KINETICS OF OXIDATION OF SOME ORGANIC COMPOUNDS BY QUINOLINIUM DICHROMATE

BY

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Declaration

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I, Girija Shankar Chaubey, 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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CURRICULUM VITAE

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 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 ketones (62,63).

The present investigation focuses attention on the kinetic features pertaining to the oxidation of various aldehydes 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 water (in the case of aliphatic aldehydes and dialdehydes), and aqueous acetic acid (in the case of long chain aliphatic aldehydes, α,β-unsaturated aldehydes and heterocyclic aldehydes), have included the following :

1. **Aliphatic Aldehydes - Chapter I**

I. Acetaldehyde, Propionaldehyde, Butyraldehyde,
Valeraldehyde, Isobutyraldehyde and Isovaleraldehyde.

II. Caproaldehyde, Heptaldehyde, Caprylicaldehyde,
Pelargonaldehyde and Caprinaldehyde.

III. Glyoxal and Glutaraldehyde.

2. **α, β-Unsaturated Aldehydes - Chapter II**

Acrylaldehyde, Methacrylaldehyde, Crotonaldehyde,
Cinnamaldehyde.

3. Heterocyclic Aldehydes - Chapter III

I. Five-membered heterocyclic aldehydes :

2-Furaldehyde, 5-Methyl-2-Furaldehyde, 5-Bromo-2-Furaldehyde, 2-Pyrrolecarbaldehyde and 2-Thiophenecarbaldehyde.

II. Six-membered heterocyclic aldehydes :

2-Pyridinecarbaldehyde and 3-Pyridinecarbaldehyde.

Chapter I – Kinetics of Oxidation of Aliphatic Aldehydes

The kinetics of oxidation of aliphatic aldehydes (acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, caprylicaldehyde, pelargonaldehyde, caprinaldehyde, isobutyraldehyde, isovaleraldehyde, glutaraldehyde and glyoxal) by quinolinium dichromate (QDC) has been studied in acid medium, using water and water-acetic acid mixtures, 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 aliphatic aldehydes studied, stoichiometric ratios, Δ[QDC] / Δ [substrate], in the range 0.63 - 0.69 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 581K. 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, suggesting that the same mechanism operated for the oxidation of all the aliphatic aldehydes 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 aliphatic aldehydes by QDC showed that :

(a) Acetaldehyde < Propionaldehyde < Butyraldehyde < Valeraldehyde;

(b) Isovaleraldehyde < Isobutyraldehyde;

(c) Caproaldehyde < Heptaldehyde < Caprylicaldehyde < Pelargonaldehyde Caprinaldehyde ; and

(d) Glutaraldehyde < Glyoxal.

The relative rates of oxidation for the aldehydes indicated that the rate of oxidation was dependent on the length of the alkyl chain of the aldehydes. Electron-releasing groups accelerated the oxidation process by increasing the electron availability at the oxygen of the aldehydic carbonyl group. This would facilitate the attack of the electrophile (protonated QDC).

The rate of oxidation of isobutyraldehyde was faster than that for isovaleraldehyde. This observed order of reactivity was due to the fact that the aldehyde function was closer to the isomethyl group in isobutyraldehyde. This proximity effect would have a direct influence on the reactivities of these two aldehydes, thereby facilitating the attack of the electrophile (protonated QDC).

The observed order of reactivity was glyoxal > glutaraldehyde . The presence of methylene groups between the two aldehyde moieties would decrease the electron availability at the oxygen of the aldehydic carbonyl group. This would prevent the attack of the electrophile (protonated QDC) as more methylene groups were inserted between the two aldehydic groups.

Aldehydes exist in three forms : (a) the hydrated aldehydes ; (b) enol-enolate ion; and (c) the free aldehydes. The species involved in the oxidation of aldehydes could be determined by the kinetic data and product analysis.

Aliphatic aldehydes are extensively hydrated in aqueous solutions. The aldehyde hydrate dissociation constants (K_d) pertaining to the reaction : $RCH(OH)_2 \overset{K_d}{\rightleftharpoons} RCHO + H_2O$ were given. From k_1 (the pseudo-first-order rate constant) and K_d , two sets of rate constants were computed. Values of

k_{Hy} were obtained by assuming that only the hydrated form appears in the rate law : $v = k_{Hy}$ [QDC] [RCH(OH)$_2$].

Similarly, k_A was calculated using the concentration of free aldehydes according to the rate law : $v = k_A$ [QDC] [RCHO]. The correlation with k_{Hy} supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen transfer reaction between the free aldehyde and QDC was very unlikely. This evidence provided additional support for the mechanistic pathway wherein the slow step was the oxidative decomposition of the chromate ester of the aldehyde hydrate. A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. The mechanistic pathway involved the rapid formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the aldehyde hydrate (step 2). The overall rate of the reaction would depend on the position of equilibrium (step 1), and the rate of the reaction (step 2).

The slow step of the reaction was the transfer of two electrons in a cyclic system. This electrocyclic mechanism for the oxidation of aldehyde hydrates by QDC involved six electrons; being a Hückel-type system (4n + 2), this was an allowed process. This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant

Under the experimental conditions employed in the present investigation, aliphatic aldehydes were oxidized by quinolinium dichromate (QDC), in acid media, giving the corresponding carboxylic acid in each case. The products obtained were characterized by FT-IR and FT-NMR analyses.

Kinetic data has been presented to establish the mechanistic pathway for the oxidation of aliphatic aldehydes by QDC as proceeding via the hydrated form of the aldehydes.

The data collected demonstrated that the QDC oxidation of aliphatic aldehydes led to the formation of the corresponding carboxylic acids, substantiating the mechanism wherein there was an attack of the oxidant on the aldehyde hydrate. There was no cleavage of the carbon-carbon bond, thus ruling out the possibility of any enolization. Under the present experimental conditions, there was no further oxidation of the products. This study has thus emphasized the efficiency of QDC reacting with aliphatic aldehydes, suggesting the possibility that such reactions could prove to be useful as a general route for the synthesis of carboxylic acids.

Chapter II – Kinetics of Oxidation of α, β-Unsaturated Aldehydes

The present work is a detailed kinetic investigation of the oxidation of α, β-unsaturated aldehydes (methacrylaldehyde, acrylaldehyde, crotonaldehyde and cinnamaldehyde) by quinolinium dichromate (QDC), in acid medium, using 50% aqueous acetic acid 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 0.66 - 0.69. 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 40% acetic acid to 60% acetic acid. Plots of log k_1 against the reciprocal of the dielectric constant were linear, with positive slopes, suggesting 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 order of reactivity observed was :

methacrylaldehyde > acrylaldehyde > crotonaldehyde > cinnamaldehyde.

The presence of the methyl group (in methacrylaldehyde), adjacent to the site of reaction (carbonyl group), enhanced the reactivity of methacrylaldehyde over that of acrylaldehyde. In crotonaldehyde, the methyl group was far removed from the site of reaction, and hence its reactivity was much less than that of methacrylaldehyde. The presence of the phenyl group in cinnamaldehyde exerted a deactivating influence on the rate of the reaction, and hence the reactivity of cinnamaldehyde was the lowest in the series.

In the present investigation, the oxidation of α, β-unsaturated aldehydes by quinolinium dichromate (QDC) in acid medium, 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 hydrate-form of the substrate.

On the basis of the kinetic results obtained in the present investigation, a mechanism was proposed for the oxidation of α, β-unsaturated aldehydes by quinolinium dichromate (QDC), in acid medium, using 50% acetic acid as the solvent.

A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. The large negative entropies of activation (ΔS^{*}) would be consistent with the formation of a cyclic intermediate in a bimolecular reaction. If the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and the conversion to the corresponding carboxylic acid could then be rationalized. The mechanistic pathway involved the formation of the ester of the aldehyde hydrate (step 1), followed by the slow oxidative decomposition of this ester (step 2).

The slow step of the reaction involved the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, as evidenced by the experimental observation that a kinetic isotope effect was observed for the oxidation of the respective aldehyde-d_1 compounds ($k_H / k_D = 6.2$), indicating a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction. This step would envisage a reaction via an electrocyclic mechanism involving six electrons ; being a Hückel-type system (4n+2), this was an allowed process. This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant.

Under the experimental conditions employed in the present investigation, α, β-unsaturated aldehydes were oxidized by quinolinium dichromate (QDC), in acid media giving the corresponding carboxylic acids in each case. The products obtained were characterized by FT- IR and FT-NMR analyses.

The data collected demonstrated that the QDC oxidation of α, β-unsaturated aldehydes led to the formation of carboxylic acids, substantiating the mechanism wherein there was an attack of the oxidant on the aldehyde hydrate. There was no cleavage of the carbon-carbon bond, thus ruling out the possibility of any enolization. This study emphasized the efficiency of QDC reacting with α, β-unsaturated aldehydes, suggesting the possibility of a regioselective route for the synthesis of carboxylic acids.

Chapter III – Kinetics of Oxidation of Heterocyclic Aldehydes

The kinetics of the quinolinium dichromate (QDC) oxidation of heterocyclic aldehydes (2-furaldehyde, 5-methyl-2-furaldehyde, 5-bromo-2-furaldehyde, 2-pyrrolecarbaldehyde, 2-thiophenecarbaldehyde, 2-pyridinecarbaldehyde and 3-pyridinecarbaldehyde) has been investigated. The reactions were followed by monitoring the absorption band at 440 nm, spectrophotometrically. For all the heterocyclic aldehydes studied, stoichiometric ratios, Δ[QDC] / Δ [substrate], in the range 0.64 – 0.70 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 aldehydes was unity. The reaction was catalyzed by acid, and the acid-catalyzed reaction showed a first-order dependence on acidity.

The oxidation of heterocyclic aldehydes by QDC was studied in solutions containing varying proportions of acetic acid 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 positive slopes, suggesting an ion-dipole type of interaction.

The oxidation of heterocyclic aldehydes was studied at different temperatures (303-323K), and the activation parameters were evaluated. The oxidation of heterocyclic aldehydes 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 :

2-furaldehyde > 2-pyrrolecarbaldehyde > 2-thiophenecarbaldehyde, which was in conformity with the decreasing electronegativities of O, N and S atoms (electronegativities were : O = 3.50; N = 3.07; S = 2.44).

For the substituted 2-furaldehydes, the observed order of reactivity was : 5-methyl-2-furaldehyde > 2-furaldehyde > 5-bromo-2-furaldehyde > 5-nitro-2-furaldehyde, which was in conformity with the inductive effects of the substituents.

The observed order of reactivity, in the case of six-membered heterocyclic aldehydes was : 2-pyridinecarbaldehyde > 3-pyridinecarbaldehyde.

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.

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrated form. The experimental rate constants (k_1) for the oxidation of the aldehydes by QDC, and the aldehyde hydrate dissociation constants (K_d) have been given for the reaction :

$$RCH(OH)_2 \overset{K_d}{\rightleftharpoons} RCHO + H_2O$$

From k_1 and K_d, two sets of rate constants for the oxidation of the aldehyde in only one of the forms present in solution were computed. The values of k_{Hy} were obtained by assuming that only the hydrate form appears in the rate law:

$$v = k_{Hy} [\,QDC\,] [\,RCH(OH)_2\,]$$

Similarly, the values of k_A were calculated using the concentration of free aldehydes according to the rate law: $v = k_A [\,QDC\,] [\,RCHO\,]$.

The correlation with k_{Hy} supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen-transfer reaction between a free aldehyde and QDC was very unlikely. Thus, the rate-accelerating effect of the electronegative substituents could be interpreted in terms of greatly increased hydration. The mechanistic pathway involved the formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the aldehyde hydrate (step 2).

The slow step of the reaction involved the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, as evidenced by the experimental observation that a kinetic isotope effect was observed for the oxidation of 2-furaldehyde-d_1 ($k_H / k_D = 5.8$). The proton was removed in the cyclic transition state (co-planarity of all the atoms involved), the centre of which resided on an electron-dense oxygen in the chromate ester. Since the five-membered heterocyclic ring system is a planar pentagon with sp^2 hybridized carbon atoms, and possesses a considerable aromatic character arising from delocalization of the two paired electrons, it would undergo a reaction via an electrocyclic mechanism involving six electrons; being a Hückel-type system (4n+2), this was an allowed process.

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

The data collected demonstrated that the application of QDC to the oxidation of heterocyclic aldehydes led to the formation of carboxylic acids, substantiating the mechanism of the oxidation reaction wherein there was an attack of the oxidant on the aldehydic function, leaving the heteroatom site intact. While highlighting the importance of QDC as an oxidant, this study emphasized the efficiency of the reactions of QDC with heterocyclic aldehydes, which could prove to be a regioselective route for the synthesis of carboxylic acids.

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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. 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. 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, $(PyH)_2Cr_2O_7$ (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 $Me_3SiOOSiMe_3$ (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 oxidaiton 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, $Py_4Ag_2Cr_2O_7$, 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 coversion 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 oxidaiton of steroidal allylic alcohols to the corresponding ketones (62). A new method for the 1,4-oxygenation of 1-alkylated cyclo-pentadienes 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-carboxylpyridinium 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 $(C_6H_5)_3P^+CH_2P^+(C_6H_5)_3Cr_2O_7^{2-}$, 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 $[ZnCr_2O_7.3H_2O]$, 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 regiospecificity 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-CrO_3 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, 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 $0^{\circ}C$. 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).

Imidazolinium fluorochromate was found to be a mild, stable and selective chromium(VI) reagent which was used for the oxidation of alcolols 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_2Cl_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	CinnamicAcid		52
Crotonaldehyde	CrotonicAcid		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), cyclic ketones (128), and α-keto acids (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

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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), having the structure

$(C_9H_7N^+H)_2Cr_2O_7^{2-}$. 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. **Aliphatic Aldehydes - Chapter I**

I. Acetaldehyde, Propionaldehyde, Butyraldehyde, Valeraldehyde, Isobutyraldehyde and Isovaleraldehyde.

II. Caproaldehyde, Heptaldehyde, Caprylicaldehyde, Pelargonaldehyde, Caprinaldehyde.

III. Glyoxal and Glutaraldehyde.

2. **α, β-unsaturated Aldehydes - Chapter II**

Acrylaldehyde, Methacrylaldehyde, Crotonaldehyde, Cinnamaldehyde.

3. **Heterocyclic Aldehydes - Chapter III**

I. **Five-membered Heterocyclic Aldehydes**

2-Furaldehyde, 5-Methyl-2-Furaldehyde, 5-Bromo-2-furaldehyde, 2-Pyrrolecarbaldehyde and 2-Thiophenecarbaldehyde.

II. **Six-membered Heterocyclic Aldehydes**

2-Pyridinecarbaldehyde and 3-Pyridinecarbaldehyde.

The present investigation is a detailed kinetic probe into the oxidation of aldehydes by quinolinium dichromate (QDC), in acid medium, in different solvent media such as water (in the case of aliphatic aldehydes and dialdehydes), 70% aqueous acetic acid (in the case of long chain aliphatic aldehydes), and 50% aqueous acetic acid (in the case of unsaturated aliphatic aldehydes and heterocyclic aldehydes), 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 mixtures), 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 all the substrates (aldehydes) 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.

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.

Quinolinium Dichromate (QDC), $(C_9H_7N^+H)_2Cr_2O_7^{2-}$

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

Acetaldehyde (S.d. Fine Chem. Ltd.), propionaldehyde, butyraldehyde valeraldehyde, isovaleraldehyde (Fluka) and isobutyraldehyde (E. Merck) were used after distillation, and their purity was checked from physical constants.

The long chain aliphatic aldehydes (caproaldehyde, heptaldehyde, caprylicaldehyde, pelargonaldehyde and caprinaldehyde) obtained from Aldrich, were all distilled before use, and their purity was checked from physical constants.

Glutaraldehyde (S.d. Fine Chem. Ltd.) and glyoxal (S.D's) were distilled and used after checking their physical constants.

2-Furaldehyde (S.d. Fine Chem. Ltd.), 5-methyl-2-furaldehyde, 2-thiophenecarbaldehyde, 2-pyridinecarbaldehyde, and 3-pyridinecarbaldehyde (Aldrich), were all distilled before use and their purity was further checked from physical constants. 5-bromo-2-furaldehyde and 2-pyrrolecarbaldehyde (Aldrich) were used after recrystallization and their purity was checked from physical constants.

Acryladehyde, methacryladehyde (Aldrich) and crotonaldehyde, cinnamaldehyde (Merck-Schuchardt) were used after distillation 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)
Acetaldehyde	20
Propionaldehyde	49
Butyraldehyde	75
Valeraldehyde	104
Caproaldehyde	131
Heptaldehyde	155
Caprylicaldehyde	170
Pelargonaldehyde	190
Caprinaldehyde	208
Isovaleraldehyde	92
Isobutyraldehyde	64
Glutaraldehyde	101
Glyoxal	50
2-Furaldehyde	162
5-Methyl-2-furaldehyde	187
5-Bromo-2-furaldehyde	82-84 (m.p)
2-Pyrrolecarbaldehyde	43-45 (m.p)
2-Thiophenecarbaldehyde	198
2-Pyridinecarbaldehyde	181
3-Pyridinecarbaldehyde	95-97
Acrylaldehyde	52
Methacryladehyde	73
Crotonaldehyde	102
Cinnamaldehyde	252

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.

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 ± 0.1°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 absoption 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 case of aliphatic aldehydes and dialdehydes), or with 50% aqueous acetic acid (in the case of heterocyclic aldehydes and α-β-unsaturated aldehydes), or with 70% aqueous acetic acid (in the case of long chain aliphatic aldehydes), 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 acetic acid). Sufficient time was allowed to compensate for any change of heat during dilution. A known volume of sulfuric acid was taken in a 10 ml standard flask, and the volume made up with water (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 ±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_I, expressed in s^{-1}, was calculated from the equation (1) :

$$k_I = (2.303 / t) \log (A_0 / A_t) \qquad (1)$$

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).

(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),

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

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

(ii) Enthalpy of activation ($\Delta H^{\neq}$)

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

(iii) Entropy of activation ($\Delta S^{\neq}$)

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

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

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

(iv) Free energy of activation ($\Delta G^{\neq}$)

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

Stoichiometry

The stoichiometric experiments were carried out under nitrogen, at the particular temperature under the conditions of $[QDC]_0$ > $[Substrate]_0$ at varying acid concentrations. The disappearance of Cr(VI) was followed, until the absorbance values became constant. The $[QDC]_\infty$ was estimated. For each oxidation reaction, the stoichiometric ratio, $\Delta[QDC] / \Delta[Substrate]$, 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 case of aliphatic aldehydes and dialdehydes), or with 50% aqueous acetic acid (in

the case of heterocyclic aldehydes and α-β-unsaturated aldehydes), or with 70% aqueous acetic acid (in the case of long chain aliphatic aldehydes) 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°C for 30 minutes. 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-i) General Procedure for the oxidation of Aliphatic Aldehydes 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, 0.015 M of substrate (0.661 g acetaldehyde, 0.871 g propionaldehyde, 1.082 g butyraldehyde, 1.29g valeraldehyde, 1.29 g isovaleraldehyde, 1.082 g isobutyraldehyde, 0.871 g glyoxal and 1.5 g glutaraldehyde), taken in 25ml of water, was added. The reaction mixture was stirred at 40°C for 1h. The colour 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 Na_2SO_4), and warmed to remove the ether. The oxidized products [acetic acid (from acetaldehyde);

propionic acid (from propionaldehyde); butyric acid (from butyraldehyde); valeric acid (from valeraldehyde); isovaleric acid (from isovaleraldehyde); iso-butyric acid (from isobutyraldehyde); oxalic acid (from glyoxal); and glutaric acid (from glutaraldehyde)] were obtained after the complete removal of ether (yield≈ 80-90%). Each reaction product obtained was subjected to IR (KBr) and NMR (300 MHz ; $CDCl_3$; Me_4Si) analysis, and characterized as follows :

(i) Acetic acid ; IR : ν 2945(br s, -OH), 2663, 1711(s, C=O) , 1405, 1350, 1291,
940, 620 cm^{-1}
^1H NMR : δ 11.1(s, 1H, 1-H), 2.3(s, 3H, 2-H_3)

(ii) Propionic acid ; IR : ν 2980(br s, -OH), 2540, 1714(s, C=O), 1467, 1234, 1079,
930, 841 cm^{-1}
^1H NMR : δ 10.2(s, 1H, 1-H), 2.4(q, 2H, 2-H_2), 1.1(t, 3H,3-H_3)

(iii) Butyric acid ; IR : ν 2972(br s, -OH), 1716(s, C=O), 1420, 1236, 1105, 937,
762, 490 cm^{-1}
^1H NMR : δ 10.3(s, 1H, 1-H), 2.3(t, 2H, 2-H_2), 1.7(m, 2H, 3-H_2),
0.9(t, 3H, 4-H_3)

(iv) Valeric acid ; IR : ν 2940(br s, -OH), 2630, 1720(s, C=O), 1427, 1220, 940,
750 cm^{-1}
^1H NMR : δ 11.2(s, 1H, 1-H), 2.3(t, 2H, 2-H_2), 1.6(m, 2H, 3-H_2),
1.2(m, 2H, 4-H_2), 0.9(t, 3H, 5-H_3)

(v) Isovaleric acid ; IR : ν 2940(br s, -OH), 2623, 1703(s, C=O), 1470, 1301, 1225,
940, 780 cm^{-1}
^1H NMR : δ 11.1(s, 1H), 2.2(m, 3H), 1.0(d, 6H)

(vi) Isobutyric acid ; IR : ν 2972(br s, -OH), 2650, 1712(s, C=O), 1465, 1280, 1080, 930, 830 cm^{-1}

^{1}H NMR : δ 11(s, 1H), 2.6(m, 1H), 1.2(d, 6H)

(vii) Oxalic acid ; IR : ν 3425(br s, -OH), 1718(s, C=O), 1685, 1406, 1262, 910, 725, 600 cm^{-1}

^{1}H NMR : δ 9.9(br s, 2H)

(viii) Glutaric acid; IR : ν 2707(br s, -OH), 1696(s, C=O), 1467, 1305, 1265, 1085, 920, 761 cm^{-1}

^{1}H NMR : δ 11.4(br s, 2H, 1-H), 2.3(t, 4H, 2-H_2), 1.6(m, 2H, 3-H_2)

(A-ii) General Procedure for the oxidation of long chain Aliphatic Aldehydes by QDC.

Water (30 ml) was taken and cooled in ice. Concentrated H_2SO_4 (7.9 g, 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, 0.015 M of substrate (1.502 g of caproaldehyde, 1.712 g of heptaldehyde, 1.92 g of caprylicaldehyde, 2.134 g of pelargonaldehyde, 2.344 g of caprinaldehyde) taken in 25 ml of 70% aqueous acetic acid , was added. The reaction mixture was stirred at 40°C for 24h 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 [caproic acid (from caproaldehyde); heptanoic acid (from heptaldehyde); caprylic acid (from caprylicaldehyde); pelargonic acid (from pelargonaldehyde); and capric acid (from caprinaldehyde)] were obtained after the complete removal of ether (yields ≈ 85-90%). Each reaction product obtained was subjected to IR (CHCl$_3$) and NMR (300 MHz ; CDCl$_3$; Me$_4$Si) analysis, and characterized as follows :

(i) Caproic acid ; IR : ν 2940(br s, -OH), 2635, 1703(s, C=O), 1455, 1280, 1210 930, 731 cm^{-1}
^{1}H NMR : δ 10.6(s, 1H, 1-H), 2.5(t, 2H, 2-H$_2$), 1.2(m, 6H, 3,4,5-H$_2$), 0.9(t, 3H, 6-H$_3$)

(ii) Heptanoic acid ; IR : ν 2930(br s, -OH), 2650, 1710(s, C=O), 1465, 1370, 1285, 1225, 930, 721 cm^{-1}
^{1}H NMR : δ 11.1(s, 1H, 1-H), 2.3(t, 2H, 2-H$_2$), 1.1-1.3(m, 8H, 3,4,5,6-H$_2$), 0.9(t, 3H, 7-H$_3$)

(iii) Caprylic acid ; IR : ν 2950(br s, -OH), 2680, 1700(s, C=O), 1465, 1380, 1295, 1215, 1115, 940, 730cm^{-1}
^{1}H NMR : δ 10.9(s, 1H, 1-H), 2.4(t, 2H, 2-H$_2$), 1.2-1.4(m, 10H, 3,4,5,6,7-H$_2$), 0.9(t, 3H, 8-H$_3$)

(iv) Pelargonic acid ; IR : ν 2940(br s, -OH), 2630, 1720(s, C=O), 1475, 1370, 1280, 1240, 940, 735 cm^{-1}
^{1}H NMR : δ 10.2(s, 1H, 1-H), 2.3(t, 2H, 2-H$_2$), 1.4-1.6(m, 12H, 3,4,5,6,7,8-H$_2$), 0.9(t, 3H, 9-H$_3$)

(v) Capric acid ; IR : ν 2945(br s, -OH), 2710, 1700(s, C=O), 1470, 1300, 1220, 1190, 1080, 940, 740 cm^{-1}

^{1}H NMR : δ 11.5(s, 1H, 1-H), 2.3(t, 2H, 2-H$_2$), 1.3-1.6(m, 14H, 3,4,5,6,7,8,9-H$_2$), 0.9(t, 3H, 10-H$_3$)

(B) General Procedure for the oxidation of Heterocyclic Aldehydes by QDC

Water (30 ml) was taken in a round bottom flask and cooled in ice. Concentrated H_2SO_4 (7.9 g, 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, 0.015 M of substrate (1.45 g of 2-furaldehyde, 1.43 g of 2-pyrrolecarbaldehyde, 1.69 g of 2-thiophenecarbaldehyde, 1.61 g of 2-pyridinecarbaldehyde and 3-pyridinecarbaldehyde, 1.66 g of 5-methyl-2-furaldehyde and 2.63 g of 5-bromo-2-furaldehyde) taken in 25 ml of 50% aqueous acetic acid solution , was added. The reaction mixture was stirred at 40 °C 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 [2-furancarboxylic acid (from 2-furaldehyde); 2-pyrrolecarboxylic acid (from 2-pyrrolecarbaldehyde); 2-thiophenecarboxylic acid (from 2-thiophenecarbaldehyde); 5-methyl-2-furancarboxylic acid (from 5-methyl-2-furaldehyde); 5-bromo-2-furancarboxylic acid (from 5-bromo-2-furaldehyde); 2-pyridinecarboxylic acid (from 2-pyridinecarbaldehyde); and 3-pyridinecarboxylic acid (from 3-pyridinecarbaldehyde)] were obtained (yield $\approx$ 80-90%) after the complete removal of ether. Each of the reaction products obtained was subjected to IR (KBr) and NMR ($CDCl_3$) analysis, and characterized as follows :

(i) 2-Furancarboxylic acid ;

IR : ν 3000, 2860(br s, -OH), 2583, 1690(s, C=O), 1470, 1305, 1245, 1020, 930, 760 cm^{-1}

^{1}H NMR : δ 10.5(s, 1H, COOH), 7.9(d, 1H, 5-H), 7.3(d, 1H, 3-H), 6.7(t, 1H, 4-H)

(ii) 2-Pyrrolecarboxylic acid ;

IR : ν 3000, 2850(br s, -OH), 1692(s, C=O), 1545, 1355, 1105, 925, 750 cm^{-1}

^{1}H NMR : δ 10.2(s, 1H, COOH), 6.9(d, 1H, 5-H), 6.7(d, 1H, 3-H), 6.2(t, 1H, 4-H)

(iii) 2-Thiophenecarboxylic acid ;

IR : ν 3090, 2850(br s, -OH), 2621, 1690(s, C=O), 1530, 1350, 1100, 910, 750 cm^{-1}

^{1}H NMR : δ 11.4(s, 1H, COOH), 7.8(d, 1H, 5-H), 7.5(d, 1H, 3-H), 7.1(t, 1H, 4-H)

(iv) 5-Methyl-2-furancarboxylic acid ;

IR : ν 2865(br s, -OH), 2630, 1645(s, C=O), 1410, 1370, 1210, 1030, 940, 810, 760 cm^{-1}

^{1}H NMR : δ 10.4(s, 1H, COOH), 7.5(d, 1H, 3-H), 7.3(d, 1H, 4-H), 2.3(s, 3H, CH_3)

(v) 5-Bromo-2-furancarboxylic acid ;

IR : ν 3130, 2565(br s, -OH), 1700(s, C=O), 1470, 1350, 1220,
1160, 1020, 940, 860, 760 cm^{-1}

^{1}H NMR : δ 10.3(s, 1H, COOH),7.5(d, 1H, 3-H), 6.6(d, 1H, 4-H)

(vi) 2-Pyridinecarboxylic acid ;

IR : ν 3030(br s, -OH), 2500, 1720(s, C=O), 1590, 1305, 1255,
1040, 830, 680 cm^{-1}

^{1}H NMR : δ 8.9(s, 1H, COOH), 8.2(d, 1H, 6-H), 8.1(d, 1H, 3-H),
7.7(m, 2H, 4,5-H)

(vii) 3-Pyridinecarboxylic acid ;

IR : ν 3030(br s, -OH), 2445, 1720(s, C=O), 1590, 1300, 1195,
830, 680 cm^{-1}

^{1}H NMR : δ 9.1(s, 1H, COOH), 8.8(s, 1H, 2-H), 8.2(d, 1H, 6-H),
7.5(m, 2H, 4,5-H)

(C) General Procedure for the oxidation of α,β- Unsaturated Aldehydes by QDC

Freshly distilled substrate solutions (0.71g of methacrylaldehyde , 0.57g of acrylaldehyde, 0.71g of crotonaldehyde, and 1.33g of cinnamaldehyde, 0.01 M) and QDC solution (9.52g, 0.02 M) were mixed in the presence of sulfuric acid (7.9g, 0.08 M) in 50% aqueous acetic acid medium at 40°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 [methacrylic acid (from methacrylaldehyde); acrylic acid (from acrylaldehyde); crotonic acid (from crotonaldehyde); and cinnamic acid (from cinnamaldehyde)], were obtained after the complete removal of ether (boiling and melting points were in agreement with literature values; yield ≈80-90%). Each reaction product obtained was subjected to IR (CCl_3) and NMR (300 MHz ; $CDCl_3$; Me_4Si) analysis, and characterized as follows :

(i) Methacrylic acid ;

IR : ν 2940(br s, -OH), 2500, 1700(s, C=O), 1640, 1455, 1381, 1200, 950, 810 cm^{-1}

^{1}H NMR : δ 11.6(s, 1H, 1-H), 6.3(d, 1H, trans to COOH), 5.6(d, 1H, cis to COOH), 2.0 (s, 3H, CH_3)

(ii) Acrylic acid ;

IR : ν 3000, 2665(br s, -OH), 1710(s, C=O), 1620, 1300, 1240, 1040, 980 cm^{-1}

^1H NMR : δ 12.1(s, 1H, 1-H), 6.1(t, 1H, 2-H), 5.9(d, 2H, 3-H_2),

(iii) Crotonic acid ;

IR : ν 2920(br s, -OH), 2600, 1700(s, C=O), 1650, 1530, 1440, 1381, 1230, 970 cm^{-1}

^1H NMR : δ 11.9(s,1H, 1-H), 6.7(s, 1H, 3-H), 5.8(s, 1H, 2-H), 2.0(d, 3H, 4-H)

(iv) Cinnamic acid ;

IR : ν 3060, 2980(br s, -OH), 1680(s, C=O), 1580, 1450, 1330, 1220, 980, 760 cm^{-1}

^1H NMR : δ 12.9(s, 1H, 1-H), 8.1(d, 1H, 3-H), 7.7(m, 5H,5,6,7,8,9-H), 6.5(d, 1H, 2-H)

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DISCUSSION

CHAPTER - I

KINETICS OF OXIDATION OF ALIPHATIC ALDEHYDES

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 aliphatic aldehydes 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 aliphatic aldehydes to their corresponding reaction products.

The oxidation of acetaldehyde by ceric sulphate was suggested to proceed to the extent of 90% to give formic acid, and the reaction was via the enol (1). The oxidation of acetaldehyde by cobaltic sulphate was suggested to proceed by the acetyl radical, yielding acetic acid as the final product (2). The oxidation of aliphatic aldehydes by one-electron reagents such as manganic pyrophosphate (3), potassium hexacyanoferrate (III) (4), and the radical $ON(SO_3K)_2$ (5), was reported to be of zero-order with respect to the oxidant. The course of these reactions was via the attack on the enolic form of the aldehydes. Acid solutions of vanadium(V) were used for the oxidation of aliphatic aldehydes, and the rates of oxidation were reported to be slower than the rate of enolization (6).

Reaction rates for the oxidation of aliphatic aldehydes by chromic acid were correlated with the aldehyde hydration equilibria. The results supported a mechanistic pathway involving a rate-determining oxidative decomposition of the chromic acid ester of an aldehyde hydrate (7).

The chromium(VI) oxidation of aliphatic aldehydes had suggested a hydrogen atom transfer from the aldehydic carbon atom to the oxidant in the rate-determining step (8).

The kinetic features of the oxidation of aliphatic aldehydes by peroxydiphosphate in aqueous sulfuric acid medium has been reported. The oxidation reaction was catalyzed by hydrogen ions, and exhibited a zero-order dependence on [aldehyde] and a first-order dependence on [oxidant]. The kinetic results were explained by a free-radical mechanism involving a phosphate radical-ion intermediate (9).

The chromium(VI) oxidation of isobutyraldehyde followed a mechanistic pathway wherein 70% of the substrate oxidation proceeded via the hydrated form, and 30% via an enol intermediate (10).

The kinetics of oxidation of aliphatic aldehydes by potassium ditelluratocuprate (III) in alkaline medium was observed to be first-order with respect to the aldehydes and Cu(III) concentrations, but showed an inverse dependence on the concentration of tellurate and hydroxide ions (11).

Ditelluratoargentate(III) in alkaline medium has been used for the oxidation of aliphatic aldehydes. The reactions were reported to be first-order in aldehyde, but showed a decrease in the rate with an increase in tellurate concentration. The rate-determining step involved a two-electron transfer from the aldehyde to the Ag(III) ions. The products of the oxidation were the corresponding carboxylic acids (12).

The kinetics of oxidation of aliphatic aldehydes by permanganate in aqueous perchloric acid was suggested to proceed via the hydrate form of the aldehyde. These reactions were first-order in aldehyde, permanganate, and hydrogen ions. The corresponding carboxylic acids were reported to be the final products (13).

The kinetics of oxidation of aliphatic aldehydes by peroxomonophosphoric acid was observed to be first-order in both, aldehyde and oxidant, but showed a complex dependence on the pH of the medium (14).

Aliphatic aldehydes were oxidized by peroxomonosulphate in aqueous perchloric acid medium. These reactions were first-order with respect to each, aldehyde and oxidant. These reactions exhibited acid catalysis, with the concurrent acid-dependent reaction pathway. The mechanism of the reaction involved a fast nucleophilic attack of the oxidant on the aldehydes, followed by the slow acid-catalyzed decomposition of the product (15).

Kinetic studies on the oxidation of aliphatic aldehydes by peroxomonosulphate in acid medium showed a first-order dependence each on the substrate and oxidant concentrations, but exhibited a complex hydrogen ion dependence. The reaction pathway involved nucleophilic substitution at the carbonyl carbon, followed by a rearrangement to give the corresponding acids as the product (16).

