KINETICS OF OXIDATION OF SOME ORGANIC SUBSTRATES BY QUINOLINIUM DICHROMATE

SUMMARY

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SUMMARY

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 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 substances 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 oxodiperoxo chromium(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);

Chaudhuri's reagent-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(TBACC); tetramethyl 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); chlorotrimethylsilane - chromium 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-carboxy pyridinium 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); cyano pyridinium 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) and chromium trioxide in the presence of wet aluminium oxide taken in hexane(37).

The most recent chromium(VI) reagent which has been introduced for the oxidation of organic substrates has been quinolinium fluorochromate(QFC), used in chloroform as solvent(38). This reagent has been used for the oxidation of alcohols, polycyclic arenes and diphenyl sulfide, and the yields reported have been excellent(38).

The reagent employed in the present investigation has been quinolinium dichromate (QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$. This reagent was first reported to have been used for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, and for the oxidation of aldehydes to acids(39). This reagent has now emerged as a very useful and versatile oxidant, and has been used for the oxidation of a variety of organic substrates. When taken in dimethylformamide or in dimethylformamide - water mixtures, in the presence of an acid, quinolinium dichromate(QDC) was found to be very efficient for the oxidation of benzyl alcohols(40), aryl alkanes(41), diphenylamines(42), polynuclear aromatic hydrocarbons(43,44), toluene and substituted toluenes(44,45), fluorene(46), amino acids(47) and benzoin(48).

The present investigation focuses attention on the kinetic features pertaining to the oxidation of various organic substrates by quinolinium dichromate(QDC) in acid medium, using dimethylformamide(DMF) and dimethylformamide - water (DMF-H_2O) mixtures as the solvent, 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 acid 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 DMF and DMF-H_2O mixtures, have included the following:

1. <u>Alcohols</u> - Chapter 1

(a) Cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol).

(b) Bicyclic alcohols (borneol and isoborneol).

(c) Allylic alcohols (geraniol and farnesol).

2. <u>Unsaturated Compounds</u> - Chapter 2.

(a) Styrene and substituted styrenes.

(b) Cinnamic acid and substituted cinnamic acids and crotonic acid.

(c) Maleic acid and fumaric acid.

Chapter 1 - Kinetics of Oxidation of Alcohols.

The kinetics of oxidation of alcohols (cyclic alcohols, bicyclic alcohols and allylic primary alcohols) by quinolinium dichromate(QDC) has been studied in acid medium, using dimethylformamide(DMF) and dimethylformamide-water(DMF-H_2O) mixtures as the solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440nm. For all the alcohols studied, stoichiometric ratios, Δ[QDC]/Δ[Substrate], in the range 0.61-0.73 were obtained. The rate of the reaction was found to be dependent on the first powers of the concentration of each reactant (substrate, oxidant and acid). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated chromium(VI) species in the rate-determining step.

The reaction has been found to be fastest in those solvent mixtures that contained the largest proportions of dimethylformamide. Plots of log k_1 (the pseudo-first-order rate constant) against the reciprocal of the dielectric constant were linear, with positive slopes. This indicated an interaction between a positive ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated chromium(VI) species.

The reactions were studied over a range of temperatures, 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 thus 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 498K. Although current views do not attach much physical significance to isokinetic temperatures, a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. It was further found that the values for the free energies of activation($\Delta G^{\neq}$) were nearly constant, indicating that the same mechanism operated for the oxidation of all the alcohols 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.

It has been earlier established that the kinetic rates of oxidation for cyclic compounds could be rationalized on the basis of the difference in strain energy between the ground state and the transition state. In cyclic systems, changes in bond hybridization had resulted in concomitant changes in angle strain, bond opposition strain or transannular strain. In the present investigation, the order of reactivity for the oxidation of cyclic alcohols by quinolinium dichromate (QDC) was observed to be:

Cyclooctanol >	cycloheptanol >	cyclopentanol >	cyclohexanol.
(8-)	(7-)	(5-)	(6-)

This order of reactivity was rationalized on the basis of a change in ring strain involved, in passing from the initial state (sp^3) to the transition state (sp^2). The major source of strain for the 5-, 7- and 8- membered ring systems arose as a result of non-bonded interactions. Such interactions would be absent in the ground state of the 6-membered ring system. The net result would be that reactions leading to the easing of some of these non-bonded interactions in 5-, 7- and 8- membered ring systems would be facilitated. The nature of the transition state would be such that this strain relief could occur, enabling the formation of a product-like transition state. For the 6- membered ring system, any deviation from the staggered conformation would be unfavourable, since this would result in a higher energy of activation. This would account for the slowness in the rate of oxidation of cyclohexanol, and would thus explain the observed order of reactivity for the cyclic alcohols (8>7>5>6).

The rates of oxidation of bicyclic alcohols have been observed to be influenced both by steric and electronic factors. The rate data on the oxidation of bicyclic alcohols by quinolinium dichromate (QDC) have been interpreted in terms of the differences in the relative stability of the alcohols and the transition states. The present data on the oxidation of bicyclic alcohols by QDC suggested that, if the strain-induced instability of the chromate ester were to determine the relative rates of oxidation, then there would be an acceleration of the rate resulting from the relief of steric strain in the chromate ester. The effect of the strain-relief factor on the relative rates of oxidation of bicyclic alcohols by QDC have thus been examined. The kinetic data showed that borneol, with an axial hydroxyl group, was more stable than the isomeric equatorial isoborneol. In isoborneol, since the chromate ester group was in the exo configuration and was more strained due to the presence of the bridged gem-dimethyl groups, there would be the distinct possibility of the hydroxyl group suffering a non-bonded repulsion from the gem-dimethyl group at C-7. This effect would be diminished when the transition state was formed. In the transition state, therefore, there would be a rate-enhancing relief of steric strain. This resulted in isoborneol being oxidized more rapidly than borneol by a factor of 2.63, thus indicating a difference in the ease of ester decomposition.

Mechanistic pathways for the oxidation of alcohols have very often been established using kinetic isotope effects. In the present investigation, kinetic isotope effects have been used to establish the structure of the transition state and the nature of bond cleavage in the rate-determining step of the reaction. The kinetic isotope effects, k_H/k_D were observed to be in the range 5.6-6.3 for the oxidation of the different alcohols studied. The high values of the kinetic isotope effects observed would suggest a cyclic transition state, with a rate-determining cleavage of the carbon-hydrogen bond. The observed k_H/k_D values obtained for the oxidation of the various alcohols (cyclohexanol, isoborneol, geraniol and farnesol) corresponded to a substantial loss of zero point energy in the transition state (4.7-5.3 kJ mol^{-1}). This indicated that the C-H bond was considerably stretched in the transition state. Thus, the high values of k_H/k_D and the high zero point energy values would establish a rate-determining cleavage of the C-H bond.

All the kinetic evidence obtained for the oxidation of alcohols by quinolinium dichromate (QDC), in acid medium, would establish that the oxidation proceeded via a mechanism which involved the formation of a cyclic chromate ester, followed by the decomposition of the ester involving the slow rupture of the C-H bond. A cyclic transition state could be postulated on the basis of the relative rates of oxidation of the cyclic alcohols studied. A conversion of the cyclic alcohols to the corresponding ketones was observed, and this process involved a change $>\text{CHOH} \longrightarrow >\text{C=O}$. The reaction intermediate could be visualized as having a cyclic structure, which would explain all the kinetic features of the oxidation reactions. The negative entropies of activation would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The decomposition of the ester could be visualized, wherein the hydrogen was bonded in the transition state to both, the alcoholic carbon atom and the oxygen atom attached to chromium. In a cyclic transition state, the electron flow could be considered for the conversion of the ester to the transition state. This could be rationalized if the chromium were to be coordinated through the alcohol O-H group. The process of electron transfer could then take place through the carbon-oxygen-chromium bond. This not only would help to facilitate the formation of the chromate ester, but would also enhance the ease of conversion to the ketone. The kinetic isotope effects observed for this process had established a cleavage of the C-H bond in the rate-determining step of the reaction. The proton was removed in the cyclic transition state (coplanarity of all the atoms being involved), the centre of which resides on an electron-dense oxygen in the chromate ester. The transition state thus postulated would envisage the transfer of electrons towards the chromium occurring by the formation of the carbon-oxygen-hydrogen bonds as well as carbon-oxygen-chromium bonds.

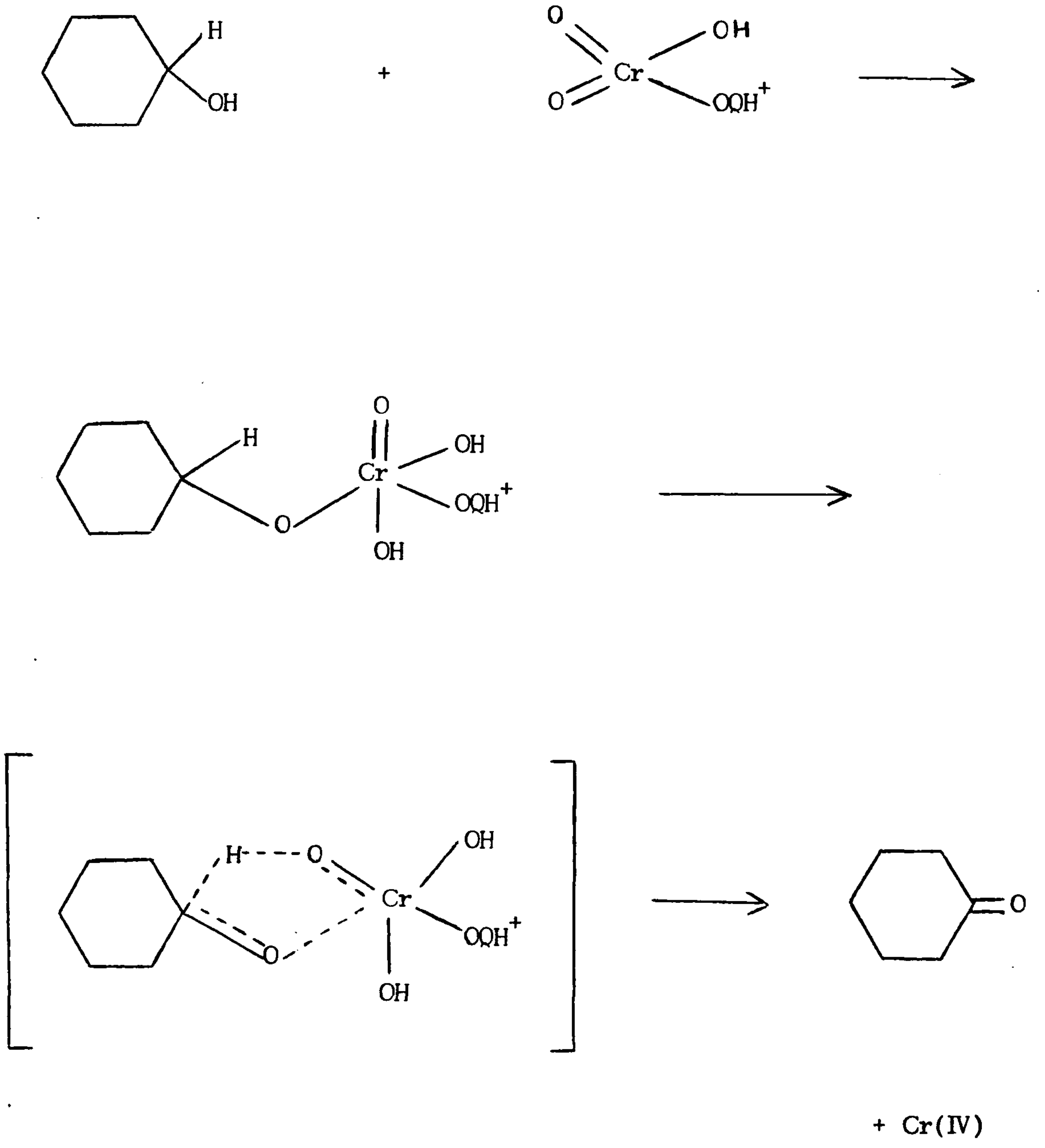
The Zimmerman treatment of electrocyclic reactions was also used to support the mechanism of these oxidation reactions. Using this topological approach to the orbital levels of the transition state, 4n+2 electrons would form a closed shell giving it stability (Hückel transition state), resulting in the reaction being an allowed process. In the present investigation, the oxidation of alcohols (cyclic, bicyclic and allylic primary alcohols) by quinolinium dichromate (QDC), in acid medium, involved the formation of a cyclic chromate ester. The second step of the reaction would involve the transfer of two electrons in a cyclic system. The electrocyclic mechanism for the oxidation of alcohols by quinolinium dichromate(QDC) clearly involved six electrons. Since this would be a Hückel-type system (4n+2), this would be an allowed process.

Under the experimental conditions employed in the present investigation, cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol) were oxidized by quinolinium dichromate (QDC) in acid medium, to the corresponding cyclic ketones in each case. The products (the respective cyclic ketones), obtained in good yields, were characterized by IR analysis, and by their respective 2,4-dinitrophenylhydrazone derivatives.

Under the experimental conditions employed in the present investigation, bicyclic alcohols (borneol and isoborneol) were oxidized by quinolinium dichromate(QDC) in acid medium to the corresponding ketone (camphor) in each case. The product (camphor), obtained in good yield, was characterized by its melting point, IR analysis and by its 2,4-dinitrophenylhydrazone derivative.

Under the experimental conditions employed in the present investigation, allylic alcohols (geraniol and farnesol) were oxidized by quinolinium dichromate (QDC) in acid medium to the corresponding aldehydes (geranial and farnesal). The products (geranial and farnesal), obtained in good yields, were characterized by IR analysis and by their respective 2,4-dinitrophenylhydrazone derivatives.

SCHEME 1



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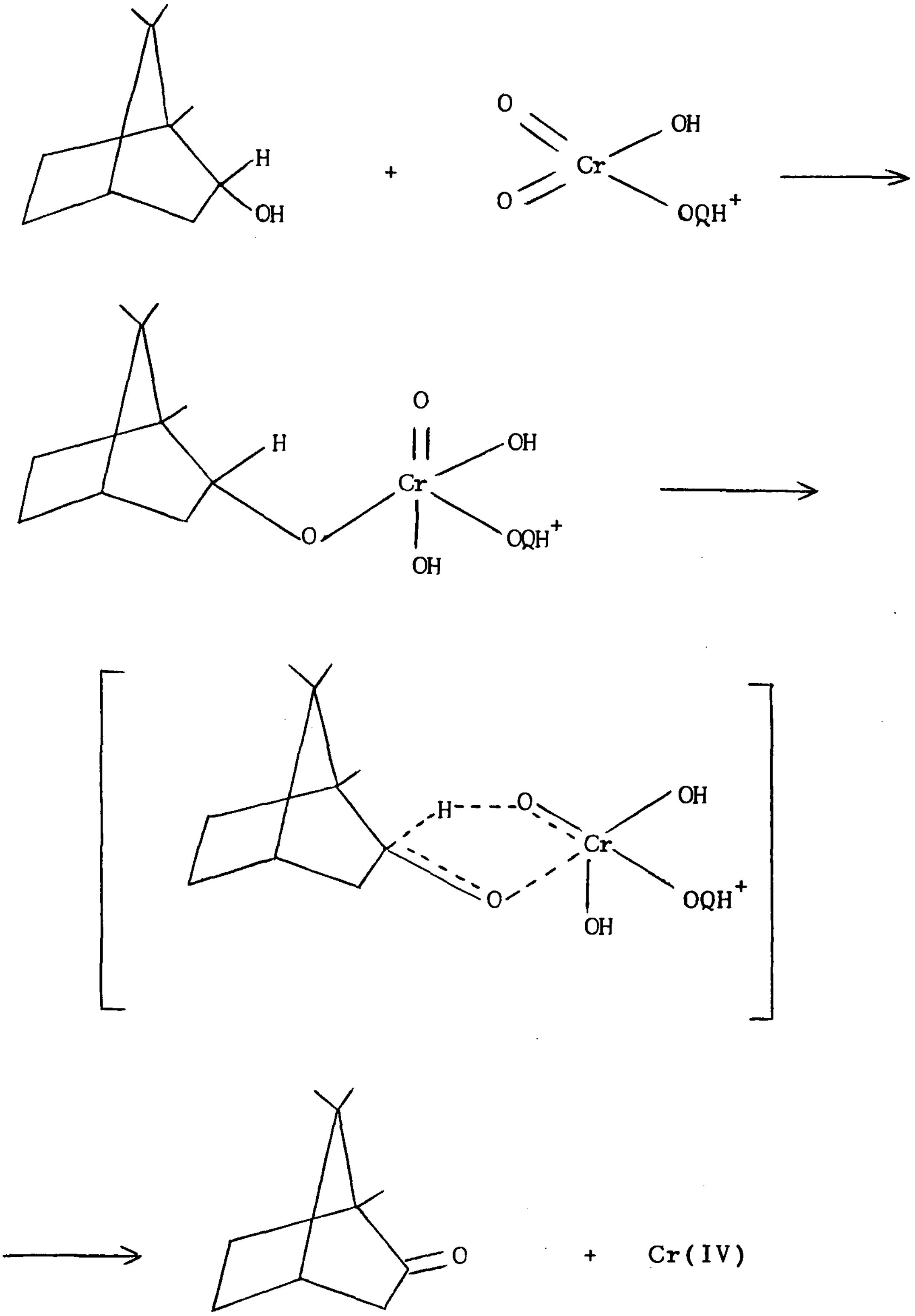
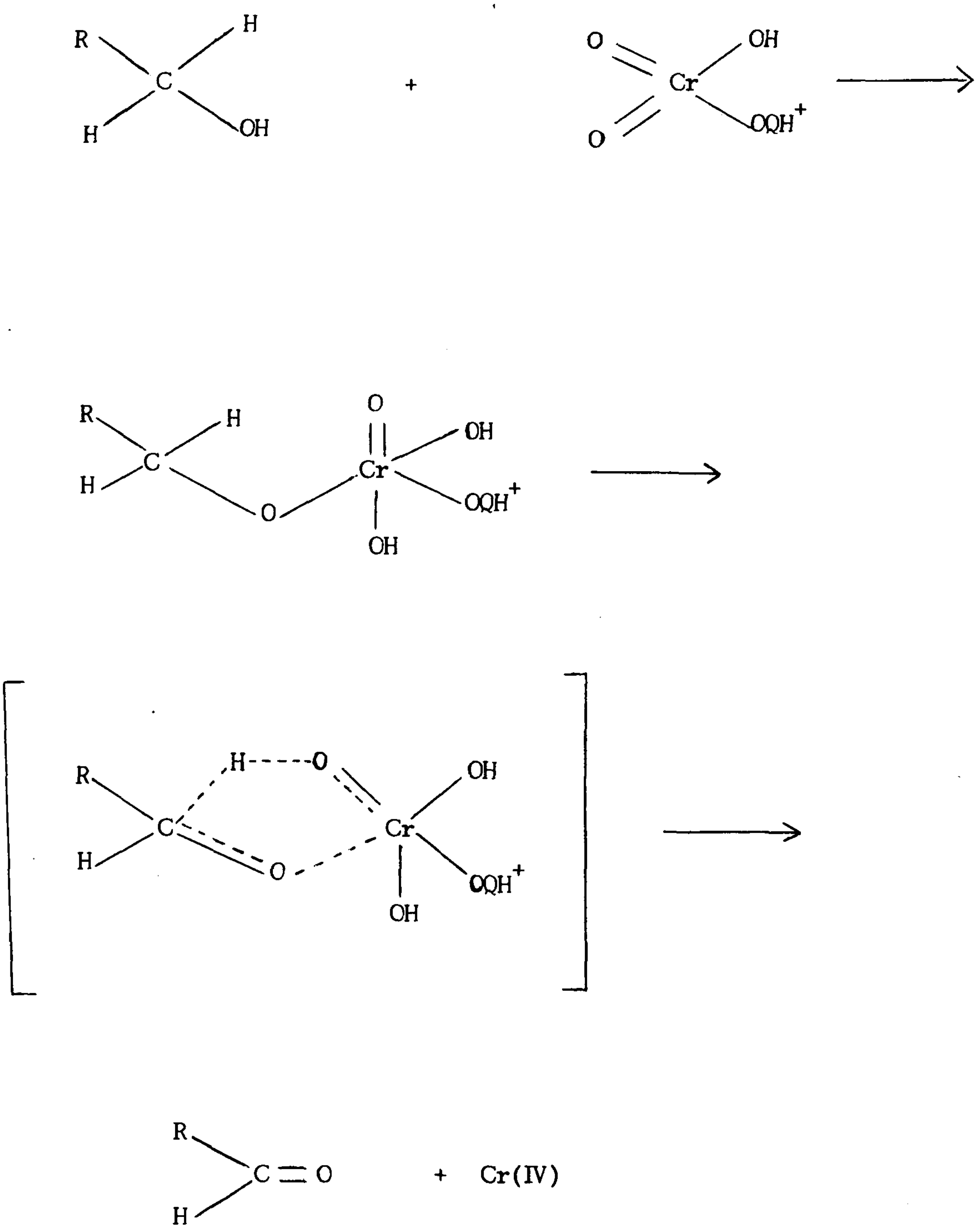


SCHEME 3



where R = C_9H_{15} (geraniol)

= $C_{14}H_{23}$ (farnesol)

Chapter 2 - Kinetics of Oxidation of Unsaturated Compounds.

The oxidation of carbon-carbon double bonds by various oxidants is an important and well-known reaction. The periodate-permanganate cleavage of alkenes has been used as a means of determining the position of double bonds in unsaturated compounds(49). Earlier work on the oxidation of styrenes have been reported wherein oxidants such as thallic ions(50-52), chromyl chloride(53,54), lead tetraacetate(55), ceric ions(56) cobaltic ions(57-59), peracetic acid(60) and acidic hexacyanoferrate(111) ions(61) have been employed. The oxidation of cinnamic acid by permanganate had resulted in a cleavage of the carbon-carbon double bond to yield benzaldehyde(62,63).

The present work is a detailed kinetic investigation of the oxidation of unsaturated compounds (styrenes, cinnamic acids, crotonic acid, maleic acid and fumaric acid) by quinolinium dichromate (QDC), in acid medium, using dimethylformamide(DMF) and dimethylformamide-water (DMF-H_2O) mixtures as the solvent, under a nitrogen atmosphere. The course of the reactions was monitored by observing the disappearance of chromium(VI) at 440nm, spectrophotometrically. The stoichiometric ratios, Δ[QDC]/Δ[Substrate], were in the range 1.30-1.38. 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 protonated chromium(VI) species would be a reactive electrophile, and hence sufficiently reactive to attack the double bond of the unsaturated compounds and bring about the oxidative cleavage of the carbon-carbon double bond.

The role of the solvent in these oxidation reactions was investigated. It was observed that the rate of oxidation was slowest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of dimethylformamide resulted in an increase in the rate of oxidation. Plots of log k_1 (pseudo-first-order rate constant) against the reciprocal of the dielectric constant were linear, with positive slopes, indicating an ion-dipole type of reaction.

The effect of changes in temperature on the rate of the reaction was studied, and the Arrhenius equation was found to be valid. The activation energies and the other activation parameters were evaluated. The reactions were characterized by fairly high positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$, which suggested that the transition state was highly solvated. 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 isokinetic temperature, obtained from the plots of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, were 313K (for styrenes) and 333K (for cinnamic acids). The similarity 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.

Structure-reactivity correlations were used to establish the nature of the transition state, and hence to deduce the mechanistic pathway of these reactions. It was observed that electron-releasing substituents accelerated the oxidation process, and electron-withdrawing groups retarded the process. Hence, a linear free energy relationship of the Hammett equation type was used to correlate the reactivity with the Hammett substituent constants. Plots of log k_1 against the σ substituent constants gave values of $\rho = -4.0$ for both, styrenes and cinnamic acids. A hydrogen abstraction mechanism was unlikely, in view of the failure to induce the polymerization of acrylonitrile and the reduction of mercuric chloride. In most hydrogen abstraction reactions, the reaction constants have small magnitudes. In the present investigation, the values obtained for the reaction constant were $\rho = -4.0$. This suggested that the transition state possessed a large degree of carbonium ion character, resulting from a large amount of positive charge developing at the carbon atom adjacent to the benzene ring (α carbon atom). Earlier studies had shown that ρ values larger than -3 suggested a fairly large degree of carbonium ion character in the transition state(64,65).

The rate data showed that cinnamic acid was oxidized at a faster rate by quinolinium dichromate(QDC), as compared to crotonic acid. In cinnamic acid, the phenyl group exerted an electron-releasing effect which counteracted, in part, the electron-attracting effect of the carboxyl group. In crotonic acid, the reaction proceeded at a slower rate because the electron-attracting properties of the carboxyl group reduced the nucleophilic properties of the double bond. The reasonable conclusion from these data was that the electron-releasing effect of the phenyl group seemed to be greater than that of the alkyl group.

In the present investigation, the kinetic data obtained revealed that maleic acid reacted marginally faster than fumaric acid. This order of reactivity was explained on the basis of steric factors. The cis-attack of the two oxygen atoms of quinolinium dichromate(QDC) resulted in the formation of a cyclic intermediate, accompanied by a change in the hybridization of the olefinic carbon atom from the sp^2 to the sp^3 state. The cis-approach of the oxidant imposed an eclipsed conformation on the maleate species. The carboxylate groups were thus brought into closer proximity to each other, before the staggered conformation in the cyclic intermediate was obtained. This resulted in the reaction taking place at a marginally faster rate for the oxidation of maleic acid than that for the oxidation of fumaric acid.

The kinetic isotope effect showed a clear distinction between the α and β carbon atoms of styrenes (and cinnamic acids) in the transition state. For the oxidation of α-deuteriostyrene and cinnamic acid -α-d, the k_H/k_D values were 0.98 and 0.99, respectively. These values were reasonable, since the benzylic carbon atom (α carbon), in going from an olefinic centre to a carbonium ion-like character, during the process of electron abstraction, would remain sp^2 in character (attack being at the β carbon). For the oxidation of β,β-dideuteriostyrene and cinnamic acid -β-d, the k_H/k_D values were 0.80 and 0.78, respectively. These values indicated that, in the rate-determining step, the oxygen atom of quinolinium dichromate(QDC) attacked the terminal carbon atom (β carbon), and the change in the state of hybridization progressed from sp^2 towards sp^3 as the new bond was being formed. The hybridization of the benzylic carbon atom (α carbon) would remain essentially sp^2 in character, since it was going from an olefinic centre to a carbonium ion-like character. Since the oxidation of styrene (and of cinnamic acid) exhibited an inverse secondary deuterium kinetic isotope effect only at the β carbon atom, this suggested that the rate-determining step of the reaction produced a carbonium ion in which the α carbon atom remained sp^2 in character. The implication of this kinetic observation was that there was negligible C_α-O bond formation, but substantial C_β-O bond formation in the transition state.

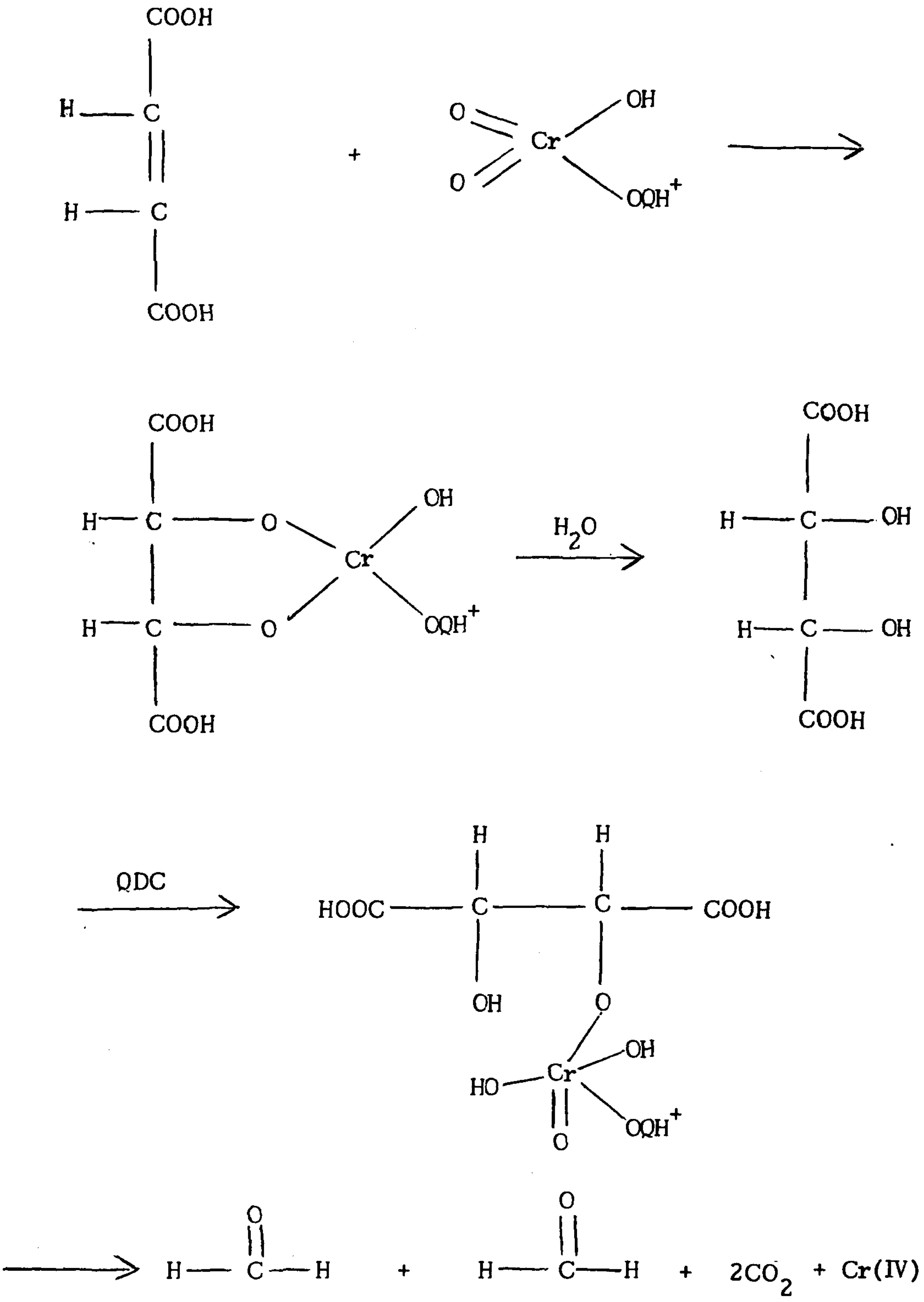
The oxidation of alkenes by chromium(VI) reagents had often led to a variety of products. In some cases, allylic oxidation predominated, while in other cases, the oxidation had resulted in the formation of epoxides, ketols, acids or ketones. It had been suggested that the oxidation of alkenes by chromic acid involved an electrophilic attack of chromium(VI) at the double bond, with the formation of a cationic intermediate in the rate-determining step. It had also been shown that the oxidation of styrene by chromyl chloride exhibited an isotope effect only at the β-carbon, suggesting that the rate-determining step of the reaction produced a carbonium ion in which the α-carbon remained sp^2 in character(66).

The reaction pathway involved an acyclic process in the rate-determining step. The formation of the carbonium ion implied substantial C_β-O bond formation, an observation which was supported by the value of $\rho = -4.0$ (for styrenes and cinnamic acids), and by the kinetic isotope effects. The acyclic mechanism was further supported by earlier ab initio calculations on the energetics of such reactions, wherein the formation of a five-membered cyclic transition state was not favoured(67). In the present investigation, the application of the topological approach to the orbital levels of the transition state indicated that not all overlapping orbitals were bonding. Since such an orbital overlap picture did not satisfy the 4n rule, it was considered to be a Möbius-type system, and hence was a forbidden process. This implied that the reaction pathway involved an alternative route. Thus, the reaction route involved an acyclic mechanism which was not subject to selection rules.

In the present investigation, all the kinetic data and experimental evidence for the oxidation of the olefinic substrates (styrene, cinnamic acid and crotonic acid) by quinolinium dichromate(QDC), in acid medium, supported a reaction pathway involving an acyclic mechanism. The observation of an isotope effect only at the β carbon atom suggested the formation of a carbonium ion wherein the α carbon atom remained sp^2 in character. This was further supported by the value of the reaction constant, $\rho = -4.0$ for both, styrenes and cinnamic acids. The thermodynamic parameters obtained also supported an acyclic transition state. Energy considerations have established that an acyclic mechanism would be an allowed process for the oxidation of these substrates by quinolinium dichromate(QDC).

For the oxidation of the substrates under consideration (styrenes, cinnamic acids and crotonic acid), the kinetic data suggested the compatibility of an electrophilic attack of the protonated form of the oxidant(QDC) on the double bond of the substrate to give a carbonium ion. The carbonium ions thus formed, from the oxidation of styrene (and cinnamic and crotonic acid), were stabilized by the phenyl group. The intermediate thus formed reacted with a nucleophile (water), in the reaction mixture, to form a second unstable intermediate. In the presence of water and excess QDC, this intermediate was converted to the cyclic chromate ester, which was cleaved to give the observed products. The products formed, from the oxidation of styrene, were benzaldehyde and formaldehyde, which were characterized by spectral methods. The products obtained, from the oxidation of cinnamic acid, were benzaldehyde and glyoxylic acid, which were characterized by spectral methods. The products obtained, from the oxidation of crotonic acid, were acetaldehyde and glyoxylic acid, which were characterized by spectral methods. The formation of these products substantiated the mechanism of the oxidation reactions, wherein there was a cleavage of the carbon-carbon bond in the final step of the reaction.

