

**KINETICS OF OXIDATION
OF KETONES BY QUINOLINIUM DICHROMATE**

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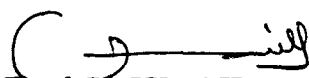
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This is being submitted to the North-Eastern Hill University for the award of degree of Doctor of Philosophy in Chemistry.



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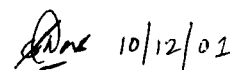
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Dedicated to My Beloved Parents

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ABSTRACT

Hexavalent chromium compounds have been widely used as oxidizing agents reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the chromium(VI) species and the solvent used. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to evince keen interest. Over the years, a large number of novel chromium(VI) oxidizing agents have been introduced especially for complex or highly sensitive substrates where great selectivity and effectiveness, coupled with mildness of conditions, are prerequisites for success.

Some of the chromium(VI) reagents which have been used as efficient oxidizing agents have included :

Chromium trioxide; chromyl chloride; Jones reagent – a solution of chromium(VI) oxide in concentrated sulfuric acid (1); Collins reagent – dipyridinium chromium(VI) oxide in dichloromethane (2) ; chromium(VI) oxide adsorbed on solid supports such as graphite, silica, alumina, silica gel, and celite (3,4); Corey's reagent – pyridinium chlorochromate (PCC) in dichloromethane (5); pyridine oxodiperoxochromium(VI) reagent – a complex of chromium pentoxide with pyridine (6); pyridinium dichromate (PDC) used either in solution in dimethylformamide or as a suspension in dichloromethane (7); bis-tetrabutyl ammonium dichromate (TBADC) in refluxing dichloromethane (8); pyridinium fluorochromate in dichloromethane (9); 4-(dimethylamino) pyridinium chlorochromate (10); tetrabutyl ammonium chlorochromate (TBACC) in chloroform (11);

bis-(trimethylsilyl) peroxide (BTSP) in dichloromethane, in the presence of pyridinium dichromate (PDC) (12); pyridinium chlorochromate (PCC) in conjunction with 3,5-dimethyl pyrazole (DMP) in dichloromethane (13,14); chromium(VI) oxide diperoxide (15); diverse chlorochromate reagents such as benzyltrimethyl ammonium chlorochromate (BTMACC), tetrabutyl ammonium chlorochromate (TMACC) in dichloroethane (16); some fluorochromates such as tetramethyl ammonium fluorochromate (TMAFC) and tetrabutyl ammonium fluorochromate (TBAFC) also in dichloroethane (16); tetrakis(pyridine) silver dichromate in refluxing benzene (17); peroxyacetic acid as the stoichiometric oxidant and a catalytic amount of 2,4-dimethylpentane-2,4-diol cyclic chromate in carbon tetrachloride-dichloromethane mixtures (18); chlorotrimethylsilanechromium trioxide (19); benzotriazole in conjunction with pyridinium chlorochromate (PCC) in dichloromethane (20); 2-cyanopyridinium chlorochromate and powdered molecular sieves in dichloromethane (21); 3-carboxy pyridinium dichromate and 4-carboxypyridinium dichromate in pyridine (22); a small quantity of anhydrous acetic acid added to pyridinium dichromate (PDC) and freshly activated molecular sieve powder in dichloromethane (23); chromium peroxide complexes (24); imidazolium dichromate (IDC) in dimethylformamide (25); pyridinium bromochromate (PBC) in chloroform (26); benzyltriethyl ammonium chlorochromate (BTACC) generated, in situ, under phase transfer conditions in refluxing chloroform (27); biphosphonium dichromate reagents (28); zinc-dichromate trihydrate in dichloromethane (29); catalytic amounts of chromium trioxide and an excess of aqueous t-butylhydroperoxide (30); cyanopyridinium chlorochromate (CPCC) in dichloromethane (31); pyridinium chlorochromate in conjunction with silica gel and by the use of the

ultrasound technique (32); pyridinium chlorochromate (PCC) in chloroform, using anhydrous acetic acid as a catalyst (33); 1-methyl imidazolium chlorochromate (MCC) and imidazolium chlorochromate (ICC) in chloroform (34); isoquinolinium chlorochromate in dichloromethane (35); ferric dichromate, polyvinylpyridine supported zinc dichromate, and polyvinylpyridine supported ferric dichromate, taken in acetonitrile (36); chromium trioxide in the presence of wet aluminium oxide taken in hexane (37); and quinolinium fluorochromate (QFC), used in chloroform as solvent (38).

The reagent employed in the present investigation has been quinolinium dichromate (QDC), $(C_9H_7N^+H)_2Cr_2O_7^{2-}$. This reagent was first reported to have been used for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, and for the oxidation of aldehydes to acids (39). This reagent has now emerged as a very useful and versatile oxidant, and has been used for the oxidation of a variety of organic substrates. When taken in dimethylformamide or in dimethylformamide - water mixtures, in the presence of an acid, quinolinium dichromate (QDC) was found to be very efficient for the oxidation of benzyl alcohols (40), arylalkanes (41), diphenylamines (42), polynuclear aromatic hydrocarbons (43,44), toluene and substituted toluenes (44,45), fluorene (46), amino acids (47), benzoin (48), styrenes (49), unsaturated acids (50), bicyclic alcohols (51), cyclic alcohols (52), diols (53,54), allylic alcohols (55), primary and secondary alcohols (56,57), α -hydroxy acids (58, 59), benzyl amines (60), anilines (61), and aromatic and aliphatic aldehydes (62,63).

The present investigation focuses attention on the kinetic features pertaining to the oxidation of various ketones by quinolinium dichromate (QDC) in acid medium,

under a nitrogen atmosphere. The rationale governing the present kinetic investigation has been to enlarge the scope of this versatile oxidizing agent, quinolinium dichromate (QDC), in acidic medium, and to provide experimental evidence for the mechanistic pathways of reactions involving diverse organic substrates. The substrates which have been used for the purpose of oxidation by quinolinium dichromate (QDC), in acid medium, using aqueous acetic acid (in the case of cyclic ketones), water (in the cases of alkanones and β -diketones) and aqueous dimethylformamide (in the cases of alkyl aryl ketone and α -ketoacids), have included the following :

1. Cyclic Ketones - Chapter I

- (a) Cyclopentanone (b) Cyclohexanone (c) Cycloheptanone
(d) Cyclooctanone

2. 2- and 3-Alkanones - Chapter II

(A) 2-Alkanones

- (a) 2-Butanone (b) 2-Pentanone (c) 2-Hexanone (d) 2-Heptanone
(e) 2-Octanone

(B) 3-Alkanones

- (a) 3-Pentanone (b) 3-Hexanone (c) 3-Heptanone (d) 3-Octanone

3. Alkyl Aryl Ketones - Chapter III

- (a) Acetophenone (b) Propiophenone (c) Butyrophenone
(d) Valerophenone

4. **β -Diketones - Chapter IV**

(a) Acetylacetone (b) Acetylacetonone (c) Benzoylacetone

5. **α -Ketoacids - Chapter V**

(a) Pyruvic acid (b) Phenylpyruvic acid

Chapter I – Kinetics of Oxidation of Cyclic Ketones

The kinetics of oxidation of cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone) by quinolinium dichromate (QDC) has been studied in acid medium, using aqueous acetic acid, as the solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440 nm. For all the cyclic ketones studied, stoichiometric ratios, $\Delta[\text{QDC}] / \Delta [\text{substrate}]$, in the range 1.98 – 2.03 were obtained. The rate of the reaction was found to be dependent on the first powers of the concentrations of each reactant (substrate, oxidant, and acid). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated dimetallic Cr(VI) species in the rate-determining step of the reaction.

The reaction has been found to be slowest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of acetic acid resulted in an increase in the rate of oxidation. Plots of $\log k_1$ (the pseudo-first-order rate constant) against the inverse of the dielectric constant were linear, with positive slopes. This suggested an interaction between a positive ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated Cr(VI) species.

The reactions were studied over a range of temperature, and it was observed that the Arrhenius equation was obeyed. Plots of $\log k_1$ against the reciprocal of temperature were linear. The activation energies and the different activation parameters were

evaluated. The reactions were characterized by negative entropies of activation. This suggested an ordered transition state, relative to the reactants. The isokinetic temperature, obtained from the plot of ΔH^\ddagger against ΔS^\ddagger , was 437K. Although current views do not attach much physical significance to isokinetic temperature, a linear correlation between ΔH^\ddagger and ΔS^\ddagger is usually a necessary condition for the validity of the Hammett equation. It was further found that the values for the free energies of activation (ΔG^\ddagger) were nearly constant, indicating that the same mechanism operated for the oxidation of all the cyclic ketones studied in this investigation.

There was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. This indicated that a one-electron oxidation was unlikely.

The observed order of reactivity for the oxidation of cyclic ketones by QDC showed that :

cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone (6 > 8 > 5 > 7).

This order of reactivity was rationalized on the basis of a change in the state of hybridization of the ketone in passing from the initial state (sp^2) to the transition state (sp^3) at the site of attack. The observed order of reactivity of cyclic ketones (6 > 8 > 5 > 7) was also explained using conformational analysis.

Correlations of rates with spectral data (IR, 1H and ^{13}C) have been used to support the nature of the cleavage product obtained.

The mechanistic pathway for the oxidation of cyclic ketones by QDC, in acid medium, involved the attack of the protonated dimetallic Cr(VI) species on the enol-form

of the substrate, in the rate-determining step, to give a cyclic monochromate ester and a Cr(VI) monomer. This cyclic monochromate ester was formed when the enol-form of the substrate was bound to Cr(VI) through the carbon-oxygen-chromium bond via an electrocyclic mechanism involving six electrons. The orbital picture showed that this was a Hückel-type system ($4n+2$); hence this would be an allowed process. The chromate ester underwent rapid decomposition which could take place through the carbon-oxygen-chromium bond, to give the final products (open-chain dibasic acids). This mechanistic pathway and the products obtained (open-chain dicarboxylic acids) established that there was the cleavage of the carbon-carbon bond in the final step of the reaction. Our mechanistic pathway finds overwhelming support from earlier investigations wherein the oxidation of cyclic ketones had established that the rate-determining step for the oxidation reactions involved an attack of the oxidant on the enol form of the substrate.

Under the experimental conditions employed in the present investigation, cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone), were oxidized by quinolinium dichromate (QDC), in acid media, giving the corresponding dicarboxylic acid in each case. The products [glutaric acid (from cyclopentanone); adipic acid (from cyclohexanone); pimelic acid (from cycloheptanone); and suberic acid (from cyclooctanone)] were characterized by FT-IR and FT-NMR analyses.

The data collected in the present investigation demonstrated that application of QDC to the oxidation of cyclic ketones resulted in the formation of the corresponding open-chain dibasic acids. This indicated the cleavage of the ring system, and also a

cleavage of the carbon-carbon bond in the final step of the reaction. Under the present experimental conditions, there was no further oxidation of the products. This experimental protocol demonstrates that application of QDC to the oxidation of cyclic ketones could prove to be a useful and general route for the synthesis of dicarboxylic acids.

Chapter II – Kinetics of Oxidation of 2- and 3- Alkanones

The present work is a detailed kinetic investigation of the oxidations of 2-alkanones (2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, and 2-octanone) and 3- alkanones (3-pentanone, 3-hexanone, 3-heptanone, and 3-octanone) by quinolinium dichromate (QDC), in acid medium, using water as the solvent, under a nitrogen atmosphere. The course of the reactions was monitored by observing the disappearance of chromium(VI) at 440 nm, spectrophotometrically. The stoichiometric ratios, $\Delta[\text{QDC}] / \Delta [\text{substrate}]$, were in the range 1.96 – 2.05. The rate of the reaction was observed to be dependent on the first powers of the concentrations of each reactant (substrate, oxidant, and acid). The rate of oxidation showed a linear increase with acidity, which suggested the participation of a protonated chromium(VI) species in the rate-determining step.

The role of the solvent in these oxidation reactions was investigated. It was observed that the rate of oxidation increased with a decrease in the polarity of the medium, in going from 0% DMF to 20% DMF. Plots of $\log k_1$ against the reciprocal of the dielectric constant were linear, with positive slopes, indicating an ion-dipole type of reaction.

The effect of changes in temperature on the rate of the reaction was studied, and the Arrhenius equation was found to be valid. The activation energies and the other activation parameters were evaluated. The negative entropies of activation (ΔS^\ddagger) indicated that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecule. The similarities in ΔG^\ddagger values for all the

substrates arose due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that all these reactions involved similar rate-determining steps.

It was observed that there was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. This indicated that a one-electron oxidation was quite unlikely.

The observed order of reactivities for the oxidation of 2- and 3- alkanones was in accordance with the structural changes in the substrates :

2-butanone > 2-octanone > 2-heptanone > 2-hexanone > 2-pentanone (for 2-alkanones);

and 3-octanone > 3-heptanone > 3-hexanone > 3-pentanone (for 3-alkanones).

These orders of reactivities were rationalized on the basis of the +I-effect of the electron-releasing alkyl groups adjacent to the carbonyl groups.

In the present investigation, the oxidation of 2- and 3- alkanones by quinolinium dichromate (QDC) in acid medium, was first-order with respect to the concentrations in each — substrate, oxidant, and acid. The first-order dependence of the rate on QDC concentration supported a reaction pathway proceeding through the enol-form of the substrate.

The rates of enolization of all the 2- and 3- alkanones were determined by the bromination method. It was found that the rates of enolization were very much greater than the rates of oxidation for all the alkanones by a factor of ~12. Since the rates of enolization were found to be much faster than the rates of oxidation, this would suggest

that the enolization step was not rate-determining. Hence, it could be concluded that the enol-form of the substrate reacted with the oxidant.

Considering the substantial evidence put forward by earlier workers on the mechanism of oxidation of 2- and 3- alkanones by different oxidizing agents, and on the basis of the kinetic results obtained in the present investigation, a mechanism was proposed for the oxidation of 2- and 3- alkanones by quinolinium dichromate (QDC), in acid medium, using water as the solvent.

The mechanistic pathway for the oxidation of 2- and 3- alkanones by QDC, in acid medium, involved the attack of the protonated QDC on the enol-form of the substrate, in the rate-determining step, to give a cyclic chromate ester and a chromium(VI) monomer. The chromate ester underwent rapid decomposition to give the final products (corresponding carboxylic acids). This mechanistic pathway and the products obtained (carboxylic acids) established that there was a cleavage of the carbon-carbon bond in the final step of the reaction. Our mechanistic pathway finds overwhelming support from earlier investigations wherein the oxidation of 2- and 3- alkanones had established that the rate-determining step for the oxidation reactions involved an attack of the oxidant on the enol-form of the substrate.

Under the experimental conditions employed in the present investigation, 2- and 3- alkanones were oxidized by quinolinium dichromate (QDC), in acid media giving the corresponding carboxylic acids in each case. These products were characterized by FT-NMR analysis.

It would be necessary to comment on the nature of the products formed from the oxidation of 2- and 3- alkanones by quinolinium dichromate (QDC) obtained in the present study. Our hypothesis opens the question of regiochemistry. There is every possibility that these 2- and 3- alkanones could also enolize to some degree to the 1-position. In that case, there would be some conversion of these alkanones to formic acid. We have examined the products of these reactions, and have not been able to detect or isolate any formic acid as a possible product. The conclusion is that, under the present experimental conditions, the enolization of these 2- and 3- alkanones took place exclusively on the 2-position.

The data collected in the present investigation demonstrated that application of QDC to the oxidation of 2- and 3- alkanones led to the formation of carboxylic acids, substantiating the mechanism of the oxidation reaction, wherein there was a cleavage of the carbon-carbon bond in the final step of the reaction. While highlighting the importance of QDC as an oxidant, this study emphasizes the efficiency of the reactions of QDC with 2- and 3- alkanones, which could prove to be a regioselective route for the synthesis of carboxylic acids.

Chapter III – Kinetics of Oxidation of Alkyl Aryl Ketones

The kinetics of the quinolinium dichromate (QDC) oxidation of alkyl aryl ketones (acetophenone, propiophenone, butyrophenone and valerophenone) has been investigated. Pseudo-first-order conditions were used (large excess of substrate over QDC). The reactions were done at constant temperature (± 0.1 K), and followed by monitoring the absorption band at 440 nm, spectrophotometrically. Rate constants were evaluated from the linear plots of $\log [QDC]$ against time. For all the alkyl aryl ketones studied, stoichiometric ratios, $\Delta[QDC] / \Delta [\text{substrate}]$, in the range 1.98 – 2.08 were obtained.

Under pseudo-first-order conditions, individual kinetic runs were first order with respect to QDC. Further, the pseudo-first-order rate constants (k_1) did not vary with the initial concentration of QDC. The order with respect to the concentrations of ketones was unity. The reaction was catalyzed by acid, and the acid-catalyzed reaction showed a first-order dependence on acidity.

The oxidation of alkyl aryl ketones by QDC was studied in solutions containing varying proportions of dimethylformamide and water. An increase in the dielectric constant of the medium increased the rate of the reaction. Linear plots of $\log k_1$ against the inverse of the dielectric constants gave negative slopes, which indicated an ion-dipole type of interaction.

The oxidation of alkyl aryl ketones was studied at different temperatures (313 - 333K), and the activation parameters were evaluated. The oxidation of alkyl aryl

ketones was characterized by negative entropies of activation, which suggested an ordered transition state, relative to the reactants. The similarity in ΔG^\ddagger values for all the substrates emphasized the probability that all these reactions involved similar rate-determining steps.

The observed order of reactivity was in accordance with the structural changes in the alkyl aryl ketones :

acetophenone > propiophenone > butyrophenone > valerophenone.

This order of reactivity was rationalized on the basis of the +I-effect of the electron-releasing alkyl groups adjacent to the carbonyl groups.

It was seen that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride, which indicated that a one-electron oxidation was quite unlikely.

In the present investigation, highlighting the oxidation of alkyl aryl ketones by quinolinium dichromate (QDC) in acid medium, using 20% DMF as the solvent, the rate of oxidation had a first-order dependence on the concentration of QDC. The first-order dependence of the rate on QDC concentration suggested that the reaction pathway was through the enol-form of the substrate. The rates of enolization of all the alkyl aryl ketones under study were determined by the bromination method. It was observed that the rates of enolization were very much greater than the rates of oxidation for the alkyl aryl ketones (by a factor of ~12). The rates of enolization being much faster than the rates of oxidation would indicate that the enolization step was not rate-determining. Hence, it would be justified to conclude that the enol-form of the substrate reacted with

the oxidant. The rate-determining step involved an attack of the protonated oxidant on the enol-form of the substrate to form a cyclic monochromate ester. The formation of this cyclic monochromate ester was followed by the transfer of two electrons in the cyclic system giving rise to cleavage products. This electrocyclic mechanism involved six electrons, and being a Hückel-type system ($4n+2$), this was an allowed process. This mechanistic pathway and the products obtained (carboxylic acids) established that there was a cleavage of the carbon-carbon bond in the final step of the reaction.

Under the experimental conditions employed in the present investigation, alkyl aryl ketones were oxidized by quinolinium dichromate (QDC), in acid medium, giving a mixture of carboxylic acids in each case. These products [formic acid and benzoic acid (from acetophenone); acetic acid and benzoic acid (from propiophenone); propionic acid and benzoic acid (from butyrophenone); and butyric acid and benzoic acid (from valerophenone)] were characterized by FT-NMR analysis.

Chapter IV – Kinetics of Oxidation of β -Diketones

The present work is a detailed kinetic investigation of the oxidations of β -diketones (acetylacetone, benzoylacetone and acetonylacetone) by quinolinium dichromate (QDC), in acid medium, using water as the solvent, under a nitrogen atmosphere. The course of the reactions was monitored by observing the disappearance of chromium(VI) at 440 nm, spectrophotometrically. The stoichiometric ratios, $\Delta[\text{QDC}] / \Delta [\text{substrate}]$, were in the range 2.64 – 2.68 for acetylacetone and benzoylacetone, and 1.98 – 2.00 for acetonylacetone.

The rates of oxidation of all the β -diketones (acetylacetone, benzoylacetone and acetonylacetone) were dependent on the first powers of the concentrations of each — substrate and oxidant.

The rates of reactions showed a first order dependence on the concentrations of the acid. The acid catalysis of the oxidation reactions must be related to the structure of the oxidant (QDC), which was converted to a protonated dimetallic Cr(VI) species. In the presence of the acid, the keto tautomer was also converted to the enol tautomer.

An increase in the polarity of the solvent medium (using water - dimethylformamide mixtures) showed an increase in the rate of the reaction. Linear plots of $\log k_1$ against the inverse of the dielectric constants gave negative slopes, which indicated an ion-dipole type of interaction. This was in accordance with the involvement of a protonated dimetallic Cr(VI) species in the rate-determining step of the reaction.

An increase in temperature resulted in an increase in the rates of the reactions. The oxidation of β -diketones was characterized by negative entropies of activation, which suggested an ordered transition state, relative to the reactants. The similarity in ΔG^\ddagger values for all the substrates were due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that all these oxidation reactions involved similar rate-determining steps.

There was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride, indicating the absence of any radical formation.

The observed order of reactivity was in accordance with the structural changes in the β -diketones :



This order of reactivity was rationalized on the basis of the inductive effect (+I-effect for the methyl group of acetylacetone, and -I-effect for the phenyl group of benzoylacetone). The greater reactivity of acetylacetone over that of acetylacetone was rationalized on the basis that the rates of oxidation were dependent on the length of the chain of these β -diketones.

The mechanism of the reaction was consistent with the fact that these oxidation reactions were catalyzed by acid. Protonation of the oxidant (QDC) would make it more amenable towards nucleophilic attack by the enol-form of the substrate on the electron deficient chromium of the oxidant. The first step involved the enolization of the ketone followed by the protonation of the oxidant (QDC). The second step was the rate-determining step, wherein the enol-form of the substrate reacted with the protonated

dimetallic oxidant, to form the cyclic monochromate ester. This was followed by the transfer of two electrons in a cyclic system giving rise to cleavage products. This electrocyclic mechanism clearly involved six electrons, and being a Hückel-type system ($4n+2$), this was an allowed process.

Under the experimental conditions employed in the present investigation, β -diketones were oxidized by quinolinium dichromate (QDC), in acid media, giving carboxylic acids in each case, accompanied by the evolution of carbon dioxide. These products [acetic acid (from acetylacetone); acetic acid and benzoic acid (from benzoylacetone); and acetic acid and acetone (from acetylacetone)] were characterized by FT-NMR analysis. These data would support the mechanism of the oxidation process wherein the cleavage of the carbon-carbon bond occurred in the final step of the reaction.

This study brings out the importance of QDC as an oxidant, and emphasizes the utility and efficiency of QDC as a reagent capable of bringing about the conversion of β -diketones to carboxylic acids.

Chapter V – Kinetics of Oxidation of α -Ketoacids

The kinetics of oxidation of α -ketoacids (pyruvic acid and phenylpyruvic acid) by quinolinium dichromate (QDC) has been studied in acid medium, using 20% dimethylformamide as solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440 nm. For both the α -ketoacids studied, stoichiometric ratios, $\Delta[\text{QDC}] / \Delta [\text{substrate}]$, in the range 0.65 – 0.70 were obtained. The rate of the reaction was found to be dependent on the first powers of the concentration of each reactant (substrate, oxidant, and acid). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated dimetallic Cr(VI) species in the rate-determining step of the reaction.

The reaction has been found to be fastest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of dimethylformamide resulted in a decrease in the rate of oxidation. Plots of $\log k_1$ (the pseudo-first-order rate constant) against the inverse of the dielectric constant were linear, with negative slopes. This suggested an interaction between an ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated Cr(VI) species.

The reactions were studied over a range of temperature, and it was observed that the Arrhenius equation was obeyed. Plots of $\log k_1$ against the reciprocal of temperature were linear. The activation energies and the different activation parameters were evaluated. The reactions were characterized by negative entropies of activation. This

suggested an ordered transition state, relative to the reactants. It was further found that the values for the free energies of activation (ΔG^\ddagger) were nearly constant, indicating that the same mechanism operated for the oxidation of both the α -ketoacids studied in this investigation.

There was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. This indicated that a one-electron oxidation was unlikely.

The observed order of reactivity was in accordance with the structural changes in the α -ketoacids. The order of reactivity observed for the oxidation of α -ketoacids was :

pyruvic acid > phenylpyruvic acid,

showing that the +I-effect of the methyl group (in pyruvic acid) was predominant over the -I-effect of the benzyl group (in phenylpyruvic acid). The activation energy was much less for the oxidation of pyruvic acid, than for phenylpyruvic acid. Furthermore, the presence of an electron-releasing group (as in pyruvic acid) accelerated the oxidation process by increasing the electron availability at the oxygen of the carbonyl group. This facilitated the attack of the electrophile (protonated QDC) on the hydrated form of the α -ketoacids. The net result would be a more facile rupture of the carbon-carbon bond in pyruvic acid, over that in phenylpyruvic acid, and hence the observed order of reactivity.

The mechanistic pathway suggested for the oxidation of pyruvic acid and phenylpyruvic acid by QDC in acid medium showed the formation of the dichromate ester resulting from a rapid reaction between the hydrated form of pyruvic acid and the protonated dimetallic Cr(VI) species. The rate-determining step of this reaction was the

decomposition of this dichromate ester to give acetic acid (in the case of pyruvic acid) and phenylacetic acid (in the case of phenylpyruvic acid) as the end products, along with the evolution of carbon dioxide.

Under the experimental conditions employed in the present investigation, α -keto acids (pyruvic acid and phenylpyruvic acid) were oxidized by quinolinium dichromate (QDC) in acid medium, giving carboxylic acids as the products in both the cases, accompanied by the evolution of carbon dioxide. These products [acetic acid (from pyruvic acid); and phenylacetic acid (from phenylpyruvic acid)] were characterized by FT-IR and FT-NMR analyses.

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INTRODUCTION

INTRODUCTION

Oxidation is an essential operation in organic synthesis and several reagents have been developed for a wide variety of transformations (1-3). Hexavalent chromium compounds have been widely used as oxidizing agents reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the chromium(VI) species and the solvent used. A large number of novel chromium(VI) oxidizing agents have been introduced, mostly in response to the needs of mildness and selectivity. Since the process of oxidation is of great value as a fundamental process in a wide scope of chemical conversions, there has been considerable interest in the development of newer chromium(VI) reagents for oxidation reactions. There exists a need for new methods, especially for complex or highly sensitive substances where great selectivity and effectiveness, coupled with mildness of conditions are prerequisites for success. New procedures are emerging, involving "non-aqueous" chromium(VI) reagents and the general idea that anhydrous conditions are more conducive to mild oxidation.

The earliest known chromium(VI) oxidants were chromium trioxide and chromyl chloride. Chromyl chloride has generally been used in carbon tetrachloride or carbon disulfide media. Chromium trioxide has been used in various kinds of reaction media such as water, acetic acid, sulfuric acid, acetic anhydride, acetone, t-butyl alcohol and pyridine.

In recent years, a large number of novel chromium(VI) oxidizing agents have been introduced, mostly in response to the needs of mildness and selectivity. The

“Jones reagent” was introduced for the oxidation of organic compounds (4-6). This reagent was a solution of chromium(VI) oxide in concentrated sulfuric acid, which was added drop wise to the substrate dissolved in acetone. The usefulness of the “Jones reagent” has been established.

Several facile oxidations of secondary alcohols were achieved with chromic acid in a two-phase system of ether and water (7). This method proved particularly suitable for the synthesis of ketones, which were susceptible to epimerization under oxidizing conditions (7).

In order to protect acid-sensitive functional groups during the oxidation of alcohols with Cr(VI) oxide, polar aprotic solvents have been used. A solution of Cr(VI) oxide in dimethylformamide, containing a trace of concentrated sulfuric acid, was able to oxidize alcohols containing acid-sensitive protecting groups. The presence of catalytic amounts of sulfuric acid was essential, accompanied by low temperatures and an inert nitrogen atmosphere (8). When a solution of Cr(VI) oxide was added to an equal volume of the substrate (alcohol), dissolved in hexamethyl phosphoric triamide (HMPT), simple axial and equatorial hydroxyl functions were oxidized, the latter at a much faster rate (9). Under the same experimental conditions, Cr(VI) oxide in HMPT was found to oxidize allylic hydroxyl functions in preference to other alcoholic groups (9). A series of primary and secondary alcohols were oxidized in 80-90% yields by a solution of sodium dichromate dihydrate, in concentrated sulfuric acid, in dimethyl sulfoxide (DMSO) at 70°C. In these oxidations, DMSO acted as a solvent and not as an

oxidant, as shown by the negligible oxidation of the substrates in the absence of dichromate (10).

One of the earliest and most widely employed chromium(VI) oxidants has been the "Collins reagent", dipyridinium-Cr(VI) oxide in dichloromethane (11). Collins reagent has been extensively used for the oxidation of primary and secondary alcohols (12-20).

The technique of using reagents intercalated in, or adsorbed on, a solid support has also been exploited in oxidations with chromium(VI) oxidizing agents. The solid supports used have included graphite, silica, alumina, silica gel and celite. As in the case of many Cr(VI) reagents, attempts were made to achieve mild reaction conditions, better selectivity and convenient isolation of the oxidation products. On heating with graphite under reduced pressure, chromium(VI) oxide was claimed to be uniformly intercalated, and the resulting substance was found to oxidize primary alcohols to aldehydes in high yields (21). Later work showed that the oxidizing agent was a surface deposit of chromium(VI) oxide on graphite (22-23). Collins reagent (11), adsorbed on celite, has been used to oxidize allylic alcohols to the corresponding aldehydes (24).

Chromium(VI) oxide, in conjunction with 3,5-dimethyl pyrazole (25), has been used to oxidize primary and secondary alcohols. This reagent was presumed to form a cyclic chromate ester that generated the corresponding carbonyl compound through intramolecular elimination. Despite the high yields of some simple aldehydes and ketones from the corresponding alcohols and near quantitative oxidation of geraniol (25), this reagent did not give satisfactory yields in a number of cases (16, 26).

For oxidation purposes, the most widely used Cr(VI) complex with pyridine has been pyridinium chlorochromate (PCC), popularly known as "Corey's reagent" (27). Its principal advantage was that this reagent was not air- or moisture-sensitive, and oxidation with it did not involve handling a large volume of solvent. Studies on the kinetics of oxidation of primary alcohols by PCC have provided important information on the mechanism of the process (28). Involvement of protonated chromium species in the rate-determining step was indicated by the catalysis of the reaction by acid, the acid-catalyzed reaction being first order. PCC did not polymerize acrylonitrile, and a hydrogen transfer hypothesis was thus not tenable. A substantial kinetic isotope effect, $k_H / k_D = 5.71$, at 303K suggested a hydride transfer in the rate-determining step. The transfer could occur directly between the alcohol and the protonated species or intramolecularly after the initial formation of a chromate ester (28). A few representative examples of oxidation of primary and secondary alcohols by PCC have been given in Table 1.

Table 1: Oxidation of Primary and Secondary Alcohols by PCC, in dichloromethane at 25°C (ref 27).

Alcohol	Product	Yield %
1-Heptanol	Heptanal	78
1-Decanol	Decanal	92
1,6-Hexanediol	Hexanedial	68
Oct-2-yn-1-ol	Oct-2-yn-al	84
Citronellol	Citronellal	82
Benzhydrol	Benzophenone	100
4-t-Butylcyclohexanol	4-t-Butylcyclohexanone	97
Presqualene alcohol	Presqualene aldehyde	78

Pyridine oxodiperoxychromium(VI), $C_5H_5N:CrO_5$, a complex of chromium pentoxide with pyridine, has been used for the oxidation of primary and secondary alcohols. This reagent was prepared by the addition of aqueous H_2O_2 to an aqueous solution of chromium(VI) oxide containing pyridine, maintained at low temperature (29).

Chromic acid supported on an ion-exchange resin has been used to oxidize primary and secondary alcohols (30). This polymer-supported reagent was prepared by the addition of the chloride form of the resin to an aqueous solution of chromium(VI)

oxide under stirring. Chromyl chloride, adsorbed on silica-alumina, was found to be an effective oxidizing agent for primary and secondary alcohols, under neutral non-aqueous conditions. This reagent was prepared by the addition of chromyl chloride, in dichloromethane, to a slurry of the adsorbent, also taken in dichloromethane (31). The instantaneous oxidation of primary and secondary alcohols, in good yields, were obtained using chromic acid adsorbed on silica gel (32). This reagent was prepared by adding a weighed amount of silica gel to a solution of chromium(VI) oxide in water (32). Pyridinium chlorochromate (PCC), supported on a polymer, was found to be an efficient system for the oxidation of alcohols to the corresponding carbonyl compounds (33). This reagent, poly[vinyl(pyridinium chlorochromate)], (PVPCC), was prepared by the addition of chromium(VI) oxide and concentrated hydrochloric acid to polyvinyl pyridine suspended in water (33). Pyridinium chlorochromate, adsorbed on alumina, has been claimed to be a better oxidizing agent than PCC taken in dichloromethane suspension (34). Thus, carveol was efficiently oxidized to carvone, and no cationic cyclization was observed during the conversion of citronellol to citronellal (34).

The difficulties in handling Collins reagent and the problem arising out of the acidic nature of Corey's reagent were overcome by the use of pyridinium dichromate, $(\text{PyH})_2\text{Cr}_2\text{O}_7$ (PDC), which was recognized as a mild and selective oxidizing agent (35). This reagent was soluble in a number of solvents, though an aprotic medium was necessary for getting satisfactory results. PDC was generally used either in solution in dimethylformamide or as a suspension in dichloromethane. Anhydrous conditions were used during oxidation with PDC, and when the oxidation was performed in dimethylformamide, the carbonyl compounds were isolated by ether extraction after

pouring the reaction mixture in water. PDC showed remarkable selectivity as an oxidizing agent. When dissolved in dimethylformamide, it clearly oxidized allylic alcohols to the corresponding α,β -unsaturated aldehydes in excellent yields. PDC in dichloromethane oxidized primary and secondary alcohols efficiently. The aldehydes obtained as products from primary alcohols did not undergo further oxidation (35).

In the presence of a mixture of ether and dichloromethane, chromium(VI) oxide was used to oxidize several secondary alcohols, in the presence of celite. The best results were obtained by the addition of solid chromium(VI) oxide to an ice-cold solution of the substrate (alcohol) in ether-dichloromethane as the solvent mixture, with celite as a suspension (36).

There have been several reports on the oxidation of primary and secondary alcohols by various chromium(VI) oxidants under phase-transfer catalysis (37-41). Some of the phase-transfer catalysts employed have included Adogen 464 (a commercially available mixture of methyltrialkyl-ammonium chloride, ref.37), tetrabutylammonium bisulfate (38,39), and tetra-n-butylammonium chloride (40,41). Allylic and benzylic alcohols were efficiently oxidized to the corresponding aldehydes with bis-tetrabutylammonium dichromate (TBADC) in refluxing dichloromethane (42).

The 2,2-bipyridine complex of chlorochromic acid was a useful oxidizing agent which had resulted in simplified procedures for the purification of the resulting carbonyl compounds. The 2,2-bipyridinium chlorochromate and the 2,2-bipyridine-chromium trioxide complex have both proved to be specially useful in oxidations of compounds with acid-sensitive protecting groups, due to the internal buffering of the

2,2-bipyridyl system. These results indicated that synthetically useful changes in the properties and reactivity of Cr(VI) reagents could be brought about by varying the amine ligand associated with chromium trioxides (43).

The pyridinium chlorochromate / H_2O_2 system has been used as an oxidative reagent for the conversion of oximes to parent carbonyl compounds in reasonably good yields (44). Pyridinium chlorochromate in dichloromethane containing 2% pyridine at 2-3°C was reported to effect the high-yield selective oxidation of the allylic hydroxyl function of a number of steroidal alcohols (45).

The oxidation of complex allylic and benzylic alcohols to the corresponding carbonyl compounds was achieved using a mild selective reagent, 4-(dimethyl amino) pyridinium chlorochromate. Secondary alcohols proved to be more reactive towards this reagent than primary alcohols. The ready preparation of this oxidizing agent, its selectivity, and the ease of using this reagent indicated its effectiveness for the oxidation of complexed allylic and benzylic alcohols (46).

The pyridinium chlorochromate-iodine system was found to be an efficient method for the conversion of enol silyl ethers to α -iodoketones in excellent yields (47). A highly selective oxidant, bis[benzyltriethyl ammonium] dichromate, was prepared and used for the oxidation of active alcohols to the corresponding carbonyl compounds, and of mercaptans to disulfides in hexamethyl phosphoric triamide (HMPT) as solvent; the yields reported were almost quantitative (48).

Since the process of oxidation in organic chemistry is of great value as a fundamental process in a wide scope of chemical conversions, there has been considerable interest in the development of newer chromium(VI) reagents for oxidation reactions. Since the introduction of pyridinium chlorochromate (27), and its extensive use as a versatile oxidant in organic synthesis (49), several new oxidizing agents have been developed, varying the amine ligand associated with the chlorochromate anion.

A new Cr(VI) reagent, pyridinium fluorochromate (PFC), was found to have certain advantages over similar oxidizing agents, in terms of the amounts of oxidant and solvent required, shorter reaction times, and high yields. In dichloromethane as solvent, PFC was found to oxidize primary and secondary alcohols to the corresponding aldehydes or ketones, respectively, and was also found to oxidize benzoin to benzil, as also anthracene and phenanthrene to their corresponding quinones (50).

At room temperature, tetrabutyl ammonium chlorochromate (TBACC), in chloroform, was used as a selective reagent for the oxidation of alcohols such as geraniol, which was converted to geranial in excellent yields (51).

Two new chlorochromate complexes were prepared and used as mild oxidizing agents. These were :

(a) 1,8-naphthyridinium chlorochromate ($C_8H_6N_2HCrO_3Cl$); and (b) pyrazinium chlorochromate ($C_4H_4N_2HCrO_3Cl$). These two reagents, taken in dichloromethane as solvent, were used to oxidize benzylic and cyclic alcohols to corresponding carbonyl products in good yields (52).

Bis-(trimethylsilyl) peroxide (BTSP), in the presence of Cr(VI), has been used to oxidize alcohols to the corresponding ketones. A solution of $\text{Me}_3\text{SiOOSiMe}_3$ (BTSP) in dichloromethane, in the presence of pyridinium dichromate, was used to oxidize borneol to camphor, as also for the conversion of cyclic alcohols to cyclic ketones in good yields (53, 54).

Pyridinium chlorochromate (PCC), in conjunction with 3,5-dimethylpyrazole (DMP), in dichloromethane as solvent, was found to be a convenient and useful reagent for the rapid and selective oxidation of steroidal allylic alcohols. The selectivity of this reagent was such that primary and secondary alcohols did not undergo significant oxidation, relative to allylic alcohols (55, 56).

Among many chromium(VI) reagents examined, pyridinium fluorochromate (PFC) was as reactive as pyridinium chlorochromate (PCC), and oxidation took place at 25°C (57). The reaction with benzyl-trimethylammonium chlorochromate (BTMACC) proceeded very slowly at 25°C , and the completion of the reaction in 1,2-dichloroethane required heating at 80°C (57). However, BTMACC was able to convert alcohols to the corresponding carbonyl compounds in very good yields. Tetrabutylammonium chlorochromate (TBACC) was also able to carry out these oxidation reactions, though with yields which were much less than the yields obtained by oxidation with BTMACC (57). Other reagents which were prepared had included tetramethylammonium fluorochromate (TMAFC), tetramethylammonium chlorochromate (TMACC) and tetrabutylammonium fluorochromate (TBAFC), but all these reagents were found to be inert for the oxidation of alcohols (57).

A useful contribution to organic synthesis was the preparation of tetrakis (pyridine) silver dichromate, $\text{Py}_4\text{Ag}_2\text{Cr}_2\text{O}_7$, which was used for the oxidation of benzylic and allylic alcohols in refluxing benzene, giving high yields of the corresponding carbonyl compounds (58).

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds has been most frequently accomplished in synthetic practice by the use of Cr(VI) reagents in amounts ranging from stoichiometric to large excess over stoichiometric (59). A new and highly effective reagent combination for the catalytic oxidation of secondary alcohols to ketones has been used (60). This reagent consisted of peroxyacetic acid as the stoichiometric oxidant and a catalytic amount of 2,4-dimethylpentane-2,4-diol cyclic chromate, using carbon tetrachloride-dichloromethane mixtures as solvent. A solution of the chromate ester was prepared from 2,4-dimethylpentane-2,4-diol and chromium trioxide in dry carbon tetrachloride. The yields of the corresponding ketones were almost quantitative, using this method (60).

A new class of Cr(VI) reagents derived from chromium trioxide and halosilanes has been developed. These reagents are highly efficient for the oxidation of alcohols to carbonyl compounds, for the oxidative coupling of mercaptans into disulfides, and for a mild cleavage of oximes to carbonyl compounds. Chlorotrimethylsilane-chromium trioxide has been shown to be an efficient oxidizing agent for the conversion of arylmethanes to benzaldehyde, and for the oxidative cleavage of some benzyl esters (61).

The use of a triazole to mediate selective Cr(VI) oxidation has been described. Benzotriazole, when used in conjunction with pyridinium chlorochromate in dichloromethane, was found to be a mild and useful reagent system for the rapid and selective oxidation of steroidal allylic alcohols to the corresponding ketones (62). A new method for the 1,4-oxygenation of 1-alkylated cyclopentadienes had made use of 2-cyanopyridinium chlorochromate and powdered molecular sieves, in dichloromethane, to give the corresponding cyclopentenones in good yields (63).

Two new Cr(VI) reagents derived from nicotinic acid and isonicotinic acid were prepared (64). 3-carboxypyridinium dichromate (nicotinium dichromate, NDC) and 4-carboxypyridinium dichromate (isonicotinium dichromate, INDC), were synthesized from chromium trioxide dissolved in a small amount of water, and nicotinic or isonicotinic acid respectively. These two reagents (NDC and INDC) have been used for the oxidations of allylic and benzylic alcohols to aldehydes, thiols to disulfides, hydroquinones to benzoquinones, and for the oxidation of polynuclear aromatic hydrocarbons (64). This reagent, 3-carboxypyridinium dichromate (NDC), proved to be an efficient reagent for the oxidation of alcohols to carbonyl compounds, in the presence of pyridine. In order to ensure complete oxidation of the substrate, the optimum molar ratio of substrate : oxidant : pyridine was found to be 1 : 2.5 : 20, respectively (65).

The efficient oxidation of alcohols to carbonyl compounds under mild conditions has been a necessary theme in organic syntheses. An improved procedure was described for the extremely rapid and efficient oxidation of alcohols, by the

addition of a small quantity of anhydrous acetic acid to pyridinium dichromate (PDC) and freshly activated molecular sieve powder, in dichloromethane, at room temperature (66).

Chromium peroxide complexes have been used as general oxidants in organic syntheses. 2,2-Bipyridylchromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, for C-C bond cleavages in 1,2-diols, the quantitative decarboxylation of α -hydroxy acids, the conversion of oximes to their carbonyl compounds, thiols to disulfides, dihydroxy phenolic compounds to quinones, benzylamine to benzaldehyde, aromatic amines to their azo compounds, and for the conversion of anthracene and phenanthrene to their quinones (67). Pyridine chromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, thiols to disulfides, anthracene to anthraquinone, and for the decarboxylation of mandelic and benzylic acids (67). Chromium peroxide etherate has also been used as an effective reagent for the oxidation of different classes of alcohols to their respective carbonyl compounds (67).

Under mild conditions, imidazolium dichromate (IDC), in dimethylformamide as solvent, was found to be a useful and selective reagent for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds, the yields being very good (68).

A phase-transfer catalysis (PTC) technique for the oxidation of benzylic, primary and secondary alcohols was reported. Benzyltriethylammonium chlorochromate, generated in situ under phase-transfer conditions, was used in refluxing

chloroform to oxidize alcohols to the corresponding carbonyl compounds in good yields (69).

Pyridinium bromochromate (PBC), in chloroform, was found to be an efficient reagent for the oxidation of benzyl alcohols, fluorenols and benzoin, giving good yields of the respective products (70).

Biphosphonium dichromate $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{Cr}_2\text{O}_7^{2-}$, was a particularly mild and selective reagent for the oxidation of primary and secondary alcohols. The oxidation of primary alcohols to aldehydes occurred without further oxidation to acid, and without any isomerization or migration of the double bond (71).

Zinc dichromate trihydrate $[\text{ZnCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}]$, in dichloromethane, was found to be a mild reagent for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones in good yields. Allyl alcohols and tricyclic allyl alcohols were observed to be resistant towards any reaction with this reagent (72).

Catalytic amounts of chromium trioxide and excess of aqueous t-butyl hydroperoxide, was found to be an effective reagent for the conversion of alcohols to carbonyl compounds, geraniol having been converted to geranial at room temperature in quantitative yields (73).

The pyridinium dichromate induced oxidative rearrangement of various enynols proceeded with complete regioselectivity giving good yields. In these rearrangements, it was observed that chromate ester formation and subsequent ring flip created severe 1,4-steric (flag pole) interaction (74).

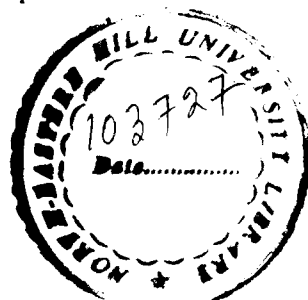
The oxidation of alcohols by pyridinium fluorochromate (PFC) in dichloromethane had yielded the corresponding carbonyl compounds in good yields. This study indicated that PFC was an efficient two-electron oxidant which was capable of participating in oxygen-transfer reactions (75). The versatility of PFC as an oxidizing agent has been brought out by the various studies which have been carried out on the oxidation of some organic substrates such as aliphatic alcohols (76), sulfides (77), and aromatic alcohols (78).

Cyano-pyridinium chlorochromate (CPCC), in dichloromethane, was found to be the reagent of choice for the conversion of alkenes to α -chloroketones, and this procedure seemed to have broad applicability (79).

Pyridinium chlorochromate (PCC), in the presence of sodium azide or sodium cyanide, was used to transform aldehydes into carbamoyl azides or acyl azides in fairly good yields (80).

Cr(VI)-oxide diperoxide has been used for the oxidation of tertiary amines. These reactions were carried out in chloroform, and the products obtained were the corresponding N-oxides in good yields. The rate law observed suggested a mechanism involving a preliminary coordination of the amine to the metal. The oxidation rate of the amines and some organic sulfides indicated a mechanism having some single-electron-transfer (SET) character (81).

By using the ultrasound technique (82), pyridinium chlorochromate in conjunction with silica gel was developed as a heterogeneous process for the oxidation



of alcohols to the corresponding carbonyl compounds (83). Using this process, borneol was converted to camphor, and geraniol was converted to geranial in excellent yields (83). The synthetic utility of pyridinium chlorochromate in chloroform was demonstrated for the oxidation of alcohols, using anhydrous acetic acid as a catalyst (84). Such anhydrous conditions have been used for the oxidation of primary and secondary alcohols by pyridinium chlorochromate (84).

With a view to provide further evidence so as to ascertain the mechanism of the oxidation of alcohols by Corey's reagent (PCC), two new Cr(VI) reagents were synthesized. These two reagents were 1-methyl imidazolium chlorochromate (MCC) and imidazolium chlorochromate (ICC). It was found that these two reagents were similar in selectivity. The mechanism for the oxidation of alcohols by these reagents was similar to that for the oxidation of the alcohols by PCC (85).

Benzotriazole was found to complex with chromium trioxide to produce a versatile new oxidant. This complex was capable of oxidizing primary alcohols to carboxylic acids, secondary alcohols to ketones, and olefin substrates to α,β -unsaturated ketones by allylic oxidation (86). Farnesol could be converted to the corresponding acid. Other amine-CrO₃ complexes have been reported to produce aldehydes from primary alcohols.

The oxidation of alcohols by isoquinolinium chlorochromate, in dichloromethane solvent, yielded the corresponding carbonyl compounds in reasonably good yields (87).

Three new Cr(VI) reagents (ferric dichromate, polyvinylpyridine supported zinc dichromate, and polyvinylpyridine supported ferric dichromate), were prepared and found to be stable, mild and efficient reagents for the oxidation of different kinds of organic compounds (88). Of these three reagents, ferric dichromate seemed to be the most efficient. When taken in acetonitrile, ferric dichromate was able to oxidize styrene to benzaldehyde, and alcohols to their corresponding carbonyl compounds in good yields (88).

The oxidation of secondary alcohols with chromium trioxide, in the presence of wet aluminium oxide in hexane, had yielded the corresponding ketones. This method was used for the oxidation of cyclic alcohols, giving good yields of the cyclic ketones. For the oxidation of geraniol by this reagent, it was observed that the reaction proceeded without any appreciable loss of double bond stereochemistry (89).

The synthetic potential of quinolinium fluorochromate (QFC), $C_9H_7NH[CrO_3F]$, and its application in the oxidation of alcohols was reported. This reagent was found to be as effective as pyridinium chlorochromate (PCC) and pyridinium fluorochromate (PFC). The major improvements have been the relatively higher solubility of QFC in non-aqueous solvents and much less pronounced acidic character, as compared to PCC and PFC (90). The versatile nature of QFC has been highlighted by the diverse types of organic substrates which have been oxidized by it. QFC in chloroform has been used to oxidize alcohols, polycyclic arenes, triphenylphosphine, trimethylsilyl ether and diphenylsulfide, and the yields reported have been excellent (91).

Kinetic studies involving the use of various chromium(VI) reagents have been reported. Pyridinium bromochromate has been employed for the kinetics of oxidation of phosphinic, phenylphosphinic and phosphorus acid (92). Pyridinium fluorochromate (PFC), in aqueous acetic acid medium, was found to be an efficient oxidant for the oxidation of secondary alcohols (93). Pyridinium chlorochromate (Corey's reagent) has been extensively employed for the oxidation of different organic substrates. In the oxidation of cinnamic acids by this reagent, a kinetic data has been used to support the mechanistic pathway for this reaction, which was characterized by a non-linear Hammett plot (94). The reaction of hydromates and hydroxyacids with pyridinium chlorochromate (PCC), in acid medium, catalysed by ruthenium(III), yielded kinetic data which suggested a mechanism involving an electron transfer reaction (95). Kinetic studies on the oxidation of some thioacids by 2,2'-bipyridinium chlorochromate has been reported (96). Quinolinium bromochromate has been selectively used for the oxidation of different alcohols in anhydrous acetic acid (97). A new chromium(VI) reagent, tetraethylammonium chlorochromate (TEACC), was introduced, and a kinetic study has been carried out on the oxidation of benzyl alcohol by this reagent in dimethylformamide solvent (98).

Quinolinium chlorochromate (QCC) was prepared by treating a solution of CrO_3 in 6M HCl with quinoline at 0°C . The orange-red compound was stable when exposed to air, moisture and light. It efficiently oxidized primary and secondary alcohols to the corresponding carbonyl compounds (99).

Butyltriphenylphosphonium dichromate (BTPPD) was found to be a mild and selective oxidizing agent which was used for the oxidation of alcohols to carbonyl compounds, thiols to disulphides, aromatic amines to azo compounds, and aromatic oximes to the corresponding carbonyl compounds (100).

Isoquinolinium fluorochromate (IFC) was introduced as a new and efficient oxidant which was used for the oxidation of different organic substrates such as alcohols and aldehydes (101).

A new and selective oxidant, isoquinolinium dichromate (IDC), was found to be an efficient reagent for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds (102).

Imidazolium fluorochromate was found to be a mild, stable and selective chromium(VI) reagent which was used for the oxidation of alcohols to the corresponding carbonyl compounds (103).

Benzyltriphenylphosphonium chlorochromate (BTPPC) was a mild and novel reagent which was used for the oxidation of benzylic and allylic alcohols under non aqueous and aprotic conditions (104).

Quinolinium dichromate (QDC), having the structure $(C_9H_7N^+ H)_2Cr_2O_7^{2-}$, has been used for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, and for the oxidation of aldehydes to acids (105). QDC is a stable orange solid, which was prepared by dissolving CrO_3 in water, adding quinoline, and collecting the product. Solutions of QDC, in dimethylformamide or suspensions in

dichloromethane, have been used for the oxidation of alcohols and aldehydes, giving good yields of the corresponding products (105). A few representative examples of the oxidation of alcohols and aldehydes by QDC are given in Table 2.

Table 2: Oxidation of alcohols and aldehydes by QDC (ref. 105).

Compound	Products	(% Yields)	
		In CH ₂ Cl ₂	In DMF
n-Butanol	n-Butanal	69	74
n-Hexanol	n-Hexanal	70	44
Benzyl Alcohol	Benzaldehyde	45	45
Cinnamyl Alcohol	Cinnamaldehyde	70	52
Benzhydrol	Benzophenone	55	48
Benzaldehyde	Benzoic Acid		55
Cinnamaldehyde	Cinnamic Acid		52
Crotonaldehyde	Crotonic Acid		85

Quinolinium dichromate (QDC) has now emerged as a very useful and versatile oxidant, which is clearly deserving of widespread application. QDC in dimethylformamide-water mixtures, in the presence of acid, has been used for the oxidation of a variety of organic substrates. Some of the organic substrates which have been oxidized by QDC in acid medium, have included benzyl alcohols (106), arylalkanes (107), diphenylamines (108), polynuclear aromatic hydrocarbons (109,110),

toluene and substituted toluenes (110,111), fluorene (112), amino acids (113), benzoin (114), styrenes (115), unsaturated acids (116), bicyclic alcohols (117), cyclic alcohols (118), diols (119, 120), allylic alcohols (121), primary and secondary alcohols (122, 123), α -hydroxy acids (124, 125), benzyl amines (126), anilines (127), and aromatic and aliphatic aldehydes (128, 129). All these reactions using QDC have highlighted the kinetic features associated with the oxidation process, and mechanistic pathways have been suggested for all these oxidation reactions (106-129).

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SCOPE OF THE PRESENT INVESTIGATION

SCOPE OF THE PRESENT INVESTIGATION

There has been a sustained interest in the development of new reagents for the effective and selective oxidation of organic substrates. The development of oxidizing agents based upon higher-valent transition metal oxo derivatives has resulted in the use of reagents derived from transition metals such as ruthenium, osmium, iron, manganese, molybdenum, chromium and vanadium. Of all such reagents, chromium(VI) oxidants seem to have proved to be the most versatile and efficient in bringing about various kinds of transformations.

The conversion of hydroxy groups to the corresponding carbonyl groups has been considered to be an important transformation in organic synthesis. Many procedures have been developed for these conversions. The use of oxochromium(VI) amine reagents in oxidative transformations has been quite extensive. These reagents have been used for the general oxidation of alcohols to carbonyl compounds, the selective oxidation of allylic and benzylic alcohols, the oxidation of organometallics, oxidative transpositions and cleavages, and oxidative cyclizations. Since the introduction of pyridinium chlorochromate (PCC, Corey's reagent) as an oxidant for the purpose of carrying out the oxidation of alcohols to the carbonyl compounds, several new oxochromium(VI) amine reagents have been developed with the purpose of achieving a desired selectivity, improvement in yield, or a modification of product outcome.

In the present investigation, the chromium(VI) reagent which has been employed for the purpose of oxidation is quinolinium dichromate (QDC),

$(C_9H_7N^+H)_2Cr_2O_7^{2-}$. This reagent has emerged as a useful and versatile oxidant, capable of oxidizing diverse kinds of organic substrates.

The purpose of this investigation has been to attempt to extend the scope of this oxidizing agent, QDC, in acid medium, and to explore and establish mechanistic pathways of reactions involving QDC with diverse organic substrates.