Sodium N-bromoarylsulphonamide (N-bromoamine) in acid medium was used to oxidize aliphatic aldehydes to the corresponding carboxylic acids. The reactions were first-order with respect to the concentrations of each of the reactants (oxidant, substrate and hydrogen ions). A mechanism involving hydride transfer from aldehyde hydrate to the oxidant was proposed (17).

The kinetics of the reaction between formaldehyde and nitric acid had suggested a two-step mechanism which accounted for the autocatalytic nature of the reaction. The product of the reaction was acetic acid (18).

The kinetics of oxidation of glyoxal by chromic acid showed a first-order dependence in glyoxal, but exhibited a gradual change from a first-order to zero-order dependence in acidity. The product formed was formic acid (19).

The oxidation of aliphatic aldehydes by N-bromobenzamide in 1: 1 (v/v) acetic acid-water resulted in the formation of the corresponding carboxylic acids. The reactions were first-order with respect to each of the reactants (substrate, oxidant and acid). The mechanism involved the transfer of a hydride ion to the oxidant in the rate-determining step of the reaction (20).

The kinetics of oxidation of formaldehyde by cerium(IV) in aqueous sulfuric acid medium, catalyzed by iridium(III), showed a first-order dependence on the concentration of cerium ions. At higher concentrations of the substrate, there was a leveling-off of the rate. A fractional order dependence in catalyst concentration was observed (21).

The kinetics of oxidation of formaldehyde to formic acid by aqua-manganese (III) ions in perchlorate medium showed an order dependence less than one in formaldehyde, but was independent of the concentration of acid. The reaction pathway was via the formation of a free radical (22).

Kinetics studies on the oxidation of aliphatic aldehydes by N-chlorosaccharin in aqueous acetic acid medium showed a first order dependence on the oxidant concentration , but an order dependence varying from one to zero with respect to acid and substrate concentrations. The products of the reactions were the corresponding acids (23).

The oxidation of long chain aliphatic aldehydes by quaternary ammonium permanganates in dichloromethane emphasized the special role of the colloidal manganese (VI) intermediate (24).

The osmium(VIII) and ruthenium(III) catalysis of the oxidation of acetaldehyde by periodate in aqueous alkaline medium indicated that osmium(VIII) was more efficient than ruthenium(III) in its catalytic behaviour. The product obtained was acetic acid (25).

The oxidation of aliphatic aldehydes by benzyltrimethyl ammonium chlorobromate to the corresponding carboxylic acids proceeded via the transfer of a hydride ion from the aldehyde hydrate to the oxidant. The reactions were found to be first order with respect to oxidant and substrate (26).

The kinetics of uncatalyzed and ruthenium(III) catalyzed oxidation of aliphatic aldehydes by pyridinium chlorochromate in aqueous acetic acid medium has been reported. The order in [oxidant] was unity in both the catalyzed and uncatalyzed reactions. However, the order with respect to [aldehyde] varied from unity to fractional, in the presence of ruthenium(III). The oxidation products were identified as the corresponding carboxylic acids (27).

The oxidation of aliphatic aldehydes by tetrabutylammonium tribromide in aqueous acetic acid resulted in the formation of the corresponding carboxylic acids. The reactions were first order with respect to oxidant and substrate concentrations. The mechanistic pathway involved the transfer of hydrogen ions from the aldehyde hydrate to the oxidant in the slow step of the reaction (28).

PRESENT WORK

The oxidation of aliphatic aldehydes is an important transformation in organic synthesis. The nature of products obtained was dependent on the nature of oxidant and the reaction conditions used. Among the many oxidizing agents which have been used for the oxidation of aliphatic aldehydes, 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 aliphatic aldehydes using a newer chromium(VI) reagent. In the present study, the chromium(VI) reagent which has been employed for the purpose of oxidation of aliphatic aldehydes, has been quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$]. All reactions were carried out in aqueous acid, under a nitrogen atmosphere. The dielectric constant of the medium was varied using acetic acid.

The aliphatic aldehydes which have been chosen for the purpose of oxidation by QDC have included:

I. Acetaldehyde, Propionaldehyde, Butyraldehyde,
Valeraldehyde, Isobutyraldehyde, and Isovaleraldehyde.

II. Caproaldehyde, Heptaldehyde, Caprylicaldehyde,
Pelargonaldehyde, and Caprinaldehyde.

III. Glyoxal and Glutaraldehyde.

Stoichiometry (vide "Experimental")

The stoichiometric experiments were performed under nitrogen at 313 K, under the conditions of $[QDC]_0 > [\text{aliphatic aldehyde}]_0$, at varying acid concentrations. The disappearance of Cr(VI) was followed until the absorbance values became constant. The $[QDC]_\infty$ was estimated. Stoichiometric ratios, $\Delta[QDC] / \Delta[\text{Substrate}]$, in the range 0.63 - 0.69, were obtained (Table 1).

Table 1 : Stoichiometries of the Oxidation of the Substrates

(*[Substrate] = 0.005 M; T = 313 K*)

$[H_2SO_4]$ / M	0.10	0.25	0.50
10^2[QDC] / M	2.50	2.60	2.70
Δ[QDC] / Δ[Acetaldehyde]	0.67	0.66	0.65
Δ[QDC] / Δ[Propionaldehyde]	0.64	0.67	0.66
Δ[QDC] / Δ[Butyraldehyde]	0.65	0.64	0.67
Δ[QDC] / Δ[Valeraldehyde]	0.63	0.68	0.66
Δ[QDC] / Δ[Caproaldehyde]	0.67	0.69	0.64
Δ[QDC] / Δ[Heptaldehyde]	0.65	0.68	0.67
Δ[QDC] / Δ[Caprylicaldehyde]	0.66	0.68	0.63
Δ[QDC] / Δ[Pelargonaldehyde]	0.65	0.67	0.68
Δ[QDC] / Δ[Caprinaldehyde]	0.69	0.67	0.66
Δ[QDC] / Δ[Isobutyraldehyde]	0.65	0.63	0.67
Δ[QDC] / Δ[Isovaleraldehyde]	0.68	0.66	0.64

The observed stoichiometric ratios conformed to the overall equations :

(a) For acetaldehyde :

$$3\,C_2H_4O + 2\,Cr^{VI} + 3\,H_2O \rightarrow 3\,C_2H_4O_2 + 2\,Cr^{III} + 6\,H^+ \qquad (1)$$

(b) For propionaldehyde :

$3\ C_3H_6O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_3H_6O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (2)

(c) For butyraldehyde :

$3\ C_4H_8O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_4H_8O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (3)

(d) For valeraldehyde :

$3\ C_5H_{10}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_5H_{10}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (4)

(e) For caproaldehyde

$3\ C_6H_{12}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_6H_{12}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (5)

(f) For heptaldehyde :

$3\ C_7H_{14}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_7H_{14}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (6)

(g) For caprylicaldehyde :

$3\ C_8H_{16}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_8H_{16}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (7)

(h) For pelargonaldehyde :

$3\ C_9H_{18}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_9H_{18}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (8)

(i) For caprinaldehyde :

$3\ C_{10}H_{20}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_{10}H_{20}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (9)

(j) For isobutyraldehyde :

$3\ C_4H_8O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_4H_8O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (10)

(k) For isovaleraldehyde :

$3\ C_5H_{10}O\ +\ 2\ Cr^{VI}\ +\ 3\ H_2O \rightarrow 3\ C_5H_{10}O_2\ +\ 2\ Cr^{III}\ +\ 6\ H^+$ (11)

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 Tables 2a, 2b, 3 and 4.

Table 2a : Dependence of Rate Constants on the Concentration of Aliphatic Aldehydes ([QDC] = 0.001 M; [H_2SO_4] = 0.5 M; T = 313 K)

10^2 [Substrate] / M	10^4 k_1 / s^{-1}			
	Acetaldehyde	**Propionaldehyde**	**Butyraldehyde**	**Valeraldehyde**
1.0	0.30	0.77	0.85	0.91
2.5	0.75	1.93	2.18	2.40
5.0	1.53	3.80	4.30	4.40
7.5	2.30	5.85	6.43	6.80
10.0	3.12	7.70	8.54	9.10
		10^2 k_2 / M^{-1} s^{-1}		
	0.3	0.77	0.85	0.91
	0.3	0.77	0.87	0.96
	0.31	0.76	0.86	0.88
	0.31	0.78	0.85	0.91
	0.31	0.77	0.85	0.91

$k_2 = k_1$ / [Substrate]

Table 2b : Dependence of Rate Constants on the Concentration of Aliphatic Aldehydes ([QDC] = 0.002 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

10^2 [Substrate] / M	$10^4\ k_1$ / s^{-1} Isovaleraldehyde	$10^4\ k_1$ / s^{-1} Isobutyraldehyde
2.0	2.10	7.10
5.0	5.30	17.50
10.0	11.10	35.60
15.0	15.60	53.30
20.0	20.90	71.50
	$10^2\ k_2$ / $M^{-1}\ s^{-1}$	
	1.05	3.55
	1.06	3.5
	1.11	3.5
	1.04	3.55
	1.05	3.57

$k_2 = k_1$ / [Substrate]

Table 3 : Dependence of Rate Constants on the Concentration of Long Chain Aliphatic Aldehydes ([QDC] = 0.001 M; [H_2SO_4] = 0.5 M; [AcOH] = 70% (v/v); T = 313 K)

	10^4 k_1 / s^{-1}				
10^2 [Substrate] / M	**Capro-aldehyde**	**Hept-aldehyde**	**Caprylic-aldehyde**	**Pelargon-aldehyde**	**Caprin-aldehyde**
1.0	6.8	7.1	7.4	7.8	8.2
2.5	17.1	17.8	18.5	19.5	20.5
5.0	34.2	35.6	36.1	39.2	41.1
7.5	51.2	53.4	56.0	57.6	61.1
10.0	67.5	72.4	74.6	78.5	83.2
	10^2 k_2 / M^{-1} s^{-1}				
	6.8	7.1	7.4	7.8	8.2
	6.8	7.1	7.4	7.8	8.2
	6.8	7.1	7.2	7.8	8.2
	6.8	7.1	7.4	7.7	8.1
	6.8	7.2	7.5	7.9	8.3

$k_2 = k_1$ / [Substrate]

Table 4 : Dependence of Rate Constants on the Concentration of Aliphatic Dialdehydes ([QDC] = 0.001 M; [H_2SO_4] = 0.5 M; T = 313 K)

10^2 [Substrate] / M	10^4 k_1 / s^{-1}	
	Glyoxal	Glutaraldehyde
1.0	31.0	1.15
2.5	76.5	2.90
5.0	158	5.92
7.5	258	8.50
10.0	311	11.6
	k_2 / M^{-1} s^{-1}	
	0.31	0.01
	0.31	0.01
	0.32	0.01
	0.34	0.01
	0.31	0.01

$k_2 = k_1$ / [Substrate]

Plots of k_1, the pseudo-first-order rate constant, against the concentrations of substrates, gave straight lines passing through the origin (Figures 1-4), indicating that the rate of oxidation was dependent on the first power of the concentration of the substrate.

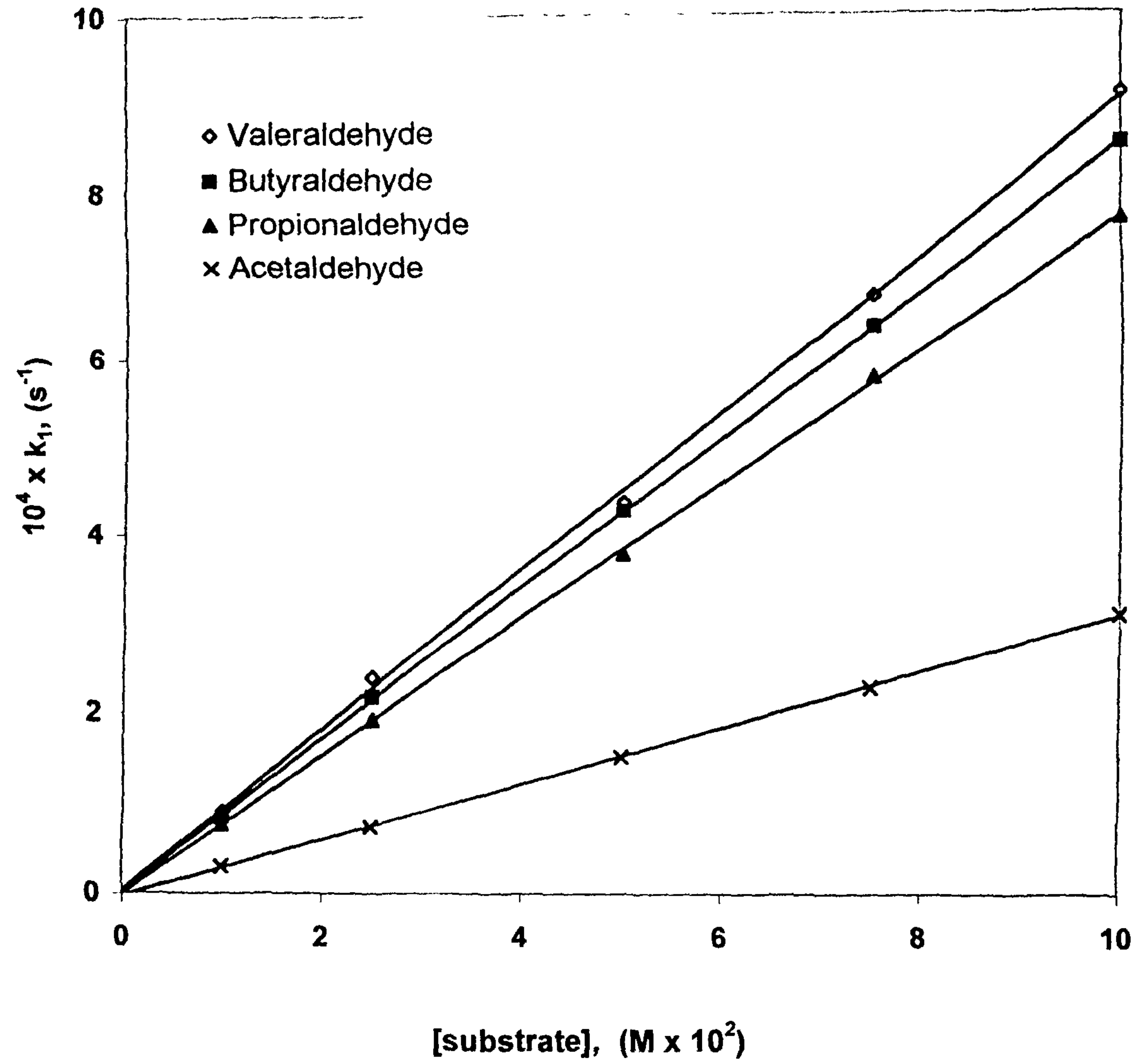


Fig. 1. Plots of k_1 against the concentrations of substrates.

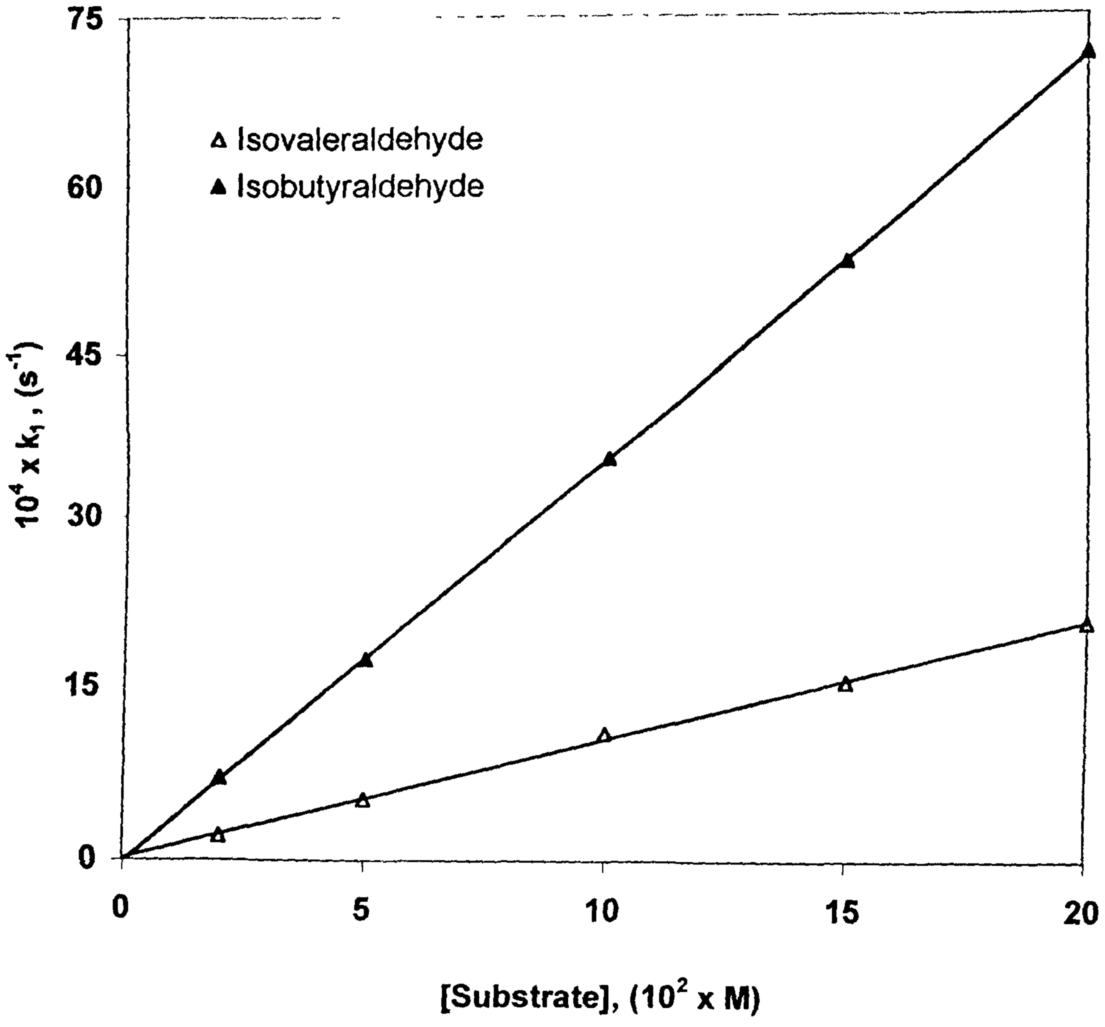


Fig. 2. Plots of k_1 against the concentrations of the substrates.

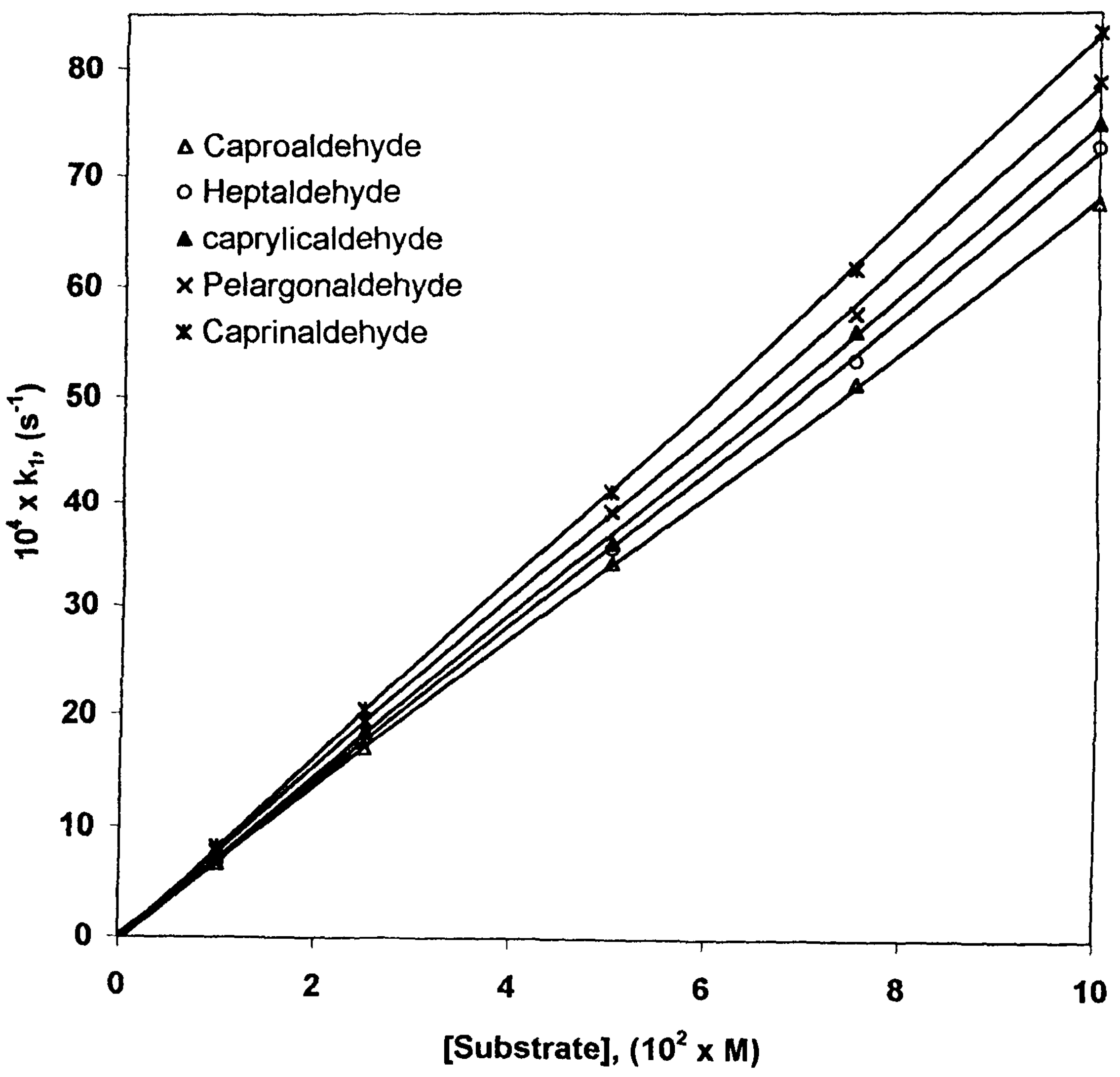


Fig. 3. Plots of k_1 against concentrations of substrates.

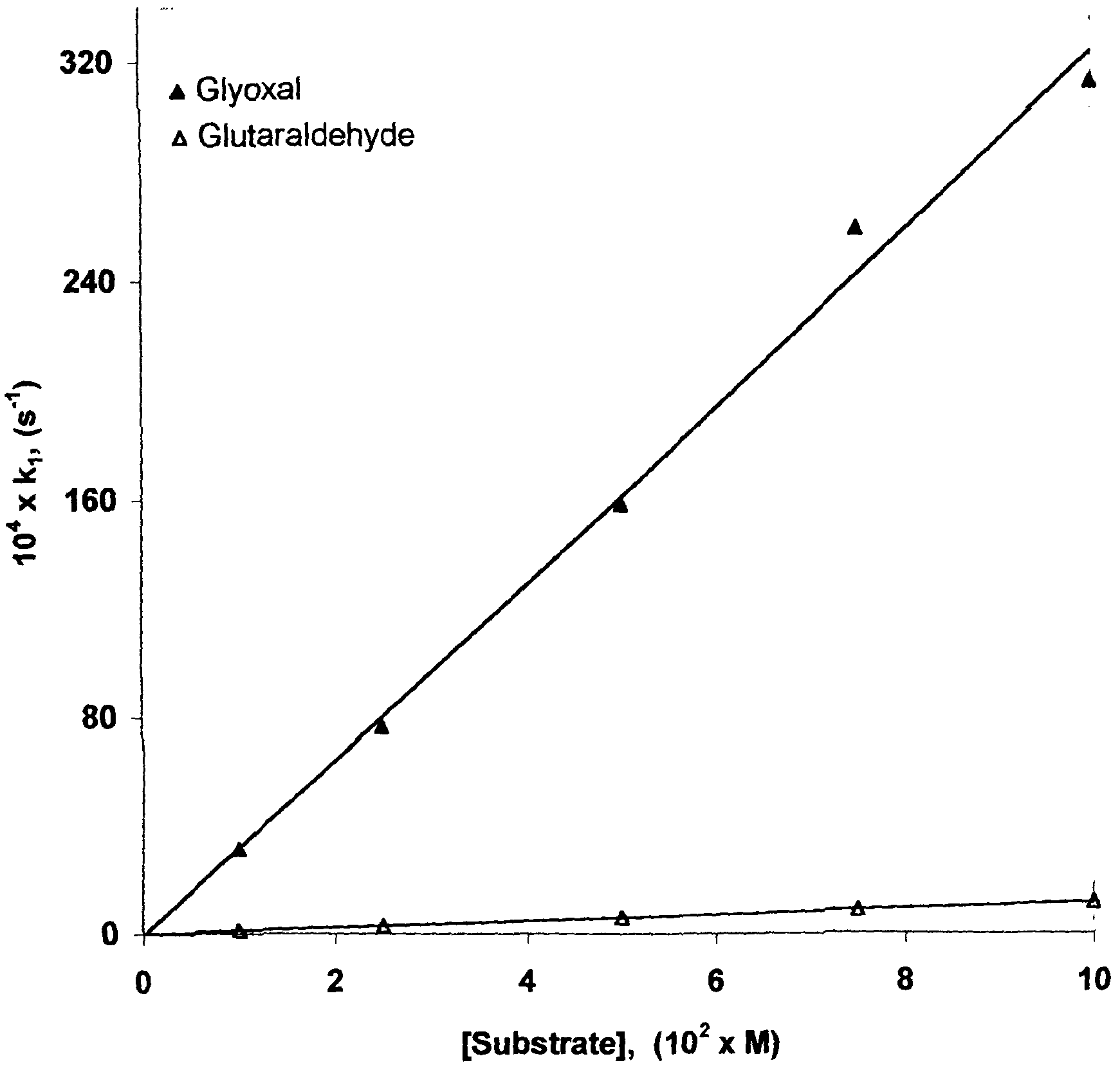


Fig. 4. Plots of k_1 against the concentrations of substrates.

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 (Tables 5a, 5b, 6 and 7).

Table 5a : Dependence of Rate Constants on the Concentration of Oxidant

([Substrate] = 0.01 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

	$10^4\ k_1 / s^{-1}$			
10^3 [QDC] / M	**Acetaldehyde**	**Propionaldehyde**	**Butyraldehyde**	**Valeraldehyde**
1.0	0.30	0.77	0.85	0.91
0.75	0.31	0.75	0.81	0.94
0.50	0.30	0.74	0.81	0.91
0.25	0.29	0.78	0.83	0.92
0.10	0.30	0.76	0.82	0.90

Table 5b : Dependence of Rate Constants on the Concentration of Oxidant

([Substrate] = 0.02 M; [H_2SO_4] = 0.5 M; T = 313 K)

10^3 [QDC] / M	10^4 k_1 / s^{-1}	
	Isovaleraldehyde	**Isobutyraldehyde**
2.0	2.10	7.10
1.5	2.15	7.18
1.0	2.18	7.20
0.5	2.11	7.15
0.2	2.17	7.13

Table 6 : Dependence of Rate Constants on the Concentration of Oxidant

[Substrate] = 0.01 M; [H_2SO_4] = 0.5 M; [AcOH] = 70% (v/v); T = 313 K)

10^3 [QDC] / M	10^4 k_1 / s^{-1}				
	Capro-aldehyde	**Hept-aldehyde**	**Caprylic-aldehyde**	**Pelargon-aldehyde**	**Caprin-aldehyde**
1.0	6.8	7.1	7.4	7.8	8.2
0.75	6.8	7.3	7.4	7.8	8.2
0.50	6.9	7.2	7.2	7.7	8.3
0.25	6.7	7.1	7.3	7.6	8.2
0.10	6.9	7.0	7.4	7.9	8.1

Table 7 : Dependence of Rate Constants on the Concentration of Oxidant

([Substrate] = 0.01 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

10^3 [QDC] / M	10^4 k_1 / s^{-1}	
	Glyoxal	**Glutaraldehyde**
1.0	31.0	1.15
0.75	31.5	1.17
0.05	30.8	1.13
0.25	31.2	1.14
0.10	31.1	1.16

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 (Tables 8a, 8b, 9 and 10).

Table 8a : Dependence of Rate Constants on the Acid Concentration for Aliphatic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; T = 313 K)

	10^4 k_1 / s^{-1}			
[H_2SO_4] / M	**Acetaldehyde**	**Propionaldehyde**	**Butyraldehyde**	**Valeraldehyde**
0.5	0.3	0.77	0.85	0.91
0.75	0.45	1.18	1.28	1.36
1.0	0.59	1.54	1.68	1.83
1.25	0.75	1.83	2.09	2.30
1.50	0.92	2.36	2.57	2.73

Table 8b : Dependence of Rate Constants on the Acid Concentration for Aliphatic Aldehydes

([Substrate] = 0.02 M; [QDC] = 0.002 M; T = 313 K)

$[H_2SO_4]$ / M	$10^4 k_1$ / s^{-1}	
	Isovaleraldehyde	Isobutyraldehyde
0.5	2.10	7.10
0.75	3.15	10.7
1.0	4.18	14.2
1.25	5.22	18.8
1.50	6.30	21.5

Table 9 : Dependence of Rate Constants on the Acid Concentration for Long Chain Aliphatic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 70% (v/v); T = 313 K)

$[H_2SO_4]$ / M	10^4 k_1 / s^{-1}				
	Capro-aldehyde	Hept-aldehyde	Caprylic-aldehyde	Pelargon-aldehyde	Caprin-aldehyde
0.5	6.8	7.1	7.4	7.8	8.2
0.75	10.2	10.8	11.4	11.8	12.4
1.0	13.9	14.0	14.8	15.6	16.5
1.25	17.2	18.8	18.7	19.5	20.7
1.50	20.4	21.5	22.6	23.4	24.8

Table 10 : Dependence of Rate Constants on the Acid Concentration for Aliphatic Dialdehydes

([Substrate] = 0.01 M; [QDC] = 0.001 M; T = 313 K)

	10^4 k_1 / s^{-1}	
$[H_2SO_4]$ / M	Glyoxal	Glutaraldehyde
0.50	31.0	1.15
0.75	45.8	1.71
1.0	61.5	2.30
1.25	76.3	2.90
1.50	91.2	3.46

Plots of log k_1 against log $[H^+]$ were linear, with slopes equal to unity (Figures 5-8), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

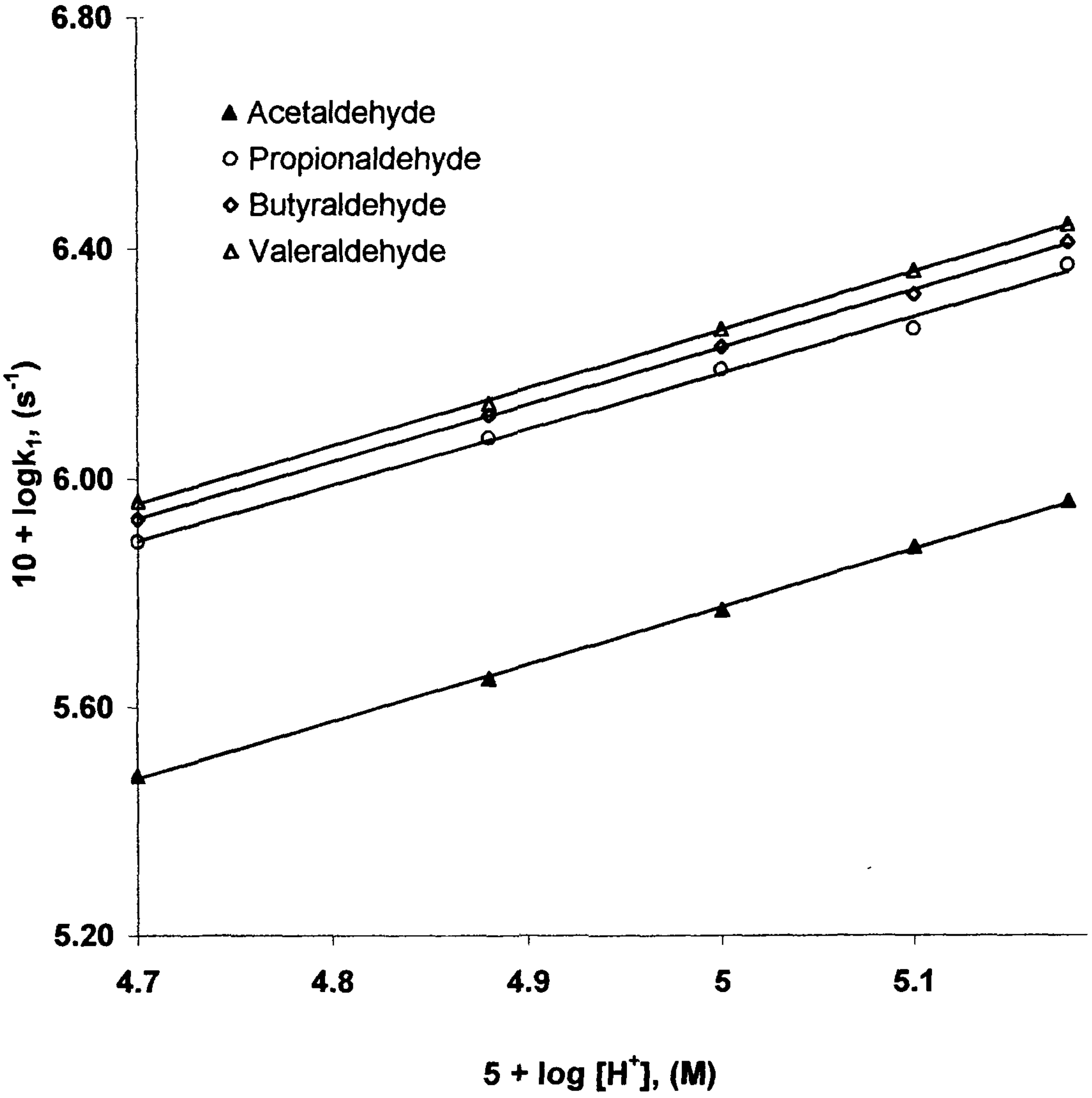


Fig. 5. Plots of log k_1 against log [H^+].