SCHEME A



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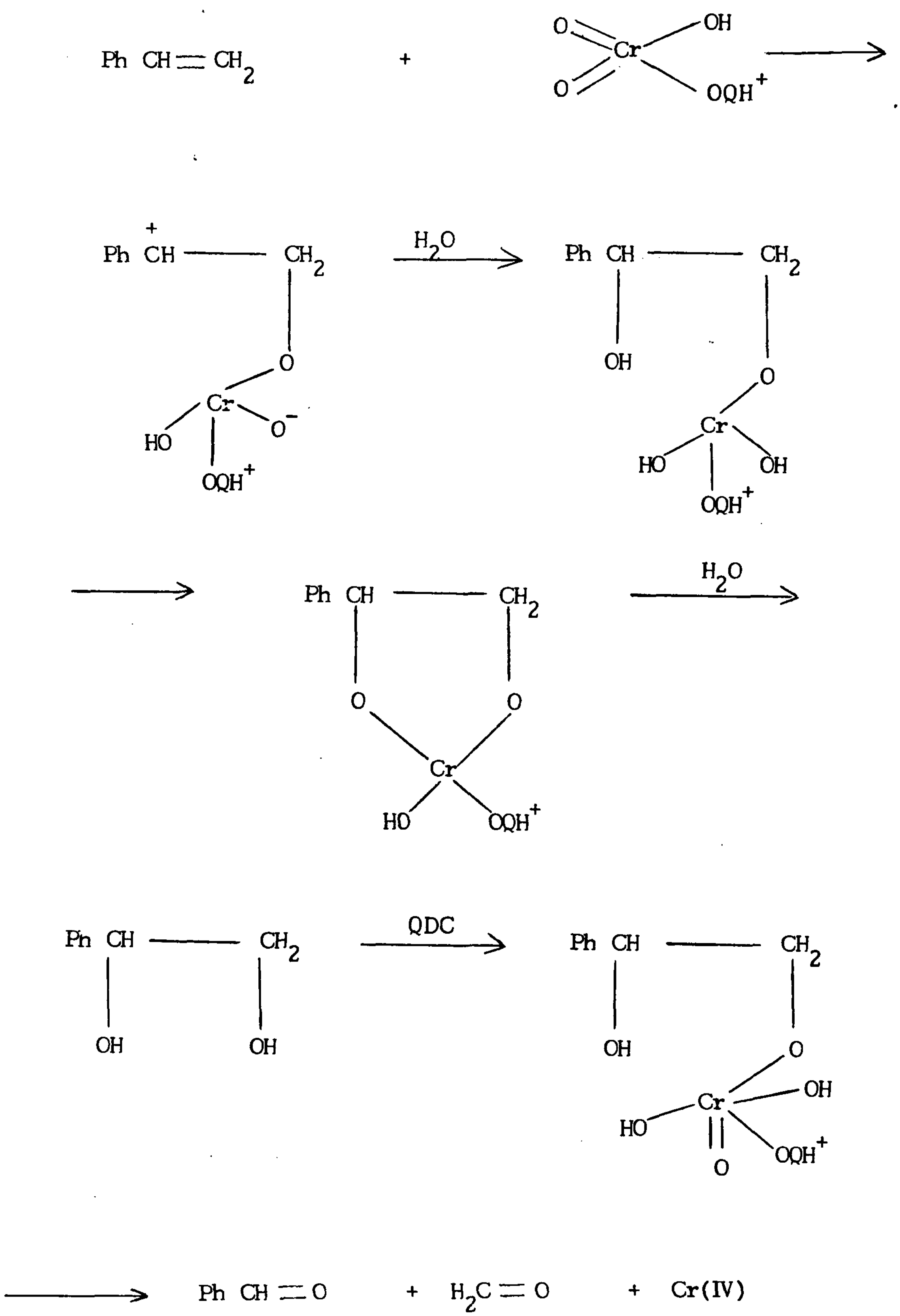

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O
O
Cr
OH
OQH+
+
Ph CH
CH2
O
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HO
O−
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OH
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CH2
O
O
Cr
HO
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CH2
OH
OH
QDC
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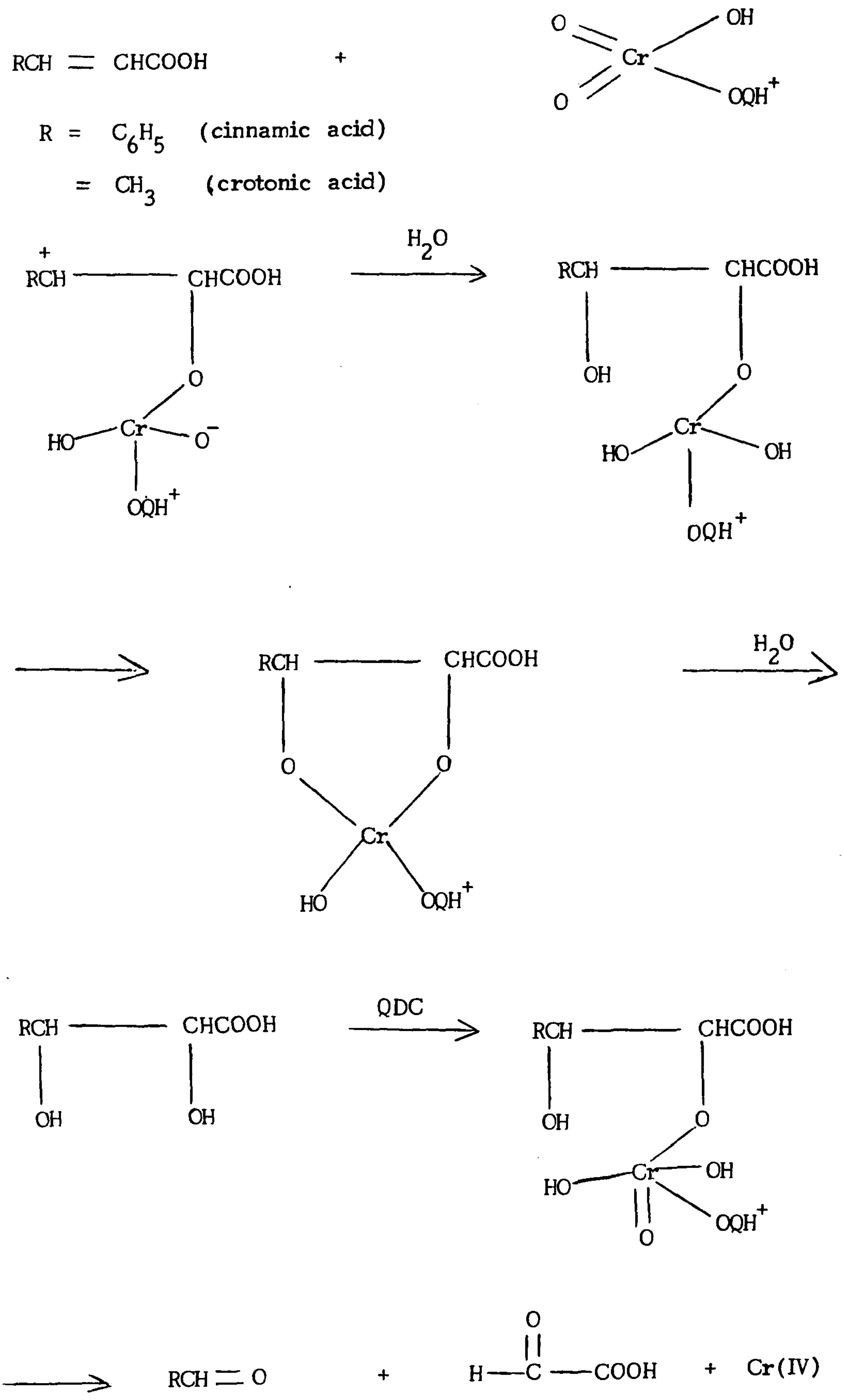
H2C=O
+
Cr(IV)

SCHEME 2


RCH = CHCOOH
+
O
O
Cr
OH
OQH+
R = C6H5 (cinnamic acid)
= CH3 (crotonic acid)
+
RCH
CHCOOH
O
HO
Cr
O−
OQH+
H2O
RCH
CHCOOH
OH
O
HO
Cr
OH
OQH+
RCH
CHCOOH
O
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Cr
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OQH+
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RCH
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QDC
RCH
CHCOOH
OH
O
HO
Cr
OH
O
OQH+
RCH = O
+
O
H—C—COOH
+
Cr(IV)

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KINETICS OF OXIDATION OF SOME ORGANIC SUBSTRATES BY QUINOLINIUM DICHROMATE

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IRONA NONGKYNRIH

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INTRODUCTION

Oxidation is an essential operation in organic syntheses 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. During the course of these reactions, the Cr(VI) compounds are reduced to the Cr(III) species.

The earliest known chromium(VI) oxidants were chromium trioxide and chromyl chloride. Chromyl chloride has generally been used in carbon tetrachloride or carbon disulfide. 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 dropwise to the substrate dissolved in acetone. The usefulness of "Jones reagent" has been well-established.

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

In order to protect acid-sensitive functional groups during the oxidation of alcohols with Cr(VI)oxide, polar aprotic solvents have been used. A solution of Cr(VI) oxide in dimethylformamide containing a trace of concentrated sulfuric acid was able to oxidize alcohols containing acid-sensitive protecting groups. The presence of catalytic amounts of sulfuric acid was essential, accompanied by low temperatures and an inert nitrogen atmosphere(8). When a solution of Cr(VI) oxide was added to an equal volume of the substrate (alcohol) dissolved in hexamethyl phosphoric triamide(HMPT), simple axial and equatorial hydroxyl functions were oxidized, the latter at a much faster rate(9). Under the same experimental conditions, Cr(VI) oxide in HMPT was found to oxidize allylic hydroxyl functions in preference to other alcoholic groups(9). A series of primary and secondary alcohols were oxidized in 80-90% yields by a solution of sodium dichromate dihydrate in concentrated sulfuric acid in dimethyl sulfoxide(DMSO) at 70°C(10). 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-dimethylpyrazole(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-ynal	84
Citronellol	Citronellal	82
Benzhydrol	Benzophenone	100
4-t-Butylcyclohexanol	4-t-Butylcyclohexanone	97
Presqualene alcohol	Presqualene aldehyde	78

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

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(31). 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). Oxidations with 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 more 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, $PyCr_2O_7$(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(36). 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 methyltrialkylammonium 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(43). 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(46). 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(50). 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 the 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(55,56). 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, 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(57). Tetrabutylammonium chlorochromate(TBACC) was also able to carry out these oxidation reactions, though with yields which were much less than the yields obtained by oxidation with BTMACC(57). Other reagents which were prepared had included tetramethylammonium fluorochromate(TMAFC), tetramethylammonium chlorochromate(TMACC) and tetrabutylammonium fluorochromate(TBAFC), but all these reagents were found to be inert for the oxidation of alcohols(57).

A useful contribution to organic synthesis was the preparation of tetrakis(pyridine) silver dichromate, $Py_4Ag_2Cr_2O_7$, 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(61). These reagents are highly efficient for the oxidation of alcohols to carbonyl compounds, for the oxidative coupling of mercaptans into disulfides, and for a mild cleavage of oximes to carbonyl compounds. Chlorotrimethylsilane-chromium trioxide has been shown to be an efficient oxidizing agent for the conversion of arylmethanes to benzaldehyde, and for the oxidative cleavage of some benzyl esters(61).

The use of a triazole to mediate selective Cr(VI) oxidation has been described(62). Benzotriazole, when used in conjunction with pyridinium chlorochromate in dichloromethane, was found to be a mild and useful reagent system for the rapid and selective oxidation of steroidal allylic alcohols to the corresponding ketones(62). A new method for the 1,4-oxygenation of 1-alkylated 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-carboxypyridinium dichromate(isonicotinium dichromate, INDC), were synthesized from chromium trioxide dissolved in a small amount of water, and nicotinic or isonicotinic acid respectively. These two reagents (NDC and INDC) have been used for the oxidations of allylic and benzylic alcohols to aldehydes, thiols to disulfides, hydroquinones to benzoquinones, and for the oxidation of polynuclear aromatic hydrocarbons(64). This reagent, 3-carboxypyridinium dichromate(NDC), proved to be an efficient reagent for the oxidation of alcohols to carbonyl compounds, in the presence of pyridine. In order to ensure complete oxidation of the substrate, the optimum molar ratio of substrate: oxidant:pyridine was found to be 1:2.5:20, respectively(65).

The efficient oxidation of alcohols to carbonyl compounds under mild conditions has been a necessary theme in organic syntheses. An improved procedure was described for the extremely rapid and efficient oxidation of alcohols, by the addition of a small quantity of anhydrous acetic acid to pyridinium dichromate(PDC) and freshly activated molecular sieve powder in dichloromethane at room temperature(66).

Chromium peroxide complexes have been used as general oxidants in organic syntheses. 2,2'-Bipyridylchromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, for C-C bond cleavages in 1,2-diols, for the quantitative decarboxylation of α-hydroxy acids, for 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(69). 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).

The suitable biphosphonium dichromate reagent, $(C_6H_5)_3P^+CH_2P^+(C_6H_5)_3Cr_2O_7^{2-}$, was a particularly mild and selective reagent for the oxidation of primary and secondary alcohols(71). 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(72). 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(74). In these rearrangements, it was observed that chromate ester formation and subsequent ring flip created a 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(75). This study indicated that PFC was an efficient two-electron oxidant which was capable of participating in oxygen-transfer reactions(75).

The versatility of pyridinium fluorochromate 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(81). 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).

The oxidation of alcohols by isoquinolinium chlorochromate, in dichloromethane solvent, yielded the corresponding carbonyl compounds in reasonably good yields(86).

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(87). 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(87).

The oxidation of secondary alcohols with chromium trioxide, in the presence of wet aluminium oxide in hexane, had yielded the corresponding ketones(88). This method was used for the oxidation of cyclic alcohols, giving good yields of the cyclic ketones(88). For the oxidation of geraniol by this reagent, it was observed that the reaction proceeded without any appreciable loss of double bond stereochemistry(88).

The most recent chromium(VI) reagent(89) which has been introduced for the oxidation of organic substrates has been quinolinium fluorochromate(QFC), $C_9H_7NH[CrO_3F]$. This reagent has been 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. 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(89).

Quinolinium dichromate(QDC), having the structure $(C_9H_7NH^+)_2Cr_2O_7^{2-}$, has been used for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, and for the oxidation of aldehydes to acids(90). 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(90). 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.90)

Compound	Product	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	Cinnamic Acid		52
Crotonaldehyde	Crotonic Acid		85

Quinolinium dichromate (QDC) has 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(91), arylalkanes(92), diphenylamines(93), polynuclear aromatic hydrocarbons(94,95), toluene and substituted toluenes(95,96), fluorene(97), amino acids(98) and benzoin(99).

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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 such reagents derived from transition metals such as ruthenium, osmium, iron, manganese, molybdenum, chromium and vanadium. Of all such reagents, chromium(VI) oxidants seemed to have proved to be the most versatile and efficient in bringing about various kinds of transformations.

The conversion of hydroxyl 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 have 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 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 is quinolinium dichromate(QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$. This reagent has emerged as a useful and versatile oxidant, capable of oxidizing diverse kinds of organic substrates. In the present study, quinolinium dichromate(QDC) has been used for the oxidation of alcohols and unsaturated compounds.

The present investigation is a detailed kinetic probe into the oxidation of various organic substrates by quinolinium dichromate(QDC) in acid medium, using dimethylformamide as the solvent, under a nitrogen atmosphere. 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 diverse organic substrates. The substrates chosen for the purpose of oxidation by quinolinium dichromate (QDC), have included the following:

1. **Alcohols** - Chapter 1
   - (a) Cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol).
   - (b) Bicyclic alcohols (borneol and isoborneol).
   - (c) Allylic alcohols (geraniol and farnesol).

2. **Unsaturated Compounds** - Chapter 2.
   - (a) Styrene and substituted styrenes.
   - (b) Cinnamic acid and substituted cinnamic acids, and crotonic acid.
   - (c) Maleic acid and fumaric acid.

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 (DMF and DMF-H_2O 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. The nature of the transition states involved in these reactions has been rationalized, based on the observed kinetic data, as also by the use of the Hammett plots and kinetic isotope effects. 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 the substrates by quinolinium dichromate(QDC), in acid medium, have been proposed.

EXPERIMENTAL

EXPERIMENTAL

Conductivity Water

Conductivity water was prepared by the following method : tap water was distilled first with alkaline potassium permanganate and then redistilled with Merck "Pro Analysi" sulfuric acid from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel (Sunvic, U.K.). 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.

N,N-Dimethylformamide

Dimethylformamide was purified by the following method: Anhydrous copper sulfate was prepared by heating copper sulfate ($CuSO_4.5H_2O$) until it turned white. The complete removal of water molecules was checked by its constant weight after repeated heating. Anhydrous copper sulfate was mixed with dimethylformamide (SDS, AR grade), and the mixture was allowed to stand for 24 hours. The solution was filtered, and the filtrate was distilled under reduced pressure (b.p. 153°C). The distillate thus collected was used as the solvent.

Quinolinium dichromate(QDC), $(C_9H_7NH^+)_2Cr_2O_7{}^{2-}$

To a stirred solution of CrO_3(100g) in water (100ml) cooled in ice, quinoline (86ml) was added in small portions. The solution was diluted with acetone (400ml), 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 730cm^{-1}, characteristic of the dichromate ion.

Substrates

All the cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol) were obtained from the Aldrich Chemical Company, and were purified by distillation, and their purity was checked from physical constants. Borneol and isoborneol were obtained from the Aldrich Chemical Company, and were purified by recrystallization, and their purity was checked from physical constants. Geraniol and farnesol were obtained from the Aldrich Chemical Company, and were distilled before use, and their purity was checked from physical constants. Styrene was a SISCO sample and was distilled. The fraction distilling at 145°C was collected. The purity of this sample was checked by IR and UV analyses, which were found to correspond to that of the styrene monomer(1). Substituted styrenes were obtained from the Aldrich Chemical Company, and were purified by distillation, and their purity was checked from physical constants.

Styrene glycol (1-phenylethane - 1,2-diol) was prepared by the standard method(2), and was obtained as white needles (m.p. 65°C).

Cinnamic acid, crotonic acid and substituted cinnamic acids were obtained from Koch-Light Laboratories (U.K.), and were purified by recrystallization, and their purity was checked from physical constants. Maleic acid and fumaric acid were SISCO samples, and were used after recrystallization.

All ir spectra were recorded on an IR 297 (Perkin Elmer) spectrophotometer, uv spectra on an UV 26 (Beckman) spectrophotometer, and nmr spectra on an EM 390 (Varian) 90 MHz NMR spectrometer.

The boiling points, melting points and the spectral data obtained for each of the substrates used, are summarized in Table 1.

Table 1

Substrate	Boiling Points or Melting Points °C	UV(nm)*
Cyclopentanol	141	-
Cyclohexanol	161	-
Cycloheptanol	185	-
Cyclooctanol	100	-
Borneol	208(m.p.)	-
Isoborneol	212(m.p.)	-
Geraniol	229	
Farnesol	140	-
Styrene	145	244, 282(A)
Styrene glycol	65(m.p.)	224(W)
p-Chlorostyrene	192	258(C)
m-Chlorostyrene	63	250(C)
p-Methoxystyrene	205	265(cH)
p-Methylstyrene	172	253(cH)
m-Methylstyrene	170	251(cH)
Cinnamic acid (trans)	133(m.p.)	268(A)
p-Methylcinnamic acid	196(m.p.)	280(A)
m-Methylcinnamic acid	80(m.p.)	270(M)
p-Chlorocinnamic acid	248(m.p.)	260(M)
m-Chlorocinnamic acid	164(m.p.)	265(M)
p-Nitrocinnamic acid	286(m.p.)	255(M)
Crotonic acid (trans)	72(m.p.)	204(A)
Maleic acid	140(m.p.)	203(A)
Fumaric acid	298(m.p.)	207(M)

*A: Ethanol; W:Water; C: Chloroform; cH: Cyclohexane; M: Methanol

Deuterated Compounds

(a) 1-Deuterocyclohexanol was prepared by the method reported earlier(3), and its purity was checked by ^{1}H-NMR spectroscopy.

(b) Isoborneol-2-d was prepared by the method reported earlier(4), and its purity was checked by ^{1}H-NMR spectroscopy.

(c) α,α-dideuteriogeraniol and α,α-dideuteriofarnesol were prepared by the method reported earlier(5), and the purity of these deuterated compounds was checked by ^{1}H-NMR spectroscopy.

(d) α-deuteriostyrene (b.p. 60°C, 30 torr) was prepared by the dehydration of 1-phenyl-ethanol-1-d with potassium hydroxide. The dehydration of 2-phenylethanol-1,1-d_2 with potassium hydroxide yielded β,β-dideuteriostyrene (b.p.54°C, 30 torr). The purity of these deuterated compounds was checked by ^{1}H-NMR spectroscopy.

(e) Cinnamic-α-d acid and cinnamic-β-d acid were prepared by the method reported earlier(6), and the purity of these deuterated compounds was checked by ^{1}H-NMR spectroscopy.

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.

Kinetic Method:

All the standard flasks and reaction vessels were of pyrex glass with well-ground stoppers. The reaction vessels used were stoppered conical flasks. All the glass apparatus used were tested for loss of solvent, and the loss was found to be negligible. The standard flasks, reaction vessels and the pipettes used were standardized, using conductivity water, and the correction was found out and applied.

An electrically operated thermostatic water bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers 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.

Spectrophotometer

For absorption measurements, the spectrophotometer used was the Digital Spectrophotometer, Type 106 (Systronics model).

The Type 106 Digital spectrophotometer was a single beam spectrophotometer having a grating of 600 lines/mm and a wave length range from 340nm to 960nm. The nominal spectral slit width was 20nm, constant over the entire range. The full scale deflection could be otained over the wavelength range of 340nm to 600nm. By the addition of a red filter and interchanging of the phototube, the range could be extended to 960nm. In order to ensure maximum sensitivity of the instrument, and to minimize the errors in measurements of optical density 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 instrument was calibrated, as specified in the instruction manual, over the range of concentrations of K_2CrO_4 in KOH solutions, so as to verify Beer's law at 370nm.

Absorption cells

The absorption cells were of 'Corning' glass and of 8 ml capacity for the spectrophotometer Type 106 (Systronics). 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 to see that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

Rate measurements

A known amount of the substrate was weighed accurately into a 10ml standard flask, dissolved and made up with the requisite quantities of dimethylformamide, so as to make the solutions of the required molarity. Quinolinium dichromate(QDC) was accurately weighed out into a 10ml standard flask, dissolved and made up in dimethylformamide. Sufficient time was allowed to compensate for any change of heat during dilution. A known volume of sulfuric acid was taken in a 10ml standard flask and made up with distilled water 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 1 hour, under a nitrogen atmosphere. Equal volumes of the two solutions of oxidant and sulfuric acid were mixed. An equal volume of the substrate solution was then introduced, and the reaction mixture mixed 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 optical density at 440nm, spectrophotometrically (Systronics digital model, Type 106).

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

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

The pseudo-first-order rate constant, k_1, expressed in $\sec^{-1}$, was calculated from the equation (2):

$$k_1 = \frac{2.303}{t} \log \frac{D_o}{D_t} \qquad (1)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time t. The logarithmic plots of optical density against time were linear, and extrapolation to zero time gave the values of D_o.

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

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

(b) Thermodynamic activation parameters

These 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),

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

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

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

$$\Delta H^{\neq} = E - RT$$

(kJ mol^{-1})

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

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

$$\Delta S^{\neq} = 2.303R \left[\log k_1 + \frac{\Delta H^{\neq}}{2.303RT} - \log \frac{kT}{h}\right]$$

$(\text{Jk}^{-1}\text{mol}^{-1})$

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

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

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

(kJ mol^{-1})

Stoichiometry

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

Tests for Radical formation

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

(1) Reduction of mercuric chloride(7):

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.

(2) Polymerization of an added olefinic monomer, such as acrylonitrile(7):

1ml of acrylonitrile (0.02M) and 2ml of substrate solution (0.2M) in DMF and H_2SO_4(4.0M) were taken in a 10ml conical flask. In a separate test-tube, 2ml of QDC solution (0.02M) 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 to accelerate the oxidation. There was no formation of polymer. Each experiment was accompanied by a blank control.

Product Analysis

The reactions were carried out in a manner similar to the kinetic experiments (using an excess of the substrate), and were allowed to proceed to completion, keeping the reaction mixture for 24 hours in an atmosphere of nitrogen, at the requisite temperature. The products obtained, from the reaction of the various substrates with the oxidant, were isolated as follows:

(A) Products obtained from the oxidation of cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol.

At the end of the reaction, the reaction mixture was extracted with ether. The ether extract was washed with water, dried over anhydrous Na_2SO_4, and then concentrated. The products obtained were the corresponding cyclic ketones (yields: 85-95%), whose boiling points agreed with those reported in the literature.

IR analysis exhibited carbonyl bands at 1750cm^{-1} (cyclopentanone), 1710cm^{-1}(cyclohexanone), 1700cm^{-1}(cycloheptanone), and 1690cm^{-1}(cyclooctanone).

An aliquot (2ml) of the reaction mixture was pipetted into 25ml of 2N HCl saturated at 0°C with 2,4-dinitrophenylhydrazine. The ketone was converted to the 2,4-dinitrophenylhydrazone(DNP), which was recrystallized from ethanol, dried and weighed. The product, in each case, was characterized by its melting point (Table 2). The yields of DNP after recrystallization, with all the cyclic alcohols, were 85-95%. In the case of cyclooctanone, the semicarbazone derivative was prepared and characterized.

Table 2

Substrate	Oxidation product	Melting point (°C) of 2,4-DNP derivatives prepared
Cyclopentanol	Cyclopentanone	145
Cyclohexanol	Cyclohexanone	160
Cycloheptanol	Cycloheptanone	148
Cyclooctanol	Cyclooctanone	167(Semicarbazone)

(B) Product obtained from the oxidation of borneol and isoborneol.

At the end of the reaction, solvent ether was added to the reaction mixture, the organic layer was washed with water, dried over anhydrous $MgSO_4$, and then concentrated.

The product was obtained as colourless crystals (yield: ∿85%), having a melting point of 179°C characteristic of camphor.

IR analysis gave a carbonyl band at $1733cm^{-1}$, and other bands at $2960cm^{-1}$ and $1043cm^{-1}$, characteristic of camphor.

The 2,4-dinitrophenylhydrazone(DNP) derivative of camphor was prepared, and recrystallized from ethanol to give orange crystals (m.p. 175°C; yield: ∿85%).

(c) Products obtained from the oxidation of geraniol and farnesol

At the end of the reaction, the reaction mixture was taken in ether. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and then concentrated. The products were the corresponding aldehydes (geranial and farnesal, respectively), whose boiling points agreed with those reported in the literature. The yields were ∿85-90%.

IR analysis gave carbonyl bands at $1695cm^{-1}$ (geranial) and $1685cm^{-1}$ (farnesal).

The 2,4-dinitrophenylhydrazone(DNP) derivatives of geranial and farnesal were prepared, and recrystallized from ethanol, dried and weighed (DNP of geranial, m.p. 108°C; DNP of farnesal, m.p. 120°C). The yields of DNP, after recrystallization, were ∿85-95%.

(D) Products obtained from the oxidation of styrene, cinnamic acid and crotonic acid.

At the end of the reaction, the reaction mixture was extracted with chloroform. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and then concentrated. Spotting on TLC plates showed two spots. The two products were separated on a silical gel column, eluted with varying proportions (100:0 to 70:30, v/v) of hexane and chloroform, concentrated and then identified as follows:

(i) <u>Products from the oxidation of styrene</u>

For the first product, an IR spectrum exhibited a carbonyl band at $1700cm^{-1}$ and certain other bands below $900cm^{-1}$ that were characteristic of benzaldehyde(8).

The second product was characterized as formaldehyde, which existed in water largely as the hydrate $[CH_2(OH)_2]$. IR analysis did not show any carbonyl band. On evaporation of the aqueous solution of formaldehyde, a solid residue was left behind, which on recrystallization from ether gave crystalline needles of 1,3,5-trioxane (m.p. 62°C).

The percentage yields of benzaldehyde and formaldehyde were 80-85% and 6-10%, respectively.

(ii) <u>Products from the oxidation of cinnamic acid</u>:

The IR spectrum exhibited a carbonyl band at $1700cm^{-1}$ and certain other bands below $900cm^{-1}$ that were characteristic of benzaldehyde(8).

The second product had a sharp melting point (98°C), and gave a positive response to the tests for both, an aliphatic aldehyde and an aliphatic acid. The phenylhydrazone (m.p. 129°C), and the 2,4-dinitrophenylhydrazone (m.p. 125°C) derivatives were prepared, suggesting that this product was glyoxylic acid. Further characterization was done by IR analysis(8,9), and this product was confirmed as glyoxylic acid.

The yields were: benzaldehyde (∿30%) and glyoxylic acid (∿ 10%). A small amount of cinnamic acid (∿5%) was recovered.

(iii) Products from the oxidation of crotonic acid:

For the first product, the IR spectrum exhibited a carbonyl band at 1730cm^{-1} and other bands in the region 2880-2670cm^{-1}, characteristic of acetaldehyde(8), and further confirmed by UV analysis(10).

The second product was glyoxylic acid, characterized as described in the earlier section, under(ii).

The yields were: acetaldehyde (∿ 80%) and glyoxylic acid (∿ 10%). A small amount of crotonic acid (∿ 5%) was recovered.

(E) Product from oxidation of maleic acid and fumaric acid.

Using the same experimental conditions that were used for the kinetic determinations, a solution of the reaction mixture was kept under nitrogen for 24 hours, at the requisite temperature. At the end of the reaction, solvent ether was added to the reaction mixture. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and then concentrated.

The product obtained was treated with an excess of 2,4-dinitrophenylhydrazine, taken in methanol and H_2SO_4 kept at 0°C. The precipitated 2,4-dinitrophenylhydrazone(DNP) was filtered, dried and recrystallized from ethanol (m.p. 168°C, yield $\sim$ 85%). This product was identical with an authentic sample of the DNP of formaldehyde. Thus only one product, formaldehyde, was obtained from the oxidation of maleic acid (and fumaric acid) by quinolinium dichromate (QDC) in acid medium, using DMF as the solvent.

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DISCUSSION

CHAPTER 1

KINETICS OF OXIDATION OF ALCOHOLS

Chromic acid has been extensively used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. 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 t-butyl chromate in a variety of solvents. The conversion of hydroxyl groups to the corresponding carbonyl groups is an important transformation in organic synthesis. Many procedures have been developed to carry out the conversions of primary and secondary alcohols to aldehydes and ketones, respectively. While developing these procedures, several newer 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 a variety of alcohols to the corresponding carbonyl compounds. The literature has been reviewed with the purpose of highlighting the various kinds of reagents which have been extensively used for the oxidation of both primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. The alcohols which have been studied have included:

(1) Cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol).

(2) Bicyclic alcohols (borneol and isoborneol).

(3) Allylic alcohols (Primary alcohols, such as geraniol and farnesol).