The substrates chosen for the purpose of oxidation by quinolinium dichromate (QDC), have included the following :

1. Cyclic Ketones - Chapter I

- (a) Cyclopentanone (b) Cyclohexanone (c) Cycloheptanone
- (d) Cyclooctanone

2. 2- and 3- Alkanones - Chapter II

(A) 2-Alkanones

- (a) 2-Butanone (b) 2-Pentanone (c) 2-Hexanone (d) 2-Heptanone
- (e) 2-Octanone

(B) 3-Alkanones

- (a) 3-Pentanone (b) 3-Hexanone (c) 3-Heptanone (d) 3-Octanone

3. Alkyl Aryl Ketones - Chapter III

- (a) Acetophenone (b) Propiophenone (c) Butyrophenone
- (d) Valerophenone

4. β -Diketones - Chapter IV

(a) Acetylacetone (b) Acetylacetone (c) Benzoylacetone

5. α -Ketoacids - Chapter V

(a) Pyruvic acid (b) Phenylpyruvic acid

The present investigation is a detailed kinetic probe into the oxidation of ketones by quinolinium dichromate (QDC), in acid medium, using water (in the cases of alkanones and β -diketones), aqueous dimethylformamide (in the cases of alkyl aryl ketones and α -ketoacids), and aqueous acetic acid (in the case of cyclic ketones), as the solvents, under a nitrogen atmosphere.

For each oxidation reaction, the stoichiometry of the reaction has been determined. The concentrations of substrate, oxidant and acid have been varied, and the effects of these variations on the reaction rates have been studied. The solvent composition has been varied (water-acetic acid mixture, in the case of cyclic ketones; and water and water-dimethylformamide mixtures, in the cases of alkanones, alkyl aryl ketones, β -diketones, and α -ketoacids), in order to study the effects of changes in the dielectric constant of the medium on the rates of the reactions. Changes in the temperature of the reaction medium have been made, and the activation parameters have been evaluated. Based on the observed kinetic data, the nature of the transition states involved in these reactions has been rationalized. For each reaction, the products have been isolated and characterized by analytical and spectral methods. Based on the observed experimental data, mechanistic pathways for the oxidation of these substrates by quinolinium dichromate (QDC), in acid medium, have been proposed.

EXPERIMENTAL

EXPERIMENTAL

Conductivity Water

Conductivity water was prepared by the following method : Tap water was distilled first with alkaline potassium permanganate and then redistilled with sulfuric acid (Merck) from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel. The conductivity water thus prepared was utilized for the preparation of all the solutions used in the kinetic determinations.

Sulfuric Acid

E. Merck sample was used after a check of its physical constants.

Perchloric Acid

E. Merck sample was used after a check of its physical constants

Acetic Acid

Acetic acid (E. Merck) was refluxed for 3 hours with chromic oxide, with the addition of a quantity of acetic anhydride corresponding to the water content of the acetic acid. The solids that separated out were filtered off, and the acid was distilled from an all-glass apparatus. Large head and tail fractions were rejected and the fraction distilling at 116°C was collected.

N,N-Dimethylformamide

Dimethylformamide was purified by the following method : Anhydrous copper sulfate was prepared by heating copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$), until it turned white. The complete removal of water molecules was checked by its constant weight after repeated heating. Anhydrous copper sulfate was mixed with dimethylformamide (SD'S, AR grade), and the mixture was allowed to stand for 24 hours. The solution was filtered and the filtrate was distilled under reduced pressure. The distillate thus collected was used as the solvent (b.p. 153°C).

Quinolinium Dichromate (QDC), $(\text{C}_9\text{H}_7\text{N}^+\text{H})_2\text{Cr}_2\text{O}_7^{2-}$

To a stirred solution of CrO_3 (100 g) in water (100 ml) cooled in ice, quinoline (86 ml) was added in small proportions. The solution was diluted with acetone (400 ml), cooled to -20°C , and the orange solid which separated out was filtered, washed with acetone, dried in vacuo and recrystallized from water (m.p. 160°C). The purity of the compound was further checked by spectral analysis. Infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730 cm^{-1} , characteristic of the dichromate ion.

Substrates

Cyclopentanone and cyclohexanone (E. Merck), and cycloheptanone and cyclooctanone (Fluka) were used after distillation, and their purity was checked from physical constants.

The 2-alkanones (2-pentanone and 2-hexanone) obtained from Fluka, and 2-butanone, 2-heptanone and 2-octanone obtained from E. Merck, were all distilled before use, and their purity was checked from physical constants. The 3-alkanones (3-hexanone, 3-heptanone and 3-octanone) obtained from E. Merck, and 3-pentanone obtained from Fluka, were all distilled before use, and their purity was checked from physical constants.

Acetophenone (E. Merck), propiophenone (Spectrochem), butyrophenone and valerophenone (Aldrich) were all distilled before use and their purity was further checked from physical constants.

Acetylacetone (SD, fine-chem. Ltd.) and acetonylacetone (E. Merck) were used after distillation and their purity was checked from physical constants. Benzoylacetone (SISCO) was used after recrystallization, and its purity was checked from physical constants.

Pyruvic acid (E. Merck) and phenylpyruvic acid (Fluka) were used after distillation and recrystallization, respectively, and their purity was checked from physical constants. The boiling points and melting points of the substrates used are summarized in Table 1.

Table 1 : Boiling Points / Melting Points of Substrates (1)

Substrate	Boiling points or Melting points (°C)
Cyclopentanone	130
Cyclohexanone	155
Cycloheptanone	179
Cyclooctanone	195
2-Butanone	80
2-Pentanone	105
2-Hexanone	127
2-Heptanone	149
2-Octanone	173
3-Pentanone	102
3-Hexanone	123
3-Heptanone	146
3-Octanone	167
Acetophenone	202
Propiophenone	218
Butyrophenone	228
Valerophenone	105
Acetylacetone	140
Acetonylacetone	191
Benzoylacetone	58 (m.p.)
Pyruvic acid	165
Phenylpyruvic acid	158 (m.p.)

Acrylonitrile

The monomer (BDH) was washed with 5% sodium hydroxide solution to remove the inhibitor (hydroquinone), and then with 3% orthophosphoric acid to remove any basic impurities. It was then washed with water, dried over anhydrous calcium chloride, and distilled under reduced pressure in an atmosphere of nitrogen. The middle fraction was collected (b.p. 77°C) and used.

Other Reagents

All other reagents used were of AnalaR grade, and were purified before use, and their boiling points/melting points were checked, and found to agree with those given in the literature.

Instruments

- (a) FT-IR spectrophotometer :- All IR spectra were recorded on FT-IR (DA-8. Bomen) spectrophotometer.
- (b) FT-NMR spectrometer :- NMR spectra were recorded on FT-NMR (300 MHz, Bruker) spectrometer.
- (c) UV-VIS spectrophotometer :- For absorption measurements, the spectrophotometer used was Beckman DU 650 (USA).

The DU 650 spectrophotometer was a single beam spectrophotometer having a wave length range from 190 nm to 1100 nm. In order to ensure maximum sensitivity of the instrument, and to minimize the errors in the measurements of absorbance due to fluctuations in voltage,

the spectrophotometer was connected to the mains through an external voltage stabilizer. This was in addition to the in-built voltage stabilizer within the instrument itself. The light source was a 15 watt tungsten lamp operated by a regulated power supply. The spectrophotometer was equipped with the computer device attachment which permitted the recording of the absorbance of unreacted Cr(VI) as a function of time at 440nm (maximum absorption of Cr(VI)). The instrument was equipped with a thermostat compartment of 1 cm cell, the temperature of which was constant to 0.1°C. The compartment was connected to a thermostat for regulating the water circulation at the desired temperature. The spectrophotometer was provided with a parallel output from a Dot Matrix Printer.

A blank reading for the instrument was taken on a cuvette filled with solvent (substrate) before the analysis began. The solvent was at the same temperature at which the analysis was performed.

- (d) Thermostat :- An electrically operated thermostatic water bath was used. It was provided with sufficient thermal lagging, suitable heaters and timers with proper cooling arrangements for continuous work. A xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperature accurately, with fluctuations of not more than $\pm 0.1^\circ\text{C}$. The temperatures were recorded by means of an accurate

sensitive thermometer, reading to tenths of a degree. The bath liquid was water, covered with a layer of liquid paraffin to minimize evaporation of water and loss of heat due to radiation.

Absorption Cells

The absorption cells were of quartz and of 4 ml capacity. All the cells were thoroughly cleaned by aqueous ethanol and acetone, and dried before they were used for the spectral measurements. After the transfer of the solution to the cell, care was taken such that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

Kinetic Measurements

For all the kinetic determinations, pseudo-first-order reaction conditions have been used, wherein the substrate was taken in large excess over that of the oxidant.

A known amount of the substrate was taken accurately in a 10 ml standard flask, and the volume made up with the requisite quantities of water (in the cases of alkanones and β -diketones), or with aqueous dimethylformamide (in the cases of alkyl aryl ketones and α -ketoacids), or with aqueous acetic acid (in the case of cyclic ketones) so as to make the solutions of the required molarity. Quinolinium dichromate (QDC) was accurately weighed out in a 10 ml standard flask, dissolved, and the volume was made up with water (or aqueous dimethylformamide or aqueous acetic acid). Sufficient time was allowed to compensate for any change of heat during dilution. A known volume of sulfuric acid (or perchloric acid) was taken in a 10 ml standard flask, and the

volume made up with water (or aqueous DMF or aqueous acetic acid) so as to make the solution of required strength. The three solutions thus prepared (substrate, oxidant and acid), were separately thermostated at the required temperature for 1h, under a nitrogen atmosphere. Equal volumes of the two solutions of oxidant and acid were mixed. A double amount of the substrate solution was then introduced, and the reaction mixture was shaken well. The reaction mixture remained homogeneous throughout the duration of the reaction.

The progress of the reaction was followed by observing the disappearance of Cr(VI). Readings were taken at regular intervals of time, by noting the decrease in absorbance at 440 nm, spectrophotometrically.

All the kinetic experiments were carried out in duplicate or triplicate, and the rate constants which were determined were found to be reproducible to within $\pm 3\%$. All reactions were performed under a nitrogen atmosphere. Since the reactions were performed at high concentrations of acid, the ionic strength was not maintained constant.

Calculations

(a) Rate constants

The pseudo-first-order rate constant, k_1 , expressed in s^{-1} , was calculated from the equation (1) :

$$k_1 = (2.303 / t) \log (A_0 / A_t) \quad (1)$$

where A_0 was the initial absorbance of the reaction mixture, and A_t was the absorbance at time t . The logarithmic plots of absorbance against time were linear, and extrapolation to zero time gave the value of A_0 .

The values of the second order rate constant, k_2 , expressed in $M^{-1} s^{-1}$, were computed by dividing the pseudo-first-order rate constant (k_1, s^{-1}) by the concentration of the substrate (M).

All values of rate constants were the average of two or more experiments, with agreement being within $\pm 3\%$.

(b) Thermodynamic activation parameters

The activation parameters were determined from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows :-

(i) Activation energy (E)

From the linear plot of $\log k_1$ against the reciprocal of temperature (T),

$$\text{Slope} = -E / 2.303R$$

$$E = -\text{slope} \times 2.303 R \quad (\text{kJ mol}^{-1})$$

(ii) Enthalpy of activation (ΔH^\ddagger)

$$\Delta H^\ddagger = E - RT \quad (\text{kJ mol}^{-1})$$

(iii) Entropy of activation (ΔS^\ddagger)

$$k_1 = kT/h \times e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

$$\Delta S^\ddagger = 2.303R [\log k_1 + \Delta H^\ddagger / 2.303RT - \log kT/h] \quad (\text{JK}^{-1} \text{mol}^{-1})$$

where k is the Boltzmann constant, h is the Planck's constant, and R is the gas constant.

(iv) Free energy of activation (ΔG^\ddagger)

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (\text{kJ mol}^{-1})$$

Stoichiometry

The stoichiometric experiments were carried out under nitrogen, at the particular temperature under the conditions of $[\text{QDC}] > [\text{Substrate}]_0$, at varying acid concentrations. The disappearance of Cr(VI) was followed, until the absorbance values became constant. The $[\text{QDC}]_\infty$ was estimated. For each oxidation reaction, the stoichiometric ratio, $\Delta[\text{QDC}] / \Delta[\text{Substrate}]$, was obtained. The individual stoichiometric equations have been shown along with the reactions of each of the substrates with the oxidant.

Test for Radical formation

Various tests were performed to determine whether radical intermediates were formed during the course of the oxidation reactions of the substrates by quinolinium dichromate (QDC), in acid medium, under nitrogen. The following tests were carried out :

(a) Reduction of mercuric chloride (2) :

It was observed that there was no reduction of mercuric chloride, thus indicating the absence of radical intermediates during the process of oxidation of the substrates by QDC.

(b) Polymerization of an added olefinic monomer, such as acrylonitrile (2) :

1 ml of acrylonitrile (0.02 M) and 2 ml of substrate solution (0.2 M) in water (in the cases of alkanones and β -diketones), or with aqueous dimethylformamide (in the cases of alkyl aryl ketones and α -ketoacids), or with aqueous acetic acid (in the case of cyclic ketones) and H_2SO_4 (4.0 M), were taken in a 10 ml conical flask. In a separate test tube, 2 ml of QDC solution (0.02 M) was taken. The two reactant solutions were placed under nitrogen, and then mixed and allowed to stand at 40° for 30 min. There was no formation of a white opalescence, indicating the absence of any polymer formation. The reaction mixture was warmed to 60°C in order to accelerate the oxidation. There was no formation of polymer. Each experiment was accompanied by a blank control.

Product Analysis

(A) General Procedure for the oxidation of Cyclic Ketones by QDC.

Water (30 ml) was taken and cooled in ice. Concentrated H_2SO_4 (8 ml, 0.15 M) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 9.52 g , 0.02 M) was added, and the mixture was warmed to 40°C for complete dissolution of the QDC. To this mixture,

0.01 M of substrate (0.89 ml cyclopentanone, 1.04 ml cyclohexanone, 1.18 ml cycloheptanone, 1.26 g cyclooctanone), taken in 25ml of 20% acetic acid (v/v), was added. The reaction mixture was stirred at 40°C for 1h until TLC showed complete reaction (entry 3 in Table 2). The color changed from yellow to green. The organic layer was extracted with ether (4 x 25 ml), and the combined organic extracts were washed with water, dried (anhydrous Na₂SO₄), and warmed to remove the ether. The crude product (obtained as a white solid) was recrystallized from hot water. The yields of the recrystallized products [glutaric acid (from cyclopentanone); adipic acid (from cyclohexanone); pimelic acid (from cycloheptanone); and suberic acid (from cyclooctanone)] have been shown in Table 2.

Table 2 : Oxidation of Cyclic Ketones at 40 °C^a

Entry	Ketone	Time (h)	Product	Yield (%) ^b
1	cyclopentanone	3	glutaric acid	80
2	cyclopentanone	4.5	glutaric acid	80
3	cyclohexanone	1	adipic acid	90
4	cyclohexanone	2	adipic acid	90
5	cycloheptanone	4.5	pimelic acid	80
6	cyclooctanone	1.5	suberic acid	84
7	cyclooctanone	2.5	suberic acid	86

^a reaction conditions as indicated in the experimental section.

^b isolated yields.

Each reaction product obtained was subjected to IR (KBr) and NMR (CDCl₃ / 1 drop DMSO-d₆) analyses, and characterized as follows:

(i) Glutaric acid ; IR : ν 2940(br s, -OH), 1688(s, C=O) , 1468, 1305, 1265, 1205, 1065, 921, 760 cm⁻¹

¹H NMR : δ 5.5(br s, 2H, 1-H), 2.3(t, 4H, 2-H₂), 1.6(m, 2H, 3-H₂)

¹³C NMR : δ 175.5(1-C), 33.2(2-C), 20.0(3-C)

(ii) Adipic acid ; IR : ν 2952(br s, -OH) 1724(s, C=O), 1462, 1428, 1408, 1278, 1193, 926, 734 cm⁻¹

¹H NMR : δ 6.8(br s, 2H, 1-H), 2.3(t, 4H, 2-H₂), 1.7(m, 4H,3-H₂)

¹³C NMR : δ 176.0(1-C) , 33.8(2-C), 24.4(3-C)

(iii) Pimelic acid ; IR : ν 2938(br s, -OH), 1663(s, C=O), 1469, 1408, 1268, 1200, 919, 731 cm⁻¹

¹H NMR : δ 5.4(br s, 2H, 1-H), 2.3(t, 4H, 2-H₂), 1.6(m, 4H, 3-H₂), 1.4(m, 2H, 4-H₂)

¹³C NMR : δ 175.37 (1-C), 33.91 (2-C), 28.50 (3-C), 24.51 (4-C)

(iv) Suberic acid ; IR : ν 2942(br s, -OH), 1695(s, C=O), 1427, 1333, 1252, 1190, 930, 796, 725, 681 cm⁻¹

¹H NMR : δ 6.7(br s, 2H, 1-H), 2.3(t, 4H, 2-H₂), 1.6(m, 4H, 3-H₂), 1.3(m, 4H, 4-H₂)

¹³C NMR : δ 175.9(1-C), 33.9(2-C), 28.6(3-C), 24.6(4-C)

(B-i) General Procedure for the oxidation of 2-Alkanones by QDC.

30 ml of water was taken and cooled in ice. Concentrated HClO_4 (4.83 ml, 0.08 M) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 9.52 g, 0.02 M) was added and the mixture was warmed to 40°C for complete dissolution of the QDC. To this mixture, 0.01 M of substrate (0.90 ml of 2-butanone, 1.07 ml of 2-pentanone, 1.23 ml of 2-hexanone, 1.40 ml of 2-heptanone, 1.57 ml of 2-octanone) taken in 25 ml of DMF, was added. The reaction mixture was stirred at 313 K for 48h under nitrogen. The organic layer was extracted four times with ether (25 ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na_2SO_4 . The oxidized products [acetic acid (from 2-butanone); acetic acid and propionic acid (from 2-pentanone); acetic acid and butyric acid (from 2-hexanone); acetic acid and pentanoic acid (from 2-heptanone); and acetic acid and hexanoic acid (from 2-octanone)] were obtained after the complete removal of ether. Each reaction product obtained was subjected to NMR (300 MHz ; CDCl_3 / 1 drop DMSO-d_6 ; Me_4Si) analysis, and characterized as follows :

(i) Acetic acid ;

$^1\text{H NMR}$: δ 8.9(s, 1H, 1- $\text{H}_{\text{acetic acid}}$), 2.2(s, 3H, 2- $\text{H}_3_{\text{acetic acid}}$),

$^{13}\text{C NMR}$: δ 165.8(C-1 $_{\text{acetic acid}}$), 14.9(C-2 $_{\text{acetic acid}}$)

(ii) Acetic acid and Propionic acid ;

$^1\text{H NMR}$: δ 10.6(s, 1H, 1- $\text{H}_{\text{propionic acid}}$), 7.3(s, 1H, 1- $\text{H}_{\text{acetic acid}}$),
2.4(q, 2H, 2- $\text{H}_2_{\text{propionic acid}}$), 2.1(s, 3H, 2- $\text{H}_3_{\text{acetic acid}}$),
1.1(t, 3H, 3- $\text{H}_3_{\text{propionic acid}}$)

^{13}C NMR : δ 181.2(C-1_{propionic acid}), 178.1(C-1_{acetic acid}), 27.5(C-2_{propionic acid}),
20.9(C-2_{acetic acid}), 8.9(C-3_{propionic acid})

(ii) Acetic acid and Butyric acid ;

^1H NMR : δ 10.3(s, 1H, 1-H_{butyric acid}), 7.3(s, 1H, 1-H_{acetic acid}),
2.3(t, 2H, 2-H_{2 butyric acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.7(m, 2H, 3-H_{2 butyric acid}), 0.9(t, 3H, 4-H_{3 butyric acid})

^{13}C NMR : δ 180.4(C-1_{butyric acid}), 178.0(C-1_{acetic acid}), 36.1(C-2_{butyric acid}),
20.9(C-2_{acetic acid}), 18.2(C-3_{butyric acid}), 13.6(C-4_{butyric acid})

(iv) Acetic acid and Pentanoic acid ;

^1H NMR : δ 8.2(s, 1H, 1-H_{pentanoic acid}), 8.1(s, 1H, 1-H_{acetic acid}),
2.4(t, 2H, 2-H_{2 pentanoic acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.6(m, 2H, 3-H_{2 pentanoic acid}), 1.2(m, 2H, 4-H_{2 pentanoic acid}),
0.9(t, 3H, 5-H_{3 pentanoic acid})

^{13}C NMR : δ 170.7(C-1_{pentanoic acid}), 163.5(C-1_{acetic acid}), 31.4(C-2_{pentanoic acid}),
27.0(C-2_{acetic acid}), 23.6(C-3_{pentanoic acid}), 22.3(C-4_{pentanoic acid}),
15.1(C-5_{pentanoic acid})

(v) Acetic acid and Hexanoic acid ;

^1H NMR : δ 8.7(s, 1H, 1-H_{hexanoic acid}), 8.1(s, 1H, 1-H_{acetic acid}),
2.5(t, 2H, 2-H_{2 hexanoic acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.2(m, 6H, 3,4,5-H_{2 hexanoic acid}), 0.9(t, 3H, 6-H_{3 hexanoic acid})

^{13}C NMR: δ 170.6(C-1_{hexanoic acid}), 163.9(C-1_{acetic acid}), 34.1(C-2_{hexanoic acid}),
31.4(C-2_{acetic acid}), 28.9(C-3_{hexanoic acid}), 24.6(C-4_{hexanoic acid}),
22.4(C-5_{hexanoic acid}), 13.9(C-6_{hexanoic acid})

(B-ii) General Procedure for the oxidation of 3-Alkanones by QDC

15 ml of water was taken and cooled in ice. Concentrated HClO₄ (4.83 ml, 0.08 M) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 4.76g, 0.01 M) was added and the mixture was warmed to 40 °C for complete dissolution of the QDC. To this mixture, 0.015 M of substrate (1.59 ml of 3-pentanone, 1.85 ml of 3-hexanone, 2.10 ml of 3-heptanone, 2.34 ml of 3-octanone) taken in 25 ml of DMF, was added. The reaction mixture was stirred at 313K for 48 h under nitrogen. The organic layer was extracted four times with ether (25 ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na₂SO₄. The oxidized products [acetic acid and propionic acid (from 3-pentanone); acetic acid and butyric acid (from 3-hexanone); acetic acid and pentanoic acid (from 3-heptanone); and acetic acid and hexanoic acid (from 3-octanone)] were obtained after the complete removal of ether. Each of the reaction products obtained was subjected to NMR (CDCl₃ / 1 drop DMSO-d₆) analysis, and characterized as follows :-

(i) Acetic acid and Propionic acid ;

¹H NMR : δ 10.6(s, 1H, 1-H_{propionic acid}), 7.3(s, 1H, 1-H_{acetic acid}),
2.4(q, 2H, 2-H_{2 propionic acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.1(t, 3H, 3-H_{3 propionic acid})

¹³C NMR : δ 181.2(C-1_{propionic acid}), 178.1(C-1_{acetic acid}), 27.5(C-2_{propionic acid}),
20.9(C-2_{acetic acid}), 8.9(C-3_{acetic acid})

(ii) Acetic acid and Butyric acid ;

$^1\text{H NMR}$: δ 10.3(s, 1H, 1-H_{butyric acid}), 7.3(s, 1H, 1-H_{acetic acid}),
2.3(t, 2H, 2-H_{2 butyric acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.7(m, 2H, 3-H_{2 butyric acid}), 0.9(t, 3H, 4-H_{3 butyric acid})
 $^{13}\text{C NMR}$: δ 180.4(C-1_{butyric acid}), 178.0(C-1_{acetic acid}), 36.1(C-2_{butyric acid}),
20.9(C-2_{acetic acid}), 18.2(C-3_{butyric acid}), 13.6(C-4_{butyric acid})

(iii) Acetic acid and Pentanoic acid ;

$^1\text{H NMR}$: δ 8.2(s, 1H, 1-H_{pentanoic acid}), 8.1(s, 1H, 1-H_{acetic acid}),
2.4(t, 2H, 2-H_{2 pentanoic acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.6(m, 2H, 3-H_{2 pentanoic acid}), 1.2(m, 2H, 4-H_{2 pentanoic acid}),
0.9(t, 3H, 5-H_{3 pentanoic acid})
 $^{13}\text{C NMR}$: δ 170.7(C-1_{pentanoic acid}), 163.5(C-1_{acetic acid}), 31.4(C-2_{pentanoic acid}),
27.0(C-2_{acetic acid}), 23.6(C-3_{pentanoic acid}), 22.3(C-4_{pentanoic acid}),
15.1(C-5_{pentanoic acid})

(iv) Acetic acid and Hexanoic acid ;

$^1\text{H NMR}$: δ 8.7(s, 1H, 1-H_{hexanoic acid}), 8.1(s, 1H, 1-H_{acetic acid}),
2.5(t, 2H, 2-H_{2 hexanoic acid}), 2.1(s, 3H, 2-H_{3 acetic acid}),
1.2(m, 6H, 3,4,5-H_{2 hexanoic acid}), 0.9(t, 3H, 6-H_{3 hexanoic acid})
 $^{13}\text{C NMR}$: δ 170.6(C-1_{hexanoic acid}), 163.9(C-1_{acetic acid}), 34.1(C-2_{hexanoic acid}),
31.4(C-2_{acetic acid}), 28.9(C-3_{hexanoic acid}), 24.6(C-4_{hexanoic acid}),
22.4(C-5_{hexanoic acid}), 13.9(C-6_{hexanoic acid})

(C) General Procedure for the oxidation of Alkyl Aryl Ketones by QDC

Freshly distilled substrate solutions (0.01 M) and QDC solution (0.02 M) were mixed in the presence of perchloric acid (0.08 M) in 20% aqueous DMF medium at 50 °C. The reaction mixture was stirred under a nitrogen atmosphere for 24h for

completion of the reaction. The organic layer was extracted four times with ether (25 ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na_2SO_4 . The oxidized products [formic acid and benzoic acid (from acetophenone); acetic acid and benzoic acid (from propiophenone); propionic acid and benzoic acid (from butyrophenone); and butyric acid and benzoic acid (from valerophenone)], were obtained after the complete removal of ether. Each reaction product obtained was subjected to NMR (300 MHz ; CDCl_3 / 1 drop DMSO-d_6 ; Me_4Si) analysis, and characterized as follows :

(i) Formic acid and benzoic acid ;

$^1\text{H NMR}$: δ 8.3(s, 1H, 1- $\text{H}_{\text{benzoic acid}}$), 8.2(s, 1H, 1- $\text{H}_{\text{formic acid}}$),
 8.0(d, 2H, 2- $\text{H}_2_{\text{benzoic acid}}$), 7.8(s, 1H, 2- $\text{H}_{\text{formic acid}}$),
 7.6(t, 2H, 3- $\text{H}_2_{\text{benzoic acid}}$), 7.5(t, 1H, 4- $\text{H}_{\text{benzoic acid}}$).

$^{13}\text{C NMR}$: δ 170.6(C-1 $_{\text{benzoic acid}}$), 165.5(C-1 $_{\text{formic acid}}$), 134.1(C-2 $_{\text{benzoic acid}}$),
 130.2(C-3 $_{\text{benzoic acid}}$), 129.6(C-4 $_{\text{benzoic acid}}$), 128.9(C-5 $_{\text{benzoic acid}}$).

(ii) Acetic acid and benzoic acid ;

$^1\text{H NMR}$: δ 11.2(s, 1H, 1- $\text{H}_{\text{benzoic acid}}$), 8.1(d, 2H, 2- $\text{H}_2_{\text{benzoic acid}}$),
 7.6(t, 2H, 3- $\text{H}_2_{\text{benzoic acid}}$), 7.5(t, 1H, 4- $\text{H}_{\text{benzoic acid}}$),
 7.3(s, 1H, 1- $\text{H}_{\text{acetic acid}}$), 2.1(s, 1H, 2- $\text{H}_3_{\text{acetic acid}}$).

$^{13}\text{C NMR}$: δ 177.3(C-1 $_{\text{acetic acid}}$), 171.4(C-1 $_{\text{benzoic acid}}$), 133.3(C-2 $_{\text{benzoic acid}}$),
 129.7(C-3 $_{\text{benzoic acid}}$), 129.1(C-4 $_{\text{benzoic acid}}$), 128.6(C-5 $_{\text{benzoic acid}}$),
 19.7(C-2 $_{\text{acetic acid}}$).

(iii) Propionic acid and Benzoic acid ;

$^1\text{H NMR}$: δ 11.6(s, 1H, 1- $\text{H}_{\text{benzoic acid}}$), 10.6(s, 1H, 1- $\text{H}_{\text{propionic acid}}$),
8.1(d, 2H, 2- H_2 benzoic acid), 7.6(t, 2H, 3- H_2 benzoic acid),
7.4(t, 1H, 4- $\text{H}_{\text{benzoic acid}}$), 2.4(q, 2H, 2- H_2 propionic acid),
1.1(t, 3H, 3- H_3 propionic acid).

$^{13}\text{C NMR}$: δ 181.4(C-1_{propionic acid}), 172.4(C-1_{benzoic acid}), 133.9(C-2_{benzoic acid}),
130.3(C-3_{benzoic acid}), 129.5(C-4_{benzoic acid}), 128.6(C-5_{benzoic acid}),
27.6(C-2_{propionic acid}), 8.9(C-3_{propionic acid}).

(iv) Butyric acid and Benzoic acid ;

$^1\text{H NMR}$: δ 11.4(s, 1H, 1- $\text{H}_{\text{benzoic acid}}$), 10.2(s, 1H, 1- $\text{H}_{\text{butyric acid}}$),
8.1(d, 2H, 2- H_2 benzoic acid), 7.6(t, 2H, 3- H_2 benzoic acid),
7.5(t, 1H, 4- $\text{H}_{\text{benzoic acid}}$), 2.3(t, 2H, 2- H_2 butyric acid),
1.7(m, 2H, 3- H_2 butyric acid), 1.0(t, 3H, 4- H_3 butyric acid).

$^{13}\text{C NMR}$: δ 180.6(C-1_{butyric acid}), 172.4(C-1_{benzoic acid}), 133.8(C-2_{benzoic acid}),
130.2(C-3_{benzoic acid}), 129.5(C-4_{benzoic acid}), 128.5(C-5_{benzoic acid}),
36.1(C-2_{butyric acid}), 18.2(C-3_{butyric acid}), 13.6(C-4_{butyric acid}).

(D) General Procedure for the oxidation of β -Diketones by QDC

Using the same experimental conditions as were used for the kinetic runs, a solution of the reaction mixture was kept under a nitrogen atmosphere for 24 h, with stirring, until the reaction had gone to completion. The evolution of CO_2 was observed. The organic layer was extracted with ether, washed with water and dried over anhydrous Na_2SO_4 . The oxidized products [acetic acid (from acetyl acetone); acetic acid and acetone (from acetonylacetone); and acetic acid and benzoic acid (from benzoyl acetone)] were obtained after the complete removal of ether. Each of the

reaction products obtained was subjected to NMR (300 MHz; CDCl₃; Me₄Si) analysis, and characterized as follows:-

(i) Acetic acid ;

¹H NMR : δ 8.9(s, 1H, 1-H), 2.2(s, 3H, 2-H₃)

¹³C NMR : δ 165.8(C-1), 14.9(C-2)

(ii) Acetic acid and acetone ;

¹H NMR : δ 8.0(s, 1H, 1-H_{acetic acid}), 2.2(s, 3H, 2-H_{3 acetic acid}),
2.0(s, 6H, 1,3-H_{3 acetone})

¹³C NMR : δ 209.5(C-2_{acetone}), 175.7(C-1_{acetic acid}), 30.7(C-1,3_{acetone}),
20.8(C-2_{acetic acid})

(iii) Acetic acid and benzoic acid ;

¹H NMR : δ 11.1(s, 1H, 1-H_{acetic acid}), 8.1(d, 2H, 2-H_{2 benzoic acid}),
8.0(s, 1H, 1-H_{benzoic acid}), 7.6(t, 2H, 3-H_{2 benzoic acid}),
7.5(t, 1H, 4-H_{benzoic acid}), 2.1(s, 3H, 2-H_{3 acetic acid})

¹³C NMR : δ 178.1(C-1_{acetic acid}), 172.2(C-2_{benzoic acid}), 133.9(C-1_{benzoic acid}),
130.3(C-3_{benzoic acid}), 128.6(C-4_{benzoic acid}), 20.8(C-2_{acetic acid})

(E) General Procedure for the oxidation of α-Ketoacids by QDC

A solution of substrate (0.01 M) was mixed with QDC solution (0.02 M) in the presence of perchloric acid (0.08 M) in 20% aqueous-DMF medium at 40°C. The reaction mixture was stirred under a nitrogen atmosphere for 24h for completion of the reaction. The evolution of CO₂ was observed. The organic layer was extracted with ether, washed with water, and dried over anhydrous Na₂SO₄. The oxidized products (acetic acid from pyruvic acid ; and phenylacetic acid from phenylpyruvic acid) were

obtained after the complete removal of ether. Each of the reaction products obtained was subjected to IR (CCl₄) and NMR (CDCl₃; Me₄Si) analyses, and characterized as follows:-

(i) Acetic acid ;

IR : ν 3030 (br s, -OH), 1717 (s, C=O), 1414, 1361, 1291, 941, 619 cm⁻¹

¹H NMR : δ 8.9 (s, 1H, 1-H), 2.2 (s, 3H, 2-H₃)

¹³C NMR : δ 165.8 (C-1), 14.9 (C-2)

(ii) Phenylacetic acid ;

IR : ν 2940 (br s, -OH), 1700 (s, C=O), 1520, 1410, 1350, 1280, 1240, 1190, 1030, 930, 680 cm⁻¹.

¹H NMR : δ 11.2 (s, 1H, 1-H), 8.1 (d, 2H, 4-H₂), 7.6 (t, 2H, 5-H₂), 7.5 (t, 1H, 6-H), 3.6 (s, 2H, 2-H₂).

¹³C NMR : δ 171.4 (C-1), 133.3 (C-3), 129.7 (C-4), 129.1 (C-5), 128.6 (C-6), 16.4 (C-2).

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DISCUSSION

CHAPTER – I

KINETICS OF OXIDATION OF CYCLIC KETONES

Chromic acid has been extensively used for the oxidation of diverse organic substrates. Some of the forms in which Cr(VI) has been used to carry out these oxidation reactions have included : chromic acid in water or in aqueous acetic acid catalyzed by mineral acid; chromic acid in water-acetone mixtures catalyzed by mineral acid; dichromate ion in acetic acid; the chromium trioxide pyridine complex; and tertiary butylchromate in a variety of solvents. Many procedures have been developed to carry out the conversions of various kinds of organic substrates to their respective products using Cr(VI) reagents. While developing these procedures, several newer Cr(VI) reagents have been introduced which have been able to carry out these oxidation processes, giving high yields of the corresponding products, and also achieving a high degree of selectivity. The synthetic utility of these newer reagents have been highlighted for the oxidation of cyclic ketones to their corresponding products. The literature has been reviewed with the purpose of highlighting the various kinds of reagents which have been used for the oxidation of cyclic ketones to their corresponding reaction products.

The kinetics of oxidation of cyclohexanone by chromic acid in aqueous perchloric acid has been reported. This reaction showed a first order dependence on the concentrations of each of the reactants — cyclohexanone, acid, and the total chromic acid concentration. The principal product of this oxidation process was adipic acid. The reaction proceeded via the enolization of cyclohexanone (1).

The kinetics of oxidation of cyclic ketones by alkaline hexacyanoferrate(III) in ethanol-water and pyridine-water mixtures at a constant ionic strength has been reported. The reactions were observed to show a first order dependence on each — substrate, oxidant and alkali concentrations. The rate-determining step involved the formation of a free radical from the enolate anion. The products obtained were the corresponding open-chain dibasic acids (2).

The kinetics of the acid permanganate oxidation of cyclohexanone showed a first order dependence on the concentrations of each of the reactants — cyclohexanone, oxidant, and the hydrogen ion. Two mechanisms were proposed for this oxidation process. The first one involved the formation of a carbocation, and the second mechanism suggested the attack of the permanganate on the enol form of the substrate. The product obtained from this oxidation reaction was mainly cyclohexane-1,2-dione (3).

The kinetics of oxidation of cyclic ketones by vanadium(V) in acid medium attempted to suggest correlations between the conformation and reactivity of these cyclic ketones. The reactions were first order each in substrate and oxidant concentrations, and showed a first order dependence on the Hammett acidity constant, h_0 . The products obtained were the corresponding open-chain dibasic acids (4).

Cerium(IV) in perchloric acid medium has been used for the oxidation of cyclic ketones. The oxidation reactions were reported to be first order each in substrate and oxidant concentrations, and showed a dependence of unity on the Hammett acidity constant, h_0 . The products obtained were the corresponding 2-hydroxyketones (5).

The kinetics of oxidation of cyclic ketones by potassium permanganate in aqueous acetic acid at constant ionic strength has been reported. The reactions were found to be first order each in the substrate and oxidant concentrations. The rate-determining step involved a two-electron transfer from the enol resulting in an oxonium ion, which was converted very rapidly to the open-chain dibasic acids (6).

The kinetics of the lead tetraacetate oxidation of cyclic ketones in different solvent mixtures showed a first order dependence on the substrate, and zero order dependence on lead tetracetate. The rate-determining step of this reaction involved the enolization of the ketones (7).

The oxidation kinetics of cyclooctanone by N-bromosuccinimide (NBS) in acid media involved an intermediate formed by the interaction between the enol form of the substrate and NBS. The reaction showed a first order dependence on each — cyclooctanone and oxidant. It was shown that one mole of cyclooctanone consumed two moles of NBS, giving cyclooctane-1,2-dione as the major product (8).

The kinetics of oxidation of cyclic ketones by chloramine-T (CAT) in aqueous ethanol medium under alkaline conditions has been studied. The reaction showed a first order dependence on the concentrations of each — CAT, substrate and alkali. The products obtained were the corresponding 1,2-diketones (9).

The kinetics and mechanism of Tl(III) oxidation of cyclic ketones showed a first order dependence on each — substrate and acid, but exhibited a zero order dependence

on oxidant. The mechanistic pathway postulated was through a rate-determining enolization. The products obtained were the corresponding acetoxy derivatives (10).

The catalytic role of ruthenium(III) in effecting facile cleavage of cyclic ketones using potassium bromate in acid medium has been reported. The reaction exhibited a first order dependence on substrate and acid concentrations, and a zero order dependence on the concentration of the oxidant. The mechanism involved the enolization of the ketones in the slow step, followed by the cleavage of the intermediate enol-Ru(III) complex by bromate. The products obtained were the corresponding cycloalkane-1,2-diones (11).

The oxidation of cyclic ketones with phenyl iodosoacetate in acetic acid-sulphuric acid media showed a first order dependence on the substrate and acid concentrations, but exhibited zero order dependence on the oxidant. The products obtained were the corresponding acetoxy compounds (12).

The kinetics of the Os(VIII)-catalyzed oxidation of cyclic ketones by periodate showed a first order dependence on the ketone, OsO_4 , and alkali concentrations in the range 0.008 – 0.038 M. These reaction exhibited zero order kinetics in [periodate]. The mechanistic pathway was an initial ester formation between Os(VIII) and the enolate ion in the rate-determining step. The final products obtained were the corresponding dibasic acids (13).

While highlighting the importance of electron-transfer oxidation reactions of organic compounds, the oxidation of cyclohexanone by tris-2,2'-bipyridylruthenium(III)

perchlorate was carried out. The rate-determining step was a non-bonded electron transfer process from the enol form of the substrate, giving rise to a free radical and a Ru(II) species (14).

The oxidation of cyclohexanone by aquacerium(IV) in acid perchlorate solution showed a first order dependence on [Ce(IV)], an order <1 on cyclohexanone, and a zero order dependence on $[H^+]$. The product obtained was adipic acid. The rate of oxidation of cyclohexanone was much greater than its rate of enolization, thereby supporting the oxidation of cyclohexanone in its keto-form (15).

The oxidation of cyclohexanone by potassium bis(tellurato)cuprate(III), in aqueous alkaline medium showed a complex dependence on both ketone and alkali concentrations. The reaction showed an inverse dependence on the concentration of tellurate ion. The rate-determining step was the conversion of the complex of (tellurato) cuprate(III) ion to a radical and a Cu(II) species (16).

The kinetics of oxidation of cyclic ketones by N-bromosaccharin in aqueous acetic acid medium showed a first order dependence with respect to [ketone] and $[H^+]$, but was independent of [oxidant]. The corresponding diketones were obtained as the products (17).

Kinetic investigations on the oxidation of cyclic ketones by bromamine-T (BAT) in perchloric acidic media have been reported. The reaction followed first order kinetics with respect to [cyclic ketones] and $[H^+]$, but exhibited a zero order dependence on

[BAT]. The rate-determining step involved the enolization of the ketone. The end products were the corresponding 1,2-diketones (18).

Correlations between structure and reactivity of cyclic ketones were attempted using trichloroisocyanuric acid in aqueous acetic acid media, in the presence of perchloric acid. The reaction was acid-catalyzed, and exhibited a first order dependence each on [acid] and [substrate], and zero order dependence on [oxidant]. The reaction pathway involved the enolization of ketone in the rate-determining step, and the reaction between enol and oxidant as the fast step. The products obtained were monochloro ketones (19).

Nitric acid has been used as a rapid, versatile, and economical oxidant for converting cyclic ketones to the corresponding dibasic acids in good yields (20).

The kinetics of oxidation of cyclic ketones by periodate in the presence of a mixture of two metal ions, such as Os(VIII) and Ru(III) as catalysts, has been studied in alkaline media. The products of oxidation in all the cases were dicarboxylic acids (21).

The kinetics of Ag(I) catalyzed oxidation of cyclic ketones by peroxydisulphate ion showed a first order dependence on $[S_2O_8^{2-}]$, [Ag(I)], and a zero order dependence on [substrate]. The mechanism was through the formation of a radical intermediate. In each case, the final product of the reaction was found to be the diketone (22).

The aqueous high pressure-temperature oxidation and enolization of cyclohexanone showed a first order dependence on [cyclohexanone] and a fractional order (0.5) on [oxygen]. The rate of oxidation was much less than the rate of enolization.

A mechanism was postulated whereby an oxygen molecule formed a transitory adduct with two enolates of cyclohexanone (23). This oxidation reaction of cyclohexanone, using aqueous high pressure - temperature conditions, was found to be strongly catalyzed by silver, iron(III), and copper ions, but not by aluminium, cobalt, manganese(II), or nickel ions (24).

The kinetics of oxidation of cyclopentanone and cyclohexanone by chloramine-B (CAB) in hydrochloric acid and perchloric acid media have been studied. The rate of oxidation showed a first order dependence on the concentrations of each of the reactants — substrate, oxidant, and acid. The formation of 1,2-diketones as the products was confirmed by spectral analysis. The mechanism involved the reaction of the enol form of the substrate with the oxidant in the rate-determining step (25).

The kinetics of electron transfer from cyclic ketones to the Ni(IV)-periodate complex in aqueous alkaline medium showed a first-order dependence each on [Ni(IV)], and [cyclic ketones], and a fractional order dependence on [OH⁻]. The products were identified as the corresponding dicarboxylic acids. The mechanism involved the formation of an adduct between the enol and the oxidant in the rate-determining step of the reaction (26).

The oxidation of cyclic ketones by acid bromate showed that the reaction was first order in both, [ketone] and [acid]. The mechanism involved the attack of the acid bromate on the enol form of the ketone in the rate-determining step of the reaction (27).

The kinetics of oxidation of cyclohexanone by dodecatungstocobaltate(III) was investigated in aqueous acidic media. A first order dependence in complex was obtained at high acid and low oxidant concentrations. A zero-order rate was obtained at high oxidant and low acid concentrations. The mechanism postulated involved the enol as the reactive species. The oxidation product was identified as adipic acid (28).

The kinetics of oxidation of cyclic ketones by diperiodatoargentate(III) in alkaline medium was studied both in the absence and presence of Os(VIII) as catalyst. The reaction rate decreased with an increase in periodate, but showed an increase with an increase in OH⁻ ions. The products obtained were the corresponding 2-hydroxy cycloalkanones (29).

The kinetics of oxidation of cyclopentanone and cyclohexanone by 2,6-dichlorophenol indophenol was investigated in the presence of alkali. The reactions showed a first order dependence on [cyclic ketones], and a second order dependence with respect to [2,6-dichlorophenol indophenol]. The final products obtained were the leuco dyes (30).

The Os(VIII)-catalyzed oxidation of cyclopentanone and cyclohexanone by alkaline hexacyanoferrate(III) ions was zero order with respect to [Fe(CN)₆]³⁻ and first order with respect [OH⁻]. The primary product of the oxidation of cyclohexanone was the corresponding α-hydroxy ketone, which was oxidized to adipic acid when an excess of [Fe(CN)₆]³⁻ was used. The rate data indicated that the keto form of the substrate was oxidized by Os(VIII) in alkaline media (31).

The kinetics of oxidation of cyclic ketones by pyridinium fluorochromate (PFC) in aqueous acetic acid media, in the presence of perchloric acid, showed a first order dependence on the concentrations of each of the reactants — oxidant, acid, and substrate. The rate-determining step involved a two electron transfer from the enol to PFC. The products obtained were the corresponding 1,2-diketones (32).

PRESENT WORK

The oxidation of cyclic ketones is an important transformation in organic synthesis. The nature of products obtained was dependent on the structure of the cyclic ketones. Among the many oxidizing agents which have been used for the oxidation of cyclic ketones, chromium(VI) reagents have proved to be versatile and efficient in performing these oxidation reactions.

The present work is a detailed kinetic investigation of the oxidation of cyclic ketones, using a newer chromium(VI) reagent. The chromium(VI) reagent which has been employed for the purpose of oxidation of cyclic ketones in the present study, has been quinolinium dichromate (QDC) in 20% acetic acid medium, in acid medium, under a nitrogen atmosphere.

The cyclic ketones which have been chosen for the purpose of oxidation by QDC have included :

(a) Cyclopentanone; (b) Cyclohexanone; (c) Cycloheptanone; and (d) Cyclooctanone

Stoichiometry (vide "Experimental")

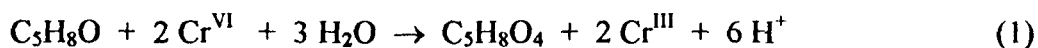
The stoichiometric experiments were performed under nitrogen at 323 K, under the conditions of $[QDC]_0 > [cyclic\ ketone]_0$, at varying acid concentrations. The disappearance of Cr(VI) was followed until the absorbance values became constant. The $[QDC]_\infty$ was estimated. Stoichiometric ratios, $\Delta[QDC] / \Delta[Substrate]$, in the range 1.98 - 2.03, were obtained (Table 1).

Table 1 : Stoichiometries of the Oxidation of the Substrates**([Substrate] = 0.005 M; T = 323 K)**

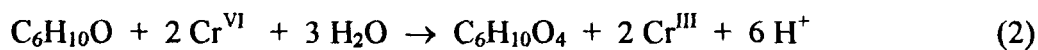
[H ₂ SO ₄] / M	0.10	0.25	0.50
10 ² [QDC] / M	2.50	2.60	2.70
Δ[QDC] / Δ[Cyclopentanone]	1.99	2.01	1.98
Δ[QDC] / Δ[Cyclohexanone]	2.03	1.98	1.99
Δ[QDC] / Δ[Cycloheptanone]	1.99	2.03	2.00
Δ[QDC] / Δ[Cyclooctanone]	2.02	1.98	2.01

The observed stoichiometric ratios conformed to the overall equations :

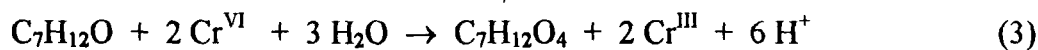
(a) For cyclopentanone :



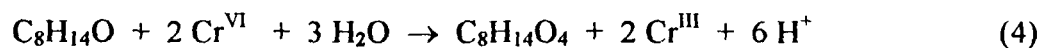
(b) For cyclohexanone :



(c) For cycloheptanone :



(d) For cyclooctanone :



Effect of Substrate

The rate of the reaction was observed to be dependent on the concentration of the substrates. The order of the reaction with respect to substrate concentration was obtained by changing the concentration of the substrate, and observing the effect on the rate of the reaction at constant [QDC] and $[H^+]$. The results have been given in Table 2.

Table 2 : Dependence of Rate Constants on the Concentration of Cyclic Ketones([QDC] = 0.001 M; [H₂SO₄] = 1.0 M; [AcOH] = 20% (v/v); T = 323 K)

[Substrate] / M	$10^4 k_1 / s^{-1}$			
	Cyclopentanone	Cyclohexanone	Cycloheptanone ^a	Cyclooctanone
0.1	0.70	3.34	0.51	2.06
0.25	1.75	8.09	1.21	5.10
0.50	3.51	16.5	2.59	10.3
0.75	5.24	24.4	-	-
1.0	7.07	33.0	-	-
	$10^3 k_2 / M^{-1} s^{-1}$			
	0.70	0.33	0.51	0.21
	0.70	0.32	0.48	0.20
	0.70	0.33	0.52	0.21
	0.69	0.32	-	-
	0.71	0.33	-	-

$k_2 = k_1 / [\text{Substrate}]$

^a sparingly soluble at concentrations higher than 0.5 M

Plots of k_1 , the pseudo-first-order rate constant, against the concentrations of substrates, gave straight lines passing through the origin (Figure 1), indicating that the rate of oxidation was dependent on the first power of the concentration of the substrate.

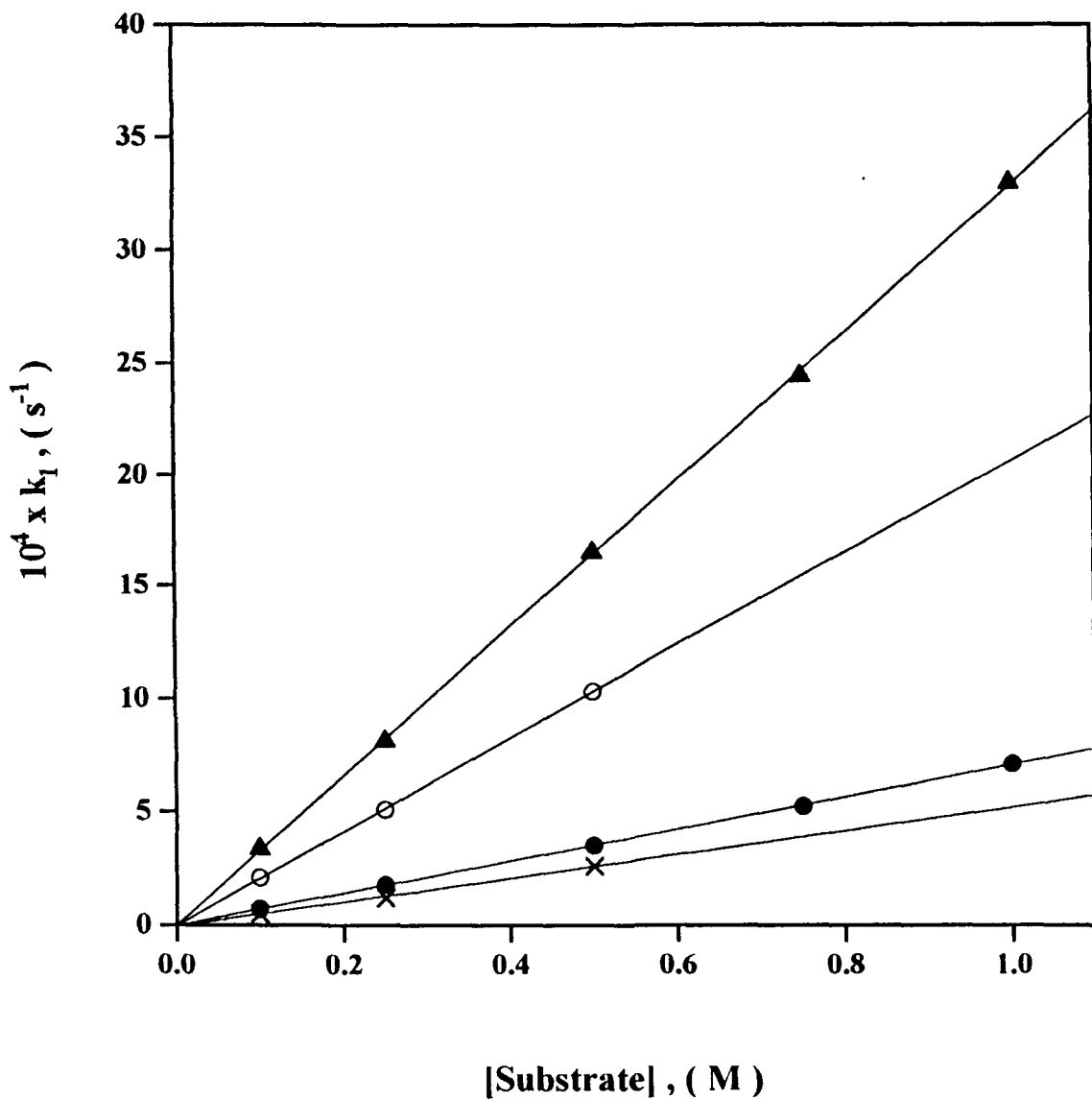


Fig. 1. Plots of k_1 against the concentrations of substrates for cyclopentanone (●), cyclohexanone (▲), cycloheptanone (×) and cyclooctanone (○).

This was further confirmed by the constancy in the values of k_2 , the second-order rate constant.

Effect of oxidant

Under pseudo-first-order conditions, individual kinetic runs were first order with respect to the concentration of the oxidant (QDC). At fixed [acid] and with the substrate taken in excess, the plots of log absorbance versus time were linear, indicating a first order dependence on QDC. When a constant concentration of substrate (large excess) was used, k_1 did not show any appreciable variation with the change in the concentration of the oxidant. This indicated a first-order dependence of the rate of the reaction on the concentration of the oxidant (Table 3)

Table 3 : Dependence of Rate Constants on the Concentration of Oxidant

([Substrate] = 0.1 M; [H₂SO₄] = 1.0 M; [AcOH] = 20% (v/v); T = 323 K)

$10^4 k_1 / s^{-1}$				
10^3 [QDC] / M	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
0.25	0.69	3.31	0.53	1.99
0.50	0.68	3.33	0.50	2.03
0.75	0.71	3.30	0.52	1.98
1.0	0.70	3.34	0.51	2.06

Effect of acid

The reaction was observed to be susceptible to changes in acid concentration, and the rate of the reaction was found to increase with an increase in the concentration of acid, in the range 0.50 M to 1.50 M (Table 4).