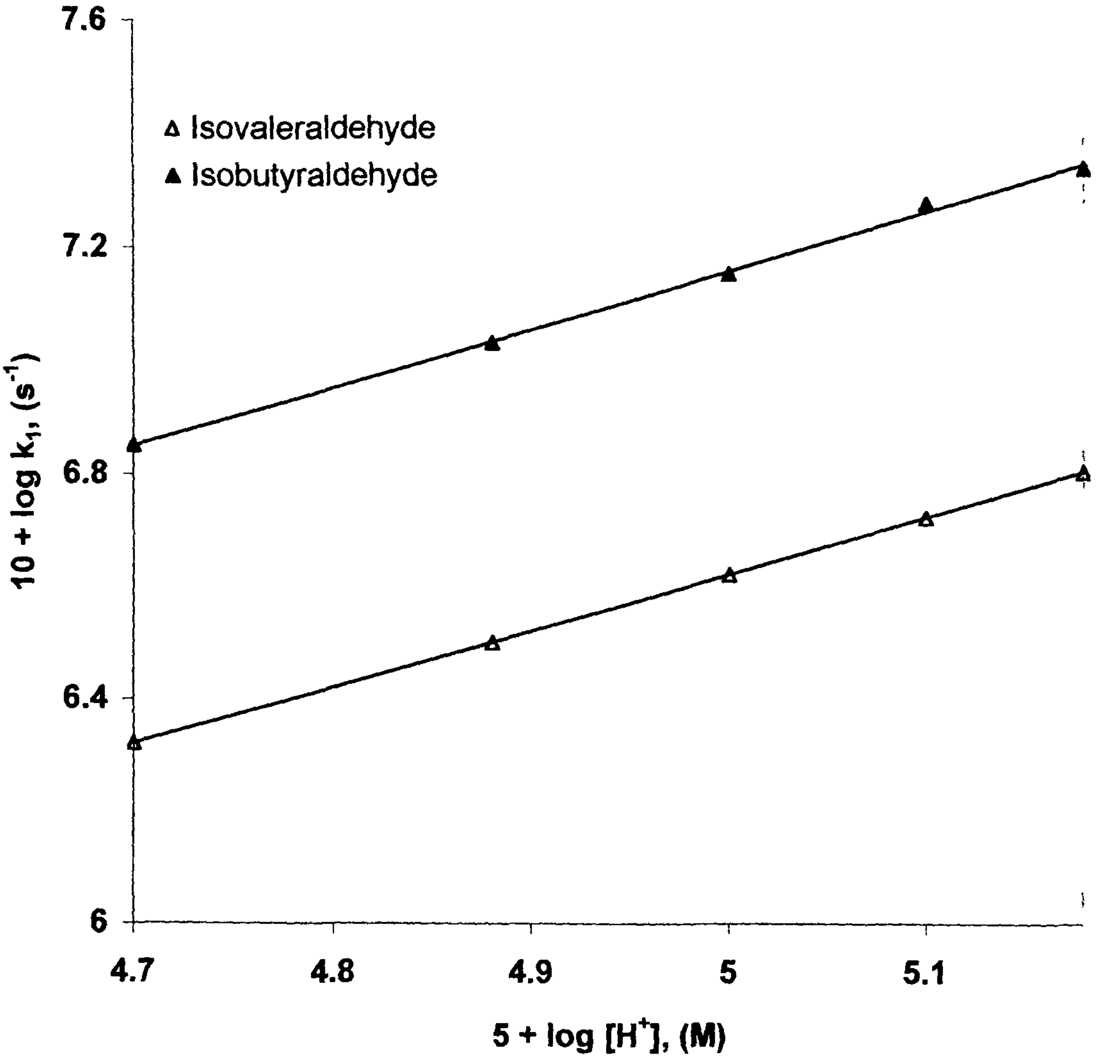


Fig. 6. Plots of log k_1 against log $[H^+]$.

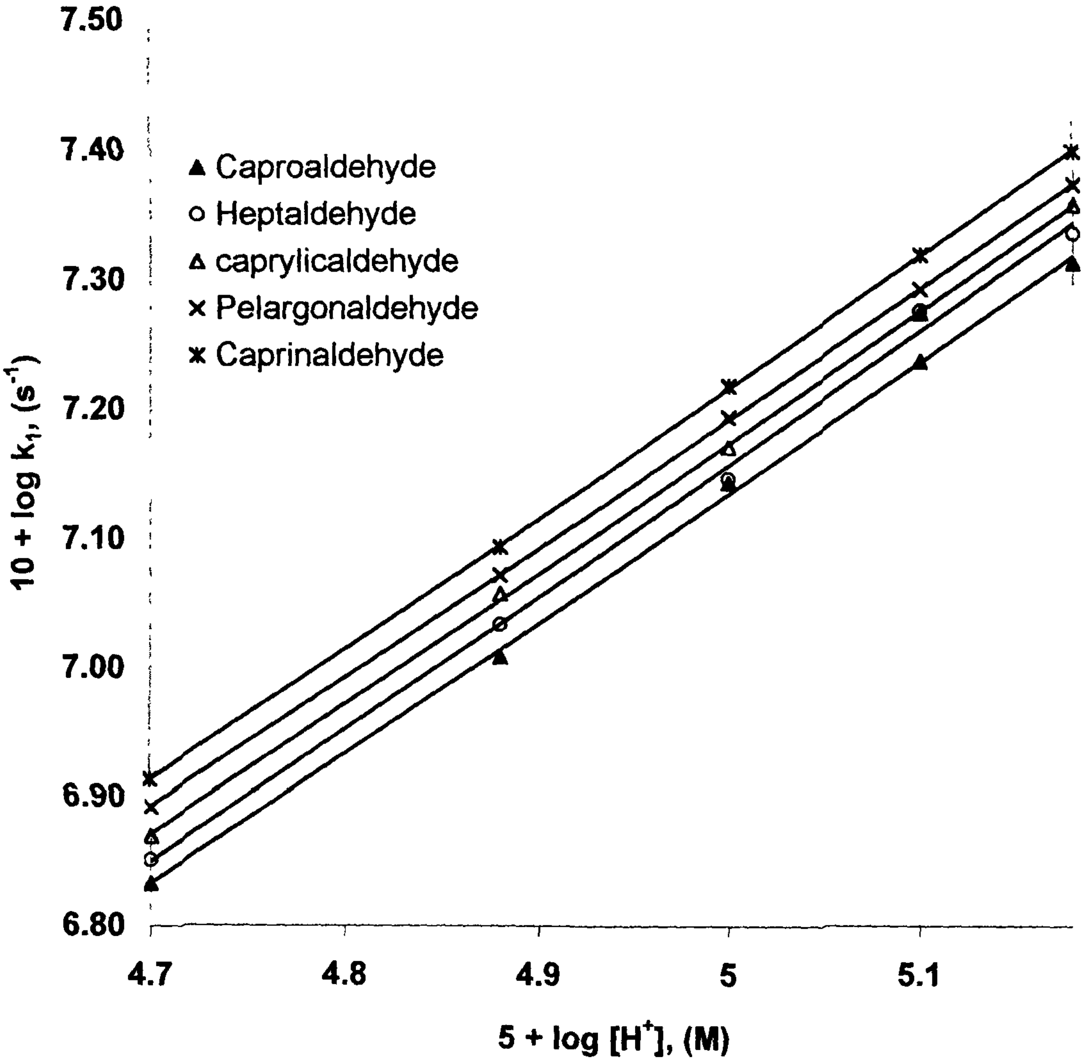


Fig. 7. Plots of log k_1 against log $[H^+]$.

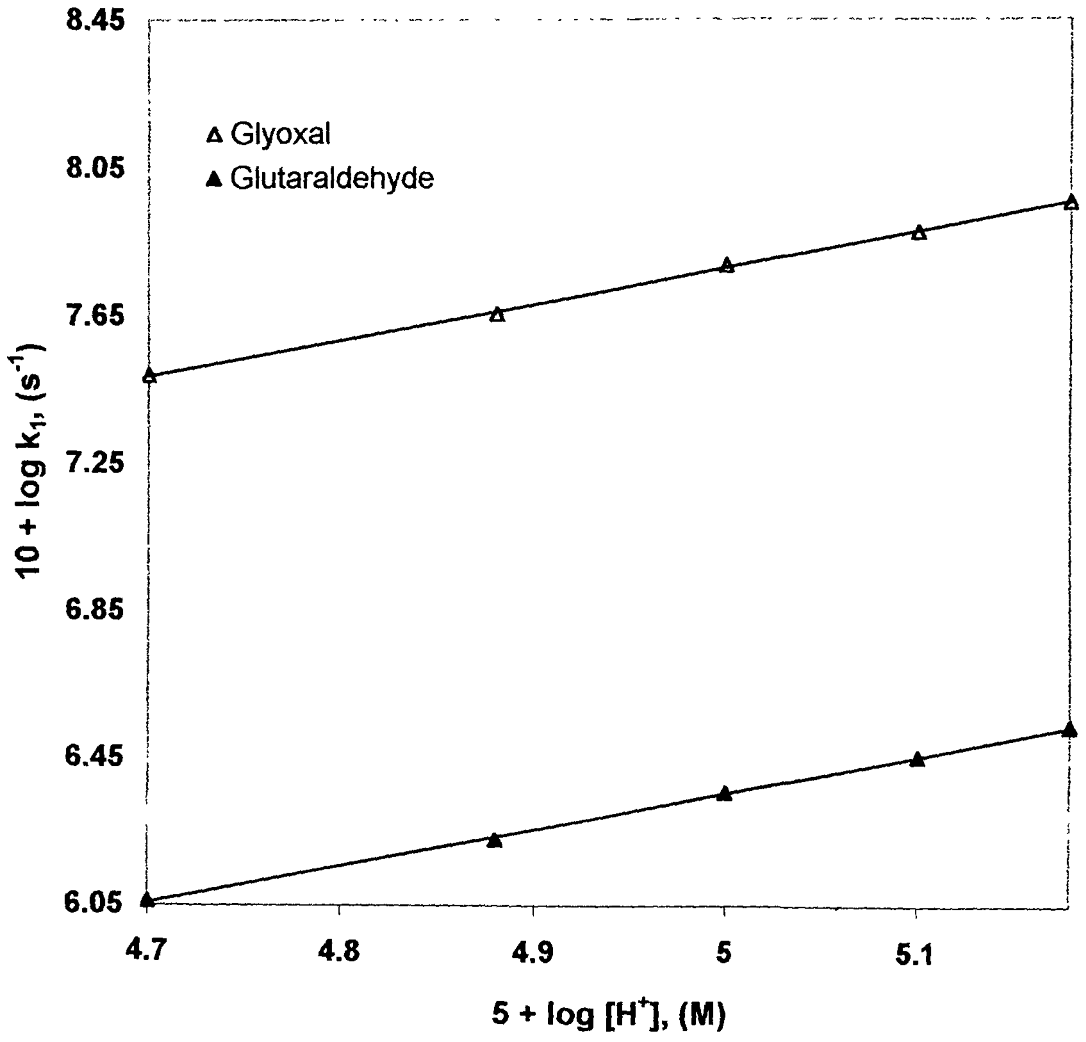


Fig. 8. Plots of log k_1 against log [H^+].

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. The acid catalysis must be related to the structure of the oxidant (QDC), which was converted to a protontated 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 $Cr_2O_7^{2-}$, besides other protonated species such as $H_2Cr_2O_7$, $HCr_2O_7^-$ and H_2CrO_4 (29). The ionization constant for $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$ was 3.0×10^{-7} 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. (30), who 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. The ionization constant for the $HCr_2O_7^-$ ion, $HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-}$ was 0.85 mol / l; hence, in solutions where $pH \geq 1$, 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 $Cr_2O_7^{2-}$. These ions are in equilibrium with each other, according to the equation given by $CrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ ($K_d = 35.5$). 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 $pH = 11$, 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 (30). 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 (31). 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 substrate.

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 :

$$\text{Rate} = -\frac{d[\text{QDC}]}{dt} = k\,[\text{Substrate}]\,[\text{QDC}]\,[\text{H}^+] \qquad (12)$$

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 (Tables 11a, 11b, 12 and 13).

Table 11a : Dependence of Rate Constants on Solvent composition for Aliphatic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

H_2O : AcOH (%, v/v)	Dielectric Constant (D)	10^4 k_1 / s^{-1}			
		Acetaldehyde	Propionaldehyde	Butyraldehyde	Valeraldehyde
100:0	73.28	0.30	0.77	0.85	0.91
95:5	69.93	0.33	0.93	1.02	1.15
90:10	66.58	0.36	1.09	1.20	1.35
85:15	63.23	0.39	1.25	1.45	1.66
80:20	59.88	0.43	1.51	1.65	1.95

Table 11b : Dependence of Rate Constants on Solvent composition for Aliphatic Aldehydes ([Substrate] = 0.02 M; [QDC] = 0.002 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

H_2O : AcOH (%, v/v)	Dielectric Constant (D)	$10^4 k_1 / s^{-1}$	
		Isovaleraldehyde	Isobutyraldehyde
100:0	73.28	2.10	7.10
95:5	69.93	2.94	11.10
90:10	66.58	3.80	16.70
85:15	63.23	4.70	21.50
80:20	59.88	5.50	26.50

Table 12 : Dependence of Rate Constants on Solvent composition for Aliphatic Dialdehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [H_2SO_4] = 0.5 M; T = 313 K

H_2O : AcOH (%, v/v)	Dielectric Constant (D)	10^4 k_1 / s^{-1}	
		Glyoxal	Glutaraldehyde
100:0	73.28	31.0	1.15
95:5	69.93	38.2	1.36
90:10	66.58	45.1	1.56
85:15	63.23	52.1	1.76
80:20	59.88	59.1	1.95

Table 13 : Dependence of Rate Constants on Solvent composition for Long Chain Aliphatic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [H_2SO_4] = 0.5 M; T = 313 K)

H_2O : AcOH (%, v/v)	Dielectric Constant (D)	10^4 k_1 / s^{-1}				
		Capro-aldehyde	Hept-aldehyde	Caprylic-aldehyde	Pelargon-aldehyde	Caprin-aldehyde
40:60	33.09	5.4	5.8	6.3	6.7	7.0
35:65	29.74	6.1	6.5	6.9	7.2	7.6
30:70	26.39	6.8	7.1	7.4	7.8	8.2
25:75	23.04	9.3	9.5	10.1	10.6	11.2
20:80	19.69	10.8	11.8	12.7	13.4	14.1

The dielectric constants for water-acetic acid mixtures have been estimated from the dielectric constants of the pure solvents (at 313 K : water = 69.9; acetic acid = 6.5) (ref. 32).

In the present investigation, in proceeding from 0% acetic acid to 20% acetic acid (Tables 11a, 11b, 12) and from 60% acetic acid to 80% acetic acid (Table 13), there was a decreases in the polarity of the medium. This decrease in the polarity of the medium resulted in an increase in the rates of the reactions. *Plots of log k_1 against the reciprocal of the dielectric constant were linear* (Figures 9-12), with positive slopes.

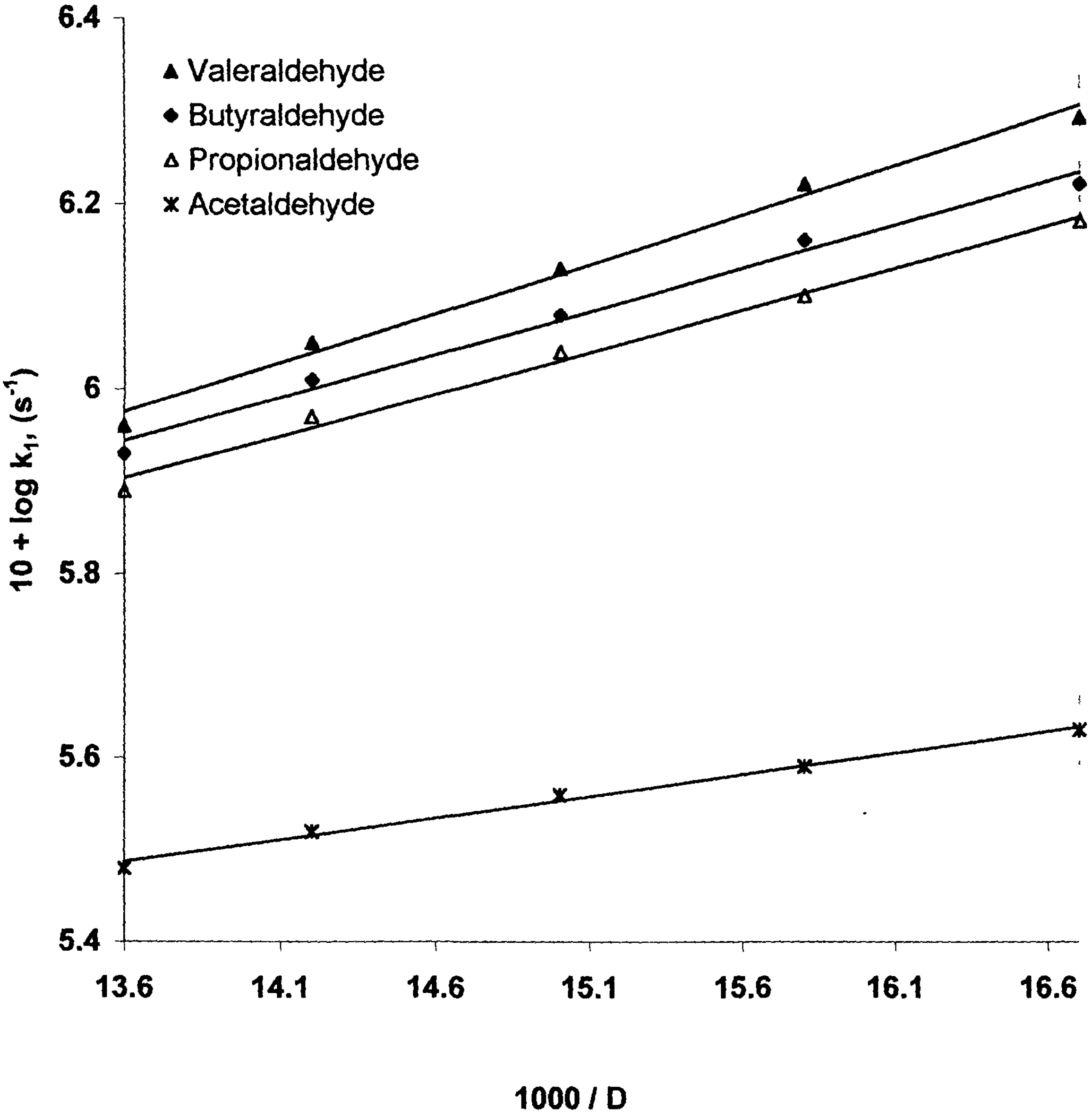


Fig. 9. Plots of log k_1 against the reciprocal of the dielectric constant.

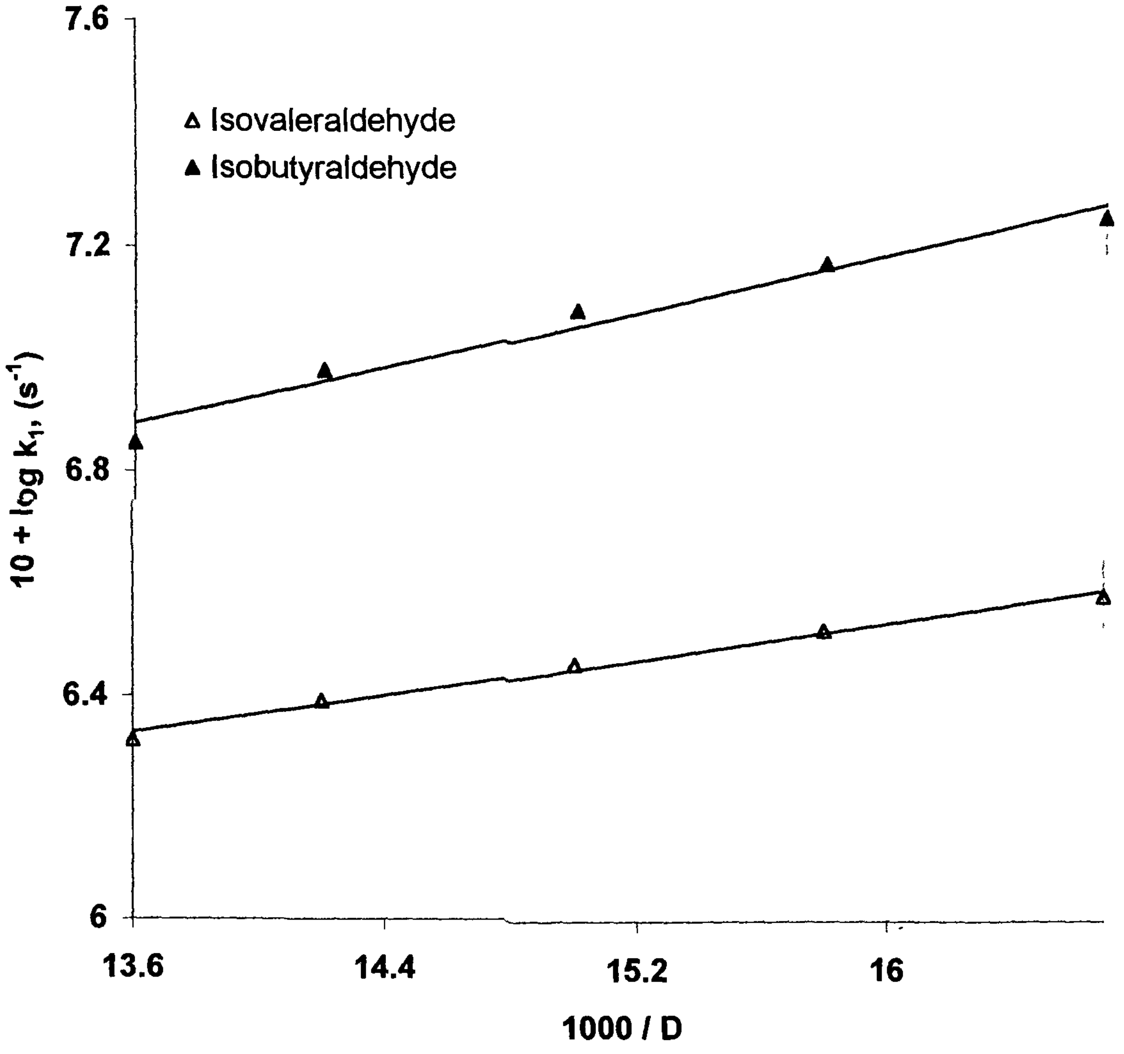


Fig. 10. Plots of log k_1 against the reciprocal of the dielectric constant.

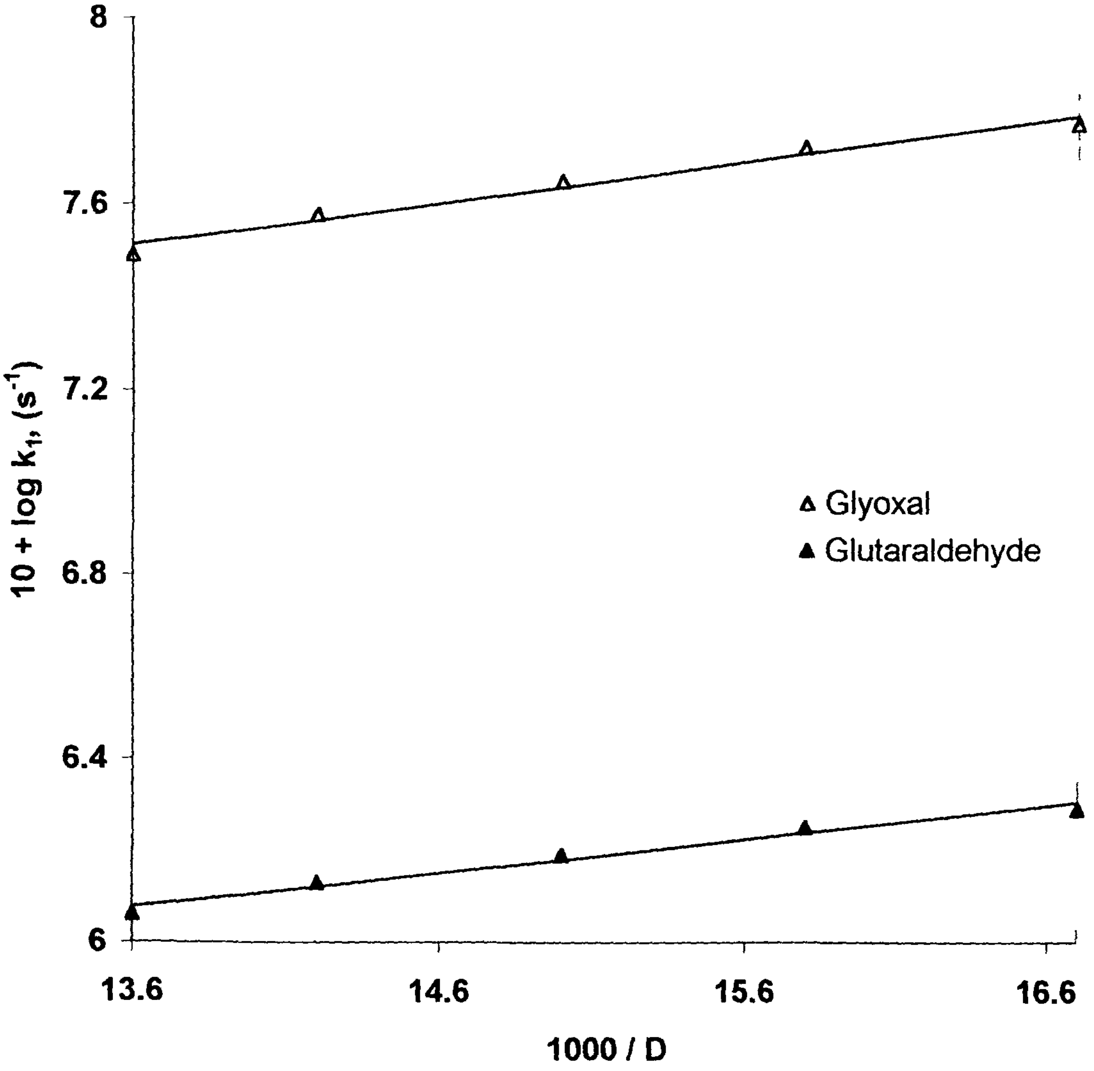


Fig. 11. Plots of log k_1 against the reciprocal of the dielectric constant.

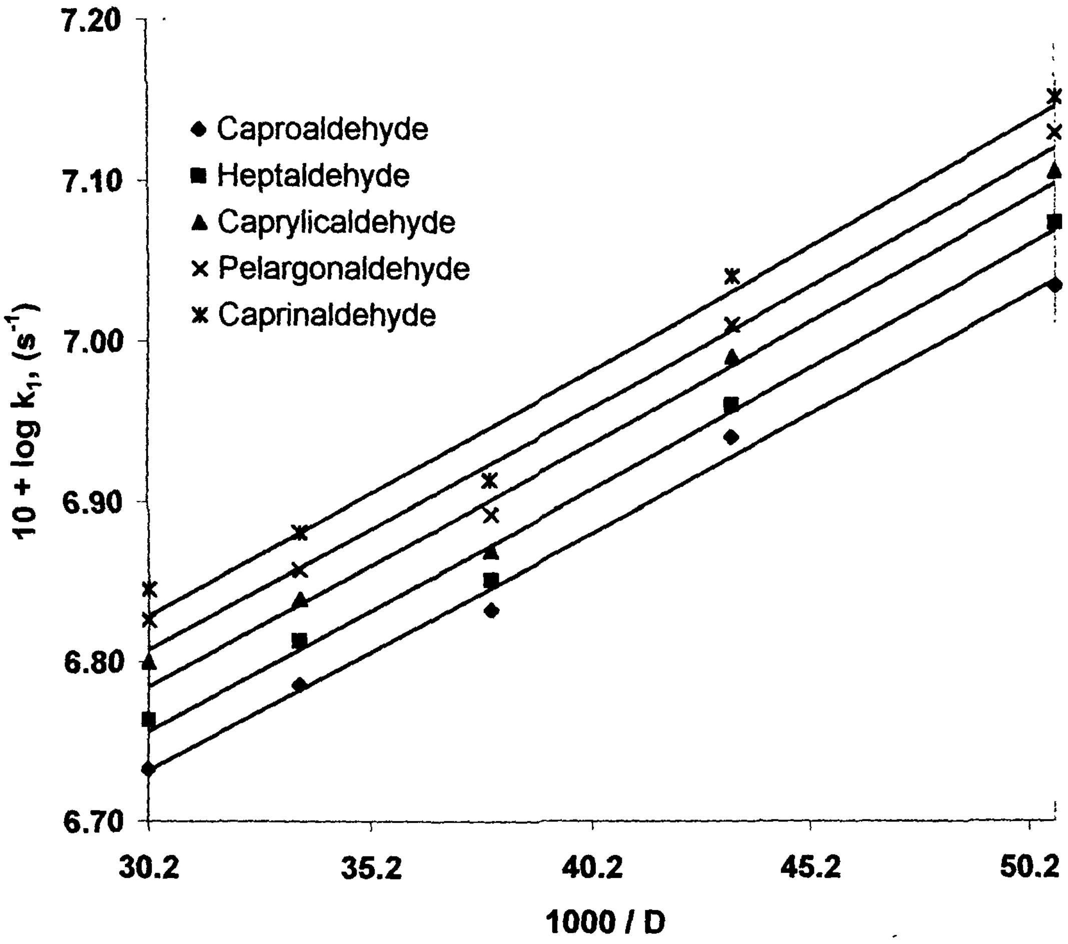


Fig. 12. Plots of log k_1 against the reciprocal of the dielectric constant.

This suggested an interaction between a positive ion and a dipole (33), and was in conformity with the experimental observation that, in the presence of an acid, there was the involvement of a protonated Cr(VI) species. The data in Tables 11a, 11b, 12 and 13 indicated that the dielectric constants for water - acetic acid mixtures were a linear function of the solvent composition used in this investigation. The 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 (34). 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 the reactions would also be dependent on factors such as solvent-solute interactions (35, 36), 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 (Tables 14a, 14b, 15 and 16).

Table 14a : Dependence of Rate Constants on Temperature for Aliphatic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; $[H_2SO_4]$ = 0.5 M)

Temperature (±0.1K)	$10^4 k_1 / s^{-1}$			
	Acetaldehyde	Propionaldehyde	Butyraldehyde	Valeraldehyde
308	0.15	0.60	0.65	0.70
313	0.30	0.77	0.85	0.91
318	0.36	1.18	1.20	1.22
323	0.44	1.45	1.60	1.58

Table 14b : Dependence of Rate Constants on Temperature for Aliphatic Aldehydes ([Substrate] = 0.02 M; [QDC] = 0.002 M; [H_2SO_4] = 0.5 M)

Temperature (±0.1K)	10^4 k_1 / s^{-1}	
	Isovaleraldehyde	Isobutyraldehyde
303	1.10	3.56
308	1.62	5.40
313	2.10	7.10
318	3.20	10.60
323	4.70	14.80

Table 15 : Dependence of Rate Constants on Temperature for Long Chain Aliphatic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 70% (v/v); [H_2SO_4] = 0.5 M)

	10^4 k_1 / s^{-1}				
Temperature (±0.1K)	Capro-aldehyde	Hept-aldehyde	Caprylic-aldehyde	Pelargon-aldehyde	Caprin-aldehyde
308	5.5	6.0	6.5	6.8	7.0
313	6.8	7.1	7.4	7.8	8.2
318	8.0	8.8	9.4	10	10.8
323	11.5	12.5	13.3	13.8	14.4

Table 16 : Dependence of Rate Constants on Temperature for Aliphatic Dialdehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [H_2SO_4] = 0.5 M)

	10^4 k_1 / s^{-1}	
Temperature (±0.1K)	Glyoxal	Glutaraldehyde
303	15.6	0.60
308	23.3	0.88
313	31.0	1.15
318	46.0	1.80
323	63.0	2.43

Plots of log k_1 against the reciprocal of temperature were linear (Figures 13-16), 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 17.

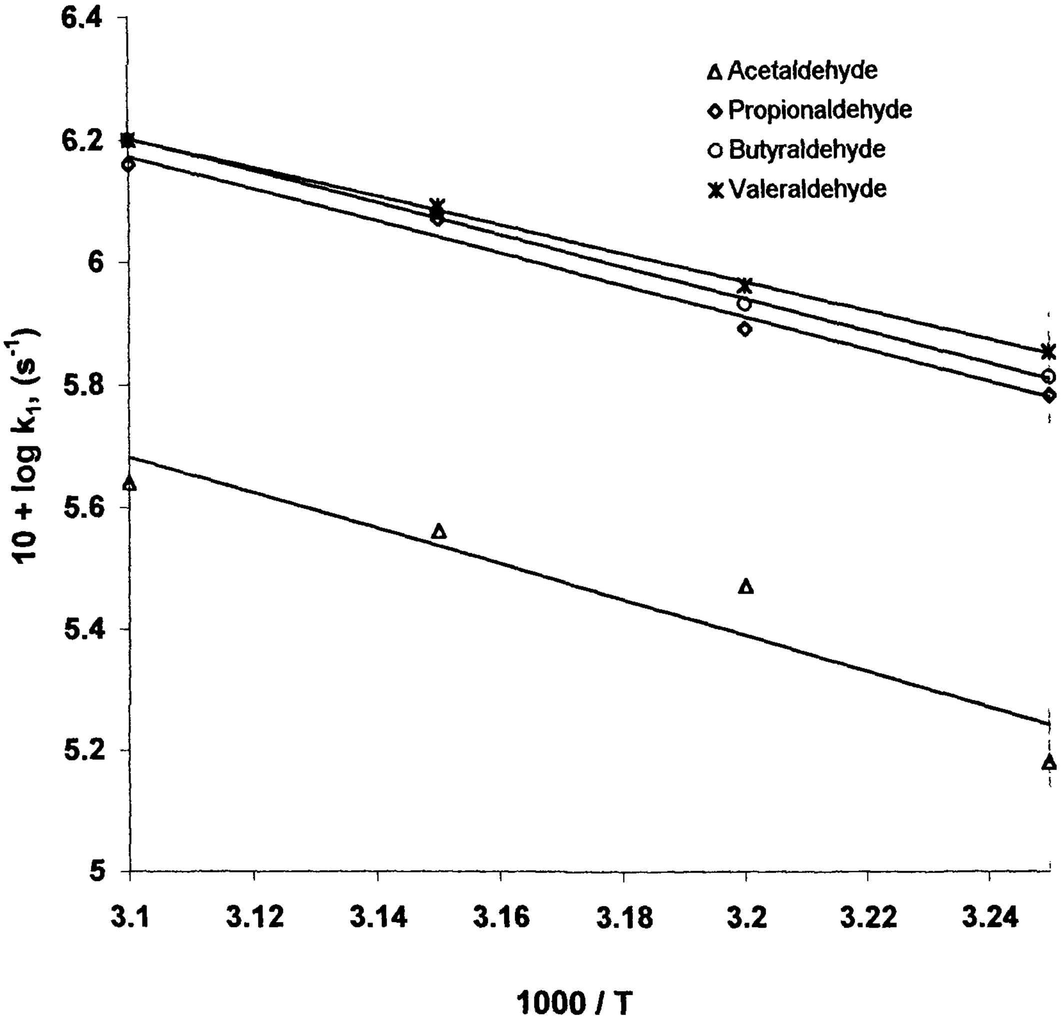


Fig. 13. Plots of log k_1 against the reciprocal of temperature.