1. Oxidation of Cyclic Alcohols

The extensive use of acid-labile protecting groups in organic syntheses prompted the use of dipyridine - Cr(VI) oxide(1) in pyridine as the reagent(2) of choice for the conversions of secondary alcohols to ketones(3). With a view to improve the oxidizing properties of dipyridine - Cr(VI) oxide, this complex was taken in dichloromethane and used for the oxidation of a variety of alcohols(4). Cyclic alcohols such as cyclohexanol were converted to cyclohexanone in 98% yield, by the use of Collins reagent(4). Pyridinium chlorochromate (Corey's reagent), in dichloromethane, was found to be an efficient reagent capable of oxidizing a wide variety of alcohols to carbonyl compounds(5). Cyclic alcohols were converted to the corresponding cyclic ketones in excellent yields by the use of Corey's reagent(5) . The reagent, poly[vinyl[(pyridinium chlorochromate)][PVPCC], prepared by the addition of Cr(VI) oxide and concentrated HCl to polyvinyl pyridine suspended in water, was used for the oxidation of cyclic alcohols to the corresponding cyclic ketones(6). The oxidation of secondary alcohols by pyridinium dichromate(PDC), in dichloromethane, gave good yields of the ketones(7). This conversion was also observed to be very efficient when carried out by PDC in dimethylformamide(7). The reagent, 2,2'-bipyridinium chlorochromate(BPCC), prepared by the addition of 2,2'-bipyridine to an equimolar mixture of chromic anhydride and dilute HCl, was found to be a useful oxidizing agent for the conversion of alcohols to the corresponding carbonyl compounds(8). Cyclic alcohols have been quantitatively converted to cyclic ketones, by the use of this reagent(8). The oxidation of cyclic alcohols by pyridinium chlorochromate, in nitrobenzene-chlorobenzene mixtures, was catalyzed by dichloro- and trichloro- acetic acid, wherein a relationship was observed between ring size and reactivity of the alcohols(9). Pentavalent Chromium complexes with 1,10-phenanthroline have been used for the oxidation of alcohols to carbonyl compounds(10). The oxidation of cyclohexanol to cyclohexanone, in 94% yield, has been achieved by the use of this Cr(V) reagent(10). Barium manganate in heterogeneous systems has been used as a good oxidizing agent for the oxidation of alcohols(11). Cyclic alcohols have been converted to cyclic ketones by $BaMnO_4$ with yields ranging between 50-60%(12,13). The synthetic potential of pyridinium fluorochromate(PFC) was investigated, and it was found that this reagent had certain advantages over similar oxidizing agents used for the oxidation of alcohols(14). Cyclohexanol was converted to cyclohexanone using PFC in dichloromethane(14). Cyclohexanol was oxidized to cyclohexanone in good yields, using solid hydrated copper permanganate in dichloromethane solvent(15). The cerium(IV) oxidation of cyclic alcohols was shown to produce the corresponding cyclic ketones almost quantitatively(16). Conformational effects in the oxidation of cyclic alcohols by ceric ions were reported, and the results were discussed in the light of the I-strain hypothesis(17). In perchloric acid medium, the conversion of cyclic alcohols to cyclic ketones was efficiently carried out using ceric ions(18). Ruthenium compounds have been used in catalytic amounts to oxidize various organic compounds with different oxidants in alkaline as well as in acid medium(19,20). The role of the ruthenate ion in the oxidation of cyclic alcohols by alkaline hexacyanoferrate(III) ions has been studied(21). The oxidation of the cyclic alcohols proceeded via the formation of a complex between Ru(VI) and the substrate, which then underwent slow decomposition in the presence of excess of alkaline hexacyanoferrate(III) ions. The products obtained were the corresponding cyclic ketones(21). Peroxyacetic acid, in the presence of a catalytic amount of 2,4-dimethylpentane-2,4-diol cyclic chromate, in dichloromethane - carbon tetrachloride mixtures was used to convert cyclic alcohols to the corresponding cyclic ketones, the reactions being characterized by very short time durations(22). The synthetic utility of halosilanes-chromium trioxide reagents as excellent oxidizing agents was brought out by the efficient conversions of alcohols to carbonyl compounds(23). Cyclohexanols were converted to cyclohexanones in good yields, using the trimethylsilylchromate reagent(23). Chromium peroxide complexes such as chromium peroxide ethereate, pyridine chromium peroxide, and 2,2'-bipyridyl chromium peroxide were found to be mild and efficient oxidants in organic synthesis. These reagents have been used for the oxidation of different types of organic compounds such as cyclohexanol which was converted to cyclohexanone in almost quantitative yield(24). Cyclic alcohols were converted to the corresponding cyclic ketones, using imidazolium dichromate(IDC) in dimethylformamide at room temperature(25). Cyclic alcohols have been oxidized to cyclic ketones by sodium bromate in the presence of a catalytic amount of hydrobromic acid(26). By this method, cyclopentanol and cyclohexanol were converted to cyclopentanone and cyclohexanone, in 93 and 96% yields, respectively(26). Anionic molybdenum-peroxo complexes have proved to be useful reagents in the oxidation of alcohols(27). The oxidation of cyclic alcohols by these complexes, taken in dichloroethane, had resulted in the formation of the corresponding cyclic ketones in quantitative yields(28). Cyclopentanol and cyclohexanol were thus oxidized to the corresponding ketones(28). Secondary alcohols have been smoothly oxidized to the ketones by dimanganese heptoxide, cycloheptanol giving cycloheptanone in 91% yield(29). Peracetic acid, in the presence of sodium bromide in acetic acid medium, has been used to oxidize alcohols to the corresponding carbonyl compounds; cyclohexanols have been converted to cyclohexanones in excellent yields(30). The oxidation of alcohols to carbonyl compounds was achieved by the use of 3-carboxy pyridinium dichromate (NDC), in the presence of pyridine(31). The oxidation of cyclohexanol to cyclohexanone by pyridinium fluorochromate(PFC) not only brought out the synthetic utility of this reagent, but also focussed on the essential details of PFC oxidations(32). The oxidation of secondary alcohols to the corresponding ketones in very high yields has been achieved in the presence of t-butyl-hypochlorite and pyridine in dichloromethane(33). In the presence of Al_2O_3, sodium bromite in dichloromethane has been used to oxidize cyclohexanol and substituted cyclohexanols to the corresponding cyclic ketones in almost quantitative yields(34). Metallic nitrates, supported on silica gel, have been found to be efficient reagents for the oxidation of secondary alcohols to the corresponding ketones(35). The oxidation of cyclic alcohols by copper nitrate-silica gel and zinc nitrate-silica gel reagents gave the corresponding ketones in high yields(36). Bis-(trimethylsilyl) peroxide(BTSP), in the presence of chromium(VI) or ruthenium(II) complexes was used to oxidize cyclic alcohols to cyclic ketones in good yields(37). The reaction of secondary alcohols with benzyltrimethyl ammonium tribromide($BTMABr_3$), in the presence of a buffer at 60°C, gave the corresponding ketones; cyclic alcohols such as cyclopentanol and cyclohexanol were converted to the corresponding cyclic ketones in reasonably good yields(38). Synthetic tetranuclear Mn(IV) complexes have been used to convert cyclohexanol to cyclohexanone in good yields(39). N-Oxo ammonium salts, in combination with sodium bromite, have been used to oxidize cyclohexanols to cyclohexanones in good yields(40). 1-Chloro benzotriazole (1-CBT), in dichloromethane or in benzene, has been used for the oxidation of cyclohexanol, giving yields of cyclohexanone ranging between 60-70%(41). Cyclohexanol was converted to cyclohexanone in 90% yield by pyridinium chlorochromate(PCC) in chloroform, using anhydrous acetic acid as a catalyst(42). Methyltrioctylammonium tetrakis(oxo-diperoxotungsto) phosphate, in combination with hydrogen peroxide as the primary oxidant, in an aqueous/organic biphase system, proved to be a versatile catalytic method for the oxidations of alcohols; cyclic alcohols were thus converted to cyclic ketones in good yields(43). The oxidation of alcohols with oxone in aprotic solvents, in the presence of "wet Al_2O_3", at room temperature, gave the corresponding ketones in good yields(44). Using this method, cyclohexanols were converted to cyclohexanones(44). The oxidation of secondary alcohols by chromium trioxide, in the presence of wet Al_2O_3 in hexane, yielded the corresponding ketones. Cyclic alcohols were thus converted to the corresponding cyclic ketones in yields greater than 90%, by the use of this method(45). Cyclic alcohols have been converted to cyclic ketones under mild conditions by acetone, in the presence of catalytic amounts of ruthenium-triphenyl phosphine complexes(46). The oxidation of alcohols to carbonyl compounds was carried out using catalytic amounts of ruthenium trichloride as catalyst and a three-fold excess of aqueous t-butyl hydroperoxide, TBHP(47). Cyclic alcohols were thus converted to the cyclic ketones in good yield with 100% selectivity(47). Trichloromelamine(TCM) in dichloromethane, at room temperature, was found to be extremely efficient in bringing about the oxidation of cyclohexanol to cyclohexanone in 90% yield(48). Chromium-substituted alumino phosphate-5 has been used as a recyclable solid catalyst for the selective oxidation of secondary alcohols, with t-butyl hydroperoxide(TBHP) as the stoichiometric oxidant. With TBHP, there was a 72% conversion of cyclohexanol to cyclohexanone, with a 73% TBHP selectivity(49). When oxygen was used as the terminal oxidant, a small amount of TBHP was added presumably to initiate the reaction. By this method, cyclohexanol was converted to cyclohexanone with 90% selectivity(49). The aerobic oxidation of secondary alcohols was carried out in toluene or tetrahydrofuran using a triple catalytic system consisting of a ruthenium complex, quinone and a cobalt macrocycle(50). Cyclohexanol was thus converted to cyclohexanone in 89% yield(50). Manganese dioxide, in the presence of a ruthenium catalyst and a quinone as the hydrogen transfer mediator, was able to bring about the oxidation of cyclic alcohols to cyclic ketones in good yields(51). Quinolinium fluorochromate(QFC), in dichloromethane, has been developed as a new Cr(VI) reagent for the oxidation of alcohols, cyclohexanol being converted to cyclohexanone in 93% yield(52).

2. Oxidation of Bicyclic Alcohols

The quantitative determination and analysis of strain in bicyclic systems was carried out with a view to ascertain the stability of bicyclic alcohols(53,54). Studies on the oxidation of bicyclic alcohols have led to the use of newer oxidizing agents which have been developed to convert borneol and isoborneol to the corresponding carbonyl compound, camphor. A solution of $Me_3SiOOSiMe_3$(BTSP), in dichloromethane, in the presence of pyridinium dichromate (PDC), has been used for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively in reasonably good yields; borneol has been converted to camphor in 98% yield(55). The oxidation of borneol by pyridinium fluorochromate(PFC) at room temperature gave a 77% yield of camphor(56). Peroxyacetic acid, in the presence of a catalytic amount of a cyclic chromate ester (using mixtures of carbon tetrachloride and dichloromethane as the solvent), was used to quantitatively convert borneol to camphor(22). The oxidation of secondary alcohols to carbonyl compounds has been carried out using sodium bromite, in dichromethane, in the presence of Al_2O_3 under mild conditions; borneol and isoborneol having been quantitatively converted to camphor(34). In the presence of

Cr(VI) or Ru(II) complexes as catalyst, bis-(trimethyl silyl) peroxide(BTSP) could convert isoborneol to camphor in 98% yield(37). By using the ultrasound technique(57), pyridinium chlorochromate, in conjunction with silica gel, was developed as a heterogeneous process to carry out the oxidation of alcohols to the corresponding carbonyl compounds(58). For example, borneol was converted to camphor in 87% yield, using this process(58). In the presence of anhydrous acetic acid as a catalyst, the synthetic utility of pyridinium chlorochromate(PCC) in chloroform was demonstrated for the oxidation of alcohols(42). Such anhydrous conditions have been used to oxidize borneol to camphor in reasonably good yields(42). The oxidation of various secondary alcohols with oxone(59) in aprotic solvents, in the presence of wet aluminium oxide, was carried out; the oxidation of borneol gave 70% yield of camphor(44). An efficient and versatile method was developed for the oxidation of primary and secondary hydroxyl groups. The ketonization of secondary alcohols was achieved with aqueous hydrogen peroxide, catalyzed by tungsten peroxo complexes (43). The reactions appeared to be relatively insensitive to geometric constraints. For example, borneol and isoborneol were both oxidized to camphor (95% yield) at similar rates (43). Organic oxoammonium salts have been used for the selective oxidation of alcohols(60). This method has been characterized by a high degree of selectivity and high yields of the products, isoborneol being converted to camphor in 97% yield(60). Tetramethyl-piperidine-1-oxyl (TEMPO), in dichloromethane, has been used for the oxidation of borneol to camphor in 86% yield(61). Mild procedures have been developed for the oxidation of alcohols which involved a ruthenium-catalyzed dehydrogenation and subsequent hydrogen transfer(46,62). A newer method involving the use of ruthenium as a catalyst has been developed, employing manganese dioxide for the oxidation of secondary alcohols(51). By this method, borneol was oxidized to camphor in 87% yield(51). The aerobic oxidation of secondary alcohols to ketones was performed in toluene or tetrahydrofuran, using a triple catalytic system consisting of a ruthenium complex, quinone and a cobalt macrocycle(50). The reaction worked well with sterically hindered alcohols, such as borneol, which was converted to camphor in 75% yield(50).

3. Oxidation of Allylic Alcohols

The first report of the use of tertiary butyl chromate for the oxidation of alcohols was the reaction involving the oxidation of primary alcohols to aldehydes(63). A solution of tertiary butyl chromate in petroleum ether was used to convert geraniol to geranial in 85% yield(63). It appeared that this reagent was specific for the oxidation of primary alcohols to aldehydes, because in some cases the conversions of secondary alcohols to ketones yielded very poor results(64). Chromium trioxide in sulfuric acid medium, in the presence of acetone as solvent, was effective in oxidizing primary alcohols to aldehydes in good yields; geraniol was converted to citral(65). The pyridine-chromium trioxide complex(1) has been extensively used for the oxidation of a wide variety of alcohols, and the oxidation of geraniol had resulted in reasonably good yields of geranial(3). This method was particularly useful with acid sensitive compounds, as also with compounds having functional groups which could be easily oxidized by chromic acid(3). A complex of chromium trioxide (in dichloromethane) and 3,5-dimethyl pyrazole(DMP) was found to be effective for the oxidation of a wide range of alcohols; geraniol was thus oxidized to geranial in 96% yield(66). This reagent (3,5-dimethyl pyrazole- chromium trioxide complex, DMP.CrO_3)

was used to carry out the allylic oxidation of many steroidal alcohols to the corresponding carbonyl compounds(67). Bis-tetrabutyl ammonium dichromate(TBADC) has been used for the rapid oxidation of allylic and benzylic alcohols, in refluxing dichloromethane; geraniol was converted to geranial in 90% yield(68). Pyridinium fluorochromate(PFC) was introduced as an efficient and versatile oxidant for the conversion of primary and secondary alcohols to the corresponding aldehydes and ketones respectively(14), and proved to be as reactive as Corey's reagent, pyridinium chlorochromate, PCC(5). Pyridinium fluorochromate(PFC) was found to be effective for the conversion of geraniol to geranial in 80% yield(56). Similar conversions of geraniol to geranial were effectively carried out by other reagents such as benzyltrimethyl ammonium chlorochromate(BTMACC) and tetrabutyl ammonium chlorochromate(TBACC), although the reactions involving these reagents required higher temperatures and longer conversion times(56). The $RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$ system has been shown to be a selective oxidant for alcohols; geraniol has been oxidized to geranial in 96% yield(55). This oxidizing reagent has also been used for the selective oxidation of allylic primary alcohols, in the presence of secondary alcohols. For example, mixtures of geraniol/4-dodecanol and geraniol/2-dodecen-4-ol were selectively oxidized to geranial in 99% and 95% yields, respectively(55). Tetrabutyl ammonium chlorochromate(TBACC) has been used as a selective reagent for the oxidation of alcohols(69). At room temperature, TBACC in chloroform was able to convert geraniol to geranial in 84% yield(69). Ruthenium dioxide hydrate acted as an oxidant with higher efficiency than manganese dioxide, and effectively catalyzed the aerobic oxidation of allylic alcohols, under mild conditions(70). By using this method, the catalytic aerobic oxidation of geraniol gave 90% yield of the product geranial which indicated that the RuO_2-catalyzed aerobic oxidation proceeded with retention of olefin stereochemistry(70). The anaerobic oxidation of geraniol by a large excess of RuO_2-hydrate, at room temperature, gave geranial with high stereospecificity(70). Imidazolium dichromate(IDC), in dimethylformamide, was found to be a mild selective reagent for the oxidation of allylic alcohols to the corresponding carbonyl compounds(25). This reagent was used to convert geraniol to geranial in 82% yield, the reaction requiring a short time duration and room temperature(25). 3-Carboxy pyridinium dichromate(NDC), prepared from nicotinic acid and chromium trioxide, was found to be an efficient reagent for the oxidation of alcohols to carbonyl compounds, in the presence of pyridine(31). The oxidation of geraniol to geranial by

NDC was a quantitative conversion, giving yields of 97% of the product, the reaction involving a very short time factor(31). The oxidation of alcohols to carbonyl compounds was achieved using catalytic amounts of chromium trioxide and excess of aqueous t-butyl hydroperoxide, TBHP(71). This method was used to oxidize geraniol to geranial in a 100% conversion at room temperature(71). The oxidation of allylic and benzylic alcohols with Co(III) acetate, in acetic acid, had resulted in quantitative conversions to the corresponding products(72). For example, the oxidation of geraniol to geranial was carried out, using this method, giving reasonably good yields of the product(72). The selective oxidation of allylic primary alcohols, in the presence of secondary alcohols, was achieved using bis-(trimethylsilyl peroxide)(BTSP), in the presence of Cr(VI) or Ru(II) catalysts. By this method, geraniol was converted to geranial in 99% yield(37). Oxochromium(VI)-amine reagents have been found to be extremely efficient in carrying out different types of oxidative transformations(73). Among these reagents, the most extensively used has been Corey's reagent, pyridinium chlorochromate, PCC(5,74). Pyridinium chlorochromate, in conjunction with silica gel, has been used for the oxidation of alcohols to carbonyl compounds. By the use of the ultrasound technique(57), pyridinium chlorochromate/silica gel has been used in a heterogeneous phase to bring about the efficient oxidation of alcohols to carbonyl compounds; geraniol has been converted to geranial in 86% yield(58). Under phase transfer catalysis(PTC) conditions, a solid mixture of $BaMnO_4$, Al_2O_3 and hydrated $CuSO_4$ selectively oxidized primary allylic alcohols such as geraniol to geranial in 91% yield(75). The use of anhydrous acetic acid as catalyst for the oxidation of alcohols has been described(42). In the presence of anhydrous acetic acid, pyridinium chlorochromate(PCC) was used to oxidize geraniol to geranial in 92% yield(42). Organic oxoammonium salts, generated by the acid-promoted disproportionation of nitroxides in solution, have been used to selectively oxidize alcohols in high yields(60). This method has been used to oxidize geraniol to geranial in 90% yield, while farnesol was converted to farnesal in 86% yield(60). The oxidation of alcohols with chromium trioxide, in the presence of wet Al_2O_3 in hexane, gave the corresponding carbonyl product in excellent yields(45). The scope of this reaction was extended to a chemoselective oxidation of the hydroxy group in a multifunctional substrate. The oxidation of geraniol at room temperature for fifteen hours gave geranial in 73% yield(45). The significant aspect of this work was that the oxidation proceeded without any appreciable loss of the double bond stereochemistry(45). The aerobic oxidation of primary alcohols to aldehydes has been achieved under mild conditions, at room temperature, using a triple catalytic system consisting of a ruthenium phosphine complex - hydroquinone - cobalt macrocycle; geraniol was thus oxidized to geranial(62). The oxidation of allylic alcohols to aldehydes was achieved with MnO_2/bentonite/microwave and MnO_2/bentonite/ultrasound, both in dry media(76). By these methods, the oxidation of geraniol gave geranial in reasonable yields(76). The oxidation of allylic alcohols by sodium percarbonate, in the presence of catalytic amounts of pyridinium dichromate (PDC) and Adogen 464, in 1,2-dichloroethane at 80°C, had resulted in a quantitative conversion to the corresponding carbonyl compound, with a high degree of selectivity(77). For example, geraniol was converted to geranial in 75% yield, with 84% selectivity(77).

PRESENT WORK

The oxidation of primary and secondary alcohols to aldehydes and ketones respectively, is an important transformation in organic synthesis. Among the many oxidizing agents which have been employed to carry out such conversions, chromium(VI) reagents are perhaps the most versatile and efficient for performing these transformations.

The present work is a detailed kinetic investigation of the oxidation of alcohols to their corresponding carbonyl compounds, using a newer Cr(VI) reagent for this purpose. The Cr(VI) reagent which has been employed for the purpose of oxidation of alcohols, in the present study, has been quinolinium dichromate(QDC) in acid medium, using dimethylformamide(DMF) as the solvent.

The alcohols which have been chosen for the purpose of oxidation by quinolinium dichromate(QDC), in the present study, have included:

(1) Cyclic Alcohols (Cyclopentanol, Cyclohexanol, Cycloheptanol and Cyclooctanol);

(2) Bicyclic Alcohols (Borneol and Isoborneol);

(3) Allylic Primary Alcohols (Geraniol and Farnesol).

Stoichiometry (Vide "Experimental")

The stoichiometries of all the oxidation reactions were determined. The stoichiometric ratios, Δ[QDC]/Δ[Substrate], in the range 0.61-0.73, were obtained (Table 1).

Table 1. Stoichiometries of the oxidation of the substrates; ([Substrate]=0.005M, T=323K)

$[H_2SO_4]$/M	0.10	0.25	0.50
10^2[QDC]/M	2.50	2.60	2.70
Δ[QDC]/Δ[Cyclopentanol]	0.65	0.68	0.71
Δ[QDC]/Δ[Cyclohexanol]	0.62	0.66	0.68
Δ[QDC]/Δ[Cycloheptanol]	0.73	0.70	0.67
Δ[QDC]/Δ[Cyclooctanol]	0.69	0.72	0.67
Δ[QDC]/Δ[Borneol]	0.62	0.66	0.68
Δ[QDC]/Δ[Isoborneol]	0.73	0.70	0.67
Δ[QDC]/Δ[Geraniol]	0.71	0.73	0.68
Δ[QDC]/Δ[Farnesol]	0.72	0.69	0.61

The observed stoichiometric ratios conformed to the overall equations:

(a) For cyclic alcohols:

$$3R_2CHOH + 2Cr^{VI} \longrightarrow 3R_2CO + 2Cr^{III} + 6H^+ \qquad (1)$$

(b) For bicyclic alcohols (borneol and isoborneol):

$$3C_{10}H_{18}O + 2Cr^{VI} \longrightarrow 3C_{10}H_{16}O + 2Cr^{III} + 6H^+ \qquad (2)$$

(c) For allylic alcohols:

$$3RCH_2OH + 2Cr^{VI} \longrightarrow 3RCHO + 2Cr^{III} + 6H^+ \qquad (3)$$

where R = C_9H_{15} (geraniol)

$C_{14}H_{23}$ (farnesol)

Effect of substrate

The rate of the reaction was found to be dependent on the concentration of the substrates. The order of the reaction with respect to substrate concentration was obtained by changing the substrate concentration, and observing the effect on the rate of the reaction at constant [QDC] and [H^+]. The results have been recorded in Tables 2-4.

Table 2. Dependence of Rate constants on the concentration of cyclic alcohols, in DMF; ([QDC]=0.001M; $[H_2SO_4]$=0.15M; T=323K)

10^2[Substrate]/M	1.0	5.0	10.0	20.0
$10^4k_1/s^{-1}$ for:				
Cyclopentanol	4.1	20.2	40.8	83.0
Cyclohexanol	2.2	11.0	22.4	44.1
Cycloheptanol	7.9	39.8	79.5	159
Cyclooctanol	10.3	51.3	104	206

Table 3. Dependence of Rate Constants on the concentration of bicyclic alcohols, in DMF; ([QDC]=0.001M; $[H_2SO_4]$=0.02M; T=323K)

10^2[Substrate] (M)	Borneol		Isoborneol	
	10^4k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)	10^4k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)
1.0	1.07	1.07	2.81	2.81
5.0	5.46	1.09	14.5	2.90
10.0	11.1	1.11	28.7	2.87
20.0	22.6	1.13	59.0	2.95

$k_2 = k_1$/[Substrate]

Table 4. Dependence of Rate Constants on the concentration of allylic alcohols, in DMF; ([QDC]=0.001M; [H_2SO_4]=0.02M; T=323K)

10^2[Substrate] (M)	Geraniol		Farnesol	
	10^4k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)	10^4k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)
1.0	1.83	1.83	2.23	2.23
5.0	9.60	1.92	11.3	2.26
10.0	18.8	1.88	23.0	2.30
20.0	38.2	1.91	45.7	2.29

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

Plots of k_1, the pseudo-first-order rate constant, against the concentrations of substrates give straight lines passing through the origin (Figures 1-2), indicating that the rate of oxidation was dependent on the first power of the concentration of the substrate. This was further confirmed by the constant 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). When a constant concentration of

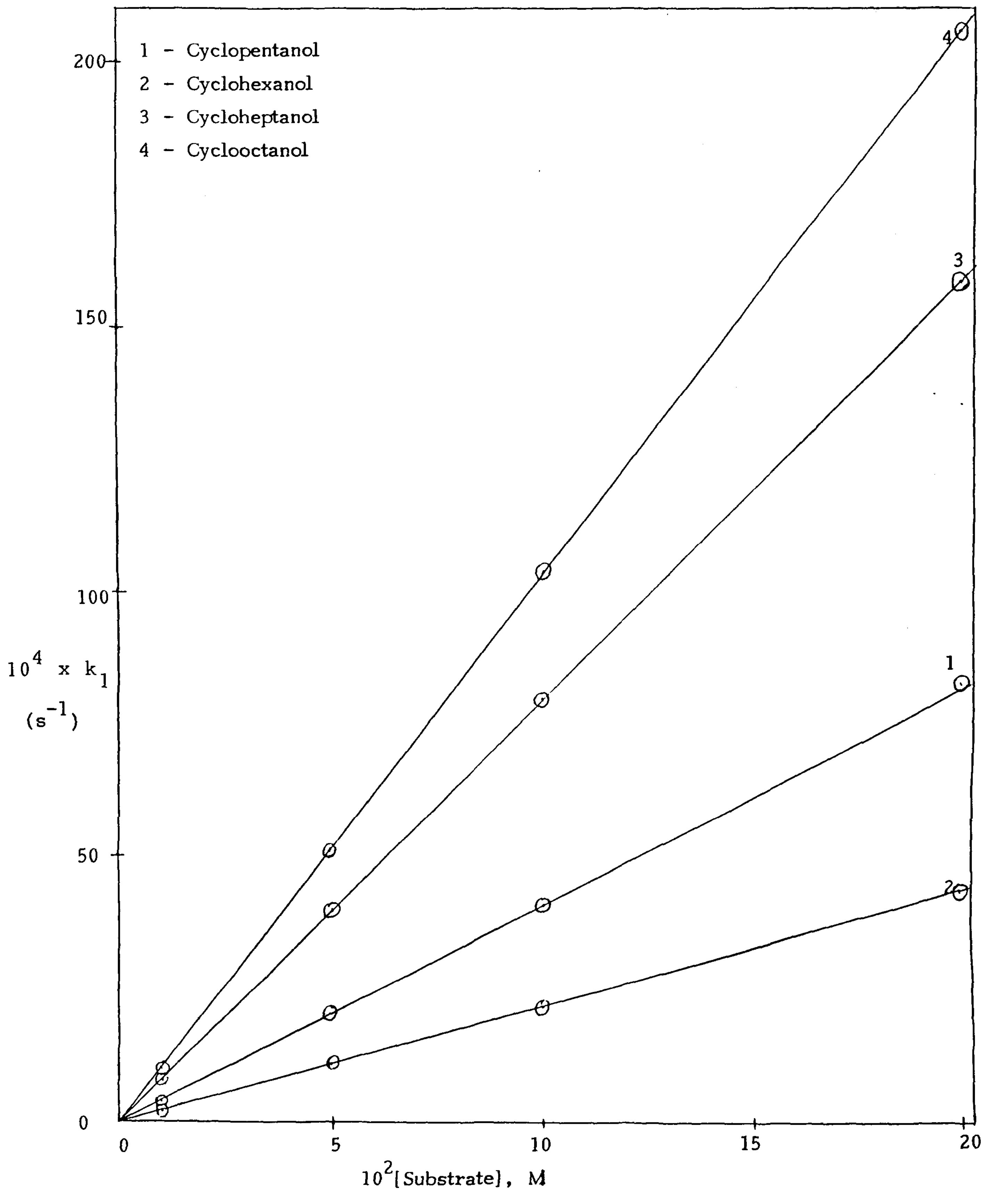


Fig.1. Plots of k_1 against the concentrations of substrates.

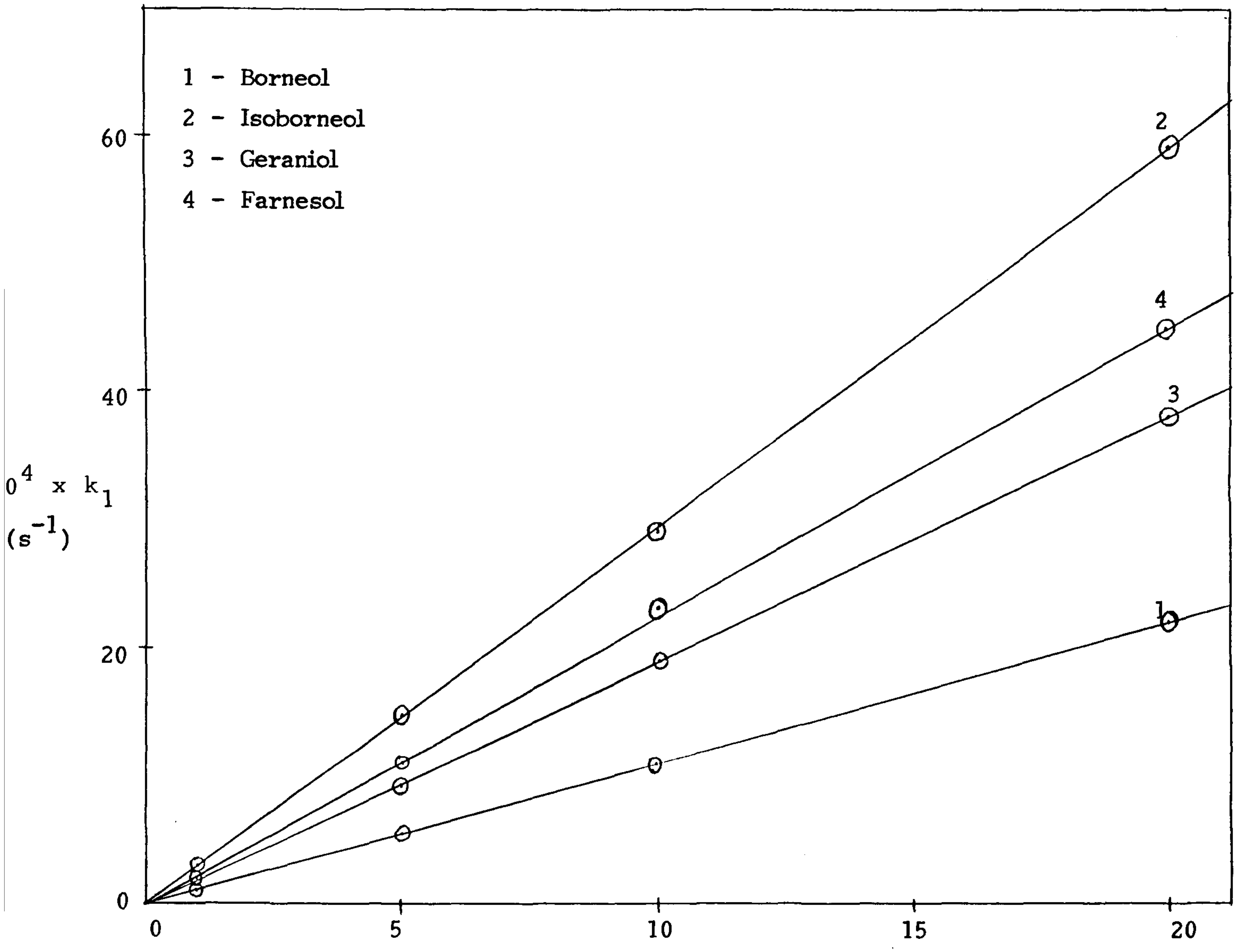


Fig.2. Plots of k_1 against the concentrations of substrates.

substrate (large excess) was used, k_1 did not show any appreciable variation with the change in the concentration of the oxidant, indicating a first-order dependence of the reaction on the concentration of the oxidant (Tables 5-6).

Table 5. Dependence of Rate Constants on the concentration of oxidant, in DMF; ([Substrate]=0.01M; $[H_2SO_4]$=0.15M; T=323K)

10^3[QDC]/M	0.10	0.25	0.50	1.0
$10^4k_1/s^{-1}$ for:				
Cyclopentanol	4.3	4.0	4.2	4.1
Cyclohexanol	2.2	2.3	2.2	2.2
Cycloheptanol	7.9	7.4	7.6	7.9
Cyclooctanol	10.2	10.6	10.1	10.3

Table 6. Dependence of Rate Constants on the concentration of Oxidant, in DMF; ([Substrate]=0.01M; $[H_2SO_4]$=0.02M; T=323K)

10^3[QDC]/M	0.10	0.25	0.50	1.0
$10^4k_1/s^{-1}$ for:				
Borneol	1.15	1.09	1.02	1.07
Isoborneol	2.84	2.75	2.88	2.81
Geraniol	1.91	1.86	1.75	1.83
Farnesol	2.41	2.29	2.33	2.23

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 the acid (Tables 7-9).

Table 7. Dependence of Rate Constants on Acid concentration for cyclic alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; T=323K)

$[H_2SO_4]$/M	0.05	0.10	0.15	0.20	0.25	0.50
$10^4k_1/s^{-1}$ for:						
Cyclopetanol	1.4	2.8	4.1	5.6	7.0	14.1
Cyclohexanol	0.74	1.5	2.2	3.0	3.7	7.4
Cycloheptanol	2.6	5.3	7.9	10.4	13.1	26.0
Cyclooctanol	3.4	6.7	10.3	13.6	17.2	34.0

Table 8. Dependence of Rate Constants on Acid concentration for bicyclic alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; T=323K)

$10^2[H_2SO_4]$/M	0.6	1.25	2.0	2.5	3.1
$10^4k_1/s^{-1}$ for:					
Borneol	0.32	0.68	1.07	1.35	1.67
Isoborneol	0.83	1.77	2.81	3.53	4.37

Table 9. Dependence of Rate Constants on Acid concentration for allylic alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; T=323K).

$[H_2SO_4]/M$	0.01	0.02	0.05	0.10	0.20
$10^4k_1/s^{-1}$ for:					
Geraniol	0.90	1.83	4.47	9.02	18.6
Farnesol	1.05	2.23	5.80	11.5	23.2

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.

The linear increase in the rate of the reaction with acidity suggested the involvement of a protonated Cr(VI) species. There have been earlier reports of the involvement of protonated Cr(VI) species in chromic acid oxidations(78). Protonated Cr(VI) species have been observed in the presence of p-toluene-sulfonic acid in nitrobenzene-dichloromethane mixtures(79).

Rate law

Under the present experimental conditions, wherein psuedo-first-order conditions have been employed for all the

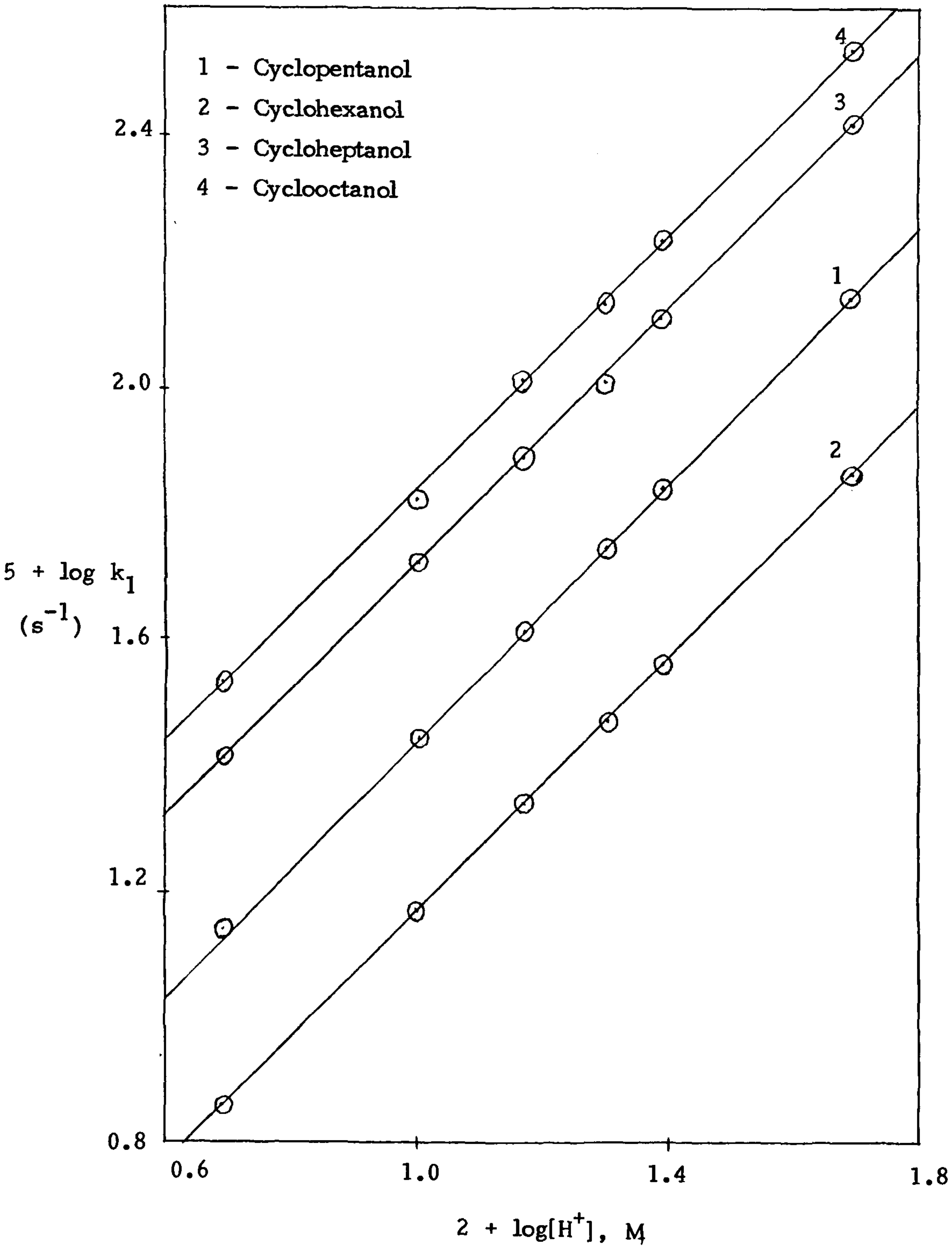


Fig.3. Plots of log k_1 against log [H^+].