Table 4 : Dependence of Rate Constants on Acid Concentration for Cyclic Ketones
([Substrate] = 0.1 M; [QDC] = 0.001 M; [AcOH] = 20% (v/v); T = 323 K)

[H ₂ SO ₄] / M	10 ⁴ k ₁ / s ⁻¹			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
0.50	0.35	1.67	0.25	0.99
0.75	0.48	2.42	0.38	1.60
1.0	0.70	3.34	0.51	2.06
1.25	0.84	4.41	0.64	2.59
1.50	1.05	5.01	0.76	3.10

Plots of log k₁ against log [H⁺] were linear, with slopes equal to unity (Figure 2), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

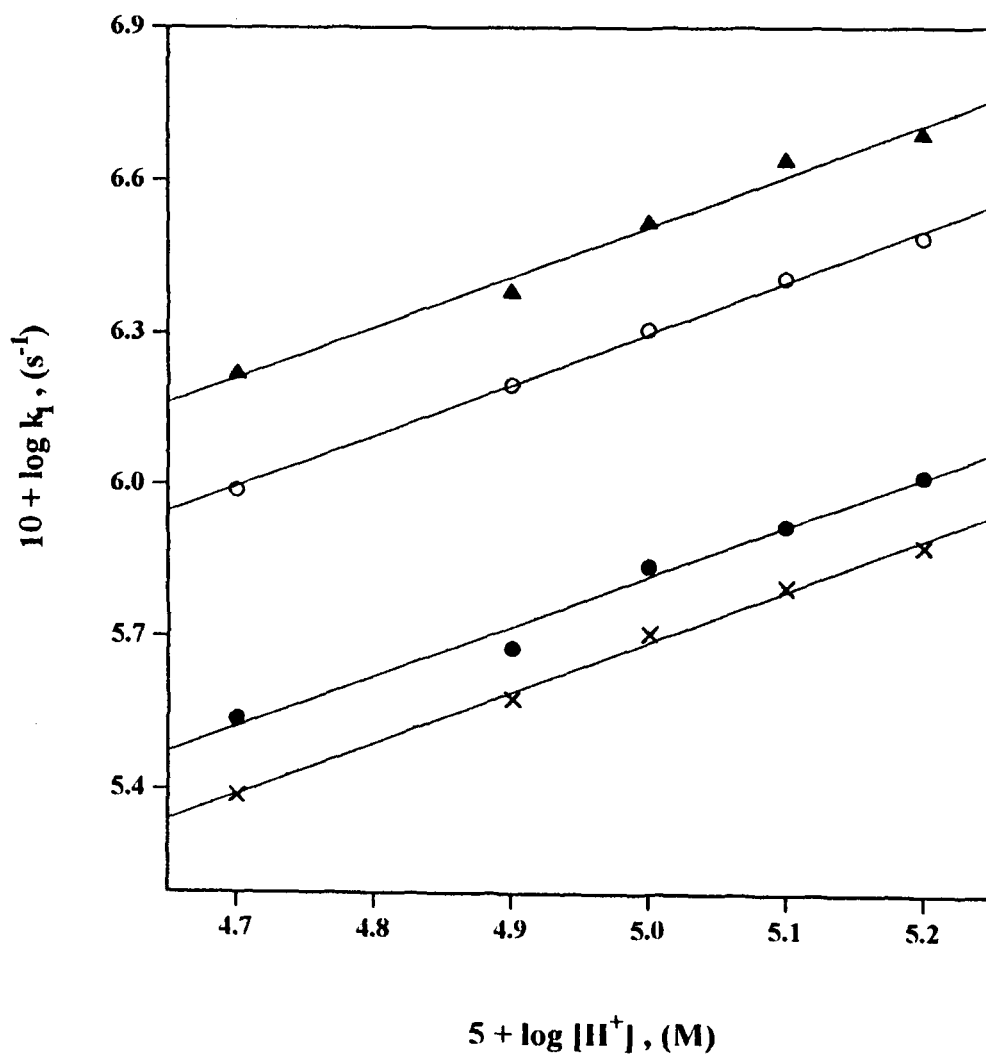


Fig. 2. Plots of $\log k_1$ against $\log [H^+]$ for cyclopentanone (●), cyclohexanone (▲), cycloheptanone (×) and cyclooctanone (○).

The linear increase in the rate of the reaction with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step. There have been earlier reports of the involvement of protonated Cr(VI) species in chromic acid oxidations (33). Protonated Cr(VI) species have been observed in earlier investigations (34). The acid catalysis must be related to the structure of the oxidant (QDC), which was converted to a protonated species at the concentrations of mineral acid used. Quinolinium dichromate is a dimetallic species, an anionic condensed form of chromic acid. Aqueous solutions of chromic acid contain ions such as CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, besides other protonated species such as $\text{H}_2\text{Cr}_2\text{O}_7$, HCr_2O_7^- and H_2CrO_4 (35). The ionization constant for $\text{HCrO}_4^- \rightleftharpoons \text{H}^+ + \text{CrO}_4^{2-}$ is $3.0 \times 10^{-7} \text{ mol / l}$; hence, in dilute aqueous acid, the concentration of CrO_4^{2-} ions is negligible. This has been amply substantiated by Michel et al. (36), who examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate HCrO_4^- does not exist in aqueous solutions of Cr(VI) compounds. The ionization constant for the HCr_2O_7^- ion, $\text{HCr}_2\text{O}_7^- \rightleftharpoons \text{H}^+ + \text{Cr}_2\text{O}_7^{2-}$ is 0.85 mol / l ; hence, in solutions where $\text{pH} \geq 1$, the ionization may be considered essentially complete. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of mineral acid will be HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. These ions are in equilibrium with each other, according to the equation given by $\text{CrO}_4^{2-} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ ($K_d = 35.5$). According to this equilibrium, an increase of the hydrochromate concentration should be significant with dilution. When the Raman lines were examined under dilution, it was established that at $\text{pH} = 11$, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion, whereas at $\text{pH} = 1.2$, it was 100% as the

$\text{Cr}_2\text{O}_7^{2-}$ ion (36). Hence, at concentrations of acid larger than 0.05 M, the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, spectral studies have shown that $\text{Cr}_2\text{O}_7^{2-}$ was the predominant species (37). In the present investigation, since the acid concentrations used were in the range 0.5 to 1.5 M, the dichromate ion (or its protonated form) would be the predominant species. Moreover, the protonated Cr(VI) species would be a more reactive electrophile capable of increasing its rate of coordination to the enol form of the cyclic ketones.

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been employed for all the kinetic runs, the observed rate law could be expressed as :

$$\text{Rate} = - \frac{d[\text{QDC}]}{dt} = k [\text{Substrate}] [\text{QDC}] [\text{H}^+] \quad (5)$$

Effect of solvent

Reactions involving ionic reactants are susceptible to solvent influences. It is hence to be expected that, in the present investigation, the solvent should be playing an important role in these reactions. In the case of each of the substrates oxidized by quinolinium dichromate, the rate of oxidation was slowest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of acetic acid resulted in an increase in the rate of oxidation (Table 5).

Table 5 : Dependence of Rate Constants on Solvent Composition for Cyclic Ketones ([Substrate] = 0.1 M; [QDC] = 0.001 M; [H₂SO₄] = 1.0 M; T = 323K)

H ₂ O:AcOH (%, v/v)	Dielectric Constant (D)	10 ⁴ k ₁ / s ⁻¹			
		Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
95:5	76.5	0.38	2.99	0.30	1.58
90:10	72.8	0.46	3.11	0.35	1.70
85:15	69.1	0.56	3.21	0.41	1.82
80:20	65.4	0.70	3.34	0.51	2.06

The dielectric constants for water-acetic acid mixtures have been estimated approximately from the dielectric constants of the pure solvents (at 323 K : water = 69.9; acetic acid = 6.5) (38).

In the present investigation, in proceeding from 5% acetic acid to 20% acetic acid, the polarity decreases. The decrease in the polarity of the medium resulted in an increase in the rate of the reaction (Table 5). Plots of log k₁ against the reciprocal of the dielectric constant were linear (Figure 3), with positive slopes. This suggested an interaction between a positive ion and a dipole (39), and was in conformity with the experimental observation that, in the presence of an acid, there was the involvement of a protonated

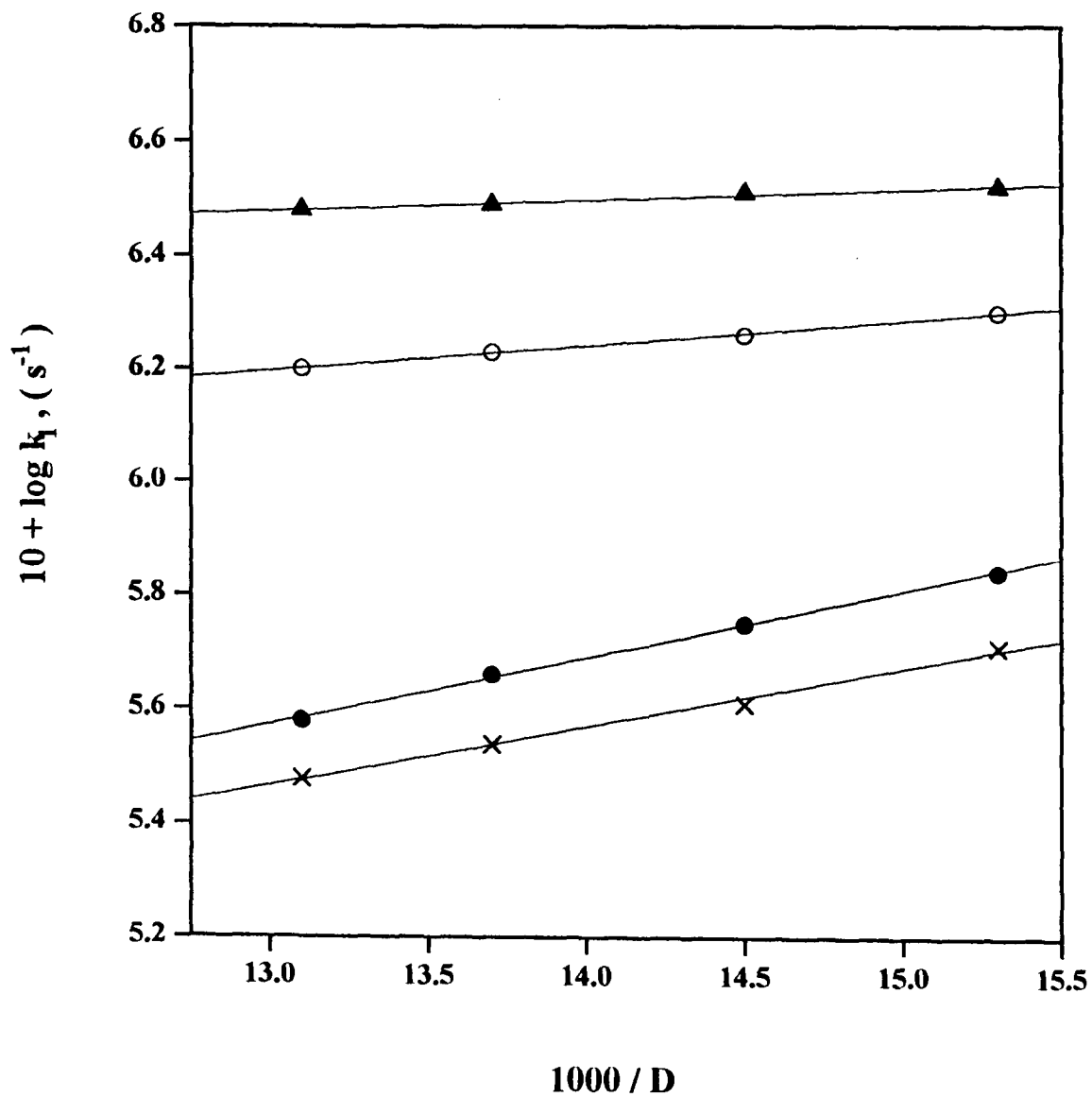


Fig. 3. Plots of $\log k_1$ against the reciprocal of the dielectric constant for cyclopentanone (●), cyclohexanone (▲), cycloheptanone (×) and cyclooctanone (○).

Cr(VI) species. The data in Table 5 indicated that the dielectric constants for water-acetic acid mixtures were a linear function of the solvent composition used in this investigation. This relationship between $\log k_1$ and $1 / D$ was thus obeyed in the range of dielectric constants used.

If the solvating power of the solvent were to be taken into consideration, one could predict a correlation between the rate of the reaction and the nature of the solvent media. It would be expected that the total solvation of an ion and a dipole (initial state) should be greater than the solvation of the transition state formed by their union. The transition state would thus be less polar than the initial state (reactants) because of the increase dispersal of charges in the transition state (40). Therefore, the decrease in the rate of oxidation, on the addition of a more polar solvent, as in the present investigation, would be the result of a progressive decrease in solvation of the transition state. The effect of a change in the solvent composition on the rates of reactions would also be dependent on factors such as solvent-solute interactions (41, 42), and on solvent structure.

Effect of temperature

The rates of the oxidation reactions were influenced by changes in temperature. It was observed that an increase in temperature resulted in an increase in the rate of the reaction (Table 6).

Table 6 : Dependence of Rate Constants on Temperature for Cyclic Ketones**([Substrate] = 0.1 M; [QDC] = 0.001 M; [H₂SO₄] = 1.0 M;****[AcOH] = 20%(v/v))**

Temperature (± 0.1K)	$10^4 k_1 / s^{-1}$			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
313	0.32	1.81	0.21	0.96
318	0.50	2.50	0.36	1.23
323	0.70	3.34	0.51	2.06
328	0.93	4.51	0.72	2.51
333	1.41	5.32	0.98	3.55

Plots of $\log k_1$ against the reciprocal of temperature were linear (Figure 4), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies of the reactions. The other activation parameters were evaluated (vide "Experimental : Calculations") and have been shown in Table 7.

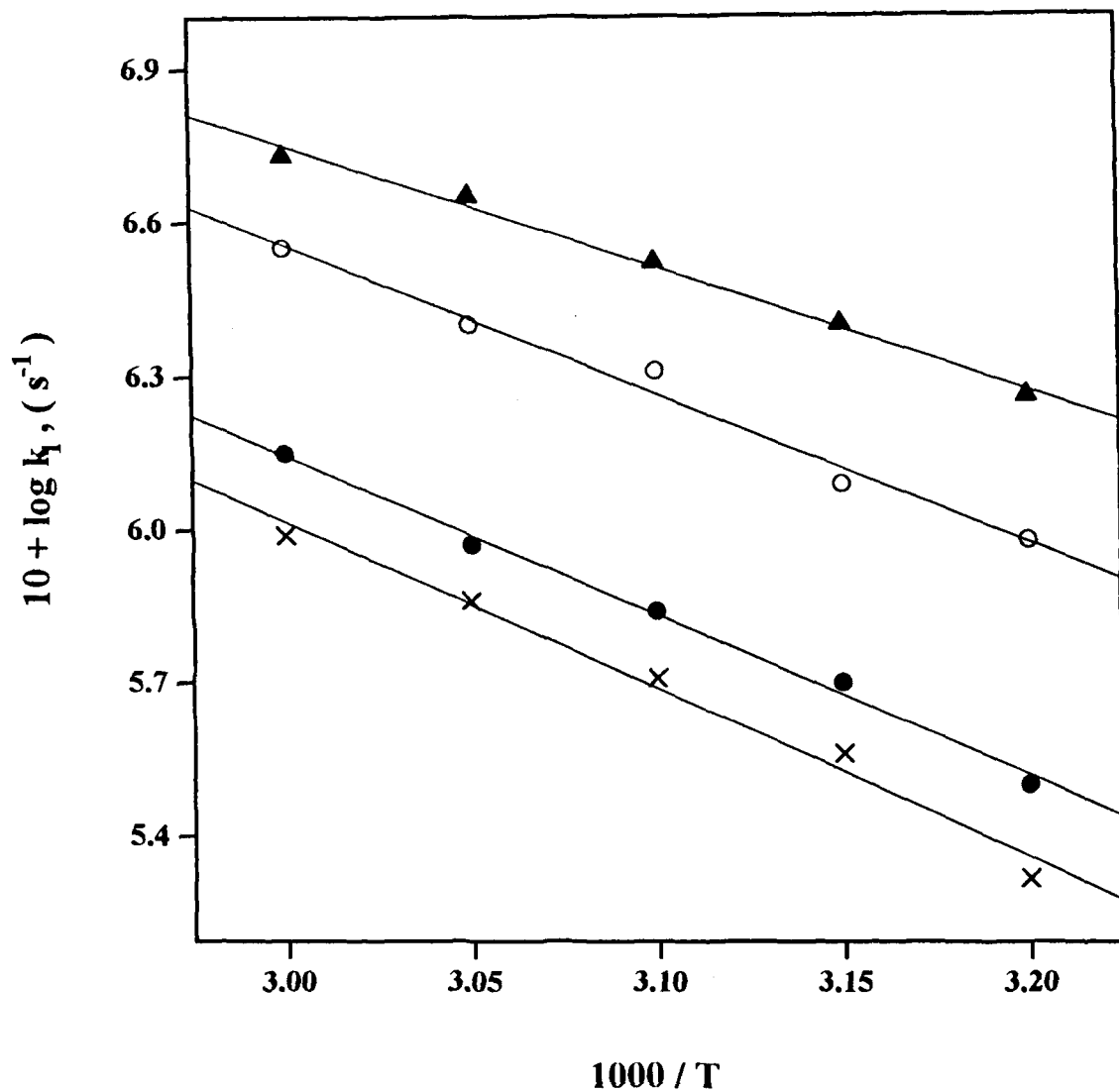


Fig. 4. Plots of $\log k_1$ against the reciprocal of temperature for cyclopentanone (●), cyclohexanone (▲), cycloheptanone (×) and cyclooctanone (○).

Table 7 : Activation Parameters for Cyclic Ketones ^a

Substrate	E (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
Cyclopentanone	63	61	-141	102
Cyclohexanone	48	47	-173	97
Cycloheptanone	65	64	-134	103
Cyclooctanone	58	56	-152	99

^aError limits : E \pm 2 kJ mol⁻¹; $\Delta H^\ddagger \pm$ 2 kJ mol⁻¹; $\Delta S^\ddagger \pm$ 5 JK⁻¹ mol⁻¹;
 $\Delta G^\ddagger \pm$ 2 kJ mol⁻¹.

The oxidation of all the substrates were characterized by negative entropies of activation. This would suggest an ordered transition state, relative to the reactants (43). The large negative values of ΔS^\ddagger in all cases thus provided support for the formation of a more rigid activated complex. Differences in solvation of the substrate in the ground state and in the transition state might also contribute to the negative entropies of activation. The similarity of ΔG^\ddagger values for the oxidation of all the substrates arose due to the changes in ΔH^\ddagger and ΔS^\ddagger values, and stressed the probability that these oxidation reactions involved similar rate-determining steps.

Isokinetic relationship

The enthalpies and entropies of activation for a reaction are linearly related by the equation

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (6)$$

where β is the isokinetic temperature. For the oxidation reactions studied in the present investigation, the activation enthalpies and entropies were linearly related. The correlation was tested and found to be valid by applying Exner's criterion (44). The isokinetic temperature, obtained from the plot of ΔH^\ddagger against ΔS^\ddagger , was 437K (Figure 5). Although current views do not attach much physical significance to isokinetic temperatures (45), a linear correlation between ΔH^\ddagger and ΔS^\ddagger is usually a necessary condition for the validity of the Hammett equation (linear free energy relationships). Further, the values for the free energies of activation (ΔG^\ddagger) were nearly constant, indicating that the same mechanism operated for the oxidation of all the cyclic ketones studied in this investigation.

Induced polymerization

In the present investigation, since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (46). This indicated that a one-electron oxidation was unlikely. Control experiments were

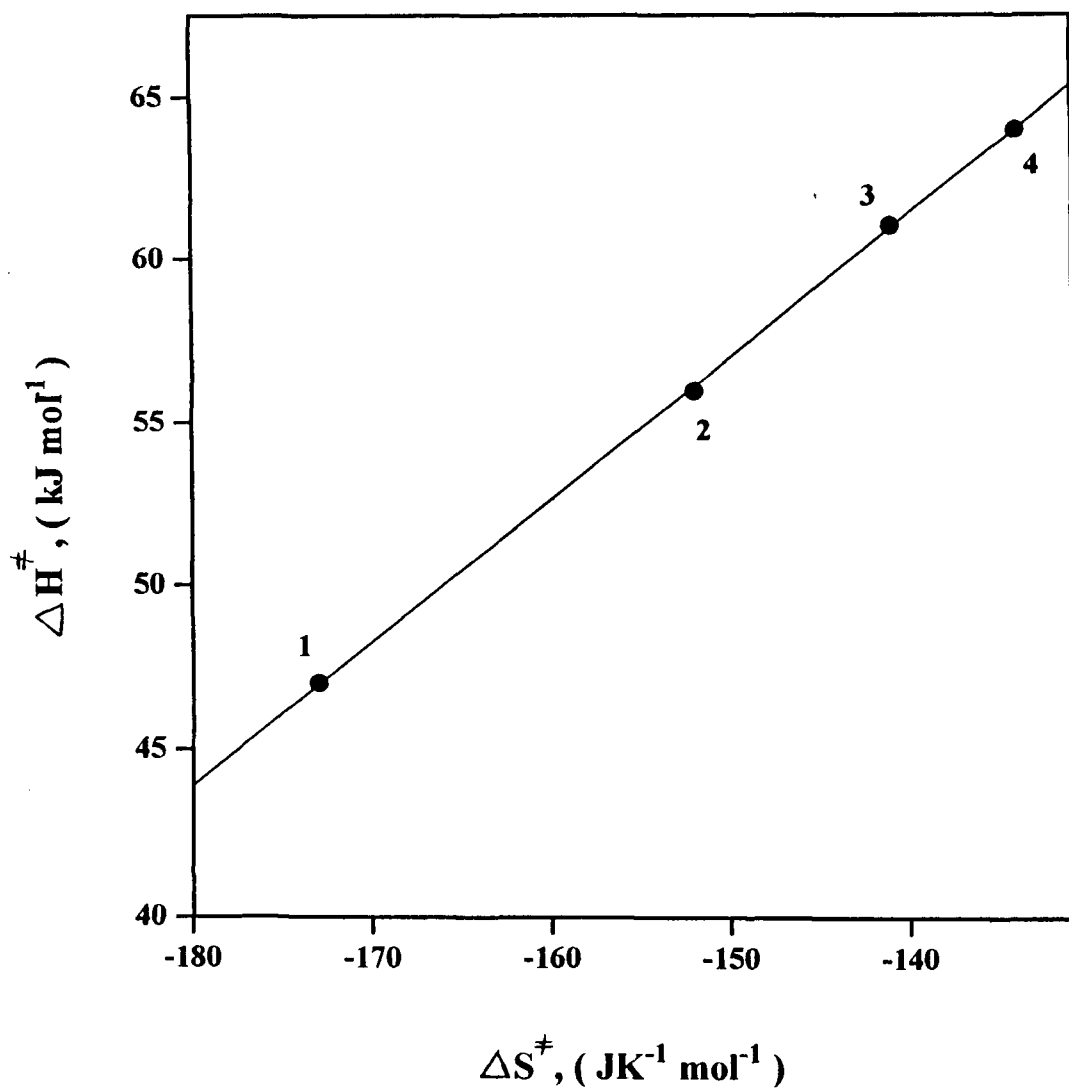


Fig. 5. Plots of ΔH^\ddagger against ΔS^\ddagger for cyclopentanone (3), cyclohexanone (1), cycloheptanone (4) and cyclooctanone (2).

performed in the absence of the respective substrates. The concentration of the oxidant (QDC) did not show any appreciable change.

Spectral data

The IR and NMR data were obtained for each of the products formed (Table 8).

Table 8 : Magnetic Resonance and Infrared Data

Cyclic Ketones	Oxidized Products	^1H (-COOH) δ (ppm)	^{13}C (-COOH) δ (ppm)	IR ($\nu_{\text{C=O}}$) (cm^{-1})
Cyclopentanone	Glutaric acid	5.49	175.50	1688
Cyclohexanone	Adipic acid	6.77	176.03	1724
Cycloheptanone	Pimelic acid	5.45	175.37	1663
Cyclooctanone	Suberic acid	6.73	175.87	1695

The magnetic resonance spectra (^1H and ^{13}C) for the oxidized products from cyclic ketones were obtained and the location of peaks for the characteristic carboxylic acid groups of the open-chain dibasic acids have been shown (Table 8). The chemical shifts are in consonance with the rates of oxidation as shown in Table 8, suggesting a direct correlation between NMR absorption and the rates of reactions. Since magnetic transitions occur very slowly in contrast to electronic transitions, the NMR spectra would correspond to an average conformation of each of the cyclic ketones under investigation.

The IR spectra were recorded for each of the products obtained from the oxidation of the cyclic ketones. The $\nu_{C=O}$ for each of the products has been shown in Table 8. A quantitative relationship was observed between the oxidation rates (shown in Table 2) and the IR stretching frequencies of the carbonyl groups (dibasic acids as the products in each case), indicating that the transition state was more product-like in character. This would favour the conversion of the ketone to a cleavage product (dibasic acids). Such a correlation provided an extremely useful semi-empirical relationship for the prediction of oxidation rates. An earlier investigation had established a quantitative correlation between $\nu_{C=O}$ and solvolysis rates for organic compounds (47).

Structural influences on the rates of oxidation

Reaction rates for cyclic compounds have been rationalized by the difference in strain energy between the ground state and the transition state of the molecule in the process considered (48). For example, the rates of oxidation of secondary alcohols with chromic acid were interpreted on the basis of an increase or decrease of steric strain during the conversion of the sp^3 hybridized alcohol to the sp^2 hybridized ketone (33, 49). For cyclic systems, in general, changes in bond hybridization produced concomitant changes in angle strain (Baeyer strain), bond opposition strain (Torsional or Pitzer strain) or transannular strain (50).

(a) Earlier work

For the oxidation of cyclic ketones by hexacyanoferrate(III) in alkaline medium, the observed order of reactivity was $6 > 5 > 8 > 7$ (2). The results were consistent

with the studies on the determination of the enol content of the cyclic alkanones (51), where it was observed that the enol content alternates with ring size $6 > 5 > 8 > 7$.

The kinetics of oxidation of cyclic ketones by V(V) in acid medium revealed an order of reactivity $6 > 5 > 8 > 7$ (4).

The kinetics of oxidation of cyclic ketones by Ce(IV) in perchloric acid medium showed that the order of reactivity was $6 > 8 > 7 \sim 5$. This order of reactivity was rationalized on the basis of conformational analysis (5).

The kinetics of oxidation of cyclic ketone by potassium permanganate in aqueous acetic acid showed the order of reactivity to be : $6 > 8 > 5 > 7$. It was suggested that the reaction proceeded via the enol form of the ketone, and the oxidant was the permanganate ion (6).

The oxidation of cyclic ketones by lead tetraacetate showed an order of reactivity $6 > 8 > 5 > 7$. It was correlated that the order of reactivity was in consonance with the stability of the enols in the series (7).

The kinetics of oxidation of cyclic ketone by thallium triacetate was investigated, and the order of reactivity observed was : $6 > 8 > 5 > 7$. The Tl(III) functions as a two-electron oxidant reacting with the enol of the ketones to give the intermediate oxonium ion in a fast step involving a two-electron transfer (10).

The kinetics of the Ru(III) catalyzed oxidation of cyclic ketones by potassium bromate in acid medium showed an order of reactivity $6 \sim 8 > 5 > 7$.

Cyclohexanone was essentially free of strain, but due to eclipsing of the carbonyl oxygen by the equatorial hydrogen at C-2 and C-6, the strain seemed to be relieved when there was a change in the state of hybridization of the carbonyl oxygen from sp^2 to sp^3 (11).

The oxidation of cyclic ketones by phenyl iodosoacetate in acetic acid – sulphuric acid media showed that the reactivity varied with ring size in the order $6 > 8 > 5 > 7$. This order of reactivity was correlated with the rate of enol formation which exhibited a similar order of reactivity (12).

The Os(VIII)-catalyzed oxidation of cyclic ketone by periodate showed the order of reactivity to be $6 > 5 > 7$. The higher rate of oxidation of cyclohexanone was ascribed to the higher enolate content of cyclohexanone responsible for the formation of the complex (13).

The reactivity pattern obtained in the case of cyclic ketones was $6 > 5 > 7$ for the oxidation of cyclic ketones by N-bromosaccharin in aqueous acetic acid medium. This order of reactivity seemed to parallel the order of their enol content (17).

A comparative study of the role of Os(VIII), Ru(III), and Os(VIII)+Ru(III) catalyzed oxidation of cyclic ketones by periodate in alkaline medium suggested an order of reactivity $6 > 5 > 7$. The higher enolization constant of cyclohexanone was taken to be the most important factor responsible for the greater reactivity of cyclohexanone (21).

The observed oxidation rate was found to decrease in the order $6 > 8 > 5 > 7$, for the oxidation of cyclic ketones by the nickel(IV) periodate complex in aqueous

alkaline medium. This was probably due to the enolic content of the cyclic ketones decreasing in the same order (26).

In the acid bromate oxidation of cyclic ketones, the order of reactivity was found to be $8 > 6 > 7$. The results were consistent with the enol contents of the cyclic ketones, wherein the higher enolization constant of cyclohexanone contributed towards its greater reactivity compared to that of cycloheptanone (27).

The Os(VIII) catalyzed and uncatalyzed oxidation of cyclic ketones by diperiodatoargentate (III), in alkaline medium, showed an order of reactivity $6 > 5 > 7$. The rate being lowest for cycloheptanone was accounted for by the twist-chair conformation of cycloheptanone which was generally presumed to be its most favoured conformation (29).

The rate constants for the oxidation of cyclic ketones by pyridinium fluorochromate (PFC) showed an order of reactivity $6 > 8 \sim 7 > 5$. The possible explanation given for this was based on the concept of I-strain in these rings (32).

(b) Present work

In the present investigation, the order of reactivity for the oxidation of cyclic ketones by quinolinium dichromate (QDC) was observed to be :

cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone ($6 > 8 > 5 > 7$).

The rationale associated with the observed order of reactivity of cyclic ketones ($6 > 8 > 5 > 7$) would become more relevant and meaningful only when conformational aspects are taken into consideration.

In its chair form, cyclohexanone would owe its unique stability to the fact that each of its energy components would be a minimum (all angles are tetrahedral and all dihedral angles are 60°). In its most common representation, the boat form is represented with a plane of symmetry (52) and an assumption that it is equally rigid (occupies a potential minimum, like the chair form). However, the boat form, unlike the chair form, is flexible in that it can exist in an entire spectrum of conformations, all possessing unstrained tetrahedral angles. While considering the continuum of conformations, the conformation of minimum non-bonded repulsions is the twist-boat (53), possessing three mutually perpendicular 2-fold symmetry axes. The form of the transition state for boat-chair interconversion can be assumed to be the bent-chair form (54). However, this form has five carbon atoms in one plane, a situation of considerable strain owing to torsional eclipsing. A more favoured model would be a form with only four carbon atoms planar, which would be similar to the half-chair cyclohexene in shape (55). This form would be the direct intermediate conformation between the chair and the twist-boat forms, all of C_2 symmetry. The inter conversion of chair to twist-boat takes place by a rotation of one bond around the 2-fold axis. Since this is the most economical route for boat-chair conversion, it is probably also the most economical pathway for deformations of the six membered cycloalkanone. Hence, the reactivity of cyclohexanone would be the highest among the cycloalkanones.

Cyclooctanone has C_{2v} symmetry, resulting in a particular type of deformed crown structure (56, 57). Since the spectra of various cyclooctane derivatives have been shown to be nearly invariant with solvent, phase and temperature changes (58), it seems

clear that cyclooctanone possesses a definite fixed conformation. There appear to be three different kinds of axial positions and three different kinds of equatorial positions, indicating that cyclooctanone is a mixture of six conformations (some possibly in negligible amounts). In cyclooctanone, the oxygen is compressed by the hydrogens at C-1 and C-5, and there is no significant relief of this compression when cyclooctanone is subjected to oxidation. Hence, the rate of oxidation of cyclooctanone would be slower than that for cyclohexanone.

The lower reactivity of cyclopentanone can be attributed to the existence of cyclopentanone in the half-chair form (stable conformation) which has greater symmetry (59).

For cycloheptanone, there are two forms which can be interconverted through major deformations of bond angles from tetrahedral. These two plane-symmetrical forms are the chair- and boat-forms. However, both forms are flexible with respect to their bond angles and may undergo pseudo-rotation. The chair form has a H-H repulsion across the axial C₃-positions, which it may relieve by pseudo-rotation. In the boat form, the half-cycle position provides minimum repulsion energy. This form has a 2-fold symmetry axis, called the twist-chair conformation (60). This would be the stable form, and would account for an extremely low reactivity of cycloheptanone when subjected to oxidation.

Supporting arguments can be given as possible explanations for the observed order of reactivity ($6 > 8 > 5 > 7$) for the oxidation of cyclic ketones by QDC. These could be based on the following :

(a) I-strain in these rings : The concept of I-strain has been invoked to explain the relative ease with which a change in bond hybridization ($sp^2 \rightarrow sp^3$) takes place in these ring compounds (61). The change may refer to the formation of a transition state or of a product, leading to a kinetic effect or a thermodynamic effect, respectively. In the rate-determining step of the reaction, one of the ring carbon atoms changes from sp^2 to sp^3 hybridization. The relative ease of such change in the state of hybridization is in the order : $6 > 8 > 5 > 7$ (62).

(b) Cyclohexanone is essentially free of strain. The strain due to eclipsing of the carbonyl oxygen by the equatorial hydrogens at C-2 and C-6 appears to be relieved when the hybridization of the carbonyl oxygen is changed from sp^2 to sp^3 .

(c) The higher reactivity of cyclohexanone is probably due to the terminal hydrogen of the nearly strainless puckered residue $(CH_2)_4$ fulfilling the stereochemical requirement for hyperconjugation with the cyclic C=C groups better than does the terminal hydrogen of the nearly flat residue $(CH_2)_3$ in cyclopentanone. This also explains the higher enol content for cyclohexanone, as compared with the other medium-ring ketones (63 a).

(d) The order of reactivity observed indicated that the even-membered cyclic ketones (C_6 and C_8) reacted much faster than the odd-membered cyclic ketones (C_5 and C_7). For even-membered ring ketones, the spectrum changed suddenly at the melting point, while in the rest of the temperature range, only slight changes were observed. For odd-membered ring ketones, the spectrum also changed, not at the melting point but at a transition point which was lower than the melting point. The change in spectrum may be attributed to the possible disappearance of one or more conformations at a given temperature.

(e) The higher reactivity of cyclohexanone is a natural consequence of higher enolic content. The enolization of ketones consists of two steps :

- (i) Equilibrium protonation of the carbonyl group
- (ii) Deprotonation of the α - carbon of the conjugate acid.

These two steps affect the rate of enolization depending on the structural factors.

(f) The enolization rate constants have been reported for the cyclic ketones (64). The higher enolization constant of cyclohexanone is probably the most important factor contributing towards greater reactivity of this ketone, compared to that of cycloheptanone. In the step involving the formation of the enol, there is a change in the state of hybridization of the ketone from sp^2 to sp^3 at the site of attack. The conversion from sp^2 to sp^3 is most favoured when it is a 6-membered ring, and least favoured when it is a 7- membered ring (65).

Mechanism

At this juncture, it would be pertinent to review the earlier work which has been carried out on the oxidation of cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone) by various oxidizing agents. This would help to unequivocally establish the mechanistic pathway, in the present study, for the oxidation of the cyclic ketones studied by quinolinium dichromate (QDC) in acid medium, using 20% AcOH (v/v) as the solvent.

Since there exists an equilibrium between the keto- and enol- form of cyclic ketones, different oxidants have been found to attack either the keto-form or the enol-

form, to give a variety of products. The literature is replete with examples of the oxidation of cyclic ketones by different oxidizing agents, and there has been evidence for the reaction taking place either through the keto- form or the enol- form, depending on the nature of the oxidant and the reaction conditions used for the oxidation process.

(i) Reactions through the keto-form of cyclic ketones

The oxidation of cyclohexanone by oxidants such as V(V), Co(III), Ce(IV), and Mn(III) in acid medium showed that these one-electron oxidants attacked the keto-form rather than the enol-form of the substrate (66). It was shown that the oxidation of cyclohexanone by V(V) was always slower than enolization, but the solvent isotope effects indicated that the oxidation by V(V) involved an attack on the ketone. The primary isotope effect showed that there was a fission of the C-H bond in the rate-determining step of the oxidation reaction. The mechanism was consistent with a cyclic hydrogen transfer which was energetically favoured over an acyclic mechanism. In the oxidation of cyclohexanone by Co(III), the rate of oxidation was much faster than the rate of enolization. The absence of a primary isotope effect implied either that the C-H bond was not broken, or that if it was broken, then it was involved in that step which was not rate-determining. The conclusion was that the formation of a cobalt-ketone complex was slower than its decomposition by oxidation. In the oxidation of cyclohexanone by cerium sulphate, the rate of oxidation was much faster than the rate of enolization. The primary isotope effect showed that the C-H bond was broken in the rate-determining step of the oxidation. It was concluded that the oxidation involved a direct attack on the ketone. Manganic sulphate oxidized cyclohexanone at a rate greater than the rate of enolization and the primary isotope effect observed ($k_H / k_D = 4.0$) was considered to be smaller than

it would be due to the enolization pre-equilibrium ($k_{11} / k_{12} \approx 8.0$). It was therefore concluded that oxidation by manganic sulphate involved a direct attack on the keto-form and that the C-H bond was broken in the rate-determining step. From these experimental observations, it was established that the oxidation of cyclohexanone by one-electron oxidants proceeded via a mechanism involving a direct attack on the keto form of the substrate. The products obtained from the oxidation of cyclohexanone by all these one-electron oxidants were the α -diketones (66).

The oxidation of cyclohexanone by mercuric perchlorate showed that the reaction proceeded via the keto form of the substrate (67).

The reactions of cyclic ketones with V(V) in acid medium showed that the mechanistic pathway was through the keto-form of the substrate (4). The experimental observations clearly showed that the enol-form of the substrate did not provide the easiest route for the one-electron oxidation of a ketone in acid medium. The oxygen of the enol-form was less nucleophilic, and a substrate-oxidant complex was visualized in the keto-form of the substrate. Hence, it was concluded that in acid medium, the mode of preferential attack was on the keto form of the substrate. The products obtained in all the cases were the corresponding open-chain dibasic acids (4).

The oxidation of cyclic ketones by Ce(IV) in perchloric acid medium suggested an attack of the oxidant on the keto form of the substrate. The formation of a free radical was observed during the course of the reaction, as evidenced from the polymerization of acrylamide. The product obtained from the oxidation of cyclohexanone was the 2-hydroxycyclohexanone (5).

The oxidation of cyclohexanone by aqueous Ce(IV) in acid perchlorate solution showed that the rate of oxidation was much greater than the rate of enolization, thereby ruling out the oxidation of cyclohexanone in the enol form. The product obtained was adipic acid, which indicated that the reaction proceeded via a carbon-carbon bond cleavage in the final step of the reaction (15).

The oxidation of cyclohexanone by potassium bis(tellurato)cuprate(III) in aqueous alkaline medium showed a complex dependence on the concentrations of ketone and alkali. The kinetic results showed that the keto form was involved in the reversible formation of a complex, which underwent dissociation, in a slow step, to give a radical and a Cu(II) species. The product obtained was 2-hydroxycyclohexanone (16).

The kinetics of Ag(I) catalyzed oxidation of cyclic ketones revealed that these reactions proceeded via a general radical mechanism. This radical was the result of the reaction of the oxidant with the keto form of the substrates. The products of the reactions were the corresponding diketones (22).

The Os(VIII)-catalyzed oxidation of cyclopentanone and cyclohexanone by alkaline hexacyanoferrate(III) yielded α -hydroxy ketone as the major product (31). In an excess of alkaline hexacyanoferrate(III), there was a further oxidation to adipic acid. An analysis of the rate data showed that the reaction proceeded via the keto-form of the substrate (31).

(ii) Reactions through the enol-form of cyclic ketones

The oxidation of cyclohexanone by chromic acid in aqueous perchloric acid medium was observed to be slower than its rate of enolization (1). Using acid-base equilibrium in H_2O and D_2O , the observed solvent effects showed that a pre-equilibrium step preceded the rate-determining step involving a complex between cyclohexanone and chromic acid. This was consistent with the view that the oxidation proceeded through a reaction between an enol molecule and unionized chromic acid. It was therefore concluded that the reaction pathway for the oxidation of cyclohexanone by chromic acid was through the enol form of the substrate. The product obtained was adipic acid, an indication that a carbon-carbon bond cleavage occurred in the final step of the reaction (1).

The oxidation of cyclohexanone by iodine, bromine, mercury(II), thallium(III), and manganese(VII) in acid medium was found to be zero order in oxidant concentration (68). This showed that the oxidation step did not control the rate of the reaction. Hence, it was concluded that the enolization step was rate-determining, and that the enol form was rapidly attacked by the oxidant. The above evidence indicated that enol molecules were very easily oxidized by two-electron oxidants of the electrophilic type. The product obtained was cyclohexane-1,2-dione (68).

The oxidation of cyclic ketones by hexacyanoferrate(III) in ethanol- H_2O and pyridine- H_2O mixtures, at a constant ionic strength, showed that the reaction involved the enolate ion of the substrate (2). The rate-determining step was the formation of a free

radical from the enolate anion. The products obtained were the corresponding open-chain dibasic acids (2).

The oxidation of cyclohexanone by acid permanganate resulted in the formation of cyclohexane-1,2-dione. The kinetic results indicated that the rate of oxidation was much slower than the rate of enolization (3). However, no conclusion could be reached regarding the exact nature of the mechanistic pathway for this oxidation reaction. The possibilities suggested were: (a) the formation of a carbocation; and (b) the attack on the enol yielding an ester, which was hydrolyzed to give an α -ketol and a Mn(V) species. The only conclusion was that the oxidation reaction proceeded through an enol intermediate (3).

The oxidation of cyclic ketones by potassium permanganate in acid medium showed that the reaction proceeded via the enol form of the ketones, and that the oxidant was the permanganate ion itself (6). The rate-determining step involved a two-electron transfer from the enol giving the carbocation, which was rapidly converted to the open-chain dibasic acids (6).

The oxidation of cyclic ketones by lead tetraacetate in different solvent media (acetic acid-sodium acetate, acetic acid-DMF) showed that the mechanistic pathway was through a rate-determining enolization step (7). The products obtained were the corresponding acetoxy derivatives (7).

The oxidation of cyclooctanone by N-bromosuccinimide (NBS) in acid media involved the interaction between the enol form of cyclooctanone and NBS in a slow step, followed by a rapid step leading to cyclooctane-1,2-dione (8).

The oxidation of cyclohexanone by periodate in alkaline medium, catalyzed by Os(VIII), indicated that the slow step involved the reaction of Os(VIII) with the enolate ion of cyclohexanone. The product obtained was adipic acid (69).

The oxidation of cyclic ketones by chloramine-T (CAT) in aqueous ethanol under alkaline conditions indicated the involvement of at least one neutral molecule in the rate-determining step. The kinetic data indicated that the enolate anion reacted with CAT, in a slow step, to form an intermediate which was rapidly converted to the corresponding 1,2-diketones (9).

The oxidation of cyclic ketones by thallium triacetate proceeded through a rate-determining enolization step (10). Thallium(III) functions as a two-electron oxidant, and reacts with the enol form of the ketone to give a carbocation, which was finally converted to the acetoxy derivative in a rapid step (10).

The Ru(III)-catalyzed oxidation of cyclic ketones by potassium bromate in acid medium indicated a mechanism involving the enolization of the ketones in the rate-determining step. This was followed by the cleavage of the intermediate enol-Ru(III) complex yielding 1,2-diketones (11).

Phenyl iodosoacetate in acetic acid-sulphuric acid media has been used for the oxidation of cyclic ketones. The slow step involved the formation of the enol from the protonated form of the ketone. The products obtained were the corresponding acetoxy derivatives (12).

The oxidation of cyclic ketones by periodate in alkaline medium, catalyzed by Os(VIII), showed that the reaction between the enolate ion and Os(VIII) was the slow step of the reaction. The products of oxidation were identified as the corresponding open-chain dibasic acids (13).

The reaction of $[\text{Ru}^{\text{III}}(\text{bipy})_3]^{3+}$ with cyclohexanone showed that the rate-determining step was a non-bonded electron transfer process from the enol form of the substrate. This gave rise to a free radical and a Ru(II) species. The product obtained was cyclohexane-1,2-dione (70).

The kinetics of oxidation of cyclic ketones by N-bromosaccharin in aqueous acetic acid medium showed that the slow step of the reaction was the formation of the enol. The subsequent step involved a fast electron-transfer to the oxidant giving rise to the diketone (17).

The kinetics of oxidation of cyclopentanone and cyclohexanone by bromamine-T (BAT) in perchloric acid media pointed to a mechanism involving the acid catalyzed enolization of the ketones in the slow step of the reaction. This was followed by a rapid reaction with BAT to give the corresponding 1,2-diketones as the final products (18).

The oxidation of cyclic ketones by trichloroisocyanuric acid in aqueous acetic acid medium, in the presence of perchloric acid, attempted to correlate structure and reactivity of the cyclic ketones. The reaction was suggested to proceed through the enolization of the protonated ketone in the rate-determining step (19).

The kinetics of oxidation of cyclic ketones by periodate in the presence of Ru(III), Os(VIII), and Ru(III) + Os(VIII) mixtures, were studied in alkaline medium. The products of oxidation were the dicarboxylic acids. For the oxidation of Ru(III), the slow step involved the interaction of the hydroxylated species of Ru(III) with the enolate ion, resulting in the formation of Ru(I) and an intermediate which was probably a carbocation. In the oxidation with Os(VIII), the formation of the ester complex between Os(VIII) and the enolate ion was shown to be the rate-determining step. For the oxidation reaction catalyzed by Ru(III) + Os(VIII) mixtures, the mechanism envisaged the formation of an initial complex between Os(VIII) and the enolate ion of cyclohexanone. This was followed by an interaction with Ru(III) to give a reactive intermediate. This intermediate underwent rearrangement, in a slow step, to give the products (21).

In the high pressure - temperature aqueous oxidation of cyclohexanone, it was observed that the rate of enolization was very much faster than the rate of oxidation, thereby supporting the intermediacy of an enol. Both 2-hydroxycyclohexanone and its corresponding hydroperoxide were isolated as the products of oxidation of cyclohexanone at low temperatures. The peroxide was reported to decompose at 120°C. Further oxidation of 2-hydroxyketone gave the adipic acid (23).

The aqueous high pressure - temperature oxidation of cyclohexanone was found to be strongly catalyzed by silver, iron(III) and copper ions, but not by aluminium, cobalt, manganese(II) or nickel ions. The rate of enolization of cyclohexanone was unaffected by the presence of copper ions under conditions of constant acidity, but was strongly catalyzed by deuterium ion and acetate ion. However, the rate of oxidation exceeded the

rate of enolization at higher copper ion concentrations. The activation energies for the catalyzed and uncatalyzed oxidation were about the same, but the entropies of activation were quite different. These experimental results established that the enol was not a major intermediate in the catalyzed reaction. It was suggested that the copper ion may form an active peroxy complex with the oxygen molecule to serve as the reactive oxidant (24).

The kinetics of oxidation of cyclopentanone and cyclohexanone by chloramine-B (CAB) in hydrochloric acid and perchloric acid media were reported. In the presence of strong acids, cycloalkanones formed the oxonium salts on protonation, leading to enolization. The products obtained were the corresponding 1,2-diketones (25).

The kinetics of electron transfer from cyclic ketones to the Ni(IV) periodate complex in aqueous alkaline medium suggested a mechanism involving a slow adduct formation between the enol and oxidant. The products of oxidation were identified as the corresponding dicarboxylic acids (26).

The oxidation of cyclic ketones by acid bromate involved a mechanism where the attack of acid bromate on the enol form of the ketone was the rate-determining step. The intermediate formed underwent a rapid decomposition to the dicarboxylic acids (27).

The oxidation of cyclohexanone by dodecatungstocobaltate(III) in aqueous acetic acid media showed that the enol form of the substrate was the reactive species. The product obtained was identified as adipic acid (28).

The kinetics of oxidation of cyclic ketones by diperiodatoargentate(III) [DPA] in alkaline medium, catalyzed by Os(VIII) has been reported. The product obtained was

2-hydroxycyclohexanone. The oxidation of these ketones was assumed to proceed via the enol form. DPA attacking the enol form was suggested from the fact that silver possessed a greater tendency to form olefinic complexes (29).

The kinetics of oxidation of cyclic ketones by 2,6-dichlorophenol indophenol in the presence of alkali has been reported. The final reaction products obtained were the leuco dyes. The reaction proceeded through the formation of the enolate ion which reacted with the oxidant to form a complex. The slow step involved the reaction of the complex with the oxidant (30).

With a view to explore aspects pertaining to conformation, reactivity and mechanism in the oxidation with cyclic ketones, pyridinium fluorochromate (PFC) was used as the oxidant. These reactions were studied in aqueous acetic acid medium in the presence of perchloric acid. The products of oxidation were the corresponding 1,2-diketones. The rate-determining step was assumed to involve a two-electron transfer from the enol to PFC leading to the formation of an α -keto ester (32).

In the present investigation involving the oxidation of cyclic ketones by QDC, the stoichiometries of the oxidation reactions (Table 1) and the observed experimental data would help to establish the mechanistic pathways of the oxidation reactions.

Some of the kinetic observations which must be taken into account are the following :



- (1) The rates of oxidation of all the substrates (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone) by QDC were dependent on the first powers of the concentrations of each — substrate and oxidant (Tables 2-3).
- (2) The rates of the reactions showed a first order dependence on the concentration of the acid (Table 4). The acid catalysis of the oxidation reactions must be related to the structure of the oxidant (QDC), which was converted to a protonated dimetallic Cr(VI) species.
- (3) A decrease in the polarity of the solvent medium (using H₂O - AcOH mixtures) resulted in an increase in the rate of the reaction (Table 5). Linear plots of log k_1 against the reciprocal of the dielectric constants (Figure 3) gave positive slopes, which indicated an ion-dipole type of interaction. This was in accordance with the involvement of a protonated Cr(VI) species in the rate-determining step of the reaction.
- (4) An increase in temperature resulted in an increase in the rates of the reactions (Table 6). The oxidations of all the substrates were characterized by negative entropies of activation (Table 7), which suggested an ordered transition state, relative to the reactants. The similarity in ΔG^\ddagger values (Table 7) for all the substrates arose due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that all these oxidation reactions involved similar rate-determining steps.
- (5) There was no induced polymerization of acrylonitrile or the reduction of mercuric chloride, indicating the absence of any radical formation.

(6) The observed order of reactivity for the oxidation of cyclic ketones was as follows : cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone (6 > 8 > 5 > 7). This order of reactivity was rationalized on the basis of a change in the state of hybridization of the ketone in passing from the initial state (sp^2) to the transition state (sp^3) at the site of attack. The observed order of reactivity of cyclic ketones (6 > 8 > 5 > 7) has also been explained using conformational aspects.

Rate determining-step

(a) Keto-form

In oxidation reactions, ketones could react either directly, or through the enol form. Oxidation rates faster than the rates of enolization have been observed with one-electron oxidants such as ceric ions (71,72), manganic ions (72), and cobaltic salts (72, 73), indicating that the ketones reacted directly. All of these oxidants underwent one-electron reduction, and the reactions occurred through a free radical mechanism (71-73). In all these reactions, it was suggested that the enol form did not provide the easiest route for a one-electron oxidation of ketones. Attack on either the keto or the enol would yield the same free radical. If these reactions were to proceed at comparable rates, the much lower concentration of enol than that of ketone would ensure that the attack on the ketone predominated. The oxygen atom of an enol would be less nucleophilic than that of a corresponding keto molecule, and hence a substrate-oxidant complex could more easily be formed from the ketonic form. Solvent isotope effect measurements were used to provide confirmatory evidence of direct attack on the keto form, and in all such

oxidations by one-electron oxidants, the salient feature was the rapid formation of the keto-oxidant complex, with the breaking down of the complex occurring in the slow step of the reaction. Subsequently, several kinetic investigations have shown that the oxidation of cyclic ketones by V(V) in acid medium (4), Ce(IV) in perchloric acid medium (5), aqueous Ce(IV) ions (15), potassium bis(tellurato) cuprate(III) (16), peroxydisulphate catalyzed by Ag(I) ions (22), and by alkaline hexacyanoferrate(III) catalyzed by Os(VIII) ions (31), all proceeded by a mechanism involving a reaction of the oxidant with the keto form of the substrates.

(b) Enol-form

There have been many reports in the literature where the oxidation of cyclic ketones by various oxidizing agents were shown to proceed via the enolization of the ketones. The oxidizing agents which have been used for this purpose have included lead tetraacetate in acetic acid and acetic acid-DMF mixtures (7), N-bromosuccinimide in acid media (8), thallium triacetate in acid medium (10), potassium bromate in acid medium (11), phenyl iodosoacetate in acetic acid-sulphuric acid media (12), N-bromosaccharin in aqueous acetic acid medium (17), bromamine-T in acid media (18), trichloroisocyanuric acid in acid media (19), and dodecatungstocobaltate(III) in aqueous acidic medium (28). In all these oxidation reactions, the kinetic data showed a zero order dependence on the concentrations of the respective oxidants. The mechanistic pathways for all these reactions involved the enolization of the ketones in the slow step of the reaction, followed by the subsequent fast interaction of the enol with the oxidant, giving the final products. In all these oxidation reactions, the final products were identified as the 1,2-diketones; acetoxy derivatives were obtained as the products of oxidation with lead tetraacetate (7)

and thallium triacetate (10). These oxidation reactions did not yield any products which would have resulted from a carbon-carbon bond cleavage.

It has been shown that the oxidation of ketones occurred via the enolic tautomer (74, 75). This conclusion was based on evidence that the oxidizable C-H bonds were the same ones which were easily broken during the process of enolization. The effects of isotopic substitution, both in the ketone and in the solvent, showed that it was possible to distinguish between attack by the oxidant directly on the ketone and its attack on the enol (1). For example, in the oxidation of cyclohexanone by chromic acid, it was suggested that the attack of chromic acid on the enol form of the substrate was a concerted process yielding an α -keto-chromite ester, which hydrolyzed to the α -ketol and Cr(IV). This concerted process could explain the rapid bromination and iodination of enols. Since enols are acids of comparable pK_a to phenols, their esterification would be very small (1). Moreover, the concerted electrophilic reactions of enols did not require reagents as active as those needed for the addition to olefins, since free carbocations were not generated (1). A similar direct attack on an enol by selenious acid was observed as a possible step in the SeO_2 oxidation of the $CO.CH_2$ group (76).

(c) Present Work

In the present investigation involving the oxidation of cyclic ketones by quinolinium dichromate (QDC), in acid medium, the rate of oxidation was first-order with respect to the concentrations of each — substrate, oxidant and acid.

An unambiguous indication of the form in which the ketone reacted can be obtained only when the two rates (of oxidation and enolization) were compared. In the

present study, since the medium was highly acidic, it has to be decided whether the enolization of the ketone was the rate-determining step or not. If the step involving enolization were to be rate-determining, then the rate of oxidation would have been independent of the concentration of QDC. The kinetic data (Table 3) showed a first order dependence on QDC concentration, thus supporting the reaction pathway to be proceeding through the enol form of the substrate. For purposes of comparison, it can be recalled that in earlier investigations, the oxidation of cyclic ketones by different oxidizing agents had shown a zero order dependence on the concentration of the oxidant (7, 8, 10-12, 17-19, 28). A zero order dependence on oxidant concentration had thus established that the rate-determining step was the acid-catalyzed enolization of cyclic ketones, and that the enol-form was rapidly attacked by the oxidant (7, 8, 10-12, 17-19, 28).

In the present work, the rates of enolization of all the cyclic ketones under study were determined by the bromination method. It was found that the rates of enolization were very much greater than the rates of oxidation for all the cyclic ketones (~12). Since the rate of enolization was found to be much faster than the rate of oxidation, this would suggest that the enolization step was not rate-determining. Hence, it could be concluded that the enol-form of the substrate reacted with the oxidant. The rate-determining step would thus involve an attack of the oxidant on the enol form of the substrate. It can be recalled that in the acid-catalyzed iodination of ketone, the essential process was the conversion of the keto form to the enol form, which was very rapidly iodinated (77).

On the basis of the relative rates of oxidation of the cyclic ketones studied (Table 9), a cyclic transition state could be postulated.

Table 9 : Rate data for the Oxidation of Cyclic Ketones, in 20%AcOH (v/v)**([Substrate] = 0.1 M; [QDC] = 0.001 M; [H₂SO₄] = 1.0 M; T = 323K)**

Substrate	10 ⁴ k ₁ / s ⁻¹	Relative Rate
Cyclopentanone	0.70	1.4
Cyclohexanone	3.34	6.5
Cycloheptanone	0.51	1.0
Cyclooctanone	2.06	4.0

The reactivity of the cyclic ketones would support a transition state in which the accessibility of the ene and the hydroxyl group of the enol at the reaction centre, were about equally important. This conformational insensitivity could be attributed to the cyclic nature of the transition state.