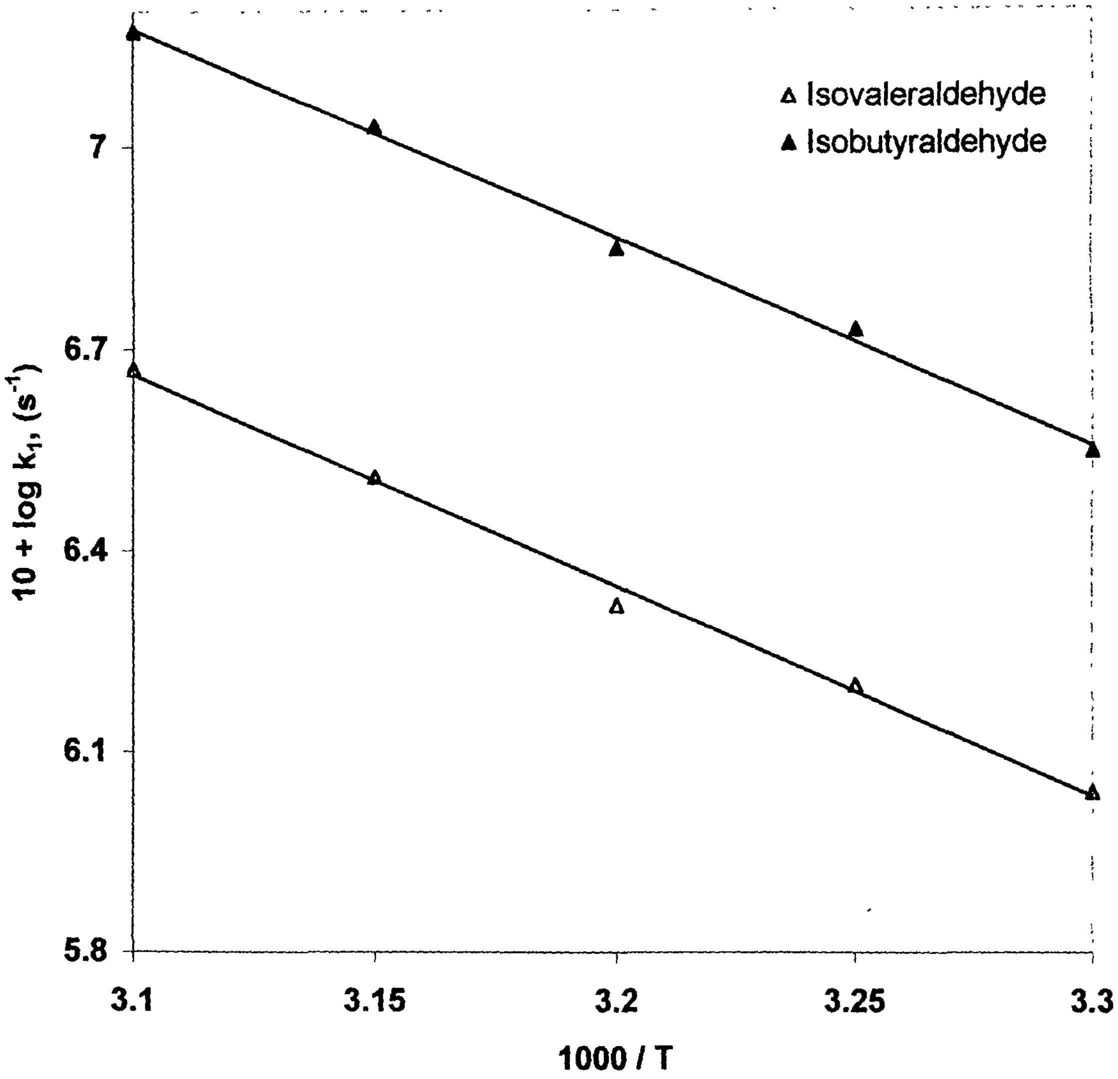


Fig.14. Plots of log k_1 against the reciprocal of temperature.

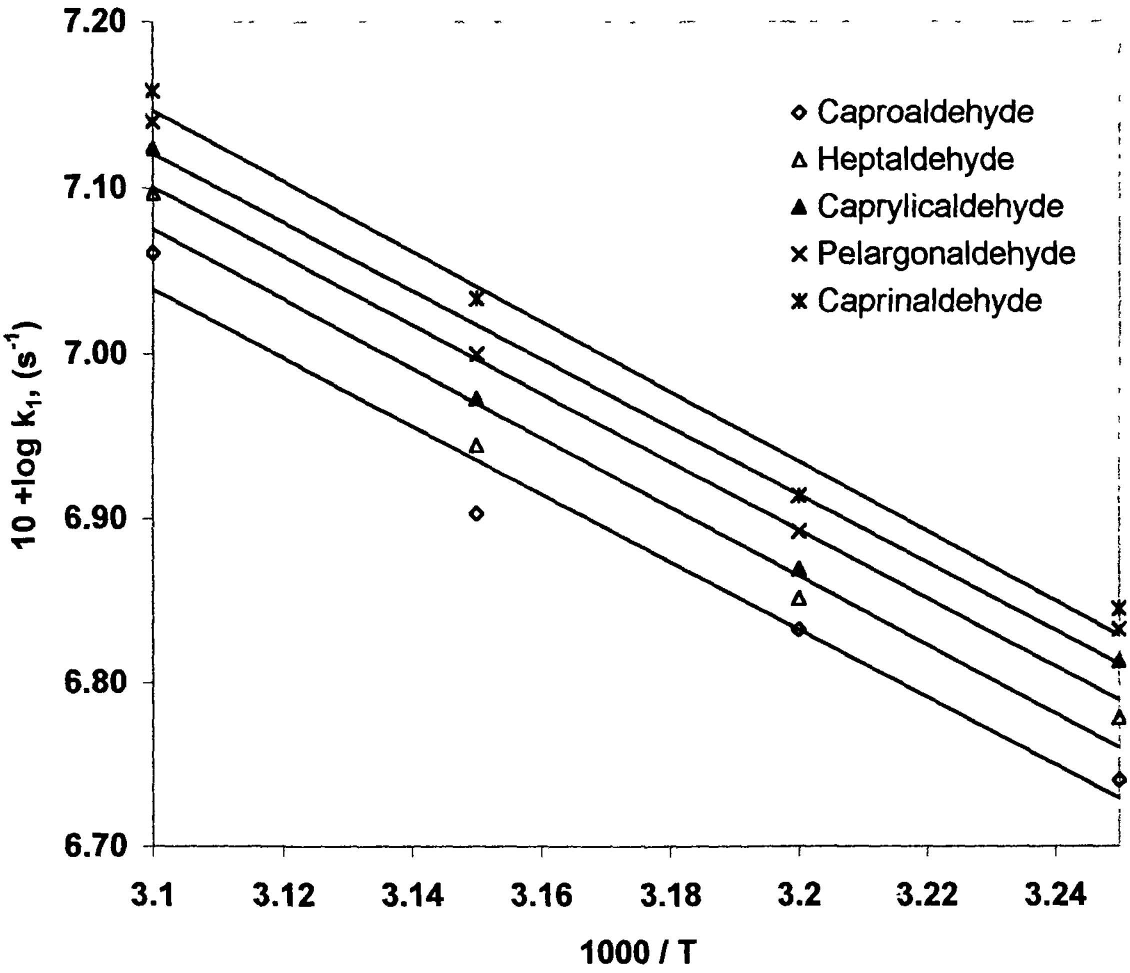


Fig. 15. Plots of log k_1 against reciprocal of temperature.

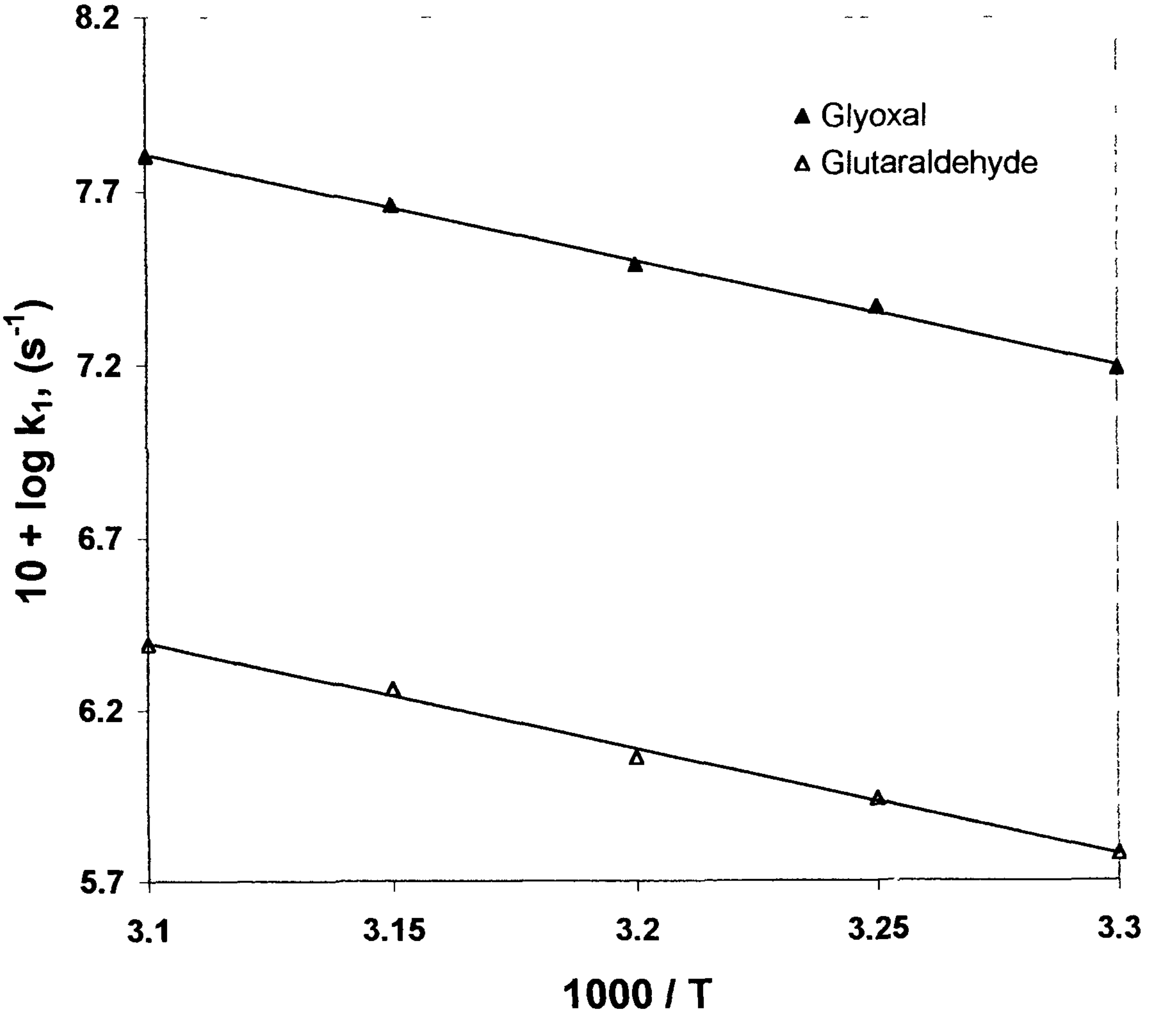


Fig. 16. Plots of log k_1 against the reciprocal of temperature.

Table 17 : Activation Parameters for Aliphatic Aldehydes

Substrate	E (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Acetaldehyde	56	54	-161	102
Propionaldehyde	54	51	-170	104
Butyraldehyde	51	48	-171	102
Valeraldehyde	45	41	-187	102
Isovaleraldehyde	60	56	-138	96
Isobutyraldehyde	58	54	-132	94
Caproaldehyde	41	39	-189	92
Heptaldehyde	40	37	-191	92
Caprylicaldehyde	38	35	-194	93
Pelargonaldehyde	37	34	-196	93
Caprinaldehyde	36	33	-198	92
Glyoxal	57	53	-121	91
Glutaraldehyde	59	56	-147	92

Error limits : E ± 2 kJ mol^{-1}; $\Delta H^{\neq}$ ± 3 kJ mol^{-1}; $\Delta S^{\neq}$ ± 5 JK^{-1} mol^{-1}; $\Delta G^{\neq}$ ± 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 (37). The large negative values of $\Delta S^{\neq}$ 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 $\Delta G^{\neq}$ values for the oxidation of all the substrates arose due to the changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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

$$\Delta H^{\neq} = \Delta H_0^{\neq} + \beta \Delta S^{\neq} \qquad (13)$$

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 (38). The isokinetic temperature, obtained from the plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, was 581K (Figure 17). Although current views do not attach much physical significance to isokinetic temperatures (39), a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 ($\Delta G^{\neq}$) were nearly constant, indicating that the same mechanism operated for the oxidation of all the aliphatic aldehydes studied in this investigation.

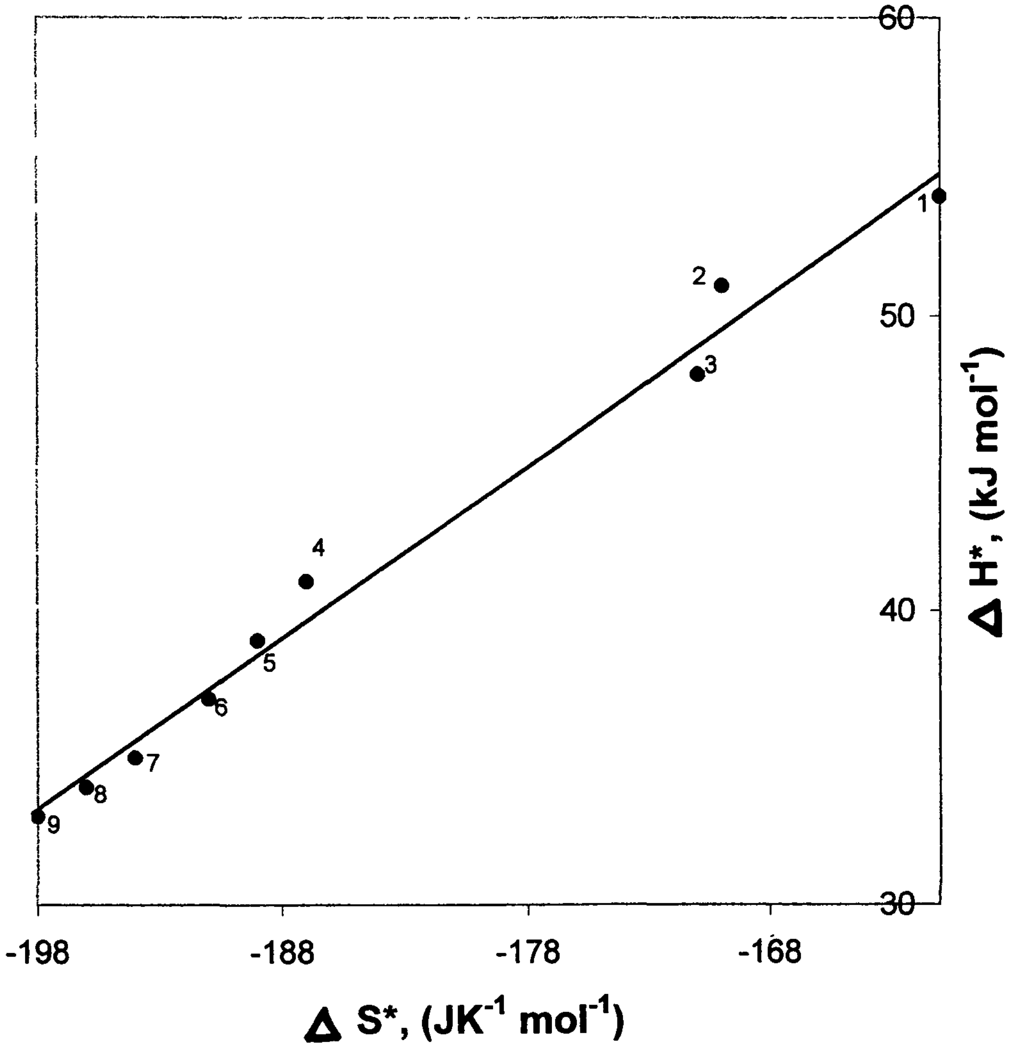


Fig. 17. Plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ for acetaldehyde (1), propionaldehyde (2), butyraldehyde (3), valeraldehyde (4), caproaldehyde (5), heptaldehyde (6), caprylicaldehyde (7), pelargonaldehyde (8), caprinaldehyde (9).

Induced polymerization

Since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was observed that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (40). This indicated that a one-electron oxidation was unlikely. Control experiments were performed in the absence of the respective substrates. The concentration of the oxidant (QDC) did not show any appreciable change.

Structure and Reactivity

It would be pertinent to examine correlations between the structures of the aldehydes and their reactivities. The data in Tables 2a, 2b, 3 and 4 have to be taken into account while establishing such correlations. The order of reactivities observed was :

a. Acetaldehyde < Propionaldehyde < Butyraldehyde < Valeraldehyde (Table 2a).

b. Isovaleraldehyde < Isobutyraldehyde (Table 2b).

c. Caproaldehyde < Heptaldehyde < Caprylicaldehyde < Pelargonaldehyde < Caprinaldehyde (Table 3).

d. Glutaraldehyde < Glyoxal (Table 4).

The relative rates of oxidation for all the aldehydes (Tables 2a, 3 and 4) indicated that the rates of oxidation were dependent on the length of the alkyl chain of the aldehydes. Electron-releasing groups (Tables 2a and 3) accelerated the oxidation process by increasing the electron availability at the oxygen of the aldehydic carbonyl group. This would facilitate the attack of the electrophile (protonated QDC), which would account for the observed order of reactivity.

The rate of oxidation of isobutyraldehyde was faster than that for isovaleraldehyde (Table 2b). The observed order of reactivity was due to the fact that the aldehyde function was closer to the isomethyl group in isobutyraldehyde. This proximity effect would have a direct influence on the reactivities of these two aldehydes, thereby facilitating the attack of the electrophile (protonated QDC). This would result in the increased rate of oxidation of isobutyraldehyde, over that of isovaleraldehyde.

The observed order of reactivity was glyoxal > glutaraldehyde (Table 4). The presence of methylene groups between the two aldehyde moieties would decrease the electron availability at the oxygen of the aldehydic carbonyl group, preventing the attack of the electrophile (protonated QDC) as more methylene groups were inserted between the two aldehydic groups. The net result was the faster rate of oxidation of glyoxal, over that of glutaraldehyde.

Mechanism

There have been several reports on the oxidation of aliphatic aldehydes by various oxidants (4, 11, 12, 41, 42). These investigations showed that the oxidation of aldehydes generally occurred either by oxidation of the terminal -CHO group or by the attack of the oxidant at the α-carbon atom. In the former case, acids were reported as the products, whereas α-hydroxy acids have been obtained in the latter case. Aldehydes exist in three forms : (a) the hydrated aldehydes ; (b) enol-enolate ion; and (c) the free aldehydes. The actual species involved in the oxidation would be determined by the kinetic data and the product analysis, and would be independent of the nature of the oxidant (one-electron or two-electron). For example, the hydrated form of the aldehyde was the reactive species in the presence of one-electron oxidants such as Cu(III) in alkaline medium (11), and Ag(II) in acid medium (41). The enol was suggested as the reactive species in the oxidation by V(V) in acid medium (12), and by hexacyanoferrate(III) in alkaline medium (4). Such contrasting situations were also reported in the presence of two-electron oxidants such as Ag (III) in alkaline medium, wherein the hydrated aldehyde was assumed to be the reactive species (12). In the oxidation of aldehydes by chloroamine-T, the enolate ion was reported to be the reactive species (42). There were some reports where the free aldehyde was suggested to be the reactive species, as in the case of Ce (IV) ions (43, 44).

It has been shown that aliphatic aldehydes are extensively hydrated in aqueous solutions (17, 45-51). The aldehyde hydrate dissociation constants (K_d) pertaining to the reaction:

$RCH(OH)_2 \overset{K_d}{\rightleftharpoons} RCHO + H_2O$ are given (Tables 18, 19).

Table 18. QDC Oxidation of Aliphatic Aldehydes at 313 K

Aldehydes	K_d	$10^4 k_1 / s^{-1}$	k_{Hy} ($M^{-2} s^{-1}$)	k_A ($M^{-2} s^{-1}$)
Acetaldehyde	0.67	0.30	2.05 ± 0.04	3.05 ± 0.05
Propionaldehyde	1.4	0.77	10.81 ± 0.15	7.70 ± 0.10
Butyraldehyde	2.1	0.85	18.09 ± 0.19	8.59 ± 0.11
Valeraldehyde	2.8	0.91	25.61 ± 1.09	9.13 ± 0.40

Table 19. QDC Oxidation of Long Chain Aliphatic Aldehydes at 313 K

Aldehydes	K_d	$10^4 k_1 / s^{-1}$	$k_{Hy} (M^{-2}s^{-1})$	$k_A (M^{-2}s^{-1})$
Caproaldehyde	2.9	6.8	198 ± 3	68.1 ± 0.6
Heptaldehyde	3.2	7.1	229 ± 2	71 ± 0.4
Caprylicaldehyde	3.7	7.4	272 ± 4	73 ±1.2
Pelargonaldehyde	4.2	7.8	326 ± 3	78 ± 0.6
Caprinaldehyde	4.5	8.2	370 ± 4	82 ± 0.3

From k_1 and K_d, two sets of rate constants were computed. Values of k_{Hy} were obtained by assuming that only the hydrated form appears in the rate law :

$$v = k_{Hy} [QDC] [RCH(OH)_2] \qquad (14).$$

Similarly, k_A was calculated using the concentration of free aldehydes according to the rate law :

$$v = k_A [QDC] [RCHO] \qquad (15).$$

The values of k_{Hy} and k_A have been shown (Tables 18 and 19). Using the σ values (52), plots of log k_{Hy} against σ were linear (r = 0.999 and 0.996), with slopes of $\rho = -1.63$ (Table 18, Figure 18), and $\rho = -1.16$ (Table 19, Figure 20). The correlation of σ with k_A gave $\rho = -1.33$ (Table 18, Figure 19), and $\rho = -0.371$ (Table 19, Figure 21).

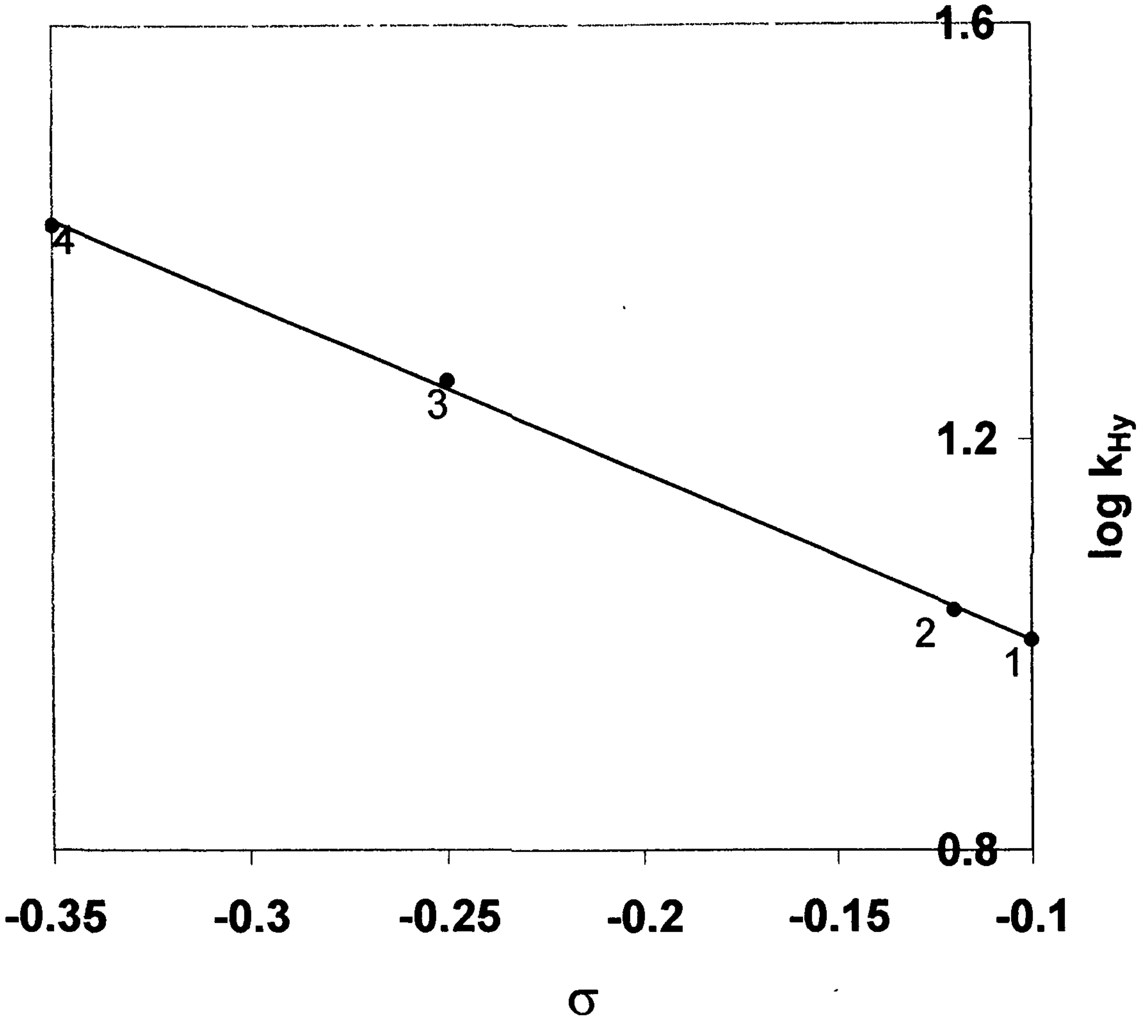


Fig. 18. Plot of σ against log k_{Hy} for acetaldehyde (1), propionaldehyde (2), butyraldehyde (3), valeraldehyde (4).

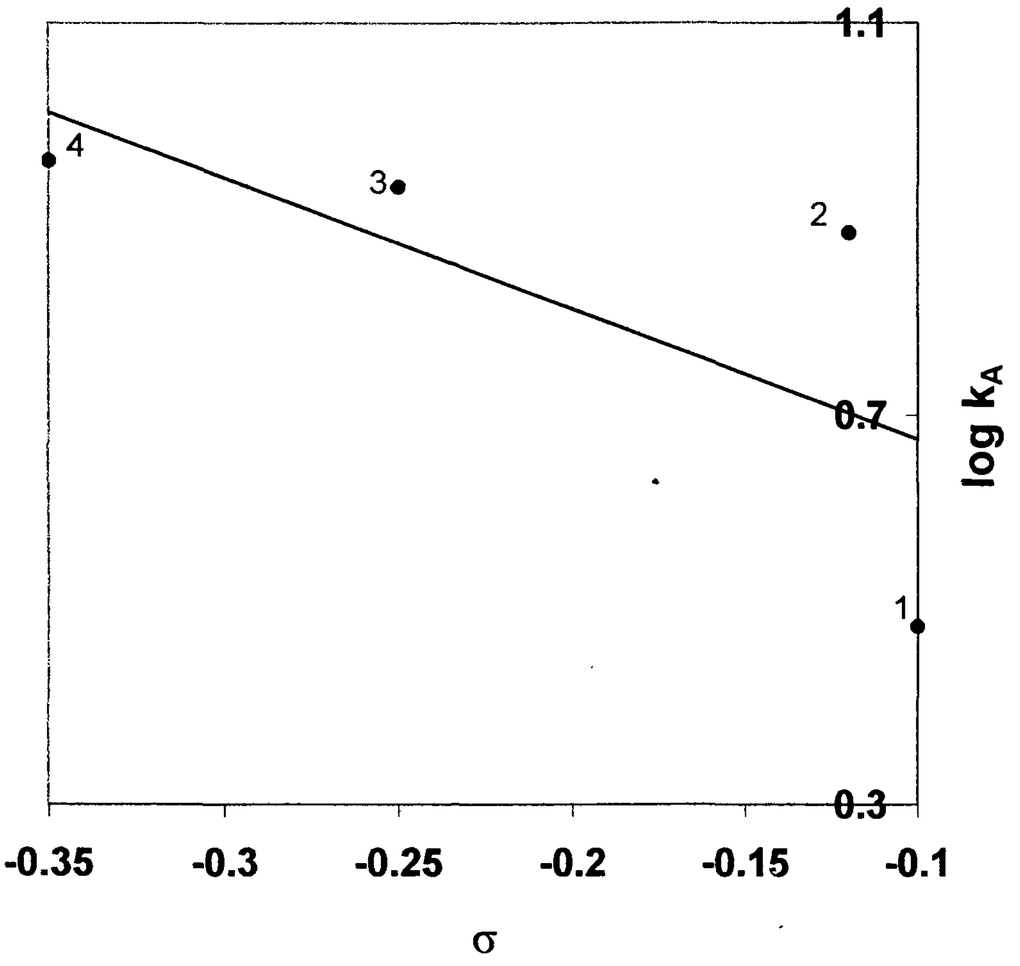


Fig. 19. Plot of σ against log k_A for acetaldehyde (1), propionaldehyde (2), butyraldehyde (3), valeraldehyde (4).

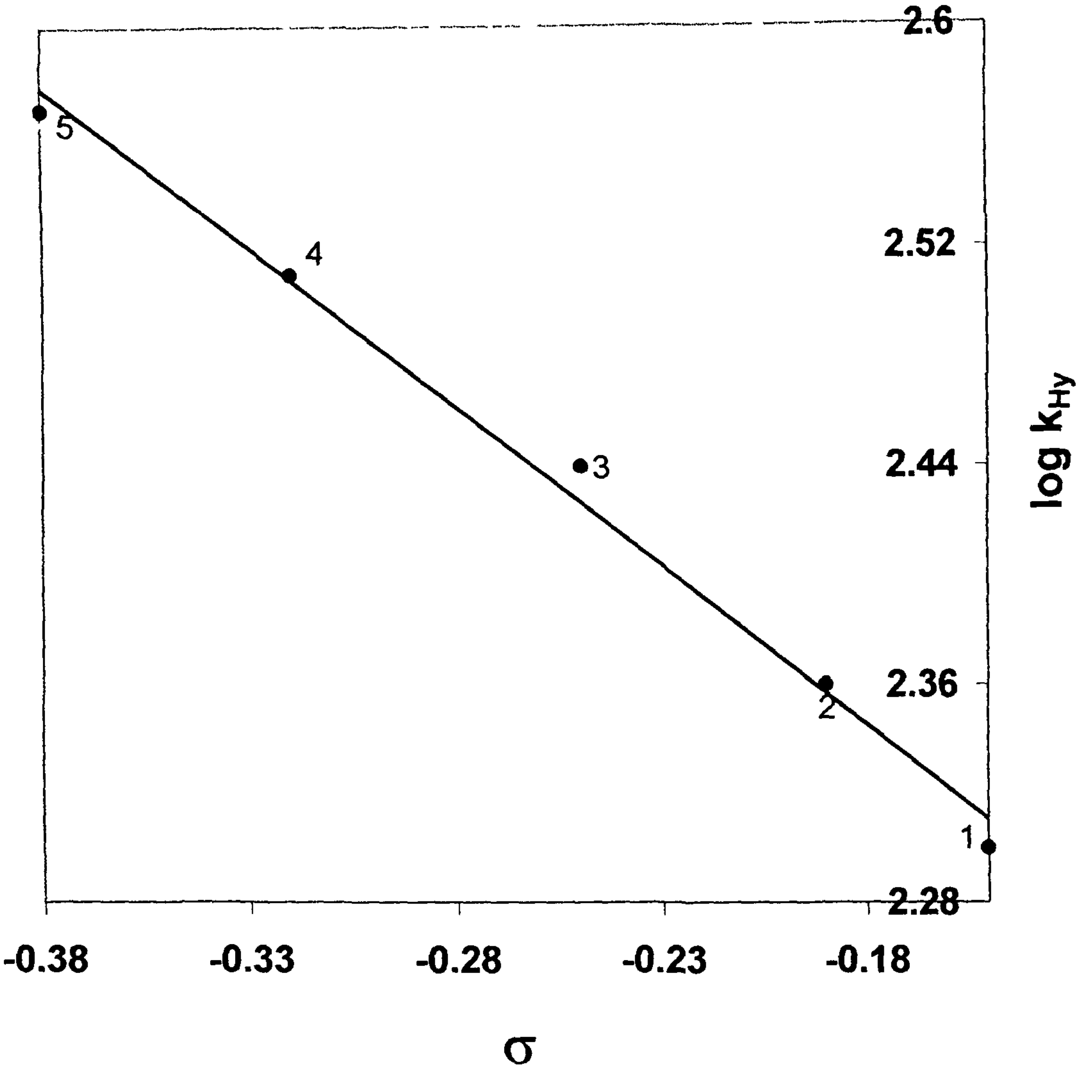


Fig. 20. Plot of σ against log k_{Hy} for caproaldehyde (1), heptaldehyde (2), caprylicaldehyde (3), pelargonaldehyde (4) caprinaldehyde (5).

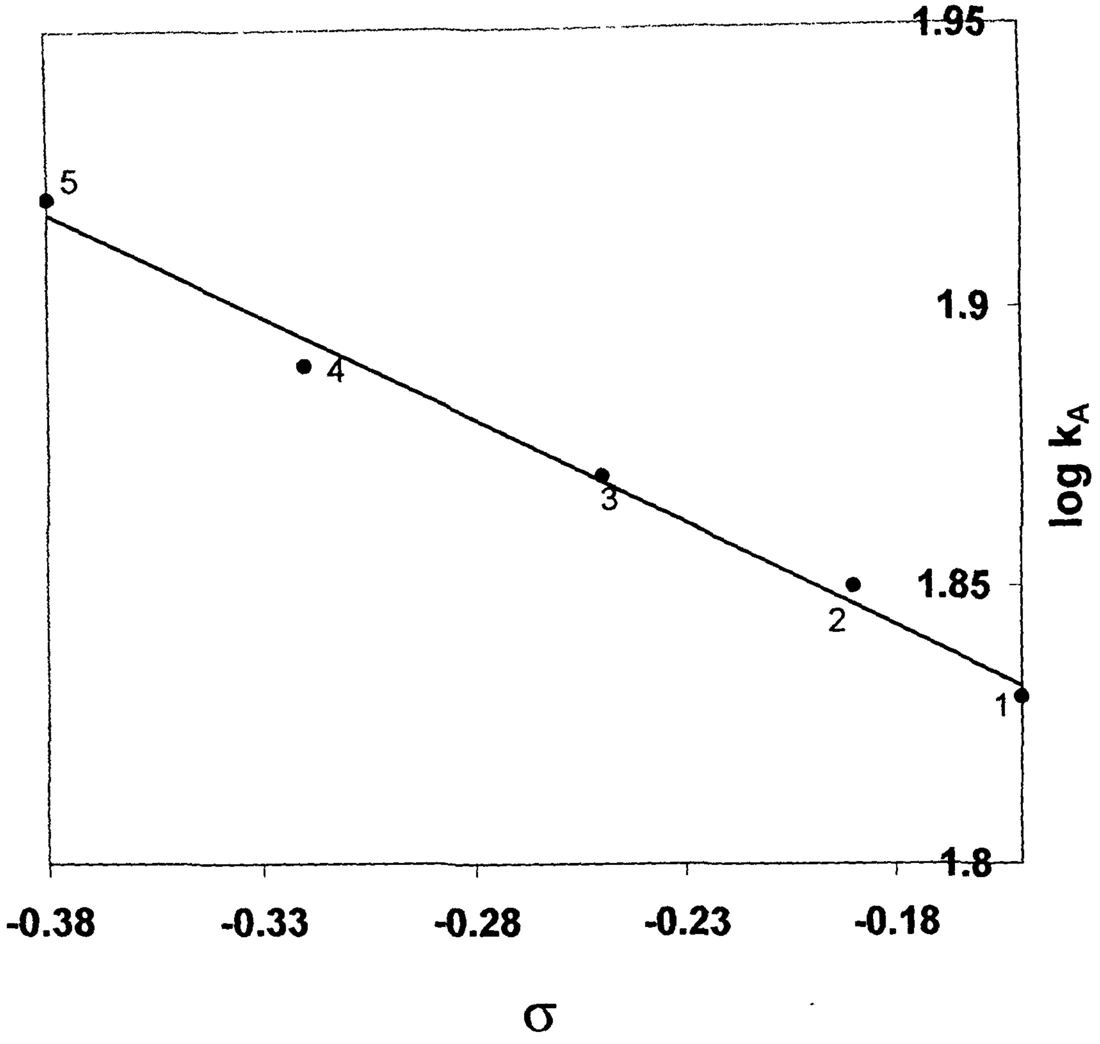


Fig. 21. Plot of σ against log k_A for caproaldehyde (1), heptaldehyde (2), caprylicaldehyde (3), pelargonaldehyde (4) caprinaldehyde (5).