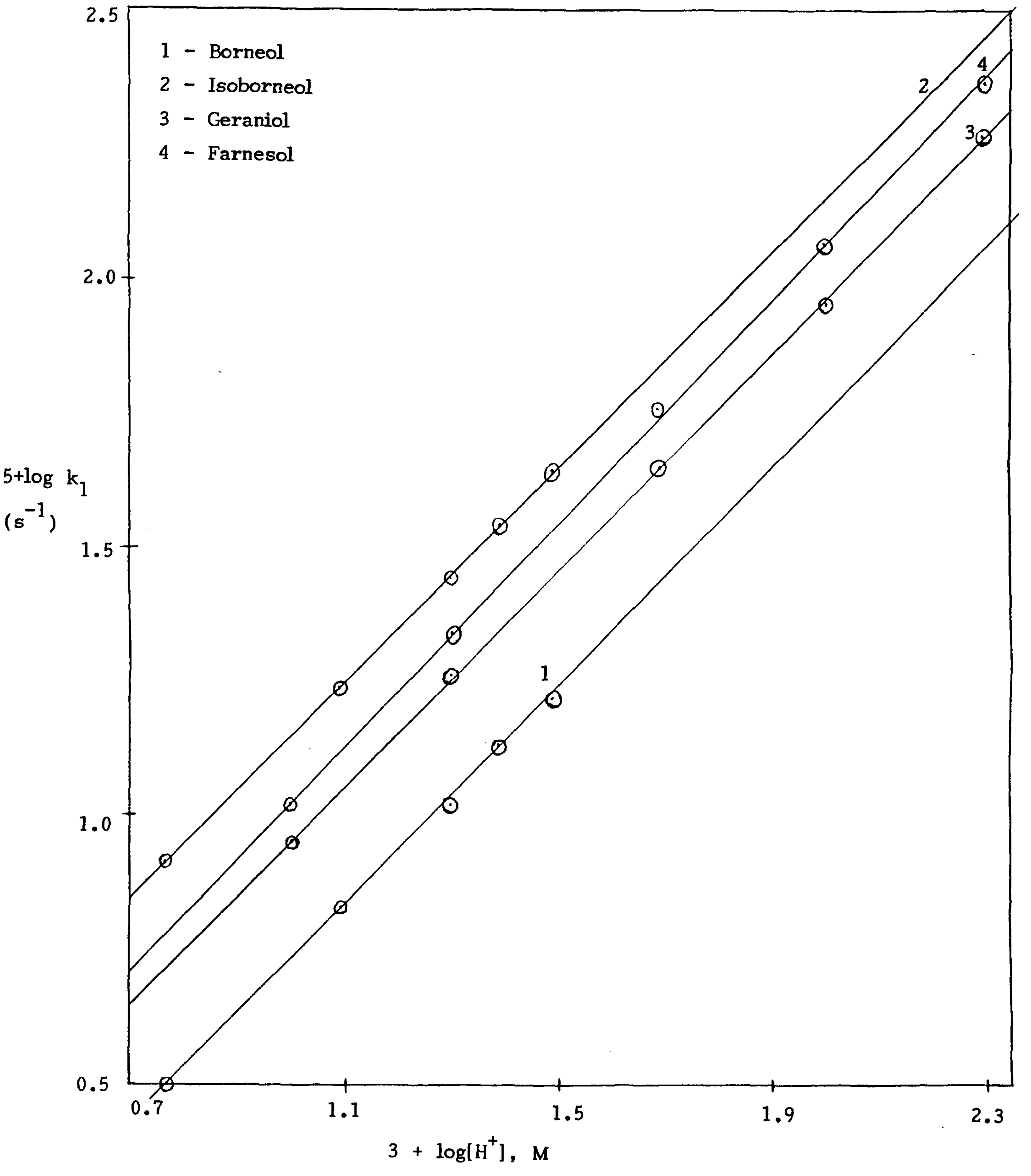


Fig.4. Plots of log k_1 against $\log[H^+]$.

kinetic runs, the observed rate law can be expressed as:

$$\text{Rate} = -\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Substrate}][\text{QDC}][\text{H}^+] \qquad (4)$$

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 all 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 dimethylformamide resulted in an increase in the rate of oxidation (Tables 10-11).

Table 10. Dependence of Rate Constants on Solvent Composition for cyclic alcohols; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.15M; T=323K).

DMF:H_2O (%, v/v)	100:0	95:5	90:10	85:15	80:20
Dielectric Constant(D)	37.6	39.7	41.8	43.9	46.1
$10^4 k_1/s^{-1}$ for:					
Cyclopentanol	4.1	3.0	2.24	1.70	1.31
Cyclohexanol	2.2	1.62	1.24	0.98	0.77
Cycloheptanol	7.9	5.25	3.66	2.49	1.82
Cyclooctanol	10.3	6.46	4.35	3.0	2.09

Table 11. Dependence of Rate Constants on Solvent Composition for bicyclic and allylic alcohols; ([Substrate]=0.01M; [QDC]=0.001M; $[H_2SO_4]$=0.02M; T=323K)

$DMF:H_2O$(%, v/v)	100:0	95:5	90:10	85:15	80:20
Dielectric Constant(D)	37.6	39.7	41.8	43.9	46.1
$10^4k_1/s^{-1}$ for:					
Borneol	1.07	0.68	0.54	0.43	0.32
Isoborneol	2.81	1.66	1.25	0.76	0.60
Geraniol	1.83	1.40	0.99	0.86	0.79
Farnesol	2.23	1.74	1.36	1.18	1.08

The dielectric constants for dimethylformamide-water mixtures have been estimated from the dielectric constants of the pure solvent(80).

In the present investigation, in proceeding from 80% dimethylformamide to 100% dimethylformamide, the polarity decreases. This decrease in the polarity of the medium caused an increase in the rate of the reaction (Tables 10-11). Plots of log k_1 against the reciprocal of the dielectric constant were linear (Figures 5,6a,6b), with positive slopes. This suggested an interaction between a positive ion and a

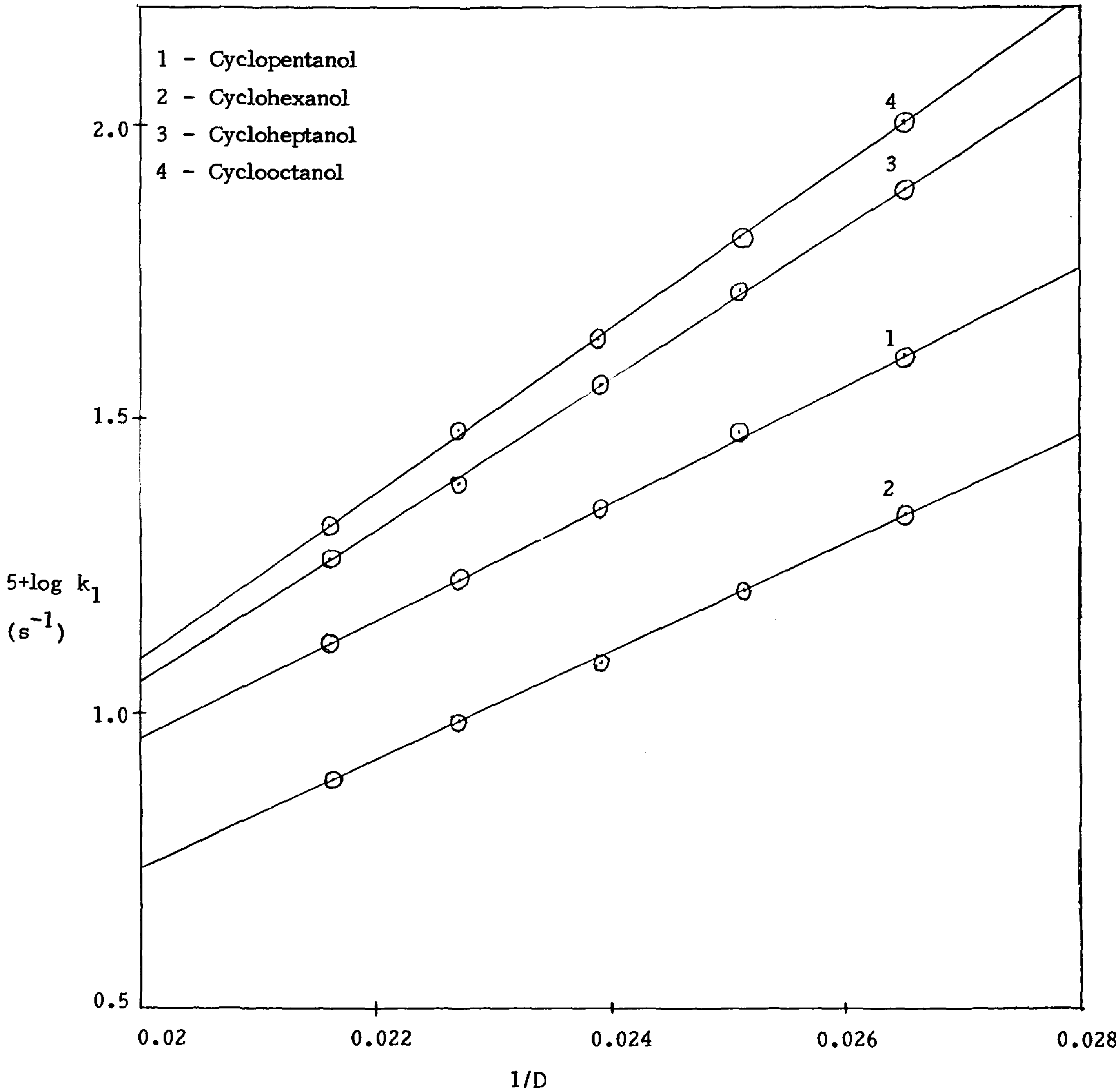


Fig. 5. Plots of log k_1 against the reciprocal of the dielectric constant.

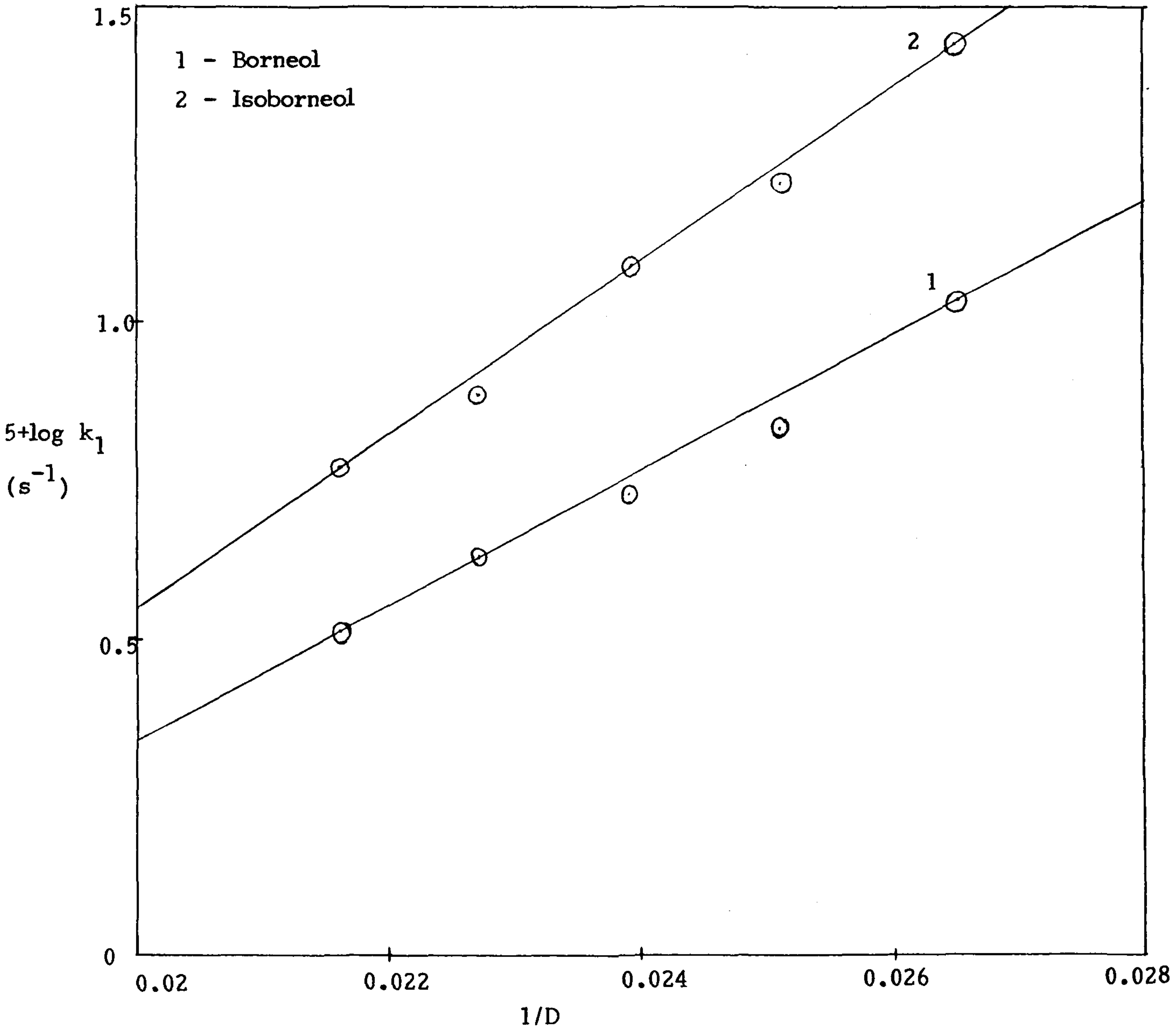


Fig. 6a. Plots of log k_1 against the reciprocal of the dielectric constant.

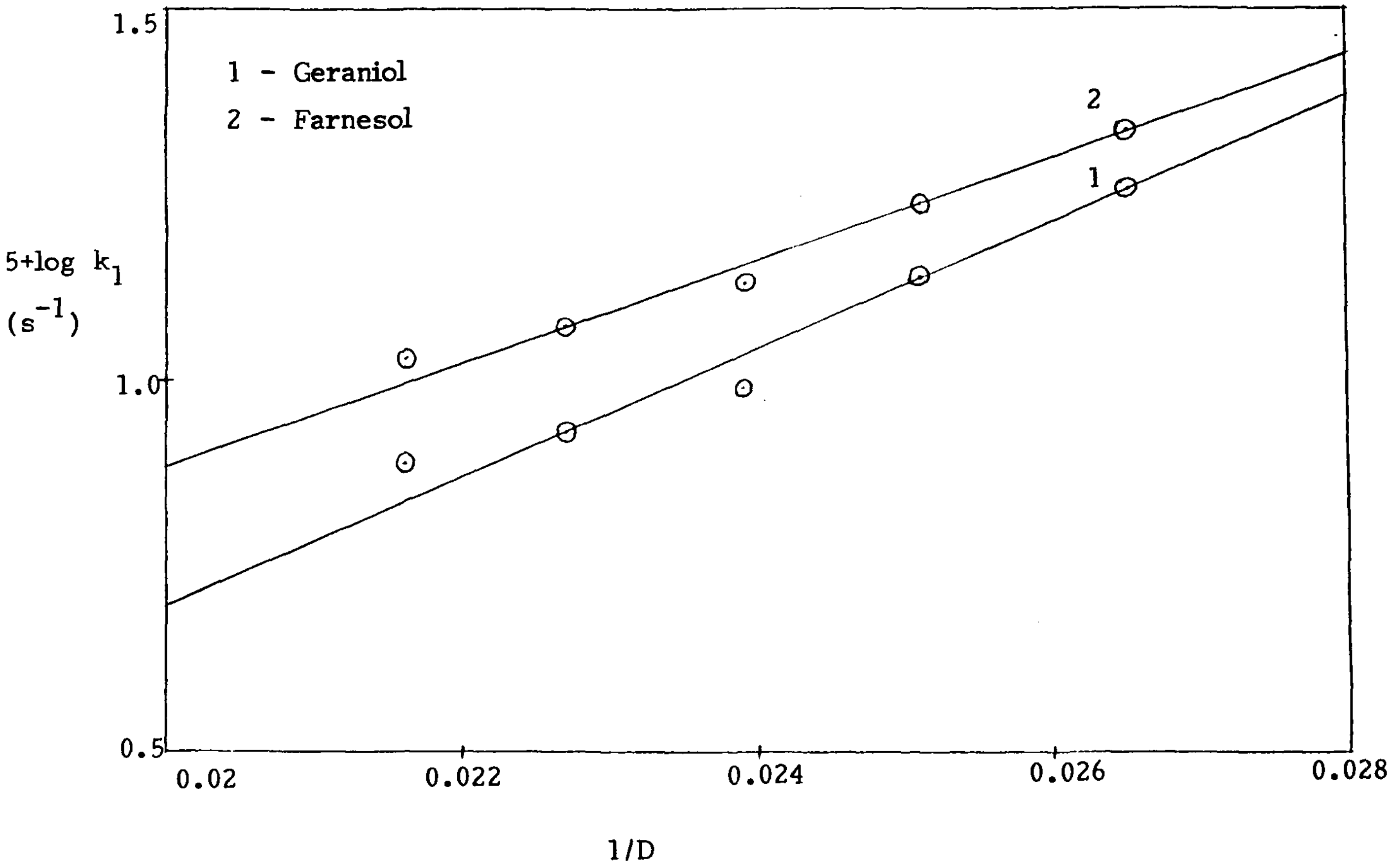


Fig. 6b. Plots of log k_1 against the reciprocal of the dielectric constant.

dipole(81), 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.

If the solvating power of the solvent were to be taken into consideration, one could qualitatively 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, in consonance with earlier observations(82). Therefore, the decrease in the rate of oxidation on the addition of a more polar solvent, as in the present investigation, would be the result of a progressive decrease in solvation of the transition state. The effect of a change in the solvent composition on the rates of reactions would also be dependent on factors such as solvent-solute interactions(83,84), and on solvent structure.

Effect of temperature

The rates of the reaction were influenced by changes in temperature (Tables 12-13).

Table 12. Dependence of Rate Constants on Temperature for cyclic alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.15M)

Temperature (±0.1K)	313	318	323	328	333
$10^4k_1/s^{-1}$ for:					
Cyclopentanol	2.75	3.39	4.10	5.01	6.17
Cyclohexanol	1.38	1.74	2.20	2.69	3.31
Cycloheptanol	5.50	6.61	7.90	9.55	11.2
Cyclooctanol	7.24	8.51	10.3	12.0	14.1

Table 13. Dependence of Rate Constants on Temperature for bicyclic and allylic alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.02M)

Temperature (±0.1K)	313	318	323	328	333
$10^4k_1/s^{-1}$ for:					
Borneol	0.46	0.69	1.07	1.60	2.36
Isoborneol	1.31	1.99	2.81	3.32	3.84
Geraniol	1.05	1.44	1.83	2.47	2.89
Farnesol	1.18	2.04	2.23	2.83	3.50

Plots of log k_1 against the reciprocal of temperature were linear (Figs. 7-8), 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 14.

Table 14. Activation Parameters for Cyclic, Bicyclic and Allylic Alcohols

Substrate	E	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	(kJ mol^{-1})	(kJ mol^{-1})	(JK^{-1}mol^{-1})	(kJ mol^{-1})
Cyclopentanol	36	33	-209	100
Cyclohexanol	39	36	-205	102
Cycloheptanol	32	29	-216	99
Cyclooctanol	29	26	-222	98
Borneol	71	68	-111	104
Isoborneol	28	25	-238	102
Geraniol	41	38	-199	102
Farnesol	39	36	-202	101

Error limits: E±2 kJmol^{-1}; $\Delta H^{\neq}$ ± 2kJmol^{-1}; $\Delta S^{\neq}$ ± 4Jmol^{-1}K^{-1}; $\Delta G^{\neq}$ ± 2kJmol^{-1})

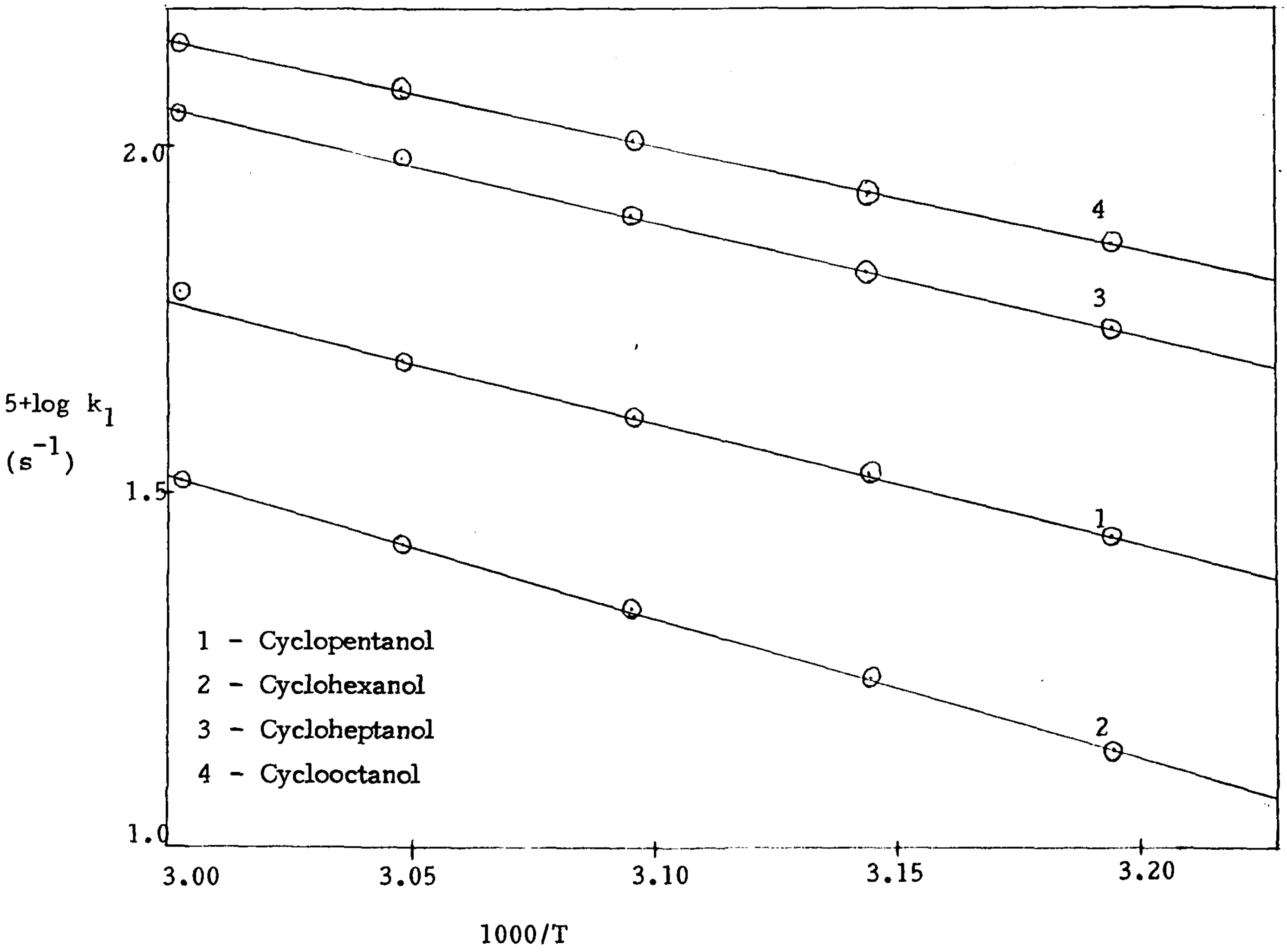


Fig. 7. Plots of log k_1 against the reciprocal of temperature.

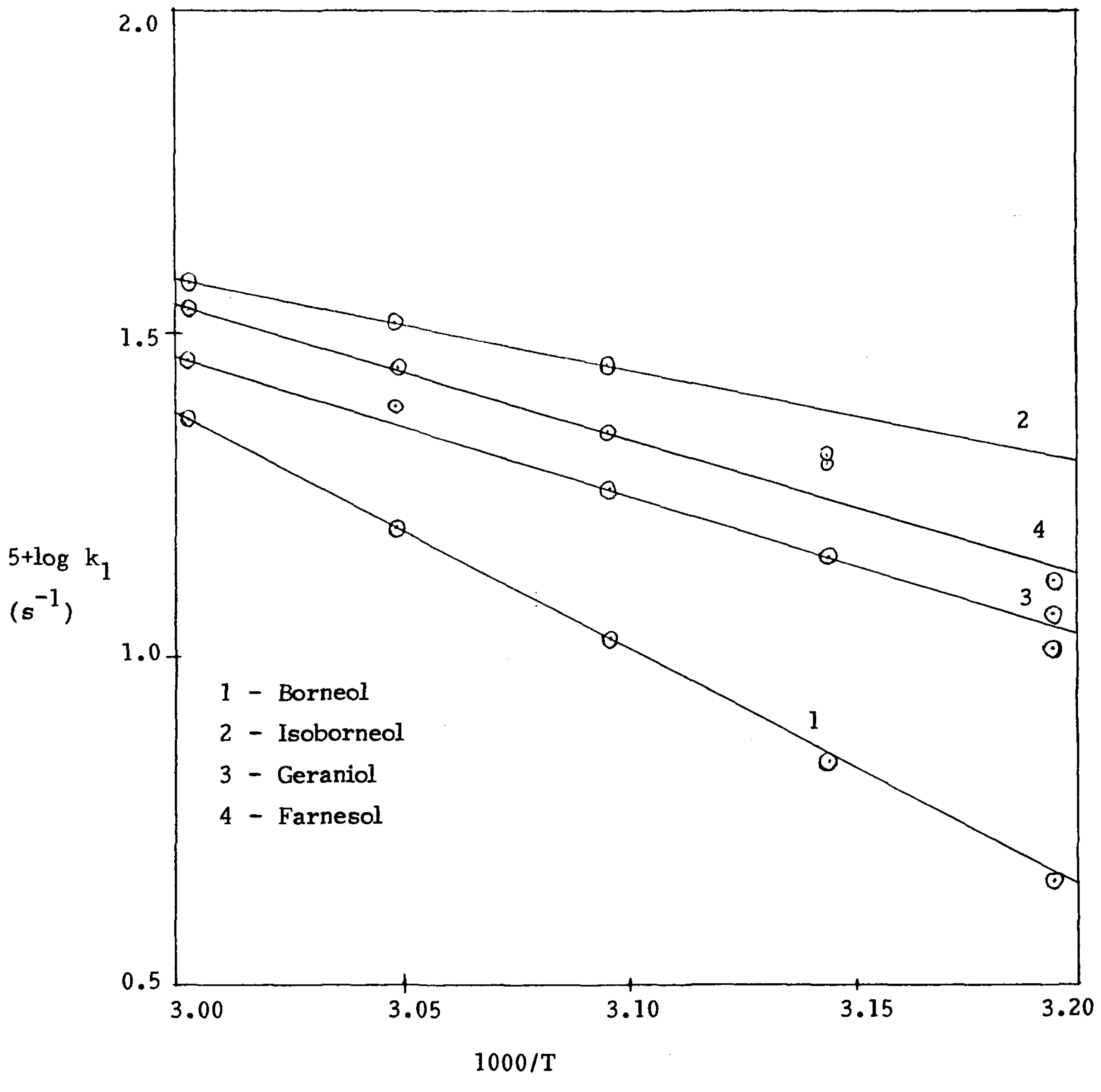


Fig. 8. Plots of log k_1 against the reciprocal of temperature.

The oxidations of all the substrates were characterized by negative entropies of activation. This would suggest an ordered transition state relative to the reactants(85). 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 all the substrates arises due to the changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, and stresses the probability that these oxidation reactions involve similar rate-determining steps.

Isokinetic relationship

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

$$\Delta H^{\neq} = \Delta H_{o}^{\neq} + \beta \Delta S^{\neq} \qquad (5)$$

where β is the isokinetic temperature. For the oxidation reactions studied in the present investigation, the activation enthalpies and entropies were linearly related. The correlation was tested and found to be valid by applying Exner's criteria(86). The isokinetic temperature, obtained from the plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, was 498K (Figure 9). Although current views do not attach much physical significance to isokinetic temperatures(87), a linear correlation between

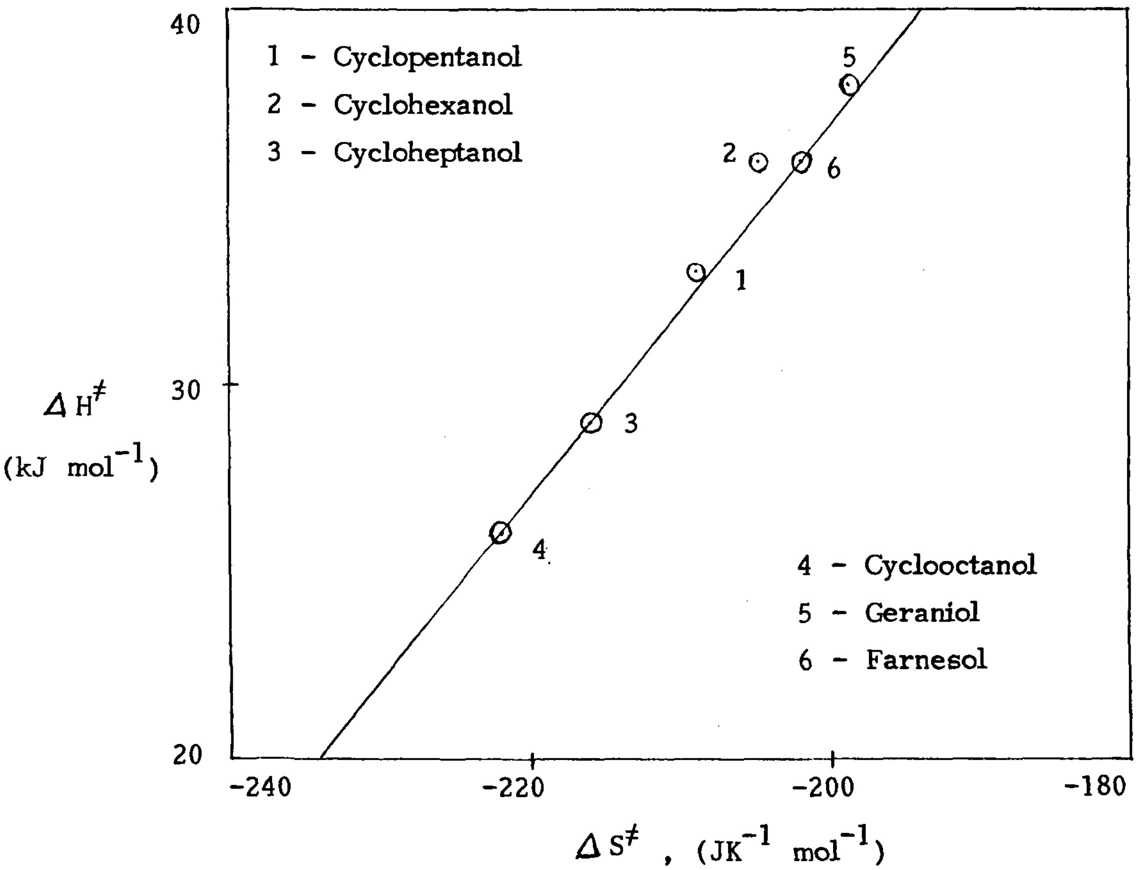


Fig. 9. Plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. Further, the values for the free energy of activation ($\Delta G^{\neq}$) were nearly constant, indicating that the same mechanism operated for the oxidation of all the alcohols studied in this investigation.

Induced polymerization

In the present investigation, since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile or the reduction of mercuric chloride(88). 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.

Structural influences on the rates of oxidation

Reaction rates for cyclic compounds have been rationalized by the difference in strain energy between the ground state and the transition state of the molecule in the process considered(89). The rates of oxidation of secondary alcohols with chromic acid have been interpreted with a decrease or increase of steric strain during the conversion of the sp^3 hybridized alcohol to the sp^2 hybridized ketone(78,90). In cyclic systems, changes in bond hybridization produced concomitant changes in angle strain (Baeyer strain), bond opposition strain (Torsional or Pitzer strain) or transannular strain(91).

For the oxidation of cyclic alcohols by chromic acid, the order observed was: 8>7>5>6. The fact that the 5-, 7- and 8- membered ring alcohols reacted faster than cyclohexanol was anticipated on the basis of other reactions involving a covalency change from four to three or five(92).

The kinetics of oxidation of cyclic alcohols by pyridinium chlorochromate (Corey's reagent) in chlorobenzene-nitrobenzene mixtures has been reported(9). The order of reactivity observed was 8>7>5>6. Similar observations were recorded in the oxidation of cyclic alcohols by chromic acid(93,94). A similar variation in the rate of the reaction with ring size was reported in the oxidation of cycloparaffins by chromic acid, wherein it was suggested that the reactivity of alicyclic compounds could be directly related to thermochemical strains in the molecule(95). The mechanism of oxidation of cyclic alcohols by pyridinium chlorochromate may be similar to those suggested for the oxidation of benzhydrol by pyridinium chlorochromate(96) and in the oxidation of benzyl alcohol by pyridinium chlorochromate(97). The intermediate formation of chromate ester was invoked to explain the rate data. The chromate ester would be better stabilized in the presence of solvent of low polarity, that is, a decrease of solvent polarity would accelerate the rate of oxidation. Further, the small variation in the rate of oxidation among the cyclic alcohols could be reconciled with the chromate ester mechanism since the chromate ester formation was likely to be little influenced by any structural changes(98,99).

The kinetics of oxidation of cyclic alcohols by V(V) in acetic acid-water mixtures at constant acidity was reported(100), and the results were discussed on the basis of the I-strain hypothesis. The order of reactivity reported was 8>7>5>6. The mechanism suggested was through a two-electron transfer.

The kinetics of oxidation of cyclic alcohols by Ce(IV) in acetic acid-water mixtures at varying acidities of perchloric acid was reported(17). The observed order of reactivity was 5>7>8>6. The mechanism involved a rate-determining O-H bond cleavage similar to what had been observed in earlier investigations(101,102).

The kinetics of oxidation of cyclic alcohols by potassium hexacyanoferrate(III) in alkaline medium(103) yielded an order of reactivity as follows: 8>7>6>5. This order of reactivity 8>7>5 was in conformity with the oxidation of cyclic alcohols by V(V) and Cr(VI), and also in consonance with the I-strain hypothesis, as sp^3 to sp^2 transitions were favoured in these rings. Cyclohexanol exists predominantly in a rigid chair form (staggered conformation), free of angular strain and bond oppositions. Hence any change of hybridization would generally be resisted and cyclohexanol would be oxidized at the slowest rate, as had been observed in the oxidations by V(V), Cr(VI) and Ceric ions. The only anamoly in the oxidation of cyclic alcohols by alkaline hexacyanoferrate(III) was the enhanced reactivity of cyclohexanol over cyclopentanol. The only explanation possible was that cyclohexanol was reacting through its flexible boat form which has bond opposition strain involving four pairs of hydrogen at the side of the boat. There was also strain due to the interference of the pair of hydrogen at the top of the boat, usually called the "bowsprit-flagpole interaction". Hence, the observed order of reactivity (8>7>6>5) for the oxidation of cyclic alcohols by alkaline hexacyanoferrate(III) could be rationalized(103).