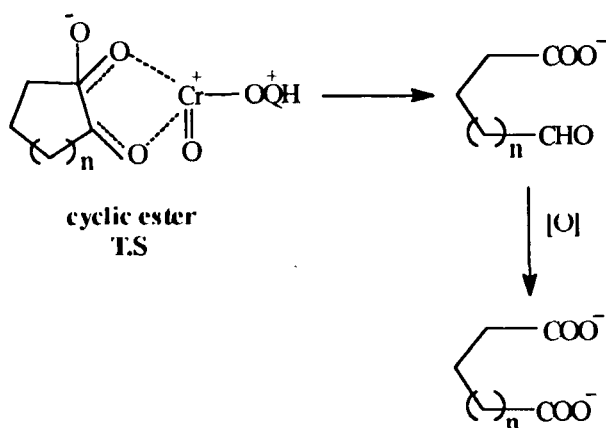
The stoichiometric conversion of the cyclic ketones to the corresponding dibasic acids involved the changes : $>=O \rightleftharpoons \geq\text{-OH} \rightarrow \text{chromate ester} \rightarrow \text{dibasic acid}$, and the rate of oxidation varied with the concentration of the acid. If the reaction intermediate were to be visualized as having a cyclic structure, then this would explain all the features of the oxidation reaction. The negative entropies of activation (Table 7) would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The similarity in ΔG^\ddagger values arose due to changes in ΔH^\ddagger and ΔS^\ddagger values

(Table 7), and stressed the probability that these oxidation reactions involved similar rate-determining steps.

As an analogy, the effect of solvent could also be examined. Pyridinium chlorochromate (PCC) has been used for the oxidation of alcohols, and the kinetic features of these reactions have been reported (78, 79). The mechanistic pathways in all these oxidations by pyridinium chlorochromate had involved the formation of a chromate ester intermediate, which would be better stabilized in the presence of solvents of low polarity. Hence, a decrease in the polarity of the solvent had shown an increase in the rate of oxidation of these alcohols by pyridinium chlorochromate (78, 79).

In the present investigation, the observed solvent effect (increase in the polarity of the solvent decreased the rate of oxidation, Table 5) provided support for a reaction pathway which involved the formation of a chromate ester intermediate. Further, the small variation in the reaction rate for the oxidation of cyclic ketones by quinolinium dichromate (Table 9), could also be reconciled with the ester mechanism, since the chromate ester formation was likely to be little influenced by structural changes (80).

A unimolecular decomposition of the cyclic ester can be written in which the chromium is bonded in the transition state to both the oxygen atoms :



Electron flow in a cyclic transition state has been earlier considered (63b, 81), and the conversion of the ester to the transition state has to be rationalized. This can be best considered in the following terms :

If the chromium were to be coordinated through the oxygen, then the process of electron transfer could take place through the carbon-oxygen-chromium bond. This would not only facilitate the formation of the cyclic chromate ester, but would also enhance the ease of conversion to the product. Such an intermediate would envisage the transfer of electrons towards the chromium, occurring by the formation of the carbon-oxygen-chromium bonds. Partly occupied orbitals could thus be used to bind the oxygen to both, carbon and chromium, in the transition state. A cyclic transition state has been suggested as the most plausible intermediate for the oxidation of primary and secondary alcohols by chromium(VI) reagents (82).

In the present investigation, the sequence of reactions involved in the oxidation of cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone) by

quinolinium dichromate (QDC) in acid medium, using 20% AcOH as the solvent, has been shown in the Scheme.

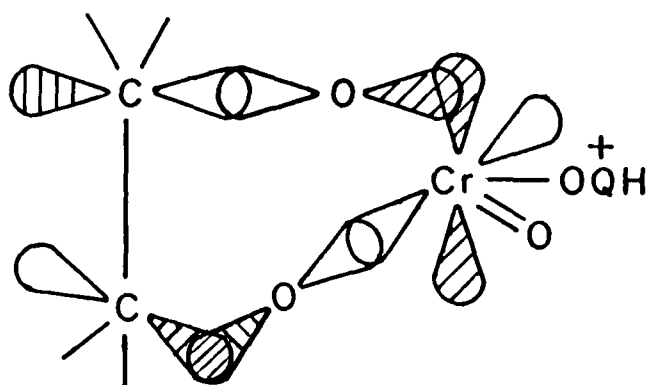
This mechanism was consistent with the fact that these oxidation reactions were catalyzed by acid (Table 4). Protonation of the oxidant (QDC) would make it more amenable towards nucleophilic attack by the enol form of the substrate on the electron-deficient chromium of the oxidant. The first step involved the enolization of the ketone, followed by the protonation of the oxidant (QDC). The second step was the rate-determining step, wherein the enol form of the substrate reacted with the protonated oxidant, in order to form the cyclic chromate ester. This would be followed by the transfer of two electrons in a cyclic system giving rise to cleavage products. This electrocyclic mechanism clearly involved six electrons; being a Hückel-type system ($4n+2$), this was an allowed process (83).

In general, oxidation reactions of organic functions by different oxidizing agents can be considered using the Zimmerman treatment of electrocyclic reactions (84). Selection rules play an important part in determining the mechanisms of many oxidation reactions. For reactions involving electrons in d-orbitals, a topological approach to the orbital levels of the transition state has been applied (84). This method classifies the transition state as either "Hückel-like" (in which all overlapping pairs of reacting orbitals are bonding), or "Möbius-like" (in which one or an odd number of anti-bonding overlaps must occur). In a Hückel transition state, $4n+2$ electrons form a closed shell (giving it stability), while $4n$ electrons are required for stable closed shells in a Möbius transition state. An "allowed" reaction may have either a Hückel-type or a Möbius-type transition

state, provided that the correct number of electrons is available to stabilize that transition state.

When chromium(VI) is reduced, the initial product chromium(IV) is unstable, but it is generally considered to be an octahedral complex (85). The d-electrons in the unexcited product must therefore be in a t_{2g} orbital (d_{xy}) which can overlap, in the reactions, using two adjacent lobes with opposite signs of the wave functions. It can therefore be considered to be locally antisymmetric (π -type). The transition state would be of the Hückel-type ($4n+2$), and hence would be an "allowed" reaction.

In the present investigation, the oxidation of cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone) by quinolinium dichromate (QDC), in acid medium, involved the formation of a cyclic chromate ester. The next step of the reaction would be the transfer of two electrons in the cyclic system. The accepted electrocyclic mechanism for the oxidation of cyclic ketones by QDC clearly involved six electrons, and the orbital picture showed that this was a Hückel-type system ($4n+2$). Hence, this would be an "allowed" process. The orbital overlap diagram is shown :



The mechanistic pathway for the oxidation of cyclic ketones by QDC in acid medium, thus involved the attack of the protonated (QDC) on the enol form of the substrate in the rate-determining step, to give a cyclic chromate ester and a chromium(VI) monomer. The chromate ester underwent rapid decomposition to give the final products (open-chain dicarboxylic acids). This mechanistic pathway and the products obtained (open-chain dicarboxylic acids) established that there was the cleavage of the carbon-carbon bond in the final step of the reaction. Our mechanistic pathway finds overwhelming support from earlier investigations wherein the oxidation of cyclic ketones had established that the rate-determining step for the oxidation reactions involved an attack of the oxidant on the enol form of the substrate. Such a mechanistic pathway has been substantiated when cyclic ketones were oxidized by various oxidants such as chromic acid (1), acid permanganate (3), potassium permanganate in aqueous acetic acid medium (6), chloramine-T in aqueous ethanol under alkaline conditions (9), periodate in alkaline medium catalyzed by Os(VIII) ions (13), tris-2,2'-bipyridyl ruthenium(III) perchlorate (71), periodate in the presence of Ru(III), Os(VIII) and Ru(III) + Os(VIII) mixtures in alkaline medium (21), chloramine-B in hydrochloric acid and perchloric acid medium (25), Ni(IV) periodate complex in aqueous alkaline medium (26), acid bromate (27), diperiodatoargentate (III) in alkaline medium using Os(VIII) as the catalyst (29), and by pyridinium fluorochromate in aqueous acetic acid medium, in the presence of perchlorate (32). Considering the substantial evidence put forward by earlier workers on the mechanism of oxidation of cyclic ketones by different oxidizing agents (1, 3, 6, 9, 13, 21, 25-27, 29, 32, 71), and on the basis of the kinetic results obtained in the present

investigation, it would be justified to propose the mechanism for the oxidation of cyclic ketones by quinolinium dichromate (QDC), in acid medium, as shown in the Scheme.

In acid medium, the oxidant QDC was converted to the protonated dimetallic Cr(VI) species, PQ [in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $\text{Cr}_2\text{O}_7^{2-}$ (37)]. The substrate (S) was converted to the enol, via its protonated form (SH^+). The reaction of the enol with the protonated QDC (PQ), in the rate-determining step, resulted in the formation of the cyclic monochromate ester (E) and a monomeric Cr(VI) species. This cyclic monochromate ester was formed when the enol form of the substrate was bound to Cr(VI) through the carbon-oxygen-chromium bond via an electrocyclic mechanism involving six electrons. The decomposition of the ester could take place through the carbon-oxygen-chromium bond of the ester (E) in a fast step, resulting in an open structure A. On oxidation with another mole of protonated QDC (PQ), A gave the corresponding dicarboxylic acid B, along with the Cr(IV) species.

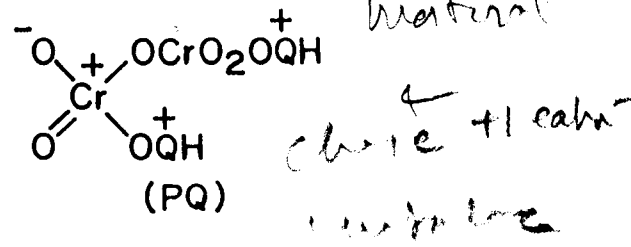
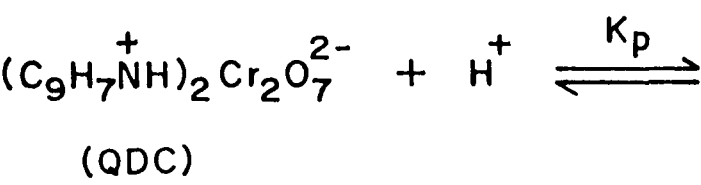
If this mechanism is correct, then the attack of the protonated QDC (PQ) on the enol form would be the crucial and rate-determining step of the reaction. Based on the mechanism shown in the Scheme, the rate law can be derived as follows :

$$- d [\text{QDC}] / dt = k_3 [\text{enol}] [\text{PQ}] \quad (6)$$

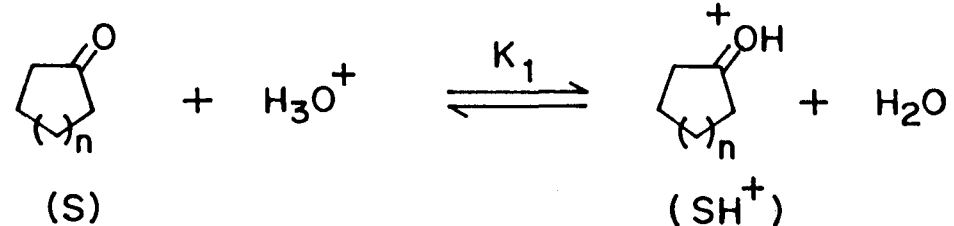
$$K_1 = [\text{SH}^+] [\text{H}_2\text{O}] / [\text{S}] [\text{H}_3\text{O}^+] \quad (7)$$

$$K_2 = [\text{enol}] [\text{H}_3\text{O}^+] / [\text{SH}^+] [\text{H}_2\text{O}] \quad (8)$$

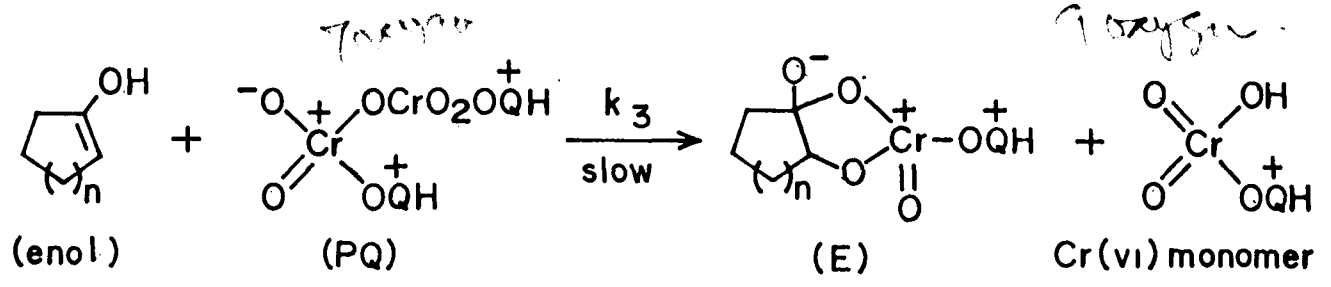
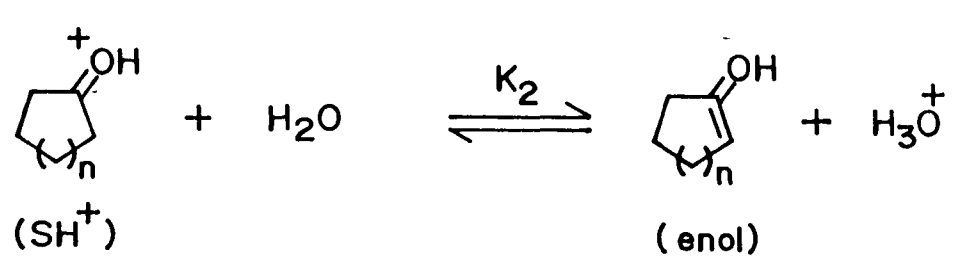
① H₂ mixture
 material



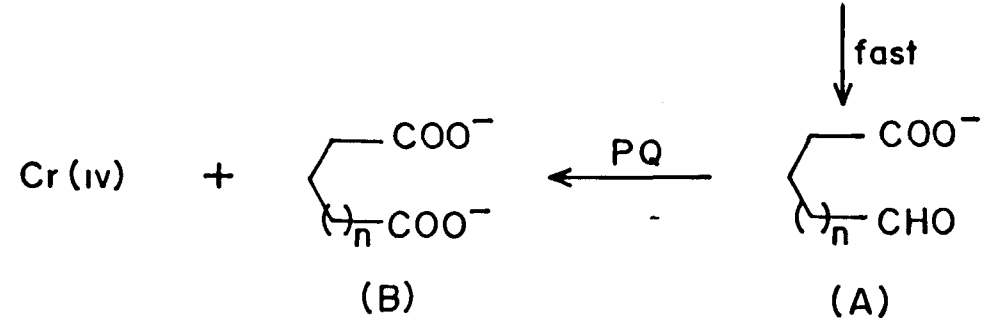
choice + 1 carb⁻
 ...



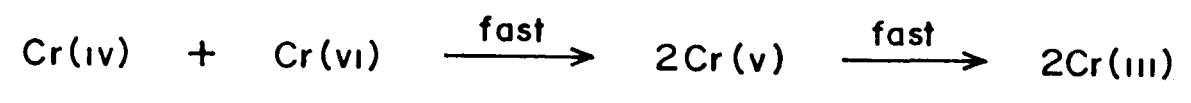
n = 1, 2, 3, 4



oxygen



what is
 fast Cr here



SCHEME

The concentrations of $[SH^+]$ in the steady state would be given by :

$$[SH^+] = K_1 [S] [H_3O^+] / [H_2O]$$

$$[SH^+] = [enol] [H_3O^+] / K_2 [H_2O]$$

Therefore, $K_1 [S] [H_3O^+] / [H_2O] = [enol] [H_3O^+] / K_2 [H_2O]$, and

$$\begin{aligned} [enol] &= K_1 [S] [H_3O^+] K_2 [H_2O] / [H_2O] [H_3O^+] \\ &= K_1 K_2 [S] \end{aligned} \quad (9)$$

Hence, the rate of the reaction would be given by

$$\begin{aligned} - d[QDC] / dt &= k_3 [enol] [PQ] \\ &= k_3 K_1 K_2 [S] [PQ] \\ &= k_3 K_1 K_2 [S] [QDC] [H^+] \end{aligned} \quad (10)$$

Since the rate of enolization was very rapid, it could be assumed that K_1 and K_2 would have very low values. This rate expression (equation 10) was in agreement with the rate law suggested for the reaction given in equation 5, and confirmed the first order dependence on the concentrations of each — substrate, oxidant, and acid. This rate law explains all the experimentally observed results.

The conversion of Cr(IV) to Cr(III) was a disproportionation reaction. For the reaction $Cr(IV) + Cr(VI) \rightarrow 2 Cr(V)$, the standard potential for the Cr(VI) - Cr(V) couple was extremely favourable ($E^0 = 0.62$ volt) (86), and this reaction would proceed rapidly. The Cr(V) - Cr(III) couple has a potential of 1.75 volt, which would enable the rapid conversion of Cr(V) to Cr(III), after the reaction with the substrate (86, 87).

Under the experimental conditions employed in the present investigation, cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone), were

oxidized by quinolinium dichromate (QDC), in acid media, giving the corresponding dicarboxylic acid in each case. The products (the respective open-chain carboxylic acids) were characterized by FT-IR and FT-NMR analyses (vide “Experimental : Product Analysis”).

It would be pertinent to recall the earlier experimental observations wherein cyclic ketones were oxidized to open-chain dicarboxylic acids in good yields, when oxidized by diverse oxidizing agents such as chromic acid (1), V(V) in acid medium (4), potassium permanganate in aqueous acetic acid (6), periodate in alkaline medium catalyzed by Os(VIII) ions (13), aqueous Ce(IV) ion in acid perchlorate (15), periodate catalyzed by Os(VIII), Ru(III), and Os(VIII) + Ru(III) mixtures (21), Ni(IV) periodate complex in aqueous alkaline medium (26), acid bromate (27), and by alkaline hexacyanoferrate (III) catalyzed by Os(VIII) ions (31). In all these oxidation reactions, the nature of the products formed (open-chain dicarboxylic acids) indicated that there was the cleavage of the carbon-carbon bond in the final step of the reaction.

The data collected in the present investigation demonstrated that application of QDC to the oxidation of cyclic ketones resulted in the formation of the corresponding open-chain dibasic acids. The nature of the products obtained indicated the cleavage of the ring system, and cleavage of the carbon-carbon bond in the final step of the reaction. Under the present experimental conditions, there was no further oxidation of the products. This experimental protocol demonstrates that application of QDC to the oxidation of cyclic ketones could prove to be a useful and general route for the synthesis of dicarboxylic acids.

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CHAPTER – II

KINETICS OF OXIDATION OF 2-ALKANONES AND 3-ALKANONES

The oxidation of 2- and 3- alkanones by various oxidizing agents have been investigated by several workers. The oxidation of 2-butanone (ethyl methyl ketone) by Mn(III) sulphate in acid medium was first order with respect to each – Mn(III) and the ketone. The rate of oxidation was independent of acidity and was unaffected by changes in solvent composition. The mechanistic pathway involved an attack by the Mn(III)-sulphate complex on the ketone. The products obtained were acetaldehyde and acetic acid (1).

The kinetics of oxidation of 2-alkanones by peroxydiphosphate in aqueous sulphuric acid medium showed that acetic acid was the main product. The oxidation obeyed second order kinetics, and the mechanism proposed was the attack of the oxidant on the keto form of the substrate in the rate-determining step (2).

The Ce(IV) oxidation of 2-butanone in perchloric acid medium followed a mechanistic pathway involving the formation of a free radical. The oxidation reactions were first order each in substrate and oxidant, and the oxidation product (in the presence of excess ketone) was confirmed as 2-hydroxyketone (3).

The oxidation of alkanones (2- and 3-) by acid permanganate in the presence of fluoride ion showed that the reactions were first order with respect to each - oxidant, ketone and hydrogen ions. It was suggested that the enol-form was involved in the oxidation process, and the products obtained were the acid and the aldehyde (4).

The kinetics of oxidation of alkanones by tris(1,10-phenanthroline) Fe(III) in aqueous acid medium indicated that the electron-donating methyl substituents enhanced the rate of electron transfer from the enol tautomer to the oxidant. The products obtained were the corresponding diketones (5).

The kinetics of oxidation of 2-butanone (ethyl methyl ketone) by potassium permanganate in aqueous acid medium showed that the reactions were first-order each in the substrate and the oxidant. Changes in the acetic acid content in the solvent did not affect the kinetic rate. The reaction proceeded via the enol form of the ketone and the oxidant was the permanganate ion. The product obtained was acetic acid (6).

The oxidation of ethyl methyl ketone by V(V) in dilute sulphuric acid was first order each in substrate, oxidant and acid. The reaction was found to be slower in sulphuric acid as compared to the rate in perchloric acid. The mechanism involved a free radical intermediate, and the product obtained was formic acid (7).

The kinetics of oxidation of 2-pentanone by lead tetraacetate showed that the reaction was first order in ketone, but zero order in lead tetraacetate. The mechanism involved the enolization of the substrate in the rate-determining step (8).

The kinetics of oxidation of 2-alkanones by sodium metaperiodate in aqueous alkaline medium, was studied both in the absence and presence of osmium tetroxide. The uncatalyzed reaction showed a first order dependence on periodate, while the order with respect to periodate was zero in the presence of osmium tetroxide. The products obtained were the corresponding acids (9).

The kinetic data on the Ce(IV) oxidation of 3-pentanone in sulphuric acid solution showed a first order dependence on both Ce(IV) and the substrate. The reaction products obtained were propionic acid and acetic acid (10).

The kinetics of oxidation of 2-butanone by chloramine-T in aqueous ethanol under alkaline conditions showed a first order dependence with respect to each — oxidant, substrate, and alkali. The mechanism of the reaction involved the reaction of the enol with the oxidant in the rate-determining step, and the product was identified as the 1,2-diketone (11).

The kinetics of oxidation of 2-alkanones by thallium triacetate showed that the reactions were first order each in substrate and acid, but zero order in oxidant. The mechanism postulated was via a rate-determining enolization. The products obtained were the corresponding acetoxy derivatives (12).

The kinetics of the Ru(III)-catalyzed oxidation of 2-alkanones by acid bromate showed that the mechanism proceeded via a rate-determining enolization step. The reaction showed a first order dependence each in substrate and acid, but exhibited a zero order dependence on the concentration of oxidant. The products obtained were the diacetyls (13).

The kinetics of oxidation of 2-butanone and 2-pentanone by phenyl iodosoacetate in aqueous acetic acid medium, in the presence of perchloric acid and sulphuric acid, showed a first order dependence with respect to substrates, but a zero order dependence

with respect to oxidant. The rate of enolization was found to be the rate-determining step of the reaction (14).

The kinetics of oxidation of 2-butanone by phenyl iodosoacetate in acetic acid-sulphuric acid media showed a first order dependence on the substrate and acid, but exhibited a zero order dependence on the oxidant. The enolization step was rate-determining and the product obtained was the acetoxy derivative (15).

The kinetics of oxidation of 2- and 3-alkanones by Ce(IV) sulphate in aqueous sulphuric acid medium, in the presence of Ru(III) chloride as the catalyst, showed a first order dependence on the ketone. The rate was inversely proportional to the square of the concentration of the acid, which tended towards a first order behaviour at lower concentration of acid. The first order dependence on lower Ru(III) concentration tended towards zero order at higher concentration of the catalyst. The rate-determining step involved the attack of the oxidant on the protonated ketones, and the products obtained were the corresponding carboxylic acids (16).

The kinetics of oxidation of 2-pentanone by N-bromosuccinimide (NBS) was studied in perchloric acid media, in the presence of mercuric acetate. A zero order dependence on NBS, and a first order dependence on both the ketones and acid were observed. The mechanism of the reaction involved the enolization as the rate-determining step, and the product obtained was the 1,2-diketone (17).

The kinetics of oxidation of 2-alkanones by N-bromosaccharin in aqueous acetic acid medium, yielded the diketones as the products. The reactions were first order each

with respect to ketone and acid, and independent of the concentration of oxidant. The rate-determining step was suggested to be the enolization of the substrate (18).

The kinetics of oxidation of 2- and 3-alkanones by N-bromoacetamide (NBA) in perchloric acid media, in the presence of mercuric acetate, showed a zero-order dependence on oxidant and a first-order dependence on both, ketone and acid. The rate-determining step involved the enolization of ketone, and the end products were identified as the corresponding diketones (19).

The kinetics of oxidation of ethyl methyl ketone by potassium bis(tellurato) cuprate(III) in aqueous alkaline medium showed a complex dependence in both ketone and alkali concentrations. The inverse dependence on tellurate ion suggested that a hydroxo mono (tellurato) species of the oxidant was involved in the reaction with the substrate. The rate-determining step was the collapse of the (tellurato)Cu(III) complex to a radical and a Cu(II) species (20).

The kinetics of oxidation of alkanones (2- and 3-) by trichloroisocyanuric acid in aqueous acetic acid medium, in the presence of perchloric acid, was studied. The reactions showed a first order dependence on acid and substrate concentrations, but exhibited a zero order dependence on the concentration of the oxidant. The enolization of the ketone was shown to be the rate-determining step. The products obtained were the monochloro ketones (21).

The kinetics of oxidation of 2-hexanone by N-bromoacetamide (NBA) in perchloric acid media, in the presence of mercuric acetate, has been reported. The major

product was the 1,2-dicarbonyl compound. The reaction order with respect to each, ketone and acid was unity, and that with respect to NBA was zero. The mechanistic pathway was through the enolization of the ketone as the rate-determining step (22).

The kinetics of oxidation of alkanones (2- and 3-) by bromamine-B (23) and bromamine-T (24) in acid medium, showed a first order dependence each on the ketone and H^+ concentrations, but was independent of the concentration of the oxidant. The mechanism involved the acid-catalyzed enolization of the ketone in the rate-determining step. The products obtained were the respective diketones (23, 24).

The kinetics of oxidation of alkanones (2- and 3-) by bromamine-B in alkaline buffer medium showed a first order dependence on oxidant, but variable dependence (one to zero) in [ketone] and [oxidant]. The products obtained were the respective diketones. The rate-determining step was the attack of HOBr on the ketone (25).

The kinetics of oxidation of alkanones (2- and 3-) by acid bromate showed a first order dependence on each – bromate, ketone and acid. The mechanism involved the attack of acid bromate on the enol form of the ketone in the rate-determining step. Carboxylic acids were obtained as the final products of oxidation (26).

The kinetics of the Ru(III) catalyzed oxidation of 2-butanone and 2-pentanone by acid potassium bromate, in the presence of Hg(II) acetate, has been studied. The reaction showed a first order dependence on the substrate, H^+ and Ru(III) concentrations, but showed zero order kinetics in bromate. The diketones were isolated as the final products. The mechanism involved the enolization as the rate-determining step (27).

Kinetic studies on the oxidation of 2-alkanones by SeO_2 in aqueous acetic acid and perchloric acid media showed a first order dependence on each - substrate, oxidant and perchloric acid. The reaction proceeded via the attack of the oxidant on the keto-form of the 2-alkanones. The products obtained were the corresponding diketones (28).

The kinetics of oxidation of 2-butanone with permanganate ions in aqueous acidic and alkaline media have been reported. In acid medium, nucleophilic addition of the permanganate to the carbonyl carbon atom was suggested. In alkaline medium, a concerted mechanism was proposed. The products obtained were oxalic acid and acetic acid (29).

PRESENT WORK

The present work is a detailed kinetic investigation of the oxidation of 2- and 3-alkanones by quinolinium dichromate (QDC), in acid medium, using water as the solvent.

The alkanones chosen for the purpose of oxidation by quinolinium dichromate (QDC) have included :

(A) 2-Alkanones

(a) 2-Butanone; (b) 2-Pentanone; (c) 2-Hexanone; (d) 2-Heptanone; and (e) 2-Octanone.

(B) 3-Alkanones

(a) 3-Pentanone; (b) 3-Hexanone; (c) 3-Heptanone; and (d) 3-Octanone.

Stoichiometry (vide “Experimental”)

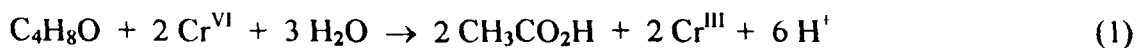
The stoichiometries of all the oxidation reactions were determined. The stoichiometric ratios, $\Delta[\text{QDC}] / \Delta[\text{Substrate}]$, were in the range 1.96-2.05 (Table 1).

Table 1 : Stoichiometries of the Oxidation of the Substrates**([Substrate] = 0.005 M; T = 323 K)**

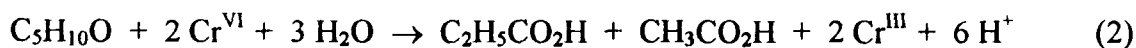
[HClO ₄] / M	0.10	0.25	0.50
10 ² [QDC] / M	2.50	2.60	2.70
Δ[QDC] / Δ[2-Butanone]	1.99	2.00	1.96
Δ[QDC] / Δ[2-Pentanone]	2.03	2.03	1.99
Δ[QDC] / Δ[2-Hexanone]	1.96	2.00	2.00
Δ[QDC] / Δ[2-Heptanone]	2.02	2.03	2.01
Δ[QDC] / Δ[2-Octanone]	1.95	2.01	2.05
Δ[QDC] / Δ[3-Pentanone]	2.05	1.98	2.03
Δ[QDC] / Δ[3-Hexanone]	1.96	2.05	2.01
Δ[QDC] / Δ[3-Heptanone]	2.02	1.98	2.02
Δ[QDC] / Δ[3-Octanone]	2.05	1.99	2.00

The observed stoichiometric ratios conformed to the overall equations :

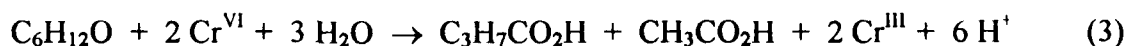
(a) For 2-butanone :



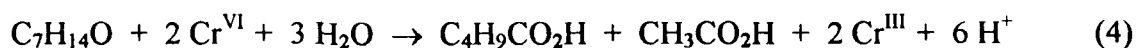
(b) For 2-pentanone :



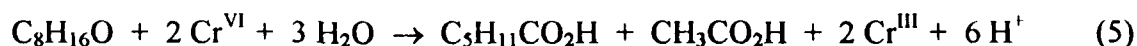
(c) For 2-hexanone :



(d) For 2-heptanone :



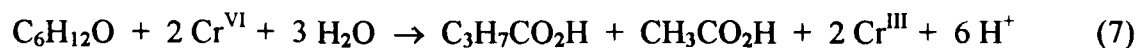
(e) For 2-octanone :



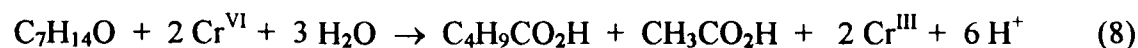
(f) For 3-pentanone :



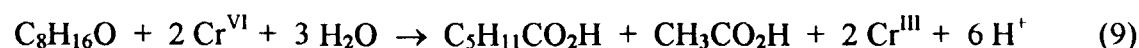
(g) For 3-hexanone :



(h) For 3-heptanone :



(i) For 3-octanone :



Effect of Substrate

The rate of the reaction was found to be dependent on the concentration of the substrates. The order of the reaction with respect to substrate concentration was obtained by changing the substrate concentration, and observing the effect on the rate of the reaction at constant [QDC] and [H⁺]. The results have been recorded in Tables 2-3.

Table 2 : Dependence of Rate Constants on the concentration of 2-Alkanones, in aqueous medium; ([QDC] = 0.001 M; [HClO₄] = 2.0 M; T = 323K)

$10^4 k_1 / s^{-1}$					
10^2 [Substrate] / M	2-Butanone	2-Pentanone	2-Hexanone	2-Heptanone ^a	2-Octanone ^a
1.0	1.52	0.48	0.65	0.81	1.12
2.5	3.81	1.24	1.62	2.12	2.81
5.0	7.62	2.42	3.25	4.02	5.58
7.5	11.4	3.60	4.82	-	-
10.0	15.2	4.82	6.53	-	-
$10^2 k_2 / M^{-1} s^{-1}$					
	1.52	0.48	0.65	0.81	1.12
	1.52	0.49	0.65	0.85	1.12
	1.52	0.48	0.65	0.80	1.11
	1.53	0.48	0.64	-	-
	1.52	0.48	0.65	-	-
$k_2 = k_1 / [\text{Substrate}]$					

^a sparingly soluble at concentrations higher than 0.05 M

Table 3 : Dependence of Rate Constants on the Concentration of 3-Alkanones in aqueous medium; ([QDC] = 0.001 M; [HClO₄] = 2.0 M; T = 323K)

$10^4 k_1 / s^{-1}$				
10^2 [Substrate] / M	3-Pentanone	3-Hexanone	3-Heptanone ^a	3-Octanone ^a
1.0	0.42	0.51	0.76	1.20
2.5	1.01	1.23	1.89	2.98
5.0	1.99	2.58	3.81	6.04
7.5	2.89	3.62	-	-
10.0	4.01	5.12	-	-
$10^2 k_2 / M^{-1} s^{-1}$				
	0.42	0.51	0.76	1.20
	0.40	0.49	0.76	1.19
	0.40	0.52	0.76	1.21
	0.38	0.48	-	-
	0.40	0.51	-	-
$k_2 = k_1 / [\text{Substrate}]$				

^a sparingly soluble at concentrations higher than 0.05 M

Plots of k_1 , the pseudo-first-order rate constant, against a ten-fold range of the concentrations of substrates (in each case), gave straight lines passing through the origin (Figures 1-2), indicating that the rate of oxidation was dependent on the first power of the concentrations of the substrates. This was further demonstrated by the constancy in the values of k_2 , the second-order rate constant.

Effect of oxidant

Under pseudo-first-order conditions, the individual kinetic runs were first-order with respect to the oxidant (QDC). At fixed [acid] and with the substrate taken in excess, the plots of log absorbance versus time were linear, indicating a first-order dependence on QDC. When a constant concentration of substrate (large excess) was used, the pseudo-first-order rate constant (k_1) did not alter appreciably with changing concentrations of the oxidant (QDC), indicating a first-order dependence on the concentration of the oxidant. The rate data have been shown in Tables 4-5.

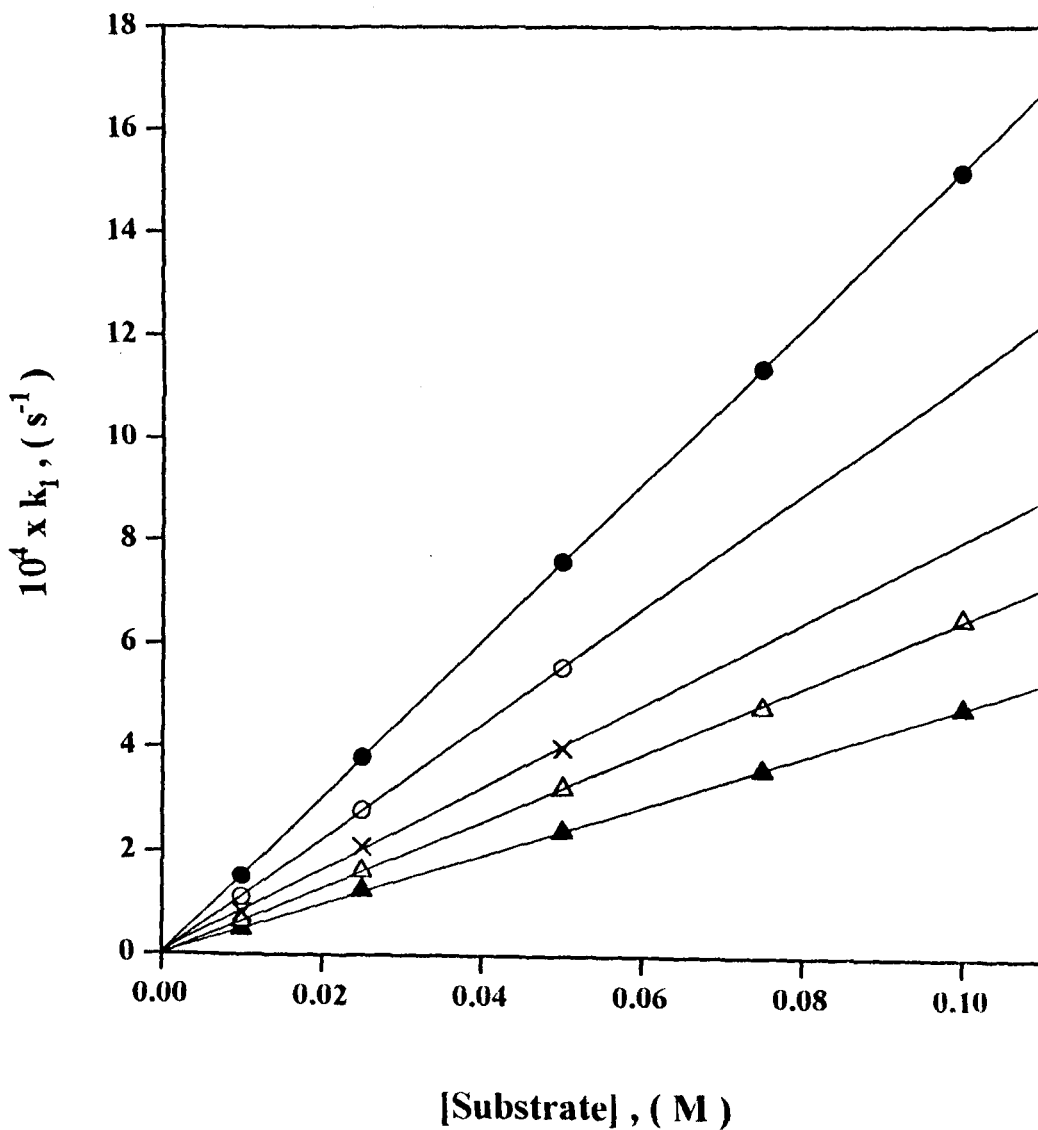


Fig. 1. Plots of k_1 against the concentrations of substrates for 2-butanone (●), 2-pentanone (▲), 2-hexanone (△), 2-heptanone (×) and 2-octanone (○).

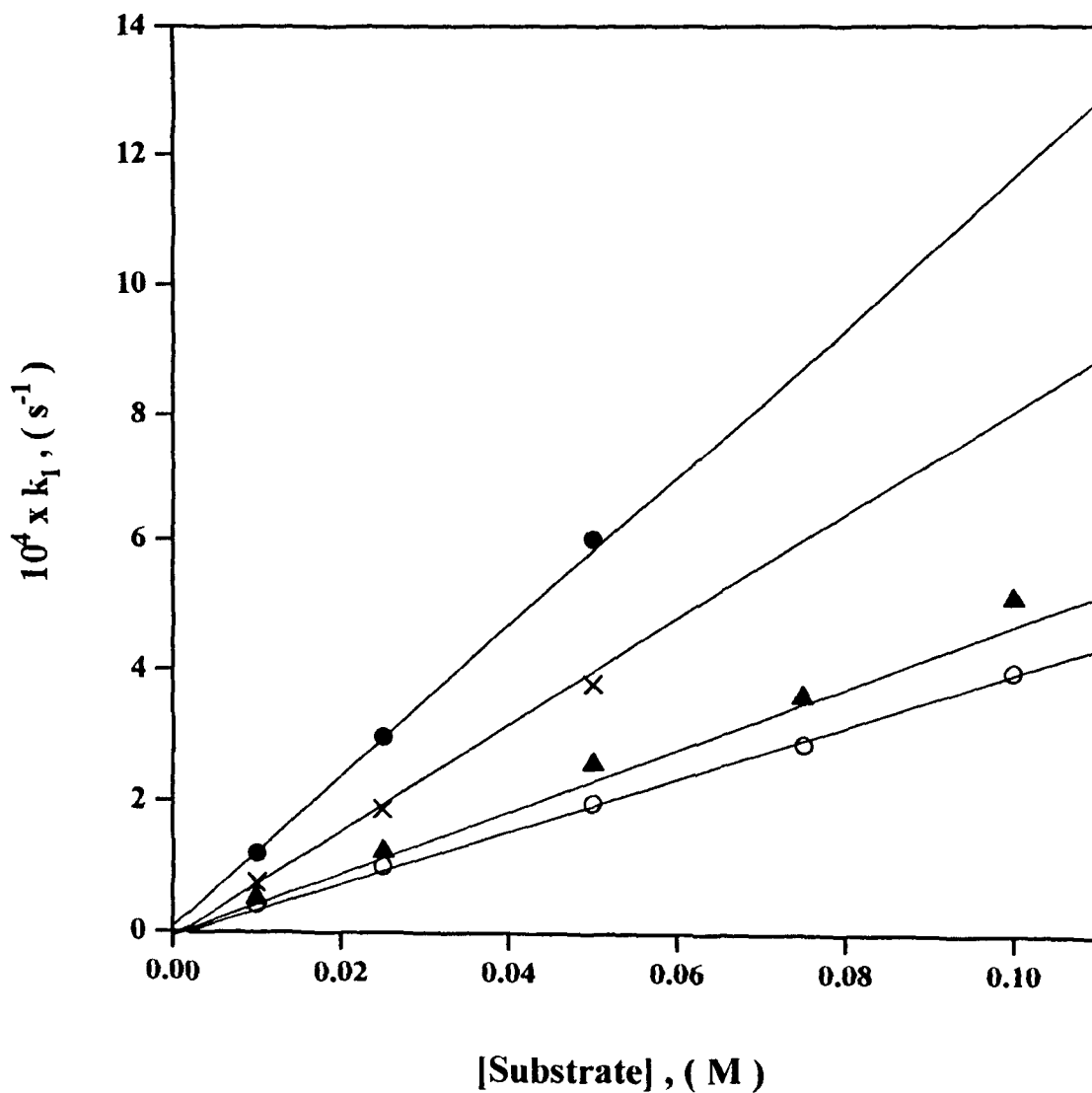


Fig. 2. Plots of k_1 against the concentrations of substrates for 3-pentanone (○), 3-hexanone (▲), 3-heptanone (×) and 3-octanone (●).

Table 4 : Dependence of Rate Constants on the concentration of Oxidant, in aqueous medium; ([Substrate] = 0.01 M; [HClO₄] = 2.0 M; T = 323K)

$10^3 [\text{QDC}] / \text{M}$	$10^4 k_1 / \text{s}^{-1}$				
	2-Butanone	2-Pentanone	2-Hexanone	2-Heptanone	2-Octanone
0.25	1.48	0.51	0.63	0.85	1.13
0.50	1.59	0.48	0.69	0.87	1.15
0.75	1.56	0.50	0.61	0.80	1.10
1.0	1.52	0.48	0.65	0.81	1.12

Table 5 : Dependence of Rate Constants on the concentration of Oxidant ([Substrate] = 0.01 M; [HClO₄] = 2.0 M; T = 323K)

$10^3 [\text{QDC}] / \text{M}$	$10^4 k_1 / \text{s}^{-1}$			
	3-Pentanone	3-Hexanone	3-Heptanone	3-Octanone
0.25	0.41	0.52	0.76	1.21
0.50	0.39	0.50	0.78	1.18
0.75	0.37	0.48	0.77	1.22
1.0	0.42	0.51	0.76	1.20

Effect of acid

The reaction was influenced by changes in acid concentration, and the rate was observed to increase with an increase in the concentration of the acid in the range 1.0 M to 3.0 M (Tables 6-7).

Table 6 : Dependence of Rate Constants on Acid concentration for 2-Alkanones, in aqueous medium; ([Substrate] = 0.01 M; [QDC] = 0.001 M; T = 323K)

[HClO ₄] / M	10 ⁴ k ₁ / s ⁻¹				
	2-Butanone	2-Pentanone	2-Hexanone	2-Heptanone	2-Octanone
1.0	0.74	0.24	0.32	0.39	0.54
1.5	1.15	0.38	0.49	0.61	0.84
2.0	1.52	0.48	0.65	0.81	1.12
2.5	1.89	0.61	0.83	1.04	1.41
3.0	2.30	0.76	0.97	1.21	1.68

Table 7 : Dependence of Rate Constants on Acid concentration for 3-Alkanones**([Substrate] = 0.01 M; [QDC] = 0.001 M; T = 323K)**

[HClO ₄] / M	10 ⁴ k ₁ / s ⁻¹			
	3-Pentanone	3-Hexanone	3-Heptanone	3-Octanone
1.0	0.22	0.26	0.37	0.62
1.5	0.33	0.39	0.58	0.90
2.0	0.42	0.51	0.76	1.20
2.5	0.54	0.64	0.96	1.51
3.0	0.64	0.77	1.15	1.82

Plots of log k₁ against log [H⁺] were linear, with slopes equal to unity (Figures 3-4), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step. There have been earlier reports of the involvement of such protonated Cr(VI) species in chromic acid oxidation reactions (30). Protonated Cr(VI) species have been observed in earlier investigations (31). The acid catalysis must be related to the structure of the oxidant (QDC), which was

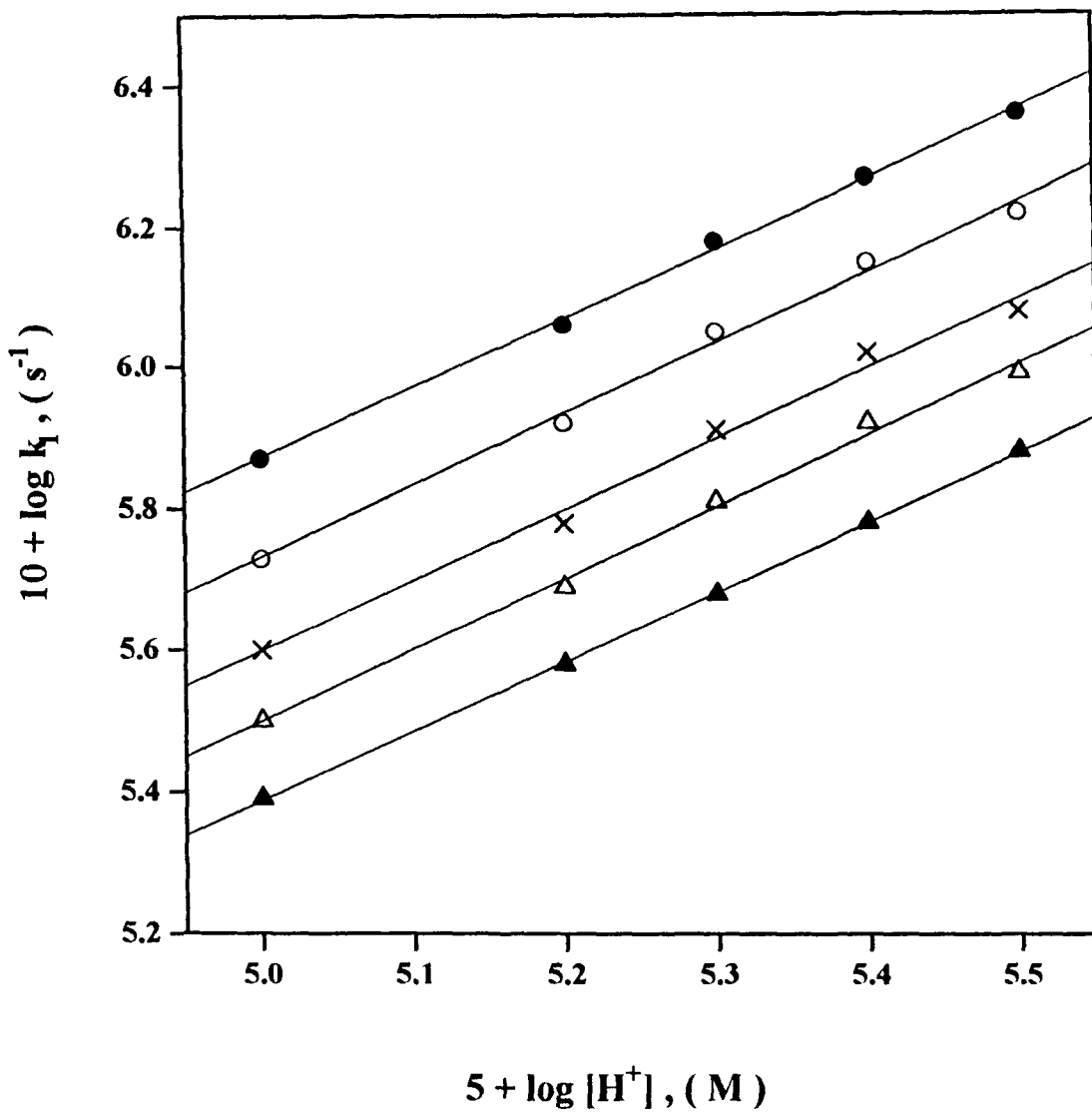


Fig. 3. Plots of $\log k_1$ against $\log [H^+]$ for 2-butanone (●), 2-pentanone (▲), 2-hexanone (△), 2-heptanone (×) and 2-octanone (○).

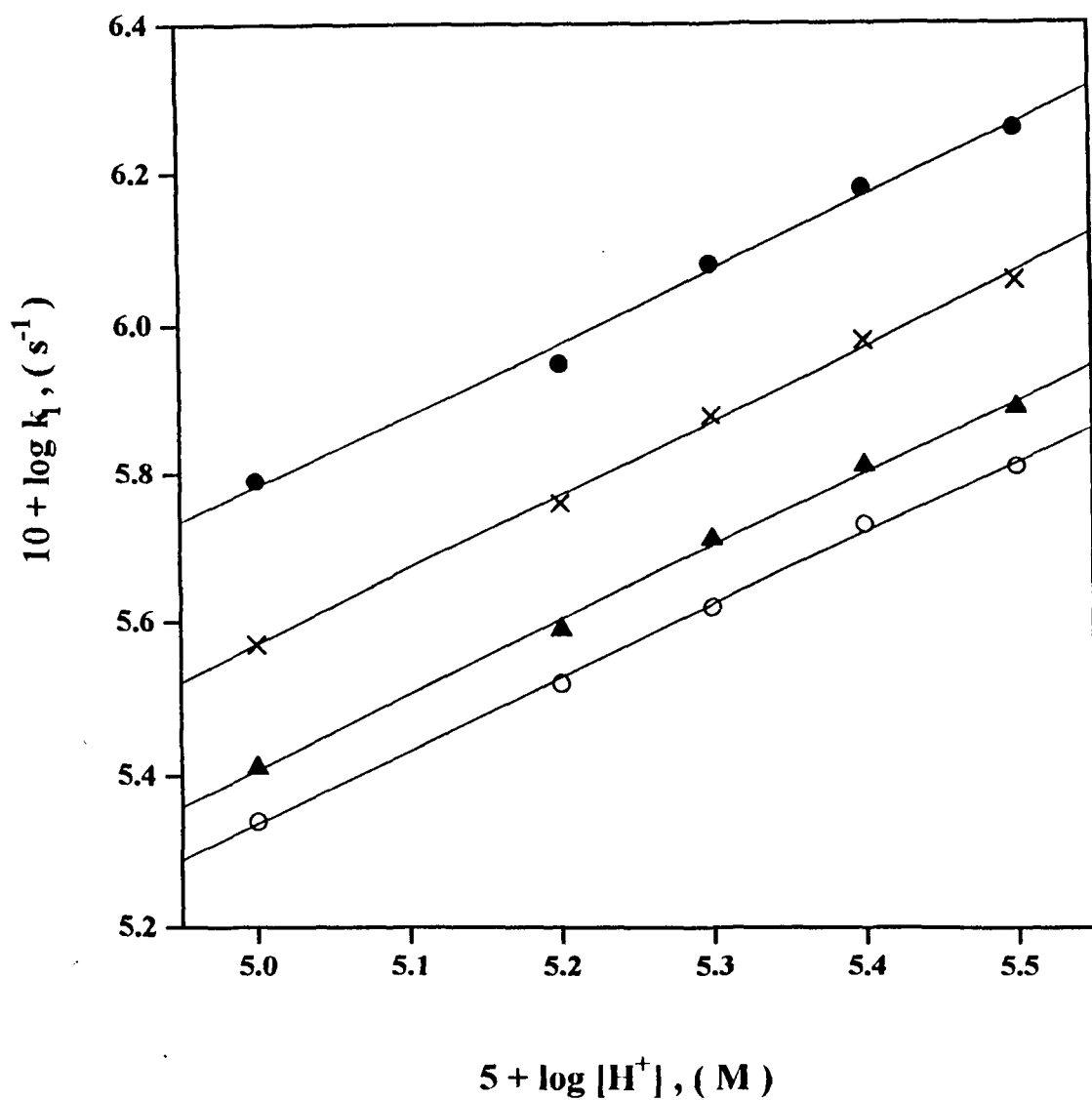


Fig. 4. Plots of $\log k_1$ against $\log [H^+]$ for 3-pentanone (O), 3-hexanone (▲), 3-heptanone (×) and 3-octanone (●).

converted to a protonated species at the concentrations of mineral acid used. Quinolinium dichromate is a dimetallic species, an anionic condensed form of chromic acid. For aqueous solutions of chromic acid, Michel et al. (32), had examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate HCrO_4^- did not exist in aqueous solutions of Cr(VI) compounds. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of mineral acid would be HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. These ions were in equilibrium with each other, according to the equation given by $2 \text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ ($K_d = 35.5$). When the Raman lines were examined under dilution, it was established that at $\text{pH} = 11$, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion, whereas at $\text{pH} = 1.2$, it was 100% as the $\text{Cr}_2\text{O}_7^{2-}$ ion (32). Hence, at concentrations of acid larger than 0.05 M, the dichromate ion (and its protonated form) would be the predominant species. In aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, spectral studies have shown that $\text{Cr}_2\text{O}_7^{2-}$ was the predominant species (33). In the present investigation, since the acid concentrations used were in the range 1.0 to 3.0 M, the dichromate ion (or its protonated form) would be the predominant species. Moreover, the protonated Cr(VI) species would be a more reactive electrophilic species and would be sufficiently reactive to attack the enol form of the alkanones.

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been employed for all the kinetic runs, the observed rate law could be expressed as :

$$\text{Rate} = - \frac{d[\text{QDC}]}{dt} = k [\text{Substrate}] [\text{QDC}] [\text{H}^+] \quad (10)$$

Effect of solvent

Reactions involving ionic reactants were influenced by the solvent. It is hence to be expected that, in the present investigation, the solvent should be playing an important role in these reactions. In the case of each of the substrates oxidized by quinolinium dichromate, the rate of oxidation was slowest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of acetic acid resulted in an increase in the rate of oxidation (Tables 8-9).

Table 8 : Dependence of Rate Constants on Solvent Composition for 2-Alkanones

([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 2.0 M; T = 323K)

H ₂ O:DMF (%, v/v)	Dielectric Constant (D)	10 ⁴ k ₁ / s ⁻¹				
		2-Butanone	2-Pentanone	2-Hexanone	2-Heptanone	2-Octanone
100:0	69.9	1.52	0.48	0.65	0.81	1.12
95:5	68.3	1.74	0.53	0.79	0.91	1.26
90:10	66.7	2.09	0.65	0.93	1.10	1.41
85:15	65.1	2.34	0.76	1.18	1.35	1.66
80:20	63.5	2.88	0.93	1.32	1.48	2.04

Table 9 : Dependence of Rate Constants on Solvent Composition for 3-Alkanones**([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 2.0 M; T = 323K)**

H ₂ O:DMF (%, v/v)	Dielectric Constant (D)	10 ⁴ k ₁ / s ⁻¹			
		3-Pentanone	3-Hexanone	3-Heptanone	3-Octanone
100:0	69.9	0.42	0.51	0.76	1.20
95:5	68.3	0.51	0.62	0.83	1.38
90:10	66.7	0.59	0.72	1.02	1.62
85:15	65.1	0.68	0.81	1.26	1.95
80:20	63.5	0.79	0.98	1.51	2.40

The dielectric constants for water-DMF mixtures have been estimated approximately from the dielectric constants of the pure solvents (at 323 K: water = 69.9; DMF = 37.6) (34).