It would be pertinent to compare our ρ values (-1.33 and -0.371), with the ρ values (ρ = +1.02 and +0.77) obtained for a series of aromatic aldehydes in 91% acetic acid (53,54). Since aromatic aldehydes were hydrated to a small extent, the observed ρ values have to be compared with our values of ρ = -1.33 and -0.371 obtained from the k_A values defined by eq. 15. The similarity between these values (ρ = +1.02 and +0.77) and our values (ρ = -1.33 and -0.371) was satisfactory in that for both cases, small values were obtained. The value of ρ could be interpreted as being due a superimposed effect of the substituents on the hydration equilibrium, wherein it had been shown that all the aldehydes oxidized by chromic acid were completely hydrated in aqueous solution (55). The correlation with k_{Hy} thus supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen transfer reaction between the free aldehyde and QDC was very unlikely. This evidence provided additional support for the mechanistic pathway wherein the slow step was the oxidative decomposition of the chromate ester of the aldehyde hydrate.

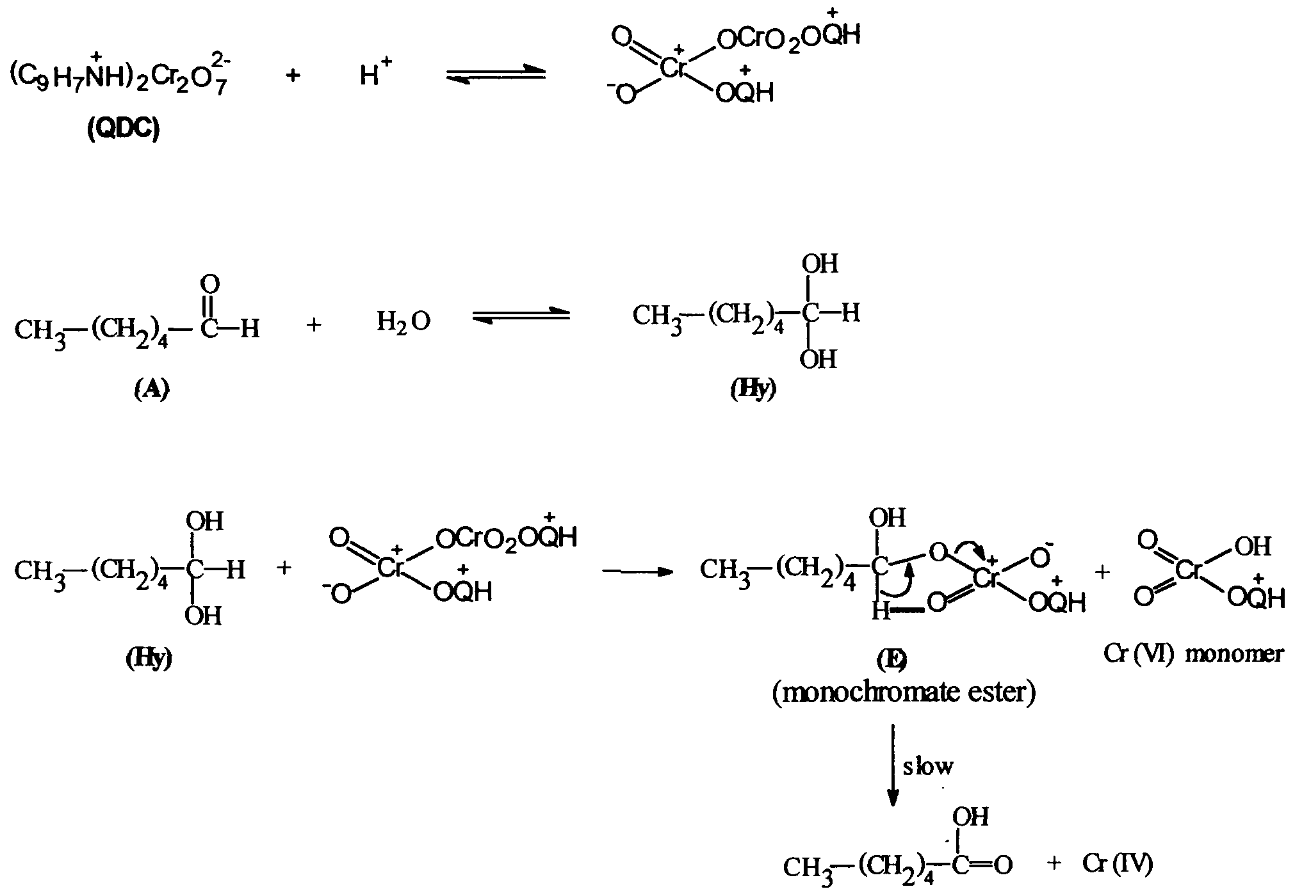
Owing to the close resemblance between aldehyde hydrates and alcohols both in structure and in many aspects of oxidation, it would be expected that there would be a similarity in the reaction intermediate and transition state of the two oxidation reactions. It has been shown that the oxidation of alcohols by chromic acid had involved the decomposition of the protonated acid chromate ester in the rate-determining step (56). In an analogous manner, the oxidation of aldehydes could be interpreted by assuming the reversible formation of a similar intermediate (an ester of the aldehyde hydrate), which would undergo decomposition in the rate-determining step. The ester of the aldehyde hydrate would thus be in equilibrium with the free aldehyde and the aldehyde hydrate (57). It would therefore be immaterial whether it was formed by a carbonyl addition reaction to the free aldehyde, or by esterification of the hydrate. It may be added that the esterification reaction has more utility since it helps to understand and predict aldehyde oxidation reactions and their relationship to the closely related oxidation of alcohols. Esterification reactions depend much less on structural changes (58), and the equilibrium constant can be regarded as independent of the structure of the ester. In the oxidation of isopropyl alcohol by chromic acid (59), a rate law was proposed which was later found to be applicable to the oxidation of primary and secondary alcohols (60-64). It was established that such oxidation reactions proceeded via the intermediate formation of a chromate ester (65,66), which then underwent decomposition to the corresponding carbonyl compound (67). The intermediate formation of the chromate ester was confirmed by a study of the oxidation of sterically hindered alcohols by chromic acid (56).

A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. If the chromium was coordinated through the O-H group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and the conversion to the corresponding carboxylic acid could be rationalized. The mechanistic pathway involved the rapid formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the aldehyde hydrate (step 2). The overall rate of the reaction would depend on the position of equilibrium (step 1), and the rate of the reaction (step 2).

In order to fully understand the mechanism of the reactions, the manner of electron transfer has to be established. The first step involved the transfer of the hydrogen atom from the -OH group (of the aldehyde hydrate) to the oxidant, enabling the formation of the ester. A unimolecular decomposition of the ester can be written in which the hydrogen is bonded in the transition state to both, the aldehydic carbon atom and the oxygen attached to chromium. Electron flow in a cyclic transition state has been considered (68,69), and could be rationalized by assuming that if the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the process of electron transfer could take place through the carbon-oxygen-chromium bond. This would not only facilitate the formation of the chromate ester, but would enhance the ease of conversion to the product. Such a transition state envisaged the transfer of electrons towards the chromium, occurring by the formation of the carbon-hydrogen-oxygen bonds, as well as the carbon-oxygen-chromium bonds.

The slow step of the reaction involved the participation of the aldehyde hydrate, QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, which was confirmed by the kinetic isotope effect observed for the oxidation of acetaldehyde ($k_H/k_D = 6.4$), which indicated a cleavage of the carbon-hydrogen bond. Similar kinetic isotope effects had been observed in earlier investigations, establishing a carbon-hydrogen bond cleavage in the rate-determining step of the reaction (70-72). The proton was thus removed in the cyclic transition state (co-planarity of all the atoms involved), the centre of which resided on an electron-dense oxygen in the chromate ester (73). This electrocyclic mechanism for the oxidation of aldehyde hydrates by QDC involved six electrons; being a Hückel-type system (4n + 2), this was an allowed process (74). This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant. The sequence of reactions has been shown in the Scheme.

SCHEME



$$\mathrm{Cr\,(IV)} + \mathrm{Cr\,(VI)} \xrightarrow{\text{fast}} 2\mathrm{Cr\,(V)}$$

$$\mathrm{Cr\,(V)} + \text{substrate} \xrightarrow{\text{fast}} \text{product} + \mathrm{Cr\,(III)}$$

The proposed mechanism is supported by the observed negative entropies of activation. As the charge separation takes place in the transition state, the two ends become highly solvated. This would result in an immobilization of a large number of solvent molecules, and would be reflected in the loss of entropy.

The mechanism for the oxidation of aliphatic aldehydes by QDC has been shown (Scheme). The conversion of Cr(IV) to Cr(III) proceeded by a disproportionation reaction. It has been shown that for the reaction given by Cr(IV) + Cr(VI) → 2 Cr(V), the standard potential for the Cr(VI) - Cr(V) couple is extremely favourable ($E^0 = 0.62$ volt) (ref. 65, 66), 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 (65, 66, 75).

If the mechanism shown in the Scheme is correct, then the attack of the protonated QDC (**PQ**) on the aldehyde hydrate (**Hy**) would be crucial, and would be favoured by the formation of the cyclic chromate ester (**E**). Based on the mechanism shown in the Scheme, the rate law has been derived as follows:

$$- d\,[QDC] / dt = k_3\,[E] = k_3\,[Hy]\,[PQ] \qquad (16),$$

where $[PQ] = K_1\,[QDC]\,[H^+]$, and $[Hy] = K_2\,[A]\,[H_2O]$.

Hence, $- d\,[QDC] / dt = K_1K_2k_3\,[A]\,[QDC]\,[H^+]$, (17),

Which showed a first order dependence on the concentrations of each (substrate, oxidant, and acid). Hence, $- 2.303\ d \log [QDC] / dt = k = K_1K_2k_3\,[A]\,[QDC]\,[H^+]$. This rate law explains all the experimentally observed results.

In the present investigation, kinetic data has been presented to establish the mechanistic pathway for the oxidation of aliphatic aldehydes by quinolinium dichromate (QDC) as proceeding via the hydrated form of the aldehydes.

The data collected in the present study demonstrated that the QDC oxidation of aliphatic aldehydes led to the formation of the corresponding carboxylic acids, substantiating the mechanism wherein there was an attack of the oxidant on the aldehyde hydrate. There was no cleavage of the carbon-carbon bond, thus ruling out the possibility of any enolization. Under the present experimental conditions, there was no further oxidation of the products. This study has thus emphasized the efficiency of QDC reacting with aliphatic aldehydes, suggesting the possibility that such reactions could prove to be useful as a general route for the synthesis of carboxylic acids.

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CHAPTER - II

KINETICS OF OXIDATION OF α, β- UNSATURATED ALDEHYDES

The oxidation of acrylaldehyde by manganic pyrophosphate showed that the rate-determining step was acid-catalyzed and did not involve the oxidant. It was suggested that the reaction pathway was via the formation of the enol. The first oxidation product was glyceraldehyde which underwent oxidative degradation giving formaldehyde and carbon dioxide (1).

Using selenium dioxide as catalyst, hydrogen peroxide was used to oxidize acrylaldehyde and methacrylaldehyde to the corresponding acids. It was found that the use of low water content resulted in higher yields of the acids (2).

The kinetics and product of the oxidation of aldehydes in acetic acid, catalyzed by metal salt have been investigated. It was observed that at high aldehyde concentration, the oxidation rate was dependent on the first power of the oxygen pressure to a fractional power of catalyst concentration. The kinetic results were explained through a mechanistic pathway proceeding via radical intermediates (3).

The liquid phase oxidation of acrylaldehyde in various solvents such as butyric and valeric acid using $Co(acac)_3$ as catalyst gave acrylic acid as the major product (4).

When α, β- unsaturated aldehydes were oxidized with peroxymonosulfuric acid (Caro acid), in the presence of alcohols (methanol, ethanol), the esters of the corresponding acids were obtained in high yield. It was proposed that these oxidation reactions proceeded through a hemiacetal peroxymonosulphate (5).

A variety of methods for the conversion of α, β- unsaturated aldehydes to corresponding carboxylic acids were explored. It was found that sodium chlorite worked well with sensitive substrates containing the α-methylene aldehyde unit. This reagent was found to effect clean oxidation and in a stereospecific manner (6).

Studies on the kinetics and mechanism of oxidation of cinnamaldehyde by chloroamine-T in HCl and H_2SO_4 medium were carried out. Various kinetic parameters were determined, and the rate-determining step involved the formation of an intermediate between a complex anion and a dipole (7).

The liquid phase oxidative cyclization of crotonaldehyde to furan was found to proceed efficiently in $CuCl_2$, CuCl , or $PdCl_2$ aqueous solutions containing alkali or ammonium halide and HCl as additives. This was observed to be a catalytic process (8).

PRESENT WORK

The present work is a detailed kinetic study of the oxidation of α,β-unsaturated aldehydes by quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], in acid medium, using 50% aqueous acetic acid as the solvent, under a nitrogen atmosphere.

The α,β-unsaturated aldehydes chosen for the purpose of oxidation by QDC have included:

Acrylaldehyde, Methacrylaldehyde, Crotonaldehyde, Cinnamaldehyde.

Stoichiometry (vide "Experimental")

The stoichiometries of the oxidation reactions were determined. The stoichiometric ratios, Δ[QDC] / Δ[Substrate], were in the range 0.66 - 0.69 (Table 1).

Table 1 : Stoichiometrics of the Oxidation of the Substrates;

([Substrate] = 0.005 M; T = 313 K)

$[H_2SO_4]$ / M	0.10	0.25	0.50
10^2[QDC] / M	2.50	2.60	2.70
Δ[QDC] / Δ[Acrylaldehyde]	0.66	0.69	0.66
Δ[QDC] / Δ[Methacrylaldehyde]	0.68	0.67	0.69
Δ[QDC] / Δ[Crotonaldehyde]	0.66	0.68	0.67
Δ[QDC] / Δ[Cinnamaldehyde]	0.66	0.67	0.68

The stoichiometry conformed to the overall equations :

(a) For acrylaldehyde :

$$3\,C_3H_4O + 2\,Cr^{VI} + 3\,H_2O \rightarrow 3\,C_3H_4O_2 + 2\,Cr^{III} + 6\,H^+ \qquad (1)$$

(b) For methacryldehyde :

$$3\,C_4H_6O + 2\,Cr^{VI} + 3\,H_2O \rightarrow 3\,C_4H_6O_2 + 2\,Cr^{III} + 6\,H^+ \qquad (2)$$

(c) For crotonaldehyde :

$$3\,C_4H_6O + 2\,Cr^{VI} + 3\,H_2O \rightarrow 3\,C_4H_6O_2 + 2\,Cr^{III} + 6\,H^+ \qquad (3)$$

(d) For cinnamaldehyde :

$$3\,C_9H_8O + 2\,Cr^{VI} + 3\,H_2O \rightarrow 3\,C_9H_8O_2 + 2\,Cr^{III} + 6\,H^+ \qquad (4)$$

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 2.

Table 2 : Dependence of Rate Constants on the Concentration of Oxidant

([Substrate] = 0.03 M; [H_2SO_4] = 0.5 M; [AcOH] = 50% (v/v); T = 313 K)

	10^4 k_1 / s^{-1}			
10^3 [QDC] / M	Methacrylaldehyde	Acrylaldehyde	Crotonaldehyde	Cinnamaldehyde
3.0	13.4	12.1	5.1	0.80
1.2	13.2	12.2	5.2	0.81
0.6	13.3	12.5	5.1	0.80
0.4	13.6	12.4	5.4	0.82
0.3	13.4	12.1	5.3	0.83

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 [H^+]. The results have been recorded in Table 3.

Table 3 : Dependence of Rate Constants on the Concentration of α, β-Unsaturated Aldehydes ([QDC] = 0.003 M; [H_2SO_4] = 0.5 M; [AcOH] = 50% (v/v); T = 313 K)

	10^4 k_1 / s^{-1}			
10^2 [Substrate] / M	Methacrylaldehyde	Acrylaldehyde	Crotonaldehyde	Cinnamaldehyde
3.0	13.4	12.1	5.1	0.80
10.0	45.6	40.1	17.1	2.60
17.5	76.1	71.1	28.5	4.10
25.0	112.0	99.8	42.5	6.20
30.0	136	120	51.0	7.80
	10^2 k_2 / M^{-1} s^{-1}			
	4.47	4.03	1.7	0.26
	4.56	4.01	1.7	0.26
	4.35	4.06	1.6	0.23
	4.48	3.99	1.7	0.25
	4.53	4.0	1.7	0.26

$k_2 = k_1$ / [Substrate]

Plots of k_1, the pseudo-first-order rate constant, against the concentrations of substrates 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.

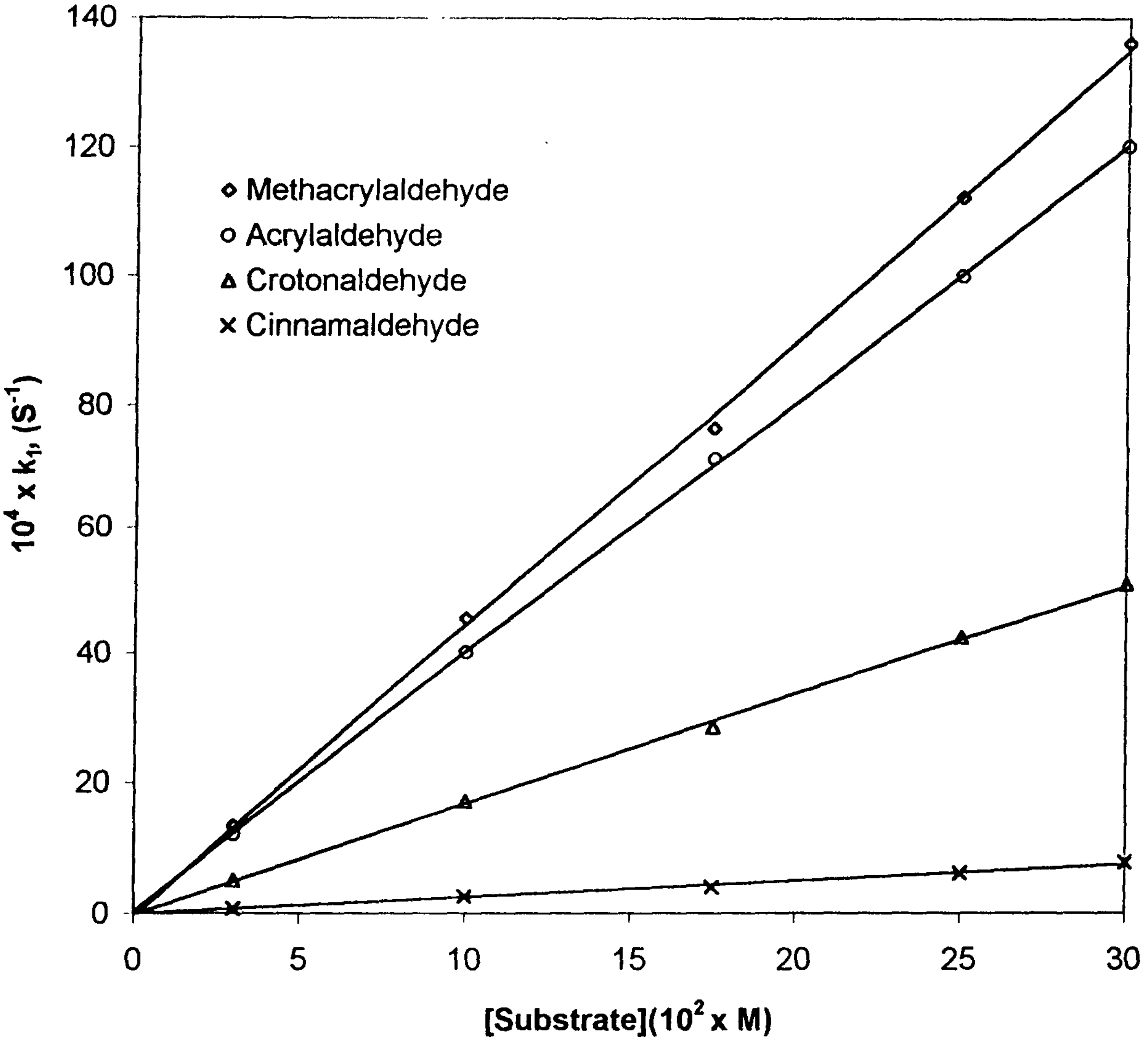


Fig. 1. Plots of k_1 against the concentrations of substrates.

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 1.50 M (Table 4).

Table 4 : Dependence of Rate Constants on the Acid Concentration for α, β- Unsaturated Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 50% (v/v); T = 313 K)

	10^4 k_1 / s^{-1}			
$[H_2SO_4]$ / M	**Methacrylaldehyde**	**Acrylaldehyde**	**Crotonaldehyde**	**Cinnamaldehyde**
0.5	13.4	12.1	5.1	0.80
0.75	20.1	18.2	7.5	1.20
1.0	27.2	24.1	10.2	1.60
1.25	34.2	30.1	12.6	2.02
1.50	40.4	36.6	15.1	2.40

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.

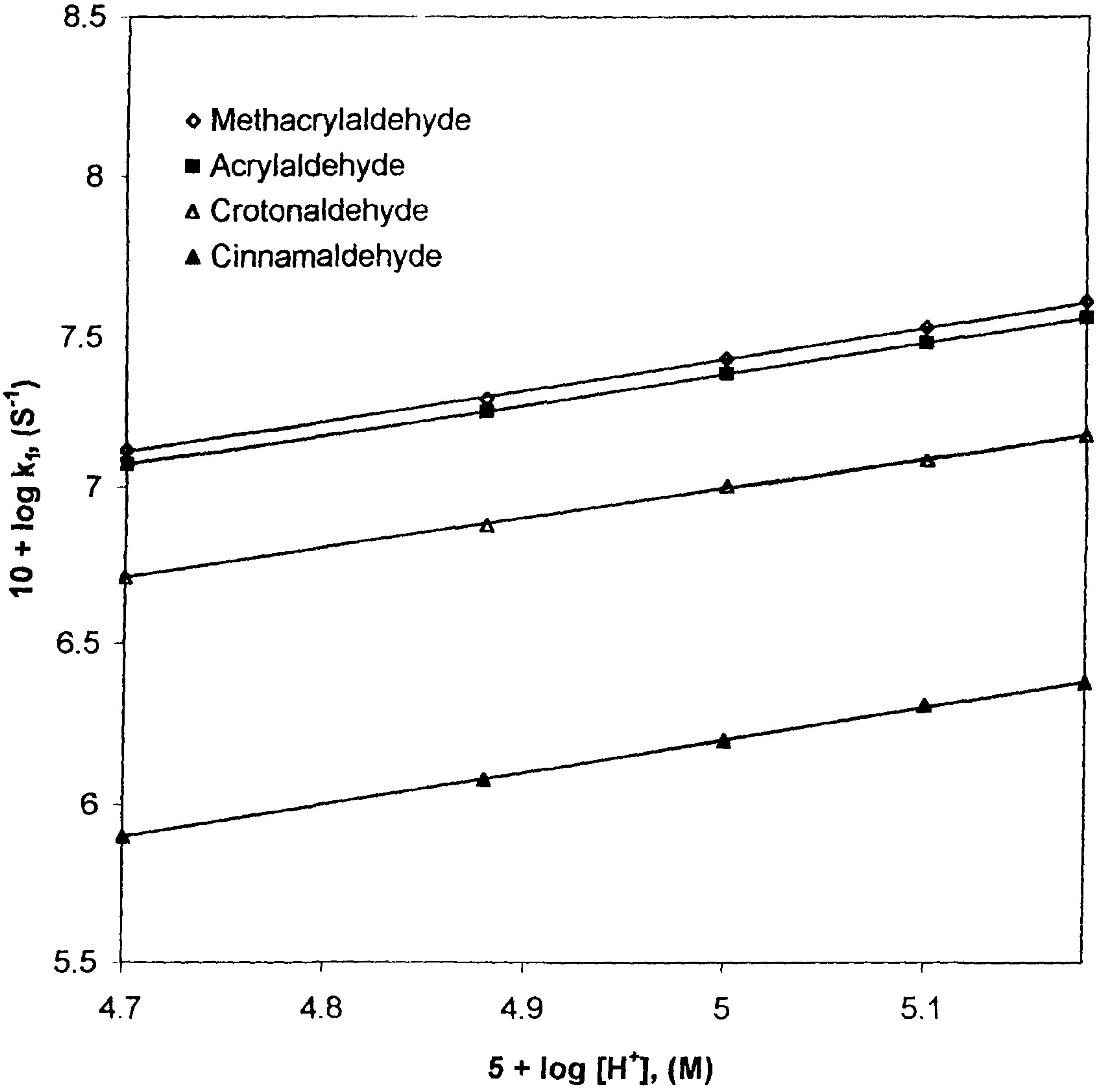


Fig. 2. Plots of log k_1 against log $[H^+]$.

The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated Cr(VI) species in the oxidation reaction. The acid catalysis was related to the structure of the oxidant (QDC), which was converted to a protontated 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 ($HCrO_4^-$) did not exist in aqueous solutions of Cr(VI) compounds (9). Of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of mineral acid would be $HCrO_4^-$ and $Cr_2O_7^{2-}$. 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 (9). 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 (10). In the present investigation, the acid concentrations used were in the range 0.5 to 1.50 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 substrate.

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 :

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

Effect of solvent

The effect of a change in the solvent composition (water-acetic acid, %, v/v) on the rate of oxidation was studied. The dielectric constants (D) of water-acetic acid mixtures were calculated (at 313 K : water = 73.28, acetic acid = 6.29) (11). It was observed that there was an increase in the rate of the reaction, with a decrease in D of the medium (Table 5).

Table 5 : Dependence of Rate Constants on Solvent composition for α, β-Unsaturated Aldehydes ([Substrate] = 0.03 M; [QDC] = 0.003 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

		10^4 k_1 / s^{-1}			
H_2O : AcOH (%, v/v)	**Dielectric Constant (D)**	**Methacryl-aldehyde**	**Acryl-aldehyde**	**Croton-aldehyde**	**Cinnam-aldehyde**
60:40	46.48	7.86	6.4	3.56	0.53
55:45	43.14	10.6	9.3	4.32	0.65
50:50	39.79	13.4	12.1	5.1	0.80
45:55	36.44	17.1	15.3	5.86	1.01
40:60	33.09	20.7	18.5	6.66	1.25

The magnitude of this effect could be analyzed by suggesting that, for the equilibrium $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, a decrease in D of the medium (increase in the acetic acid content), would favour the dichromate form over the chromate form. If ion-pairs were to be formed in this medium, it would be expected that they would have a higher ion-pair association constant for the dichromate ion, and this would again favour the dichromate ion.

In the present investigation, in proceeding from 40% acetic acid to 60% acetic acid, the polarity decreases. The decrease in the polarity of the medium caused an increase in the rate of the reaction (Table 5). Although the range of D used for these reactions was not large, plots of log k_1 versus 1/D were found to be linear, with positive slopes (Figure 3). This suggested an interaction between a positive ion and a dipole (12), and was in consonance with the experimental observation that, in the presence of an acid, the rate-determining step involved a protonated 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.

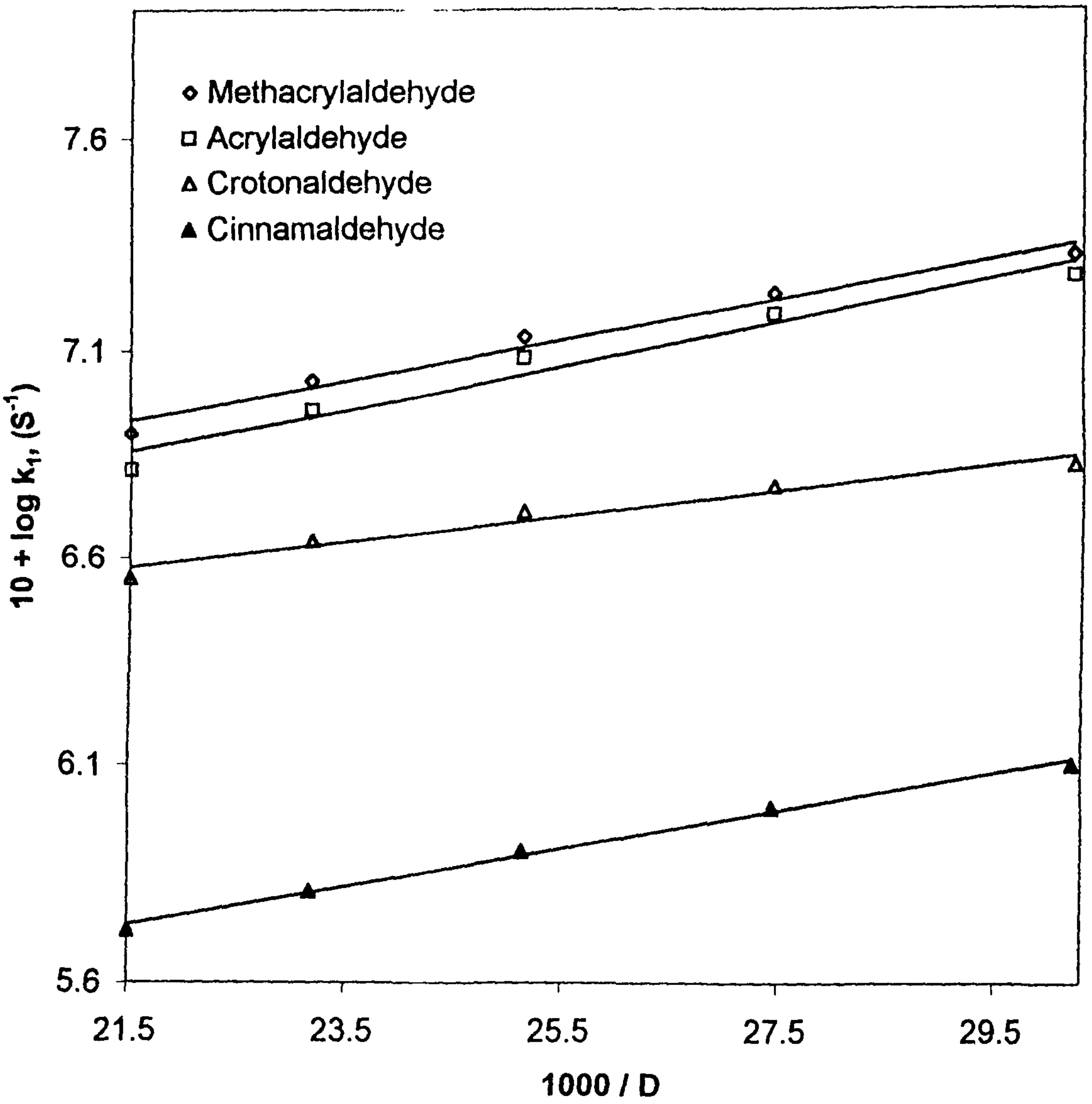


Fig. 3. Plots of log k_1 against the reciprocal of the dielectric constant.

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 and Activation parameters for α, β- Unsaturated Aldehydes ([Substrate] = 0.03 M; [QDC] = 0.003 M; [AcOH] = 50% (v/v); [H_2SO_4] = 0.5 M)

Temperature (±0.1K)	10^4 k_1 / s^{-1}			
	Methacrylaldehyde	Acrylaldehyde	Crotonaldehyde	Cinnamaldehyde
303	7.1	6.2	2.51	0.31
308	10.3	9.1	3.9	0.62
313	13.4	12.1	5.1	0.80
318	20.1	18.5	7.69	1.30
323	27.1	24.7	11.1	1.60
E (kJ mol^{-1})	55	57	61	66
$\Delta H^{\neq}$ (kJ mol^{-1})	52	54	57	63
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-135	-129	-127	-123
$\Delta G^{\neq}$ (kJ mol^{-1})	92	92	94	95

Error limits : E ± 2 kJ mol^{-1}; $\Delta H^{\neq}$ ± 3 kJ mol^{-1}; $\Delta S^{\neq}$ ± 5 JK^{-1} mol^{-1}; $\Delta G^{\neq}$ ± 2 kJ mol^{-1}

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 the Arrhenius equation. The activation parameters (vide "Experimental : Calculations") have been shown in Table 6. The negative values of $\Delta S^{\neq}$ provided support for the formation of a rigid activated complex. The constancy in $\Delta G^{\neq}$ values suggested the probability of a common mechanism being applicable for the oxidation of all the substrates.