The kinetics of oxidation of cyclic alcohols by barium manganate in alkaline medium had yielded an order of reactivity 8>7>5>6 (12), and the results were explained on the basis of the I-strain hypothesis(89).

In the present study, the order of reactivity for the oxidation of cyclic alcohols by quinolinium dichromate (QDC) was observed to be: 8>7>5>6 (Table 15).

Table 15. Order of Reactivity for the Oxidation of Cyclic Alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.15M; T=323K)

Substrate	$10^4k_1/s^{-1}$	$k_{relative}$
Cyclopentanol	4.1	1.86
Cyclohexanol	2.2	1.00
Cycloheptanol	7.9	3.59
Cyclooctanol	10.3	4.68

This order of reactivity could be rationalized on the basis of a change in ring strain involved on passing from the initial state (sp^3) to the transition state (sp^2). In the 5-, 7- and 8- membered ring systems, the primary source of strain arises as a result of non-bonded interactions. Such interactions would be absent in the ground state of the 6-membered ring system (staggered form). The net result would be that reactions leading to the easing of some of these non-bonded interactions in 5-, 7- and 8- membered ring systems would be facilitated. Earlier work has shown that the non-bonded interactions of the alcohols are mostly, if not entirely, relieved(104). The structure of the transition state must be such that this strain relief could occur, enabling the postulation of a product-like transition state. On the contrary for the 6-membered ring system, any deviation from the staggered conformation would be unfavourable since this would entail a higher energy of activation. This would account for the slowness in the rate of oxidation of cyclohexanol (Table 15).

While considering conformational effects for cyclic alcohols and their reactivities, it would be pertinent to observe that the cis- and trans-4-t-butyl cyclohexanols would represent a pair of conformationally pure equatorial and axial cyclohexanols with no α- or β- substituents. Thus the rates of reactions of the cyclohexanols and their derivatives would provide useful information on the differences to be expected from the equatorial or axial disposition of the reactive group on the chair form of the cyclohexane ring. It has been shown that the cis-4-t-butyl cyclohexanol, with an axial hydroxyl group, was oxidized more rapidly by chromium trioxide in aqueous acetic acid than the trans-isomer (with its equatorial hydroxyl group), by a factor ranging between 2-3. Thus the sequence of rates was taken as qualitatively typical(105) of axial and equatorial isomers. The relative rates of oxidation at 25°C were shown to be(106):

Cis-4-t-butylcyclohexanol	=	3.01
Cyclohexanol	=	1.24
trans-4-t-butylcyclohexanol	=	1.00

The rates of oxidation of bicyclic alcohols are influenced both by steric and electronic factors. The measurement of the relative stability of exo and endo epimeric alcohols of [2.2.1] bicycloheptane derivatives are particularly useful in attempting to analyze the rates of oxidation of bicyclic alcohols. While interpreting the rate data on the oxidation of bicyclic alcohols by quinolinium dichromate(QDC), it is imperative to look at the relative instabilities of the intermediate chromate esters. For a two-step reaction involving a fast prior equilibrium, followed by a slow decomposition of the intermediate, the rate of product formation would be independent of the relative stability of the intermediate. This independence arises because of a change in the rate of decomposition, due to a change in the stability of the intermediate. This, in turn, might be compensated by a change in the concentration of the intermediate. Thus, the relative rates of oxidation of bicyclic alcohols by quinolinium dichromate(QDC) would be determined by the differences in the relative stability of the alcohols and their transition states.

The rate data for the acid-catalyzed oxidation of secondary alcohols by quinolinium dichromate(QDC) in dimethylformamide, has been shown in Table 16.

Table 16. Rate data for the oxidation of secondary alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.02M; T=323K).

Alcohol	$10^4 k_1/s^{-1}$	$k_{relative}$
Borneol	1.07	3.7
Isoborneol	2.81	9.7
α-Norborneol (endo)	0.61	2.1
β-Norborneol (exo)	0.41	1.4
Cyclohexanol	0.29	1.0

The present data on the oxidation of secondary alcohols by QDC seem to suggest that if the strain-induced instability of the chromate ester were to determine the relative rates of oxidation, then there would be a rate-accelerating effect resulting from the relief of steric strain in the chromate ester. The present kinetic results would help to understand the extent of the influence of strain relief in determining the rate of chromate ester decomposition. For this purpose, the effect of strain relief factor on the relative rates of oxidation of alcohols of [2.2.1] bicycloheptane derivatives by QDC have been examined. The results in Table 16 show that borneol, with an axial hydroxyl group, is more stable than the isomeric equatorial isoborneol. In isoborneol, the chromate ester group is in the exo configuration, and is more strained due to the bridge gem-dimethyl groups. The hydroxyl group suffers non-bonded repulsion from the gem-dimethyl group at C-7, this effect being diminished when the transition state is formed. There is a rate-enhancing relief of steric strain in the transition state, and isoborneol is oxidized more rapidly than borneol by a factor of 2.63. This indicates a difference in the ease of ester decomposition. Such a conclusion is supported by the results obtained for the oxidation of norborneols. Here, the rate order of the endo and exo epimers is inverted. When their reactivities towards oxidation by QDC are considered, α-norborneol (endo) is more reactive than β-norborneol (exo) by a factor of 1.5 (Table 16). α-Norborneol (endo) forms the endo-chromate ester with greater difficulty and is more unstable than β-norborneol (exo), due to the strain induced by non-bonded interaction with the axial transannular hydrogen(105). The strain relieved by ester decomposition outweighs the ease of chromate ester formation, while determining the relative rates of reactions of the epimers.

From this analysis, there is another significant point to be taken into consideration. The difference in the rates of oxidation between isoborneol and α-norborneol(endo) gives a factor of 4.6 (Table 16). This suggests that the determining factor in the decomposition of the chromate ester relates to steric hindrance and non-bonded repulsions, both factors contributing to the instability of the chromate ester.

Similar reasoning would be valid for the series, α-norborneol(endo) > cyclohexanol (Table 16). The factor of 2.1 which distinguishes the oxidation rates of α-norborneol (endo) and cyclohexanol is a pointer to the strain and steric hindrance developed by substitution in the axial position of the boat structure of α-norborneol (endo).

Kinetic Isotope Effects

When an atom in a reactant molecule is replaced by its isotope, there is often a change in the rate of the reaction. Such changes are known as kinetic isotope effects or deuterium isotope effects, and are expressed as k_H/k_D (107-109). These effects are most marked when a hydrogen atom is replaced by a deuterium atom, since this would correspond to a relative change in the mass of the atom. The change in the rate of the reaction arises because of a change in the average vibrational energy (called the Zero-point vibrational energy) of the molecule. The ground state vibrational energy of a bond depends on the mass of the atoms and is lower when the reduced mass of the molecule is higher. Therefore, C-D and O-D bonds have lower energies in the ground state than the corresponding C-H and O-H bonds, respectively. Complete dissociation of a deuterium bond, therefore, requires more energy than that for a corresponding hydrogen bond in the same environment. The difference in bond dissociation energy observed for C-D and C-H bonds, in the dissociation of methane, is about 9.7kJ/mol (110). Thus, if the C-H or an O-H bond is considerably weakened or broken in the rate-determining step, the substitution of hydrogen by deuterium would lower the rate.

Kinetic isotope effects generally range from 1 (no isotope effect at all) to about 9 or 10 (111), although k_H/k_D values greater than 10 have been reported in some reactions(112,113).

The study of kinetic isotope effects has proved to be a valuable diagnostic tool for the determination of the mechanistic pathways of reactions.

Mechanistic pathways for the oxidation of alcohols have very often been established, using kinetic isotope effects. For the oxidation of secondary alcohols by chromic acid, the mechanism involved the rapid formation of a chromate ester, and the slow step of the reaction was the decomposition of this ester(114). Removal of the hydrogen on the carbinol carbon was part of the slow step, as shown by the fact that 2-deutero-2-propanol reacted about six times slower than 2-propanol(115).

The oxidation of ethanol by Ce(IV) in perchloric acid had shown the formation of a cerium(IV)-alcohol complex (116). The ceric sulfate oxidation of cyclohexanol had given a rate law which indicated a cerium(IV)-alcohol complex formation(117). The kinetic isotope effect for the ceric sulfate oxidation of α-deuterocyclohexanol gave a value of k_H/k_D = 1.9, which suggested that this reaction proceeded by a mechanism which involved the breaking of the α-C-H bond in the rate determining step(118). An acyclic mechanism was suggested to explain the low value of the isotope effect (118). The oxidation of cyclohexanol by aqueous cobaltic perchlorate had shown a small kinetic isotope effect, k_H/k_D = 1.72 at 10°C(119). This low value of the isotope effect was similar to what had been earlier observed for the Co(III) oxidation of cyclohexanol(120). The low values for the kinetic isotope effects observed for the oxidation of cyclohexanol by ceric ions(118) and by cobaltic ions(119) had established an acyclic mechanism with a rate-determining cleavage of the carbon-hydrogen bond. Calculations had shown that the kinetic isotope effect depended on the geometry of the transition state and exhibited low values of k_H/k_D (in the range 1-2) for non-linear configurations(121). The bromine oxidation of cyclohexanol with k_H/k_D=2.9 was a possible example of a six-membered transition state(122,123).

The oxidation of cyclohexanol by vanadium(V) in sulfuric acid solution, as also in perchloric acid solution, was observed to be first order with respect to both, V(V) and cyclohexanol(124). The kinetic isotope effect observed, k_H/k_D=4.5 (in sulfuric acid) and 3.6 (in perchloric acid) at 50°C, had indicated that the C-H or C-D bond of the carbinol group was involved in the rate-determining step of the reaction. This value of the kinetic isotope effect suggested a mechanism which involved a cyclic transfer of the α-H atom portion of the metal ion coordination sphere(124).

In the present investigation, the kinetic isotope effects have been studied with a view to establish the structure of the transition state and the nature of bond cleavage in the rate-determining step of the reaction. The rates of oxidation of some deuterated alcohols have been determined, and the kinetic isotope effects have been shown in Table 17.

Table 17. Kinetic Isotope Effects for the Oxidation of Alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.02M; T=323K).

Substrate	$10^5 k_1/s^{-1}$	k_H/k_D
Cyclohexanol	22.0	
Cyclohexanol-1-d	3.79	5.8
Isoborneol	28.1	
Isoborneol-2-d	4.46	6.3
Geraniol	18.3	
α,α-Dideuteriogeraniol	3.27	5.6
Farnesol	22.3	
α,α-Dideuteriofarnesol	3.84	5.8

The high values of the kinetic isotope effects observed (Table 17) would suggest a cyclic transition state with a rate-determining cleavage of the carbon-hydrogen bond.

It has been shown that the oxidations of primary and secondary alcohols by chromium(VI) had involved esterification and base-catalyzed, or cyclic, decomposition of the ester by the slow rupture of the carbon-hydrogen bond(125). Generally, for a cyclic mechanism with a rate-determining carbon-hydrogen bond cleavage, the k_H/k_D values were fairly high, as seen from the oxidation of primary and secondary alcohols by various oxidizing agents(115,124,126,127). The relevant data on the kinetic isotope effects have been shown in Table 18.

Table 18. Kinetic Isotope Effects for the Oxidation of Primary and Secondary Alcohols by different Oxidants.

Alcohol	Oxidant	k_H/k_D	Zero Point Energy ($kJmol^{-1}$)^f
Cyclohexanol	V(V)	4.5^a	3.8
Isopropanol	Cr(VI)	7.0^b	5.9
Ethanol	PCC	5.7^c	4.8
Propanol	PCC	6.7^d	5.6
Cyclohexanol	QDC	5.8^e	4.9
Isoborneol	QDC	6.3	5.3
Geraniol	QDC	5.6	4.7
Farnesol	QDC	5.8	4.9

^{a}ref.115; ^{b}ref.124; ^{c}ref.126; ^{d}ref.127; ^{e}this work; ^{f}ref.107

If kinetic isotope effects for C-H bonds were due to differences in activation energies alone, then the energy difference for C-H and C-D bonds could be calculated from the zero point energy differences for the linear stretching of these bonds(107). The values of the kinetic isotope effects observed when cyclohexanol was oxidized by ceric ions(118), cobaltic ions(119) and Mn(III) ions(122) corresponded to a much smaller difference of energy ($\sim$1.25 kJ/mol). This indicated that, with these three oxidants, the transition state involved a more strongly bound hydrogen atom. On the contrary, the observed k_H/k_D values obtained for the oxidation of cyclohexanol by different oxidants(Table 18), corresponded to a substantial loss of zero point energy in the transition state (3.8 kJ/mol or more). This indicated that the C-H bond was considerably stretched in the transition state. In general, high zero point energy values would indicate that the C-H bond was considerably stretched in the transition state(107), and the high values of k_H/k_D would thus establish a rate-determining cleavage of the carbon-hydrogen bond.

Mechanism

Based on the stoichiometries of the oxidation reactions (Table 1), and the observed experimental data, the mechanistic pathways of the reactions have to be considered.

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

(1) The rates of oxidation of all the substrates (cyclic alcohols, bicyclic alcohols and allylic alcohols) were dependent on the first powers of the concentrations of each — substrate and oxidant (Tables 2-6).

(2) The rates of the reactions showed a first order dependence on the concentration of the acid (Tables 7-9). The acid catalysis of the oxidation reactions must be related to the structure of the oxidant(QDC). The oxidant was thus converted to a protonated Cr(VI) species.

(3) A decrease in the polarity of the solvent medium (using DMF-water mixtures) resulted in an increase in the rate of the reaction (Tables 10-11). Linear plots of log k_1 against the reciprocal of the dielectric constants (Figs. 5-6) gave positive slopes, which indicated an ion-dipole type of interaction. This was in accordance with the involvement of a protonated Cr(VI) species.

(4) An increase in temperature resulted in an increase in the rates of the reactions (Tables 12-13). The

oxidations of all the substrates were characterized by negative entropies of activation (Table 14), which suggested an ordered transition state, relative to the reactants. The similarity in $\Delta G^{\neq}$ values (Table 14) for all the substrates arose due to changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, and emphasized the probability that all these oxidation reactions involved similar rate-determining steps.

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

(6) The observed order of reactivity for the oxidation of the substrates was as follows:

(a) Cyclic Alcohols: 8 > 7 > 5 > 6 (Table 15),

(b) Bicyclic Alcohols: Isoborneol > Borneol (Table 16),

Norborneols: α-Norborneol(endo) > β-Norborneol(exo) (Table 16)

(c) Allylic Primary Alcohols: Farnesol > Geraniol (Table 4)

For the cyclic alcohols, the order of reactivity was rationalized on the basis of a change in ring strain involved in passing from the initial state (sp^3) to the transition state (sp^2).

For the borneol-isoborneol pair, isoborneol was more reactive than borneol, since the hydroxy group suffered non-bonded repulsion from the gem-dimethyl group.

For the norborneols, it was observed that α-norborneol(endo) was more reactive than β-norborneol(exo), because of the non-bonded repulsion from the neighbouring hydrogen atoms.

(7) The kinetic isotope effects observed were as follows (Table 17):

Substrate	k_H/k_D
Cyclohexanol	5.8
Isoborneol	6.3
Geraniol	5.6
Farnesol	5.8

The high values of the kinetic isotope effects observed suggested a cyclic transition state, with a rate-determining cleavage of the carbon-hydrogen bond.

(8) The zero point energy values were as follows (Table 18):

Substrate	Zero point energy ($kJ\ mol^{-1}$)
Cyclohexanol	4.9
Isoborneol	5.3
Geraniol	4.7
Farnesol	5.9

The high zero point energy values indicated that the carbon-hydrogen bond was considerably stretched in the transition state, supporting a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction.

At this juncture, it would be pertinent to review the earlier work which has been carried out on the oxidation of alcohols (cyclic, bicyclic and allylic alcohols) by various oxidizing agents. This would help to unequivocally establish the mechanistic pathways for the oxidation of all the substrates studied by quinolinium dichromate(QDC) in acid medium, using dimethylformamide(DMF) as the solvent.

The oxidation of a secondary alcohol, such as isopropyl alcohol, by chromic acid in aqueous acetic acid, catalyzed by mineral acid, was observed to give a quantitative yield of acetone(114). A solution of chromic acid in dilute sulfuric acid, when added to a solution of a secondary alcohol, taken in acetone, yielded the ketone(128). It was observed that the reaction proceeded more rapidly in acetone than in acetic acid. Further, in the oxidation of secondary alcohols, the ketone formed was effectively protected against further oxidation because of the large excess of acetone(128). Potassium dichromate, in glacial acetic acid, was observed to be a useful reagent for the oxidation of secondary alcohols(129). The chromium trioxide-pyridine complex(1) was found to be very effective for the oxidation of steroidal alcohols, giving high yields of the ketone(2). A solution of t-butyl chromate, in petroleum ether, effected the oxidation of primary alcohols to aldehydes in excellent yields(63). This same reagent was found to oxidize secondary alcohols to ketones in high yields(130).

The reactions of primary and secondary alcohols, with chromic acid, had resulted in the rapid formation of the esters of chromic acid(131-133), which underwent ready decomposition to the corresponding carbonyl compounds(133).

The first attempt to unravel the mechanism of oxidation of alcohols by chromic acid was made by Westheimer, who studied the oxidation of isopropyl alcohol(114). This work could be summarized as follows:

(a) the reaction was acid-catalyzed, with the rate being proportional to the first (or higher) power of the hydrogen ion concentration (or the acidity constant);

(b) the reaction was much faster in acetic acid solution than in mineral acid of the same acidity constant;

(c) the transition state was a monochromium species; and

(d) the carbon-hydrogen bond at the carbinol carbon was broken in the rate-determining step.

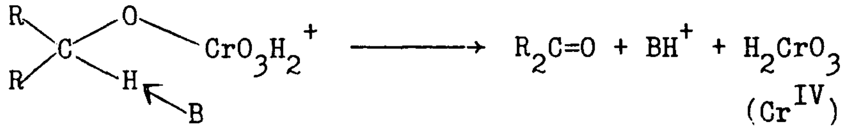
The rate law for the oxidation of isopropyl alcohol by chromic acid was found to be(114):

$$\nu = k_a[HCrO_4^-][R_2CHOH][H^+]+k_b[HCrO_4^-][R_2CHOH][H^+]^2 \qquad (6).$$

This rate law was later found to be applicable to the oxidation of many other primary and secondary alcohols (134-138). A kinetic isotope effect, $k_H/k_D=7.0$, was observed for the oxidation of isopropyl alcohol by chromic acid(115). A similar value for the kinetic isotope effect was observed for the oxidation of ethanol by chromic acid(134,139,140). The reactions proceeded more rapidly in deuterium oxide than in water, which indicated the existence of a prior equilibrium step involving protonation(141). The kinetic isotope effect observed for these reactions confirmed that the slow step of the reaction had involved the cleavage of the carbon-hydrogen bond. All these kinetic data helped in establishing the overall nature of the oxidation of alcohols by chromic acid. These data helped to confirm the earlier observations of Westheimer that the pathway for the oxidation of alcohols by chromic acid had involved the intermediate formation of a chromate ester(131-133), which then underwent decomposition to give the corresponding carbonyl compound(133). This was further confirmed by the oxidation of a group of steroidal alcohols by the pyridine-chromium trioxide complex, giving yields of ketone in the range 87-92%(142-144). Later evidence had demonstrated that the acid chromate ester was formed in the reaction between isopropyl alcohol and chromic acid(145). The O-H bond of the alcohol was probably not intact in the transition state (ethers are relatively inert to chromium VI), nor being broken in the transition state (because of the positive solvent isotope effect observed in this reaction, ref.141). The conclusion that the chromate ester was a reactive intermediate in this oxidation reaction, thus seemed reasonable (131-133). Indeed, the oxidation of sterically hindered alcohols by chromic acid had established the intermediate formation of the chromic acid ester(146).

The work of Westheimer on the oxidation of isopropyl alcohol by chromic acid thus helped to establish that chromate esters of alcohols were formed under the reaction conditions. The following mechanism was put forward in which the chromate ester decomposed by the loss of a proton to any available base (probably a water molecule):

$$R_2CHOH + HCrO_4^- + 2H^+ \rightleftharpoons R_2CHOCrO_3H_2^+ + H_2O$$



The work on the induced oxidation of added substrates had examined the further fate of the chromium(IV) intermediate formed in such reactions, and had established that eventually Cr(IV) was converted to a chromium(III) species(132,147).

It has already been established that the oxidation of primary and secondary alcohols by chromium(VI) proceeded via a mechanism which involved the formation of a chromate ester, followed by base-catalyzed, or cyclic, decomposition of the ester by the slow-rupture of the C-H bond(125). The oxidation of cyclohexanol by ceric ions(118) and cobaltic ions(119) had exhibited kinetic isotope effects with the values of $k_H/k_D = 1.9$ and 1.7 respectively, and had established an acyclic mechanism with the cleavage of the C-H bond in the rate-determining step. Theoretical calculations had shown that the primary kinetic isotope effect was dependent on the geometry of the transition state, and exhibited low values of k_H/k_D (in the range 1-2) for non-linear configurations(121). The oxidation of cyclohexanol by bromine had yielded a value of $k_H/k_D = 2.9$, and the pathway involved the formation of a six-membered transition state (122,123). It has been shown that for the oxidation of alcohols by V(V) and Cr(VI) reagents, the kinetic isotope effects were much more pronounced, and the mechanistic pathway involved the formation of a cyclic transition state. Generally, for a cyclic mechanism, with a rate-determining C-H bond cleavage, the k_H/k_D values were fairly high, as seen from the oxidation of both primary and secondary alcohols by various oxidants(115,124,126,127). The data for the kinetic isotope effects has been shown in Table 18.

The zero point energy values (Table 18) indicated that there was considerable stretching of the carbon-hydrogen bond in the transition state(107), supporting a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction.

A cyclic transition state could be postulated on the basis of the relative rates of oxidation of the cyclic alcohols studied (Table 19).

Table 19. Rate data for the oxidation of cyclic alcohols, in DMF; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=0.15M; T=323K).

Substrate	$10^4k_1/s^{-1}$	Relative Rate
Cyclopentanol	4.1	1.9
Cyclohexanol	2.2	1.0
Cis-4-t-Butylcyclohexanol	2.3	1.0
trans-4-t-Butylcyclohexanol	2.2	1.0
Cycloheptanol	7.9	3.6
Cyclooctanol	10.3	4.7

It is significant that the relative rates of oxidation of cis- and trans-4-t-butylcyclohexanol were equal. With a linear transition state, the cis-isomer having an axial hydroxyl group should react faster than the trans-isomer having an equatorial hydroxyl group, the approach of the oxidant to the trans-isomer being more difficult. The similar reactivity of this epimeric pair of alcohols supports a transition state in which the accessibility of both, the hydrogen and the hydroxyl group at the reaction centre, are about equally important. It is pertinent to observe that the oxidation of the same pair of alcohols by molecular bromine(148) or N-bromosuccinimide(149) occurs with a similar conformational insensitivity attributed to the cyclic nature of the transition state.

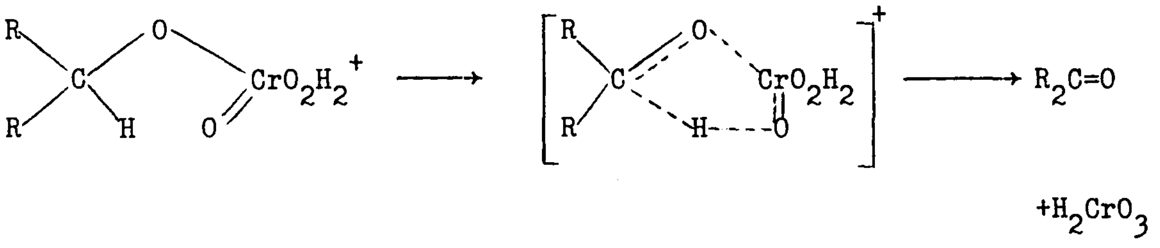
A stoichiometric conversion of the cyclic alcohols to the corresponding ketones was observed, and this process involved the change $>CHOH \longrightarrow >C=O$. If the reaction intermediate were to be visualized as having a cyclic structure, then this would explain all the features of the oxidation reaction. The negative entropies of activation (Table 14) would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The similarity of $\Delta G^{\neq}$ values arises due to changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values (Table 14), and stresses the probability that these oxidation reactions involve similar rate-determining steps.

Pyridinium chlorochromate(PCC) has been used for the oxidation of alcohols, and the kinetic features of these reactions have been reported(79,97). The mechanistic pathways in all these oxidations by pyridinium chlorochromate had involved the formation of a chromate ester intermediate, which would be better stabilized in the presence of solvents of low polarity. Hence, a decrease in the polarity of the solvent had shown an increase in the rate of oxidation of these alcohols by pyridinium chlorochromate(79,97).

In the present investigation, the observed solvent effect (increase in the polarity of the solvent decreased the rate of oxidation, Tables 10-11) provided support for a reaction pathway which involved the formation of a chromate ester intermediate.

Further, the small variation in the reaction rate for the oxidation of cyclic alcohols by quinolinium dichromate (Table 19), can also be reconciled with the ester mechanism, since the chromate ester formation was likely to be little influenced by structural changes(99).

A unimolecular decomposition of the ester can be written in which the hydrogen is bonded in the transition state to both the alcoholic carbon atom and the oxygen atom attached to chromium:



A similar transition state, with the hydrogen being transferred as a proton, had been suggested in an earlier investigation(150). Electron flow in a cyclic transition state has been earlier considered (151,152), and the conversion of the ester to the transition state has to be rationalized. This can be best considered in the following terms:

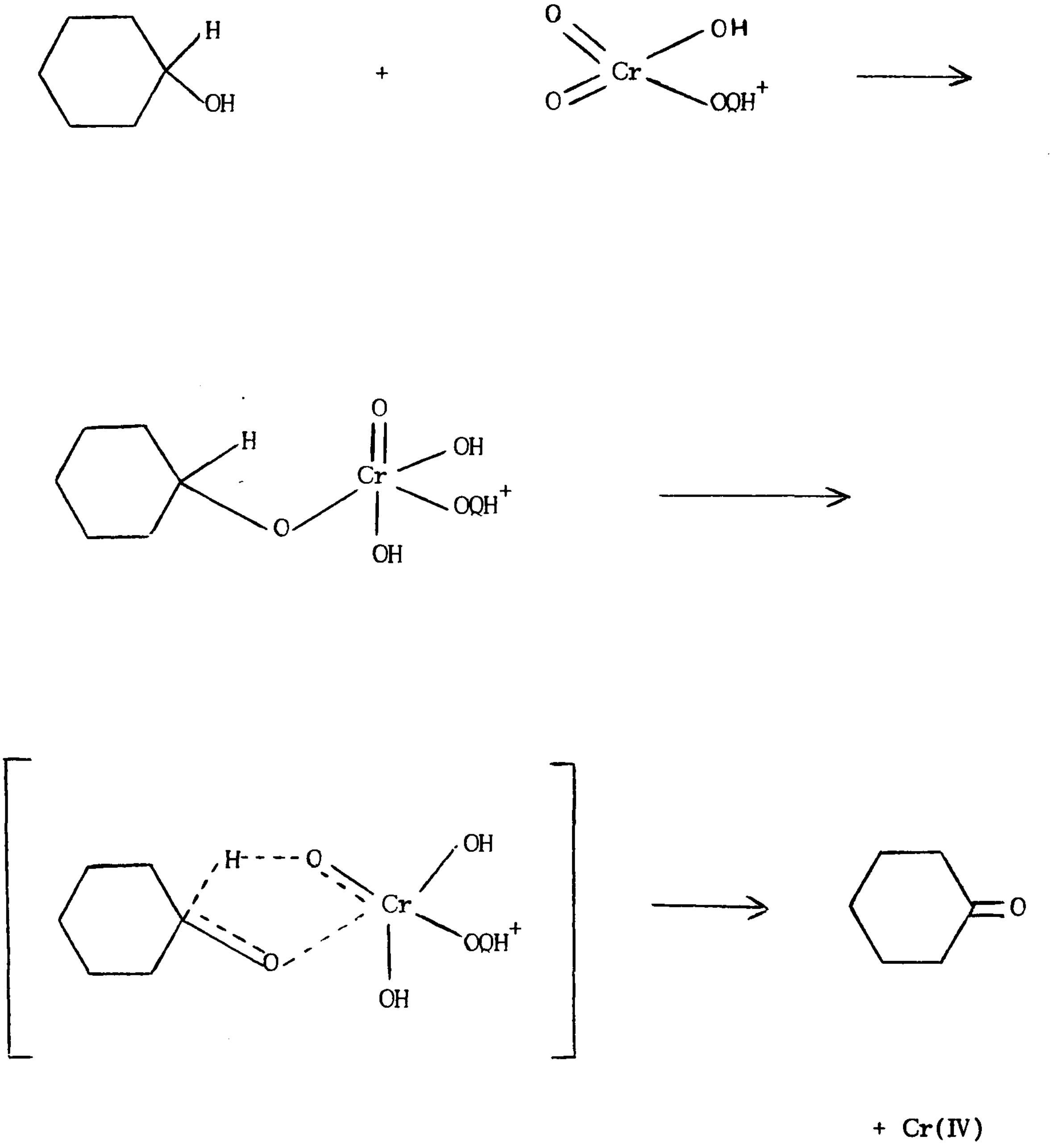
If the chromium were to be coordinated through the alcohol O-H group, then the process of electron transfer could take place through the carbon-oxygen-chromium bond. This would not only facilitate the formation of the chromate ester, but would also enhance the ease of conversion to the ketone. The observed kinetic isotope effects (Table 17) indicated a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction, similar to observations reported in earlier investigations (115,124,126,127). The proton is removed in the cyclic transition state (in which there would be the coplanarity of all the atoms involved), the centre of which resides on an electron-dense oxygen in the chromate ester(153). Such a transition state would envisage 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. Partly occupied orbitals are thus used to bind the transferred hydrogen to both, carbon and oxygen, in the transition state. A cyclic transition state has been suggested as the most plausible intermediate for the oxidation of primary and secondary alcohols by chromium(VI) reagents(154).

In the present investigation, the sequence of reactions involved in the oxidation of alcohols (cyclic alcohols, bicyclic alcohols and allylic alcohols) by quinolinium dichromate(QDC) in acid medium, using DMF as the solvent, has been shown in Schemes 1-3.

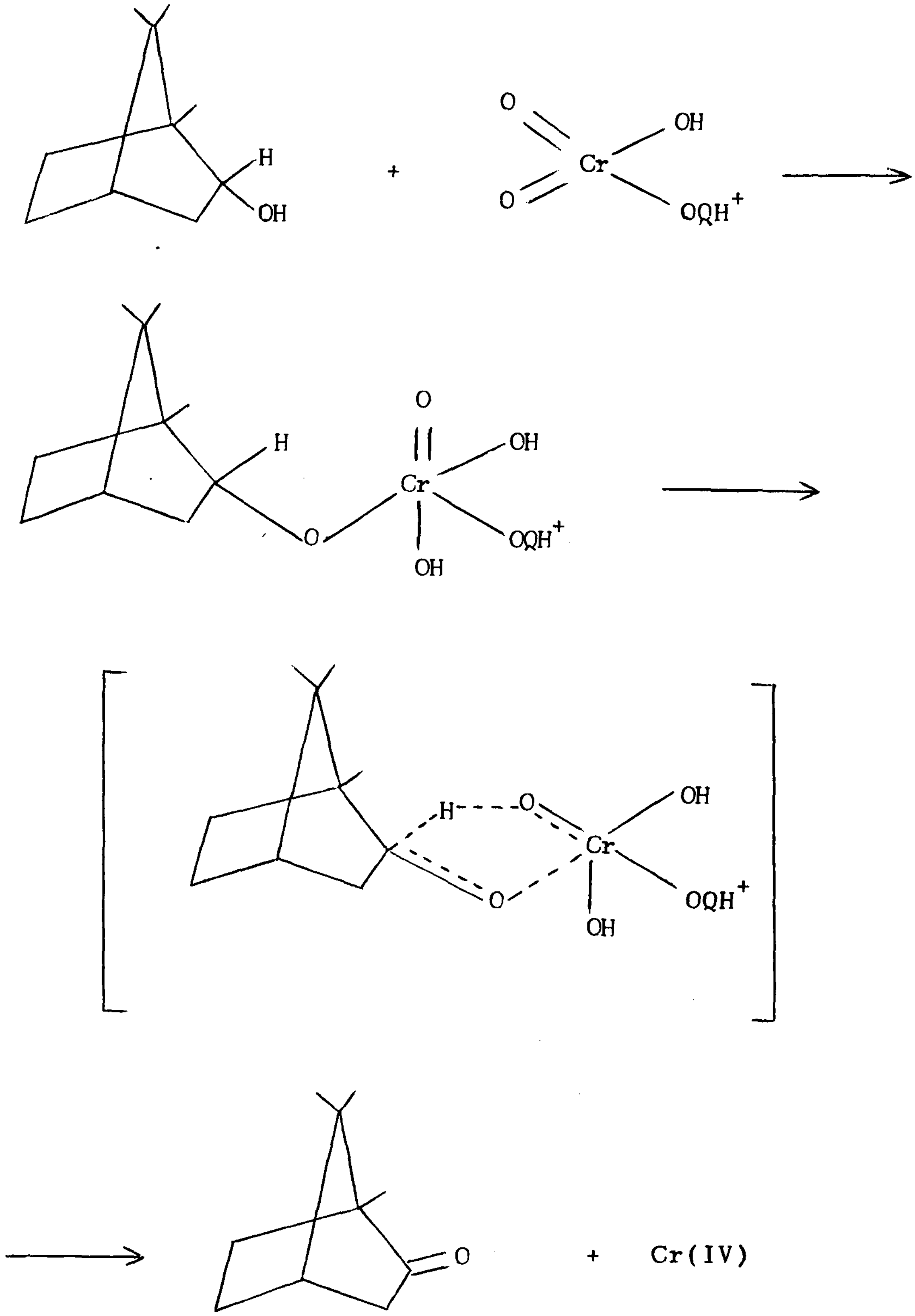
The mechanism is consistent with the fact that these oxidation reactions are catalyzed by acid (Tables 7-9). Protonation of the oxidant(QDC) would make it more amenable towards nucleophilic attack by alcohol on the electron-deficient chromium of the oxidant. The first step involved the transfer of the hydrogen atom from the O-H group of the alcohol to the oxidant, in order to form the chromate ester. The O-H fission must be the first step of this reaction. The large values obtained for the kinetic isotope effects (Table 17) confirmed that the cleavage of the carbon-hydrogen bond must occur in the second step of the reaction, which would be the rate-determining step of the reaction. In the second step of the reaction, two electrons are transferred in a cyclic system.