In the present investigation, in proceeding from 0% DMF to 20% DMF, the polarity decreases. The decrease in the polarity of the medium caused an increase in the rate of the reaction (Tables 8-9). Plots of log k₁ against the reciprocal of the dielectric constant were linear (Figures 5-6), with positive slopes. This suggested an interaction between a positive ion and a dipole (35), and was in consonance with the experimental observation that, in the presence of an acid, the rate-determining step involved a

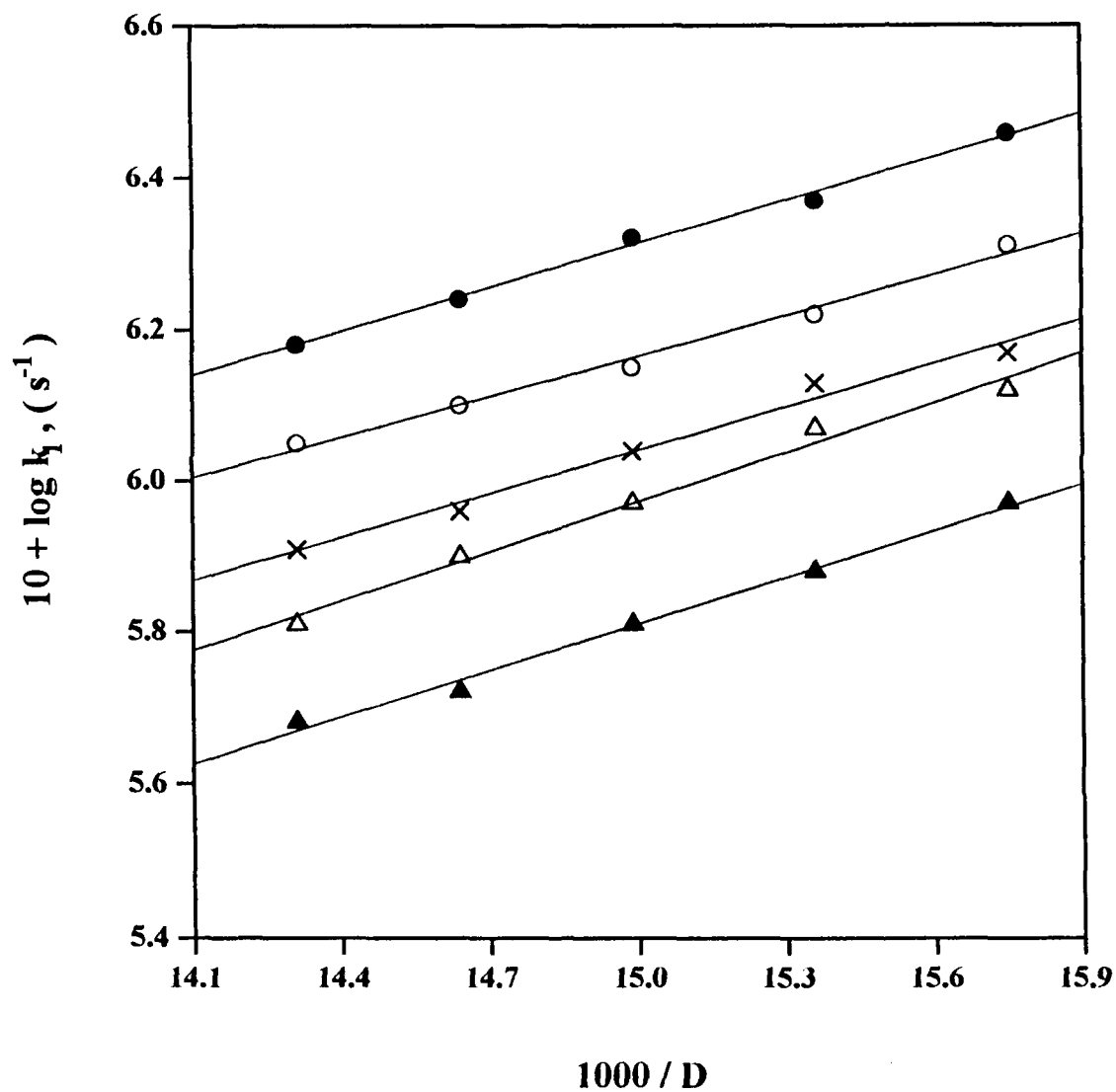


Fig. 5. Plots of $\log k_1$ against the reciprocal of the dielectric constant for 2-butanone (●), 2-pentanone (▲), 2-hexanone (△), 2-heptanone (×) and 2-octanone (○).

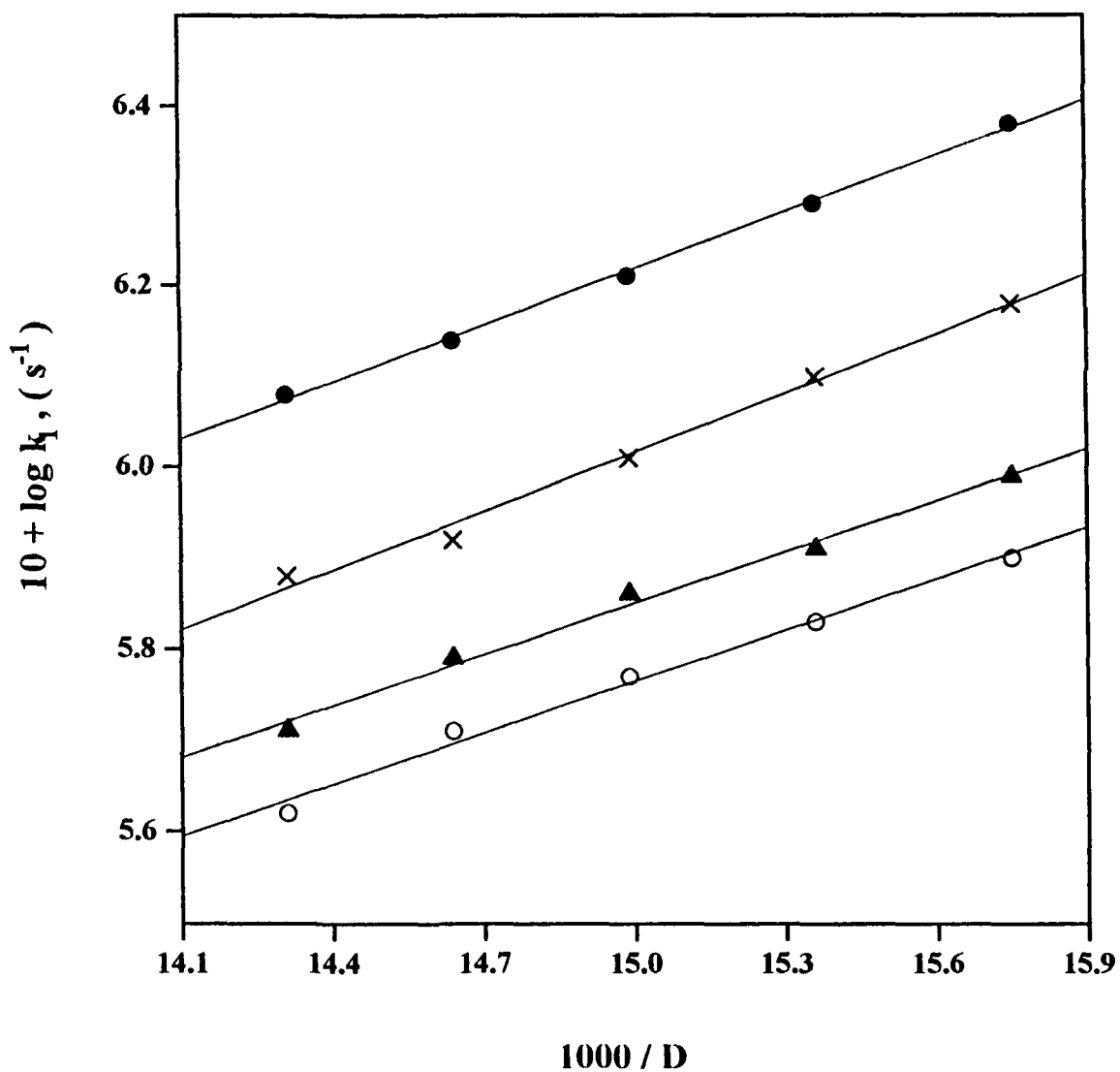


Fig. 6. Plots of $\log k_1$ against the reciprocal of the dielectric constant for 3-pentanone (○), 3-hexanone (▲), 3-heptanone (×) and 3-octanone (●).

protonated Cr(VI) species. The data in Tables 8-9 indicated that the dielectric constants for water-DMF mixtures were a linear function of the solvent composition used in this investigation. This relationship between $\log k_1$ and $1 / D$ was thus obeyed in the range of dielectric constants used.

On the basis of the solvating power of the solvent, a correct prediction of a qualitative nature could be made regarding the rate of the reaction in different solvent media. It would be expected that the total solvation of an ion and a dipole (initial state) should be greater than the solvation of the transition state formed by their union. The transition state would be less polar than the initial state (reactants), because of the increased dispersal of charges in the transition state (36). Hence, the decrease in the rate of oxidation on the addition of a more polar solvent, as in the present investigation, would be the result of a progressive decrease in solvation of the transition state. The effect of a change in the solvent composition on the reaction rates would also be dependent on factors such as solvent-solute interactions (37, 38), and on solvent structure.

Effect of temperature

The rates of the reactions were influenced by changes in temperature. It was observed that an increase in temperature resulted in an increase in the rate of the reaction (Tables 10-11).

Table 10 : Dependence of Rate Constants on Temperature for 2-Alkanones, in aqueous medium; ([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 2.0 M)

Temperature (± 0.1K)	$10^4 k_1 / s^{-1}$				
	2-Butanone	2-Pentanone	2-Hexanone	2-Heptanone	2-Octanone
313	0.53	0.14	0.22	0.30	0.39
318	1.02	0.28	0.32	0.45	0.72
323	1.52	0.48	0.65	0.81	1.12
328	2.46	0.81	1.23	1.51	2.04
333	3.47	1.38	1.70	2.04	2.69

Table 11 : Dependence of Rate Constants on Temperature for 3-Alkanones**([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 2.0 M)**

Temperature (± 0.1K)	$10^4 k_1 / s^{-1}$			
	3-Pentanone	3-Hexanone	3-Heptanone	3-Octanone
313	0.18	0.24	0.33	0.50
318	0.25	0.36	0.50	0.76
323	0.42	0.51	0.76	1.20
328	0.68	0.81	1.07	1.62
333	0.98	1.23	1.62	2.24

Plots of $\log k_1$ against the reciprocal of temperature were linear (Figures 7-8), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies (vide "Experimental : Calculations"). The other activation parameters were evaluated, and have been shown in Tables 12-13.

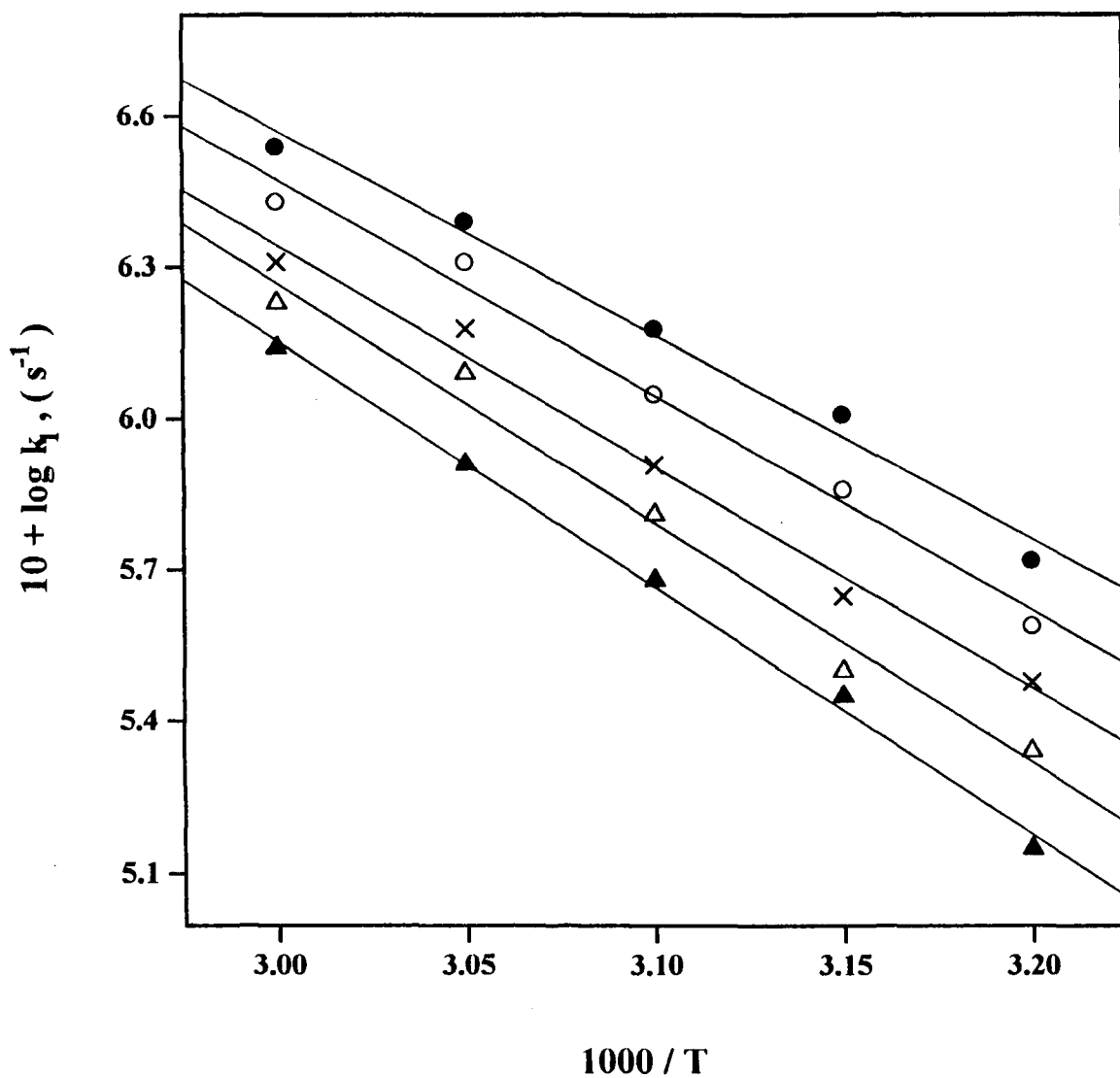


Fig. 7. Plots of $\log k_1$ against the reciprocal of temperature for 2-butanone (●), 2-pentanone (▲), 2-hexanone (△), 2-heptanone (×) and 2-octanone (○).

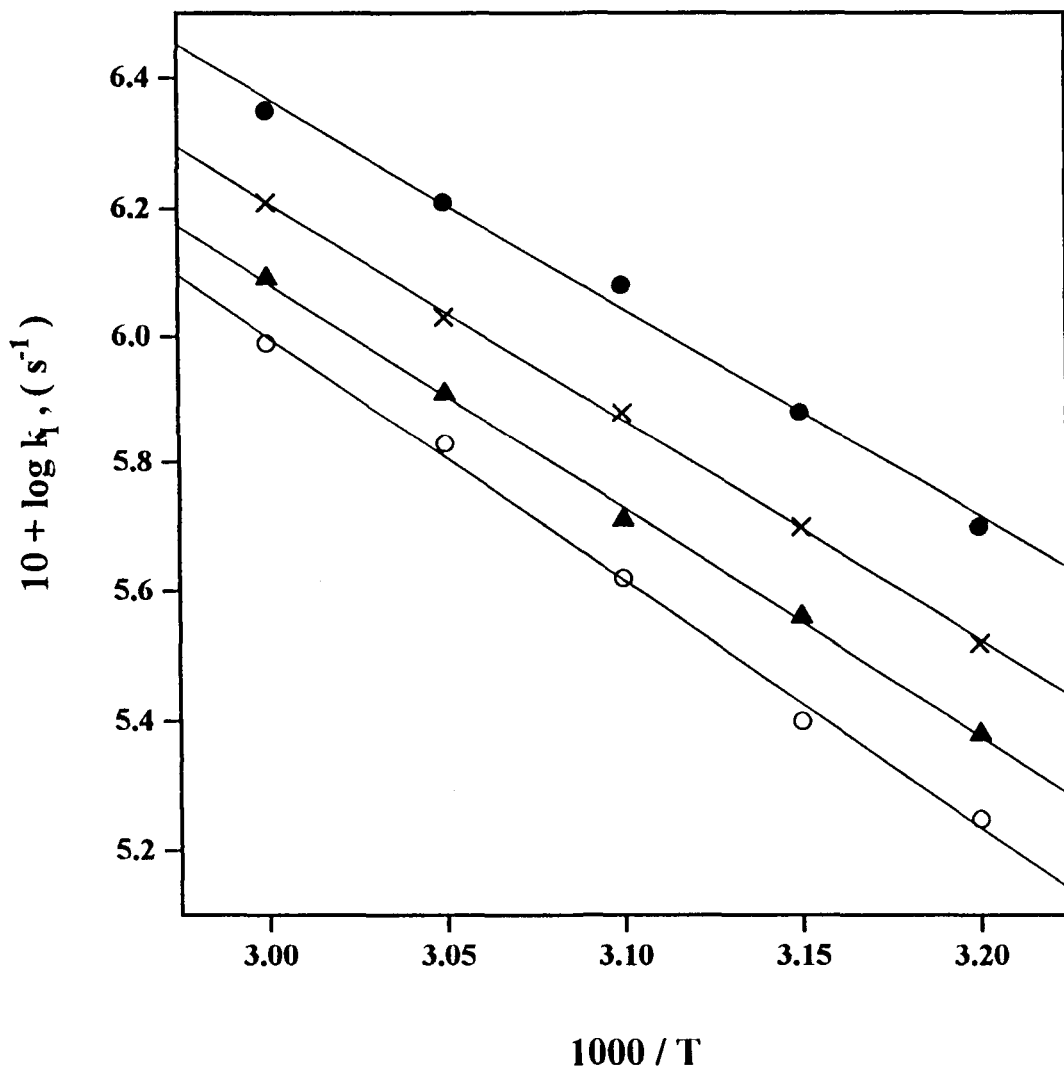


Fig. 8. Plots of $\log k_1$ against the reciprocal of temperature for 3-pentanone (O), 3-hexanone (\blacktriangle), 3-heptanone (\times) and 3-octanone (\bullet).

Table 12 : Activation Parameters for 2-Alkanones ^a

Substrate	E (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
2-Butanone	81	78	-78	101
2-Pentanone	97	95	-34	105
2-Hexanone	95	92	-43	104
2-Heptanone	87	85	-62	103
2-Octanone	86	83	-66	102

^a Error limits : E \pm 2 kJ mol⁻¹; $\Delta H^\ddagger \pm$ 2 kJ mol⁻¹; $\Delta S^\ddagger \pm$ 5 JK⁻¹ mol⁻¹; $\Delta G^\ddagger \pm$ 2 kJ mol⁻¹.

Table 13 : Activation Parameters for 3-Alkanones ^a

Substrate	E (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
3-Pentanone	86	82	-102	104
3-Hexanone	81	77	-117	103
3-Heptanone	79	74	-121	102
3-Octanone	67	63	-152	101

^a Error limits : E \pm 2 kJ mol⁻¹; $\Delta H^\ddagger \pm$ 2 kJ mol⁻¹; $\Delta S^\ddagger \pm$ 5 JK⁻¹ mol⁻¹; $\Delta G^\ddagger \pm$ 2 kJ mol⁻¹.

The high positive values of the enthalpies of activation (ΔH^\ddagger) and the free energies of activation (ΔG^\ddagger) indicated that the transition state was highly solvated. The oxidation of all the substrates were characterized by negative entropies of activation. This would suggest that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecules (39). Differences in solvation of the substrate in the ground state and the transition state might also contribute, to some extent, to the negative entropies of activation. The similarity of ΔG^\ddagger values for all the substrates arose due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that all these reactions involved similar rate-determining steps.

Isokinetic relationship

The enthalpies and entropies of activation for a reaction were linearly related by the equation

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (11)$$

where β was the isokinetic temperature. For the oxidation reactions studied in the present investigation, the activation enthalpies and entropies were linearly related. The correlation was tested and found to be valid by applying Exner's criteria (40). The isokinetic temperature, obtained from the plot of ΔH^\ddagger against ΔS^\ddagger , was 385K (for 2-alkanones) and 382K (for 3-alkanones) (Figures 9-10). Although current views do not attach much physical significance to isokinetic temperatures (41), a linear correlation between ΔH^\ddagger and ΔS^\ddagger is usually a necessary condition for the validity of the Hammett equation (linear free energy relationships). The linear trend between the

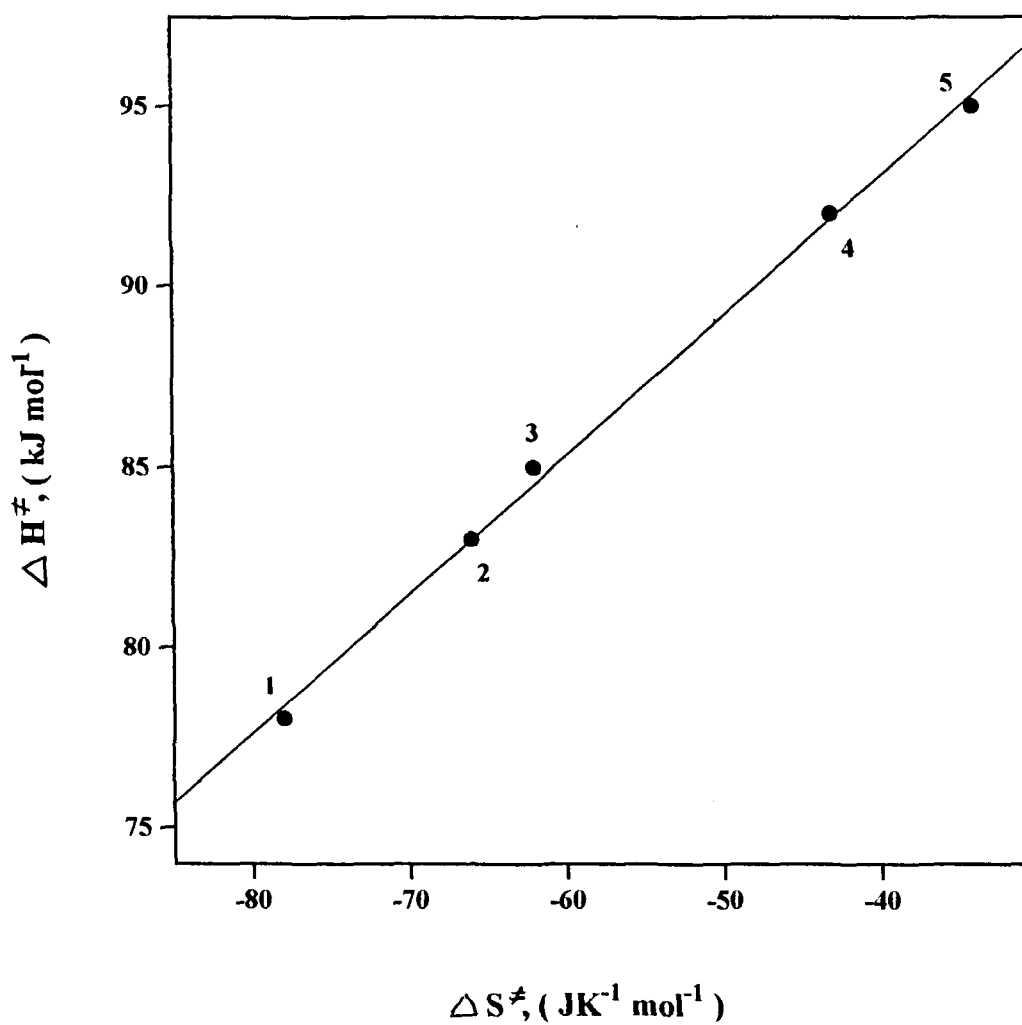


Fig. 9. Plots of ΔH^\ddagger against ΔS^\ddagger for 2-butanone (1), 2-pentanone (5), 2-hexanone (4), 2-heptanone (3) and 2-octanone (2).

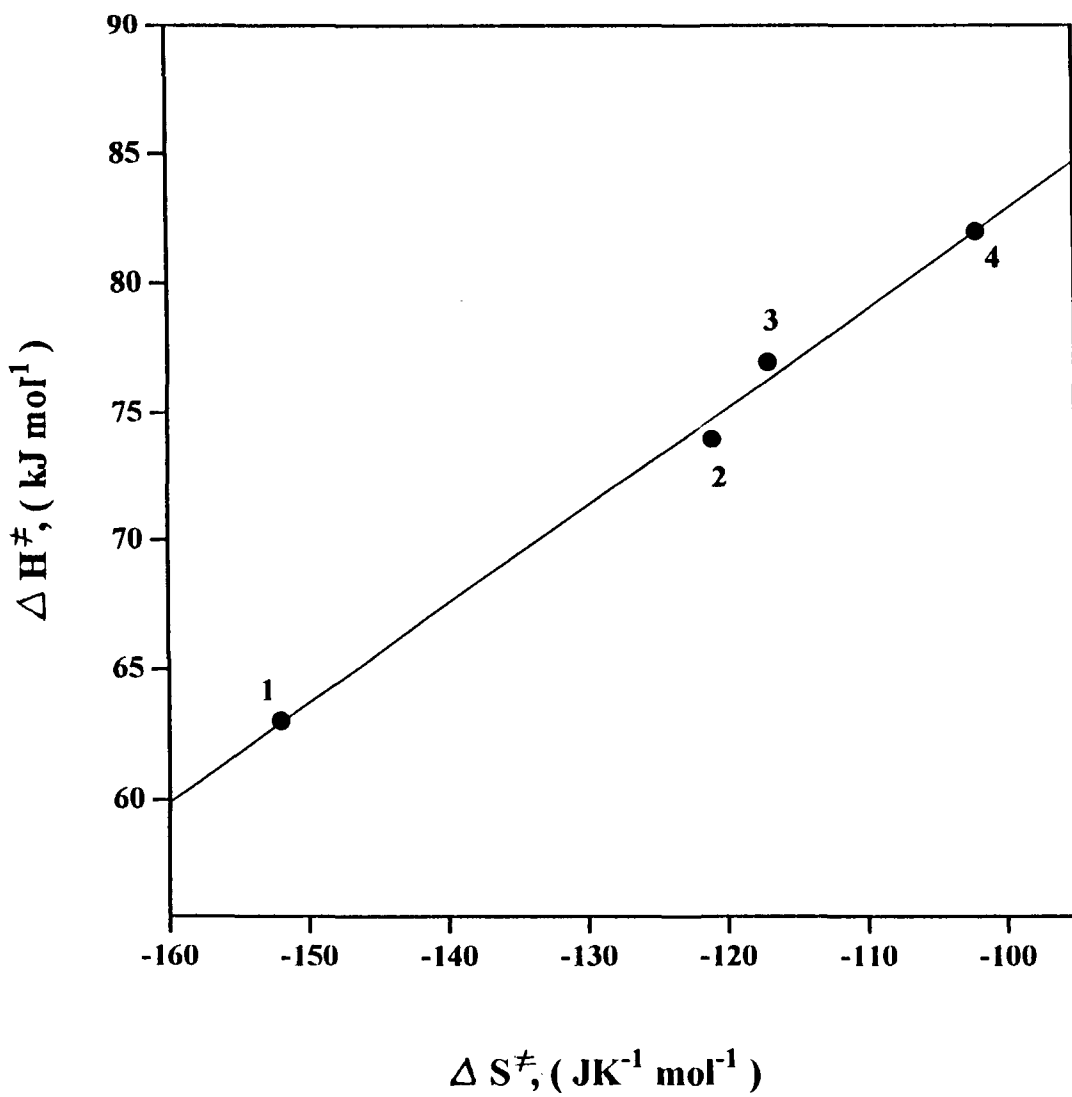


Fig. 10. Plots of ΔH^\ddagger against ΔS^\ddagger for 3-pentanone (4), 3-hexanone (3), 3-heptanone (2) and 3-octanone (1).

enthalpies and entropies of activation further established that all these reactions were controlled by both parameters, ΔH^\ddagger and ΔS^\ddagger . Further, the values for the free energy of activation (ΔG^\ddagger) were nearly constant, indicating that the same mechanism operated for the oxidation of all the alkanones (2- and 3-) studied in this investigation.

Induced polymerization

In the present investigation, since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (42). This indicated that a one-electron oxidation was quite unlikely. Control experiments were performed, in the absence of the respective substrates. The concentration of QDC did not show any appreciable change.

Relative rates of oxidation

In the present investigation, the order of reactivity was in accordance with the structural changes in the 2-alkanones and 3-alkanones :

2-butanone > 2-octanone > 2-heptanone > 2-hexanone > 2-pentanone (for 2-alkanones);

and 3-octanone > 3-heptanone > 3-hexanone > 3-pentanone (for 3-alkanones).

The formation of the enol would be assisted by the electron-releasing group adjacent to the carbonyl group. The ascending order of reactivity was observed as the length of the alkyl group adjacent to the carbonyl group increased. The tendency of alkyl groups to increase the electron density on the α -carbon would check the loss of the

proton attached to the same α -carbon atom. Hence, an increase in the +I-effect of the alkyl groups would increase the rate of the reaction. The enhanced reactivity of 2-butanone calls for an explanation. Considering the fact that the length of the alkyl chain was the shortest in 2-butanone, as compared to the longer chains in the series of 2-alkanones, the higher rate of oxidation of 2-butanone could be due to a dominant hyperconjugative effect called into play to meet the demand of a suitably placed double bond. Such an explanation has been used for the enhanced reactivity of 2-butanone when oxidized by selenium dioxide in aqueous acidic medium (28). It would be justified to suggest that since the site of attack was at the carbon-carbon double bond, there would be a greater steric effect for the longer chains of the other alkanones, as compared to that for 2-butanone. Since the steric effect would be the least for 2-butanone, it would be envisaged that the reactivity of 2-butanone would be higher than that for the other members of this series. Hence, the observed order of reactivity for the 2-alkanones (Table 2).

Mechanism

There exists the distinct possibility of an equilibrium between the keto- and enol form of alkanones. Hence, it could be visualized that different oxidants would attack either the keto form or the enol form to give different products. It would be worthwhile to examine the evidence for the oxidation of alkanones proceeding via the keto form or the enol form, depending upon the type of oxidant and the different reaction conditions employed for the oxidation process.

(i) Reactions through the keto form of 2- and 3- alkanones

The oxidation of 2-butanone with Mn(III) sulphate showed that the enolization step was an acid-catalyzed reaction, whereas the oxidation step was independent of acidity (1). An increase in the proportion of acetic acid in the solvent mixture favoured a reaction involving protonation, and the acid-catalyzed enolization of the 2-butanone was an example of such a reaction. It was observed that the rate of oxidation was much faster than the rate of enolization, which clearly proved that the oxidation of 2-butanone by Mn(III) sulphate proceeded via a direct attack on the keto form. This was followed by the rate-determining step to give a radical, which was then oxidized by several fast steps to acetaldehyde and acetic acid (1).

The oxidation of 2-butanone and 2-pentanone by peroxydiphosphate in aqueous sulfuric acid medium showed that the rate of oxidation was much greater than the rate of enolization. The slow step involved the attack of the oxidant on the keto form of the substrate (2).

The kinetics of oxidation of 2-butanone by Ce(IV) in perchloric acid medium showed the reaction of the oxidant on the keto form of the substrate to yield a keto complex. The decomposition of this complex gave a radical species in the rate-determining step (3).

Potassium bis(tellurato)cuprate(III) was used to oxidize 2-butanone in aqueous alkaline medium. The alkali dependence showed that OH^- was used up either in the

reversible formation of the enolate ion or in the abstraction of a proton from the bis(tellurato) cuprate(III) ion. Kinetic evidence showed that the OH^- ion was involved in the latter process. The first step involved the reaction of the ketone with the oxidant to yield a complex. It was proposed that this complex collapsed to a radical and a Cu(II) species. In the final step of the reaction, the radical underwent a rapid reaction with a second Cu(II) moiety to form the product. Thus, this kinetic investigation provided evidence of the direct attack on the ketonic form of alkanone (20).

The kinetics of oxidation of 2- and 3- alkanones by bromamine-B in alkaline buffer medium showed a first-order dependence on oxidant, but a variable dependence (one to zero) on ketone. It was shown that the substrate interacted through the keto form. The rate-determining step was the reaction between the ketone and HOBr to give an intermediate, which underwent a rapid reaction to yield the diketones as the final products (25).

The kinetics of oxidation of 2-alkanones by selenium dioxide in aqueous acetic acid and perchloric acid media showed that the redox process occurred via an attack of the oxidizing species on the keto form of the 2-alkanones. The kinetic data obtained ruled out the possibility of enolization as the rate-determining step. The rate-determining step involved a new oxygen-selenium bond formation, followed by the loss of a water molecule (28).

The kinetics of oxidation of 2-butanone with permanganate ions in aqueous acid and alkaline media has been studied. In acid medium, the slow enolization was followed by rapid halogen addition, and the reaction showed a zero order dependence on halogen

concentration. It was suggested that the attack of the permanganate ion took place via a nucleophilic addition on the carbon atom of the carbonyl group, resulting in the formation of an intermediate permanganate ester. In alkaline medium, permanganate ion reacted with the enolate anion in a concerted process. In both the processes, the electrophilic attack of halogen and the electron abstraction by the permanganate ion (that is, oxidation) took place at the same site of the molecule. The final products of this oxidation reaction were acetic acid and oxalic acid, indicating that a cleavage of the carbon-carbon bond had taken place in the final step of the reaction (29).

(ii) Reactions through the enol form of 2- and 3- alkanones

The kinetics of oxidation of 2-alkanones by acid permanganate, in the presence of fluoride ions, showed that the oxidation was slower than the acid-catalyzed enolization of the ketone. The magnitude of the solvent effect and the correlation between the relative rates of oxidation and enolization suggested that the enol form was involved in the oxidation process. The products obtained were aldehyde and acid (4).

The kinetics of oxidation of 2-butanone and 3-pentanone by tris(1,10-phenanthroline)Fe(III) in aqueous acidic medium were consistent with the mechanism involving oxidation of the enol tautomer by the oxidant. The products obtained were the diketones (5).

The kinetics of oxidation of 2-butanone by potassium permanganate in aqueous acetic acid at constant ionic strength showed that the reactions proceeded via the enol form of the ketone. The rate-determining step involved a two-electron transfer from the enol resulting in a carbocation, which was rapidly converted to the products (6).

The kinetics of oxidation of 2-butanone by V(V) in acid medium showed that the rate of enolization was much faster than the rate of oxidation. It was suggested that the ketone could be reacting through an enol intermediate giving an enol-V(V) complex, which was subsequently converted to formic acid (7).

The kinetics of oxidation of 2-alkanones by lead tetraacetate, in acetic acid-sodium acetate medium, showed a zero-order dependence on the concentration of the oxidant. The mechanistic pathway involved the rate-determining enolization of the ketones. The products obtained were the acetoxy derivatives (8).

The kinetics of oxidation of 2-alkanones by sodium metaperiodate in aqueous alkaline medium was studied both in the absence and presence of osmium tetroxide. In the absence of osmium tetroxide, the reaction showed a first order dependence on periodate. In the presence of osmium tetroxide catalyst, the order dependence with respect to periodate was shown to be zero. The large negative entropies of activation for the catalyzed reaction suggested the cyclic nature of the transition state, giving an enolate-OsO₄ complex. The rate-determining step was the reaction of the enolate reacting with the Os(VIII) ion. The products obtained were the corresponding acids (9).

The Ce(IV) oxidation of 3-pentanone in sulphuric acid solution showed a first order dependence on the oxidant. The oxidation process was via the reaction of the enol with the oxidant. The reaction product was identified as the corresponding carboxylic acid (10).

The oxidation of 2-butanone by chloramine-T in aqueous ethanol under alkaline conditions suggested the involvement of an enolate anion in the rate-determining step of the reaction. The intermediate formed reacted with the oxidant in a fast step, to give the 1,2-diketones (11).

The kinetics of oxidation of 2-alkanones by thallium triacetate, in acid medium, showed a zero-order dependence on the concentration of the oxidant. The rate-determining step was the enolization of the ketone. It was observed that the thallium(III) reacted with the enol-form of the ketone to give an intermediate carbocation in a two-electron transfer step, yielding the acetoxy derivatives as products (12).

The kinetics of the Ru(III)-catalyzed oxidation of 2-alkanones by potassium bromate in acid medium showed a zero-order dependence on the concentration of the oxidant. The mechanism involved the enolization of the ketones in the rate-determining step, followed by the cleavage of the intermediate enol-Ru(III) complex to yield the diacetyl as the products (13).

The kinetics of oxidation of 2-alkanones by phenyl iodosoacetate in aqueous acetic acid medium, in the presence of perchloric acid and sulfuric acid, have been reported. These reactions showed a zero-order dependence with respect to the concentration of oxidant. The mechanism suggested involved the enolization of the ketone in the rate-determining step of the reaction, followed by oxidation of the enol in a fast step (14).

The reactions of 2-alkanones with phenyl iodosoacetate in aqueous acetic acid-sulfuric acid mixtures yielded the acetoxy derivatives as the final products. The reactions showed a zero-order dependence on the concentration of the oxidant, and the mechanism suggested was via a process of enolization in the rate-determining step (15).

The oxidation of 2-butanone and 3-pentanone by Ce(IV) sulphate in aqueous sulfuric acid medium, catalyzed by Ru(III) chloride, proceeded via the formation of an activated complex between Ru(III) and the protonated ketone in the rate-determining step. Kinetic data revealed a zero-order dependence with respect to the oxidant. The final oxidation products were characterized as the carboxylic acids (16).

A zero-order dependence on oxidant concentration was observed in the reactions between 2-alkanones and N-bromosuccinimide, in perchloric acid medium, in the presence of mercuric acetate. Solvent isotope effects pointed to a mechanism wherein the oxidation proceeded through the enol form of the substrate. The products obtained were the corresponding 1,2-diketones (17).

The kinetics of oxidation of 2-alkanones by N-bromosaccharin in aqueous acetic acid medium showed that the rate was independent of the concentration of the oxidant. The rate-determining step was the enolization of the corresponding ketone. The final products obtained were the 1,2-diketones (18).

The kinetics of oxidation of 2-butanone and 3-pentanone by N-bromoacetamide (NBA) in perchloric acid medium, in the presence of mercuric acetate, showed a zero-order dependence on NBA, and a first-order dependence on both substrate and acid.

The rate-determining step was the enolization of the ketone followed by a rapid reaction of the enol with NBA to give the corresponding diketones (19).

The kinetics of oxidation of 2-butanone and 3-pentanone by trichloroisocyanuric acid in aqueous acetic acid, in the presence of perchloric acid, revealed a zero-order dependence on [oxidant], and a first-order dependence on each – acid and substrate. Kinetic data supported the acid-catalyzed enolization of ketones as the rate-determining step. The subsequent reaction between the enol and the oxidant was the fast step. The products obtained were the monochloro ketones (21).

The kinetics of oxidation of 2-hexanone by N-bromoacetamide (NBA) in perchloric acid, in the presence of mercuric acetate, showed a first-order dependence on the ketone and acid, and a zero-order dependence with respect to NBA. The mechanistic route for NBA oxidation was suggested to be through the enol form of the ketone. It was established that the oxidation reaction proceeded through enolization in the rate-determining step, followed by a rapid reaction between the enol and NBA to give the corresponding 1,2-dicarbonyl compound as the final product (22).

The kinetics of oxidation of 2- and 3- alkanones by bromamine-B (BAB) and bromamine-T (BAT) in perchloric acid medium showed a first-order dependence on ketone and H^+ , but the rate was independent of the concentration of the oxidant. The suggested mechanism involved the acid-catalyzed enolization of the ketone in the rate-determining step, followed by a fast interaction between enol and oxidant to give the diketones as the final products (23, 24).

The kinetics of oxidation of 2-alkanones by acid bromate showed a first-order dependence on each – bromate, ketone and acid. The mechanism proposed involved the attack of acid bromate on the enol form of the ketone in the rate-determining step of the reaction. The resulting intermediate underwent rapid decomposition to give the carboxylic acids as the final products (26).

The respective diketones were obtained as the products of oxidation of 2-butanone and 2-pentanone by acid solutions of potassium bromate, catalyzed by Ru(III), in the presence of mercuric acetate. The kinetic results showed a zero-order dependence on bromate, but a first-order dependence with respect to the concentrations of the substrate, acid and catalyst. The rate-determining step was the formation of the enol. This was followed by a rapid conversion of the intermediate to the products (27).

(iii) Present Investigation

In the present investigation, based on the stoichiometries of the oxidation reactions (Table 1), and the observed experimental data, the mechanistic pathways for the oxidation of the 2-alkanones (2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, and 2-octanone) and the 3-alkanones (3-pentanone, 3-hexanone, 3-heptanone, and 3-octanone) by quinolinium dichromate (QDC) in aqueous acid medium, has to be rationalized. While suggesting mechanistic pathways for these oxidation reactions, the following kinetic observations have to be taken into consideration :

- (1) the rates of the reactions were dependent on the first powers of the concentrations of each — substrate and oxidant (Tables 2-5). This kinetic behaviour was

consistent with a mechanism involving a rate-determining reaction between the enol form of the substrate and the oxidant;

- (2) the rates of the reactions were dependent on the first powers of the concentrations of the acid (Table 6-7). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated dimetallic Cr(VI) species in the rate-determining step of the reaction;
- (3) the rates of the reactions were decreased, with an increase in the polarity of the medium, using water-DMF mixtures (Table 8-9). Plots of $\log k_1$ against the reciprocal of the dielectric constants (Figs 5-6) were linear, with positive slopes. This indicated an interaction between a positive ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated dimetallic Cr(VI) species;
- (4) the rate of the oxidation reactions showed an increase with an increase in temperature (Tables 10-11). The negative entropies of activation (Tables 12-13), suggested that the transition state formed was considerably rigid, resulting in a decrease in the degrees of freedom of the molecules. The similarity in ΔG^\ddagger values (Tables 12-13) for all the substrates were due to changes in ΔH^\ddagger and ΔS^\ddagger values, and suggested that all these oxidation reactions involved similar rate-determining steps;
- (5) there was no induced polymerization of acrylonitrile or the reduction of mercuric chloride, indicating the absence of any radical formation; and
- (6) the observed order of reactivities for the oxidation of 2- and 3- alkanones was in accordance with the structural changes in the substrates :

2-butanone > 2-octanone > 2-heptanone > 2-hexanone > 2-pentanone (for 2-alkanones) (Table 2); and

3-octanone > 3-heptanone > 3-hexanone > 3-pentanone (for 3-alkanones) (Table 3).

These orders of reactivities were rationalized on the basis of the + I-effect of the electron-releasing alkyl groups adjacent to the carbonyl groups.

It would be worthwhile to summarize the evidence for the reactions of 2- and 3-alkanones proceeding via the keto-form or the enol-form of the substrates. The rates of oxidation have been observed to be faster than the rates of enolization for the reactions of alkanones with oxidants such as Mn(III)sulphate in acid medium (1), peroxydiphosphate in aqueous sulfuric acid medium (2), Ce(IV) in perchloric acid medium (3), potassium bis(tellurato) Cu(III) in aqueous alkaline medium (20), bromamine-B in alkaline buffer medium (25), selenium dioxide in aqueous acetic acid and perchloric acid media (28), and permanganate in aqueous acidic and alkaline media (29). In all these reactions, it was established that the oxidation of alkanones proceeded by a direct attack on the keto form of the substrate. In some of these cases, the rate-determining step was the reaction between the keto form of the substrate and the oxidant (2, 25, 28). In the reactions of alkanones with Ce(IV) in perchloric acid medium (3), potassium bis(tellurato) Cu(III) in aqueous alkaline medium (20), and with permanganate in aqueous acidic media (29), the rate-determining step was the decomposition of the complex formed between the keto form of the substrate and the oxidant.

In the oxidation of 2-butanone by manganese(III) sulphate, the first step was the rapid, reversible formation of complex between the ketone and the manganese(III) sulphate complex, followed by the rate-determining step to give a radical, which on oxidation by several fast steps gave the products (1).

There have been several reports emphasizing the enolization of the ketones as the significant step in the oxidation of 2- and 3- alkanones. These can be categorized as follows :

(a) in the oxidation of 2-butanone by V(V) in the presence of sulfuric acid and perchloric acid, the enolization step was very rapid. It was suggested that the ketone reacted through an enol intermediate which formed a complex with V(V). In the rate-determining step, this enol-V(V) complex underwent decomposition to give formic acid as the major product (7). The Ru(III) chloride-catalyzed oxidation of 2- and 3- alkanones by Ce(IV) sulphate, in aqueous sulfuric acid medium, showed that the oxidation proceeded via the formation of an activated complex between Ru(III) and the protonated ketone in the rate-determining step (16). This was followed by a fast reaction between the Ru(III) hydride and a Ce(IV) species. The products obtained were the respective carboxylic acids (16);

(b) in the oxidation of 2-butanone and 2-pentanone by acidic potassium bromate solution, catalyzed by Ru(III), the rate-determining step involved the reaction of the protonated ketone and the oxidant to give an intermediate which underwent a rapid conversion to the respective diketones (27); and

(c) for the oxidation of 2- and 3- alkanones by a variety of oxidizing agents, the rate-determining step was characterized as the enolization of the ketones. These reactions have included oxidation processes involving 2- and 3- alkanones with lead tetraacetate in acetic acid-sodium acetate medium (8), thallium triacetate in acidic medium (12), potassium bromate in acid medium (13), phenyl iodosoacetate in aqueous acetic acid medium in the presence of perchloric acid and sulfuric acid (14), phenyl iodosoacetate in acetic acid-sulfuric acid media (15), N-bromosuccinimide in perchloric acid media in the presence of mercuric acetate (17), N-bromosaccharin in aqueous acetic acid medium (18), N-bromoacetamide in perchloric acid medium in the presence of mercuric acetate (19), trichloroisocyanuric acid in aqueous acetic acid medium in the presence of perchloric acid (21), N-bromoacetamide in perchloric acid medium in the presence of mercuric acetate (22), bromamine-B in perchloric acid medium (23), and with bromamine-T in the presence of perchloric acid medium (24).

In all the oxidation reactions, kinetic data showed a zero-order dependence on the concentrations of the particular oxidant used. This zero order dependence on oxidant concentration had established that the rate-determining step was the acid-catalyzed enolization of the 2- and 3-alkanones, and that the enol form reacted with the oxidant, in a fast step, to give the products. The nature of the products formed showed that there was no cleavage of the carbon-carbon bond in the final step of the reaction ((8, 12-15, 17-19, 21-24).

In the present investigation, focusing on the oxidation of 2- and 3- alkanones by quinolinium dichromate (QDC) in acid medium, the rate of oxidation was first-order with

respect to the concentrations of each - substrate, oxidant and acid. The first-order dependence of the rate on QDC concentration supported a reaction pathway proceeding through the enol form of the substrate. The rates of enolization of all the 2- and 3-alkanones were determined by the bromination method. It was found that the rates of enolization were very much greater than the rates of oxidation for all the alkanones by a factor of ~12. Since the rates of enolization were found to be much faster than the rate of oxidation, this would suggest that the enolization step was not rate-determining. Hence, it could be concluded that the enol-form of the substrate reacted with the oxidant. The rate-determining step would thus involve an attack of the oxidant on the enol form of the substrate. It can be recalled that in the acid-catalyzed iodination of ketone, the essential process was the conversion of the keto-form to the enol-form, which was very rapidly iodinated (43).

On the basis of the relative rates of oxidation of the 2- and 3- alkanones studied (Table 14), a cyclic transition state could be postulated.

Table 14 : Rate data for the Oxidation of 2- and 3- Alkanones, in aqueous medium**([Substrate] = 0.1 M; [QDC] = 0.001 M; [H₂SO₄] = 1.0 M; T = 323K**

Substrate	10⁴ k₁ / s⁻¹	Relative Rate
2-Alkanones		
2-Butanone	1.52	3.2
2-Pentanone	0.48	1.0
2-Hexanone	0.65	1.3
2-Heptanone	0.81	1.7
2-Octanone	1.12	2.3
3-Alkanones		
3-Pentanone	0.42	1.0
3-Hexanone	0.51	1.2
3-Heptanone	0.76	1.8
3-Octanone	1.20	2.9

The reactivity of the 2- and 3- alkanones would support a transition state in which the accessibility of the ene and the hydroxyl group of the enol to the reaction centre, were about equally important. This conformational insensitivity could be attributed to the cyclic nature of the transition state.

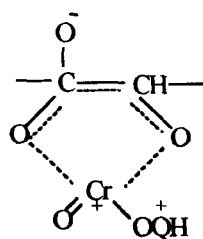
The stoichiometric conversion of the 2- and 3- alkanones to the corresponding carboxylic acids involved the changes : $>=O \rightleftharpoons \gg-OH \rightarrow$ chromate ester \rightarrow carboxylic acid, and the rate of oxidation varied with the concentration of the acid. If the reaction intermediate were to be visualized as having a cyclic structure, then this would explain all the features of the oxidation reaction. The negative entropies of activation (Tables 12-13) would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The similarity in ΔG^\ddagger values arose due to changes in ΔH^\ddagger and ΔS^\ddagger values (Tables 12-13), and stressed the probability that these oxidation reactions involved similar rate- determining steps.

Considering the effect of the solvent, it has been observed that pyridinium chlorochromate (PCC) was used for the oxidation of alcohols, and the kinetic features of these reactions have been reported (44, 45). The mechanistic pathways in all these oxidations by pyridinium chlorochromate had involved the formation of a chromate ester intermediate, which was better stabilized in the presence of solvents of low polarity. Hence, a decrease in the polarity of the solvent had shown an increase in the rate of oxidation of these alcohols by pyridinium chlorochromate (44, 45). In the present investigation, the observed solvent effect (increase in the polarity of the solvent decreased the rate of oxidation, Tables 8-9) provided support for a reaction pathway which involved the formation of a chromate ester intermediate.

Further, the small variation in the reaction rate for the oxidation of 2- and 3- alkanones by quinolinium dichromate (Table 14), could be reconciled with the ester

mechanism, since the chromate ester formation was likely to be little influenced by structural changes (46).

A unimolecular decomposition of the cyclic ester could be written in which the chromium was bonded in the transition state to both the oxygen atoms :



**cyclic ester
T.S**

Electron flow in a cyclic transition state has been earlier considered (47, 48), and the conversion of the ester to the transition state could be best considered in the following terms :

If the chromium was coordinated through the oxygen, then the process of electron transfer could take place through the carbon-oxygen-chromium bond. This would facilitate the formation of the cyclic chromate ester, and also enhance the ease of conversion to the product. Such an intermediate would envisage the transfer of electrons towards the chromium, occurring by the formation of the carbon-oxygen-chromium bonds. Partly occupied orbitals were thus used to bind the oxygen to both, carbon and chromium in the transition state.

In the present investigation, the sequence of reactions involved in the oxidation of 2-alkanones (2-butanone, 2-pentanone, 2-hexanone, 2-heptanone and 2-octanone) and

3-alkanones (3-pentanone, 3-hexanone, 3-heptanone and 3-octanone) by quinolinium dichromate (QDC) in acid medium has been shown in Scheme 1 and Scheme 2.

The mechanism is consistent with the fact that these oxidation reactions were catalyzed by acid (Tables 6-7). Protonation of the oxidant (QDC) would make it more amenable towards nucleophilic attack by the enol form of the substrate on the electron-deficient chromium of the oxidant. The first step involved the enolization of the ketone followed by the protonation of the oxidant (QDC). The second step was the rate-determining step, wherein the enol form of the substrate reacted with the protonated oxidant, in order to form the cyclic chromate ester. This was followed by the transfer of two electrons in a cyclic system giving rise to cleavage products. This electrocyclic mechanism involved six electrons; and being a Hückel-type system ($4n+2$), this was an allowed process (49).

In general, oxidation reactions of organic functions by different oxidizing agents could be considered using the Zimmerman treatment of electrocyclic reactions (50). Selection rules played an important part in determining the mechanisms of many oxidation reactions. For reactions involving electrons in d-orbitals, a topological approach to the orbital levels of the transition state can be applied (50). This method classified the transition state as either "Hückel-like" (in which all overlapping pairs of reacting orbitals were bonding), or "Möbius-like" (in which one or an odd number of anti-bonding overlaps must occur). In a Hückel transition state, $4n+2$ electrons formed a closed shell (giving it stability), while $4n$ electrons were required for stable closed shells in a Möbius transition state. An "allowed" reaction may have either a Hückel-type or a

Möbius-type transition state, provided that the correct number of electrons was available to stabilize that transition state.

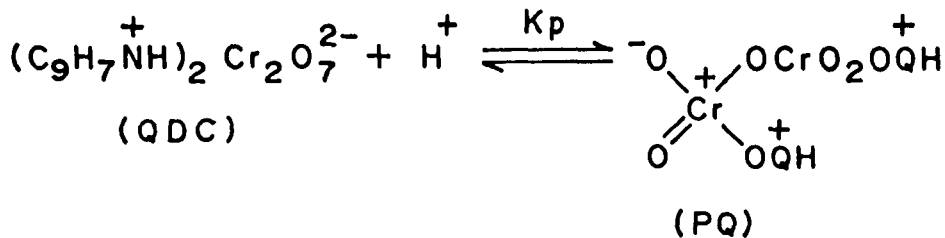
When chromium(VI) was reduced, the initial product chromium(IV) was unstable, but it was generally considered to be an octahedral complex (51). The d-electron in the unexcited product must therefore be in a t_{2g} orbital (d_{xy}) which can overlap, in the reactions, using two adjacent lobes with opposite signs of the wave functions. It can therefore be considered to be locally antisymmetric (π -type). The transition state would be of the Hückel-type ($4n+2$), and hence would be an allowed reaction.

In the present investigation, the oxidation of 2-alkanones (2-butanone, 2-pentanone, 2-hexanone, 2-heptanone and 2-octanone) and 3-alkanones (3-pentanone, 3-hexanone, 3-heptanone and 3-octanone) by quinolinium dichromate (QDC), in acid medium, involved the formation of a cyclic chromate ester. The next step of the reaction would be the transfer of two electrons in the cyclic system. This electrocyclic mechanism for the oxidation of alkanones by QDC involved six electrons, and the orbital picture showed that this was a Hückel-type system ($4n+2$). Hence, this would be an allowed process.