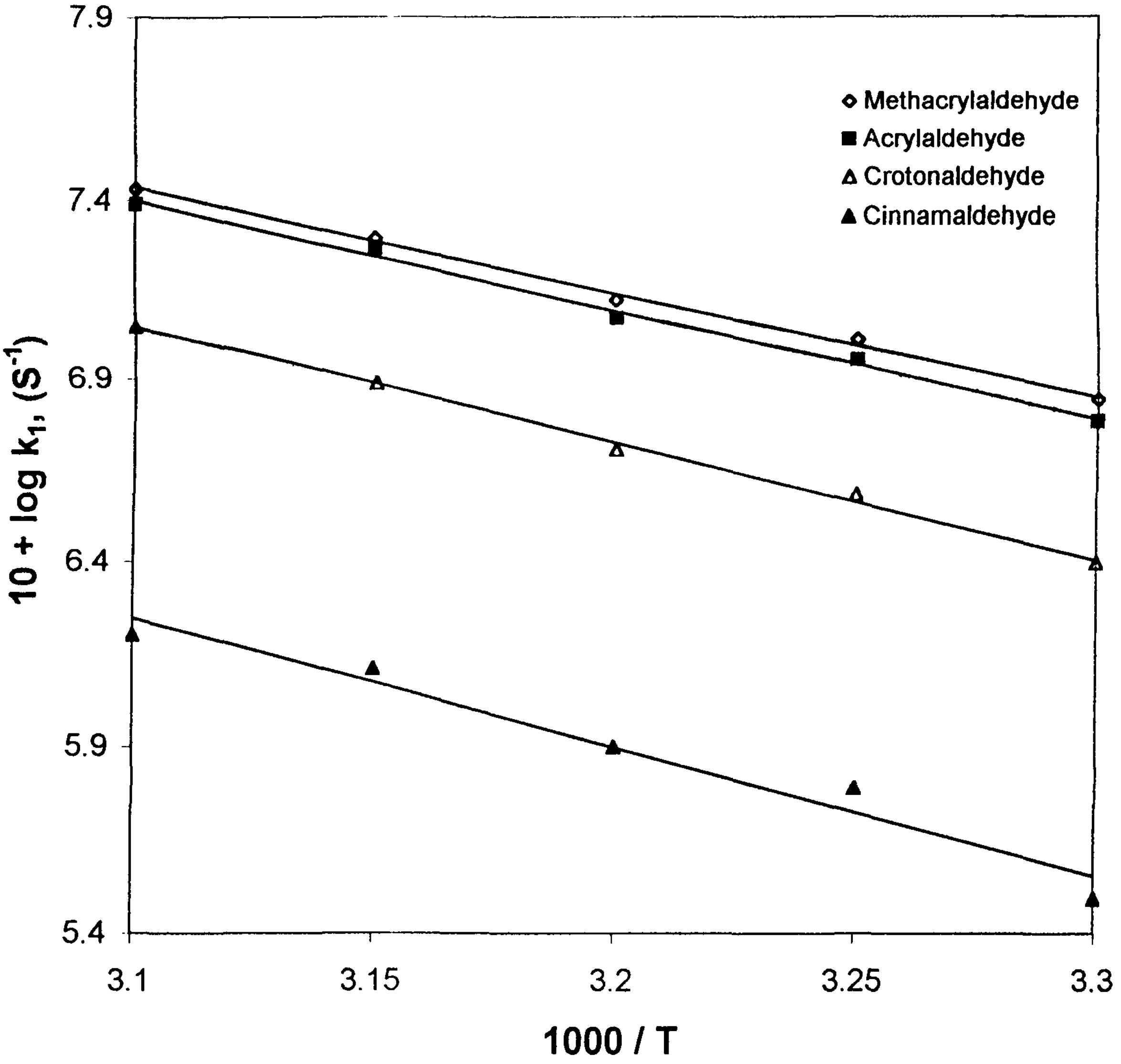


Fig. 4. Plots of log k_1 against the reciprocal of temperature.

Induced polymerization

It was observed that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride (13). This indicated that a one-electron oxidation was unlikely. Control experiments were performed in the absence of the respective substrates. The concentration of the oxidant (QDC) did not show any appreciable change.

Structure and Reactivity

The rate data (Table 2) showed that both acrylaldehyde and methacrylaldehyde underwent a fairly rapid oxidation. It would be justified to assume that the oxidation process did not involve an enolization step. The enolization of acrylaldehyde would have yielded hydroxyallene, which would be improbable. Further, methacrylaldehyde underwent a rapid reaction even though there was no enolizable hydrogen atom. The argument that unsaturated aldehydes could undergo a reaction involving the hydration of the double bond to form a β-hydroxyaldehyde was ruled out, since no such intermediate was isolated during the course of the reaction. The order of reactivity observed for the oxidation of α,β-unsaturated aldehydes by QDC was:

methacrylaldehyde > acrylaldehyde > crotonaldehyde > cinnamaldehyde (Table 2). The kinetic data showed that methacrylaldehyde was oxidized at a slightly faster rate than acrylaldehyde. This would suggest that an α-methyl group has a marginal accelerating influence on the rate of the reaction. The presence of the methyl group (in methacrylaldehyde), adjacent to the site of reaction (carbonyl group), would enhance the reactivity of methacrylaldehyde over that of acrylaldehyde. In crotonaldehyde, the methyl group was far removed from the site of reaction, and hence its reactivity would be much less than that of methacrylaldehyde. The presence of the phenyl group in cinnamaldehyde would exert a deactivating influence on the rate of the reaction, and hence the reactivity of cinnamaldehyde would be the lowest in the series.

Mechanism

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrated form (14-21). Table 7 records the experimental rate constants (k_1) for the oxidation of the aldehydes by QDC. The aldehyde hydrate dissociation constants (K_d) pertaining to the reaction :

$$RCH(OH)_2 \xrightleftharpoons{K_d} RCHO + H_2O \qquad (6)$$

are also given.

Table 7. QDC Oxidation of α,β-Unsaturated Aldehydes at 313 K

Aldehydes	K_d	$10^4\ k_1 / s^{-1}$	$k_{Hy}\ (M^{-1}\ s^{-1})$	$k_A\ (M^{-1}\ s^{-1})$
Methacrylaldehyde	2.3	13.4	34.4 ± 0.53	14.9 ± 0.30
Acrylaldehyde	1.7	12.1	22.8 ± 0.24	13.4 ± 0.13
Crotonaldehyde	1.1	5.1	5.92 ± 0.05	5.4 ± 0.27
Cinnamaldehyde	0.6	0.8	0.51 ± 0.02	0.85 ± 0.04

From k_1 and K_d, two sets of rate constants for the oxidation of the aldehyde in only one of the forms present in solution were computed. The values of k_{Hy} were obtained by assuming that only the hydrate form appears in the rate law: $v = k_{Hy} [QDC] [RCH(OH)_2]$ (7).

Similarly, the values of k_A were calculated using the concentration of free aldehyde according to the rate law: $v = k_A [QDC] [RCHO]$ (8).

The values of k_{Hy} and k_A have been shown in Table 7. Using the σ values as reported by Taft et al (22), a plot of log k_{Hy} against σ was linear (Figure 5), with a slope of $\rho = - 0.92$ ($r = 0.993$). On the other hand, the correlation of σ with k_A (Figure 6) gave a value of $\rho = - 0.56$ ($r = 0.997$).

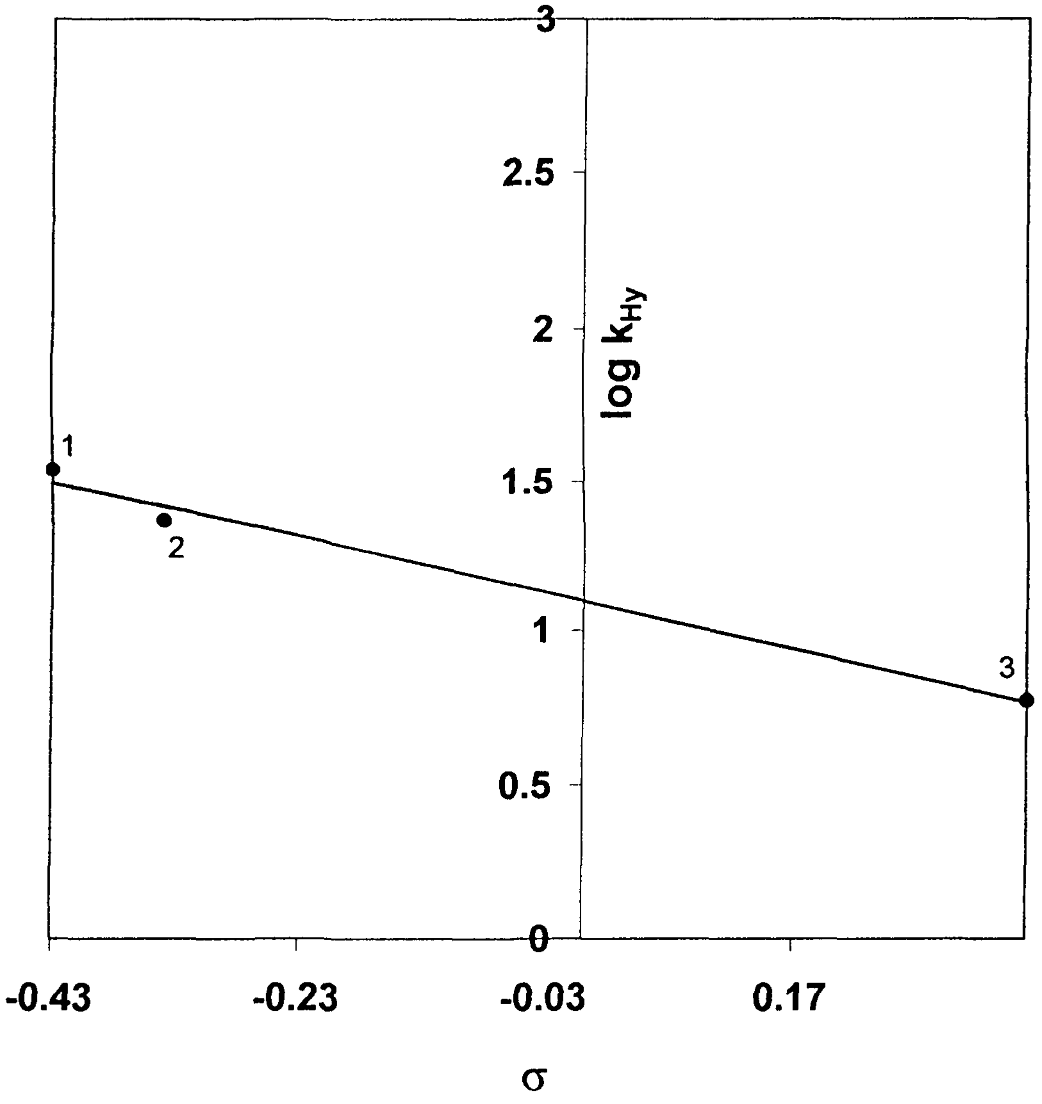


Fig. 5. Plot of σ against log k_{Hy} for methacrylaldehyde (1), acrylaldehyde (2), crotonaldehyde (3).

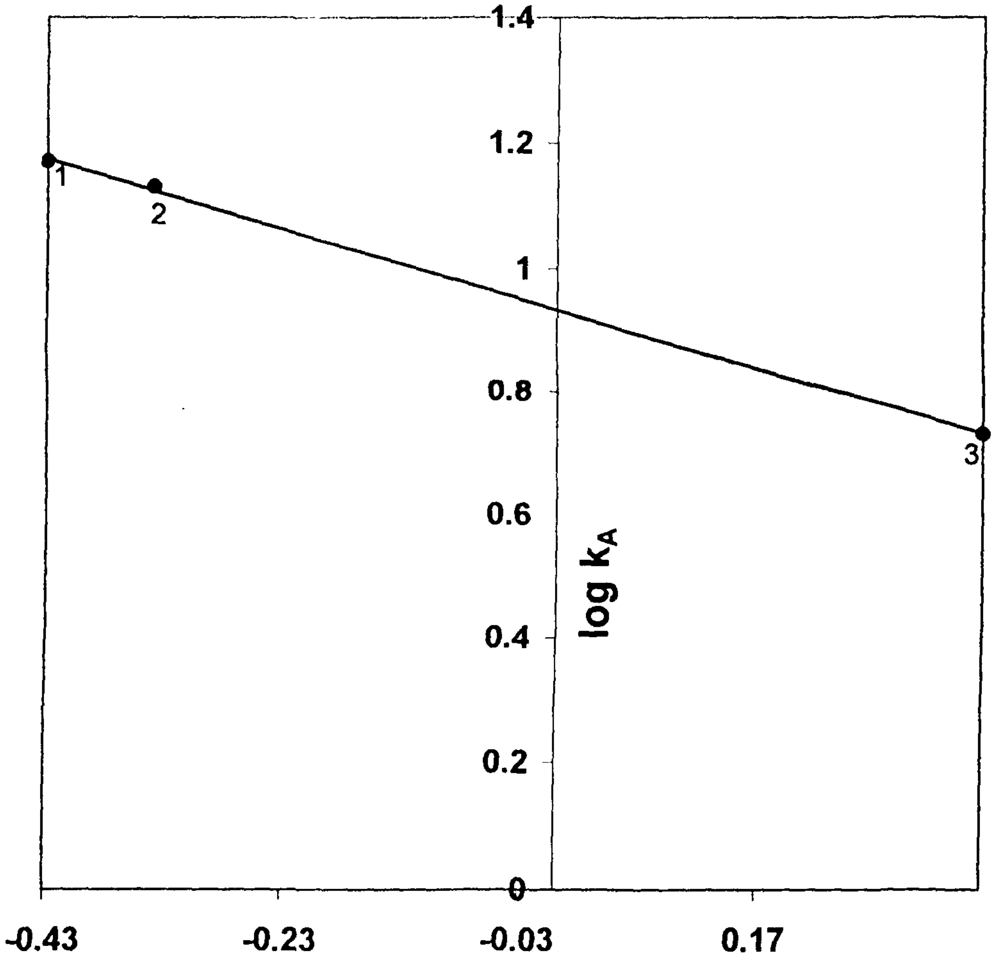


Fig. 6. Plot of σ against log k_A for methacrylaldehyde (1), acrylaldehyde (2), crotonaldehyde (3).

It would be pertinent to compare the ρ value of - 0.56, obtained in this study, with the ρ values obtained for a series of aromatic aldehydes in 91% acetic acid (23,24). Since aromatic aldehydes were hydrated only to a small extent, the observed ρ values (ref. 23, 24) have to be compared with the value of ρ obtained using the k_A values for aliphatic aldehydes, as defined by eq. 8. It can be seen that there is some similarity between these values ($\rho = +1.02$ and $+ 0.77$) (ref. 23,24) and our value ($\rho = -0.56$), which was numerically very small. The negative value of ρ could be interpreted as being due to a superimposed effect of the substituents on the hydration equilibrium. A similar effect was observed in the oxidation of aldehydes oxidized by chromic acid, wherein it was shown that the aldehydes were completely hydrated in aqueous solution (25). In the chromic acid oxidation of benzaldehyde, it was shown that the reaction proceeded by way of the chromic acid ester of hydrated benzaldehyde as the intermediate (26). In this investigation, the correlation with k_{Hy} supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen transfer reaction between a free aldehyde and QDC was very unlikely. Thus, the rate-accelerating effect of the substituents could be interpreted in terms of greatly increased hydration (Table 1). This similarity provided additional support for the mechanistic pathway suggested, in the present investigation, that the rate-determining step was the oxidative decomposition of the chromate ester of an aldehyde hydrate. The hydrated forms of the substrates would remain as undissociated molecules (since $[H^+]$ would be much greater than the dissociation constants of the substrates), in the range of acid concentrations used in the present investigation

(0.5 – 1.50 M). It was therefore suggested that the protonated QDC reacted with the hydrated form of the α,β-unsaturated aldehydes to give the corresponding acids.

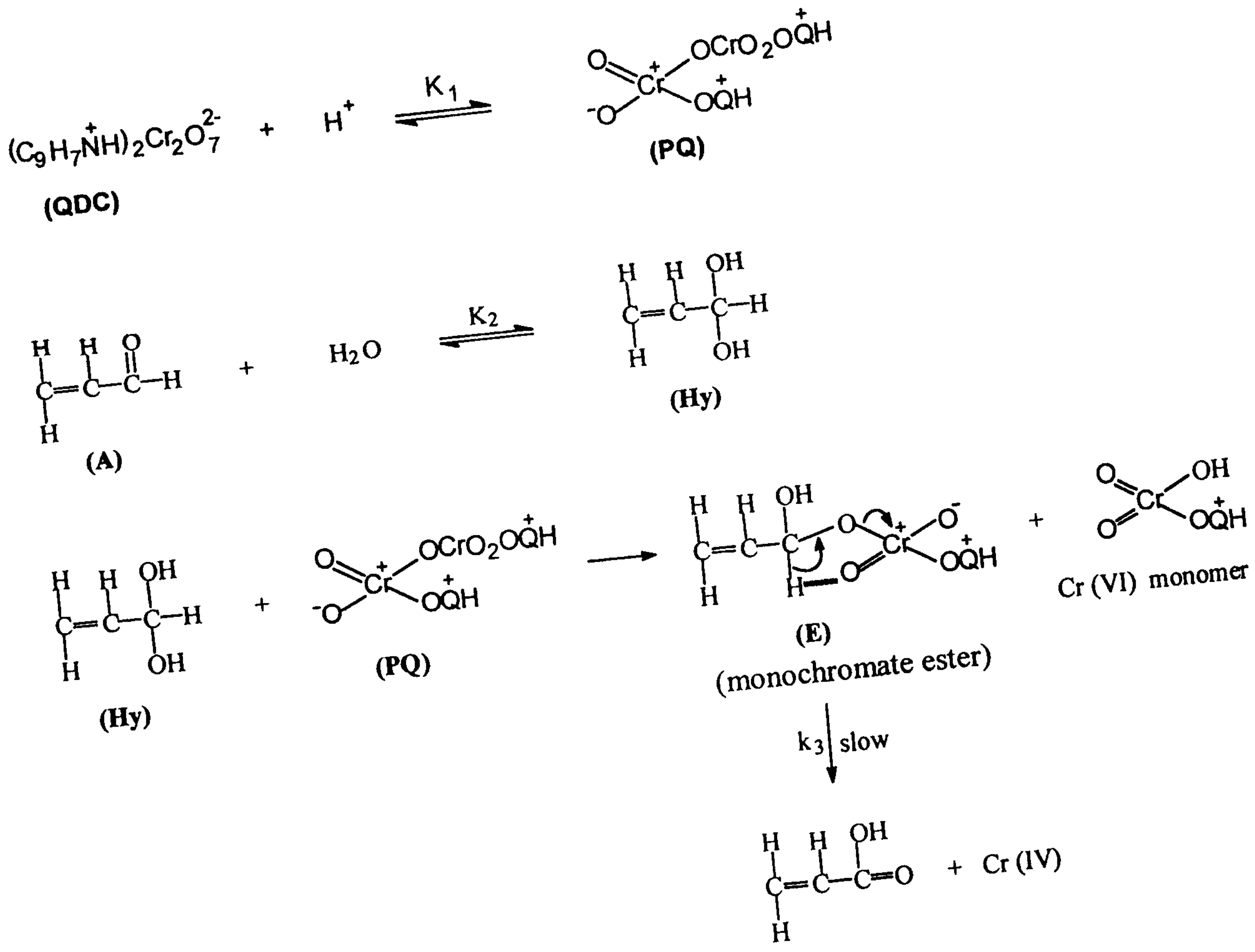
The close resemblance between aldehyde hydrates and alcohols both in structure and in many aspects of oxidation, would imply a similarity in the nature of the two oxidation reactions. For the oxidation of alcohols by chromic acid, the rate-determining step involved the decomposition of the protonated acid chromate ester (27). In an analogous manner, the oxidation of aldehydes would also proceed via the formation of a similar intermediate (an ester of the aldehyde hydrate), which would then undergo decomposition in the rate-determining step. It has been established that the hydration of the aldehydes was not the rate-determining step for the oxidation reaction (28). There would be an equilibrium between the ester of the aldehyde hydrate with the free aldehyde and the aldehyde hydrate. This ester could be formed either by a carbonyl addition reaction to the free aldehyde or by esterification of the hydrate (29). The esterification reaction would be more probable, since it would help to understand and predict aldehyde oxidation reactions and their relationship to the closely related oxidation of alcohols.

If the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and the conversion to the corresponding carboxylic acid could then be rationalized. The mechanistic pathway involved the formation of the ester of the aldehyde hydrate (step 1), followed by the slow oxidative decomposition of this ester (step 2).

Electron flow in a cyclic transition state could be rationalized as follows : if the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the process of electron transfer could take place through the carbon-oxygen-chromium bond (30). This would enable the formation of the chromate ester, and enhance the ease of conversion to the product. Such a transition state envisaged the transfer of electrons towards the chromium, by the formation of the carbon-hydrogen -oxygen bonds, as well as by the carbon-oxygen-chromium bonds.

The slow step of the reaction involved the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, as evidenced by the experimental observation that a kinetic isotope effect was observed for the oxidation of the respective aldehyde-d_1 compounds ($k_H / k_D = 6.2$), indicating a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction. The proton was removed in the cyclic transition state (co-planarity of all the atoms involved), the centre of which resided on an electron-dense oxygen in the chromate ester (31). This step would envisage a reaction via an electrocyclic mechanism involving six electrons; being a Hückel-type system (4n+2), this would be an allowed process (32). This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant. The sequence of reactions for the oxidation of α, β-unsaturated aldehydes by QDC, in an acid medium, has been shown in the Scheme.

Scheme



$$\text{Cr (IV)} + \text{Cr (VI)} \xrightarrow{\text{fast}} 2\text{Cr (V)}$$

$$\text{Cr (V)} + \text{substrate} \xrightarrow{\text{fast}} \text{product} + \text{Cr (III)}$$

In an acid medium, the oxidant QDC was converted to the protonated dimetallic chromium(VI) species (**PQ**) [in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $Cr_2O_7^{2-}$ (ref. 10)]. The substrate (**A**) 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 monochromate ester (**E**) and a Cr(VI) monomer. The monochromate ester (**E**) underwent decomposition in the rate-determining step to give the product (the corresponding acid), along with the Cr(IV) species. The conversion of Cr(IV) to Cr(III) proceeded by a disproportionation reaction. It was shown that for the reaction Cr(IV) + Cr(VI) → 2 Cr(V), the standard potential for the Cr(VI) - Cr(V) couple was extremely favourable ($E^0 = 0.62$ volt) (33), 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 of Cr(V) with the substrate (33,34).

If the mechanism shown in the Scheme is correct, then the attack of the protonated QDC (**PQ**) on the aldehyde hydrate (**Hy**) would be crucial, and would be favoured by the formation of the cyclic chromate ester (**E**).

Based on the mechanism shown in the Scheme, the rate law has been derived as follows:

$$-d[QDC]/dt = k_3[E] = k_3[Hy][PQ], \quad (9)$$

where $[PQ] = K_1[QDC][H^+]$, and $[Hy] = K_2[A][H_2O]$.

Hence, $$-d[QDC]/dt = K_1K_2k_3[A][QDC][H^+], \quad (10)$$

which showed a first order dependence on the concentrations of each (substrate, oxidant, and acid). Hence, $-2.303\ d\log[QDC]/dt = k = K_1K_2k_3[A][QDC][H^+]$. This rate law explains all the experimentally observed results.

The kinetic data collected demonstrated that the QDC oxidation of α, β-unsaturated aldehydes led to the formation of carboxylic acids, substantiating the mechanism wherein there was an attack of the oxidant on the aldehyde hydrate. There was no cleavage of the carbon-carbon bond, thus ruling out the possibility of any enolization. While highlighting the importance of QDC as an oxidant, this study emphasized the efficiency of QDC reacting with α, β-unsaturated aldehydes, suggesting the possibility of a regioselective route for the synthesis of carboxylic acids.

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CHAPTER - III

KINETICS OF OXIDATION OF HETEROCYCLIC ALDEHYDES

The oxidation of heterocyclic aldehydes by various oxidizing agents have been investigated by several workers. Kinetic studies on the oxidation of 2-furaldehydes by alkaline permanganate revealed that the reaction followed two pathways (1). The minor pathway was independent of hydroxyl ions concentration, while the major mechanism was dependent on the first power of hydroxyl ion concentration. Both reaction pathways were first order with respect to the concentrations of substrates and permanganate ions. The kinetic data were consistent with the formation of the hydrate anion of the substrates, followed by hydride anion transfer to permanganate ion in the rate-determining step (major mechanism). The mechanism for the OH^- ion-independent pathway involved a direct attack of permanganate ion on the substrate to give the permanganate ester, which then underwent decomposition in the rate-determining step of the reaction (1).

Ceric ammonium sulphate in sulfuric acid was used to oxidize 2-furaldehyde to 2-furancarboxylic acid in 25% (v/v) acetic acid-water medium. The reaction showed a first order dependence on the concentrations of each reactant (substrate, oxidant and acid). A free radical mechanism was suggested for the oxidation reaction (2).

The kinetics of oxidation of 2-furaldehyde by thallic perchlorate showed a first order dependence on the concentrations of substrate and oxidant, but exhibited zero order dependence on the concentration of acid. The oxidation product was 2-furancarboxylic acid (3).

The kinetics of oxidation of heterocyclic aldehydes by acid bromate in H_2SO_4 - HOAc medium have been studied. The reaction was first order in each, $[BrO_3^-]$ and [substrate], but showed second order dependence in $[H^+]$. The products of oxidation were the corresponding carboxylic acids (4).

The oxidation of pyridoxal by dichromate ion in aqueous perchloric acid medium showed a first order dependence on each of the reactants (substrate, oxidant and acid). The reduction of Cr(VI) to Cr(III) proceeded via the formation of a Cr(V) intermediate complex (5).

The oxidation of 2-pyridinecarbaldehyde by dichromate in acid medium has been studied. The rate of the reaction was dependent on the first power of the concentrations of oxidant and acid, but exhibited second order dependence on the concentration of substrate. The rate-determining step of the reaction involved the decomposition of the ester via a hydride anion transfer reaction (6).

The kinetics of oxidation of 2-furaldehyde by chromic acid have been studied in 70% acetic acid-water (v/v) medium. The reaction showed first order dependence each with respect to oxidant, substrate and hydrogen ion concentration, and 2-furancarboxylic acid was obtained as the final product of the reaction (7).

The kinetics of oxidation of 2-furaldehyde by quinolinium chlorochromate have been studied in 60% acetic acid-water (v/v) medium. The reaction showed first order dependence on each of the species (substrate, oxidant and acid). The addition of Mn^{2+} ions resulted in a retardation of the rate, which confirmed that a two-electron transfer process was involved in the reaction (8).

PRESENT WORK

In the oxidation of heterocyclic aldehydes, there exists the possibility of the reaction taking place either at the heteroatom or at the aldehydic function. The aims of the present investigation were:

(a) to highlight the effect of the heteroatom on the rate of the reaction; and

(b) to determine the site of attack of the oxidant.

The present study was carried out to examine the kinetic features of the oxidation of heterocyclic aldehydes by quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], in an acid medium, in 50% acetic acid-water (v/v), under a nitrogen atmosphere.

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

I. Five-membered heterocyclic aldehydes :

2-Furaldehyde, 5-Methyl-2-Furaldehyde, 5-Bromo-2-Furaldehyde,
2-Pyrrolecarbaldehyde and 2-Thiophenecarbaldehyde.

II. Six-membered heterocyclic aldehydes :

2-Pyridinecarbaldehyde and 3-Pyridinecarbaldehyde.

Stoichiometry (vide "Experimental")

The stoichiometries of all the oxidation reactions were determined. The stoichiometric ratios, Δ[QDC] / Δ[Substrate], were in the range 0.64 - 0.70 (Table 1).

Table 1 : Stoichiometries of the Oxidation of the Substrates ([Substrate] = 0.005 M; T = 313 K)

$[H_2SO_4]$ / M	0.10	0.25	0.50
10^2[QDC] / M	2.50	2.60	2.70
Δ[QDC] / Δ[2-Furaldehyde]	0.65	0.66	0.68
Δ[QDC] / Δ[5-Methyl-2-Furaldehyde]	0.64	0.70	0.67
Δ[QDC] / Δ[5-Bromo-2-Furaldehyde]	0.65	0.66	0.69
Δ[QDC] / Δ[2-Pyrrolecarbaldehyde]	0.68	0.67	0.70
Δ[QDC] / Δ[2-Thiophenecarbaldehyde]	0.67	0.65	0.69
Δ[QDC] / Δ[2-Pyridinecarbaldehyde]	0.67	0.70	0.68
Δ[QDC] / Δ[3-Pyridinecarbaldehyde]	0.69	0.67	0.65

The observed stoichiometric ratios conformed to the overall equations :

(a) For 2-furaldehyde :

$$3\ C_5H_4O_2 + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_5H_4O_3 + 2\ Cr^{III} + 6\ H^+ \qquad (1)$$

(b) For 5-methyl-2-furaldehyde :

$$3\ C_6H_6O_2 + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_6H_6O_3 + 2\ Cr^{III} + 6\ H^+ \qquad (2)$$

(c) For 5-bromo-2-furaldehyde :

$$3\ C_5H_3BrO_2 + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_5H_3BrO_3 + 2\ Cr^{III} + 6\ H^+ \qquad (3)$$

(d) For 2-pyrrolecarbaldehyde :

$$3\ C_5H_5NO + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_5H_5NO_2 + 2\ Cr^{III} + 6\ H^+ \qquad (4)$$

(e) For 2-thiophenecarbaldehyde :

$$3\ C_5H_4SO + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_5H_4SO_2 + 2\ Cr^{III} + 6\ H^+ \qquad (5)$$

(f) For 2-pyridinecarbaldehyde :

$$3\ C_6H_5NO + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_6H_5NO_2 + 2\ Cr^{III} + 6\ H^+ \qquad (6)$$

(g) For 3-pyridinecarbaldehyde :

$$3\ C_6H_5NO + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_6H_5NO_2 + 2\ Cr^{III} + 6\ H^+ \qquad (7)$$

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 2a and 2b.

Table 2a : Dependence of Rate Constants on the Concentration of Heterocyclic Aldehydes ([QDC] = 0.001 M; [H_2SO_4] = 0.5 M; [AcOH] = 50% (v/v); T = 313 K)

	10^4 k_1 / s^{-1}				
10^2 [Substrate] / M	5-Methyl-2-Furaldehyde	2-Furaldehyde	5-Bromo-2-Furaldehyde	2-Pyrrole-carbaldehyde	2-Thiophene-carbaldehyde
1.0	1.5	1.25	1.1	1.18	1.14
2.5	3.8	3.12	2.6	2.91	2.83
5.0	7.8	6.21	5.6	5.90	5.67
7.5	12.1	9.32	8.3	8.71	8.50
10.0	15.6	12.5	11.0	11.8	11.2
	10^3 k_2 / M^{-1} s^{-1}				
	15.0	12.5	11.0	11.8	11.4
	15.2	12.5	10.4	11.6	11.3
	15.6	12.4	11.2	11.8	11.3
	16.1	12.4	11.0	11.6	11.3
	15.6	12.5	11.2	11.8	11.2

$k_2 = k_1$ / [Substrate]

Table 2b : Dependence of Rate Constants on the Concentration of Heterocyclic Aldehydes ([QDC] = 0.001 M; [H_2SO_4] = 0.5 M; [AcOH] = 50% (v/v); T = 313 K)

10^2 [Substrate] / M	10^4 k_1 / s^{-1}	
	2-Pyridinecarbaldehyde	3-Pyridinecarbaldehyde
1.0	2.34	2.01
2.5	5.9	5.1
5.0	12.3	10.1
7.5	18.1	15.1
10.0	24.0	20.0
	10^3 k_2 / M^{-1} s^{-1}	
	23.4	20.1
	23.6	20.4
	24.6	20.2
	24.1	20.1
	24.0	20.0

$k_2 = k_1$ / [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 (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.

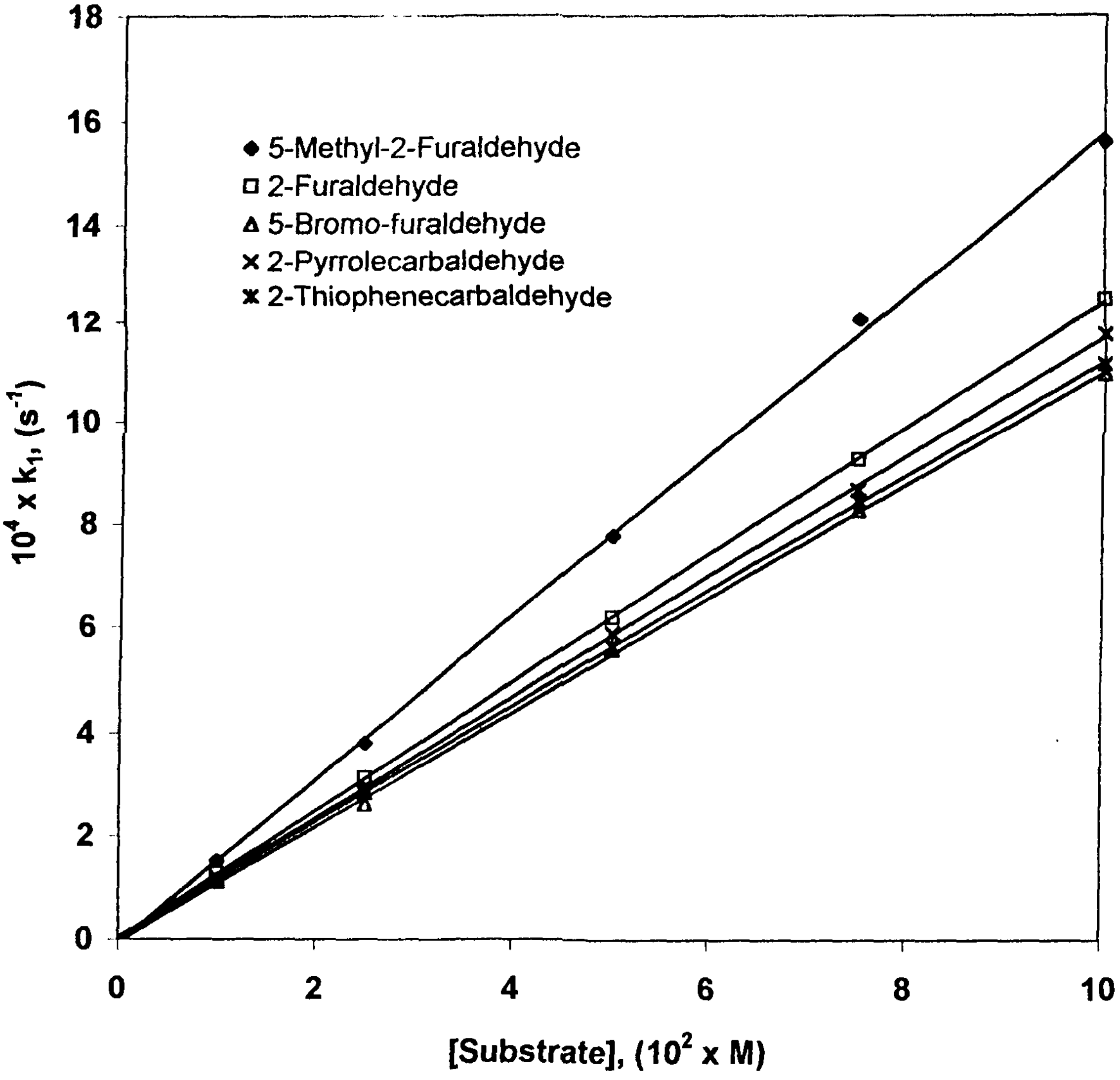


Fig. 1. Plots of k_1 against the concentrations of substrates.