In general, oxidation reactions of organic functions by different oxidizing agents can be considered using the Zimmerman treatment of electrocyclic reactions(155). Selection rules play an important part in determining the

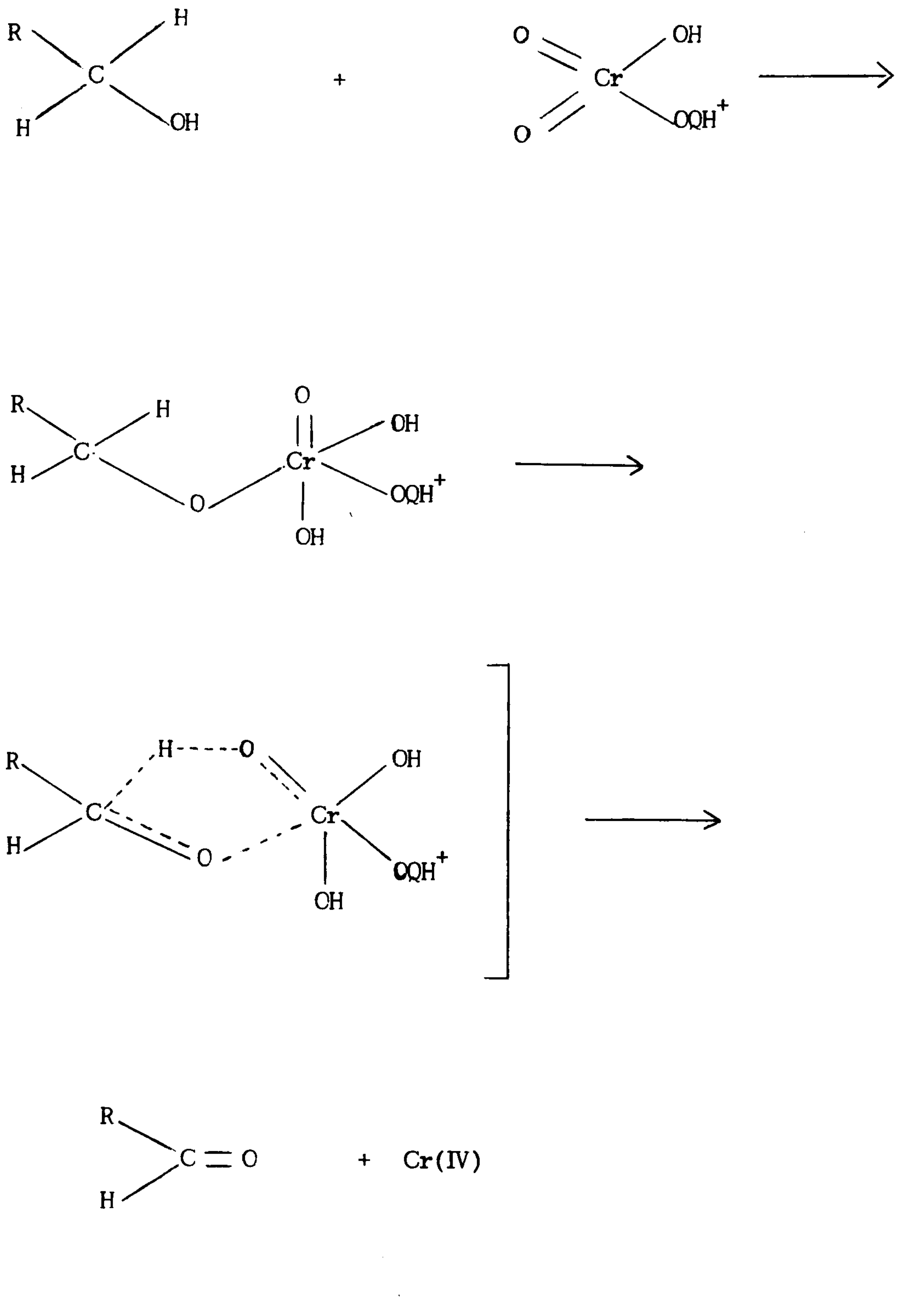
SCHEME 1



SCHEME 2



SCHEME 3



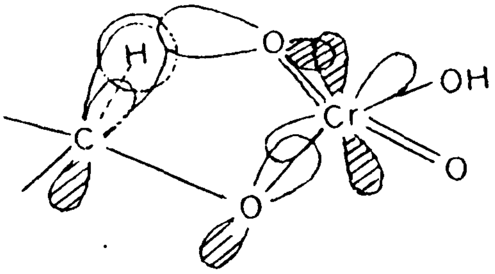
where R = $C_9 H_{15}$ (geraniol)

= $C_{14} H_{23}$ (farnesol)

mechanisms of many oxidation reactions. For reactions involving electrons in d orbitals, a topological approach to the orbital levels of the transition state has been applied (155). This method classifies the transition state as either "Hückel-like" (in which all overlapping pairs of reacting orbitals are bonding), or "Möbius-like" (in which one or an odd number of antibonding overlaps must occur). In a Hückel transition state, 4n+2 electrons form a closed shell (giving it stability), while 4n electrons are required for stable closed shells in a Möbius transition state. An "allowed" reaction may have either a Hückel-type or a Möbius-type transition state, provided that the correct number of electrons is available to stabilize that transition state.

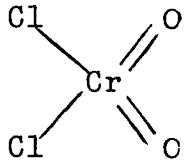
When chromium(VI) is reduced, the initial product chromium(IV) is unstable, but it is generally considered to be an octahedral complex(156). The d-electrons in the unexcited product must therefore be in a t_{2g} orbital(d_{xy}) which can overlap, in the reactions, using two adjacent lobes with opposite signs of the wavefunctions. It can therefore be considered to be locally antisymmetric (π-type). The transition state would be of Hückel-type (4n+2), and hence would be an allowed reaction.

In the present investigation, the oxidation of alcohols (cyclic, bicyclic and allylic alcohols) by quinolinium dichromate(QDC), in acid medium, involved the formation of a cyclic chromate ester. The second step of the reaction would be the transfer of two electrons in a cyclic system. The accepted electrocyclic mechanism for the oxidation of alcohols by QDC clearly involves 6 electrons, and the orbital picture shows that this is a Hückel-type system (4n+2). Hence, this would be an allowed process. The orbital overlap diagram is shown.



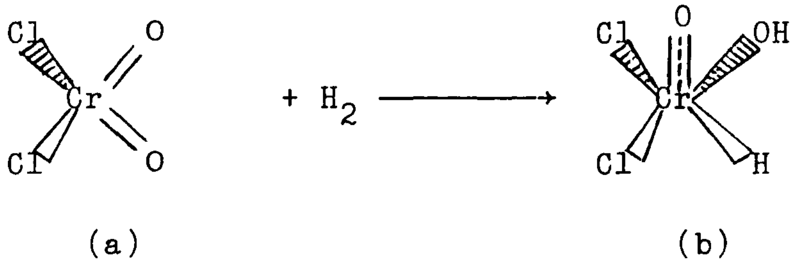
The results of a mechanistic study using ab initio theoretical methods have been used to suggest a plausible mechanistic sequence for the oxidation of alcohols by chromyl chloride(157). The primary reaction step was the addition of either a σ or a π bond across a Cr-O π bond.

This process was dependent on whether there was an extra (spectator) oxo group on the metal. Chromyl chloride, CrO_2Cl_2, can be written as 1:



1

The two dπ orbitals are each used to form a π-bond to each of the two oxo groups. Thus, including the σ bonds, both oxo groups are connected to the metal through double bonds. The second oxo group of the dioxo species plays an important role. For example, the addition of H_2 across the metal-oxo bond (in CrO_2Cl_2) can be represented as



(1)

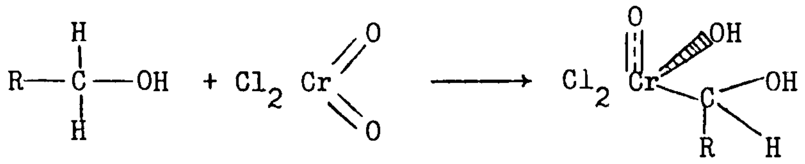
This process is exothermic, with $\Delta G^{\neq} = 29\ kJmol^{-1}$. In 1(b), there are four σ-bonded ligands (two Cl, one OH, and one H) and an oxo bond. Thus, the chromium can use both dπ orbitals to bond to a single oxygen. The result is a triple metal-oxo bond. In reaction 1, the spectator oxo group (the one not involved in the bond) changes from a double bond to a triple bond, thereby stabilizing the product. That is, the spectator oxo group drives the reaction.

For the oxidation of alcohols by chromyl chloride, it was suggested that the first step was one of the following:

(a) addition across the O-H bond

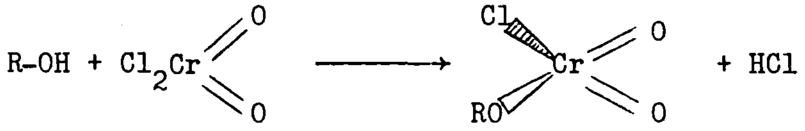
(2)

(b) addition across a C-H bond



(2)

(c) simple ligand substitution with a chloride



(3)

The energetics of these pathways, using ethanol as the substrate, suggested that chromyl chloride was a viable oxidant for water-insoluble alcohols, and that alcohols would subsequently be oxidized to aldehydes or ketones.

Under the experimental conditions employed in the present investigation, cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol) were oxidized by quinolinium dichromate(QDC), in acid medium, giving the corresponding cyclic ketones in each case. The products (the respective cyclic ketones) were characterized by IR analysis, and by the formation of the respective 2,4-dinitrophenylhydrazone derivatives (Vide Experimental: Product Analysis).

It would be pertinent to recall the earlier experimental observations wherein cyclic alcohols were oxidized to cyclic ketones in good yields, when oxidized by diverse oxidizing agents such as sodium bromate in the presence of catalytic amounts of hydrobromic acid(26), the peroxo and oxodiperoxo complexes of molybdenum containing the Bu_4N^+ cation in dichloroethane(27,28), pyridinium chlorochromate(PCC) in chloroform in the presence of anhydrous acetic acid as a catalyst(42), hydrogen peroxide catalyzed by quarternary ammonium (phosphonium) tetrakis (oxodiperoxo tungsto) phosphates(43), chromium trioxide in the presence of wet Al_2O_3 in hexane(45), acetone in the presence of catalytic amounts of $RuCl_2(PPh_3)_3$ complex(46), molecular oxygen or tertiary-butyl hydroperoxide in the presence of chromium substituted aluminophosphate-5 as a catalyst(49), trichloromelamine(TCM) in dichloromethane(48), catalytic amounts of $RuCl_3$ and a three-fold excess of aqueous tertiary-butyl hydroperoxide(47), a triple catalytic system (consisting of a ruthenium complex, quinone and a cobalt macrocycle) taken in toluene at 100°C (50), and by manganese dioxide in the presence of a catalytic system consisting of a ruthenium complex and 2,6-ditertiary-butyl 1,4-benzoquinone(51).

Under the experimental conditions employed in the present investigation, bicyclic alcohols (borneol and isoborneol) were oxidized by quinolinium dichromate(QDC), in acid medium, giving the corresponding ketone (camphor) in each case. The product (camphor) was characterized by its melting point, IR analysis and by its 2,4-dinitrophenylhydrazone derivative (Vide Experimental : Product Analysis).

It has been established that bicyclic alcohols, such as borneol and isoborneol, have been converted to the corresponding ketone (camphor) in good yields by the use of different oxidizing agents such as the pyridinium dichromate - $Me_3SiOOSiMe_3$ system(55), the ultrasound technique using pyridinium chlorochromate(PCC) in conjunction with silica gel(58), pyridinium chlorochromate(PCC) in the presence of anhydrous acetic acid as a catalyst(42), oxone taken in acetonitrile solvent in the presence of wet Al_2O_3 (44), hydrogen peroxide catalyzed by tungsten peroxo complexes(43), organic oxoammonium salts(60,61), the triple catalytic system (consisting of a ruthenium complex, quinone and a cobalt macrocycle) taken in toluene at 100°C (50), and by manganese dioxide in the presence of a catalytic system consisting of a ruthenium complex and 2,6-ditertiarybutyl 1,4-benzoquinone(51).

Under the experimental conditions employed in the present investigation, allylic alcohols (geraniol and farnesol) were oxidized by quinolinium dichromate(QDC), in acid medium, giving the corresponding aldehydes (geranial and farnesal), respectively. The products (geranial and farnesal) were characterized by IR analysis, and further identified by the respective 2,4-dinitrophenylhydrazone derivatives (Vide Experimental : Product Analysis).

There has been overwhelming experimental evidence to show that allylic alcohols (geraniol and farnesol) have been oxidized to the corresponding aldehydes (geranial and farnesal), respectively, in good yields by a variety of oxidizing agents such as the chromium trioxide-pyridine complex(1), tertiary-butyl chromate in petroleum ether(63,64), chromic acid in acetone(65), a complex of chromium trioxide (in dichloromethane) and 3,5-dimethylpyrazole(66), bis-tetrabutylammonium dichromate(TBADC) in refluxing dichloromethane(68), tetrabutylammonium chlorochromate(TBACC) at room temperature and in refluxing chloroform(69), the $RuCl_2(PPh_3)_3$ - $Me_3SiOOSiMe_3$ system in dichromethane(55), the pyridinium dichromate - $Me_3SiOOSiMe_3$ system in dichloromethane(55), the RuO_2 catalyzed aerobic oxidation(70), pyridinium fluorochromate(PFC)(56), benzyltrimethylammonium chlorochromate(56), imidazolium dichromate(IDC) in DMF(25), the oxoperoxo complex of molybdenum containing the Bu_4N^+ cation in dimethylformamide as solvent(28), 3-carboxypyridinium dichromate(NDC) in pyridine(31), Co(III) acetate in acetic acid(72), organic oxoammonium salts(60), ultrasound promoted oxidation using pyridinium chlorochromate/ silica gel(58), phase transfer catalysis involving a solid mixture of $BaMnO_4$, Al_2O_3 and hydrated $CuSO_4$(75), the $RuCl_2(PPh_3)_3$ catalyzed oxidation using benzoquinone as the oxidant and a cobalt macrocycle(62), pyridinium chlorochromate(PCC) using anhydrous acetic acid as the catalyst(42), chromium trioxide in the presence of wet Al_2O_3 in hexane(45), MnO_2/bentonite/ microwave and MnO_2/bentonite/ultrasound both in dry media(76), and sodium percarbonate in the presence of catalytic amounts of pyridinium dichromate and Adogen 464 in 1,2-dichloroethane at 80°C(77).

It has been observed that when allylic alcohols such as geraniol, nerol and cinnamyl alcohol were oxidized by the pyridine-chromium trioxide complex, good yields of the corresponding aldehydes were obtained(3). The formation of the aldehydes, in each of these cases, indicated that the pyridine-chromium trioxide complex did not oxidize any of the other functional groups present, and did not in any way affect the double bonds(3). The catalytic aerobic oxidation of geraniol by ruthenium dioxide at 70°C gave 90% yield of geranial with 95% selectivity(70). Similar oxidation of nerol by ruthenium dioxide gave 94% of neral(70). The anaerobic oxidation of these isomeric alcohols, geraniol and nerol, by a large excess of RuO_2 hydrate at room temperature, gave the corresponding aldehydes (geranial and neral), respectively, with high stereospecificity(70). These results showed that the RuO_2-catalyzed aerobic oxidation of geraniol proceeded with retention of olefin stereochemistry, and confirmed that the double bonds were not affected.

Allylic alcohols were more reactive than their saturated counterparts. Geraniol reacted twice as fast as 1-dodecanol, the reaction proceeding with high stereospecificity(55). Only one product (geranial) was obtained. Thus, primary allylic alcohols, such as geraniol, were oxidized to α,β-unsaturated aldehydes (geranial) in high yields. No epoxy alcohols were detected in the oxidation with either $RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$, or pyridinium dichromate-$Me_3SiOOSiMe_3$ system(55). The selective oxidation of primary alcohols, in the presence of secondary alcohols, has also been carried out using the $RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$ system. While primary allylic alcohols gave the α,β-unsaturated aldehydes in high yields, the coexisting secondary alcohols were recovered almost unchanged. The reactions of this oxidant system(55) with geraniol/4-dodecanol and geraniol/2-dodecen-4-ol gave yields of the corresponding aldehyde/ketone in the ratios 99/3 and 95/6 respectively, thus establishing that primary allylic alcohols (geraniol) were selectively oxidized to the aldehyde (geranial).

In the oxidation of geraniol by the oxoperoxo complex of molybdenum containing the Bu_4N^+ cation, 20% of 2,3-epoxygeranial was formed together with 80% of geranial (28). This indicated that the oxidation of the primary alcohol (geraniol) predominated over the epoxidation of the highly nucleophilic trialkyl-substituted 6,7-double bond(158). Further, the nature of the solvent seemed to be significant in determining the chemoselectivity of geraniol epoxidation. In passing from nitromethane to dimethylformamide as solvent, the yield of geranial was raised from 68% to 95%, thus indicating that the oxidation of geraniol was more facile in dimethylformamide as solvent(28).

In the present investigation, the oxidation of *geraniol* *and* *farnesol* by quinolinium dichromate(QDC), in acid medium, using dimethylformamide as the solvent, had resulted in the formation of the corresponding aldehydes (geranial and farnesal), respectively, in good yields. The formation of the corresponding aldehydes indicated that QDC, in acid medium, did not oxidize any of the other functional groups present, and substantiated the earlier conclusions(3,28,70,157) that the double bonds remained intact after the process of oxidation.

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CHAPTER 2

KINETICS OF OXIDATION OF UNSATURATED COMPOUNDS

The oxidation of carbon-carbon double bonds by various oxidants has been studied by many workers. The oxidation of ethylene by thallic ions(1), Rh(III) chloride(2), chromyl chloride(3), aqueous Pd(II) chloride(4,5), and by Pd(II) in conjunction with Cu(II) ions(6,7) had yielded the aldehyde as the major product. The oxidation of propene by thallic ions(8), and by mercuric salts of strong acids(9), had given the aldehydes in good yields. Carbon-carbon double bonds could be readily cleaved by RuO_4, whereas with OsO_4 there was no cleavage of these bonds(10). The greater tendency of RuO_4 to attack double bonds decreases its selectivity as compared to OsO_4. For example, OsO_4 oxidizes pyrene only at the 4,5 bond, whereas RuO_4 attacked non-specifically to give a mixture of products(11). Catalytic amounts of RuO_4 in aqueous acetone were able to cleave carbon-carbon double bonds having less than four substituents, giving the aldehyde in over 80% yields(12). An efficient method for the oxidation of alkenes was the use of periodate and catalytic amounts of permanganate in neutral solution (13,14). The periodate-permanganate cleavage of alkenes has been used as a means of determining the position of double bonds in unsaturated compounds(15-17). The oxidation of olefins by permanganate has been observed to be accompanied by a certain amount of carbon-carbon bond cleavage(18), and under acidic conditions, cleavage products generally predominate(19-21). The oxidation of unsaturated compounds by permanganate(22), and by phenyl iodosoacetate catalyzed by Ru(III) have been studied(23). Using copper sulphate as a phase transfer reagent, permanganate dissolved in t-butyl alcohol has been used for the oxidation of olefins to the corresponding aldehydes(24). Pd-Cu catalysts, using t-butyl alcohol as the solvent, have been employed to oxidize olefins to the corresponding aldehydes with a great deal of selectivity(25). Oxidation of alkenes by alkyl hydroperoxides, using an active manganese catalyst, had resulted in efficient conversions to the corresponding aldehydes in good yields(26). The reactivity of carbon-carbon double bonds was demonstrated in the Gif oxidation involving the cleavage of olefins to the corresponding carbonyl compounds(27).

1. Oxidation of Styrene and substituted styrenes:

The oxidation of styrene and substituted styrenes by various oxidants has been investigated by several workers. The alkaline permanganate oxidation of styrene had resulted in the formation of phenylglyoxylic acid in 55-69% yield, with the formation of the hydroxy ketone as the probable intermediate(28). When a styrene derivative was oxidized by permanganate, cleavage gave a product with a two carbon side-chain, in addition to the expected product(29). The Co(III)oxidation of styrene had involved a direct attack of the cobaltic ion at the double bond by electron transfer, with the formation of a reactive radical ion(30). The oxidation of methylstyrenes by Co(III) acetate has been reported(31,32). The oxidation of styrene by chromyl chloride in CCl_4 solution was dependent on the first powers of the concentrations of both - substrate and oxidant, and had involved a rate determining attack of the oxidant on the carbon-carbon double bond(33,34). The reaction of styrene and substituted styrenes with Tl(III) acetate in methanol and in acetic acid have been investigated(35,36). The use of Tl(III) nitrate in methanol for the oxidation of p-methoxystyrene has been reported(37). The oxidation of styrene has been carried out using oxidants such as lead tetraacetate (38), ceric ions(39), and peracetic acid(40). The oxidation of styrene and substituted styrenes by hexacyanoferrate(III) in acid media was dependent on the first powers of the concentrations of substrate, oxidant and acid. The major product was benzaldehyde, obtained by the cleavage of the carbon-carbon double bond(41). Chloro (tetraphenylporphyrinato) Chromium(III), abbreviated as (TPP)CrCl, has been used as a catalyst, in conjunction with hydrogen peroxide as the oxygen source, to convert styrene to benzaldehyde in reasonably good yields(42,43). When reacted with (TPP)CrCl/ iodosylbenzene, styrene underwent cleavage to give benzaldehyde(44,45). Using didecyldimethyl ammonium bromide(DDAB) as the phase transfer catalyst, styrene in 1,2-dichloroethane containing ruthenium chloride trihydrate was oxidized by H_2O_2 to give a good yield of benzaldehyde(46). Ruthenium polyoxytungstates have been used as catalysts in the liquid phase oxidation of styrene by sodium periodate, resulting in the formation of benzaldehyde(47). Styrene has been oxidized to benzaldehyde in good yields by H_2O_2 catalyzed by metallosilicalite xerogels of the type MO_x-SiO_2, where M is Ti^{IV}, V^{V}, Mo^{VI}, W^{VI}, Se^{IV}(48). Molecular oxygen was used for the liquid phase oxidation of styrene taken in dimethylphthalate; the products obtained were benzaldehyde and styrene oxide in a 1:1 ratio(49).

2. Oxidation of Cinnamic and Crotonic acids:

Aqueous neutral permanganate was used to oxidize cinnamic acid at 100°C to give 87% benzaldehyde and 13% phenylglyceric acid(18). The oxidation of cinnamic acid by permanganate in acid medium(50) and in alkaline medium(51) had resulted in the cleavage of the carbon-carbon bond to yield benzaldehyde. The permanganate oxidation of unsaturated carboxylic acids showed that in basic solutions (above pH 12) permanganate was reduced to manganate, and the diol was obtained as the major product(52). At lower pH, Mn(IV) was formed, and there was cleavage resulting in the formation of the ketol(52). In the permanganate oxidation of crotonic acid, there was direct spectrophotometric evidence for the formation of two Mn(V) intermediates(53). The oxidation of crotonic acid by Co(III) in H_2SO_4 at 25°C has been studied(30). The oxidations of cinnamic and crotonic acids by Mn(III) acetate in 90% acetic acid were observed to be radical processes, and the products were benzaldehyde and acetaldehyde, respectively(54). The decarboxylative chlorination of cinnamic and crotonic acids by chloramine-T has been observed(55). The V(V) oxidation of cinnamic acid was observed to obey a second order rate law(56). The oxidations of cinnamic acid and crotonic acid have been carried out by alkaline hexacyanoferrate(III), using OsO_4 as a catalyst(57,58). The use of Os(VIII) as a catalyst has been reported for the oxidation of cinnamic acid by periodic acid(59), and by chromic acid(60). The formation of a cyclic intermediate was suggested in the reaction between cinnamic acid and hexavalent manganese in aqueous alkaline medium(61). The Os(VIII)catalyzed oxidation of cinnamic acid by acid bromate had envisaged complex formation between the substrate and Os(VIII), with concomitant electron transfer(62). The kinetics of oxidation of cinnamic and crotonic acids by hexacyanoferrate(III), in acid media, showed that the primary reaction was the direct attack of the protonated species of hexacyanoferrate(III) at the double bond by a process of electron transfer, with the formation of a cationic intermediate(63). Cinnamic acid was oxidized to benzaldehyde by acid bromate(64). In the presence of moist alumina as the solid support and dichloromethane as the solvent, permanganate has been used to cleave the carbon-carbon double bond in cinnamic acid and 4-nitro-cinnamic acid to give high yields of benzaldehyde and 4-nitrobenzaldehyde respectively(65). The kinetics of oxidation of unsaturated carboxylic acids by methyltributylammonium permanganate in dichloromethane had shown a first order dependence on each of the reactants and had yielded a value of $\rho = 1.11$(66).

3. Oxidation of Maleic and Fumaric acids:

The oxidative cleavage of olefinic bonds by OsO_4, RuO_4, RuO_4^{2-} and MnO_4^- is known to proceed through a cyclic intermediate(20,67,68). The Ru(III)-catalyzed oxidation of maleic and fumaric acids by phenyliodosylacetate had resulted in the formation of formic acid as the major product(23). The Ru(III)-catalyzed oxidation of maleic and fumaric acids by N-bromosuccinimide (in the presence of mercuric acetate, sulfuric acid and acetic acid), had exhibited a first order dependence on the oxidant and a fractional order dependence on the concentration of the substrate(69). The oxidation of fumaric acid by acid permanganate led to cleavage of the molecule at the double bond, and at one of the carbon-carbon single bonds(70). The oxidation of maleic and fumaric acids by hexavalent manganese in aqueous alkaline media followed Michaelis-Menten kinetics and suggested the formation of a cyclic intermediate between Mn(VI) and the substrate; the product obtained was oxalic acid(61). The periodate oxidation of maleic and fumaric acids, catalyzed by Os(VIII) in acid medium, had yielded formic acid as the final product(59). The kinetics of Os(VIII) - catalyzed chromic acid oxidation of maleic and fumaric acids was studied in aqueous acetic acid media, in the presence of perchloric acid(60). The

Os(VIII)-catalyzed oxidation of maleic and fumaric acids by acid bromate had involved the formation of an intermediate ester complex which underwent subsequent reaction to yield the diols(62). The kinetics of oxidation of maleic and fumaric acids by osmium tetroxide in aqueous alkaline medium had involved the formation of an Os(VIII)-acid complex which underwent subsequent disproportionation to give oxalic acid(71). The oxidation of maleic acid by the peroxydisulfate ion, catalyzed by Ag(I) ions, was observed to be independent of the concentration of maleic acid, but showed a first order dependence on the concentration of peroxydisulfate and Ag(I) ions(72). The oxidation of maleic and fumaric acids by V(V) in acid medium, using Pd(II) as the catalyst, had exhibited zero order dependence on V(V), and first order dependence on both, the catalyst and the unsaturated acids(73).

PRESENT WORK

The present work is a detailed kinetic investigation of the oxidation of unsaturated compounds by quinolinium dichromate(QDC), in acid medium, using dimethylformamide as the solvent.

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

(1) Styrene and substituted styrenes.

(2) Cinnamic acid and substituted cinnamic acids, and Crotonic acid.

(3) Maleic acid and Fumaric acid.

Stoichiometry (Vide 'Experimental'):

The stoichiometries of all the oxidation reactions were determined. The stoichiometric ratios, Δ[QDC]/Δ [Substrate], were in the range 1.30-1.38 (Table 1).

Table 1. Stoichiometries of the oxidation of the substrates; ([Substrate]=0.005M; T=313K).

$[H_2SO_4]$/M	0.0	0.10	0.25	0.50
10^2[QDC]/M	2.50	2.60	2.70	2.80
Δ[QDC]/Δ[Styrene]	1.33	1.36	1.30	1.33
Δ[QDC]/Δ[Cinnamic Acid]	1.35	1.33	1.38	1.30
Δ[QDC]/Δ[Crotonic Acid]	1.37	1.30	1.33	1.36
Δ[QDC]/Δ[Maleic Acid]	1.33	1.37	1.30	1.35
Δ[QDC]/Δ[Fumaric Acid]	1.30	1.36	1.35	1.33

The stoichiometry conformed to the overall equations:

(a) For Styrene:

$$3C_8H_8+4Cr^{VI}+6H_2O \longrightarrow 3C_7H_6O+3CH_2O+4Cr^{III}+12H^+ \quad (1)$$

(b) For Cinnamic and Crotonic Acids:

$$3RCH{=}CHCOOH+4Cr^{VI}+6H_2O \longrightarrow 3RCHO+3C_2H_2O_3+4Cr^{III}+12H^+ \quad (2)$$

(where R = $-C_6H_5$, $-CH_3$)

(c) For Maleic and Fumaric Acids:

$$3C_4H_4O_4+4Cr^{VI}+6H_2O \longrightarrow 6CH_2O+6CO_2+4Cr^{III}+12H^+ \quad (3)$$

Effect of Substrate

The rate of the reaction was found to be dependent on the concentration of the substrate. The order of the reaction with respect to the substrate was obtained by changing the substrate concentration, and observing the effect on the rate at constant [QDC] and [H^+]. The results have been recorded in Tables 2-4.

Table 2. Dependence of Rate Constants on the concentration of Styrene; ([QDC]=0.001M; [H_2SO_4]=1.5M; T=313K).

10^2[Styrene] (M)	10^4k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)
1.0	1.46	1.46
5.0	7.35	1.47
7.5	11.0	1.47
10.0	14.8	1.48
15.0	22.1	1.47
20.0	30.0	1.50

Table 3. Dependence of Rate Constants on the concentrations of Cinnamic and Crotonic Acids; ([QDC]=0.001M; $[H_2SO_4]$=1.5M; T=313K).

10^2[Substrate] (M)	Cinnamic Acid 10^4k_1 (s^{-1})	Cinnamic Acid 10^2k_2 ($M^{-1}s^{-1}$)	Crotonic Acid 10^4k_1 (s^{-1})	Crotonic Acid 10^2k_2 ($M^{-1}s^{-1}$)
1.0	1.49	1.49	1.30	1.30
5.0	7.50	1.50	6.62	1.32
7.5	11.2	1.48	9.80	1.31
10.0	15.3	1.53	13.2	1.32
15.0	22.6	1.51	19.9	1.33
20.0	31.1	1.56	26.6	1.33

Table 4. Dependence of Rate Constants on the concentrations of Maleic and Fumaric Acids; ([QDC]=0.001M; $[H_2SO_4]$=2.0M; T=313K).

10^2[Substrate] (M)	Maleic Acid 10^4k_1 (s^{-1})	Maleic Acid 10^2k_2 ($M^{-1}s^{-1}$)	Fumaric Acid 10^4k_1 (s^{-1})	Fumaric Acid 10^2k_2 ($M^{-1}s^{-1}$)
1.0	1.82	1.82	1.61	1.61
5.0	9.0	1.80	8.0	1.60
7.5	13.6	1.82	12.1	1.61
10.0	18.2	1.82	15.8	1.58
15.0	27.0	1.80	24.3	1.62
20.0	37.0	1.85	32.2	1.61

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

Effect of Oxidant

Under pseudo-first-order conditions, the individual kinetic runs were first order with respect to the oxidant (QDC). 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 Table 5.

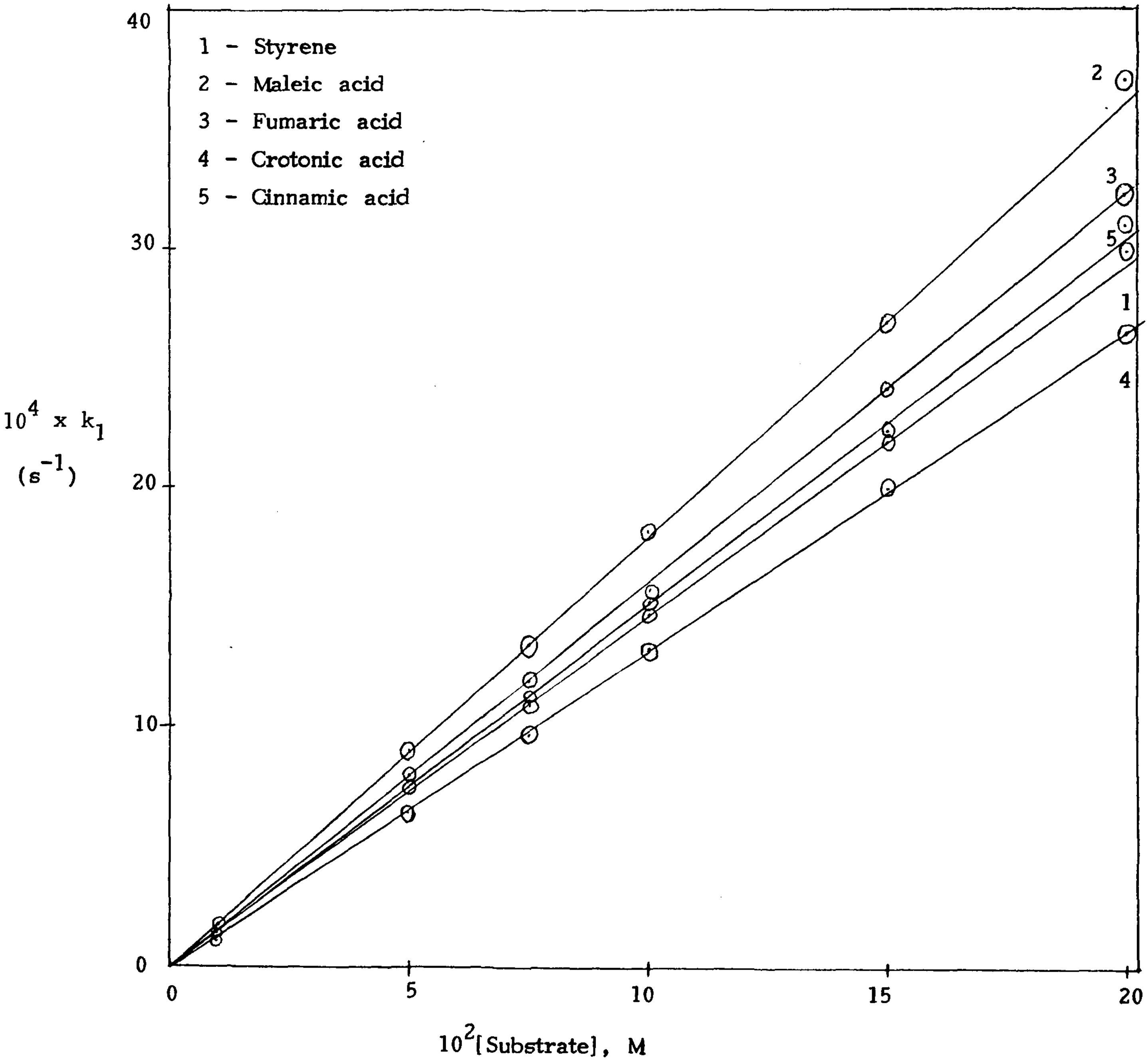


Fig.1. Plots of k_1 against the concentrations of substrates.