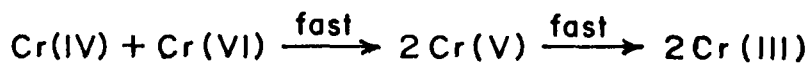
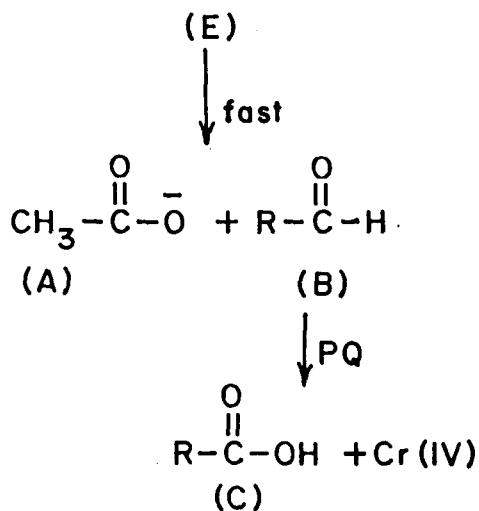
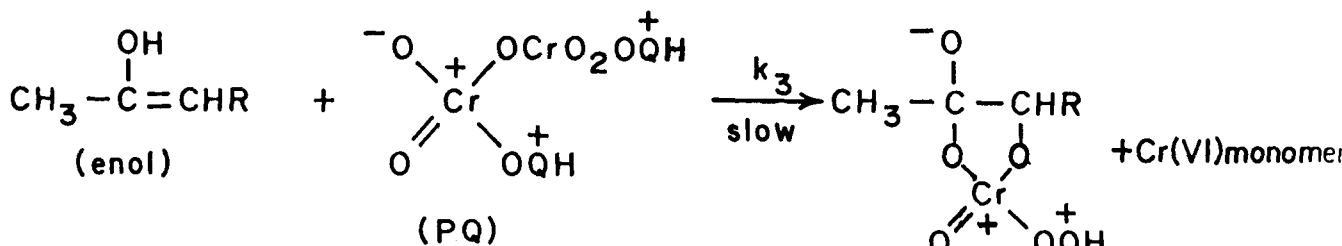
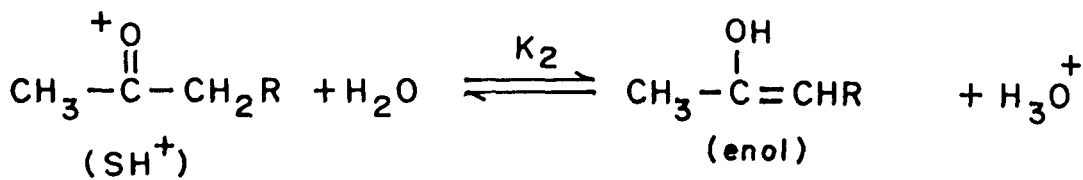
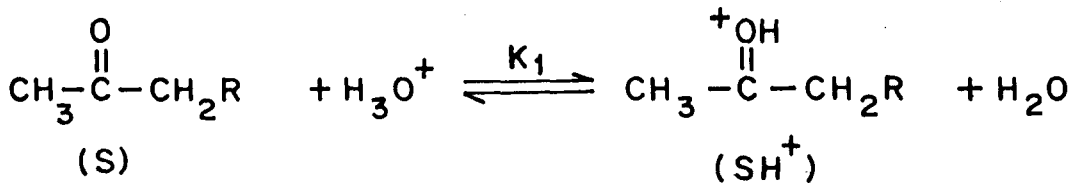
The mechanistic pathway for the oxidation of 2- and 3- alkanones by QDC, in acid medium, thus involved the attack of the protonated QDC on the enol form of the substrate in the rate-determining step, to give a cyclic chromate ester and a chromium(VI) monomer. The chromate ester underwent rapid decomposition to give the final products (corresponding carboxylic acids). This mechanistic pathway and the products obtained

(carboxylic acids) established that there was a cleavage of the carbon-carbon bond in the final step of the reaction. Our mechanistic pathway finds overwhelming support from earlier investigations, wherein the oxidation of 2- and 3- alkanones had established that the rate-determining step for the oxidation reactions involved an attack of the oxidant on the enol form of the substrate. Such a mechanistic pathway has been substantiated when these alkanones were oxidized by various oxidants such as acid permanganate in the presence of fluoride ions (4), tris(1,10-phenanthroline) Fe(III) in aqueous solutions containing sulfuric acid or perchloric acid (5), potassium permanganate in aqueous acetic acid (6), sodium metaperiodate in alkaline medium in the absence and presence of osmium tetroxide as catalyst (9), chloramine-T in aqueous ethanol under alkaline conditions (11), and potassium bromate in acid medium (26). Considering the substantial evidence put forward by earlier workers on the mechanism of oxidation of 2- and 3- alkanones by different oxidizing agents (4-6, 9, 11, 26), and on the basis of the kinetic results obtained in the present investigation, it would be justified to propose the mechanism for the oxidation of 2- and 3- alkanones by quinolinium dichromate (QDC), in acid medium, as shown in Scheme 1 and Scheme 2.

In acid medium, the oxidant QDC was converted to the protonated dimetallic Cr(VI) species (PQ) [in the acid range for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $\text{Cr}_2\text{O}_7^{2-}$ (37)]. The substrate (S) was converted to the enol, via its protonated form (SH^+). The reaction of the enol with the protonated QDC (PQ), in the rate-determining step, resulted in the formation of cyclic monochromate ester (E) and a monomeric Cr(VI) species. This cyclic monochromate ester was formed when the enol form of the substrate was bound to Cr(VI) through the

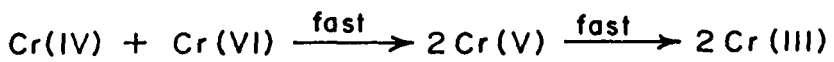
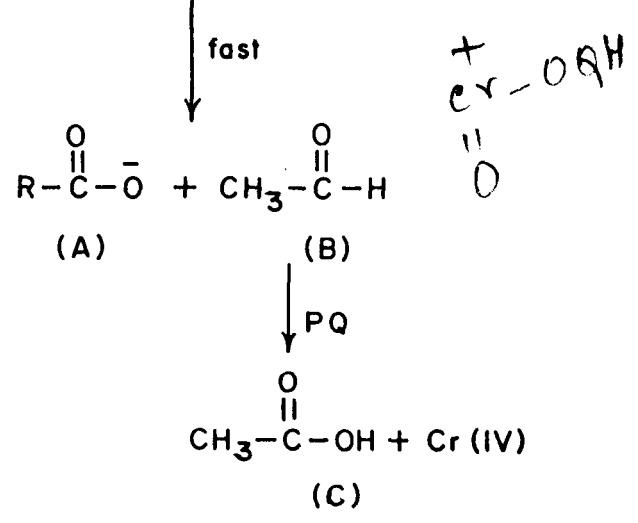
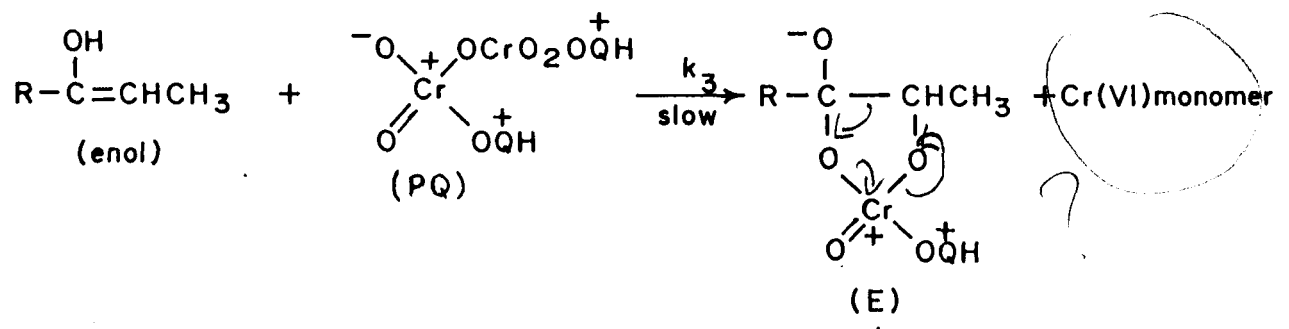
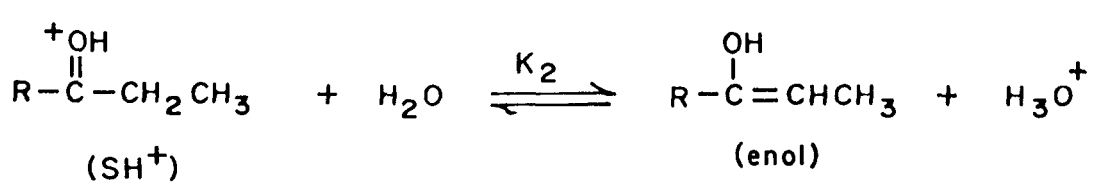
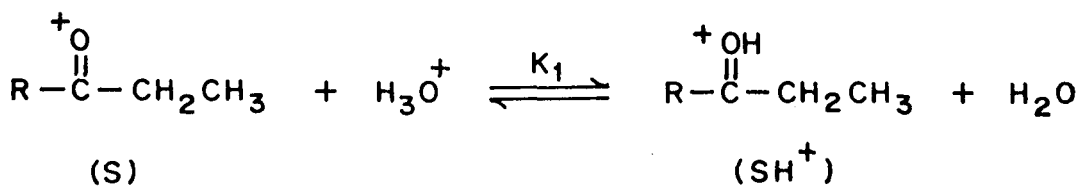
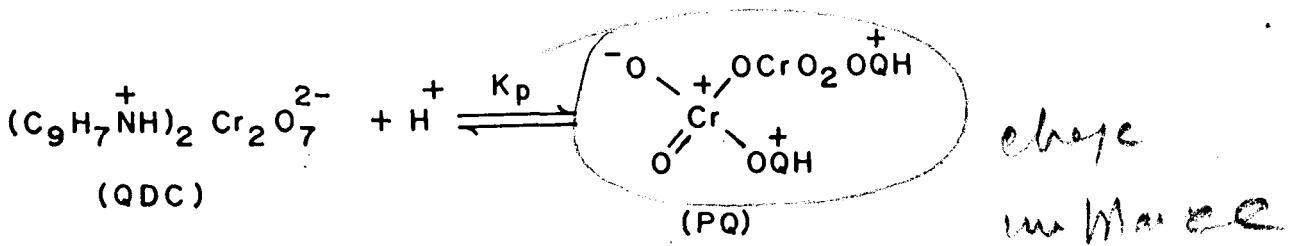


chise
... ..



R = -Me(2-butanone); -Et(2-pentanone); -Pr(2-hexanone); -Bu(2-heptanone);
-Pen(2-octanone)

SCHEME-1



R = -Et (3-pentanone); -Pr (3-hexanone); -Bu (3-heptanone); -Pen (3-octanone)

SCHEME 2

carbon-oxygen-chromium bond via an electrocyclic mechanism involving six electrons . The decomposition of the ester could take place through the carbon-oxygen-chromium bond of **E** in a fast step, resulting in open structures **A** (carboxylic acid) and **B** (aldehyde). On oxidation with another mole of protonated QDC (**PQ**), **B** gave the corresponding carboxylic acid **C**, along with Cr(IV) species.

The conversion of Cr(IV) to Cr(III) was a disproportionation reaction. For the reaction $\text{Cr(IV)} + \text{Cr(VI)} \rightarrow 2 \text{Cr(V)}$, the standard potential for the Cr(VI) - Cr(V) couple was extremely favorable ($E^0 = 0.62 \text{ volt}$) (52), and this reaction would proceed rapidly. The Cr(V) - Cr(III) couple has a potential of 1.75 volt, which would enable the rapid conversion of Cr(V) to Cr(III), after the reaction with the substrate (52, 53).

Under the experimental conditions employed in the present investigation , 2- and 3- alkanones were oxidized by quinolinium dichromate (QDC), in acid media, giving the corresponding carboxylic acids in each case. These products were characterized by FT-NMR analysis (vide "Experimental : Product Analysis").

It would be pertinent to recall the earlier experimental observations wherein 2- and 3- alkanones were oxidized to carboxylic acids in good yields, when oxidized by diverse oxidizing agents such as potassium permanganate in aqueous acetic acid (6), sodium metaperiodate in aqueous alkaline medium in the absence and presence of osmium tetroxide as catalyst (9), and by potassium bromate in acid medium (26). In all these oxidation reactions, the nature of the products formed (the corresponding carboxylic acids) indicated that there was the cleavage of the carbon-carbon bond in the final step of the reaction.

It would be necessary to comment on the nature of the products formed from the oxidation of 2- and 3- alkanones by quinolinium dichromate (QDC) obtained in the present study. Our hypothesis opens the question of regiochemistry. There is every possibility that these 2- and 3- alkanones could also enolize to some degree to the 1-position. In that case, there would be some conversion of these alkanones to formic acid. We have examined the products of these reactions, and have not been able to detect or isolate any formic acid as a possible product. The conclusion was that, under the present experimental conditions, the enolization of these 2- and 3- alkanones took place exclusively on the 2-position.

The data collected in the present investigation demonstrated that application of QDC to the oxidation of 2- and 3- alkanones led to the formation of carboxylic acids, substantiating the mechanism of the oxidation reaction, wherein there was a cleavage of the carbon-carbon bond in the final step of the reaction. While highlighting the importance of QDC as an oxidant, this study emphasized the efficiency of the reactions of QDC with 2- and 3- alkanones, which could prove to be a regioselective route for the synthesis of carboxylic acids.

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CHAPTER – III

KINETICS OF OXIDATION OF ALKYL ARYL KETONES

The oxidation of alkyl aryl ketones has been reported in many investigations. Primary and secondary kinetic isotope effects in the oxidation of acetophenone by chromic acid showed that removal of the three hydrogen atoms of the methyl group was equally possible. In the case of the deuterated acetophenone, the rate data showed the possibility of the removal of hydrogen as well as deuterium from the $-\text{CH}_2\text{D}$ group (1).

The kinetics of oxidation of para methoxy acetophenone by chromic acid, in acidic medium, suggested that the rapid step was the formation of a complex between the substrate and the oxidant, and a second order dependence with respect to [acid]. Kinetic evidence was given for the participation of both HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ in this oxidation reaction (2).

The oxidation of methyl aryl ketones by acid permanganate, in the presence of fluoride ions, gave formaldehyde and the corresponding benzoic acid as the products. The oxidation was first order with respect to each — ketone, oxidant and H^+ ions. Kinetic data showed that the rate of oxidation was slower than the rate of acid-catalyzed enolization (3).

Chloramine-T (CAT) in acid medium was used for the oxidation of acetophenone. The oxidation reaction was first order each in ketone, CAT and acid. On the basis of the experimental results, the oxidation of acetophenone was the reaction between the enol form of the ketone and HOCl , to give benzoic acid (4).

The kinetics of oxidation of acetophenones by potassium permanganate, in aqueous acetic acid medium at constant ionic strength, showed a first-order dependence each in the substrate and oxidant. It was shown that electron-withdrawing groups facilitated the oxidation as a result of an increase in the relative stability of the enol. The mechanistic pathway was via the enol form of the ketones. The rate-determining step involved a two-electron transfer from the enol resulting in the formation of a carbocation, which was converted to the corresponding benzoic acid (5).

The kinetics of oxidation of acetophenones by chloramine-T (CAT) in aqueous ethanol, under alkaline conditions, showed a first order dependence on the concentrations of the substrate, oxidant and alkali. The effect of ρ on the reaction rate was found to be negligible. The Hammett plot for the oxidation of acetophenones gave a ρ value of +1.2, suggesting that electron-withdrawing groups accelerated the oxidation process. The mechanism suggested was the reaction between the enolate anion and CAT in the rate-determining step to form an intermediate, which reacted in a fast step with another molecule of CAT to give phenacyldehyde (6).

The kinetics of oxidation of acetophenones by thallium triacetate, in acid medium, showed a first-order dependence each in substrate and acid, but exhibited a zero-order dependence in the oxidant. The kinetic results showed that the rate-determining step was the enolization of the ketones. The subsequent reaction between the enol and thallium(III) resulted in the formation of an intermediate carbocation, which was finally converted to the methoxy derivatives (7).

Phenyl iodosoacetate in aqueous acetic acid medium, in the presence of perchloric acid and sulfuric acid, was used for the oxidation of acetophenones. The reactions were first-order with respect to substrate and zero-order with respect to oxidant. At lower acidities, the dependence of the reaction was fractional, while at higher acidities, the dependence was unity. The rate-determining step was shown to be the enolization of the ketones, followed by the oxidation of the enol in a fast step (8).

The kinetics of oxidation of acetophenone by alkaline hexacyanoferrate(III) showed a first order dependence on the concentrations of each — substrate, oxidant and alkali. Solvent effects on the rates suggested that the reaction was of the ion-ion type (9).

Structural effects on the rates of the reactions between acetophenone and phenyl iodosoacetate have been reported. The kinetic results showed a first order dependence on the concentrations of the ketone and acid, but exhibited a zero order dependence on the oxidant. The mechanism proposed was the acid catalyzed enolization as the rate-determining step, followed by a fast reaction with the oxidant to give ω -acetoxyacetophenone (10).

The kinetics of oxidation of acetophenones by chloramine-T in aqueous ethanol showed that electron-releasing groups enhanced the rate of oxidation. The product obtained was benzoic acid. This study provided kinetic evidence for the steric enhancement of resonance (11).

The reaction of acetophenones with Mn(III) acetate, in the presence of ammonium chloride, gave the corresponding chloro derivatives as the reaction products. The reaction pathway suggested was via the formation of the radical intermediate (12).

The kinetics of oxidation of acetophenones by iodate in 50% aqueous methanol medium, in the presence of sulfuric acid, showed that the reaction was first order with respect to each — substrate, oxidant and acid. A mechanism involving the electrophilic attack of IO_2^+ on the methyl carbon atom of acetophenone was proposed as the rate-determining step. The products obtained were the corresponding diiodo-acetophenones (13).

In aqueous organic solvents, acetophenone was oxidized with dilute nitric acid to give dibenzoylfurazane-2-oxide, benzoic acid and benzoyl formic acid. The reaction rate was found to obey first order kinetics with respect to acetophenones and acid, but was independent of the concentration of the oxidant (14).

The kinetics of oxidation of acetophenones by trichloroisocyanuric acid was studied in aqueous acetic acid medium, in the presence of perchloric acid. The reaction showed a first-order dependence each in acid and substrate concentrations, and a zero-order dependence in [oxidant]. The kinetic data supported the acid-catalyzed enolization of the ketone as the rate-determining step, and the subsequent reaction between enol and oxidant as the fast step. The products obtained were the monochloro ketones (15).

The kinetics of oxidation of acetophenones by alkaline hexacyanoferrate(III) in 50% methanol-water mixtures, at constant ionic strength, showed that electron-

withdrawing groups in the ring facilitated the oxidation reaction. This investigation was carried out to provide evidence for the steric enhancement of resonance. The product obtained was benzoic acid (16).

The kinetics of the uncatalyzed and Os(VIII)-catalyzed oxidation of acetophenones by doperiodatoargentate(III) showed that the reactions were first order in substrate. For the uncatalyzed reaction, the order with respect to Ag(III) was unity, while in the presence of Os(VIII) as catalyst, the order with respect to Ag(III) was zero. The product obtained was phenacyl alcohol. The mechanism involved the formation of a complex between OsO₄ and the enol. The rate-determining step of the reaction was the breakdown of the complex (17).

The kinetics of oxidation of propiophenone and butyrophenone by N-bromosaccharin in aqueous acetic acid medium, in the presence of mercuric acetate showed a first order dependence on the concentrations of each — substrate, oxidant and acid. The order of reactivity was propiophenone > butyrophenone. The mechanistic pathway involved the reaction between the protonated form of the ketone with HOBr and the free oxidant in the rate-determining step (18).

The acid bromate oxidation of alkyl aryl ketones showed a first-order dependence each in bromate, ketone and acid. The mechanism proposed was the attack of the acid bromate on the enol form of the ketone in the rate-determining step, followed by a fast decomposition of the intermediate to give the carboxylic acids as the final products. The order of reactivity was found to be acetophenone > propiophenone > butyrophenone,

showing that the +I-effect became more pronounced, resulting in a decrease in the oxidation rate in this series (19).

The rate of oxidation of acetophenones by Ce(IV) in aqueous acetic acid slowed down over a range of cetyltrimethyl ammonium bromide (CTAB) concentrations exceeding the cmc values. The rate data was rationalized on the basis of a reaction between the acetophenones situated on the micelles surface and active Ce(IV) species in the bulk aqueous phase (20).

The kinetics of oxidation of acetophenones by diperiodatonickelate(IV), in the absence of Os(VIII), exhibited a first order dependence on the concentration of oxidant, substrate and alkali. In the presence of Os(VIII), the rate was independent of the concentration of oxidant, and exhibited fractional order dependence with respect to substrate and alkali concentrations. The order with respect to Os(VIII) was unity. The products of oxidation were the corresponding benzoic acid, and formaldehyde. The mechanism of the reaction involved the enolization of the ketone (21).

The kinetics of oxidation of alkyl aryl ketones by acid iodate in aqueous methanol medium exhibited a first order dependence on the concentrations of both ketone and iodate. The reaction was catalyzed by acid, and a medium of low dielectric constant favoured the oxidation process. The rate of oxidation was slower than the rate of enolization of the ketones. The mechanistic pathway proposed involved the attack of IO_2^+ on the enol form of the ketone, in the rate-determining step, giving an intermediate carbocation. The corresponding methoxy derivatives were obtained as the products (22).

PRESENT WORK

The present work is a detailed kinetic study of the oxidation of alkyl aryl ketones by quinolinium dichromate (QDC), in acid medium, using 20% dimethylformamide (DMF) as the solvent.

The alkyl aryl ketones chosen for the purpose of oxidation by QDC have included:

(a) Acetophenone ; (b) Propiophenone ; (c) Butyrophenone ; and (d) Valerophenone

Stoichiometry (vide "Experimental")

The stoichiometries of all the oxidation reactions were determined. The stoichiometric ratios, $\Delta[\text{QDC}] / \Delta[\text{Substrate}]$, were in the range 1.98-2.08 (Table 1).

Table 1 : Stoichiometries of the Oxidation of the Substrates;

([Substrate] = 0.005 M; T = 323 K)

$[\text{HClO}_4] / \text{M}$	0.10	0.25	0.50
$10^2[\text{QDC}] / \text{M}$	2.50	2.60	2.70
$\Delta[\text{QDC}] / \Delta[\text{Acetophenone}]$	1.99	2.01	2.05
$\Delta[\text{QDC}] / \Delta[\text{Propiophenone}]$	2.07	2.06	2.08
$\Delta[\text{QDC}] / \Delta[\text{Butyrophenone}]$	1.98	1.99	2.02
$\Delta[\text{QDC}] / \Delta[\text{Valerophenone}]$	2.00	1.98	2.04

The stoichiometry conformed to the overall equations :

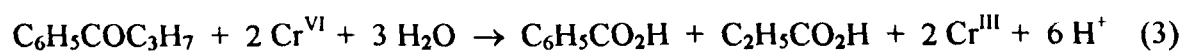
(a) For acetophenone :



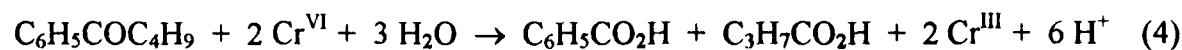
(b) For propiophenone :



(c) For butyrophenone :



(d) For valerophenone :



Effect of Substrate

The rate of the reaction was found to be dependent on the concentration of the substrates. The order of the reaction with respect to substrate concentration was obtained by changing the substrate concentration, and observing the effect on the rate of the reactions at constant [QDC] and $[\text{H}^+]$. The results have been recorded in Table 2.

Table 2 : Dependence of Rate Constants on the concentration of Alkyl ArylKetones; ([QDC] = 0.001 M; [HClO₄] = 2.0 M; [DMF] = 20%(v/v);

T = 323K)

10^2 [Substrate] / M	$10^4 k_1 / s^{-1}$			
	Acetophenone	Propiophenone	Butyrophenone	Valerophenone
1.0	0.92	0.56	0.48	0.45
2.5	2.28	1.44	1.21	1.05
5.0	4.62	2.73	2.38	1.97
7.5	6.67	3.98	3.68	3.33
10.0	9.18	5.52	4.99	4.34
	$10^2 k_2 / M^{-1} s^{-1}$			
	0.92	0.56	0.48	0.45
	0.91	0.58	0.48	0.42
	0.92	0.55	0.48	0.39
	0.89	0.53	0.49	0.44
	0.92	0.55	0.50	0.43

$K_2 = k_1 / [\text{Substrate}]$

Plots of k_1 , the pseudo-first-order rate constant, against a ten-fold range of the concentrations of substrates (in each case), gave straight lines passing through the origin (Figure 1). This indicated that the rate of oxidation was dependent on the first power of

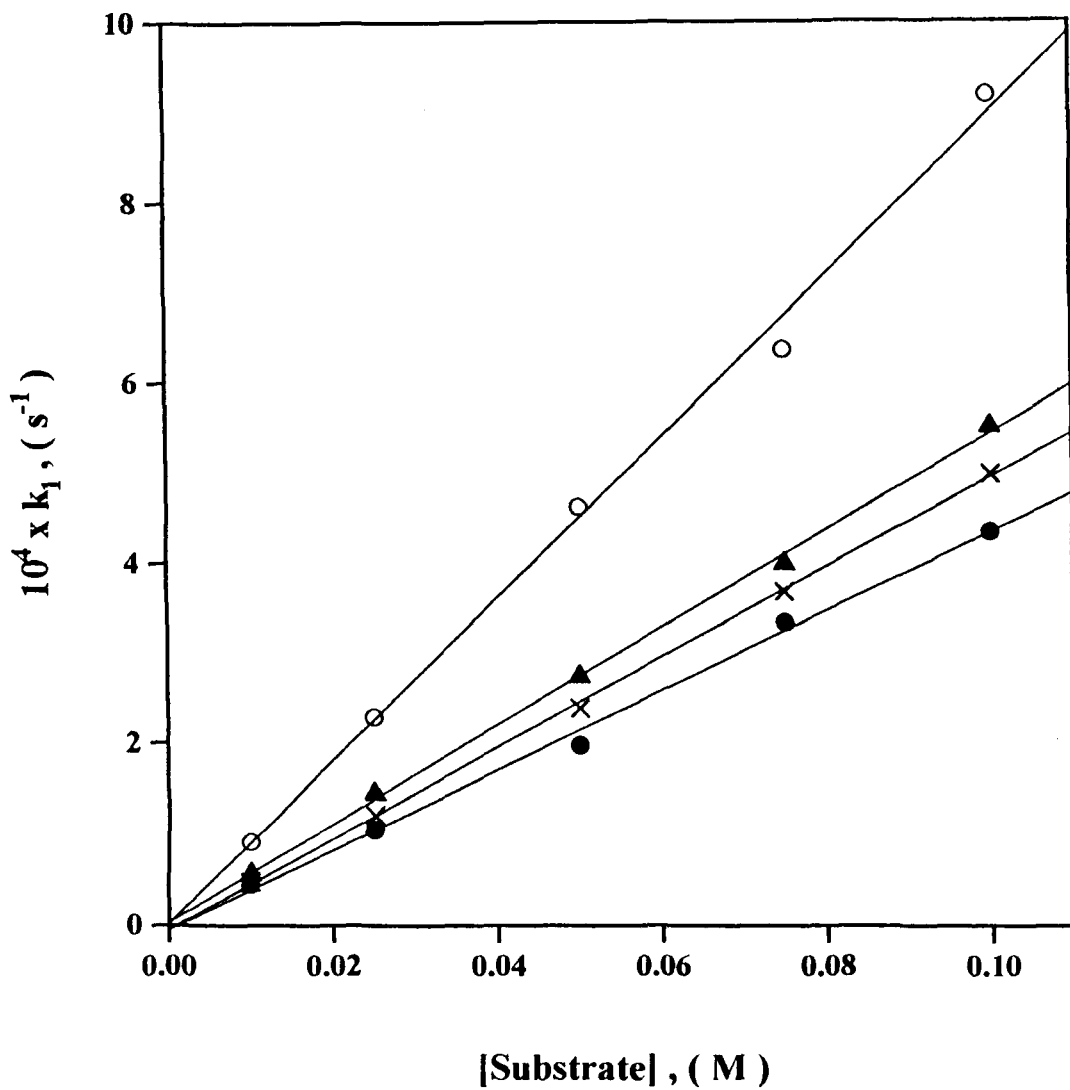


Fig. 1. Plots of k_1 against the concentrations of substrates for acetophenone (○), propiophenone (▲), butyrophenone (×) and valerophenone (●).

the concentrations of the substrates. This was further demonstrated by the constancy in the values of k_2 , the second-order rate constant.

Effect of oxidant

Under pseudo-first-order conditions, the individual kinetic runs were first-order with respect to the oxidant (QDC). At fixed [acid] and with the substrate taken in excess, the plots of log absorbance versus time were linear, indicating a first order dependence on QDC. When a constant concentration of substrate (large excess) was used, the pseudo-first-order rate constant (k_1) did not alter appreciably with changing concentrations of the oxidant (QDC). This indicated a first-order dependence of the rate on the concentration of the oxidant. The rate data have been shown in Table 3.

Table 3 : Dependence of Rate Constants on the concentration of Oxidant;

([Substrate] = 0.01 M; [HClO₄] = 2.0 M; [DMF] = 20%(v/v); T = 323K)

10^3 [QDC] / M	$10^4 k_1 / s^{-1}$			
	Acetophenone	Propiophenone	Butyrophenone	Valerophenone
0.25	0.87	0.51	0.43	0.40
0.50	0.84	0.59	0.41	0.46
0.75	0.93	0.53	0.49	0.43
1.0	0.92	0.56	0.48	0.45

Effect of acid

The reaction was influenced by changes in the acid concentration, and the rate was observed to increase with an increasing concentration of the acid in the range 0.50 M to 3.0 M (Table 4).

Table 4 : Dependence of Rate Constants on Acid concentration for Alkyl Aryl Ketones;
([Substrate] = 0.01 M; [QDC] = 0.001 M; T = 323K)

$10^4 k_1 / s^{-1}$				
[HClO ₄] / M	Acetophenone	Propiophenone	Butyrophenone	Valerophenone
0.5	0.23	0.14	0.12	0.11
1.0	0.45	0.27	0.23	0.24
1.5	0.69	0.44	0.35	0.37
2.0	0.92	0.56	0.48	0.45
2.5	1.17	0.73	0.62	0.55
3.0	1.38	0.86	0.72	0.67

Plots of $\log k_1$ against $\log [H^+]$ were linear, with slopes equal to unity (Figure 2), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

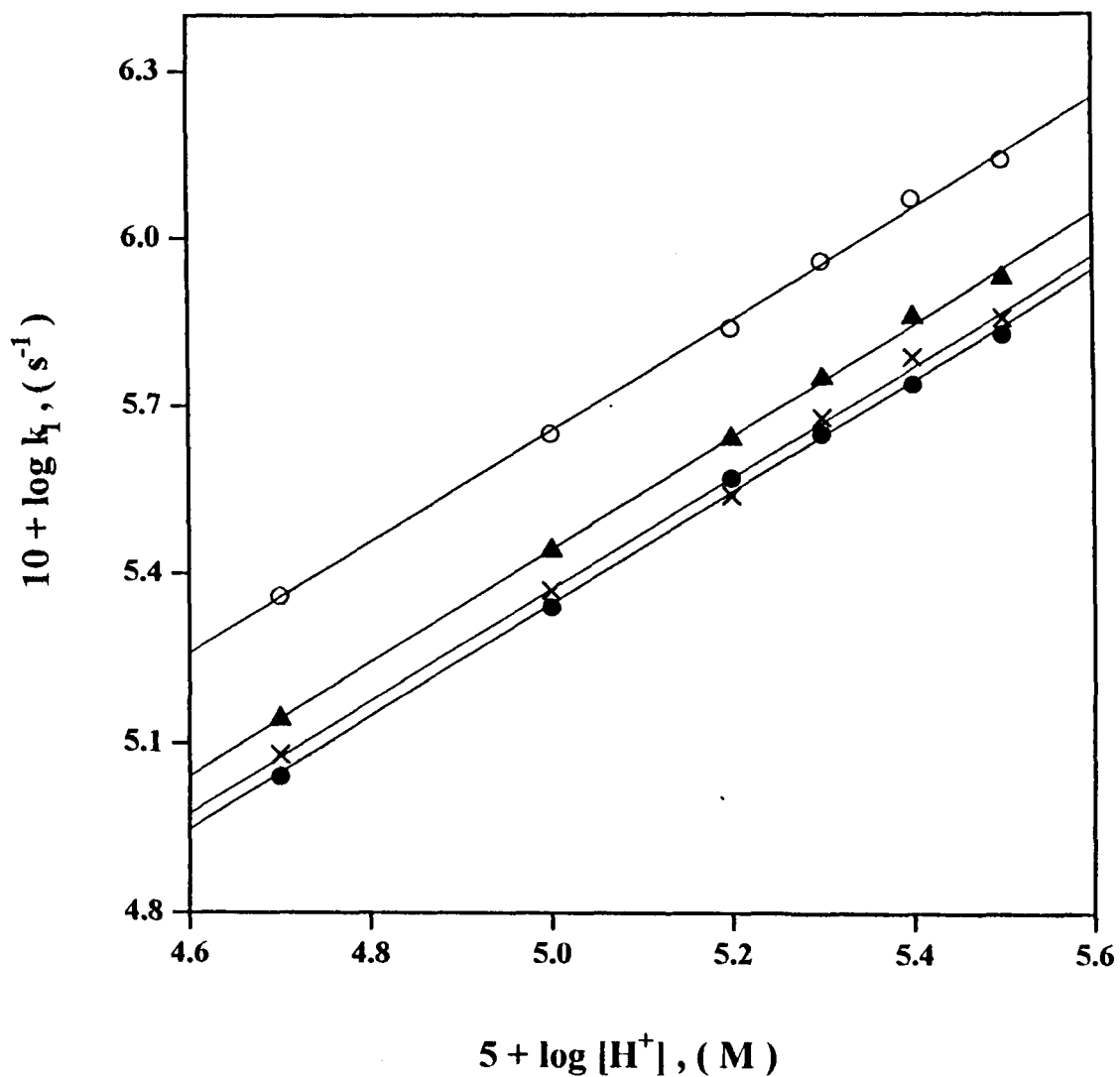


Fig. 2. Plots of $\log k_1$ against $\log [\text{H}^+]$ for acetophenone (\circ), propiophenone (\blacktriangle), butyrophenone (\times) and valerophenone (\bullet).

The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step. There have been earlier reports of the involvement of such protonated Cr(VI) species in chromic acid oxidation reactions (23). Protonated Cr(VI) species have been observed in the presence of p-toluenesulfonic acid in nitrobenzene-dichloromethane mixtures (24). The acid catalysis must be related to the structure of the oxidant (QDC), which was converted to a protonated species at the concentration of mineral acid used. Quinolinium dichromate is a dimetallic species, an anionic condensed form of chromic acid. An examination of aqueous solutions of chromic acid was carried out by Michel et al. (25), who examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate HCrO_4^- does not exist in aqueous solutions of Cr(VI) compounds. The ionization constant for the HCr_2O_7^- ion, $\text{HCrO}_7^- \rightleftharpoons \text{H}^+ + \text{Cr}_2\text{O}_7^{2-}$ is 0.85 mol/l; hence, in solutions where $\text{pH} \geq 1$, the ionization may be considered essentially complete. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of mineral acid would be HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. These ions are in equilibrium with each other, according to the equation given by $2\text{HCr}_2\text{O}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ ($K_d = 35.5$). When the Raman lines were examined under dilution, it was established that at $\text{pH} = 11$, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion, whereas at $\text{pH} = 1.2$, it was 100% as the $\text{Cr}_2\text{O}_7^{2-}$ ion (25). Hence, at concentrations of acid larger than 0.05 M, the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, spectral studies have shown that $\text{Cr}_2\text{O}_7^{2-}$ was the predominant species (26). In the present investigation, since the acid concentrations used were in the range 0.50 to 3.0 M, the

dichromate ion (or its protonated form) would be the predominant species. Moreover, the protonated Cr(VI) species would be a more reactive electrophilic species and would be sufficiently reactive to attack the enol form of the alkyl aryl ketones.

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been employed for all the kinetic runs, the observed rate law could be expressed as :

$$\text{Rate} = - \frac{d[\text{QDC}]}{dt} = k [\text{Substrate}] [\text{QDC}] [\text{H}^+] \quad (5)$$

Effect of solvent

Reactions involving ionic reactants are susceptible to solvent influences. In the present investigation, the solvent was observed to play an important role. The acid-catalyzed oxidation of the substrates was studied in solutions containing varying proportions of water and dimethylformamide (DMF). For each of the substrates oxidized by QDC, the rate of oxidation was fastest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of DMF resulted in a decrease in the rate of oxidation (Table 5).

Table 5 : Dependence of Rate Constants on Solvent Composition for Alkyl Aryl**Ketones; ([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 2.0 M;****T = 323K)**

H₂O:DMF (%, v/v)	Dielectric Constant (D)	10⁴ k₁ / s⁻¹			
		Acetophenone	Propiophenone	Butyrophenone	Valerophenone
95:5	68.3	1.41	0.83	0.69	0.65
90:10	66.7	1.17	0.78	0.65	0.55
85:15	65.1	1.05	0.66	0.54	0.50
80:20	63.5	0.92	0.56	0.48	0.45

The dielectric constants for water - DMF mixtures have been estimated approximately from the dielectric constants of the pure solvents (at 323 K: water = 69.9; DMF = 37.6) (27).

In the present investigation, in going from 5% DMF to 20% DMF, the polarity decreased. This decrease in the polarity of the medium caused a decrease in the rate of the reaction (Table 5). Plots of log k₁ against the inverse of dielectric constants were linear, with negative slopes (Figure 3). This suggested an interaction between an ion and a dipole (28), and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated dimetallic Cr(VI) species. The data in

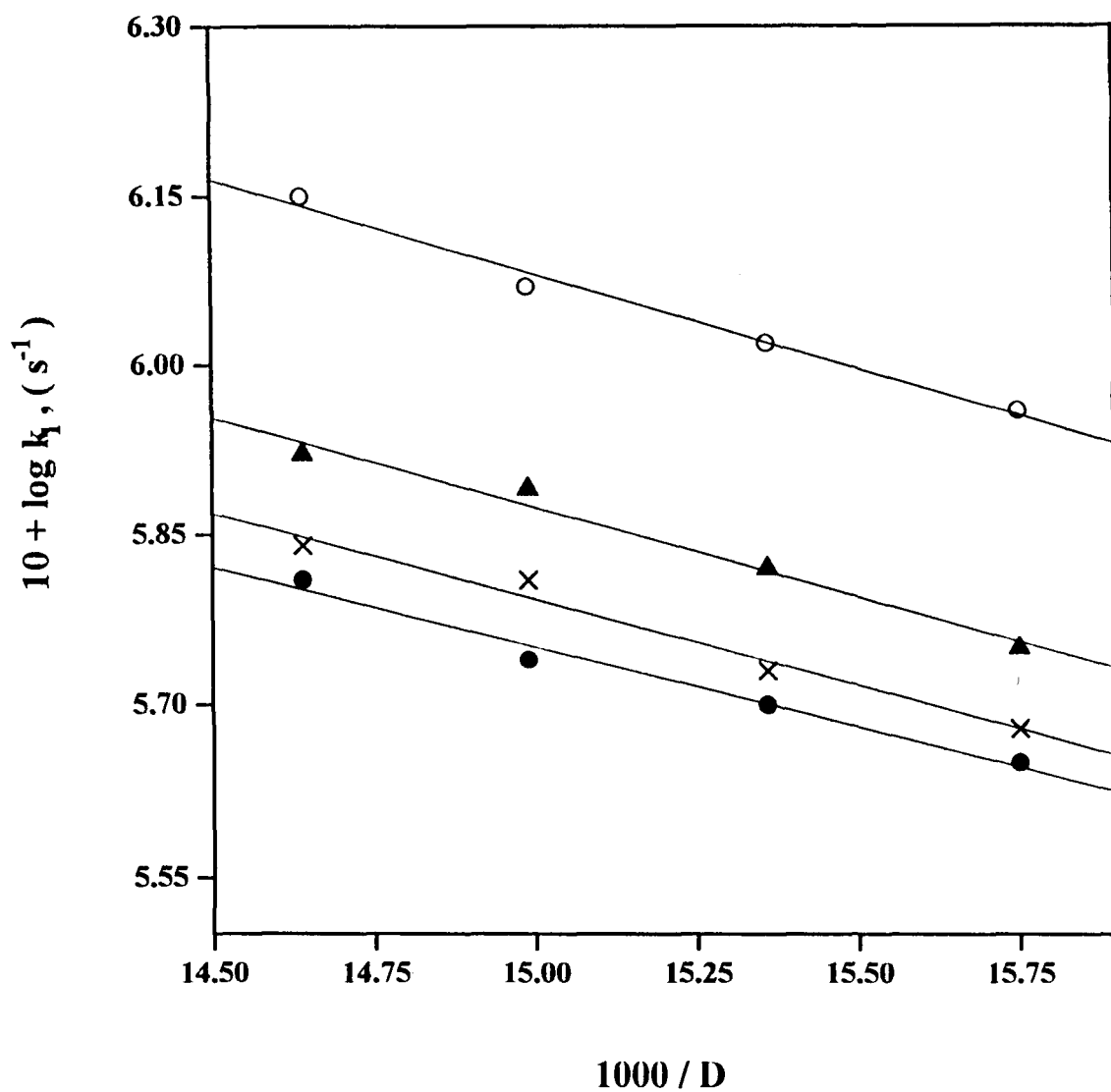


Fig. 3. Plots of $\log k_1$ against the reciprocal of the dielectric constant for acetophenone (○), propiophenone (▲), butyrophenone (×) and valerophenone (●).

Table 5 indicated that the dielectric constants for water - DMF mixtures were a linear function of the solvent composition used in this investigation. This relationship between $\log k_1$ and $1 / D$ was thus obeyed in the range of dielectric constants used.

It would be expected that the total solvation of an ion and a dipole (initial state) should be lesser than the solvation of the transition state formed by their union. The transition state would thus be more polar than the initial state (reactants), because of the decrease dispersal of charges in the transition state (29). In the present investigation, the addition of a more polar solvent resulted in an increase in the rate of oxidation. This arises as a result of a progressive increase in solvation of the transition state. The effect of a change in the solvent composition on the reaction rates would also be dependent on factors such as solvent-solute interactions (30, 31), and on solvent structure.

Effect of temperature

The rates of the reactions were influenced by changes in the temperature (Table 6).

Table 6 : Dependence of Rate Constants on Temperature for Alkyl Aryl Ketones;**([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 2.0 M;****[DMF] = 20%(v/v))**

$10^4 k_1 / s^{-1}$				
Temperature ($\pm 0.1K$)	Acetophenone	Propiophenone	Butyrophenone	Valerophenone
313	0.51	0.21	0.17	0.16
318	0.71	0.36	0.29	0.26
323	0.92	0.56	0.48	0.45
328	1.15	0.67	0.62	0.59
333	1.55	0.98	0.95	0.91

Plots of $\log k_1$ against the inverse of temperature were linear (Figure 4), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies (vide "Experimental : Calculations"). The activation parameters have been evaluated, and have been shown in Table 7.

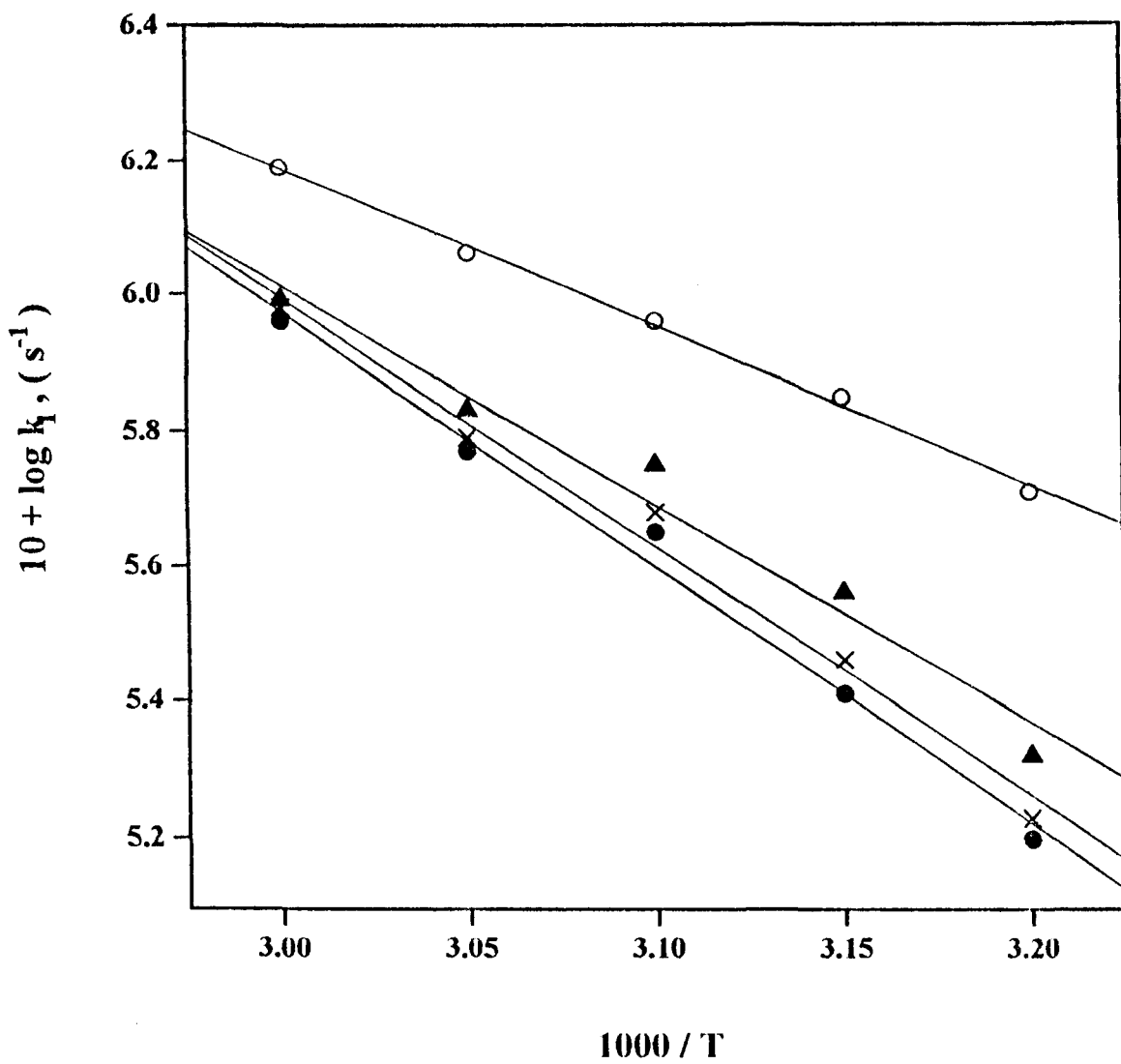


Fig. 4. Plots of $\log k_1$ against the reciprocal of temperature for acetophenone (○), propiophenone (▲), butyrophenone (×) and valerophenone (●).

Table 7 : Activation Parameters for Alkyl Aryl Ketones

Substrate	E (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
Acetophenone	49	44	-186	102
Propiophenone	66	62	-137	103
Butyrophenone	77	73	-112	104
Valerophenone	75	74	-107	105

Error limits : E \pm 2 kJ mol⁻¹; $\Delta H^\ddagger \pm$ 2 kJ mol⁻¹; $\Delta S^\ddagger \pm$ 5 JK⁻¹ mol⁻¹; $\Delta G^\ddagger \pm$ 2 kJ mol⁻¹.

The fairly high positive values of the enthalpies of activation (ΔH^\ddagger) and the free energies of activation (ΔG^\ddagger) indicated that the transition state was highly solvated. The oxidation of all the substrates was characterized by negative entropies of activation. This would suggest that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecules (32). Differences in the extent of solvation of the substrates, in the ground state and in the transition state, might also contribute to the negative entropies of activation. The similarity of ΔG^\ddagger values for all the substrates arose due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that all these reactions involved similar rate-determining steps.

Isokinetic relationship

The enthalpies and entropies of activation for a reaction are linearly related by the equation

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (6)$$

where β is the isokinetic temperature. For the oxidation reactions studied in the present investigation, the activation enthalpies and entropies were linearly related. The correlation was tested and found to be valid by applying Exner's criteria (33). The isokinetic temperature, obtained from the plot of ΔH^\ddagger against ΔS^\ddagger , was 385K (for alkyl aryl ketones) (Figure 5). Although current views do not attach much physical significance to isokinetic temperatures (34), it is sufficient to state that a linear correlation between ΔH^\ddagger and ΔS^\ddagger is usually a necessary condition for the validity of the Hammett equation (linear free energy relationships). The linear trend between the enthalpies and entropies of activation further established that all these reactions were controlled by both parameters, ΔH^\ddagger and ΔS^\ddagger . Further, the values for the free energies of activation (ΔG^\ddagger) were nearly constant, indicating that the same mechanism operated for the oxidation of all the alkyl aryl ketones studied in this investigation.

Induced polymerization

In the present investigation, since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (35). This indicated that a one-electron oxidation was quite unlikely. Control experiments were

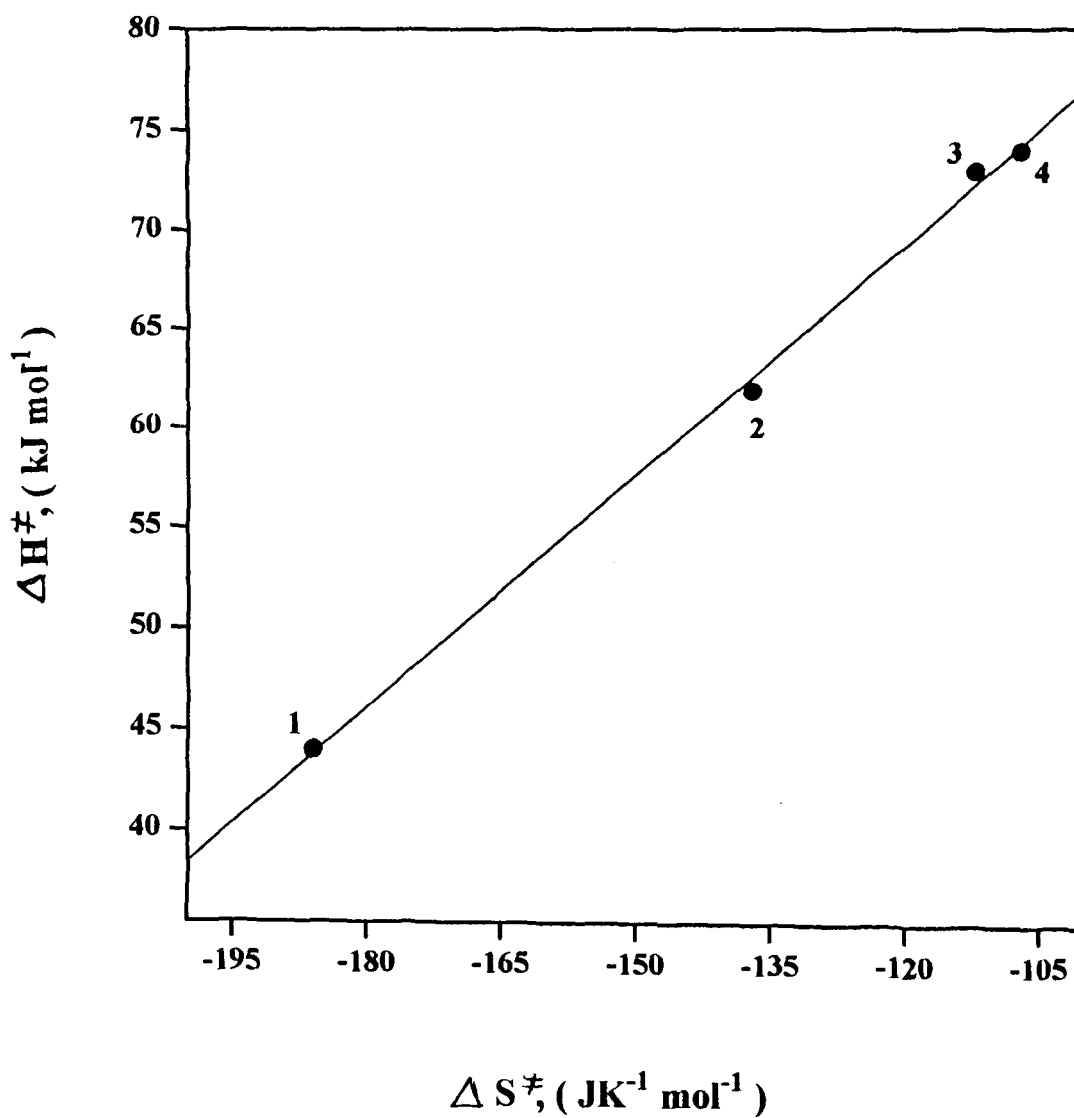


Fig. 5. Plots of ΔH^\ddagger against ΔS^\ddagger for acetophenone (1), propiophenone (2), butyrophenone (3) and valerophenone (4).

performed, in the absence of the respective substrates. The concentration of QDC did not show any appreciable change.

Relative rates of oxidation

In the present investigation, the order of reactivity was in accordance with the structural changes in the alkyl aryl ketones :

acetophenone > propiophenone > butyrophenone > valerophenone (Table 2).

Owing to the inductive effect, the presence of the methyl group in propiophenone enhances the electron density at the carbon atom adjacent to the carbonyl group. The ease of deprotonation from this carbon atom in propiophenone would decrease, as compared to that in acetophenone, due to the electron-withdrawing nature of the phenyl group. This would result in a decrease in the enolic content of propiophenone. The overall effect would be a decrease in the rate of oxidation, as observed by the rate data in Table 2. The +I-effect becomes more pronounced with respect to butyrophenone and valerophenone, due to the presence of the C₂H₅ and C₃H₇ groups respectively, resulting in a further decrease in the rate of oxidation (Table 2). The tendency of alkyl groups to decrease the electron density on the α -carbon would check the loss of the proton attached to the same α -carbon atom. Thus, an increase in the +I-effect of the alkyl groups would result in a decrease in the rate of the reaction. Hence, the observed order of reactivity for the alkyl aryl ketones (Table 2).

Mechanism

Since there exists an equilibrium between the keto- and enol- forms of ketones, different views have been expressed on the form of ketone (keto- or enol-form) which undergoes a reaction with different oxidants. The correlations which emerge from these studies can be categorized as follows :

- (a) when carboxylic acids were the major products, the oxidation was through a rate-determining attack of the oxidant on the enol form of the ketone, as for example in oxidations with acid permanganate (3), chloramine-T in acid medium (4), potassium permanganate in acid medium (5), and acid bromate (19). The kinetic data for all these oxidation reactions showed a first order dependence on the concentrations of the oxidants. It was also observed that the rate of oxidation was slower than the rate of acid-catalyzed enolization (3-5, 19);
- (b) when carboxylic acids were the major products, the oxidation was through the rate-determining enolization of the ketone, as for example in the oxidation with chloramine-T (11);
- (c) when diketones were formed, the rate-determining step involved the reaction between the protonated form of the ketone and the oxidant, as in the oxidation with N-bromosaccharin . The order dependence with respect to the concentration of the oxidant was found to be unity (18);
- (d) when monochloroketones were the major products, the rate-determining step involved the enolization of the ketone, as in the oxidation with

trichloroisocyanuric acid. The reaction showed a zero-order dependence on the concentration of the oxidant. This supported the acid-catalyzed enolization of the ketone as the rate-determining step, followed by the reaction between the enol and the oxidant in a fast step (15).

- (e) when a methoxy derivative was the final product, there was the rate-determining attack of the oxidant on the enol form of the ketone leading to the formation of an intermediate carbocation, as in the oxidation with acid iodate (22). This reaction exhibited a first-order dependence each on the substrate and oxidant. Kinetic data showed that the rate of oxidation was much slower than the rate of enolization of the ketone (22);
- (f) when a methoxy derivative was the final product, the rate-determining step was the reaction of the enol with oxidant, as for example, in the oxidation with acid iodate (13). The reaction was first order with respect to the concentrations of substrate and oxidant, and the oxidation process was catalyzed by acid. It was further shown that the rate of enolization was faster than the rate of oxidation. The first-order dependence of the rate on the concentration of the oxidant ruled out the possibility of the enolization step being rate-determining (13);
- (g) when acetoxy derivatives were obtained as the final products, the rate-determining step involved the enolization of the ketone, as for example, in oxidations with thallium triacetate in aqueous medium (7), and phenyl iodosoacetate in acidic medium (10). These reactions exhibited a zero-order dependence on the concentrations of the oxidant, and a first-order dependence on

the concentration of the substrate. The rates of oxidation were faster than the rates of enolization (7, 10);

- (h) when an aldehyde was the major product, the rate-determining step was the reaction of the enolate anion with the oxidant, as for example, in the oxidation with chloramine-T in alkaline medium. The reaction showed a first-order dependence on the concentrations of the oxidant and substrate (6);
- (i) when phenacyl alcohol was obtained as the final product, the rate-determining step was the decomposition of the complex formed between the ketone and the oxidant, as for example, in the oxidation with diperiodatoargentate(III) in alkaline medium (17). Both the uncatalyzed and catalyzed reactions followed first-order kinetics in [substrate], while the order in Ag(III) was unity in the absence of Os(VIII) and zero in the presence of Os(VIII) catalyst (17);
- (j) when a mixture of three products were obtained (benzoyl furazan-2-oxide, benzoic acid and benzoyl formic acid), the rate-determining step was the enolization of acetophenone, as for example, in the oxidation with nitric acid (14). The kinetic results were explained by the enolization of acetophenone, and the rate-determining step was the deprotonation of the conjugate acid of acetophenone (14); and
- (k) when benzoic acid and formaldehyde were obtained as the final products, the uncatalyzed reaction with diperiodatonickelate(IV) involved the reaction of the enol with oxidant as the rate-determining step of the reaction (21). When the

same reaction was carried out in the presence of Os(VIII) as the catalyst, the rate-determining step was the decomposition of the complex formed between Os(VIII) and the enol form of the ketone (21). The involvement of the enol species was supported by an increase in the rate with an increase in $[\text{OH}^-]$, and a decrease in the rate with an increase in the concentration of the oxidant (21).