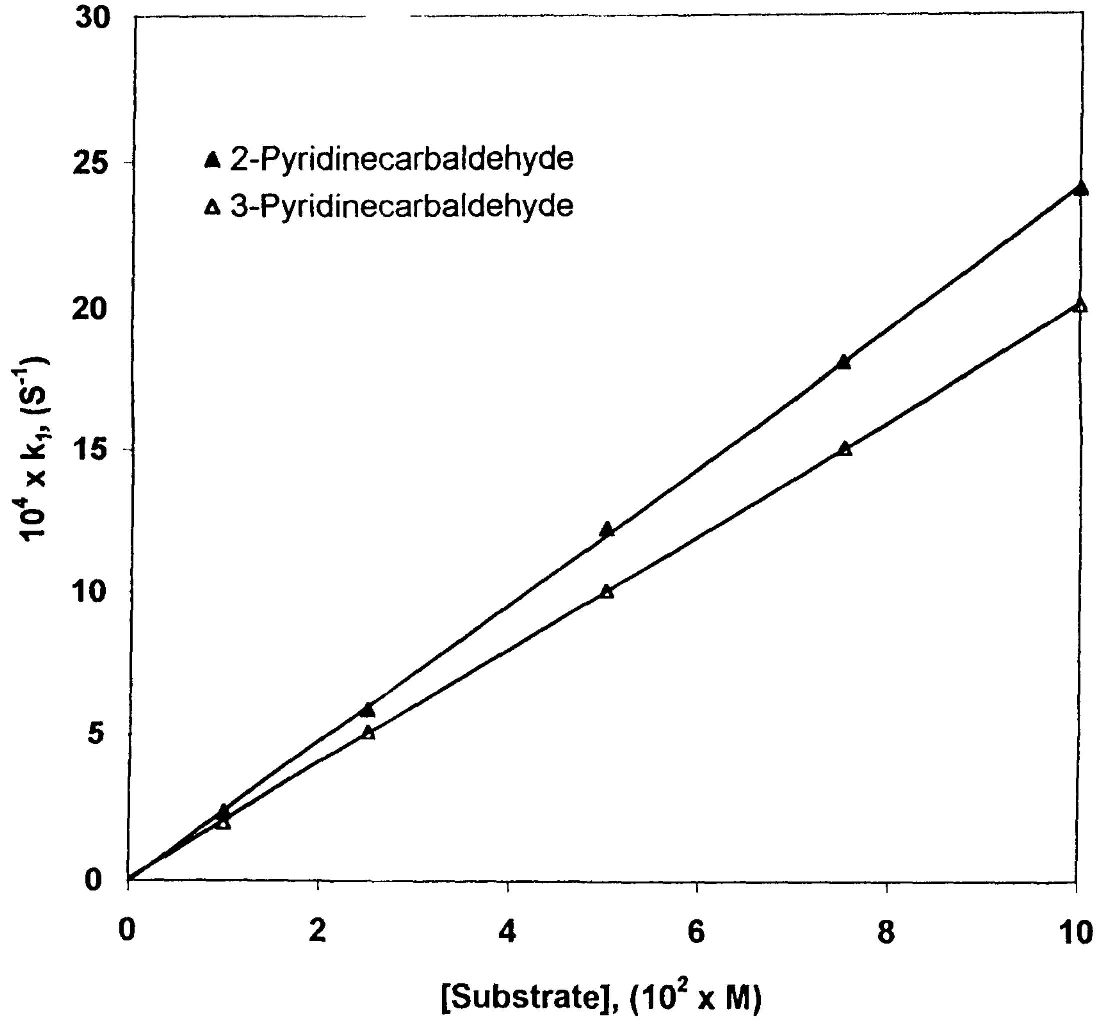


Fig. 2. Plots of k_1 against the concentrations of substrates.

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 3a and 3b.

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

[Substrate] = 0.01 M; [H_2SO_4] = 0.5 M; [AcOH] = 50% (v/v); T = 313 K)

	$10^4\ k_1\ /\ s^{-1}$				
10^3 [QDC] / M	5-Methyl-2-Furaldehyde	2-Furaldehyde	5-Bromo-2-Furaldehyde	2-Pyrrole-carbaldehyde	2-Thiophene-carbaldehyde
1.0	1.5	1.25	1.1	1.18	1.14
0.75	1.52	1.22	1.12	1.15	1.14
0.50	1.5	1.25	1.09	1.18	1.13
0.25	1.45	1.24	1.1	1.19	1.15
0.10	1.43	1.27	1.15	1.14	1.12

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

[Substrate] = 0.01 M; [H_2SO_4] = 0.5 M; [AcOH] = 50% (v/v); T = 313 K)

10^3 [QDC] / M	10^4 k_1 / s^{-1}	
	2-Pyridinecarbaldehyde	**3-Pyridinecarbaldehyde**
1.0	2.34	2.01
0.75	2.33	2.03
0.50	2.34	2.02
0.25	2.35	2.01
0.10	2.32	2.0

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 0.5 M to 1.5 M (Tables 4a and 4b).

Table 4a : Dependence of Rate Constants on the Acid Concentration for Heterocyclic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 50% (v/v); T = 313 K)

$[H_2SO_4]$ / M	$10^4\ k_1\ /\ s^{-1}$				
	5-Methyl-2-Furaldehyde	**2-Furaldehyde**	**5-Bromo-2-Furaldehyde**	**2-Pyrrole-carbaldehyde**	**2-Thiophene-carbaldehyde**
0.5	1.5	1.25	1.1	1.18	1.14
0.75	2.3	1.88	1.7	1.75	1.64
1.0	3.1	2.50	2.15	2.36	2.20
1.25	3.7	3.20	2.7	2.90	2.70
1.50	4.6	3.80	3.4	3.55	3.40

Table 4b : Dependence of Rate Constants on the Acid Concentration for Heterocyclic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 50% (v/v); T = 313 K)

$[H_2SO_4]$ / M	10^4 k_1 / s^{-1}	
	2-Pyridinecarbaldehyde	**3-Pyridinecarbaldehyde**
0.5	2.34	2.01
0.75	3.48	3.02
1.0	4.63	4.01
1.25	5.84	5.03
1.50	7.02	6.05

Plots of log k_1 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.

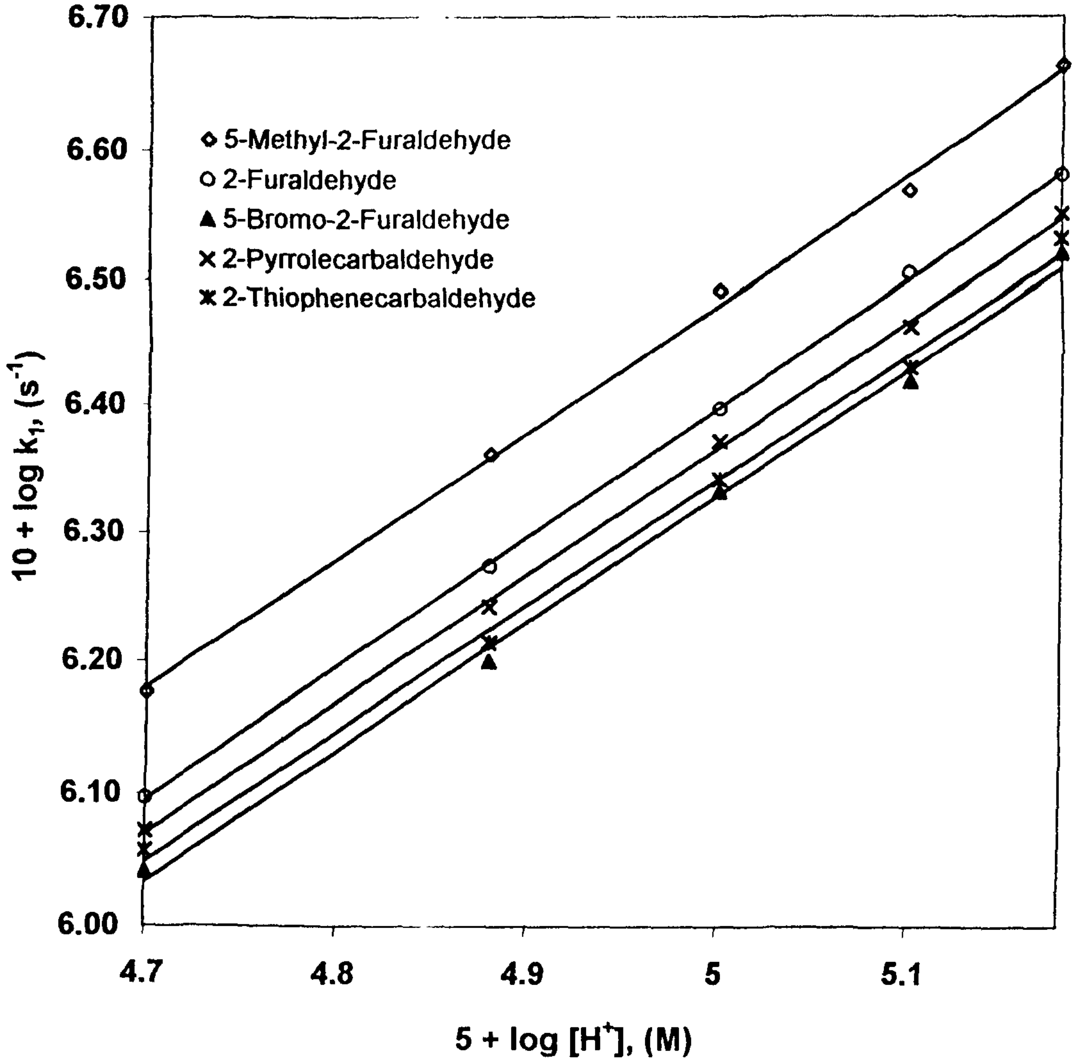


Fig. 3. Plots of log k_1 against log [H^+].

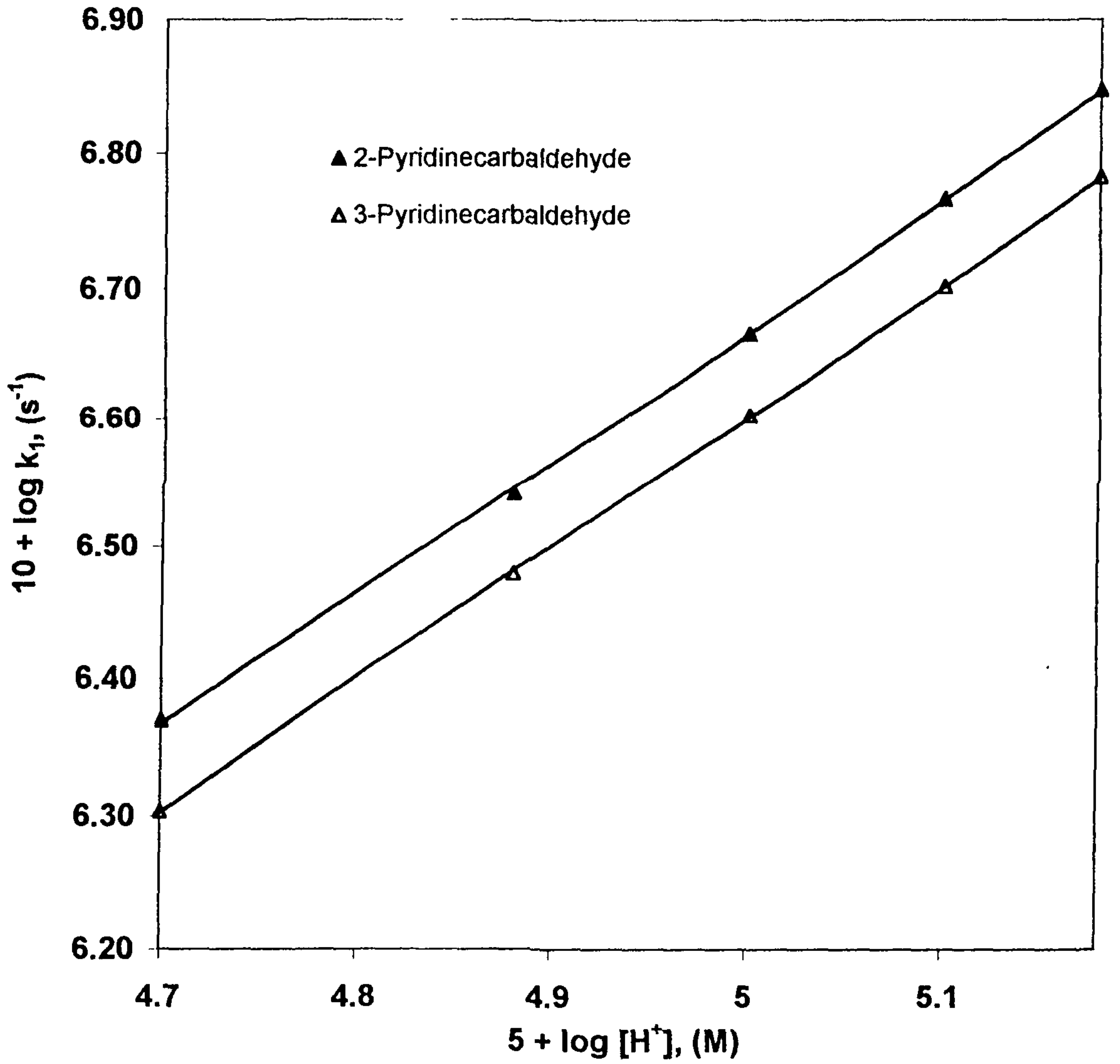


Fig. 4. Plots of log k_1 against log [H^+].

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 (9,10). The acid catalysis must be related to the structure of the oxidant (QDC), which was converted to a protontated 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. (11) 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 $Cr_2O_7^{2-}$. These ions were in equilibrium with each other, according to the equation given by $2\ HCr_2O_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ ($K_d = 35.5$). 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 (11). 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 $K_2Cr_2O_7$, spectral studies have shown that $Cr_2O_7^{2-}$ was the predominant species (12). 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 electrophilic species and would be sufficiently reactive to attack the substrate (heterocyclic aldehydes).

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 :

$$\text{Rate} = -\frac{d[\text{QDC}]}{dt} = k\,[\text{Substrate}]\;[\text{QDC}]\;[\text{H}^+] \qquad (8)$$

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 5a and 5b).

Table 5a : Dependence of Rate Constants on Solvent composition for Heterocyclic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [H_2SO_4] = 0.5 M; T = 313 K)

		10^4 k_t / s^{-1}				
H_2O : AcOH (%, v/v)	**Dielectric Constant (D**	**5-Methyl-2-Furaldehyde**	**2-Furaldehyde**	**5-Bromo-2-Furaldehyde**	**2-Pyrrole-carbaldehyde**	**2-Thiophene-carbaldehyde**
50:50	39.79	1.5	1.25	1.1	1.18	1.14
45:55	36.44	2.2	1.82	1.3	1.58	1.41
40:60	33.09	3.1	2.51	1.69	2.09	1.78
35:65	29.74	4.5	3.80	2.4	2.95	2.51
30:70	26.39	7.5	3.60	3.4	4.27	3.55

Table 5b : Dependence of Rate Constants on Solvent composition for Heterocyclic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; $[H_2SO_4]$ = 0.5 M; T = 313 K)

H_2O : AcOH (%, v/v)	Dielectric Constant (D)	$10^4\ k_1 / s^{-1}$	
		2-Pyridinecarbaldehyde	3-Pyridinecarbaldehyde
50:50	39.79	2.34	2.01
45:55	36.44	2.95	2.57
40:60	33.09	3.55	3.09
35:65	29.74	4.68	4.07
30:70	26.39	6.03	5.37

The dielectric constants for water-acetic acid mixtures have been estimated approximately from the dielectric constants of the pure solvents (at 313 K: water = 73.28; acetic acid = 6.29) (13).

In the present investigation, in proceeding from 50% acetic acid to 70% acetic acid, the polarity decreases. It was observed that an increase in the water content of the medium showed a decrease in the rate of oxidation (Table 5a and 5b). The magnitude of this effect could be analyzed by suggesting that, for the equilibrium $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, a decrease in the dielectric constant of medium (increase in the acetic acid content) would favour the dichromate form over the chromate form. If ion-pairs were to be formed in this medium, it would be expected that they would have a higher ion-pair association constant for the dichromate ion, which would again favour the dichromate ion. The absence of any salt effects on the rate of oxidation indicated that the reaction was not of the ion-ion type. If the reaction was assumed to involve two neutral molecules, then the plot of log k_1 versus (D-1) / (2D+1) would have been linear; this was not found to be so. Although the range of dielectric constants used for these reactions was not large, plots of log k_1 versus 1/D were found to be linear, with positive slopes (Figures 5-6). This suggested an interaction between a positive ion and a dipole (14), and was in consonance with the experimental observation that, in the presence of an acid, the rate-determining step involved a protonated Cr(VI) species. The data in Tables 5a and 5b 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.

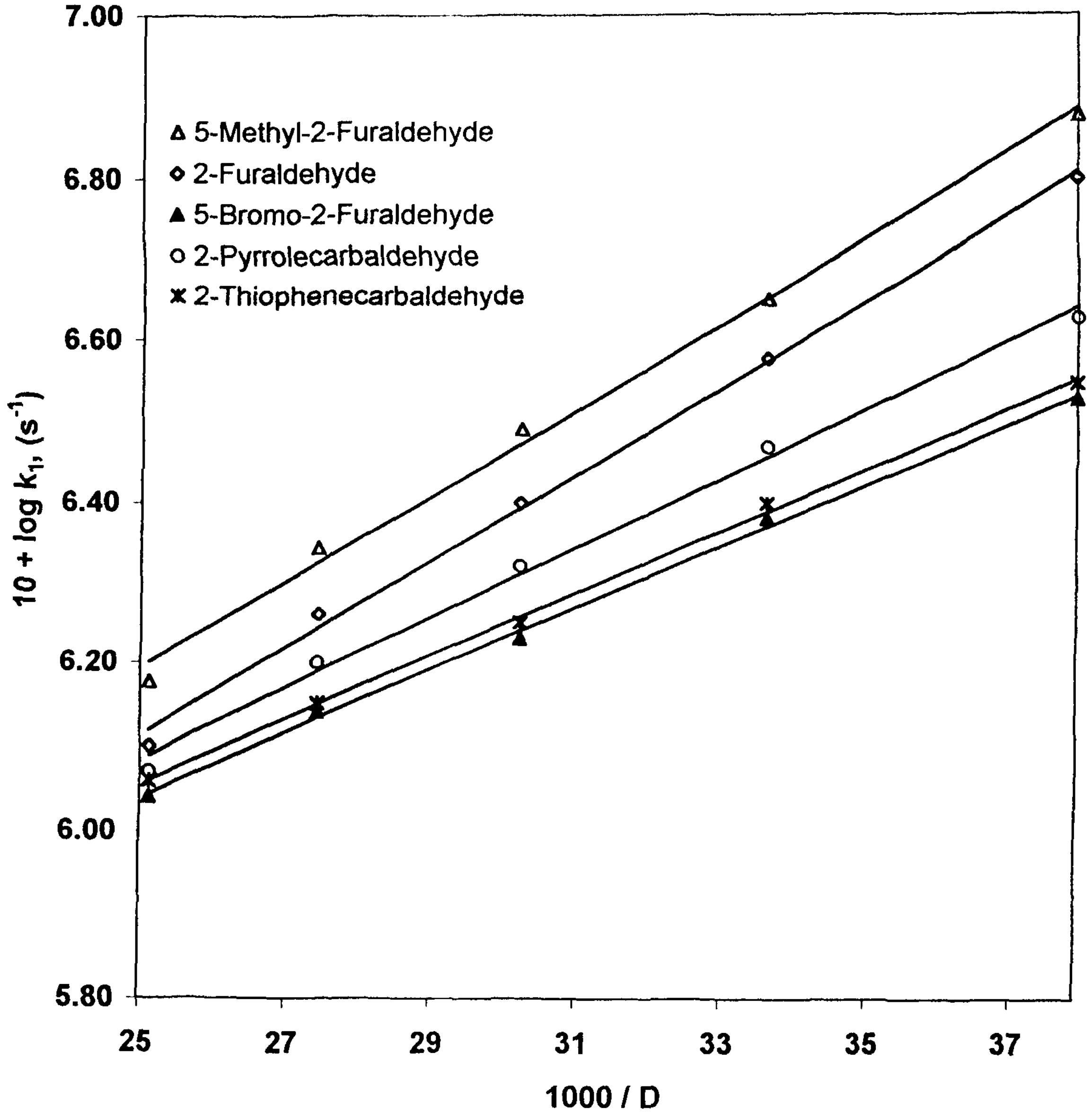


Fig. 5. Plots of log k_1 against the reciprocal of the dielectric constant.

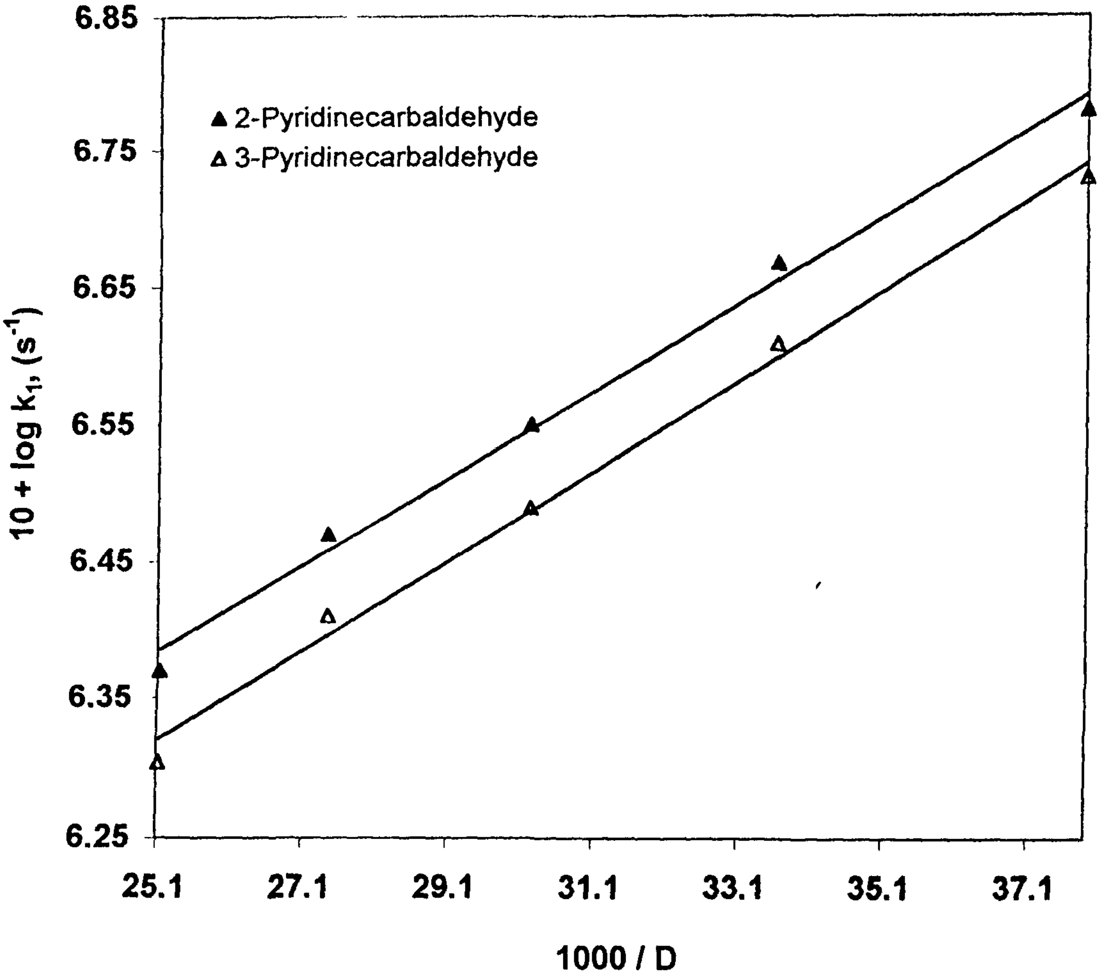


Fig. 6. Plots of log k_1 against the reciprocal of the dielectric constant.

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 6a and 6b).

Table 6a : Dependence of Rate Constants on Temperature for Heterocyclic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 50% (v/v); $[H_2SO_4]$ = 0.5 M)

	10^4 k_1 / s^{-1}				
Temperature (±0.1K)	**5-Methyl-2-Furaldehyde**	**2-Furaldehyde**	**5-Bromo-2-Furaldehyde**	**2-Pyrrole-carbaldehyde**	**2-Thiophene-carbaldehyde**
303	0.75	0.62	0.55	0.59	0.56
308	1.1	0.94	0.83	0.89	0.84
313	1.5	1.25	1.1	1.18	1.14
318	2.1	1.78	1.6	1.74	1.71
323	2.8	2.54	2.2	2.41	2.35

Table 6b : Dependence of Rate Constants on Temperature for Heterocyclic Aldehydes ([Substrate] = 0.01 M; [QDC] = 0.001 M; [AcOH] = 50% (v/v); $[H_2SO_4]$ = 0.5 M)

Temperature (±0.1K)	$10^4\ k_1 / s^{-1}$	
	2-Pyridinecarbaldehyde	3-Pyridinecarbaldehyde
303	1.25	1.07
308	1.83	1.58
313	2.34	2.01
318	3.42	3.02
323	4.57	4.04

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 Table 7.

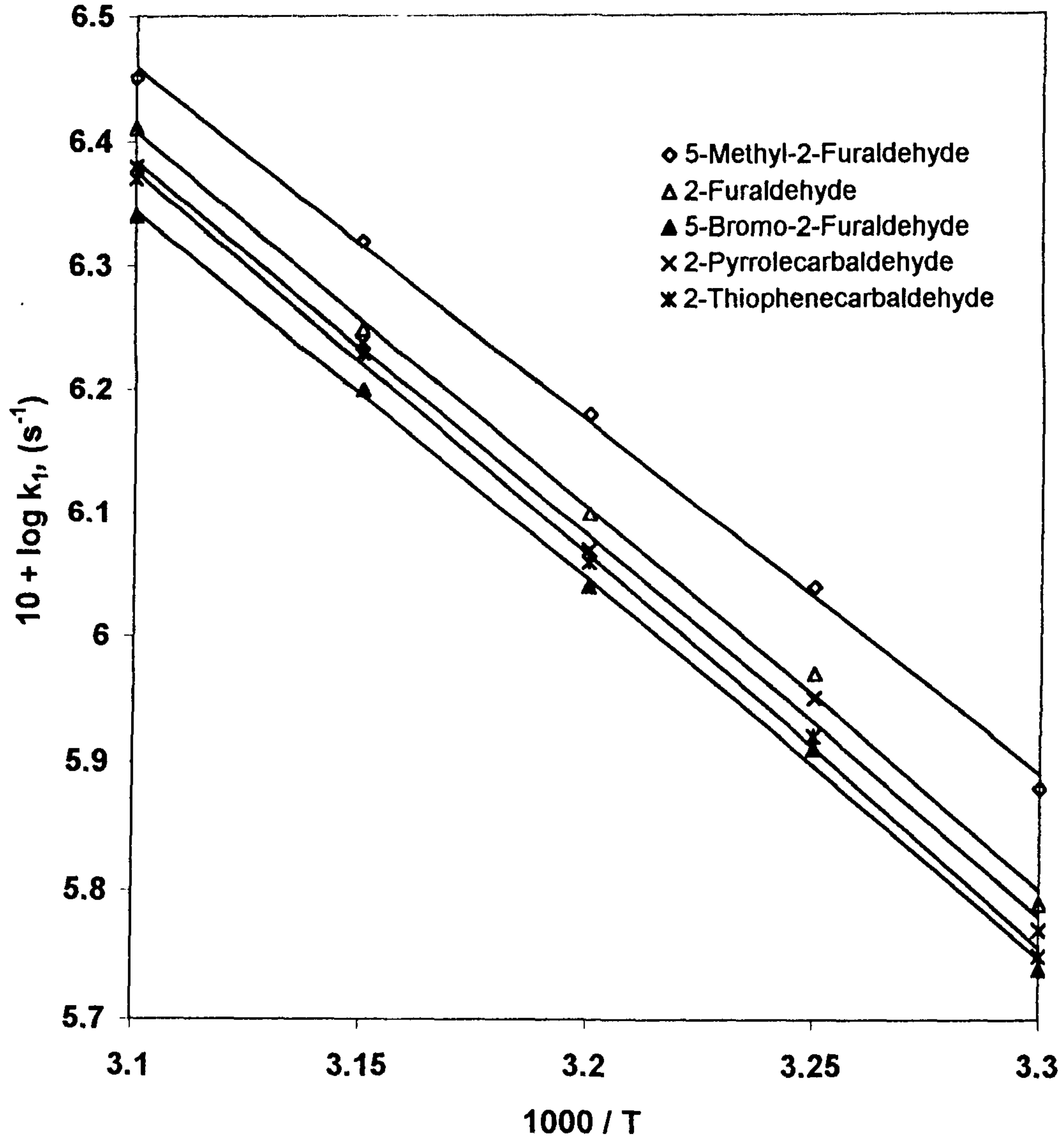


Fig. 7. Plots of log k_1 against the reciprocal of temperature.

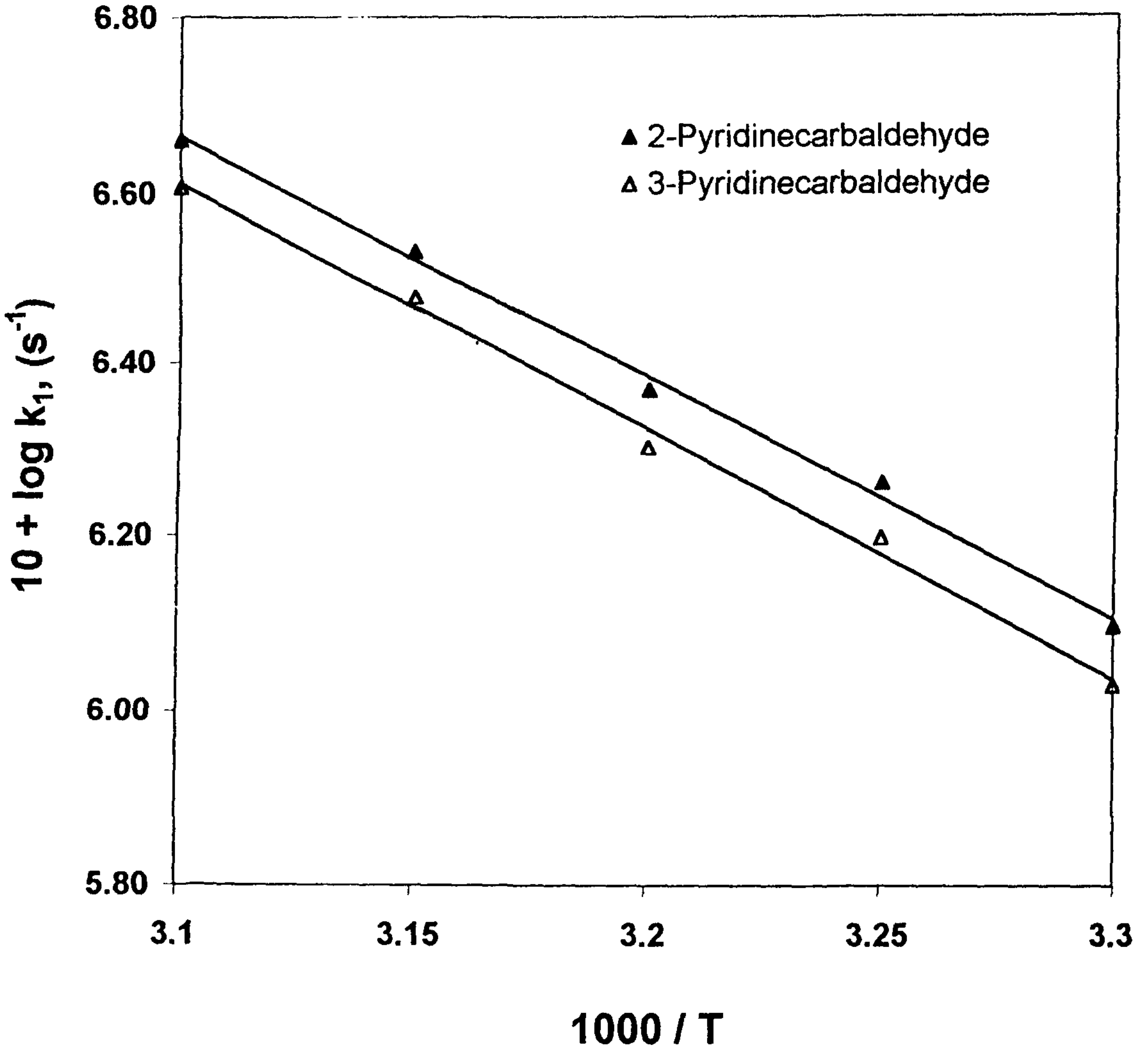


Fig. 8. Plots of log k_1 against the reciprocal of temperature

Table 7 : Activation Parameters for Heterocyclic Aldehydes

Substrate	E (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
5-Methyl-2-Furaldehyde	52	49	-157	98
2-Furaldehyde	54	51	-152	100
5-Bromo-2-Furaldehyde	55	52	-151	98
2-Pyrrolecarbaldehyde	57	54	-145	99
2-Thiophenecarbaldehyde	59	56	-142	99
2-Pyridinecarbaldehyde	52	49	-158	96
3-Pyridinecarbaldehyde	54	51	-152	96

Error limits : E ± 2 kJ mol^{-1}; $\Delta H^{\neq}$ ± 3 kJ mol^{-1}; $\Delta S^{\neq}$ ± 5 JK^{-1} mol^{-1}; $\Delta G^{\neq}$ ± 2 kJ mol^{-1}

The high positive values of the enthalpies of activation ($\Delta H^{\neq}$) and the free energies of activation ($\Delta G^{\neq}$) 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 (15). 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 $\Delta G^{\neq}$ 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.

Isokinetic relationship

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

$$\Delta H^{\neq} = \Delta H_0^{\neq} + \beta \Delta S^{\neq} \qquad (11)$$

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 (16). The isokinetic temperature, obtained from the plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, was 436K (Figure 9). Although current views do not attach much physical significance to isokinetic temperatures (17), a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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, $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Further, 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 heterocyclic aldehydes studied in this investigation.