Table 5. Dependence of Rate Constants on the concentration of Oxidant; ([Substrate]=0.01M; $[H_2SO_4]$=1.5M; T=313K).

10^4[QDC]/M	1.0	5.0	7.5	10.0
$10^4k_1/s^{-1}$ for:				
Styrene	1.38	1.40	1.41	1.46
Cinnamic Acid	1.47	1.45	1.44	1.49
Crotonic Acid	1.30	1.33	1.38	1.30
Maleic Acid[a]	1.78	1.80	1.75	1.82
Fumaric Acid[a]	1.60	1.62	1.58	1.61

[a] 2.0M H_2SO_4

Effect of Acid

The reaction was susceptible to changes in acid concentration, and the rate was observed to increase with an increase in the concentration of the acid (Tables 6-7).

Table 6. Dependence of Rate Constants on the concentration of Acid; ([Substrate]=0.01M; [QDC]=0.001M; T=313K).

$[H_2SO_4]$/M	1.0	1.25	1.50	1.75	2.0
$10^4k_1/s^{-1}$ for:					
Styrene	0.95	1.22	1.46	1.71	1.92
Cinnamic Acid	1.04	1.26	1.49	1.78	2.10
Crotonic Acid	0.87	1.08	1.30	1.53	1.70

Table 7. Dependence of Rate Constants on the concentration of Acid; ([Substrate]=0.01M; [QDC]=0.001M; T=313K).

$[H_2SO_4]$/M	1.5	1.75	2.0	2.25	2.50
$10^4k_1/s^{-1}$ for:					
Maleic Acid	1.36	1.60	1.82	2.04	2.30
Fumaric Acid	1.22	1.40	1.61	1.84	2.06

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

The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated Cr(VI) species in the rate determining step. There have been earlier reports of the involvement of such Cr(VI) species in chromic acid oxidation reactions(74). Protonated Cr(VI) species have been observed in the presence of p-toluene sulfonic acid in nitrobenzene-dichloromethane mixtures(75). Moreover, the protonated Cr(VI) species would be a reactive electrophilic species and would be sufficiently reactive to attack the double bond of the unsaturated compounds (styrene, cinnamic and crotonic acids, maleic and fumaric acids),

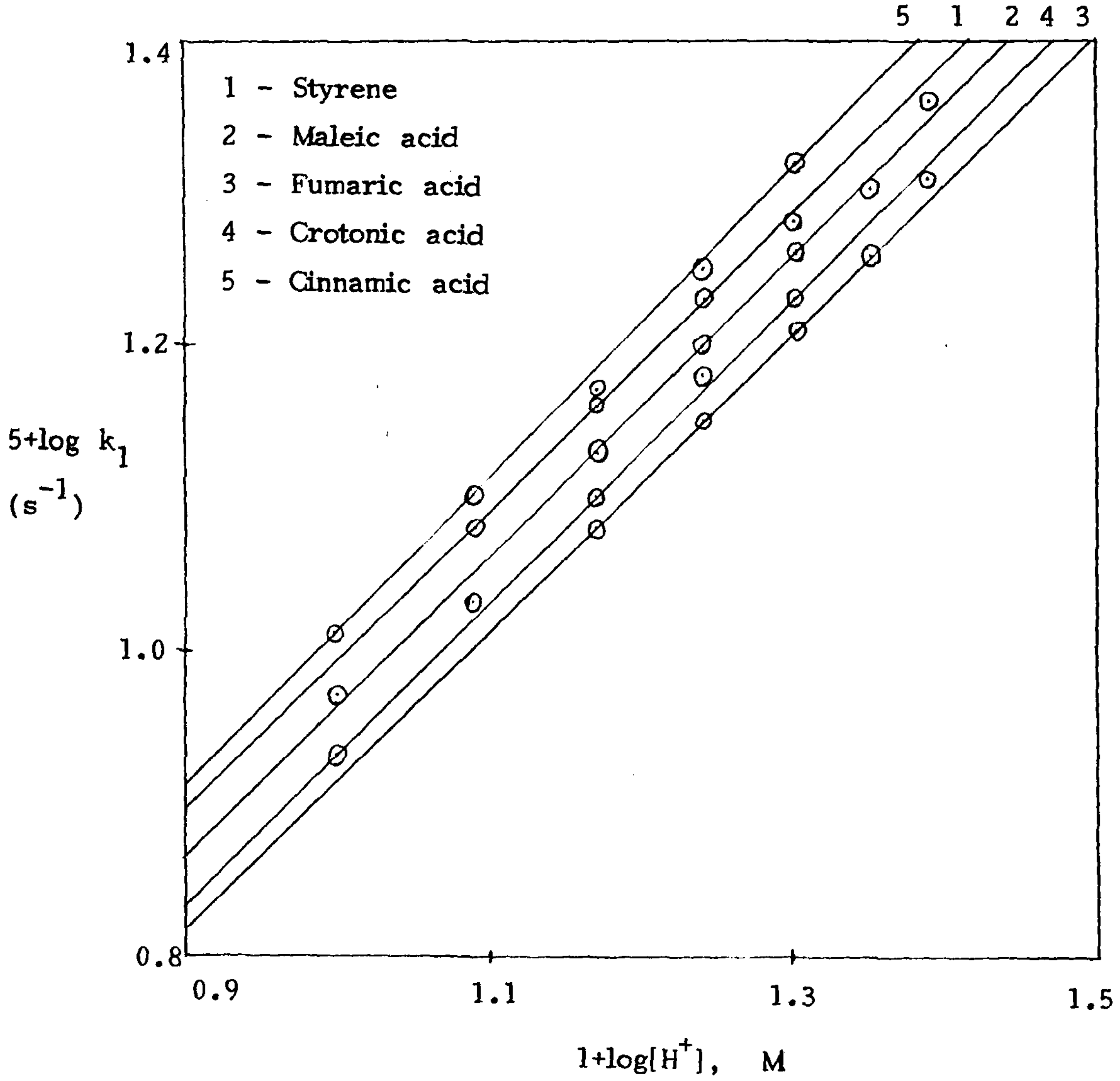


Fig. 2. Plots of log k_1 against log[H^+].

and bring about the oxidative cleavage of the carbon-carbon double bond.

Rate law

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

$$\text{Rate} = -\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Substrate}][\text{QDC}][\text{H}^+] \qquad (4)$$

Effect of Solvent

Reactions involving an ionic reactant are susceptible to solvent influences. It is hence to be expected that, in the present investigation, the solvent should be playing an important part. 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 dimethylformamide had resulted in an increase in the rate of oxidation (Table 8).

Table 8. Dependence of Rate Constants on Solvent Composition; ([Substrate]=0.01M; [QDC]=0.001M; [H_2SO_4]=1.5M; T=313K).

DMF : H_2O(%, v/v)	100:0	95:5	90:10	85:15	80:20
Dielectric Constant(D)	37.6	39.7	41.8	43.9	46.1
$10^4k_1/s^{-1}$ for:					
Styrene	1.46	1.22	1.08	0.89	0.77
Cinnamic Acid	1.49	1.27	1.04	0.84	0.70
Crotonic Acid	1.30	1.05	0.87	0.71	0.60
Maleic Acid[a]	1.82	1.51	1.29	1.08	0.95
Fumaric Acid[a]	1.61	1.31	1.15	1.00	0.87

[a] 2.0M H_2SO_4

The dielectric constants for dimethylformamide-water mixtures have been estimated from the dielectric constants of the pure solvents(76).

In the present investigation, in going from 80% DMF to 100% DMF, the polarity decreases. This decrease in the polarity of the medium caused an increase in the rate of the reaction (Table 8). Plots of log k_1 against the reciprocal of the dielectric constant were linear (Figs. 3-4) with positive slopes. This suggested an interaction between a positive ion and a dipole(77), and was in consonance with the observation that, in the presence of an acid,

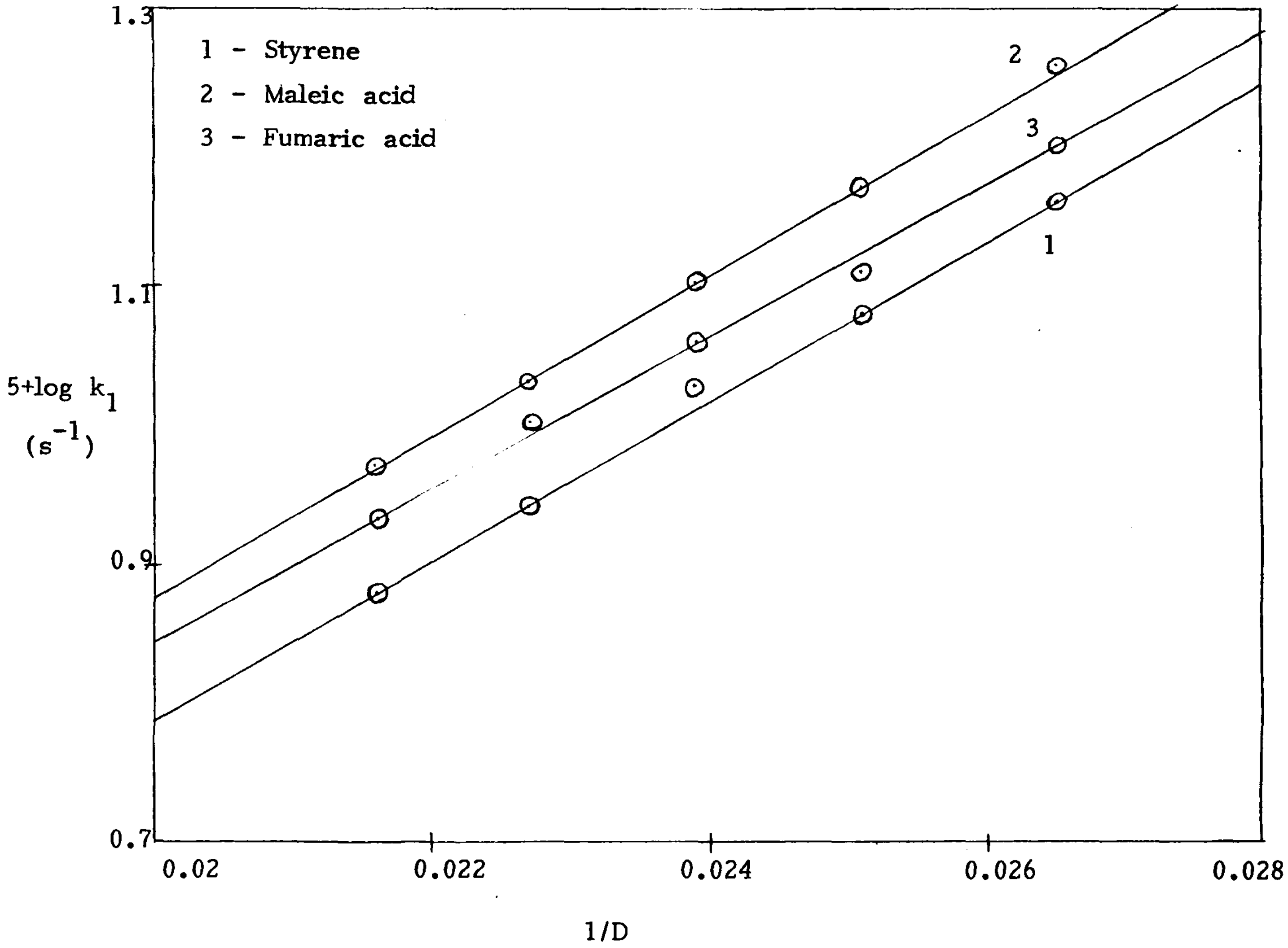


Fig.3. Plots of log k_1 against the reciprocal of the dielectric constant.

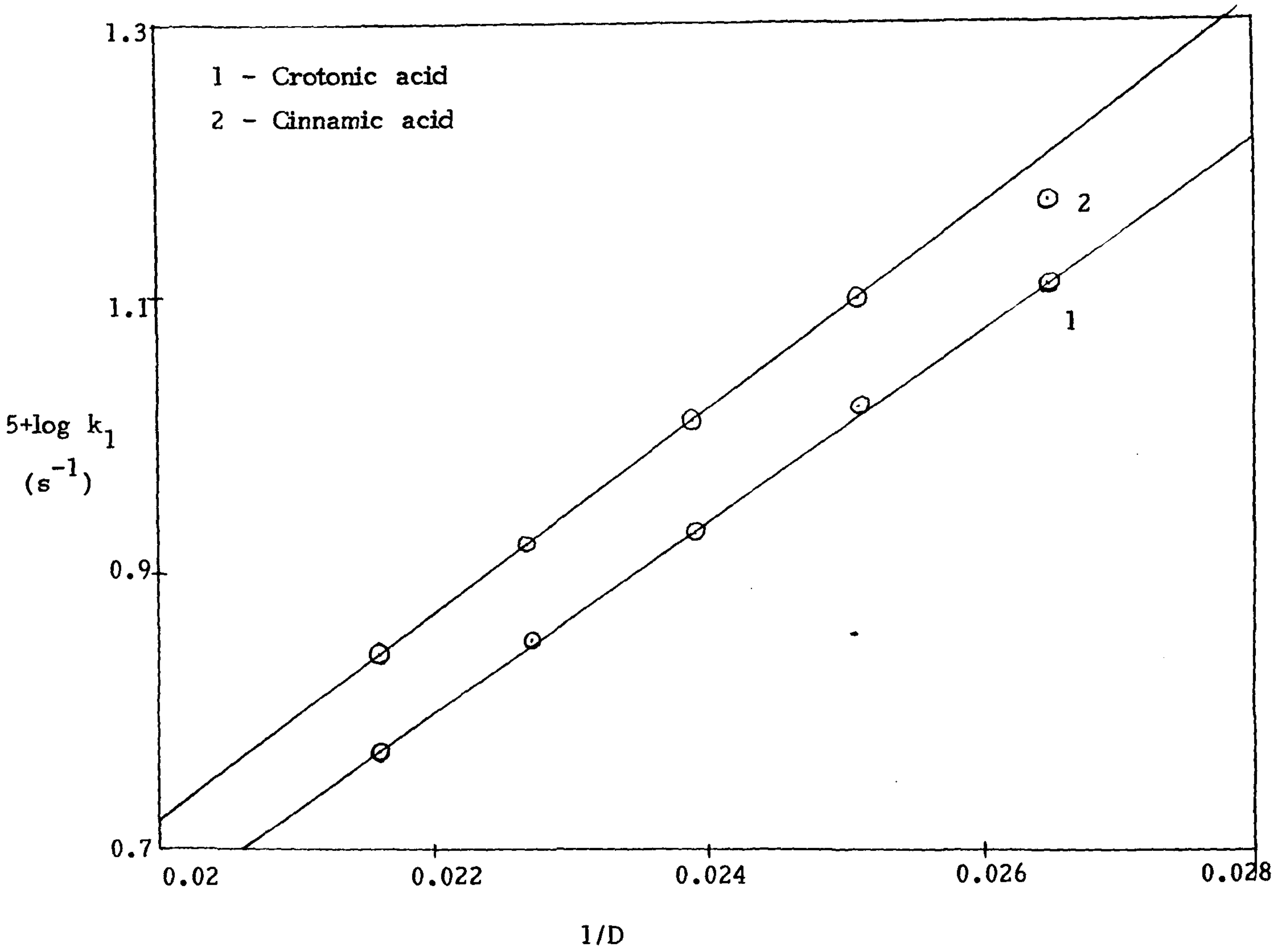


Fig. 4. Plots of log k_1 against the reciprocal of dielectric constant.

the rate-determining step involved a protonated Cr(VI) species.

On the basis of the solvating power of the solvent, a correct prediction of a qualitative nature could be made regarding the rate of the reaction in different solvent media. Solvent polarity can be used to rationalize the rate of the reaction and to account for the formation of a cationic intermediate. The decrease in the rate of the reaction with increasing proportions of water (that is, a more polar medium), may be related, in part, to the conversion of the substrate to a positively charged species. A similar explanation had been advanced to account for the formation of a positively charged species, in the nitration of some aromatic compounds in sulfuric acid media(78). The observed dependence of the reaction rate on solvent polarity (Table 8) supported the separation of charge in the transition state. In the rate-determining step, therefore, the conversion of the substrate to a cationic intermediate would involve a destruction of charge. This would lead to a decrease in the rate of reaction, in going from a less polar to a more polar solvent medium (that is, increasing proportions of water). The effect of a change in the solvent composition on reaction rates would also depend on factors such as solvent-solute interactions(79,80), and on solvent structure.

Effect of temperature

The rates of the reactions were influenced by changes in temperature (Tables 9-10).

Table 9. Dependence of Rate Constants on Temperature (±0.1K) for the oxidation of Styrenes by QDC ($10^4 k_1/s^{-1}$) in the presence of acid; [Styrenes]=0.01M; [QDC]=0.001M; [H_2SO_4]=1.5M.

Substituent	303K	308K	313K	318K	323K
H-(Styrene)	0.56	0.92	1.46	2.40	3.51
m-methyl	1.01	1.82	2.88	4.47	6.92
p-methyl	3.09	4.79	7.60	10.9	15.9
p-methoxy	7.24	12.0	20.0	31.6	47.9
p-chloro	0.04	0.07	0.14	0.23	0.39
m-chloro	-	0.02	0.04	0.07	0.12

Table 10. Dependence of Rate Constants on Temperature (±0.1K) for the oxidation of Cinnamic Acids by QDC ($10^4k_1/s^{-1}$) in the presence of acid; [Cinnamic Acids]=0.01M; [QDC]=0.001M; $[H_2SO_4]$=1.5M.

Substituent	303K	308K	313K	318K	323K
p-methyl	1.15	2.04	3.57	6.03	10.2
m-methyl	0.76	1.32	2.25	3.80	6.31
H(Cinnamic Acid)	0.49	0.85	1.49	2.42	4.10
p-chloro	0.17	0.30	0.56	1.02	1.86
m-chloro	0.09	0.17	0.32	0.58	1.02
p-Nitro	0.01	0.03	0.05	0.09	0.14
Crotonic acid	0.40	0.72	1.30	2.31	3.98
Maleic acid[a]	0.54	1.01	1.82	3.23	5.60
Fumaric acid[a]	0.45	0.87	1.61	2.94	5.33

[a] $[H_2SO_4]$=2.0M

Plots of log k_1 against the reciprocal of temperature were linear (Figs. 5-6), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies (vide 'Experimental' : Calculations). The other activation parameters were evaluated, and have been shown in Tables 11-12.

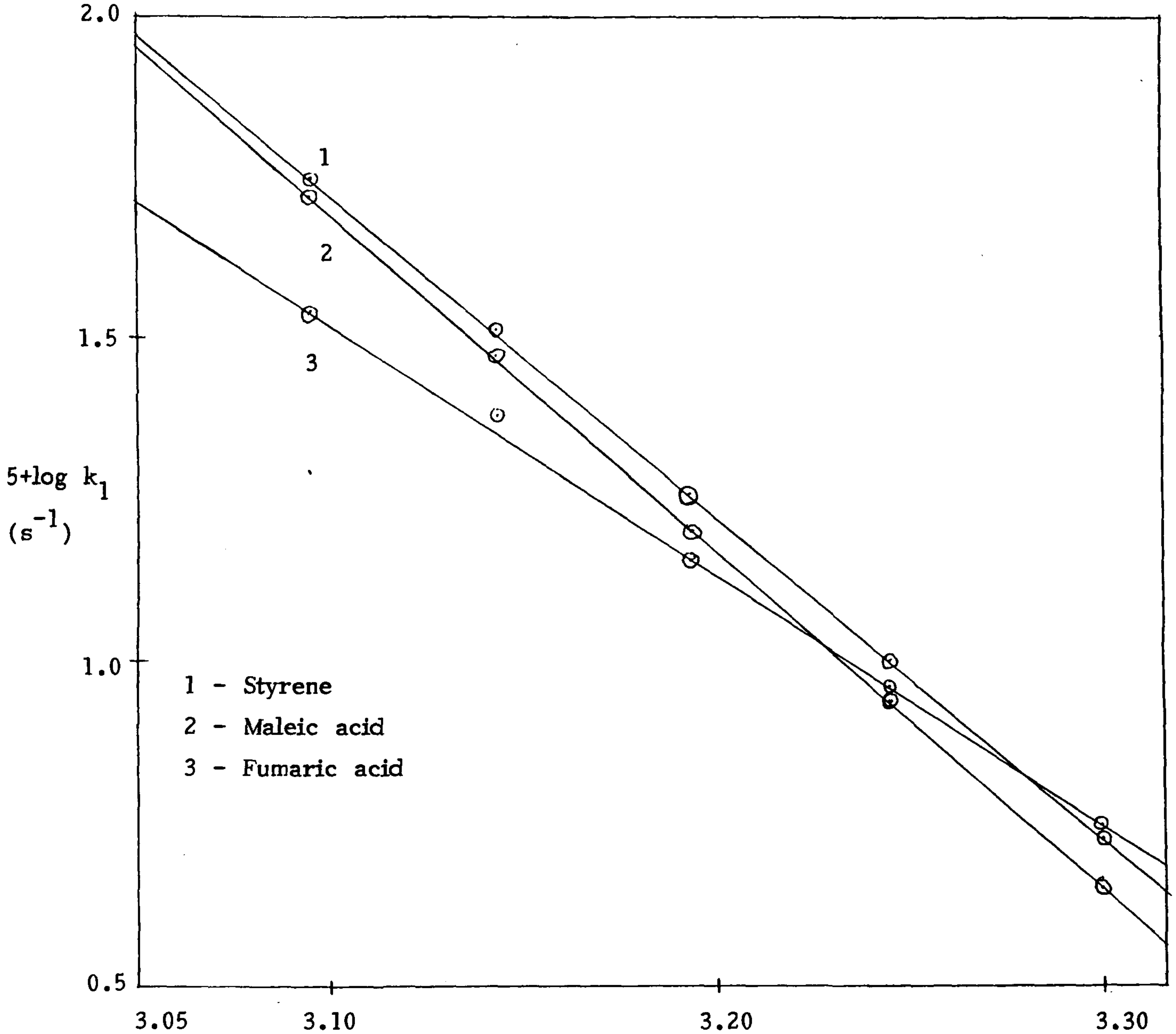


Fig. 5. Plots of log k_1 against the reciprocal of temperature.

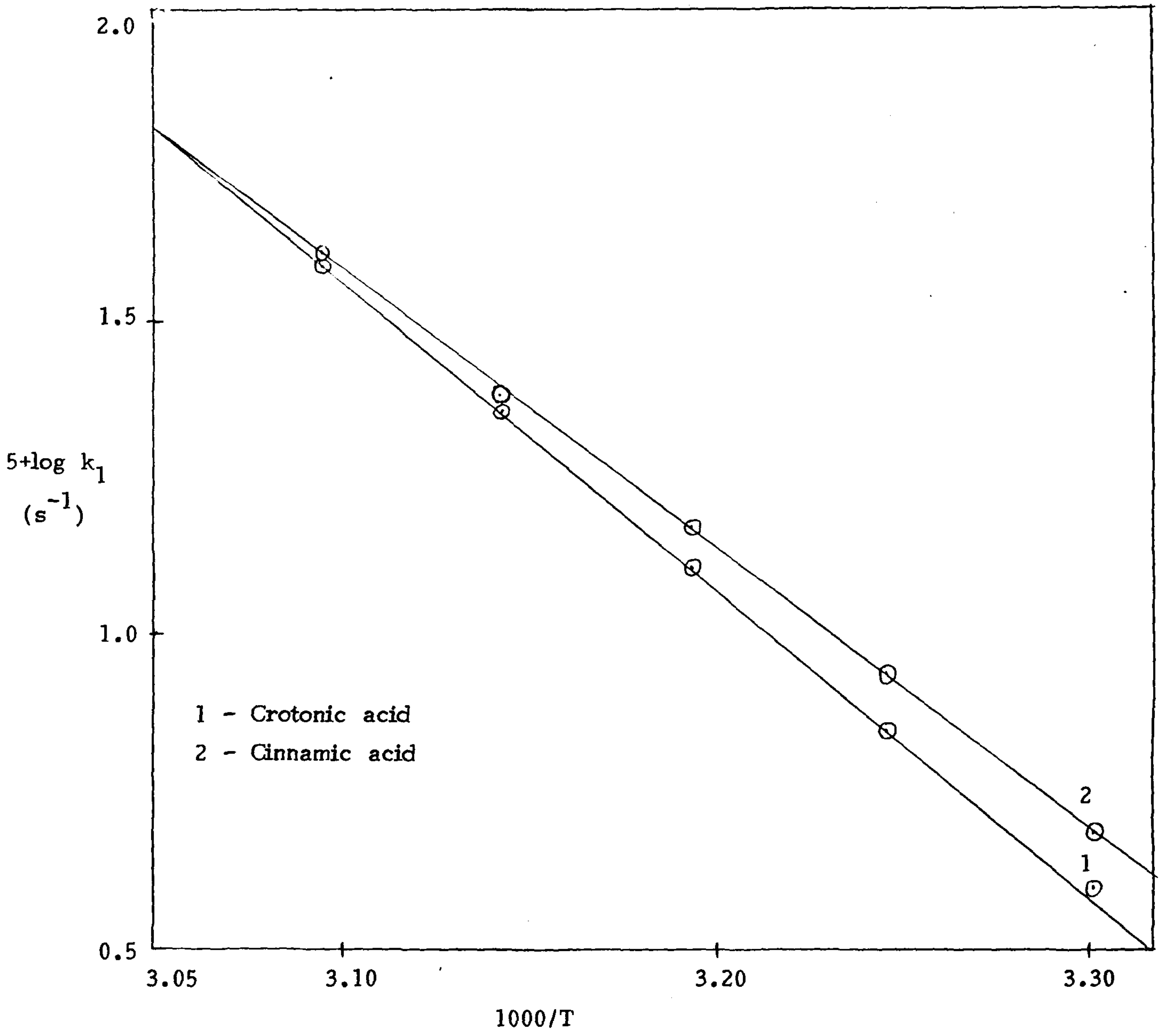


Fig. 6. Plots of log k_1 against the reciprocal of temperature.

Table 11. Activation Parameters (styrenes).

Substituent	E (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1}mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
H(styrene)	75	72	- 93	101.1
m-Methyl-	70	67	-105	99.9
p-Methyl-	63	60	-130	100.7
p-Methoxy-	44	41	-190	100.5
p-Chloro-	82	79	-70	100.9
m-Chloro-	85	82	-60	100.8

Error Limits: $\Delta H^{\neq}$ ± 2kJmol^{-1};
$\Delta S^{\neq}$ ± 3JK^{-1}mol^{-1};
$\Delta G^{\neq}$ ± 2kJ mol^{-1}.

Table 12. Activation Parameters (Cinnamic acids).

Substituent	E (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1}mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
H(Cinnamic acid)	85	82	-57	100.1
p-Methyl-	78	75	-78	99.4
m-Methyl-	82	79	-67	100.0
p-Chloro-	88	85	-50	100.7
m-Chloro-	90	87	-42	101.1
p-Nitro-	94	91	-32	101.0
Crotonic acid	96	93	-23	100.0
Maleic acid	96	93	-18	99
Fumaric acid	100	97	- 8	99

Error Limits: $\Delta H^{\neq}$±2kJmol^{-1}; $\Delta S^{\neq}$±2JK^{-1}mol^{-1}; $\Delta G^{\neq}$±2kJ mol^{-1}.

The fairly 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 oxidations of all the substrates were characterized by negative entropies of activation. This would suggest that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecules(81). Differences in the solvation of the substrates in the ground state and transition state might also contribute, to some extent, to the negative entropies of activation(82). The similarity 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 of these reactions involved similar rate-determining steps.

Isokinetic relationship

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

$$\Delta H^{\neq} = \Delta H_{o}^{\neq} + \beta \Delta S^{\neq} \qquad (5)$$

where β is the isokinetic temperature. For these oxidation reactions, the activation enthalpies and entropies can be linearly related. The correlation was tested and found to be valid by applying Exner's criteria(83). The plots between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were linear (Figs. 7-8), and the isokinetic temperatures were 313K (for styrenes) and 333K (for cinnamic acids). Although current views do not attach much physical significance to isokinetic temperatures(84), it is sufficient to state that a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. 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 $\Delta S^{\neq}$.

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(85). This indicated that a one-electron oxidation was quite unlikely. Control experiments were performed, in the absence of the substrates. The concentration of QDC did not show any appreciable change.

Structural influences on the rate of oxidation

Since structure-reactivity correlations give an insight into the nature of the transition state and throw

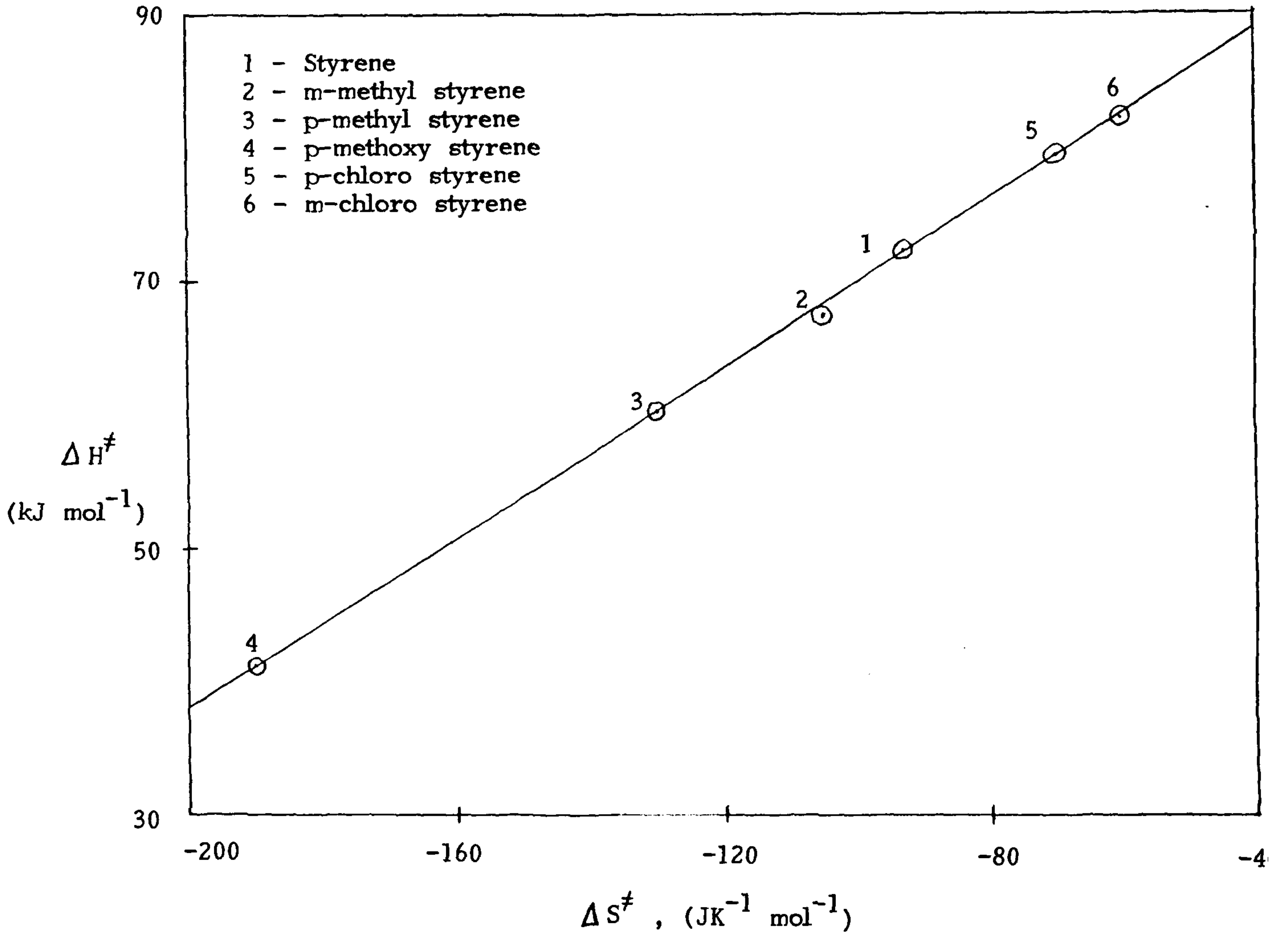


Fig. 7. Plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$

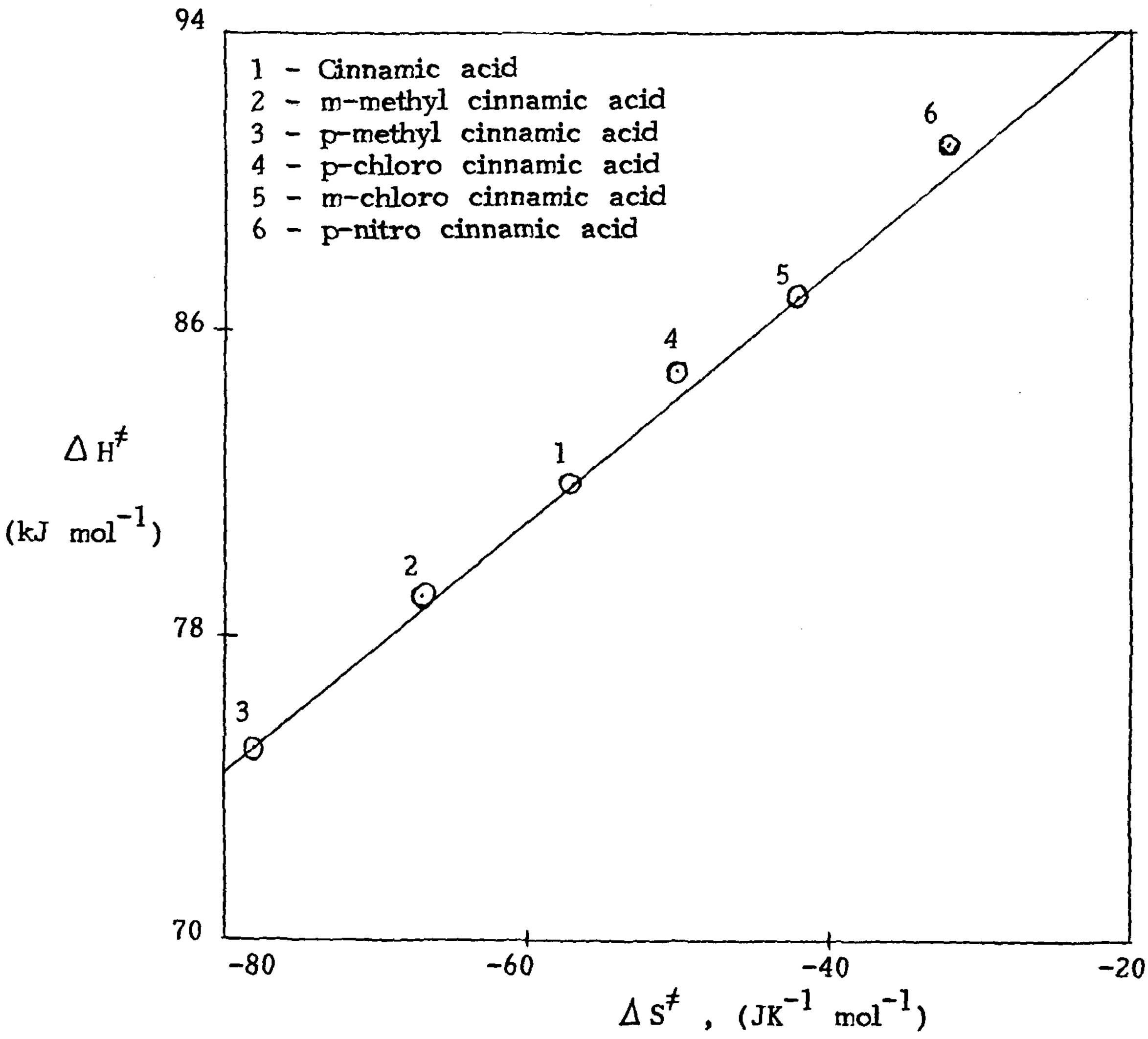


Fig. 8. Plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$

some light on the mechanistic pathway of the reaction, an attempt was made to obtain a linear free energy relationship using the Hammett equation. The rates of oxidation of styrenes and of cinnamic acids by QDC, in acid medium, using dimethylformamide as the solvent, have been shown in Tables 9-10 (Dependence of Rate Constants on Temperature). Inspection of the data in Tables 9-10 reveals that electron-releasing substituents accelerated the oxidation process and electron-attracting groups retarded the process. Hence, a linear free energy relationship of the Hammett equation type should correlate the reactivity with the Hammett substituent constants(86). Linear free energy relationships are of great value in summarizing and understanding the influences of molecular structure on chemical reactivity. The magnitude of the reaction constant (ρ) depends mainly on the ability of the bridging atom to acquire and stabilize charge in the activated complex. Plots of log k_1 against the σ substituent constants(86) gave values of $\rho = -4.0$ for both, the styrenes and the cinnamic acids (Figs. 9-10). A hydrogen abstraction mechanism is unlikely, in view of the failure to induce the polymerization of acrylonitrile, or to bring about the reduction of mercuric chloride. It has been earlier observed that in most hydrogen abstraction reactions, the reaction constants have small magnitudes(87-90).