Based on the stoichiometries of the oxidation reactions (Table 1), and the observed experimental data, the mechanistic pathway for the oxidation of the alkyl aryl ketones (acetophenone, propiophenone, butyrophenone and valerophenone) by quinolinium dichromate (QDC) in acid medium, using 20% DMF as solvent, has to be rationalized. While suggesting mechanistic pathways for these oxidation reactions, the following kinetic observations have to be taken into consideration :

- (1) the rates of oxidation of all the alkyl aryl ketones (acetophenone, propiophenone, butyrophenone and valerophenone) were dependent on the first powers of the concentrations of each — substrate and oxidant (Tables 2-3, Figure 1);
- (2) the rates of reactions showed a first order dependence on the concentrations of the acid (Table 4, Figure 2). The acid catalysis of the oxidation reactions must be related to the structure of the oxidant (QDC), which was converted to a protonated dimetallic Cr(VI) species. In presence of the acid, the keto tautomer was also converted to the enol tautomer;
- (3) an increase in the polarity of the solvent medium (using water - dimethylformamide mixtures) showed an increase in the rate of the reaction (Table 5). Linear plots of $\log k_1$ against the inverse of the dielectric constants

(Figure 3) gave negative slopes, which indicated an ion-dipole type of interaction.

This was in accordance with the involvement of a protonated dimetallic Cr(VI) species;

- (4) an increase in temperature resulted in an increase in the rates of the reactions (Table 6). The oxidation of alkyl aryl ketones was characterized by negative entropies of activation (Table 7), which suggested an ordered transition state, relative to the reactants. The similarity in ΔG^\ddagger values (Table 7) for all the substrates were due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that all these oxidation reactions involved similar rate-determining steps;
- (5) there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride, indicating the absence of any radical formation; and
- (6) the observed order of reactivity was in accordance with the structural changes in the alkyl aryl ketones :

acetophenone > propiophenone > butyrophenone > valerophenone (Table 2).

This order of reactivity was rationalized on the basis of the +I-effect of the electron-releasing alkyl groups adjacent to the carbonyl groups.

In the present investigation, highlighting the oxidation of alkyl aryl ketones by quinolinium dichromate (QDC) in acid medium, using 20% DMF as the solvent, the rate of oxidation was first-order with respect to the concentrations of each — substrate, oxidant and acid. The first-order dependence of the rate on QDC concentration suggested that the reaction pathway was through the enol form of the substrate . The rates of

enolization of all the alkyl aryl ketones under study were determined by the bromination method. It was observed that the rates of enolization were very much greater than the rates of oxidation for all the alkyl aryl ketones (by a factor of ~12). The rates of enolization being much faster than the rates of oxidation would indicate that the enolization step was not rate-determining. Hence, it would be justified to conclude that the enol form of the substrate reacted with the oxidant. The rate-determining step involved an attack of the oxidant on the enol form of the substrate.

On the basis of the relative rates of oxidation of the alkyl aryl ketones (Table 8), a cyclic transition state could be postulated.

Table 8 : Rate data for the Oxidation of Alkyl Aryl Ketones;

([Substrate] = 0.1 M; [QDC] = 0.001 M; [H₂SO₄] = 1.0 M;

[DMF] = 20%DMF(v/v); T = 323K

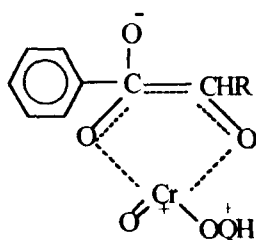
Substrate	$10^4 k_1 / s^{-1}$	Relative Rate
Acetophenone	0.92	2.0
Propiophenone	0.56	1.2
Butyrophenone	0.48	1.1
Valerophenone	0.45	1.0

The reactivity of the alkyl aryl ketones would support a cyclic transition state in which there would be the possibility of an equally equivalent accessibility of the ene and the hydroxyl group of the enol to the reaction centre. This conformational insensitivity could be attributed to the cyclic nature of the transition state.

The stoichiometric conversion of the alkyl aryl ketones to the corresponding carboxylic acids involved the changes : $>=O \rightarrow \gg-OH \rightarrow$ chromate ester \rightarrow carboxylic acid, and the rate of oxidation varied with the concentration of the acid. If the reaction intermediate was visualized as having a cyclic structure, then this would explain all the features of the oxidation reaction. The negative entropies of activation (Table 7) would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The similarity in ΔG^\ddagger values arose due to changes in ΔH^\ddagger and ΔS^\ddagger values (Table 7), and stressed the probability that these oxidation reactions involved similar rate-determining steps.

In the present investigation, the observed solvent effect (increase in the polarity of the solvent increased the rate of oxidation, Table 5) provided support for a reaction pathway which involved the formation of a cyclic chromate ester intermediate. Further, the small variation in the reaction rate for the oxidation of alkyl aryl ketones by quinolinium dichromate (Table 8) could also be reconciled with the ester mechanism, since the cyclic chromate ester formation was likely to be little influenced by structural changes (36).

A unimolecular decomposition of the cyclic monochromate ester can be written in which the chromium is bonded in the transition state to both the oxygen atoms :



**cyclic ester
T.S**

Electron flow in a cyclic transition state has been earlier considered (37, 38), and the conversion of the ester to the transition state can be best considered in the following terms :

If the chromium were to be coordinated through the oxygen, then the process of electron transfer could take place through the carbon-oxygen-chromium bond. This would facilitate the formation of the cyclic monochromate ester, and would also enhance the ease of conversion to the product. The formation of such an intermediate would envisage the transfer of electrons towards the chromium, occurring by the formation of the carbon-oxygen-chromium bonds. Partly occupied orbitals were thus used to bind the oxygen to both, carbon and chromium, in the transition state.

In the present investigation, the sequence of reactions involved in the oxidation of alkyl aryl ketones (acetophenone, propiophenone, butyrophenone and valerophenone) by quinolinium dichromate (QDC) in acid medium using 20%DMF as the solvent, has been shown in the Scheme.

The mechanism was consistent with the fact that these oxidation reactions were catalyzed by acid (Table 4). Protonation of the oxidant (QDC) would make it more

amenable towards nucleophilic attack by the enol form of the substrate on the electron-deficient chromium of the oxidant. The first step involved the enolization of the ketone followed by the protonation of the oxidant (QDC). The second step was the rate-determining step, wherein the enol form of the substrate reacted with the protonated oxidant to form the cyclic chromate ester. This was followed by the transfer of two electrons in a cyclic system giving rise to cleavage products. This electrocyclic mechanism involved six electrons, and being a Hückel-type system ($4n+2$), this was an allowed process (39).

In general, oxidation reactions of organic functions by different oxidizing agents could be considered using the Zimmerman treatment of electrocyclic reactions (40). Selection rules play an important part in determining the mechanisms of many oxidation reactions. For reactions involving electrons in d-orbitals, a topological approach to the orbital levels of the transition state has been applied (40), in which the transition state can be either "Hückel-like" (in which all overlapping pairs of reacting orbitals are bonding), or "Möbius-like" (in which one or an odd number of anti-bonding overlaps must occur). In a Hückel transition state, $4n+2$ electrons formed a closed shell (giving it stability), while $4n$ electrons were required for stable closed shells in a Möbius transition state. An "allowed" reaction could have either a Hückel-type or a Möbius-type transition state, provided that the correct number of electrons was available to stabilize that transition state.

When chromium(VI) was reduced, the initial product chromium(IV) was unstable, but it was generally considered to be an octahedral complex (41). The

d-electron in the unexcited product must therefore be in a t_{2g} orbital (d_{xy}) which can overlap, in the reactions, using two adjacent lobes with opposite signs of the wave functions. It could therefore be considered to be locally antisymmetric (π -type). The transition state would be of the Hückel-type ($4n+2$), and hence would be an allowed reaction.

In the present investigation, the oxidation of alkyl aryl ketones (acetophenone, propiophenone, butyrophenone and valerophenone) by quinolinium dichromate (QDC), in acid medium, using 20%DMF as the solvent, involved the formation of a cyclic chromate ester. The next step of the reaction was the transfer of two electrons in a cyclic system. This accepted electrocyclic mechanism for the oxidation of alkyl aryl ketones by QDC involved six electrons, and being a Hückel-type system ($4n+2$), this would be an allowed process.

The mechanistic pathway for the oxidation of alkyl aryl ketones by QDC in acid medium, using 20% DMF as solvent, thus involved the attack of the protonated QDC (dimetallic Cr(VI) species) on the enol form of the substrate in the rate-determining step, to give a cyclic monochromate ester and a chromium(VI) monomer. This cyclic monochromate ester underwent rapid decomposition to give the final products (mixtures of carboxylic acids). This mechanistic pathway and the products obtained (carboxylic acids) established that there was a cleavage of the carbon-carbon bond in the final step of the reaction. Our mechanistic pathway finds overwhelming support from earlier investigations wherein the oxidation of alkyl aryl ketones had established that the rate-determining step for the oxidation reactions involved an attack of the oxidant on the enol

form of the substrate. Such a mechanistic pathway has been substantiated by earlier investigations, wherein it was shown that alkyl aryl ketones were oxidized by various oxidants such as acid permanganate in the presence of fluoride ions (3), chloramine-T in 25% aqueous acetic acid (4), potassium permanganate in aqueous acetic acid at constant ionic strength (5), chloramine-T in aqueous ethanol under alkaline conditions (6), acid iodate in 50% aqueous methanol medium (13), acid bromate (19), diperiodatonickelate(IV) in alkaline medium (21), and by acid iodate in aqueous methanol (22). Considering the evidence put forward by earlier workers on the mechanism of oxidation of alkyl aryl ketones by different oxidizing agents (3-6, 13, 19, 21-22), and on the basis of the kinetic data obtained in the present investigation, it would be justified to suggest the mechanistic pathway of the oxidation of alkyl aryl ketones by QDC, in acid medium, as shown in the Scheme.

In acid medium, the oxidant QDC was converted to the protonated dimetallic Cr(VI) species (PQ) [in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $\text{Cr}_2\text{O}_7^{2-}$ (26)]. The substrate (S) was converted to the enol, via its protonated form (SH^+). The reaction of the enol with the protonated QDC (PQ), in the rate-determining step, resulted in the formation of the cyclic monochromate ester (E) and a monomeric Cr(VI) species. This cyclic monochromate ester was formed when the enol form of the substrate was bound to Cr(VI) through the carbon-oxygen-chromium bond via an electrocyclic mechanism involving six electrons. The decomposition of this cyclic ester could take place through the carbon-oxygen-chromium bond of the ester (E) in a fast step. The transfer of two electrons in this cyclic system resulted in open structures A (carboxylic acid) and

B (aldehyde). On oxidation with another mole of protonated QDC (PQ), **B** was converted to the corresponding carboxylic acid **C** along with Cr(IV) species.

The conversion of Cr(IV) to Cr(III) was a disproportionation reaction. For the reaction $\text{Cr(IV)} + \text{Cr(VI)} \rightarrow 2 \text{Cr(V)}$, the standard potential for the Cr(VI) - Cr(V) couple was extremely favorable ($E^0 = 0.62$ volt) (42), and this reaction would proceed rapidly. The Cr(V) - Cr(III) couple has a potential of 1.75 volt, which would enable the rapid conversion of Cr(V) to Cr(III), after the reaction with the substrate (42, 43).

Under the experimental conditions employed in the present investigation, alkyl aryl ketones were oxidized by quinolinium dichromate (QDC), in acid media, giving a mixture of carboxylic acids in each case. These products [formic acid and benzoic acid (from acetophenone); acetic acid and benzoic acid (from propiophenone); propionic acid and benzoic acid (from butyrophenone); and butyric acid and benzoic acid (from valerophenone)] were characterized by FT-NMR analysis (vide "Experimental : Product Analysis").

It would be justified to recall the earlier experimental observations, wherein alkyl aryl ketones were converted to carboxylic acids medium in good yields, when oxidized by diverse oxidizing agents such as acid permanganate in the presence of fluoride ions (3), chloramine-T in 25% aqueous acetic acid medium (4), potassium permanganate in aqueous acetic acid medium at constant ionic strength (5), chloramine-T in aqueous ethanol (11), acid bromate (19), and by diperiodatonickelate(IV) in alkaline medium (21). In all these oxidation reactions, the nature of the products formed (mixture of carboxylic

acids) established that, in the final step of the reaction, there was the cleavage of the carbon-carbon bond.

In the present investigation, the kinetic data and the nature of the products obtained clearly showed that the oxidation of alkyl aryl ketones by QDC yielded a mixture of carboxylic acids as the final products. These data would substantiate the mechanism of the oxidation process wherein there was the cleavage of the carbon-carbon bond in the final step of the reaction. This study highlighted the importance of QDC as an oxidant, and emphasized the utility and efficiency of QDC as a reagent capable of converting the alkyl aryl ketones to carboxylic acids. These reactions could prove to be of importance and utility in the synthesis of carboxylic acids.

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CHAPTER - IV

KINETICS OF OXIDATION OF β -DIKETONES

A review of the chemical literature pertaining to the reactions of metal ions with β -diketones reveals the formation of 1:1 complexes. The reaction between acetylacetone and cupric ion to form the monocomplex in water and in methanol showed two separate reactions. The concentration dependence of the rate constants suggested a mechanism which involved the direct reversible reaction between the solvated copper(II) ion and both the tautomers of acetylacetone (keto and enol). The enol tautomer was seen to be reacting much faster than the keto tautomer. For the reaction between the enol form and the copper(II) ion, the rate-determining step was the closure of the six membered ring. For the reaction between the keto form and copper(II) ion, the rate-determining step was the metal ion catalyzed proton transfer from the keto tautomer (1).

The kinetics of the reaction of β -diketones with metal ions such as nickel(II), cobalt(II), copper(II), and iron(II), at constant ionic strength showed the formation of the monocomplexes. It was further established that the keto form of the substrate did not react with the metal ions, while the enol form reacted by parallel acid-independent and inverse-acid pathways. The kinetic data were discussed in terms of a sterically controlled substitution mechanism as also a mechanism in which the loss of proton from the ligand was an important rate-determining factor (2).

The kinetics of the reaction of iron(III) with acetylacetone showed that the keto and enol tautomers both reacted with iron(III) by parallel acid independent and inverse acid pathways (3).

The kinetics of the reaction of nickel(II) and acetylacetone to form the monocomplex was reported in water and aqueous methanol medium. It was shown that the keto tautomer did not react directly with nickel(II). The kinetic data pointed to a mechanism in which nickel(II) reacted with the enol form of the ligand (4).

The kinetics of the reaction between vanadyl ion and acetylacetone to form the monocomplex was studied in aqueous solutions. The kinetic data were consistent with a mechanism in which the vanadyl ion reacted with the enol form of the substrate (5).

The kinetics of the reaction of uranyl ion, $[\text{UO}_2]^{2+}$ with acetylacetone in methanol – water solutions showed that $[\text{UO}_2]^{2+}$ ion reacted with the enol form of the substrate, as also with the keto tautomer (6).

The kinetics of the reactions of different metal ions (nickel(II), cobalt(II), copper(II) and iron(III)) with substituted acetylacetones have been reported. It has been shown that the kinetic data were consistent with a mechanism in which the metal ions reacted exclusively with the enol tautomer of the β -diketone, and that the keto tautomer was inert in all cases (7).

The oxidation kinetics of acetylacetone and benzoylacetone in sulfuric acid medium, using vanadium(V) as the oxidant, showed a first order dependence each on the oxidant, substrate and acid. It was suggested that the reactivity of benzoylacetone being higher than that of acetylacetone was probably due to a conjugative effect (8).

The kinetics of the reaction of chromium(III) and acetylacetone in aqueous solution showed that the mechanistic pathway was the reaction of the metal ion with the enol tautomer of acetylacetone. It was shown that the substitution of hexaaquachromium(III) was via an interchange-associative (I_a) mechanism wherein the enolate ion did not participate to any appreciable extent in the complex formation reaction (9).

The kinetics of oxidation of acetylacetone by chloramine-T (CAT) and bromamine-T (BAT), in the presence of hydrochloric acid, at constant ionic strength, has been reported. Michaelis-Menten type of kinetics was proposed. The mechanism involved the simultaneous catalysis by H^+ and Cl^- ions, and the interaction of haloamine species with the enol form of the diketone (10).

The kinetics of oxidation of acetylacetone by chloramine-B (CAB), in the presence of hydrochloric acid, at constant ionic strength, showed that the rate was first-order in [CAB], and fractional order each in acetylacetone and acid. The mechanism involved the interaction of the haloamine species with the enol form of the diketone (11).

The kinetics of oxidation of acetylacetone by bromamine-T (BAT) and bromamine-B (BAB) in alkaline buffer showed that the rates were first-order in oxidant, and fractional order each in substrate and alkali. The mechanism involved the reaction of the substrate with the OBr^- to form an intermediate, which was subsequently oxidized to the carboxylic acid (12).

The kinetics of oxidation of acetylacetone by cerium(IV) perchlorate in perchloric acid medium showed a first-order dependence on substrate and oxidant, but a zero-order dependence each on the acid concentration. An outer sphere mechanism was suggested for this oxidation process. The final product obtained was acetic acid (13).

The kinetics of the thallium(III) perchlorate oxidation of acetylacetone and benzoylacetone in acetic acid – water media, in the presence of perchloric acid, showed a first-order dependence in substrate and acid, but a zero-order dependence in oxidant. The mechanism involved the rate-determining enolization of the substrate (14).

PRESENT WORK

It was of interest to study the kinetic features of the reactions of chromium(VI) with β -diketones in order to examine the mechanistic features of the reaction between β -diketones and this metal ion. For this purpose, in our present work, we have carried out a detailed kinetic investigation of the oxidation of β -diketones by a chromium(VI) reagent, quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], in perchloric acid medium, under a nitrogen atmosphere.

The β -diketones chosen for the purpose of oxidation by QDC have included:

(a) Acetylacetone ; (b) Benzoylacetone ; and (c) Acetylacetonone

Stoichiometry (vide "Experimental")

The stoichiometries of all the oxidation reactions were determined. The stoichiometric ratios, $\Delta[QDC] / \Delta[Substrate]$, were obtained in the range 2.64 - 2.68 for acetylacetone and benzoyl acetone, and 1.98 - 2.00 for acetylacetonone (Table 1).

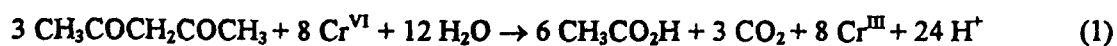
Table 1 : Stoichiometries of the Oxidation of the Substrates;

([Substrate] = 0.005 M; T = 303 K)

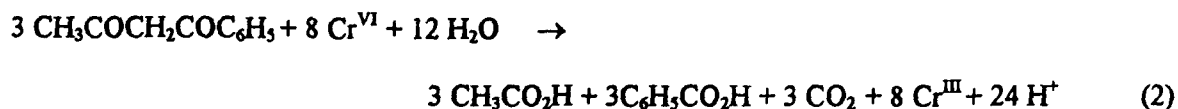
[HClO ₄] / M	0.10	0.25	0.50
10 ² [QDC] / M	2.50	2.60	2.70
Δ[QDC] / Δ[Acetylacetone]	2.66	2.64	2.68
Δ[QDC] / Δ[Benzoylacetone]	2.67	2.68	2.65
Δ[QDC] / Δ[Acetylacetone]	1.99	1.98	2.00

The stoichiometry conformed to the overall equations :

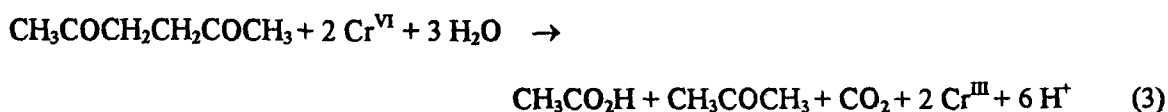
(a) For acetylacetone :



(b) For benzoylacetone :



(c) For acetylacetone :



Effect of Substrate

The rates of the reactions were found to be dependent on the concentrations of the substrates. The order of the reaction with respect to the substrate was obtained by

changing the substrate concentration, and observing the effect on the rates of the reactions at constant [QDC] and $[H^+]$. The results have been recorded in Table 2.

Table 2 : Dependence of Rate Constants on the concentration of β -Diketones in aqueous medium; ([QDC] = 0.001 M; $[HClO_4]$ = 0.4 M; T = 303K)

10^2 [Substrate] /M	$10^3 k_1 / s^{-1}$		
	Acetylacetone	Benzoylacetone	Acetylacetone
1.0	13.5	7.62	0.59
2.5	35.2	20.1	1.61
5.0	69.1	38.5	2.89
7.5	99.4	55.3	4.52
10.0	135.6	77.1	5.80
	$10 k_2 / M^{-1} s^{-1}$		
	13.5	7.62	0.59
	14.1	8.04	0.64
	13.8	7.70	0.59
	13.3	7.37	0.60
	13.6	7.71	0.58
$k_2 = k_1 / [\text{Substrate}]$			

Plots of k_1 , the pseudo-first-order rate constant, against a ten-fold range of the concentrations of substrates (in each case), gave straight lines passing through the origin (Figure 1). This indicated that the rate of oxidation was dependent on the first power of

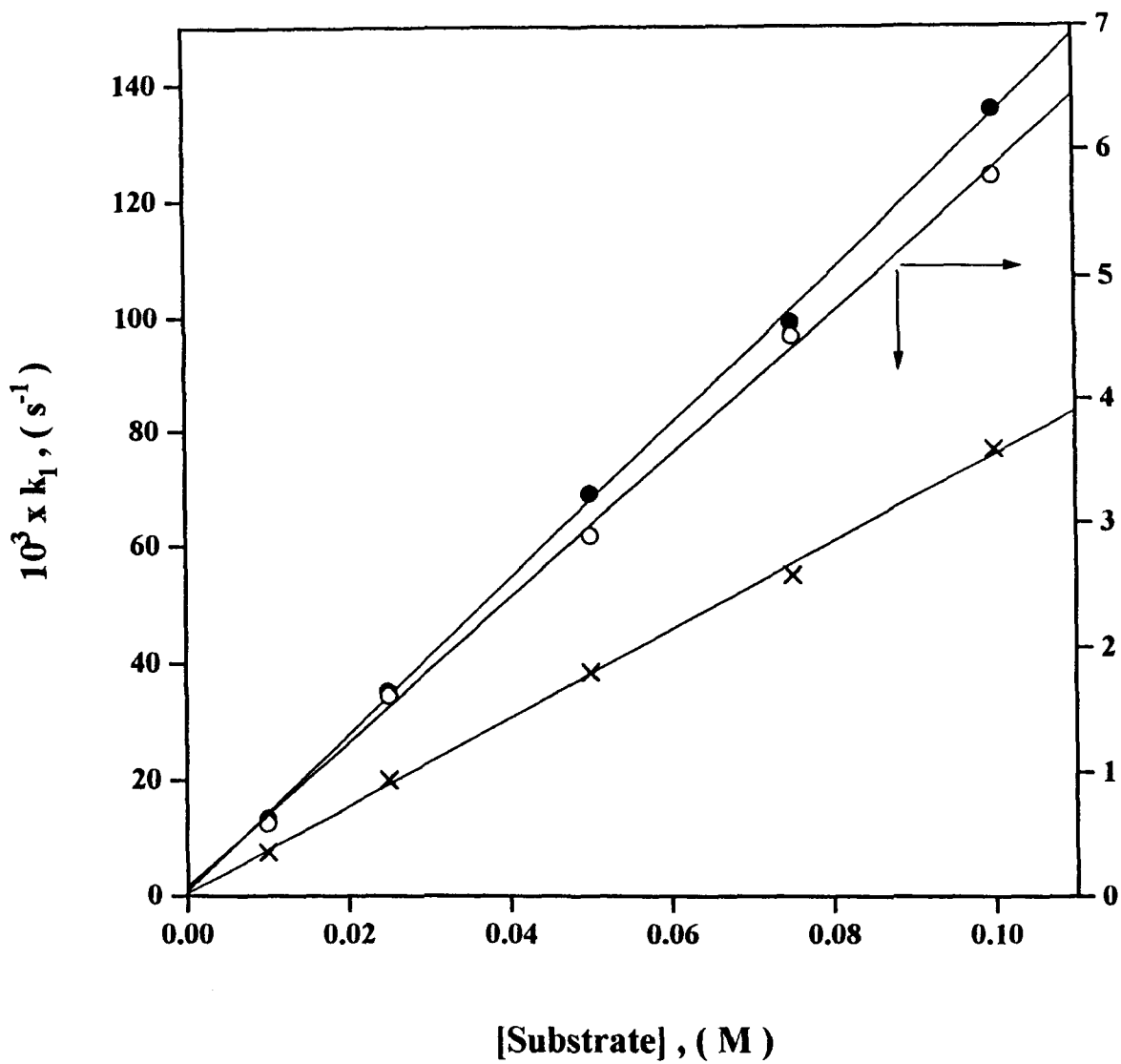


Fig.1. Plots of k_1 against the concentrations of substrates for acetylacetone (●), benzoylacetone (×) and acetylacetone (○).

the concentrations of the substrates. This was further demonstrated by the constancy in the values of k_2 , the second-order rate constant.

Effect of oxidant

Under pseudo-first-order conditions, the individual kinetic runs were first-order with respect to the oxidant (QDC). At fixed [acid] and with the substrate taken in excess, the plots of log absorbance versus time were linear, indicating a first order dependence on QDC. When a constant concentration of substrate (large excess) was used, the pseudo-first-order rate constant (k_1) did not alter appreciably with changing concentrations of the oxidant (QDC), indicating a first-order dependence of the rate on the concentration of the oxidant. The rate data have been shown in Table 3.

Table 3 : Dependence of Rate Constants on the concentration of Oxidant in aqueous medium; ([Substrate] = 0.01 M; [HClO₄] = 0.4 M; T = 303K)

10^3 [QDC] / M	$10^3 k_1 / s^{-1}$		
	Acetylacetone	Benzoylacetone	Acetonylacetone
0.25	13.6	7.70	0.62
0.50	13.6	7.60	0.58
0.75	13.4	7.66	0.61
1.0	13.5	7.62	0.59

Effect of acid

The reaction was influenced by changes in the acid concentration, and the rate was observed to increase with an increasing concentration of the acid, in the range 0.10 to 0.80 M (Table 4).

Table 4 : Dependence of Rate Constants on Acid concentration for β -Diketones in aqueous medium; ([Substrate] = 0.01 M; [QDC] = 0.001 M; T = 303K)

[HClO ₄] / M	$10^3 k_1 / s^{-1}$		
	Acetylacetone	Benzoylacetone	Acetonylacetone
0.1	3.16	1.86	0.14
0.2	5.89	3.31	0.25
0.3	8.91	5.49	0.35
0.4	13.5	7.62	0.59
0.5	17.0	8.91	0.72
0.6	20.9	11.0	0.85
0.7	24.5	12.9	0.98
0.8	26.9	15.2	1.18

Plots of $\log k_1$ against $\log [H^+]$ were linear, with slopes equal to unity (Figure 2), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step. There have been earlier reports of the involvement of such protonated Cr(VI) species in chromic acid oxidation reactions (15). The acid catalysis must be related to the structure of the oxidant (QDC), which was converted to a protonated species at the concentration of mineral acid used. Quinolinium dichromate is a dimetallic species, an anionic condensed form of chromic acid. Michel et al. examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate $HCrO_4^-$ does not exist in aqueous solutions of Cr(VI) compounds (16). Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of mineral acid would be $HCrO_4^-$ and $Cr_2O_7^{2-}$. When the Raman lines were examined under dilution, it was established that at $pH = 11$, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion, whereas at $pH = 1.2$, it was 100% as the $Cr_2O_7^{2-}$ ion (16). Hence, at concentrations of acid larger than 0.05 M, the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $K_2Cr_2O_7$, spectral studies have shown that $Cr_2O_7^{2-}$ was the predominant species (17). In the present investigation, since the acid concentrations used were in the range 0.10 to 0.80 M, the dichromate ion (existing as protonated dimetallic Cr(VI) species) would be the predominant species. Moreover, the protonated dimetallic Cr(VI) species would be a

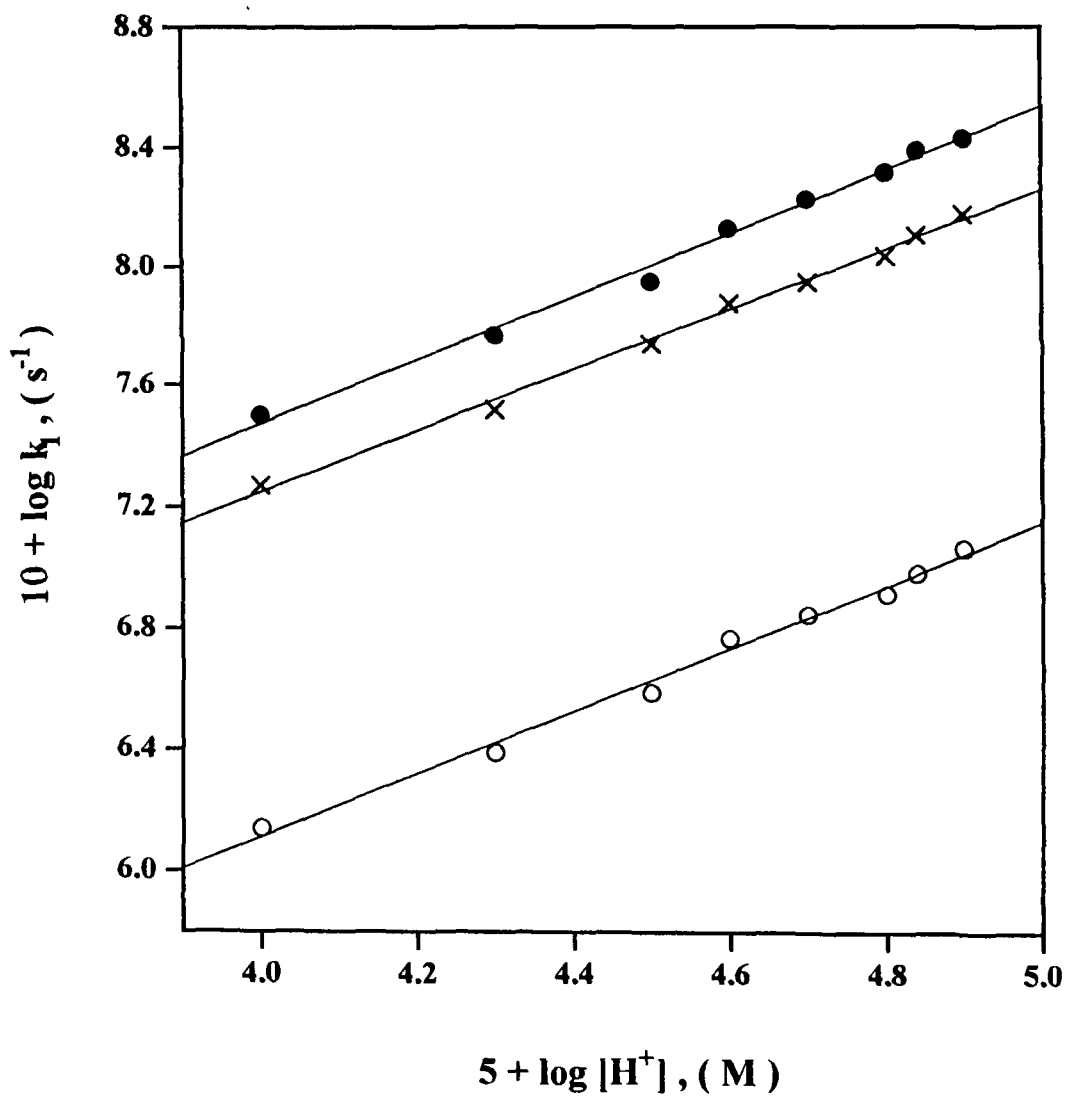


Fig. 2. Plots of $\log k_1$ against $\log [H^+]$ for acetylacetone (●), benzoylacetone (×) and acetylacetone (○).

more reactive electrophile capable of increasing its rate of coordination to the enol form of the β -diketones.

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been employed for all the kinetic runs, the observed rate law could be expressed as :

$$\text{Rate} = - \frac{d[\text{QDC}]}{dt} = k [\text{Substrate}] [\text{QDC}] [\text{H}^+] \quad (4)$$

Effect of solvent

The acid-catalyzed oxidation of the substrates was studied in solutions containing varying proportions of water and DMF. For each of the substrates oxidized by QDC, the rate of oxidation was fastest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of DMF resulted in a decrease in the rate of oxidation (Table 5).

Table 5 : Dependence of Rate Constants on Solvent Composition for β -Diketones;**([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 0.4 M; T = 303K)**

H ₂ O:DMF (%, v/v)	Dielectric Constant (D)	10 ³ k ₁ / s ⁻¹		
		Acetylacetone	Benzoylacetone	Acetylacetonone
100:0	76.7	13.5	7.62	0.59
95:5	74.7	11.5	6.46	0.38
90:10	72.8	7.59	3.80	0.26
85:15	70.8	6.03	2.14	0.19
80:20	68.9	2.57	1.48	0.15

The dielectric constants for water - DMF mixtures have been estimated approximately from the dielectric constants of the pure solvents (at 303 K: water = 76.7; DMF = 37.6) (18).

In the present investigation, in going from 0% DMF to 20% DMF, the polarity decreased. This decrease in the polarity of the medium caused a decrease in the rate of the reaction (Table 5). Plots of log k₁ against the inverse of dielectric constants were linear with negative slopes (Figure 3). This suggested an interaction between an ion and a dipole (19), and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated dimetallic Cr(VI) species.

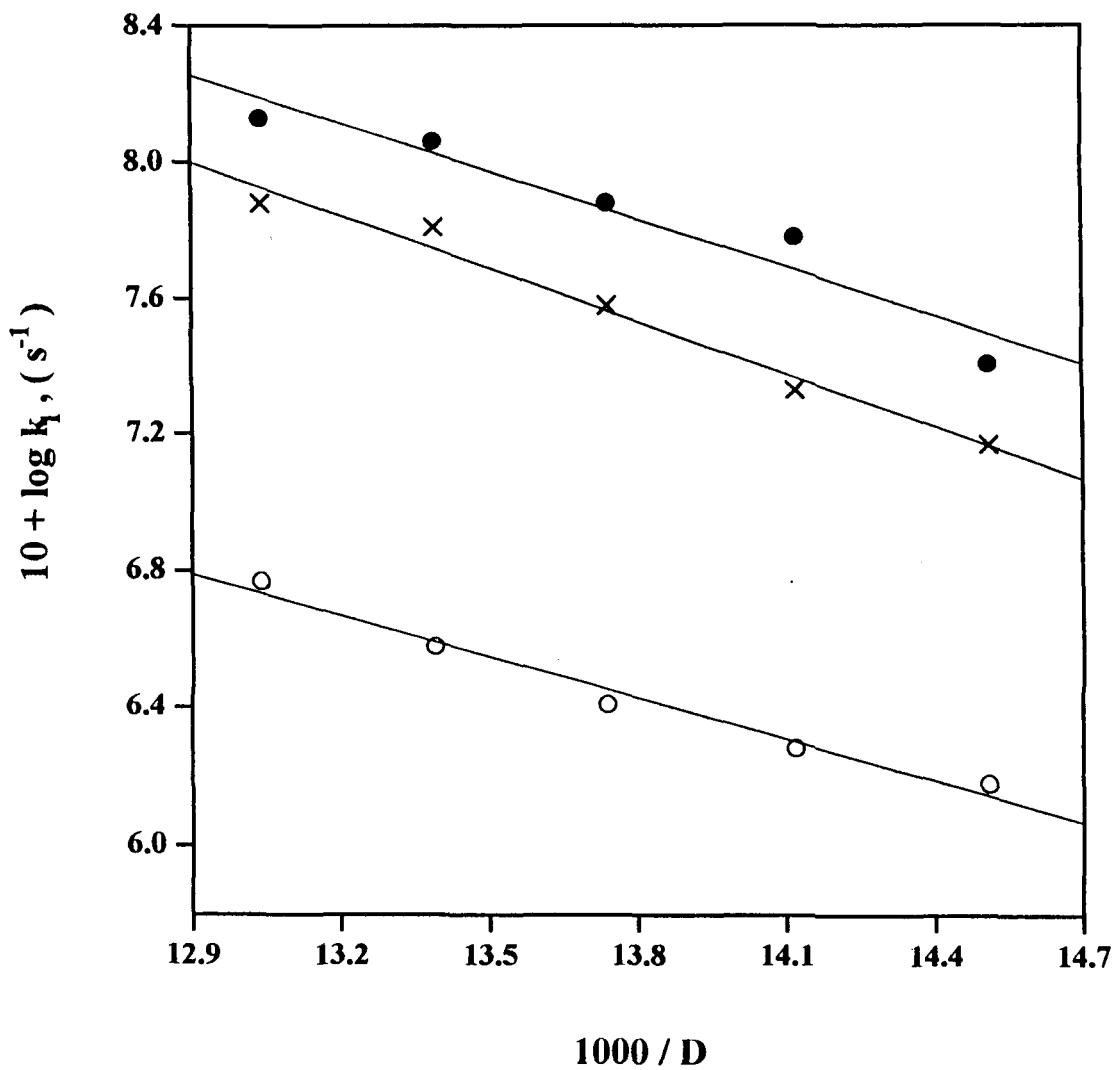


Fig. 3. Plots of $\log k_1$ against the reciprocal of the dielectric constant for acetylacetone (●), benzoylacetone (×) and acetonylacetone (○).

It would be expected that the total solvation of an ion and a dipole (initial state) should be less than the solvation of the transition state. The transition state would thus be more polar than the initial state (reactants), because of the decreased dispersal of charges in the transition state (20). In the present investigation, the addition of a more polar solvent resulted in an increase in the rate of oxidation. This arose as a result of a progressive increase in solvation of the transition state.

Effect of temperature

The rates of the reactions were influenced by changes in the temperature. The rate of the reaction was found to increase with an increase in the temperature (Table 6).

Table 6 : Dependence of Rate Constants on Temperature for β -Diketones in aqueous medium; ([Substrate] = 0.01 M; [QDC] = 0.001 M; [HClO₄] = 0.4 M)

Temperature (± 0.1 K)	$10^3 k_1 / s^{-1}$		
	Acetylacetone	Benzoylacetone	Acetylacetone
298	10.2	5.37	0.34
303	13.5	7.62	0.59
308	19.1	11.2	0.87
313	28.2	15.5	1.35
318	38.0	21.9	2.19

A linear correlation between $\log k_1$ and the reciprocal of temperature in the range 298 –318 K was observed (Figure 4), suggesting the validity of Arrhenius equation. The activation parameters (vide “Experimental : Calculations”) are shown in Table 7.

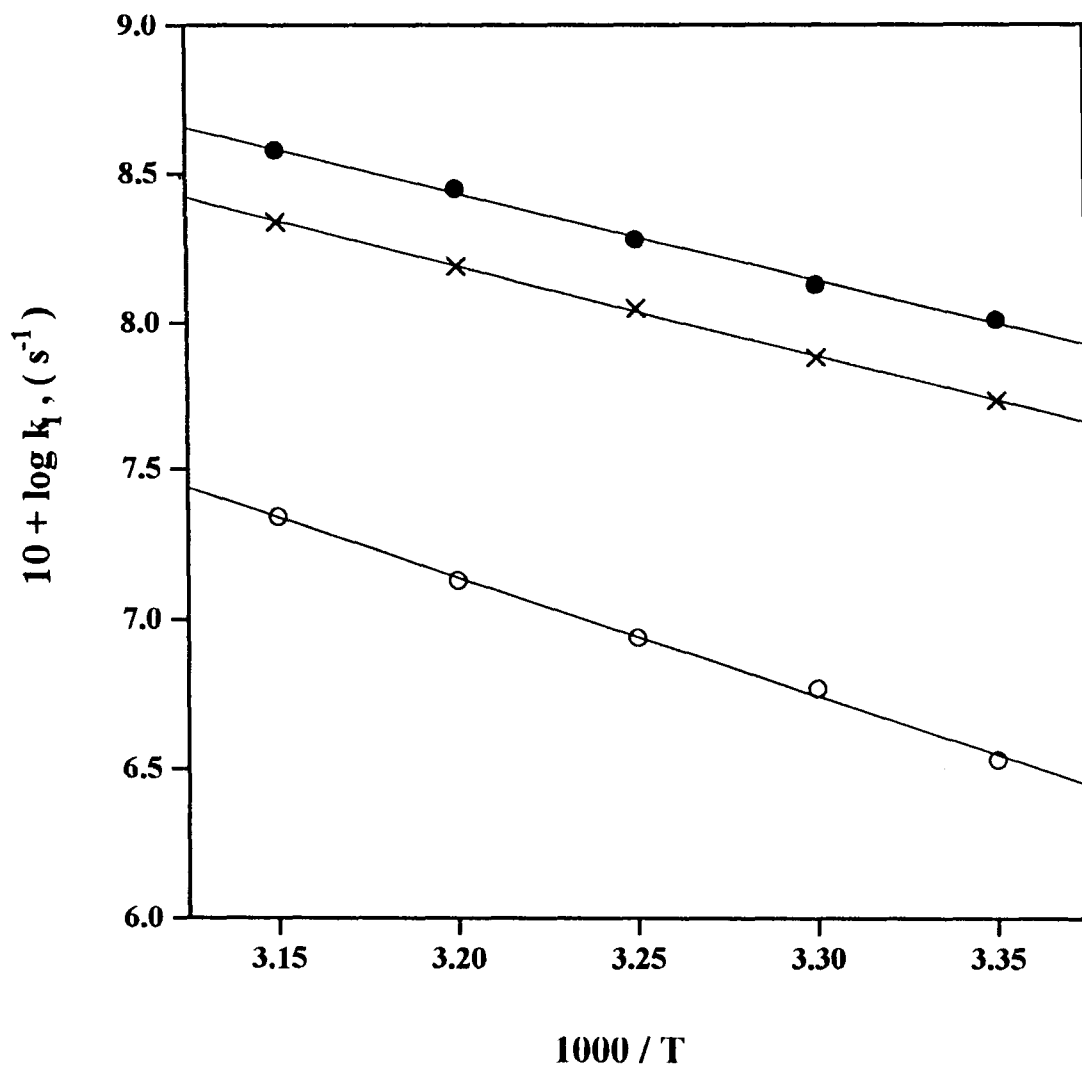


Fig. 4. Plots of $\log k_1$ against the reciprocal of temperature for acetylacetone (\bullet), benzoylacetone (\times) and acetonylacetone (\circ).

Table 7 : Activation Parameters for β -Diketones

Substrate	E (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (JK ⁻¹ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)
Acetylacetone	56	50	-115	85
Benzoylacetone	59	53	-111	86
Acetylacetonone	76	69	-79	89

Error limits : E \pm 2 kJ mol⁻¹; $\Delta H^* \pm$ 2 kJ mol⁻¹; $\Delta S^* \pm$ 3 JK⁻¹ mol⁻¹; $\Delta G^* \pm$ 2 kJ mol⁻¹

The negative values of ΔS^* provided support for the formation of a rigid activated complex. The constancy in ΔG^* values suggested that a common mechanism was applicable for the oxidation of all the substrates (acetylacetone, benzoylacetone and acetylacetonone), by QDC.

Induced polymerization

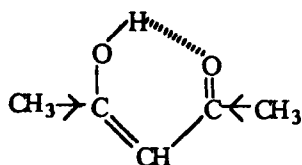
In the present investigation, since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (21). This indicated that a one-electron oxidation was quite unlikely. Control experiments were performed, in the absence of the respective substrates. The concentration of QDC did not show any appreciable change.

Structural influences on the rates of oxidation

In the present investigation, the order of reactivity was in accordance with the structural changes in the β -diketones:

acetylacetone > benzoylacetone > acetylacetonone (Table 2).

When the reactivities of acetylacetone and benzoylacetone were compared, it was observed that acetylacetone was more reactive as compared to benzoylacetone (Table 2). Benzoylacetone has a greater enol content as compared to acetylacetone; but the enol form of acetylacetone was more stabilized. The +I-effect of the two methyl groups in acetylacetone helped to stabilize the chelate ring of the enol :



In benzoylacetone, the -I-effect of the phenyl group makes it less stable, when compared to acetylacetone. Further, the value of ΔS^\ddagger for the QDC reaction with benzoylacetone ($-111 \text{ JK}^{-1} \text{ M}^{-1}$) was greater than that for the QDC reaction with acetylacetone ($-115 \text{ JK}^{-1} \text{ M}^{-1}$). This was in conformity with the observation that bulky groups (as in benzoylacetone) hindered the reaction, increasing the entropy of activation.

When the reactivities of acetylacetone and acetylacetonone were compared, it was observed that acetylacetone was far more reactive than acetylacetonone (Table 2). This showed that the rate of oxidation was dependent on the length of the chain of these

β -diketones. In acetylacetone, the presence of the two methylene groups between the two carbonyl moieties resulted in a decrease in the electron density at the carbon atom adjacent to the carbonyl group. The ease of deprotonation from this carbon atom would decrease, as compared to that in acetylacetone. This resulted in a decrease in the enolic content of acetylacetone, and prevented the attack of the electrophile (protonated dimetallic Cr(VI) species), as more methylene groups were inserted between the two carbonyl groups. Hence, this would result in a retardation in the rate of oxidation of acetylacetone, as compared to that of acetylacetone. Also, the enol form of acetylacetone was more stabilized, as compared to that in acetylacetone, since the +I-effect of the two methyl groups in acetylacetone helps to stabilize the chelate ring of the enol. Further, the value of ΔS^\ddagger for the QDC reaction with acetylacetone ($-79 \text{ JK}^{-1} \text{ M}^{-1}$) was more than that for the QDC reaction with acetylacetone ($-115 \text{ JK}^{-1} \text{ M}^{-1}$). This was in conformity with the observation that the presence of the two methylene groups (as in acetylacetone) hindered the reaction, increasing the entropy of activation.

Mechanism

In oxidation reactions, it has been observed that ketones reacted either directly or through the enol form. The rates of oxidation being faster than the rates of enolization were observed when ceric (22, 23), manganic (23), and cobaltic salts (23, 24) were used as oxidants, indicating that the ketones reacted directly. All these oxidants underwent a one-electron reduction, and the reaction occurred through a free radical mechanism

(22-24). The kinetics of oxidation of acetylacetone by bromamine-T (BAT) and bromamine-B (BAB) in alkaline buffer showed that the rate of the reaction was first-order in oxidant, and fractional-order each in [substrate] and $[\text{OH}^-]$ (12). It was observed that with an increase in pH, $[\text{OBr}^-]$ increased; at higher pH, OBr^- ion was suggested to be the most likely species responsible for oxidizing the diketone. The OBr^- formed in the first step of the reaction reacted with the substrate (as the carbanion) to give a substrate-oxidant complex. This complex underwent a reaction with alkali, in the rate-determining step, to give an intermediate, which on further oxidation with two moles of OBr^- , resulted in the formation of formic acid and acetic acid (12).

The kinetics of the complex formation reactions of β -diketones with a number of metal ions have been reported (1-7). In most of these investigations, it was reported that the metal species reacted with the protonated enol tautomer of the β -diketone. The slow rate of reaction of copper(II) with the enol tautomer of acetylacetone was explained in terms of a sterically controlled substitution mechanism due to the formation of a six-membered ring (1). It was shown that due to intramolecular hydrogen bonding, the protonated enol tautomer was a poor entering group (2,3). An inverse correlation was found between the degree of retardation of the rate and the hardness of the metal species. This suggested that the stability of a precursor complex was important in determining the overall rate constant (7).

For the reactions of chromium(III) with β -diketones, it was observed that the rate of formation of the chromium(III) – acetylacetone complex was considerably more rapid than the rate of solvent exchange on the metal ion (9). This showed that complex

formation took place via an interchange – associative (I_a) mechanism, wherein the enolate ion did not participate to any appreciable extent in the complex formation reaction (9).

In all these kinetic investigations, it was shown that the keto form of the acetylacetones did not show any appreciable reaction with the metal ions (1-7, 9). Overwhelming kinetic evidence had established that the reactions between acetylacetone and metal ions involved a mechanism wherein the enol tautomer took part in the reaction (1-7, 9).

The oxidation kinetics of acetyl acetone and benzoyl acetone in sulfuric acid, using vanadium(V) as the oxidant, revealed a first order dependence in each – substrate, oxidant and acid. The values of the activation parameters suggested a carbon-hydrogen bond fission in the final step of the reaction. Conjugation effects were used to explain the enhanced reactivity of benzoylacetone over that of acetylacetone (8).

Kinetic data on the oxidation of acetylacetone by chloramine-T (CAT) and bromamine-T (BAT), in the presence of hydrochloric acid at constant ionic strength, showed a first order dependence on the oxidant, and fractional order dependence in substrate and acid concentrations. It was shown that acetylacetone reacted in the enol form to form the substrate-oxidant complex. This complex underwent decomposition, in a rate-determining step, to give formic acid and acetic acid (10).

Chloramine-B (CAB) in the presence of hydrochloric acid, at constant ionic strength, was used for the oxidation of acetylacetone. The rate was first order in oxidant, and fractional order each in [substrate] and $[H^+]$. The mechanism showed the

simultaneous catalysis by H^+ and Cl^- ions. The interhalogen intermediate species formed from CAB, H^+ and Cl^- reacted with the enol form of the substrate to give a substrate-oxidant complex. The rate-determining step was the decomposition of this complex to give formic acid and acetic acid as the final products (11).

The kinetics of oxidation of acetylacetone by cerium(IV) perchlorate in perchloric acid medium showed a first order dependence each in substrate and oxidant, but exhibited a zero order dependence on the concentration of the acid. The mechanism involved the formation of a radical intermediate which underwent reaction with cerium(IV), in the rate-determining step. The resulting intermediate was converted to acetic acid in the final step, along with the evolution of carbon dioxide. The evolution of carbon dioxide clearly showed that decarboxylation had taken place in the final step of the reaction (13).

Kinetic analysis of the thallium(III) perchlorate oxidation of acetylacetone and benzoylacetone, in acetic acid-water mixtures, in the presence of perchloric acid was carried out. The reactions were first order each in substrate and acid, but were found to be zero order in oxidant. The zero-order dependence in oxidant implied that enolization took place in the rate-determining step. This was further supported by the experimental observation that the rate of oxidation was faster than the rate of bromination. Triones were identified as the products of these oxidation reactions (14).

Based on the stoichiometries of the oxidation reactions (Table 1), and the observed experimental data, the mechanistic pathways for the oxidation of the β -diketones (acetylacetone, benzoylacetone and acetonylacetone) by quinolinium dichromate (QDC) in perchloric acid medium in aqueous medium, has to be rationalized.

While suggesting mechanistic pathways for these oxidation reactions, the following kinetic observations have to be taken into consideration:

- (1) the rates of oxidation of all the β -diketones (acetylacetone, benzoylacetone and acetylacetonone) were dependent on the first powers of the concentrations of each — substrate and oxidant (Tables 2-3, Figure 1);
- (2) the rates of reactions showed a first order dependence on the concentrations of the acid (Table 4, Figure 2). The acid catalysis of the oxidation reactions must be related to the structure of the oxidant (QDC), which was converted to a protonated dimetallic Cr(VI) species. In presence of the acid, the keto tautomer was also converted to the enol tautomer;
- (3) an increase in the polarity of the solvent medium (using water - DMF mixtures) showed an increase in the rate of the reaction (Table 5). Linear plots of $\log k_1$ against the inverse of the dielectric constants (Figure 3) gave negative slopes, which indicated an ion-dipole type of interaction. This was in accordance with the involvement of a protonated dimetallic Cr(VI) species in the rate-determining step of the reaction;
- (4) an increase in temperature resulted in an increase in the rates of the reactions (Table 6). The oxidation of β -diketones was characterized by negative entropies of activation (Table 7), which suggested an ordered transition state, relative to the reactants. The similarity in ΔG^\ddagger values (Table 7) for all the substrates emphasized the probability that all these oxidation reactions involved similar rate-determining steps;

- (5) there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride, indicating the absence of any radical formation; and
- (6) the observed order of reactivity was in accordance with the structural changes in β -diketones:

acetylacetone > benzoylacetone > acetylacetylacetone (Table 2).

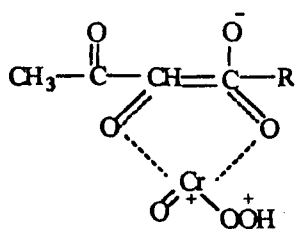
The order of reactivity was rationalized on the basis of the inductive effect (+I-effect for the methyl group of acetylacetone, and -I-effect for the phenyl group of benzoylacetone). The greater reactivity of acetylacetone over that of acetylacetylacetone was rationalized on the basis that the rates of oxidation were dependent on the length of the chain of these β -diketones.

In the present investigation, focusing attention on the oxidation of β -diketones by quinolinium dichromate (QDC) in perchloric acid medium, the rate of oxidation was first-order with respect to the concentrations of each — substrate, oxidant and acid. The first-order dependence of the rate on QDC concentration suggested that the reaction pathway was through the enol form of the substrate. The rates of enolization of all the β -diketones were determined by the bromination method. It was observed that the rates of enolization were very much greater than the rates of oxidation for all the β -diketones (by a factor of ~15). The rates of enolization being much faster than the rates of oxidation, would indicate that the enolization step was not rate-determining. Hence, it would be justified to conclude that the enol form of the substrate reacted with the oxidant. The rate-determining step involved an attack of the oxidant on the enol form of the substrate.

The stoichiometric conversion of the β -diketones to the corresponding products involved the changes : $>=O \rightleftharpoons \gg-OH \rightarrow$ chromate ester \rightarrow carboxylic acid + CO_2 ; and the rate of oxidation varied with the concentration of the acid. If the reaction intermediate were to be visualized as having a cyclic structure, then this would explain all the features of the oxidation reaction. The negative entropies of activation (Table 7) would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The similarity in ΔG^\ddagger values arose due to changes in ΔH^\ddagger and ΔS^\ddagger values (Table 7), and stressed the probability that these oxidation reactions involved similar rate-determining steps.

In the present investigation, the observed solvent effect (increase in the polarity of the solvent increased the rate of oxidation, Table 5) provided support for a reaction pathway which involved the formation of a cyclic monochromate ester intermediate.

A unimolecular decomposition of the cyclic monochromate ester could be written in which the chromium was bonded in the transition state to both the oxygen atoms :



cyclic ester
T.S

Electron flow in a cyclic transition state has been earlier considered (25, 26), and the conversion of the ester to the transition state can be best considered in the following terms :

If the chromium was coordinated through the oxygen, then the process of electron transfer could take place through the carbon-oxygen-chromium bond. This would facilitate the formation of the cyclic monochromate ester, also enhance the ease of conversion to the product. Such an intermediate would envisage the transfer of electrons towards the chromium, occurring by the formation of the carbon-oxygen-chromium bonds. Partly occupied orbitals were used to bind the oxygen to both, carbon and chromium in the transition state.

In the present investigation, the sequence of reactions involved in the oxidation of β -diketones (acetylacetone, benzoylacetone and acetylacetone) by quinolinium dichromate (QDC) in perchloric acid medium, has been shown in the Scheme.