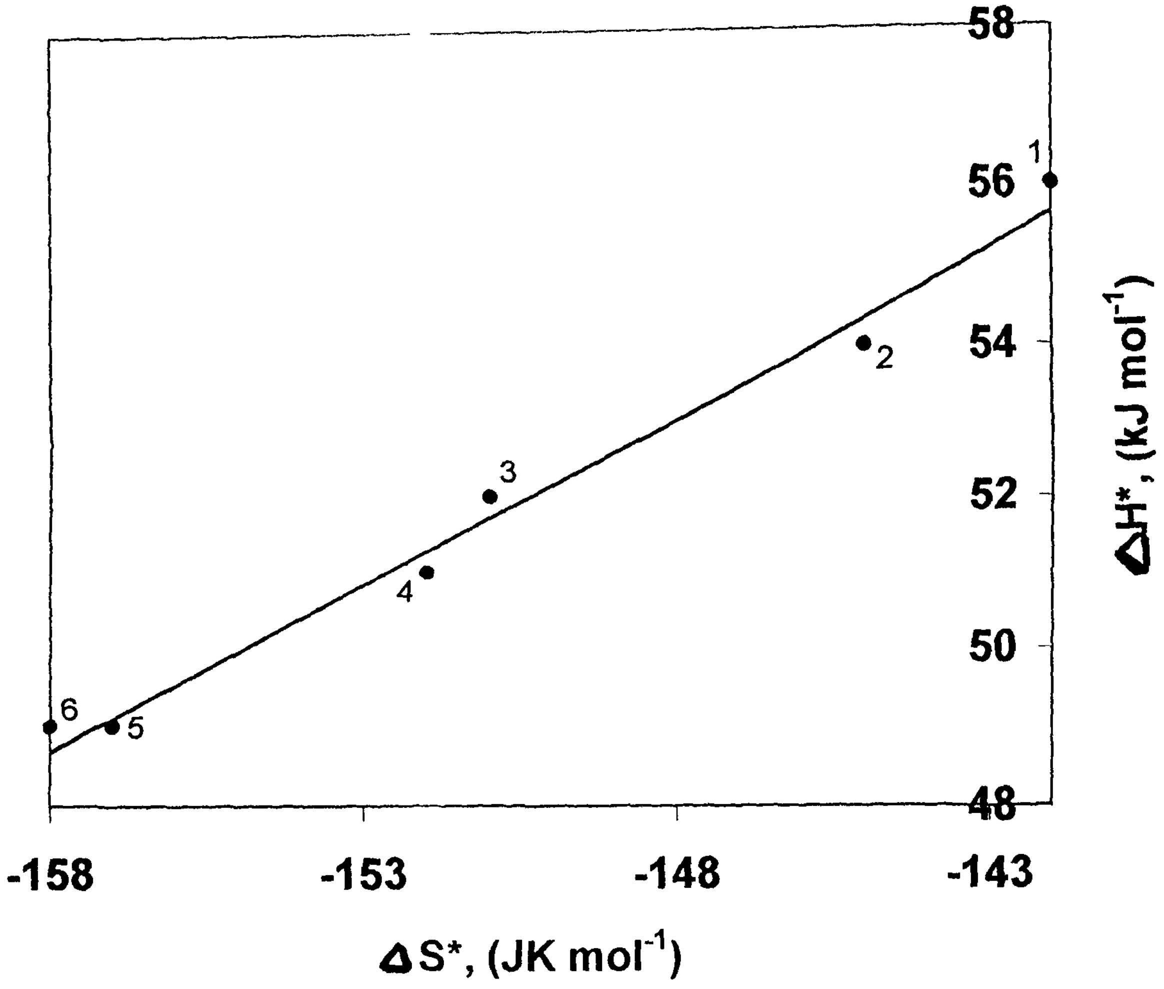


Fig. 9. Plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ for 2-thiophenecarbaldehyde (1), 2-pyrrolecarbaldehyde (2), 5-bromo-2-carbaldehyde (3), 2-furaldehyde (4), 3-pyridinecarbaldehyde (4), 5-methyl-2-furaldehyde (5), 2-pyridinecarbaldehyde (6).

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 (18). 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.

Structure and Reactivity

The heteroatoms are strong resonance donors in these five–membered ring systems, an effect which completely overrides their inductive withdrawal. By treating these rings as transmitting systems, one could look for a correlation between the structure and the reactivity of these heterocyclic aldehydes. The observed order of reactivity was : 2-furaldehyde > 2-pyrrolecarbaldehyde > 2-thiophenecarbaldehyde (Table 2a), which was in conformity with the decreasing electronegativities of O, N and S atoms (electronegativities were : O = 3.50; N = 3.07; S = 2.44) (ref. 19). The inference was that electronegative substituents increased the oxidation rates by increasing the equilibrium concentrations of the chromate ester of the aldehyde hydrate. This would thus account for the order of the observed reactivity (Table 2a).

For the substituted 2-furaldehydes, the observed order of reactivity was : 5-methyl-2-furaldehyde > 2-furaldehyde > 5-bromo-2-furaldehyde > 5-nitro-2-furaldehyde, which was in conformity with the inductive effects of the substituents. The inference was that the electron-releasing substituent (methyl) increased the oxidation rate by increasing the equilibrium concentration of the chromate ester of the aldehyde hydrate, while the electron-withdrawing substituent (nitro) decreased the oxidation rate. This would thus account for the observed order of reactivity of substituted 2-furaldehydes (Table 2a).

The observed order of reactivity, in the case of six-membered heterocyclic aldehydes was : 2-pyridinecarbaldehyde > 3-pyridinecarbaldehyde.

It was observed that having the aldehydic function at the 2-position or the 3-position had a marginal effect on the rate of the reaction, with the 2-isomer reacting faster than the 3-isomer (Table 2b). This suggested that the geometric requirement of the interaction of the aldehydic function with the protonated QDC in the transition state was relatively insensitive to any steric effects.

Mechanism

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrated form (20-27). The experimental rate constants (k_1) for the oxidation of the aldehydes by QDC and the aldehyde hydrate dissociation constants (K_d) pertaining to the reaction

$$RCH(OH)_2 \overset{K_d}{\rightleftharpoons} RCHO + H_2O \qquad (10)$$

are given in Tables 8-9.

Table 8. QDC oxidation of Heterocyclic Aldehydes at 313 K

Aldehydes	K_d	$10^4\ k_1/s^{-1}$	$k_{Hy}\ (M^{-2}\,s^{-1})$	$k_A\ (M^{-2}\,s^{-1})$
2-Furaldehyde	1.29	1.25	16.56 ± 1.28	12.84 ± 1.28
2-Pyrrolecarbaldehyde	0.92	1.18	10.99 ± 0.41	11.94 ± 0.45
2-Thiophenecarbaldehyde	0.84	1.14	9.53 ± 0.17	11.34 ± 0.20

Table 9. QDC oxidation of Heterocyclic Aldehydes at 313 K

Aldehydes	K_d	$10^4\ k_1/s^{-1}$	$k_{Hy}\ (M^{-2}\,s^{-1})$	$k_A\ (M^{-2}\,s^{-1})$
2-Furaldehyde	1.29	1.25	16.56 ± 1.28	12.84 ± 1.28
5-Bromo-2-Furaldehyde	1.16	1.1	12.68 ± 1.2	10.93 ± 0.27
5-Methyl-2-Furaldehyde	1.23	1.5	18.45 ± 1.15	15.5 ± 0.63
5-Nitro-2-Furaldehyde	1.09	1.03	11.22 ± 1	9.77 ± 0.3

From k_t and K_d, two sets of rate constants for the oxidation of the aldehyde in only one of the forms present in solution were computed. The values of k_{Hy} were obtained by assuming that only the hydrate form appears in the rate law :

$$v = k_{Hy} [\,QDC\,] [\,RCH(OH)_2\,] \qquad (11).$$

Similarly, the values of k_A were calculated using the concentration of free aldehydes according to the rate law :

$$v = k_A [\,QDC\,] [\,RCHO\,] \qquad (12).$$

The values of k_{Hy} and k_A are given in Tables 8 -9. Using the σ values derived from a consideration of the electrophilic substitution for the hetero systems (28) :

(i) a plot of $\log k_{Hy}$ against σ was linear ($r = 0.9632$), with a slope of $\rho = + 3.0$ (Figure 10; from the data given in Table 8). On the other hand, the correlation of σ with k_A (Figure 11) gave a value of $\rho = + 0.675$ ($r = 0.994$);

(ii) a plot of $\log k_{Hy}$ against σ was linear ($r = 0.999$), with a slope of $\rho = + 0.509$ (Figure 12; from the data given in Table 9). Correlation of σ with k_A (Figure 13) gave a value of $\rho = 0.423$ ($r = 0.979$).

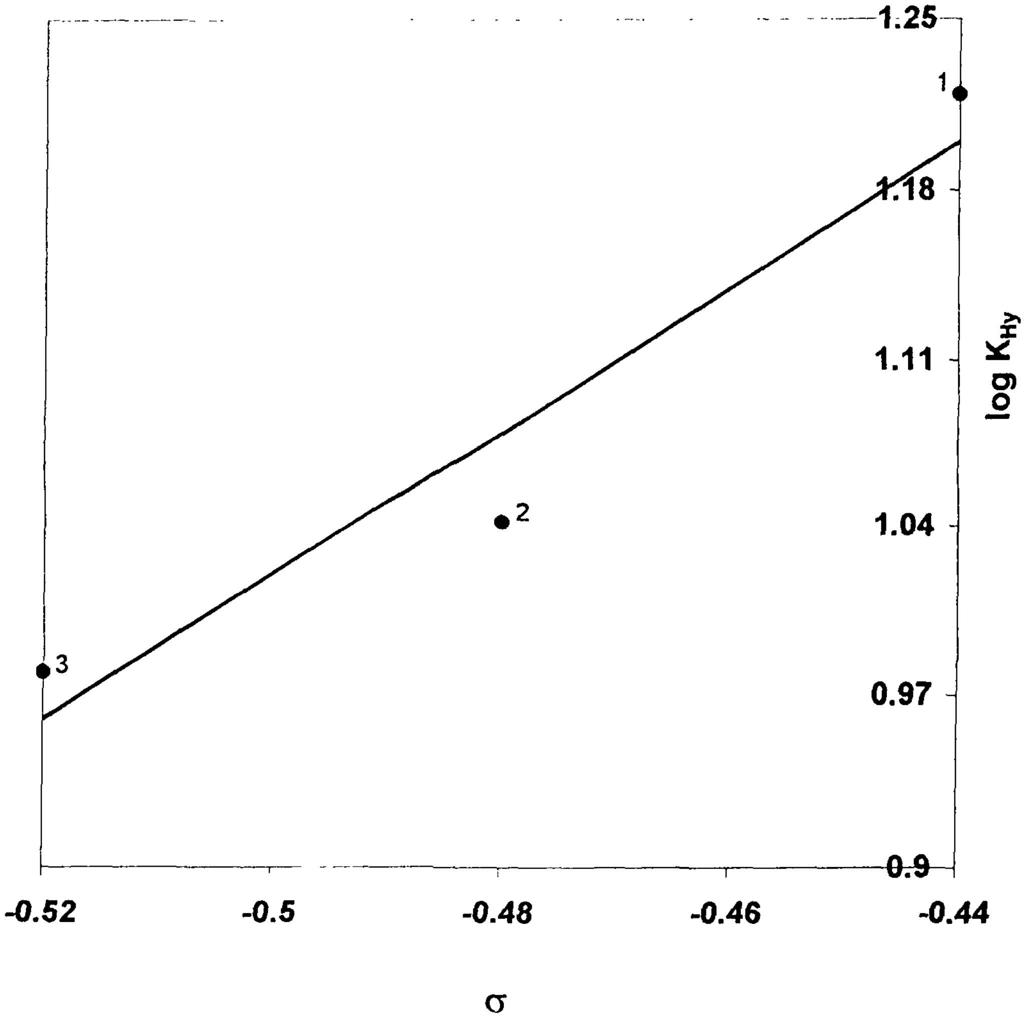


Fig. 10. Plot of σ against log k_{Hy} for 2-furaldehyde (1), 2-pyrrolecarbaldehyde (2), 2-thiophenecarbaldehyde (3).

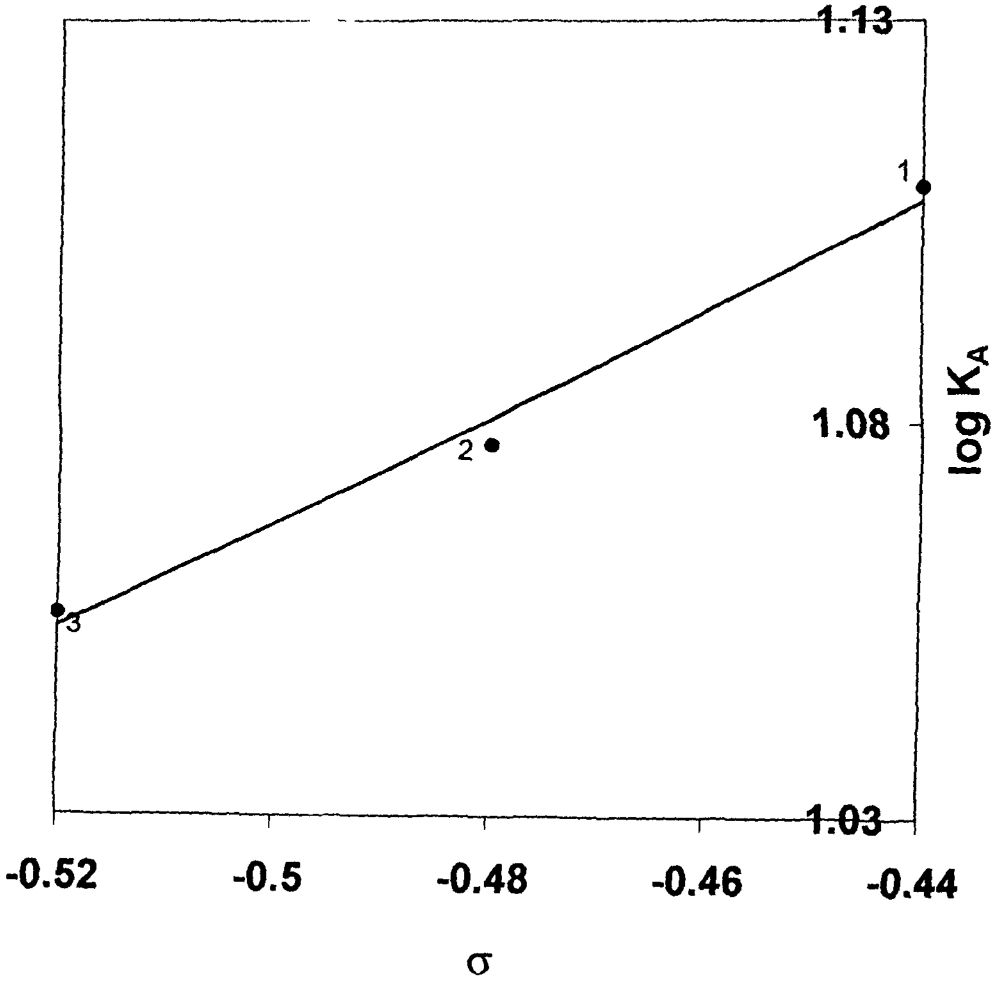


Fig. 11. Plot of σ against log k_A for 2-furaldehyde (1), 2-pyrrolecarbaldehyde (2), 2-thiophenecarbaldehyde (3).

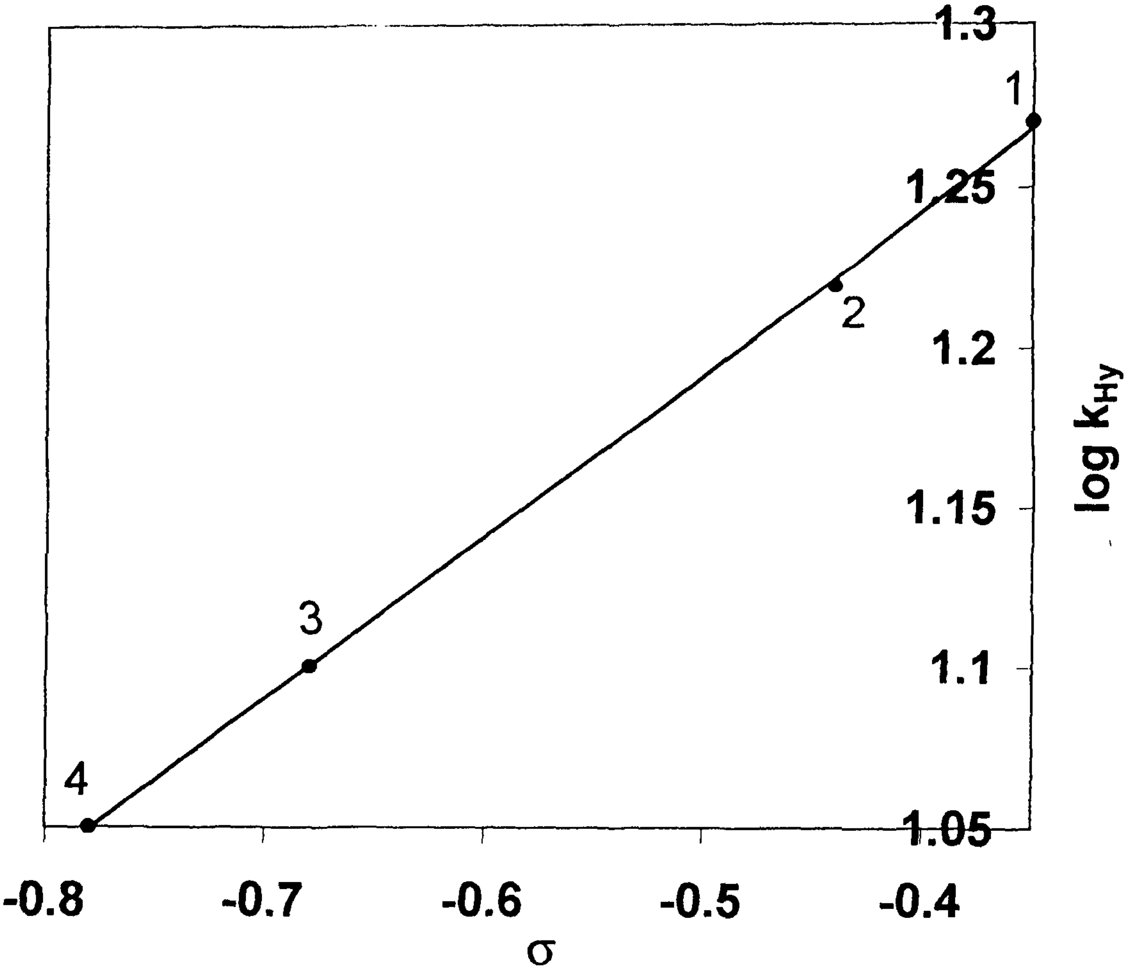


Fig. 12. Plot of σ against log k_{Hy} for 5-methyl-2-furaldehyde (1), 2-furaldehyde (2), 5-bromo-2-furaldehyde (3), 5-nitro-2-furaldehyde (4).

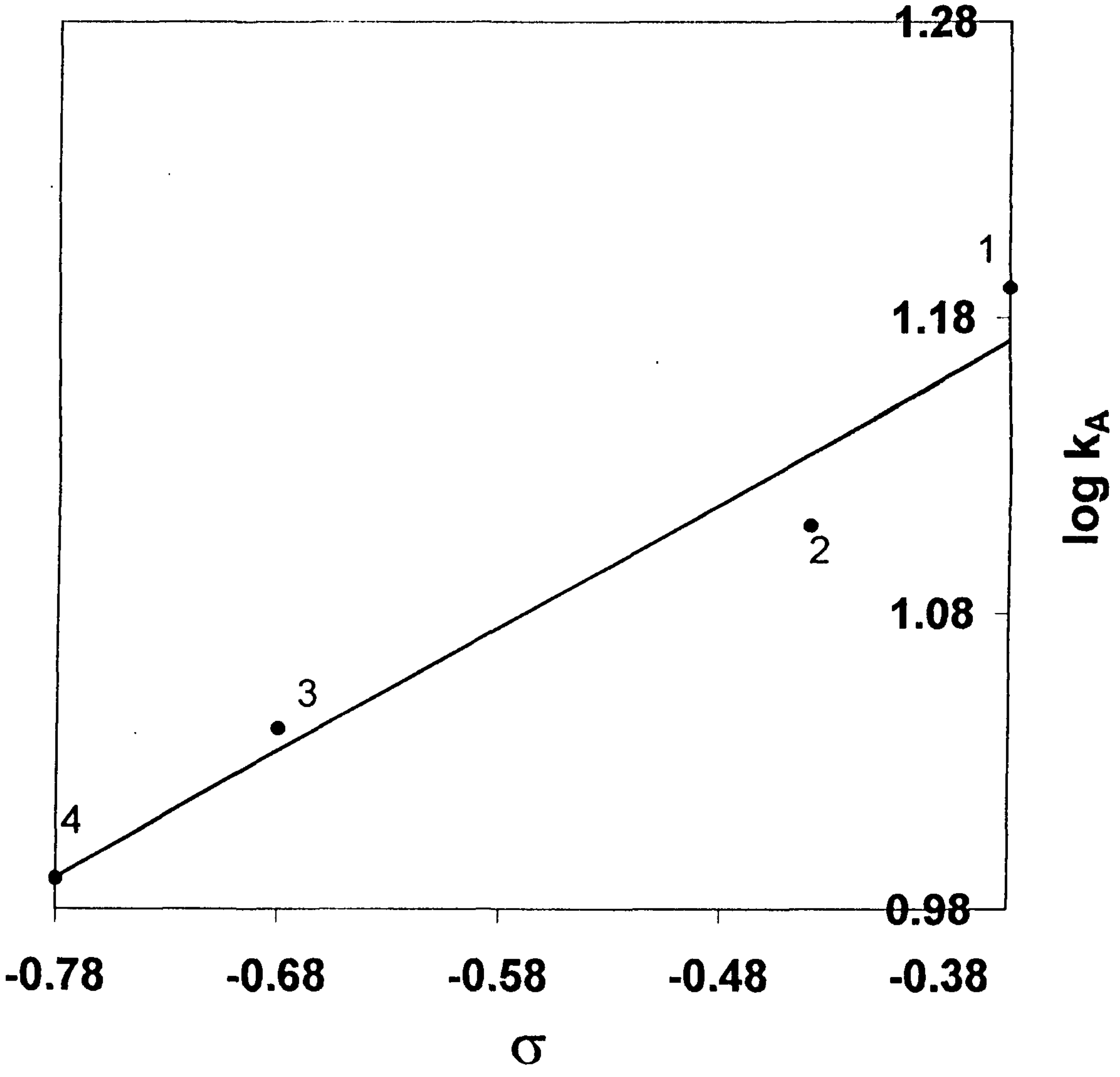


Fig. 13. Plot of σ against log k_A for 5-methyl-2-furaldehyde (1), 2-furaldehyde (2), 5-bromo-2-furaldehyde (3), 5-nitro-2-furaldehyde (4).

It would be pertinent to compare the ρ values of + 0.675 and + 0.423 (obtained in this study), with the ρ values obtained for a series of aromatic aldehydes in 91% acetic acid (29,30). Since aromatic aldehydes were hydrated only to a small extent, the similarity between these values ($\rho = +1.02$ and +0.77) (ref. 29,30) and our value ($\rho = +0.675$ and +0.423) was satisfactory in that for both cases, small positive values were obtained. The positive value of ρ could be interpreted as being due a superimposed effect of the ring substituents on the hydration equilibrium, wherein it had been shown that all the aldehydes oxidized by chromic acid were completely hydrated in aqueous solution (31). Earlier work on the oxidation of benzaldehyde by chromic acid had shown that a Hammett plot of the data yielded a good straight line with a slope ρ = + 1.06 (ref. 32). Later work on the chromic acid oxidation of benzaldehyde had shown that the reaction proceeded by way of the chromic acid ester of hydrated benzaldehyde as an intermediate (33). In the present investigation, the correlation with k_{Hy} supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen-transfer reaction between a free aldehyde and QDC was very unlikely. Thus, the rate-accelerating effect of the electronegative substituents could be interpreted in terms of greatly increased hydration (Tables 8 and 9). This similarity provided additional support for the mechanistic pathway suggested in the present investigation, that the rate-determining step was the oxidative decomposition of the chromate ester of an aldehyde hydrate. The hydrated forms of the substrates would remain as undissociated molecules (since $[H^+]$ would be much greater than the dissociation constants of the substrates), in the range of the acid concentrations used in the present study (0.5 – 1.50 M). It was therefore suggested that the protonated QDC reacted with the hydrated form of the heterocyclic aldehydes to give the corresponding acids.

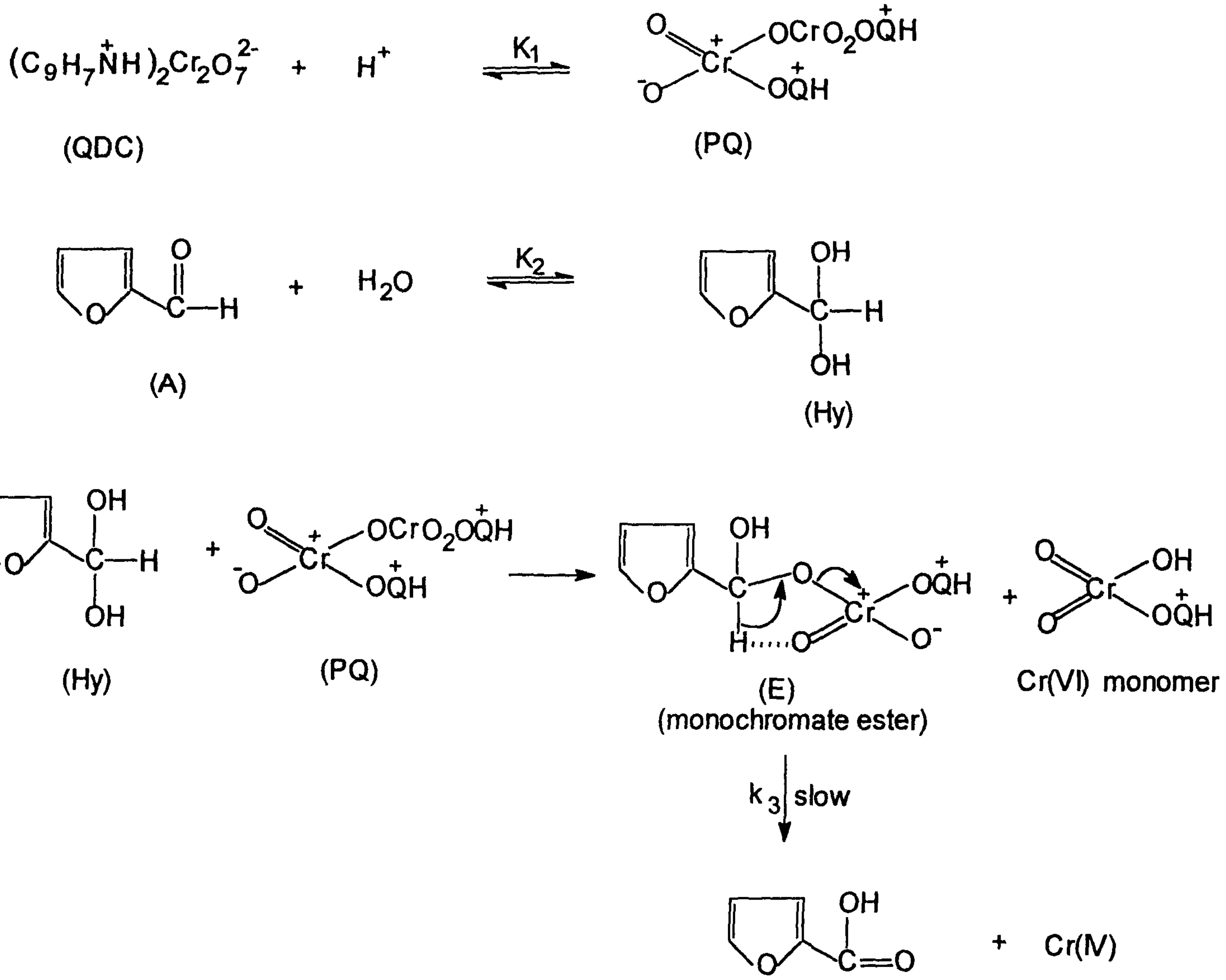
The close resemblance between aldehyde hydrates and alcohols, both in structure and in many aspects of oxidation, would result in a similarity in the two oxidation reactions. In the oxidation of alcohols by chromic acid, it was established that the rate-determining step involved the decomposition of the protonated acid chromate ester (34). By analogy, the oxidation of aldehydes should proceed via the formation of a similar intermediate (an ester of the aldehyde hydrate), which would undergo decomposition in the rate-determining step. It has been shown that the hydration of the aldehydes was not rate-determining for the oxidation reaction (35). The ester of the aldehyde hydrate would be in equilibrium with the free aldehyde and the aldehyde hydrate, and could be formed either by a carbonyl addition reaction to the free aldehyde or by esterification of the hydrate (36). The esterification reaction would be more likely, and would help to understand and predict aldehyde oxidation reactions and their relationship to the closely related oxidation of alcohols.

A cyclic structure for the reaction intermediate would explain all of the features of the oxidation reaction. If the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and conversion to the corresponding carboxylic acid could be rationalized. The mechanistic pathway involved the formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the aldehyde hydrate (step 2).

Electron flow in a cyclic transition state can be rationalized by assuming that if the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the electron-transfer process could take place through the carbon-oxygen-chromium bond (37). This would facilitate the formation of the chromate ester, and enhance the ease of conversion to the product. Such a transition state envisaged the transfer of electrons towards the chromium, occurring by the formation of the carbon- hydrogen - oxygen bonds, as well as by the carbon-oxygen-chromium bonds.

The slow step of the reaction involved the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, as evidenced by the experimental observation of a kinetic isotope effect for the oxidation of 2-furaldehyde-d_1 ($k_H / k_D = 5.8$). The proton was removed in the cyclic transition state (co-planarity of all the atoms involved), the centre of which resided on an electron-dense oxygen in the chromate ester (38). Since the five-membered heterocyclic ring system is a planar pentagon with sp^2 hybridized carbon atoms, possessing considerable aromatic character arising from delocalization of the two paired electrons, it would undergo a reaction via an electrocyclic mechanism involving six electrons; being a Hückel-type system (4n+2), this was an allowed process (39). This mechanism was supported by the observation that the reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant. The sequence of reactions for the oxidation of heterocyclic aldehydes by QDC, in an acid medium, is shown in the Scheme.

SCHEME



$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \xrightarrow{\text{fast}} 2\mathrm{Cr(V)}$$

$$\mathrm{Cr(V)} + \text{substrate} \xrightarrow{\text{fast}} \text{product} + \mathrm{Cr(III)}$$

In an acid medium, the oxidant QDC was converted to the protonated dimetallic chromium (VI) species **(PQ)** [in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $Cr_2O_7^{2-}$ (ref. 12)]. The substrate **(A)** 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 monochromate ester **(E)** and a Cr(VI) monomer. The monochromate ester **(E)** underwent decomposition in the rate-determining step to give the product (the corresponding acid), along with the Cr(IV) species. The conversion of Cr(IV) to Cr(III) proceeded by a disproportionation reaction. It was shown that 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) (ref. 40) 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 of Cr(V) with the substrate (40,41).

If the mechanism shown in the Scheme is correct, then the attack of the protonated QDC **(PQ)** on the aldehyde hydrate **(Hy)** would be crucial, and would be favoured by the formation of the cyclic chromate ester **(E)**.

Based on the mechanism shown in the Scheme, the rate law has been derived as follows:

$$- d\,[QDC] / dt = k_3\,[E] = k_3\,[Hy]\,[PQ], \qquad (13)$$

where $[PQ] = K_1\,[QDC]\,[H^+]$, and $[Hy] = K_2\,[A]\,[H_2O]$.

Substituting the values of [PQ] and [Hy] in eq. 5 (taking the activity of water to be unity), we obtain :

$$- d\,[QDC] / dt = K_1K_2\,k_3\,[A]\,[QDC]\,[H^+] \qquad (14).$$

From this rate expression (eq. 14), it is clear that the reaction exhibited a first-order dependence with respect to the concentrations of each (substrate, oxidant, and acid). Hence, $- 2.303\ d \log [QDC] / dt = k = K_1K_2\,k_3\,[A]\,[QDC]\,[H^+]$. This rate law explains all of the experimentally observed results.

The kinetic data collected established that the application of QDC to the oxidation of heterocyclic aldehydes led to the formation of carboxylic acids. The mechanistic pathway for the oxidation reaction was via an attack of the oxidant on the aldehydic function of the substrate, leaving the heteroatom site intact. This investigation highlighted the importance of QDC as an oxidant, and emphasized the efficiency of the reactions of QDC with heterocyclic aldehydes. It can be suggested that these reactions might prove to be useful and significant as regioselective routes for the synthesis of carboxylic acids.

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LIST OF PUBLICATIONS

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   Girija S. Chaubey and Mahendra K. Mahanti*
   Oxidation Communication, **23**, 500 (2000).

2. Kinetics of oxidation of 2- furfural by quinolinium dichromate.
   G. G. Kharnaior, **G.S. Chaubey** and M.K. Mahanti*
   Oxidation Communication, **24**, 377 (2001).

3. Kinetics of the oxidation of heterocyclic aldehydes by quinolinium dichromate.
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4. Kinetics features of the oxidation of aliphatic dialdehydes by quinolinium dichromate.
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5. Kinetics of oxidation of 3-alkanones by quinolinium dichromate.
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6. Oxidation of heterocyclic aldehydes by quinolinium dichromate : A kinetic study.
   Girija S. Chaubey, Simi Das and Mahendra K. Mahanti*
   Heterocyclic Communications, (Accepted)

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Don Bosco College Tura	Physics, Chemistry, Mathematics, Biology	1991	Pre-University (Science)

Computer Proficiency : WINDOW 9x, MS OFFICE, BASIC programming and special programs to deal with scientific computations and simulations.

- Having hands on experience with Instruments like UV-VISIBLE and FT-IR Spectrophotometers.

SCHOLARSHIP / FELLOWSHIP AWARDED

1990 - 92	National Scholarship for Two years.
1999 - present date :	Research Scholarship from Government of Meghalaya for the Ph.D. Programme.

WORKING EXPERIENCE

- Worked as a Post-Graduate Teacher in Chemistry for a period for five months from August 1997 to December 1997 in Secondary School, Tura, Meghalaya.
- Have been guiding Master's degree Chemistry students during their project work since 1998.

RESEARCH PUBLICATIONS

1. Kinetics and mechanism of oxidation of valeraldehyde by quinolinium dichromate.
   Girija S. Chaubey and M.K. Mahanti*
   Oxidation Communication, **23**, 500 (2000).
2. Kinetics of oxidation of 2- furfural by quinolinium dichromate.
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   Oxidation Communication, **24**, 377 (2001).
3. Kinetics of the oxidation of heterocyclic aldehydes by quinolinium dichromate.
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   Bull. Chem. Soc. Japan, **75**, 2215 (2002).
4. Kinetics features of the oxidation of aliphatic dialdehydes by quinolinium dichromate.
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5. Kinetics of oxidation of 3-alkanones by quinolinium dichromate.
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   Oxidation Communication, **25**, 000 (2002). (In Press).

6. Oxidation of heterocyclic aldehydes by quinolinium dichromate : A kinetic study.
   Girija S. Chaubey, Simi Das and Mahendra K. Mahanti*
   Heterocyclic Communications, (Accepted)
7. Quinolinium dichromate oxidation of aliphatic aldehydes : A kinetic study.
   Girija S. Chaubey, Simi Das and Mahendra K. Mahanti*
   Croatica Chemica Acta (In review)
8. Kinetics of the oxidative cleavage of α-keto acids by quinolinium dichromate.
   Simi Das, **Girija S. Chaubey** and Mahendra K. Mahanti*
   Kinetics and Catalysis (In review)
9. Kinetic studies on the oxidation of aliphatic aldehydes by quinolinium dichromate.
   Girija S. Chaubey, Simi Das and Mahendra K. Mahanti* (submitted).
10. Kinetics of oxidation of α, β-unsaturated aldehydes by quinolinium dichromate.
    Girija S. Chaubey, Simi Das and Mahendra K. Mahanti* (submitted).

CONFERENCES / SEMINARS ATTENDED

- Participated in a National Conference on Surfactants, Emulsions and Biocolloids organized jointly by Department of Chemistry, North-Eastern Hill University, Shillong and Indian Society for Surface Science and Technology during October 3-5, 2001.

- Attended a two-day Seminar on "Atomic Energy and Societal Development in India" sponsored by Department of Atomic Energy during September 17-18, 2002 at North-Eastern Hill University, Shillong.

- Presented a paper entitled "Kinetics of the oxidation of heterocyclic aldehydes by quinolinium dichromate" at the 72ND Annual Session of the National Academy of Sciences, India, held at the North-Eastern Hill University, Shillong, during October 25-27, 2002.

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