KINETICS OF OXIDATION OF KETONES BY QUINOLINIUM DICHROMATE

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SUBMITTED
IN FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY
OF
NORTH-EASTERN HILL UNIVERSITY
SHILLONG, INDIA
2001

The North-Eastern Hill University

Declaration

Month : December Year : 2001

I, Simi Das, hereby declare that the subject matter of thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/ Institute

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Dedicated to My Beloved Parents

ACKNOWLEDGEMENTS

It is a great pleasure to express my sincere gratitude to my Reverential Supervisor ***Prof. M.K. MAHANTI*** *for his valuable guidance, motivation and constant help at every step during my research tenure. Sir, I really owe you.*

I am extremely thankful to ***Prof. K. Ismail****, Head, Department of Chemistry, North-Eastern Hill University, Shillong, for his useful suggestions and to provide me all the necessary facilities in the department to carry out my research work.*

It is my privilege to place on record Prof. S.N. Bhat for his encouragement and inspiration from time to time which I got during my research tenure.

I would like to thank all the faculty members, Department of Chemistry for their help during my research tenure.

I wish to appreciate the cooperation rendered by my research colleagues Girija and Chin.

I also thank all the research scholars of Department of Chemistry for their sincere cooperation and to all my well wishers.

My thanks also go to all the project students who worked in my Lab.

I wish to thank all the non-teaching staff of the Department of Chemistry, NEHU, Shillong for their help in technical work.

I would like to acknowledge RSIC, NEHU, Shillong for providing me the instrumental facilities.

I owe my thanks to the authorities of North-Eastern Hill University for their co-operation and help in all the administrative and technical aspects during my stay in the campus.

I gratefully acknowledge the financial assistance received from the Department of Chemistry, North-Eastern Hill University under the Special Assistance Programme of UGC during my research tenure.

I also thank the Directorate of Public Instruction, Meghalaya for providing scholarship to carry out my Ph.D. work.

I am indebted to My Dearest Husband, Dr. K. Gunaseelan who not only gave enough time but also gave a lot of moral support and inspiration to me for achieving this goal.

I express my deepest sense of gratitude to my parents, brother, sister and brother-in-law for their constant encouragement and moral support in my academic career without which I would not have reached this stage. I owe them.

Finally, I thank the Almighty God for showering His blessings upon me in achieving my goals.

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Dated Shillong,
The 10th Dec. 2001

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DISCUSSION

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 and 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) Acetonylacetone (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, Δ[QDC] / Δ [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 $\Delta H^{\neq}$ against $\Delta S^{\neq}$, was 437K. Although current views do not attach much physical significance to isokinetic temperature, a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 ($\Delta G^{\neq}$) 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, ^{1}H 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, Δ[QDC] / Δ [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 ($\Delta S^{\neq}$) indicated that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecule. The similarities in $\Delta G^{\neq}$ values for all the substrates arose due to changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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, Δ[QDC] / Δ [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 $\Delta G^{\neq}$ 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, Δ[QDC] / Δ [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 $\Delta G^{\neq}$ values for all the substrates were due to changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 :

acetylacetone > benzoylacetone > acetonylacetone.

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 acetonylacetone 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 catlayzed by acid. Protonation of the oxidant (QDC) would make it more amenable towards nulceophilic 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 bimetallic 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 electrocylic 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 acetonylacetone)] 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, Δ[QDC] / Δ [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 ($\Delta G^{\neq}$) 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 oxiation 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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