The mechanism is consistent with the fact that these oxidation reactions were catalyzed by acid (Table 4). Protonation of the oxidant (QDC) would make it more amenable towards nucleophilic attack by the enol form of the substrate on the electron-deficient chromium of the oxidant. The first step involved the enolization of the ketone followed by the protonation of the oxidant (QDC). The second step was the rate-determining step, wherein the enol form of the substrate reacted with the protonated dimetallic oxidant, to form the cyclic monochromate ester. This was followed by the transfer of two electrons in a cyclic system giving rise to cleavage products. This

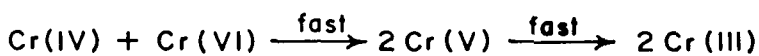
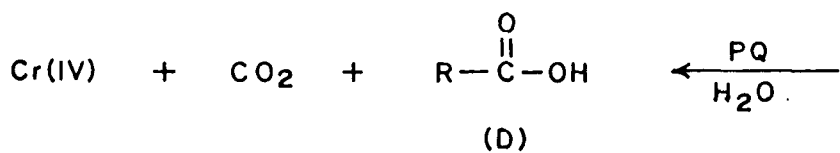
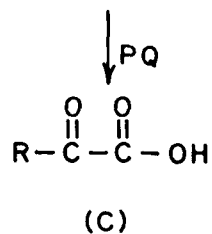
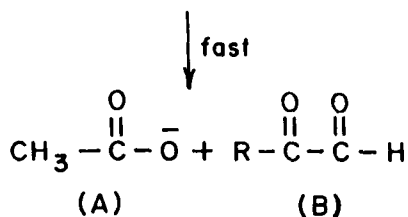
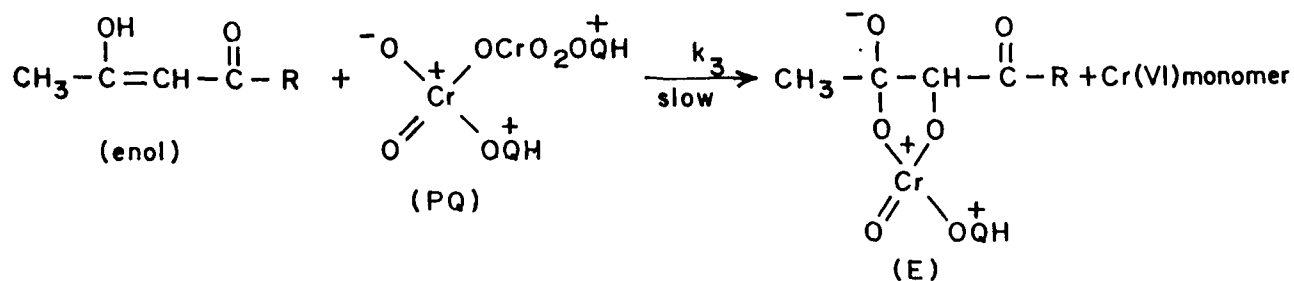
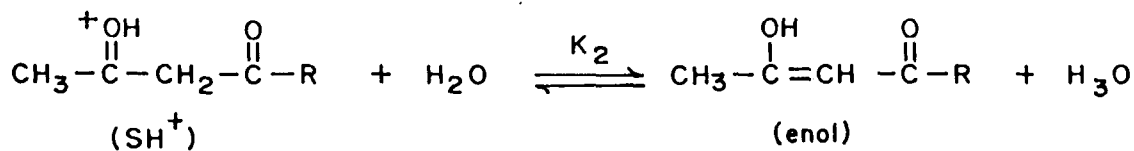
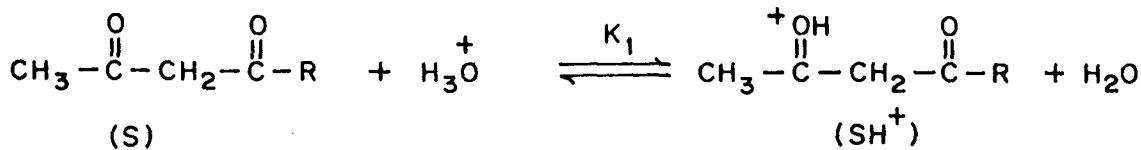
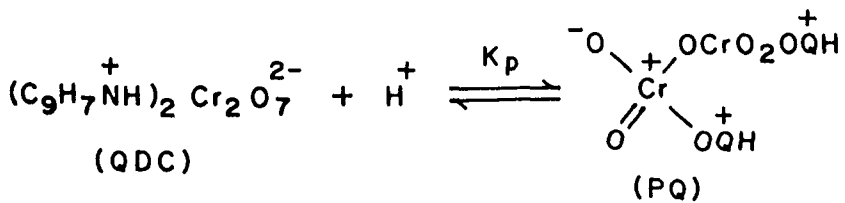
electrocyclic mechanism clearly involved six electrons, and being a Hückel-type system ($4n+2$), this was an allowed process (27).

The mechanistic pathway for the oxidation of β -diketones by QDC in acid medium, involved the attack of the protonated QDC (dimetallic Cr(VI) species) on the enol form of the substrate in the rate-determining step, to give a cyclic monochromate ester and a chromium(VI) monomer. This cyclic monochromate ester underwent rapid decomposition to give the final products (carboxylic acids in the case of acetylacetone and benzoylacetone, and a mixture of carboxylic acid and acetone in the case of acetonylacetone). This mechanistic pathway and the products obtained (carboxylic acids in the cases of acetylacetone and benzoylacetone and a mixture of carboxylic acid and acetone in the case of acetonylacetone) established that there was a cleavage of the carbon-carbon bond in the final step of the reaction. Our mechanistic pathway finds overwhelming support from earlier investigations wherein the oxidation of β -diketones had established that the rate-determining step for the oxidation reactions involved an attack of the oxidant on the enol form of the substrate. Such a mechanistic pathway finds support from earlier investigations wherein it was shown that β -diketones reacted with different metal ions such as copper(II) ions in water and methanol media (1), nickel(II), cobalt(II), copper(II), iron(III) ions at constant ionic strength (2, 7), iron(III) ions at constant ionic strength (3), nickel(II) in water and in aqueous methanol (4), vanadium(V) in aqueous medium (5), uranyl ions in methanol-water solutions (6), and with chromium(III) in aqueous solutions at constant ionic strength (9). Taking into account all the evidence suggested by the earlier investigations on the mechanism of the reactions of β -diketone with different metal ions (1-7, 9), and on the basis of the

kinetic data obtained in the present investigation, it would be justified to propose the mechanism for the oxidation of β -diketones by QDC, in acid medium, as shown in the Scheme.

In acid medium, the oxidant QDC was converted to the protonated dimetallic Cr(VI) species (PQ) [in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $\text{Cr}_2\text{O}_7^{2-}$ (17)]. The substance (S) was converted to the enol, via its protonated form (SH^+). The reaction of the enol with the protonated QDC (PQ), resulted in the formation of the cyclic monochromate ester (E) in the rate-determining step of the reaction. This cyclic monochromate ester was formed when the enol form of the substrate was bound to Cr(VI) through the carbon-oxygen-chromium bond via an electrocyclic mechanism involving six electrons. The decomposition of this cyclic ester could take place through the carbon-oxygen-chromium bond of the ester (E) in a fast step. The transfer of two electrons in this cyclic system resulted in open structures A (carboxylic acid) and B (aldehyde). On oxidation with another mole of protonated QDC (PQ), B was converted to C, which on hydration with protonated QDC (PQ) gave the corresponding carboxylic acid D, with the evolution of carbon dioxide.

The conversion of Cr(IV) to Cr(III) was a disproportionation reaction. For the reaction $\text{Cr(IV)} + \text{Cr(VI)} \rightarrow 2 \text{Cr(V)}$, the standard potential for the Cr(VI) - Cr(V) couple was extremely favorable ($E^0 = 0.62$ volt) (28), and this reaction would proceed rapidly. The Cr(V) - Cr(III) couple has a potential of 1.75 volt, which would enable the rapid conversion of Cr(V) to Cr(III), after the reaction with the substrate (28, 29).



R = -Me (acetylacetone); -Ph (benzoylacetone)

SCHEME

Under the experimental conditions employed in the present investigation, β -diketones were oxidized by quinolinium dichromate (QDC), in acid media, giving carboxylic acids in each case. These products [acetic acid (from acetylacetone); acetic acid and benzoic acid (from benzoylacetone); and acetic acid and acetone (from acetonylacetone)] were characterized by FT-NMR analysis (vide "Experimental : Product Analysis").

It would be appropriate to recall the earlier work on the oxidation of β -diketones, wherein these substrates were converted to carboxylic acids in good yields. The conversion of β -diketones to carboxylic acids have been carried out by different oxidizing agents such as chloramine-T and bromamine-T in the presence of acid at constant ionic strength (10), chloramine-B in the presence of acid at constant ionic strength (11), bromamine-T and bromamine-B in alkaline buffer medium (12), and by cerium(IV) perchlorate in perchloric acid medium (13). For all these oxidation reactions (10-13), the nature of the products formed clearly established the cleavage of the carbon-carbon bond in the final step of the reaction.

In the present investigation, the observed kinetic data and the nature of the products obtained showed that the oxidation of β -diketones (acetylacetone and benzoylacetone) by QDC yielded a mixture of carboxylic acids as the final products, accompanied by the evolution of carbon dioxide. The oxidation of acetonylacetone by QDC, in acid medium, had resulted in the formation of acetic acid and acetone as the final products, with the evolution of carbon dioxide. These data would support the

mechanism of the oxidation process wherein the cleavage of the carbon-carbon bond occurred in the final step of the reaction.

This study brings out the importance of QDC as an oxidant, and emphasizes the utility and efficiency of QDC as a reagent capable of bringing about the conversion of β -diketones to carboxylic acids.

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CHAPTER - V

KINETICS OF OXIDATION OF α -KETO ACIDS

The importance of α -keto acids in biochemical transformations has been well demonstrated (1). Pyruvic acid has an important role to play in many metabolic pathways. It has been shown that pyruvic acid is an intermediate in carbohydrate metabolism, and can be subjected to a variety of reactions giving rise to different products (2).

Pyruvic acid was oxidized quantitatively to acetic acid and carbon dioxide, when the oxidation was carried out using manganic pyrophosphate as the oxidant. It was shown that the reaction proceeded via the formation of a chelated manganic complex, and that enolization was not involved (3).

The kinetics of oxidation of pyruvic acid by chromium(VI) showed a first-order dependence with respect to the substrate and acid concentrations. It was observed that there was a decrease in the rate of oxidation with an increase in the initial concentration of chromium(VI). This was interpreted as indicating that HCrO_4^- was the reactive species under the experimental conditions used (4).

The kinetics of oxidation of pyruvic acid by periodate in the pH range 0 - 9 showed that the order dependence was unity in each — substrate and oxidant. It was suggested that IO_4^- was the only reactive periodate species, and the product obtained was acetic acid (5).

The kinetics of oxidation of pyruvic acid by alkaline hexacyanoferrate(III) showed a first-order dependence each with respect to oxidant, substrate and alkali. It was suggested that the reaction proceeded through the hydrated form of the substrate. This was supported by the formation of acetic acid as the product, which could have resulted only if pyruvic acid reacted through its hydrated form (6).

The reaction between pyruvic acid and alkaline hexacyanoferrate(III), catalyzed by Os(VIII), showed a first-order dependence on the concentrations of substrate, OH⁻ and Os(VIII). However, the rate of the reaction was independent of the concentration of the oxidant. It was proposed that the substrate reacted with the OH⁻ to give an intermediate, which reacted with Os(VIII) in the rate-determining step, to give acetic acid and Os(VI) as the products (7).

The kinetics of oxidation of pyruvic acid by V(V), in acid medium, showed a first-order dependence on both the oxidant and substrate. The order with respect to the acid was less than unity. It was suggested that V(V) reacted with the hydrated form of pyruvic acid, in the rate-determining step, to give a free radical, V(V), and carbon dioxide. The subsequent rapid reaction of the free radical with V(V) gave acetic acid (8).

The kinetics of the reaction between pyruvate and alkaline hexacyanoferrate(III) proceeded via the formation of a free radical. The rate of the reaction was dependent on the first powers of the concentrations of each — pyruvate, oxidant and alkali. The free radical formed was rapidly oxidized to acetic acid and oxalic acid, with the evolution of carbon dioxide (9).

The oxidation of pyruvic acid by Ce(IV) in acid medium showed that CeSO_4^{2-} was the reactive species. The reaction was proposed to be a one-electron process resulting in a substrate-oxidant complex. The decomposition of this complex was the rate-determining step which yielded a free radical and carbon dioxide (10).

PRESENT WORK

The present work is a detailed kinetic study of the oxidation of α -keto acids by quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], in acid medium, using 20% dimethylformamide (DMF) as the solvent.

The α -keto acids chosen for the purpose of oxidation by QDC have included:

(a) Pyruvic acid ; and (b) Phenylpyruvic acid

Stoichiometry (vide "Experimental")

The stoichiometries of both the oxidation reactions were determined. The stoichiometric ratios, $\Delta[QDC] / \Delta[Substrate]$, were in the range 0.65 - 0.70 (Table 1).

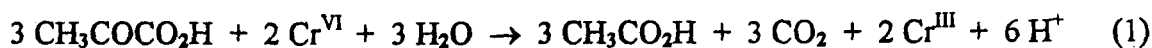
Table 1 : Stoichiometries of the Oxidation of the Substrates;

([Substrate] = 0.005 M; T = 313 K)

[HClO ₄] / M	0.10	0.25	0.50
10 ² [QDC] / M	2.50	2.60	2.70
$\Delta[QDC] / \Delta[Pyruvic\ acid]$	0.65	0.70	0.68
$\Delta[QDC] / \Delta[Phenylpyruvic\ acid]$	0.69	0.67	0.66

The stoichiometry conformed to the overall equations :

(a) For pyruvic acid :



(b) For propiophenone :



Effect of Substrate

The rate of the reaction was found to be dependent on the concentrations of the substrates. The order of the reaction with respect to substrate concentration was obtained by changing the substrate concentration, and observing the effect on the rate of the reactions at constant [QDC] and $[\text{H}^+]$. The results have been recorded in Table 2.

Table 2 : Dependence of Rate Constants on the concentration of α -Keto Acids;
 ([QDC] = 0.001 M; [HClO₄] = 0.1 M; [DMF] = 20%(v/v); T = 33K)

10^3 [Substrate] / M	$10^5 k_1 / s^{-1}$	
	Pyruvic acid	Phenylpyruvic acid
1.0	-	0.18
2.5	-	0.47
5.0	2.73	0.95
10.0	5.29	1.62
25.0	13.2	-
50.0	28.3	-
	$10^2 k_2 / M^{-1} s^{-1}$	
	-	0.18
	-	0.19
	0.55	0.19
	0.53	0.16
	0.53	-
	0.57	-

$k_2 = k_1 / [\text{Substrate}]$

Plots of k_1 , the pseudo-first-order rate constant, against the concentrations of substrates (in both the cases), gave straight lines passing through the origin (Figure 1). This indicated that the rate of oxidation was dependent on the first power of the concentrations of the substrates. This was further demonstrated by the constancy in the values of k_2 , the second-order rate constant.

Effect of oxidant

Under pseudo-first-order conditions, the individual kinetic runs were first-order with respect to the oxidant (QDC). At fixed [acid] and with the substrate taken in excess, the plots of log absorbance versus time were linear, indicating a first order dependence on QDC. When a constant concentration of substrate (excess) was used, the pseudo-first-order rate constant (k_1) did not alter appreciably with changing concentrations of the oxidant (QDC), indicating a first-order dependence of the rate on the concentration of the oxidant. The rate data have been shown in Table 3.

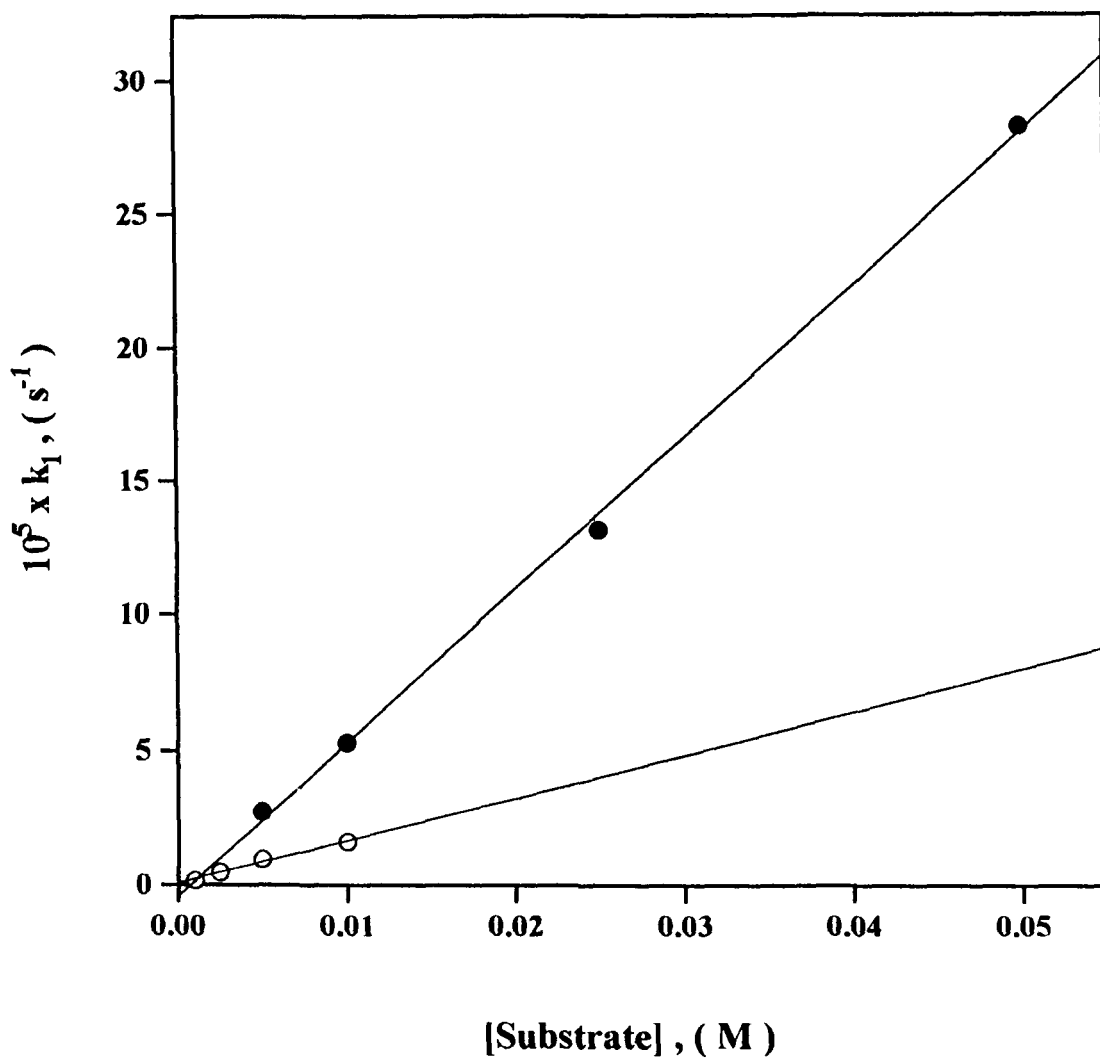


Fig. 1. Plots of k_1 against the concentrations of substrates for pyruvic acid (●) and phenylpyruvic acid (○).

**Table 3 : Dependence of Rate Constants on the concentration of Oxidant;
 ([Substrate] = 0.005 M; [HClO₄] = 0.1 M; [DMF] = 20%(v/v);
 T = 313K)**

10^3 [Substrate] / M	$10^5 k_1 / s^{-1}$	
	Pyruvic acid	Phenylpyruvic acid
0.25	2.66	0.99
0.50	2.76	0.91
0.75	2.70	0.89
1.0	2.73	0.95

Effect of acid

The reaction was influenced by changes in the acid concentration, and the rate was observed to increase with an increasing concentration of the acid in the range 0.05 M to 0.25 M (Table 4).

Table 4 : Dependence of Rate Constants on Acid concentration for α -Keto Acids;

([Substrate] = 0.005 M; [QDC] = 0.001 M; [DMF] = 20%(v/v);

T = 313K)

[HClO ₄] / M	10 ⁵ k ₁ / s ⁻¹	
	Pyruvic acid	Phenylpyruvic acid
0.05	1.34	0.48
0.10	2.73	0.95
0.15	3.97	1.40
0.20	5.31	1.93
0.25	6.55	2.47

Plots of log k₁ against log [H⁺] were linear, with slopes equal to unity (Figure 2), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated Cr(VI) species in the oxidation reaction. There have been earlier reports of the involvement of such protonated Cr(VI) species in chromic acid oxidation reactions (11). The acid catalysis was related to the structure of the oxidant (QDC), which was converted to a protonated species at the concentration of mineral acid used. Quinolinium dichromate is a dimetallic species, an anionic condensed form of chromic acid. Michel

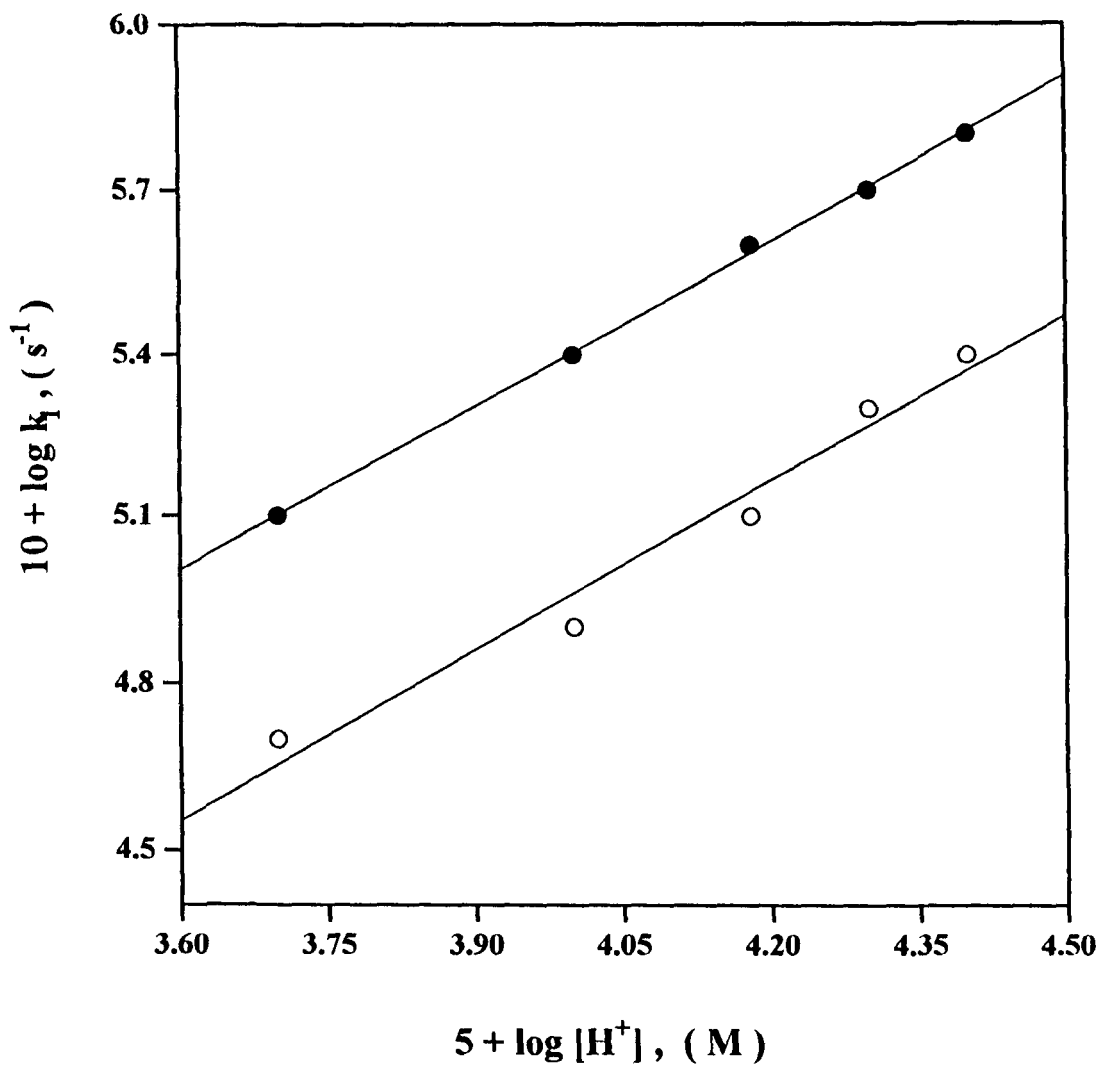


Fig. 2. Plots of $\log k_1$ against $\log [H^+]$ for pyruvic acid (●) and phenylpyruvic acid (○).

et al. examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate HCrO_4^- did not exist in aqueous solutions of Cr(VI) compounds (12). Of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of mineral acid would be HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. When the Raman lines were examined under dilution, it was established that at $\text{pH} = 11$, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion, whereas at $\text{pH} = 1.2$, it was 100% as the $\text{Cr}_2\text{O}_7^{2-}$ ion (12). Hence, at concentrations of acid larger than 0.05 M, the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, spectral studies have shown that $\text{Cr}_2\text{O}_7^{2-}$ was the predominant species (13). In the present investigation, the acid concentrations used were in the range 0.05 to 0.25 M. Hence, the dichromate ion (existing as the protonated dimetallic Cr(VI) species) would be the predominant species. Moreover, the protonated dimetallic Cr(VI) species would be a more reactive electrophile capable of increasing its rate of coordination to the hydrated form of the substrates.

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been employed for all the kinetic runs, the observed rate law could be expressed as :

$$\text{Rate} = - \frac{d[\text{QDC}]}{dt} = k [\text{Substrate}] [\text{QDC}] [\text{H}^+] \quad (3)$$

Effect of solvent

In the present investigation, the acid-catalyzed oxidation of the substrates was studied in solutions containing varying proportions of water and DMF. For both the substrates (pyruvic acid and phenylpyruvic acid) oxidized by QDC, the rate of oxidation was fastest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of DMF resulted in a decrease in the rate of oxidation (Table 5).

Table 5 : Dependence of Rate Constants on Solvent Composition for α -Keto Acids;
([Substrate] = 0.005 M; [QDC] = 0.001 M; [HClO₄] = 0.1 M; T = 313K)

H ₂ O:DMF	Dielectric Constant (D)	10 ⁵ k ₁ / s ⁻¹	
		Pyruvic acid	Phenylpyruvic acid
100:0	73.3	7.24	-
95:5	71.5	6.52	-
90:10	69.7	5.21	-
85:15	67.9	4.03	1.02
80:20	66.2	2.73	0.95
75:25	64.4	-	0.84
70:30	62.6	-	0.71
65:35	60.8	-	0.54

The dielectric constants for water - DMF mixtures have been estimated approximately from the dielectric constants of the pure solvents (at 313 K : water = 73.3 ; DMF = 37.6) (14).

In the present investigation, in going from 0% DMF to 35% DMF, the polarity decreased. This decrease in the polarity of the medium caused a decrease in the rate of the reaction (Table 5). Plots of $\log k_1$ against the inverse of dielectric constants were linear, with negative slopes (Figure 3). This suggested an interaction between an ion and a dipole (15), and was in consonance with the observation that, in the presence of an acid, these oxidation reactions involved a protonated dimetallic Cr(VI) species. The transition state would thus be more polar than the initial state (reactants), because of the decrease dispersal of charges in the transition state (16). In the present investigation, the addition of a more polar solvent resulted in an increase in the rate of oxidation. This arose as a result of a progressive increase in solvation of the transition state.

Effect of temperature

The rates of the reactions were influenced by changes in the temperature. The rate of the reaction was found to increase with an increase in the temperature (Table 6).

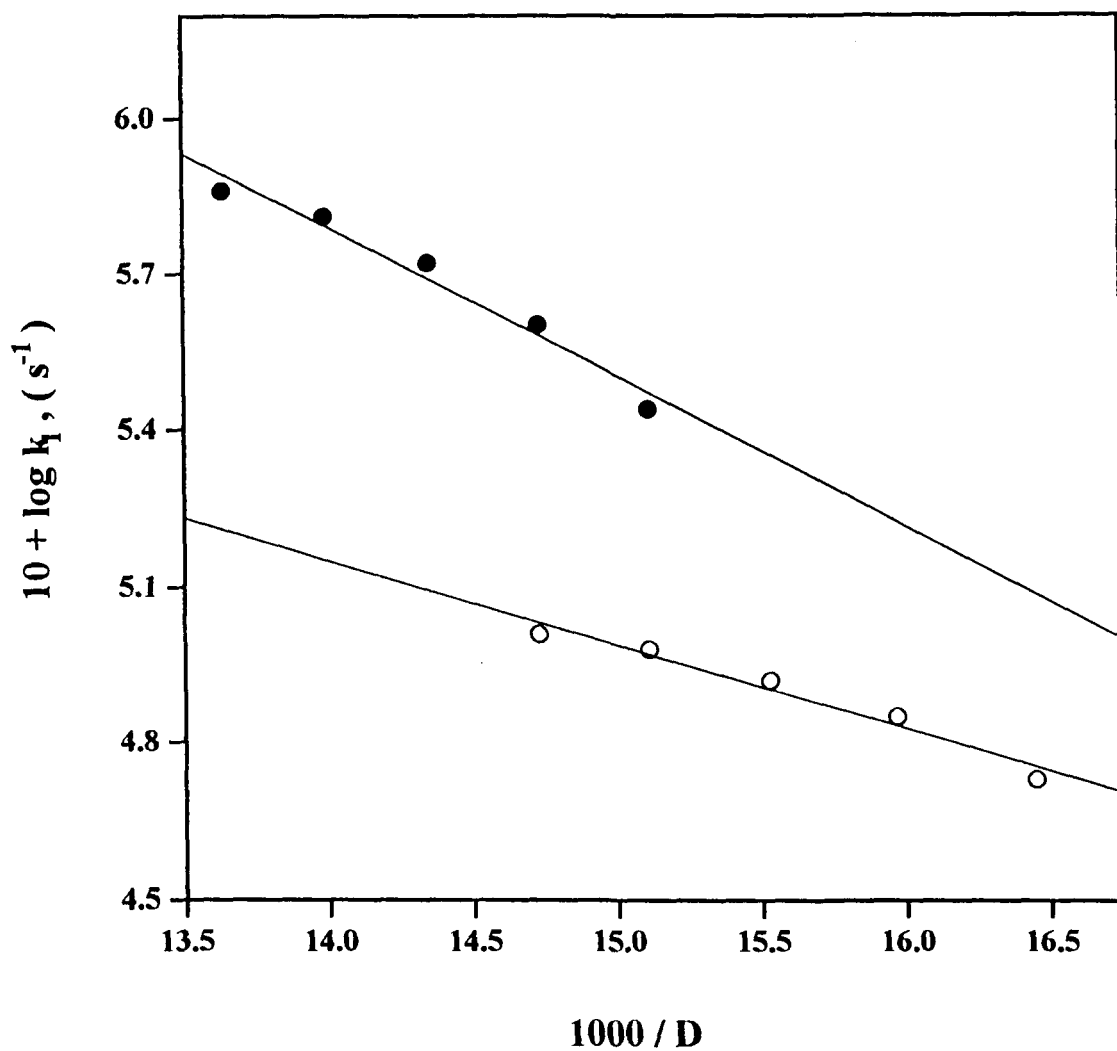


Fig. 3. Plots of $\log k_1$ against the reciprocal of the dielectric constant for pyruvic acid (●) and phenylpyruvic acid (○).

Table 6 : Dependence of Rate Constants on Temperature for α -Keto Acids;**([Substrate] = 0.005 M; [QDC] = 0.001 M; [HClO₄] = 0.1 M;****[DMF] = 20%(v/v))**

Temperature (± 0.1 K)	$10^5 k_1 / s^{-1}$	
	Pyruvic acid	Phenylpyruvic acid
303	1.23	0.39
308	1.90	0.62
313	2.73	0.95
318	4.07	1.32
323	5.62	2.24

A linear correlation between $\log k_1$ and the reciprocal of temperature in the range 303 –323 K was observed (Figure 4), suggesting the validity of Arrhenius equation. The activation parameters (vide “Experimental : Calculations”) have been shown in Table 7.

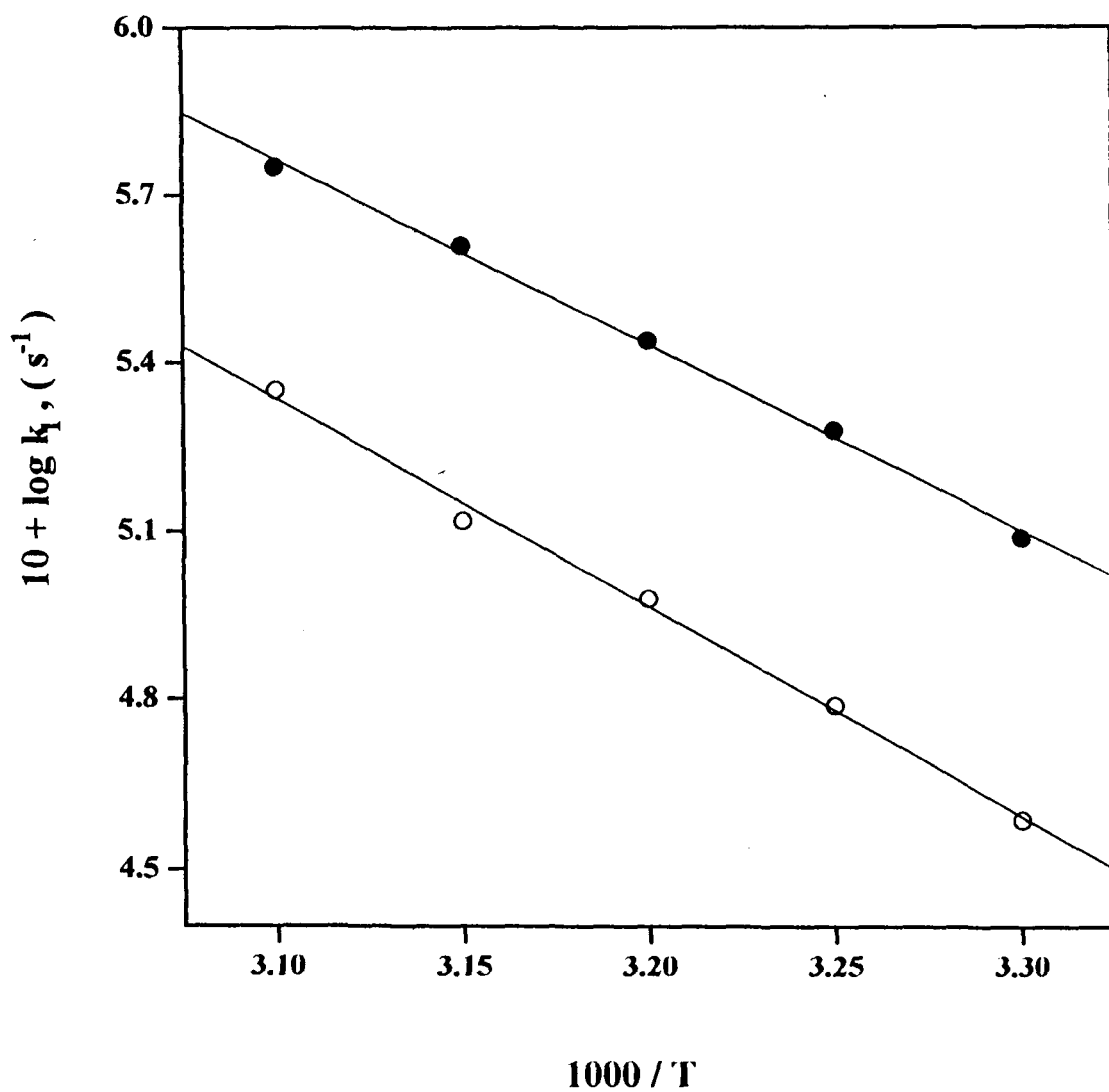


Fig. 4. Plots of $\log k_1$ against the reciprocal of temperature for pyruvic acid (●) and phenylpyruvic acid (○).

Table 7 : Activation Parameters for α -Keto Acids

Substrate	E (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (JK ⁻¹ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)
Pyruvic acid	63	59	-144	102
Phenylpyruvic acid	71	67	-129	105

Error limits : E \pm 3 kJ mol⁻¹; $\Delta H^* \pm$ 3 kJ mol⁻¹; $\Delta S^* \pm$ 5 JK⁻¹ mol⁻¹; $\Delta G^* \pm$ 2 kJ mol⁻¹.

The negative values of ΔS^* provided support for the formation of a rigid activated complex. The constancy in ΔG^* values suggested that a common mechanism was applicable for the oxidation of both the substrates (pyruvic acid and phenylpyruvic acid).

Mechanism

It has been shown that the oxidation of pyruvic acid by manganic pyrophosphate did not proceed by enolization but by a cyclic intermediate which was kinetically detectable, and which underwent homolytic fission to yield an acyl radical; this radical reacted further to form acetic acid, with the evolution of carbon dioxide. It was suggested that carbon dioxide was liberated in the primary oxidation process. The rate-determining step was the breakdown of the manganic pyrophosphate-pyruvic acid complex (3).

The reaction between pyruvic acid and chromium(VI), in the presence of perchloric acid, showed that the reaction involved the hydrated form of pyruvic acid. A first-order dependence on the concentration of acid suggested that the proton may add on to the substrate molecule forming a protonated species. This protonated substrate molecule reacted with chromium(VI) to give a carbocation in the rate-determining step of the reaction. This carbocation was converted to acetic acid in the final step of the reaction, with the evolution of carbon dioxide (4).

The kinetics of oxidation of pyruvic acid by periodate in the pH range 0 - 9 showed that the initial step of oxidation was the nucleophilic attack of the periodate monoanion, IO_4^- , on the oxo-group of pyruvic acid. It was established that the reaction between pyruvic acid and periodate monoanion gave a cyclic intermediate in the rate-determining step. This intermediate underwent disproportionation to give acetic acid as the product (5).

The kinetics of oxidation of pyruvic acid by alkaline hexacyanoferrate(III) was carried out in the absence and presence of Os(VIII) as catalyst. In the absence of Os(VIII), the substrate reacted with OH^- to give a free radical in the rate-determining step. The free radical underwent further oxidation to give acetic acid and carbon dioxide as the products. It was suggested that the formation of acetic acid would be expected only when pyruvic acid reacted through its hydrated form. In the presence of Os(VIII) as catalyst, a complex was formed by the interaction of pyruvic acid and Os(VIII). This complex reacted with OH^- , in the rate-determining step, to give acetic acid and Os(VI) (6,7).

The oxidation of pyruvic acid by V(V) in the presence of perchloric acid showed that the reaction proceeded via the hydrated form of pyruvic acid. It was suggested that the V(V) reacted with the hydrated pyruvic acid, in the rate-determining step, to give a free radical, V(IV) and carbon dioxide. The further reaction of the free radical with V(V) yielded the final product, which was identified as acetic acid (8).

The reaction between sodium pyruvate and hexacyanoferrate(III), in alkaline medium, showed that the oxidant reacted with the hydrated form of pyruvic acid to give a free radical in the rate-determining step. The radical was then rapidly oxidized to give acetic acid and oxalic acid, accompanied by the evolution of carbon dioxide (9).

The Ce(IV) oxidation of pyruvic acid was studied in sulfuric acid - perchloric acid media. The rate data suggested that CeSO_4^{2-} was the most reactive of the Ce(IV) - sulfate complexes present in the system. The oxidation reaction was a one-electron process involving the formation of a pyruvic acid - Ce(IV) complex. The decomposition of this complex was rate-determining, resulting in the formation of a free radical and the evolution of carbon dioxide. The final product was acetic acid (10).

In all the oxidation reactions mentioned above, the common feature was that all the reactions were carried out by one-electron oxidants (3, 6-10). These oxidation reactions all proceeded via homolytic fission resulting in the formation of free radical intermediates, along with the evolution of carbon dioxide (3, 6-10). In the present investigation involving the oxidation of pyruvic acid and phenylpyruvic acid by QDC in acid medium, the addition of acrylonitrile to the reaction mixture did not result in any

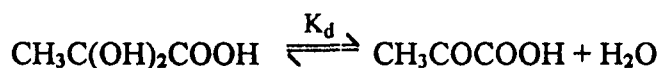
polymerization, and the addition of mercury(II) chloride did not result in any reduction. The absence of radical formation indicated that QDC did not behave as a one-electron oxidant.

Based on the stoichiometries of the oxidation reactions (Table 1), and the observed experimental data, the mechanistic pathways for the oxidation of the α -keto acids (pyruvic acid and phenylpyruvic acid) by quinolinium dichromate (QDC) in acid medium, using 20% DMF as solvent, has to be rationalized. While suggesting mechanistic pathways for these oxidation reactions, the following kinetic observations have to be taken into consideration :

- (1) the rates of oxidation of both the α -keto acids (pyruvic acid and phenylpyruvic acid) were dependent on the first powers of the concentrations of each — substrate and oxidant (Tables 2-3, Figure 1) ;
- (2) the rates of reactions showed a first order dependence on the concentrations of the acid (Table 4, Figure 2). The acid catalysis of the oxidation reactions must be related to the structure of the oxidant (QDC). The oxidant was thus converted to a protonated dimetallic Cr(VI) species in the presence of acid ;
- (3) an increase in the polarity of the solvent medium (using water - DMF mixtures) showed an increase in the rate of the reaction (Table 5). Linear plots of $\log k_1$ against the inverse of the dielectric constants (Figure 3) gave negative slopes, which indicated an ion-dipole type of interaction. This was in accordance with the involvement of a protonated dimetallic Cr(VI) species ;

- (4) an increase in temperature resulted in an increase in the rates of the reactions (Table 6). The oxidation of α -keto acids was characterized by negative entropies of activation (Table 7), which suggested an ordered transition state, relative to the reactants. The similarity in ΔG^\ddagger values (Table 7) for both the substrates was due to changes in ΔH^\ddagger and ΔS^\ddagger values, and emphasized the probability that both these oxidation reactions involved similar rate-determining steps ;
- (5) there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (17), indicating the absence of any radical formation ; and
- (6) the observed order of reactivity was in accordance with the structural changes in the α -keto acids. The order of reactivity observed for the oxidation of α -keto acids was: pyruvic acid > phenylpyruvic acid (Table 2), showing that the +I-effect of the methyl group (in pyruvic acid) was predominant over the -I-effect of the benzyl group (in phenylpyruvic acid). The activation parameters obtained indicated that the activation energy was much less for the oxidation of pyruvic acid, than for phenylpyruvic acid. Futhermore, the presence of an electron-releasing group (as in pyruvic acid) accelerated the oxidation process by increasing the electron availability at the oxygen of the carbonyl group. This facilitated the attack of the electrophile (protonated QDC) on the hydrated form of the α -keto acids. The net result would be a more facile rupture of the carbon-carbon bond in pyruvic acid, over that in phenylpyruvic acid, and hence the observed order of reactivity.

It has been shown that α -keto acids are hydrated in aqueous solution [18-20] and the dissociation constant (K_d) for the hydrated form of pyruvic acid was 0.42 [18] for the reaction:



From k_1 (Table 2) and K_d , two rate constants referring to the oxidation of pyruvic acid in only one of the forms present in solution were computed. The value of k_{hy} was obtained by assuming that only the hydrated form appears in the rate law:

$$v = k_{hy} [\text{QDC}] [\text{CH}_3\text{C}(\text{OH})_2\text{COOH}] \quad (4).$$

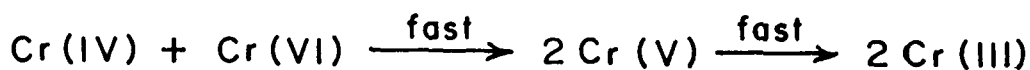
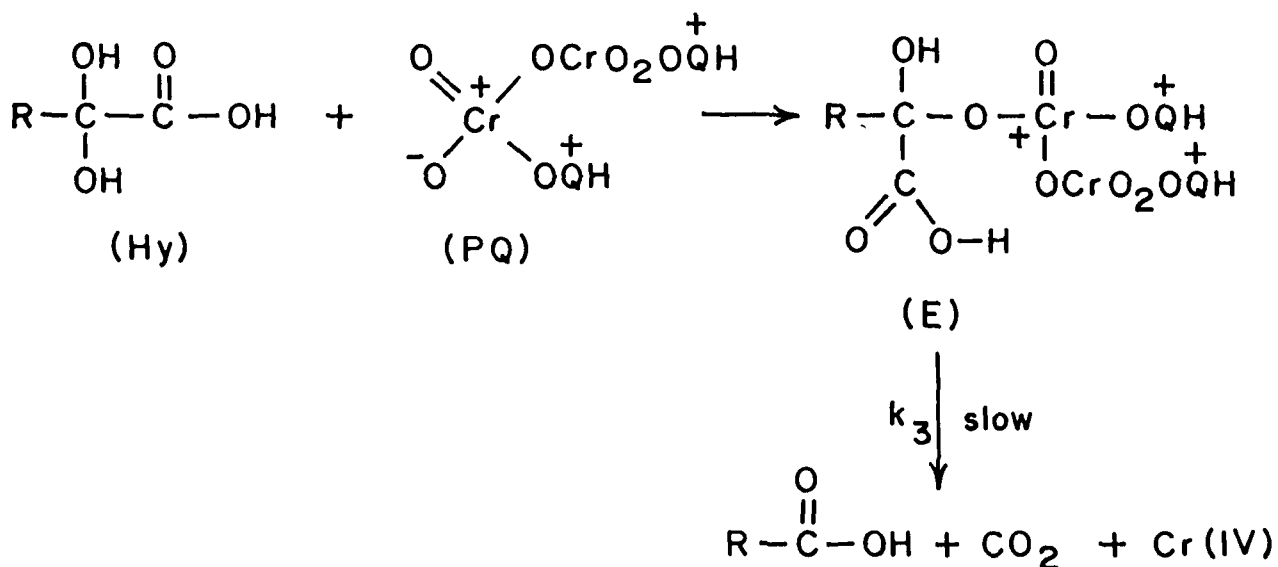
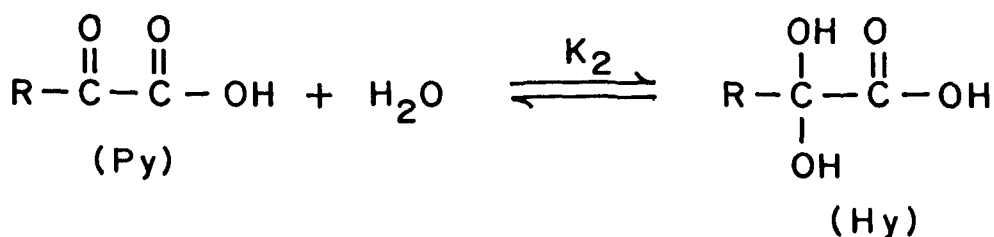
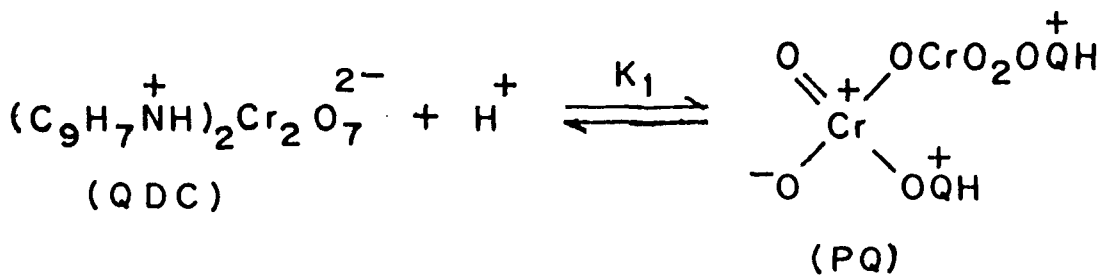
The value of k_{hy} was $2.28 \pm 0.16 \text{ M}^{-2} \text{ s}^{-1}$. Similarly, the value of k_{py} was calculated using the concentration of free pyruvic acid according to the rate law:

$$v = k_{py} [\text{QDC}] [\text{CH}_3\text{COCO}(\text{OH})] \quad (5).$$

The value of k_{py} was $5.42 \pm 0.38 \text{ M}^{-2} \text{ s}^{-1}$. Pyruvic acid is a strong organic acid with the value of $K_a = 3.2 \times 10^{-3}$ at 25°C [18, 19, 21], and a hydration constant, $K_h = 3.1$. Consequently in the pH range studied, the extent of hydration of pyruvic acid increases. Thus, the hydrated form of pyruvic acid would remain as an undissociated molecule (since $[\text{H}^+] \gg K_a$), in the range of acid concentrations used in the present study (0.05 – 0.25 M). It is therefore suggested that QDC reacts with the hydrated form of the α -keto acids. In the present investigation, it has been observed that QDC reacts quantitatively with pyruvic acid to give acetic acid and CO_2 (and with phenylpyruvic

acid to give phenylacetic acid and CO_2). Consequently, the corresponding enol, $\text{CH}_2=\text{C}(\text{OH})\text{COOH}$, which (by analogy with the enolic forms of simple ketones), should be more extensively oxidized, did not appear to be involved. The formation of acetic acid (and phenylacetic acid) from the oxidation of pyruvic acid (and phenylpyruvic acid) as the final products supported the mechanistic pathway of these reactions proceeding via the hydrated form of the α -keto acids. On the other hand, if the reaction proceeded via the process of enolization, then the reaction products would have been oxalic acid and not acetic acid (and phenylacetic acid), as obtained in the present investigation. Hence, the presence of only one product of oxidation (acetic acid from pyruvic acid, and phenylacetic acid from phenylpyruvic acid) justified the mechanism suggested for the oxidation of pyruvic acid and phenylpyruvic acid by QDC in acid medium.

All the experimental results would suggest a mechanistic pathway for the oxidation reaction as shown in the Scheme. In acid medium, the oxidant QDC was converted to the protonated dimetallic Cr(VI) species (PQ) [in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $\text{Cr}_2\text{O}_7^{2-}$ (13)]. The substrate (Py) was converted to the hydrated form (Hy). The reaction of the hydrated form (Hy) with the protonated QDC (PQ) resulted in the formation of the dichromate ester (E), which underwent decomposition, in the rate-determining step, to give the product identified as acetic acid (from pyruvic acid), and phenylacetic acid (from phenylpyruvic acid), with the evolution of carbon dioxide. The oxidation reaction thus occurred by a rupture of the carbon-carbon bond. The formation of acetic acid would be expected only when the hydrated form of pyruvic acid acts as a reducing substrate [4,22]. On the other hand, if it were to be suggested that the pyruvic acid



R = -Me (pyruvic acid); -CH₂Ph (phenylpyruvic acid)

SCHEME

underwent enolization, and not hydration, then the product obtained would have been oxalic acid (and not acetic acid, as obtained in the present study). Hence, the enolization of α -keto acids was ruled out.

Based on the mechanism shown in the Scheme, the rate law can be derived as follows :

$$- d [\text{QDC}] / dt = k_3 [\text{E}] = k_3 [\text{Hy}] [\text{PQ}] \quad (6)$$

$$\text{where } [\text{PQ}] = K_1 [\text{QDC}] [\text{H}^+] \text{ and } [\text{Hy}] = [\text{Py}] [\text{H}_2\text{O}].$$

Substituting these values of [PQ] and [Hy] in eq. 6 (taking the activity of H_2O to be equal to unity), we get :

$$- d [\text{QDC}] / dt = K_1 K_2 k_3 [\text{Py}] [\text{QDC}] [\text{H}^+] \quad (7)$$

Since the equilibria given by K_1 and K_2 are rapid, it can be assumed that K_1 and K_2 would have very small values. This rate expression (eq. 7) confirmed the first order dependence of the rate on the concentrations of each — substrate, oxidant, and acid. This rate law explains all the experimentally observed results.

The conversion of Cr(IV) to Cr(III) was a disproportionation reaction. For the reaction $\text{Cr(IV)} + \text{Cr(VI)} \rightarrow 2 \text{Cr(V)}$, the standard potential for the Cr(VI) – Cr(V) couple was extremely favorable ($E^0 = 0.62$ volt), and this reaction would proceed rapidly [23]. The Cr(V) – Cr(III) couple has a potential of 1.75 volt, which would facilitate the rapid conversion of Cr(V) to Cr(III), after the reaction with the substrate [23, 24].

The mechanistic pathway suggested for the oxidation of pyruvic acid and phenylpyruvic acid by QDC, in acid medium, showed the formation of the dichromate ester resulting from a rapid reaction between the hydrated form of pyruvic acid and the protonated dimetallic Cr(VI) species. The rate-determining step was the decomposition of this dichromate ester to give acetic acid (in the case of pyruvic acid) and phenylacetic acid (in the case of phenylpyruvic acid) as the products, along with the evolution of carbon dioxide. This mechanism finds support from earlier work involving oxidants such as manganic pyrophosphate in aqueous medium (3) and Ce(IV) in sulfuric acid – perchloric acid medium (10). In the oxidation with manganic pyrophosphate, there was the liberation of carbon dioxide in the primary oxidation process, followed by the breakdown of the manganic pyrophosphate – pyruvic acid complex in the rate-determining step, to yield the final product (3). In the reaction between pyruvic acid and Ce(IV) in acid medium, there was the formation of a complex between pyruvic acid and Ce(IV). The rate-determining step was the decomposition of this complex, yielding a free radical, with the evolution of carbon dioxide (10).

Under the experimental conditions employed in the present investigation, α -keto acids (pyruvic acid and phenylpyruvic acid) were oxidized by quinolinium dichromate (QDC) in acid medium, giving carboxylic acids as the products in both the cases, accompanied by the evolution of carbon dioxide. These products [acetic acid (from pyruvic acid); and phenylacetic acid (from phenylpyruvic acid)] were characterized by FT-IR and FT-NMR analyses (vide “Experimental : Product Analysis”).

Earlier investigations have shown that pyruvic acid was converted to acetic acid in good yields when the oxidations were carried out by manganic pyrophosphate in aqueous medium (3), chromic acid in perchloric acid medium (4), periodate in the pH range 0 – 9 (5), alkaline hexacyanoferrate(III) in the absence and presence of Os(VIII) as catalyst (6, 7), V(V) in perchloric acid medium (8), hexacyanoferrate(III) in alkaline medium (9) and by Ce(IV) in sulfuric acid – perchloric acid media (10). In all these oxidation reactions, the nature of the products formed (acetic acid and carbon dioxide) established that there was a cleavage of the carbon-carbon bond in the final step of the reaction.

In the present investigation, the kinetic data and the nature of the products obtained [acetic acid (from pyruvic acid); and phenylacetic acid (from phenylpyruvic acid)] clearly showed that the oxidation of these substrates by QDC yielded the carboxylic acids as the final products. These data substantiated the mechanism of the oxidation process, wherein there was the cleavage of the carbon-carbon bond in the final step of the reaction. This study emphasizes the utility and efficiency of QDC as a reagent capable of converting α -keto acids to the carboxylic acids. This reaction sequence could prove useful as a route for the synthesis of carboxylic acids.

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LIST OF PUBLICATIONS

1. "Kinetics and Mechanism of Oxidation of Cyclohexanone by Quinolinium Dichromate"
Simi Das and Mahendra K. Mahanti*
Oxidation Commun., 23, 495 (2000).
2. "Kinetics of Oxidation of Pyruvic Acid by Quinolinium Dichromate"
C.B. Lyndoh, Simi Das and Mahendra K. Mahanti*
Oxidation Commun., 24, (2001) (in Press).

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Pre-University (English, Alternative English, Maths,
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Working Experience

Worked as a Post-graduate teacher in Chemistry for a period of six months from July 1997 to December 1997 in Kendriya Vidhyalaya, Shillong.

Have been guiding Master degree Chemistry students during their project work since 1998.

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Awards

1. Recipient of National scholarship during 1989 – 1990.
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Research Publications

1. "Kinetics and Mechanisms of oxidation of cyclohexanone by Quinolinium dichromate"
Simi Das, Mahendra K. Mahanti*
Oxid. Commun., 23, 495 (2000).
2. Kinetics of Oxidation of Pyruvic acid by Quinolinium dichromate
C.B. Lyngdoh, Simi Das, Mahendra K. Mahanti*
Oxid. Commun., 24, (2001) (in press).

Conference / Seminar Attended

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