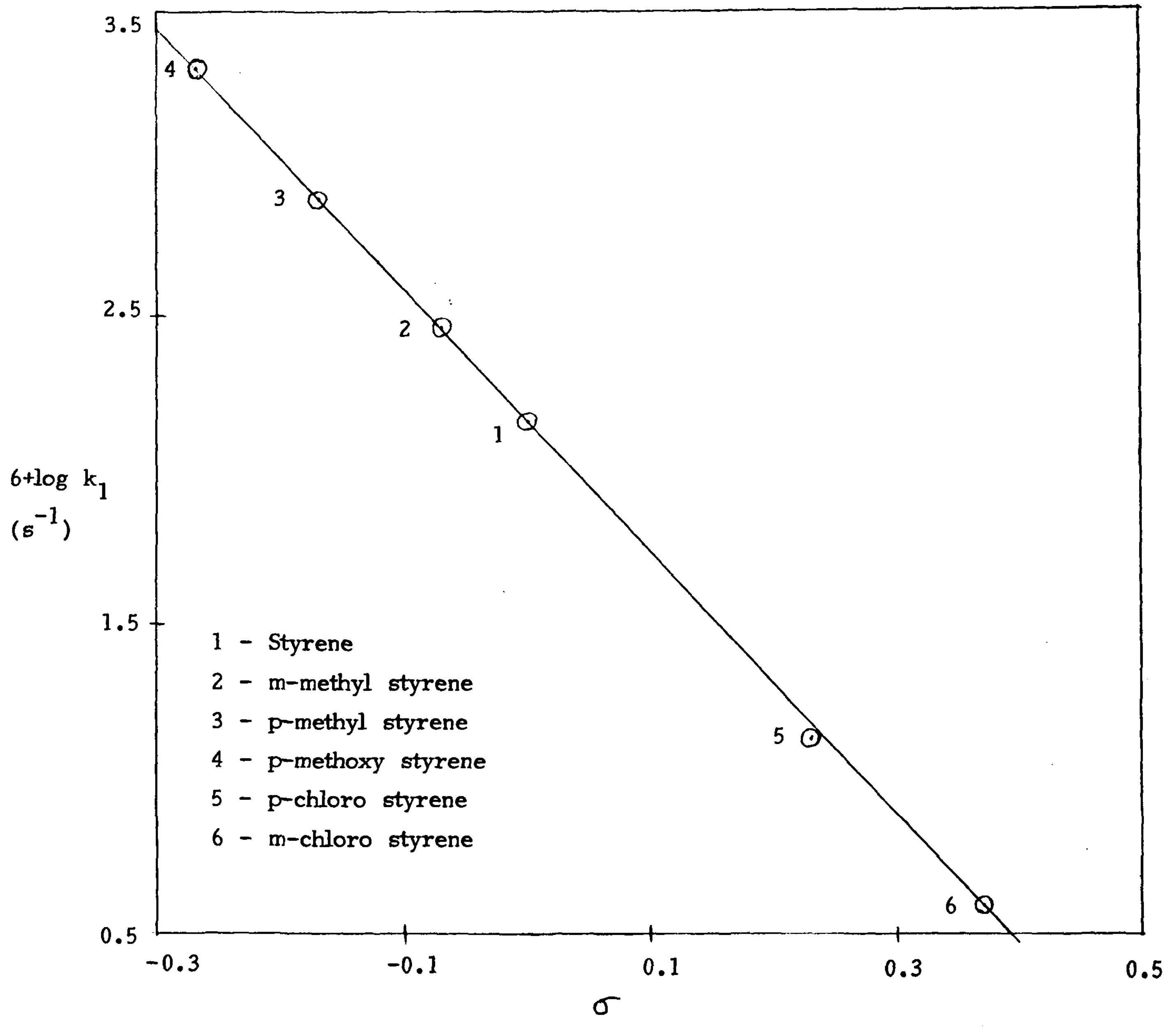


Fig. 9. Plot of log k_1 against substituent constant.

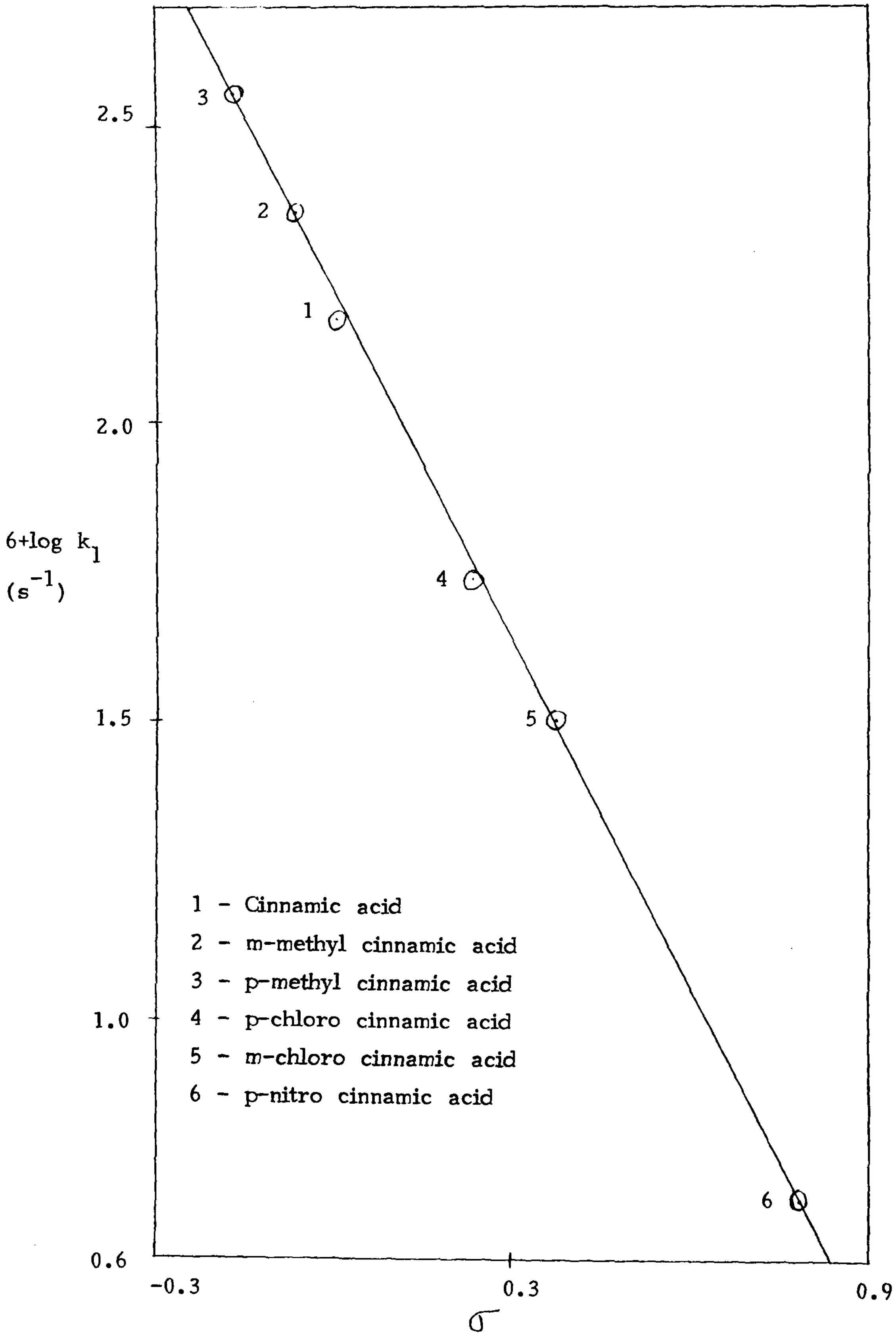


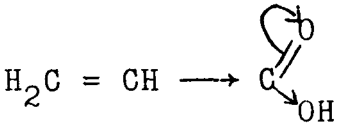
Fig.10. Plot of log k_1 against substituent constant.

In the present investigation, the values obtained for the reaction constant ρ were = -4.0, for styrenes and cinnamic acids (Tables 9-10; Figs. 9-10). This suggested that the transition state possessed a large degree of carbonium ion character, resulting from a large amount of positive charge developing at the carbon atom adjacent to the benzene ring (α-carbon atom). Earlier studies had shown that ρ values larger than -3.0 suggested a fairly large degree of carbonium ion character in the transition state(91-99).

Olefins are nucleophilic substances, and modifications in structure which increase the electron density of the ethylenic system, and thereby increase its nucleophilic properties, result in an increase in the rate of reaction of the olefins with electrophilic substances. Thus, in the reaction of olefins with electrophiles (e.g., bromine), it has been observed that the successive substitution of electron-releasing groups, such as methyl, for the hydrogen atom attached to the double bond, causes an increase in the rate of the reaction. This is because electron-releasing groups, by increasing the electron density of the ethylenic system, increase its nucleophilic properties and thereby cause a more rapid attack by the electrophilic (electron-poor) bromine ion (Br^+). Conversely, the introduction of electron-attracting groups, such as carboxyl, causes a reduction in the rate of the reaction because of the effect of such groups in diminishing the nucleophilic properties of the double bond. These electron shifts can be represented as:

$CH_3 \longrightarrow CH = CH_2$ Increased nucleophilic properties

(Propylene)



Decreased nucleophilic properties

(acrylic acid)

The concept that an increase or decrease in electron density of the ethylenic system results in an increase or decrease in the nucleophilic properties of the double bond, may be used to explain the differences in reaction rates of olefins with quinolinium dichromate(QDC).

When electron-releasing groups are attached to, or are in close proximity to, the double bond, the reaction rate is increased because of the increased electron density of the ethylenic system (e.g., styrene), which results in an increase in the nucleophilic properties of the double bond. The phenyl group acts as an electron-releasing group in styrene and 1-phenyl-1-propene, since their specific reaction rates with quinolinium dichromate are greater than those for ethylene and propylene, respectively.

Table 13. Rate Constants for the reactions of Olefins with QDC ($10^4k_1/s^{-1}$). ([Olefins]=0.01M; [QDC]=0.001M; [H_2SO_4]=1.5M; T=313K).

Ethylene	0.04	Styrene	1.46
Propylene	0.54	1-phenyl-1-propene	5.52

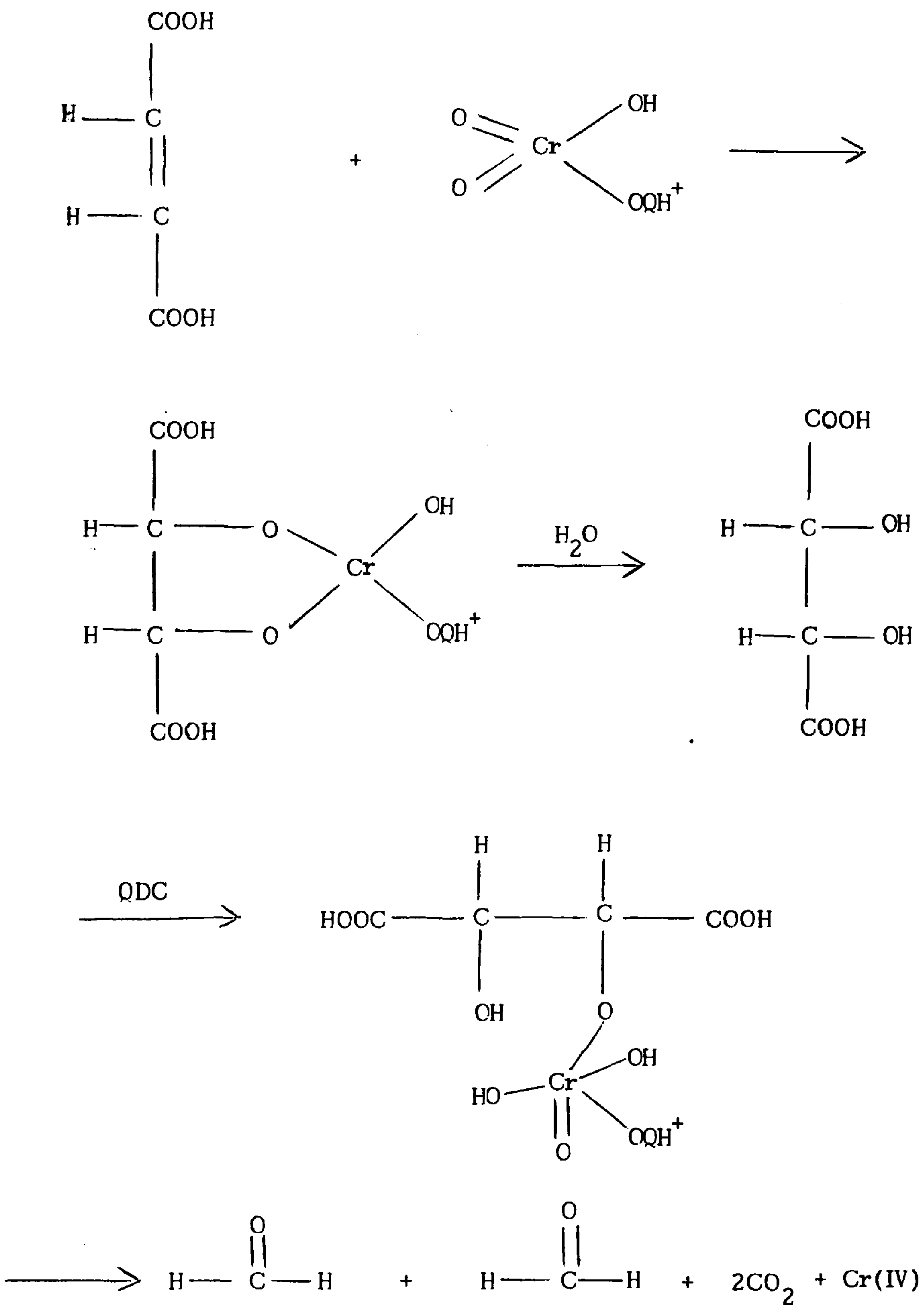
Cinnamic acid was oxidized at a faster rate by QDC, as compared to crotonic acid (k_1=1.49x$10^{-4}s^{-1}$ for cinnamic acid, and k_1=1.30x$10^{-4}s^{-1}$ for crotonic acid, at 313K). This indicated that phenyl conjugation was responsible for an acceleration in the rate of oxidation. In cinnamic acid, the phenyl group exerts an electron-releasing effect which counteracts, in part, the electron-attracting effect of the carboxyl group. In crotonic acid, the reaction proceeds at a slower rate because the electron-attracting properties of the carboxyl group reduce the nucleophilic properties of the double bond. It would thus be reasonable to conclude that the electron-releasing effect of the phenyl group was greater than that of the alkyl group. This was borne out from the experimental observations that under similar conditions of oxidation by quinolinium dichromate (QDC) at 313K, the rates of oxidation of:

(a) styrene was greater than that of propylene (Table 13);

(b) cinnamic acid was greater than that of crotonic acid (Table 3).

The data in Table 4 revealed that maleic acid reacted marginally faster than fumaric acid. Steric factors could account for the difference in specific reaction rates of the cis- and trans-isomers. The cis attack of two oxygen atoms of quinolinium dichromate(QDC) would result in the formation of a cyclic intermediate. This would be accompanied by a change in the hybridization of the olefinic carbon atom from sp^2 to sp^3. The cis approach of QDC would first impose an eclipsed conformation on the maleate species. The carboxylate groups would be brought into closer proximity to each other before the staggered conformation in the cyclic intermediate was reached. The reaction would then take place at a marginally higher rate for the oxidation of maleic acid than that for fumaric acid. The steric strain in the cis structure could be rationalized as a dominant electrostatic effect. The reaction sequence for the oxidation of maleic and fumaric acids by quinolinium dichromate(QDC) in acid medium has been shown in Scheme A.

SCHEME A



COOH
H
C
C
H
COOH
+
O
O
Cr
OH
OOH+
COOH
H
C
O
Cr
OH
H
C
O
OOH+
COOH
H2O
COOH
H
C
OH
H
C
OH
COOH
QDC
H
H
HOOC
C
C
COOH
OH
O
OH
HO
Cr
O
OOH+
O
H
C
H
+
O
H
C
H
+
2CO2
+ Cr(IV)

Kinetic Isotope Effect

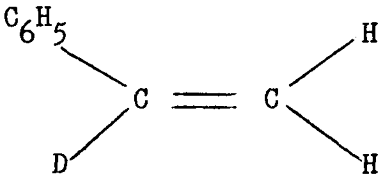
The kinetic isotope effect has been studied, in order to determine the nature of the intermediate formed in the rate-determining step of these oxidation reactions. Secondary kinetic deuterium isotope effects can be used to gain an insight into the changes in hybridization occurring at an isotopically substituted carbon atom, as the reactants proceed from the ground state to the transition state(100). These effects are related to the change in vibrational energy of the C-H versus C-D out-of-plane bending modes. Since the potential energy curve for a C-H (sp^2) bond is a relatively shallow parabola, the zero-point energies of the C-H and C-D reactants are relatively close. However, the potential curve for a C-H (sp^3) bond is a relatively steeper parabola, so that the zero-point energy of a C-D bond is substantially less than that of a C-H bond. Therefore, the energy of activation for an $sp^2 \longrightarrow sp^3$ change in hybridization is lower for the deuterated compound, and the kinetic isotope effect is inverse ($k_H < k_D$).

The kinetic isotope effect data has been shown in Table 14 (styrenes and cinnamic acids).

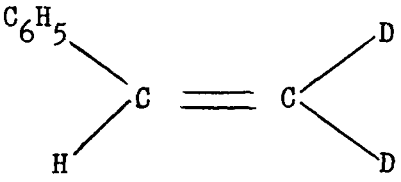
Table 14. Kinetic Isotope Effect ([Substrate]=0.01M; [QDC]=0.001M; $[H_2SO_4]$=1.5M; T=313K).

Substrate	$10^4 k_1/s^{-1}$	k_H/k_D
Styrene	1.46	
α-Deuteriostyrene (1)	1.49	0.98
β,β-Dideuteriostyrene (2)	1.83	0.80
Cinnamic acid	1.49	
Cinnamic acid-α-d (3)	1.51	0.99
Cinnamic acid-β-d (4)	1.91	0.78

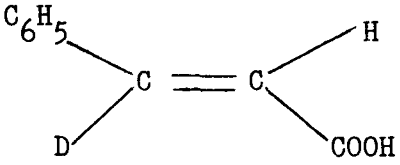
The isotope effect data in Table 14 shows a clear distinction between the α- and β- carbon atoms of styrenes (and cinnamic acids) in the transition state



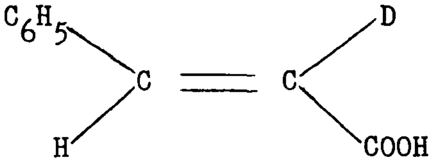
(1)



(2)



(3)



(4)

An inverse secondary kinetic deuterium isotope effect ($k_H/k_D<1$) would indicate that one or more carbon atoms would undergo a change in the state of hybridization from sp^2 to sp^3 between the ground state and the transition state(101,102). Electron abstraction from the double bond of 1 or 2 (for styrenes) and of 3 or 4 (for cinnamic acids), accompanied by the development of a partial positive charge at the benzylic carbon atom (α-carbon), would give a negligible secondary deuterium isotope effect for the oxidations of 1 and 3, and an inverse secondary deuterium kinetic isotope effect for the oxidations of 2 and 4. For the oxidation of 1, $k_H/k_D=0.98$, and for the oxidation of 3, $k_H/k_D=0.99$ (Table 14). These values are reasonable, since the benzylic carbon atom (α-carbon), in going from an olefinic centre to a carbonium ion-like character during the process of electron abstraction would remain sp^2 in character (attack being at the β carbon atom). For the oxidation of 2, $k_H/k_D=0.80$, and for the oxidation of 4, $k_H/k_D=0.78$ (Table 14). These values indicated that in the rate-determining step, the oxygen atom of quinolinium dichromate (QDC) attacked the β carbon atom, and the change in the state of hybridization progressed from sp^2 towards sp^3 as the new bond was being formed. At the same time, the hybridization at the benzylic carbon atom (α carbon) would be essentially sp^2 in character, since it was going from an olefinic centre to a carbonium ion-like character. Since the oxidation of styrene and of cinnamic acid exhibited an inverse secondary deuterium kinetic isotope effect only at the β carbon atom (Table 14), this would suggest that the rate-determining step of the reaction produced a carbonium ion in which the α-carbon atom remained sp^2 in character. This implied that in the transition state, there was substantial C_β-O bond formation, but negligible C_α-O bond formation, when QDC attacked the double bond of styrene (and cinnamic acid). Moreover, only one C-O bond of the product was formed in the transition state. This could be attributed either to the retention of a small amount of π-bond character in the transition state (that is, C_β not fully sp^3), or to a weak interaction between the oxygen lone pairs and the partially positive p orbital on the α-carbon atom. If the latter situation were to be operative, destabilization of the positive charge at C_α would enhance the C_α-O interaction in the transition state. This would lead to changes in the hybridization at C_α and give rise to a measurable inverse isotope effect. Such an effect has been observed in the bromination of α-deuteriopara-substituted styrenes(103). Since styrene and cinnamic acid did not give rise to an observable α-carbon isotope effect (Table 14), the conclusion was that, in the transition state, some fractional π-bonding was retained between C_{α} and C_{β}.

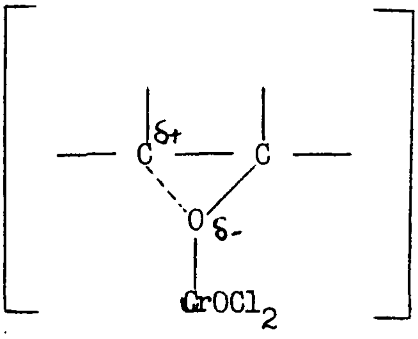
A partial change in hybridization of the reactant carbons from sp^2 to sp^3 between the ground state and the activated complex was predicted, on theoretical grounds, to give an inverse secondary deuterium kinetic isotope effect (k_H/k_D less than 1), as was observed in earlier investigations(104-112).

Mechanism

The oxidation of alkenes by Cr(VI) reagents had often led to a variety of products. In some cases, allylic oxidation seemed to predominate, while in other cases the oxidation had resulted in the formation of an epoxide, ketols, acids or ketones. For example, the chromic acid oxidation of tetraphenyl ethylenes had yielded the epoxide when the chromic acid concentration used was quite low. At higher concentrations of chromic acid, however, the major product obtained was benzophenone(113). The oxidation of some steroidal double bonds had led to ketols, or had resulted in allylic oxidation wherein there was a migration of the double bond(114). It was suggested that the oxidation of alkenes by chromic acid involved an electrophilic attack of Cr(VI) at the double bond, in a manner similar to what had been observed in the addition of bromine to an alkene in a polar medium(115). The chromic acid oxidation of conjugated dienes to enediones(116-118) had suggested an initial electrophilic attack, analogous to the 1,4-addition of bromine to dienes. The reactions of alkenes with chromyl chloride(119) and with chromic acid(120) had involved electrophilic additions to the double bond. The simultaneous addition across the double bond had been suggested in the oxidation of 1-methylfenchene to camphor, in which there was no rearrangement; the mechanism had involved the formation of a cyclic ester intermediate(121). On oxidation with aqueous chromic acid, 1,1-diphenylethylene gave benzophenone and acetone (cleavage products), which suggested that the epoxide was not an intermediate in the reaction(122-124). The reaction of cyclohexene with chromyl chloride had resulted in the formation of chlorohydrins, which did not seem to be stereospecific(125). The rate of this reaction showed an increase with increasing alkyl substitution at the double bond; there was evidence for electrophilic addition in this oxidation reaction(125).

Chromyl chloride has been used for the conversion of carbon-carbon double bonds to carbonyl compounds(126-129). Aldehydes were obtained from disubstituted ethylenes, while tetrasubstituted ethylenes were oxidized to ketones. The first step of this reaction involved an electrophilic attack of chromyl chloride to give a 1:1 adduct(119,129-138). It has been postulated that epoxides were possible intermediates in the oxidation of carbon-carbon double bonds (33,34,128-129,139-143), and the kinetic data suggested that chromyl chloride was the preferred chromium(VI) oxidant for the conversion of 2,2-disubstituted alkenes to aldehydes in high yields(127,129).

The kinetic data obtained from the chromyl chloride oxidation of alkenes(33,34,139-141) suggested a rate-determining step involving a slightly unsymmetrical three-membered cyclic activated complex, A, with partial positive charge development at the more highly substituted carbon atom(34):



(A)

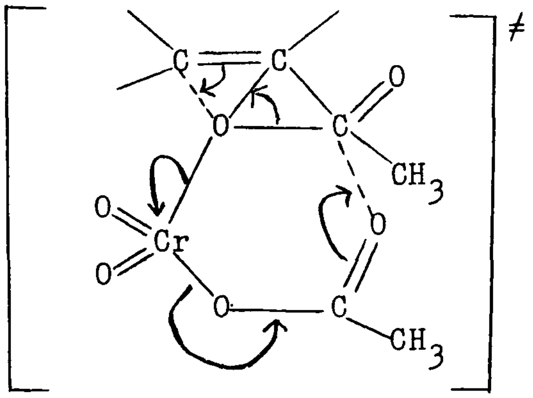
This reaction did not appear to be very sensitive to steric hindrance, and the large negative entropies of activation indicated a rigid orientation of reactants in the activated complex. The kinetic data for the chromyl chloride oxidation of styrenes suggested that the activated complex was slightly polar with a small partial positive charge at the benzylic carbon atom(33,139). It was also shown that chromyl chloride reactions proceeding via three-membered cyclic activated complexes reacted faster with 1,1-diphenylethylene than with styrene by a factor of 12.8 (139). This experimental observation indicated that stabilization resulting from the extended conjugated system appeared to be favourable in addition reactions involving three-membered cyclic activated complexes. Steric factors were also important in this oxidation reaction, as seen from the fact that there was a decrease in the rate of the reaction with an increase in phenyl substitution at the carbon-carbon double bond(139). Thus, for the oxidation of alkenes by chromyl chloride, conclusive evidence was obtained for electrophilic addition, showing that the carbon-carbon double bond had, indeed, been affected(33,34). A cationic intermediate was suggested to have been formed in the rate-determining step of this reaction(139). If attack had taken place at only one of the carbons before the transition state was achieved, it would have been expected to produce an inverse isotope effect only at that carbon. The oxidation of styrene by CrO_2Cl_2 exhibited an isotope effect only at the β-carbon(139), suggesting that the rate-determining reaction produced a carbonium ion in which the α-carbon remained sp^2 in character (eq.1)

$$PhCH = CH_2 + CrO_2Cl_2 \longrightarrow Ph\underset{\alpha}{\overset{+}{C}}HCH_2OCrOCl+Cl^- \qquad (1)$$

The oxidation of carbon-carbon double bonds with chromyl acetate and chromic acid had resulted in the formation of a large variety of compounds such as epoxides, glycols, aldehydes, ketones, acids and cleavage products. In contrast, the oxidation of unsaturated hydrocarbons by chromyl chloride had yielded aldehydes and ketones in good yields. Styrenes underwent a reaction with chromyl chloride to give adducts consisting of one part oxidant and one part reductant(130,133). Hydrolyses of these adducts gave aldehydes and ketones, as a result of structural rearrangements(33,126,144). Although the oxidations of carbon-carbon double bonds by chromic acid, chromyl acetate and chromyl chloride gave different products due to the diverse reaction conditions, it was reasonable to suggest the possibility of similar reaction pathways for the three oxidants. Cyclic epoxide-like three-membered ring activated complexes were proposed for the chromic acid oxidation of alkenes in aqueous media and in aqueous acetic acid media(145-148). However, there seemed to be a change in mechanism occurring in the chromic acid oxidation of styrenes(148). It is pertinent to note that epoxides have been isolated in the chromic acid oxidation of styrenes (122-124), cyclohexene(149), and allylic alcohols(150).

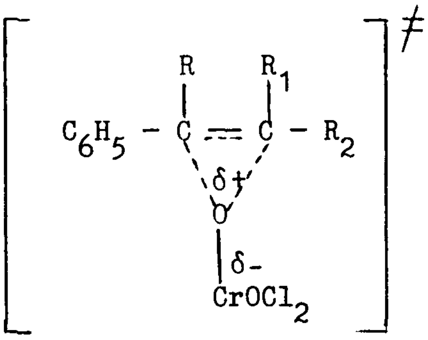
Chromyl acetate has been used to oxidize carbon-carbon double bonds to carbonates, epoxides, acids, diols and carbonyl compounds(122-124,145,146,151). A three-membered cyclic activated complex was suggested as the structure for the activated complex in these oxidation reactions. A similar mechanism was involved in the oxidation of cycloalkenes to dialdehydes, using chromyl trichloroacetate(152).

An activated complex resembling I was proposed for the chromyl acetate oxidation of alkenes and styrenes (123,145-147).:

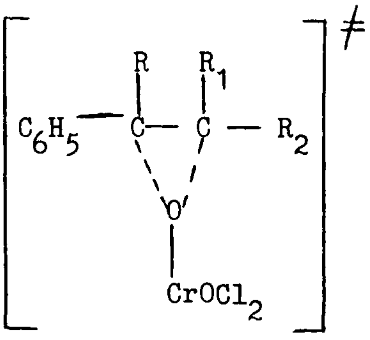


(I)

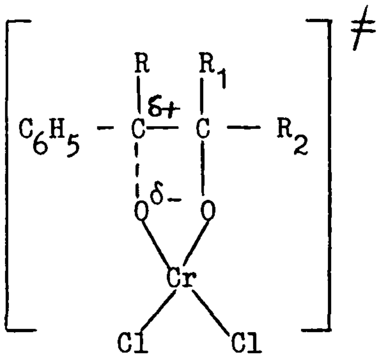
The carbonyl products obtained in the chromyl chloride oxidation of styrenes had resulted from an isomerization of the epoxide intermediates which could be formed from II, III or IV :



II



III



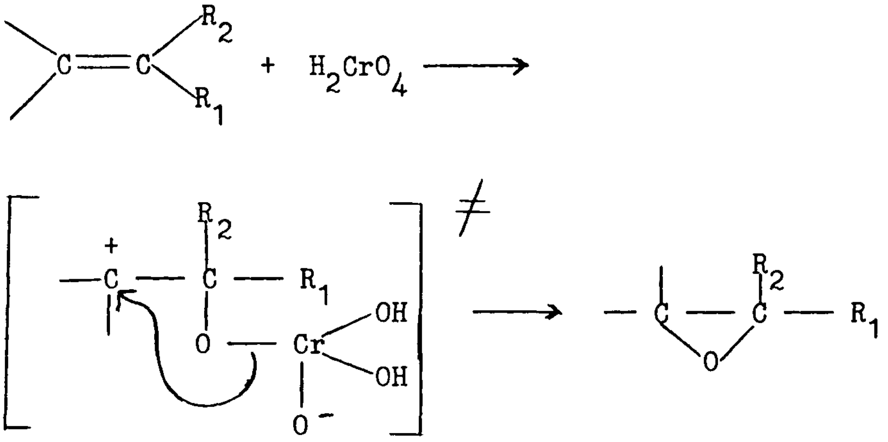
IV

Structure II could also represent the activated complex in the rate-determining step for the chromyl chloride oxidation of alkenes and cycloalkenes. From the relative rates, solvent effects, thermodynamic data, magnitude of ρ values and the secondary deuterium kinetic isotope effects, it was concluded that electrophilic addition of chromyl chloride to styrene probably involved an activated complex resembling II or IV in the rate-determining step.

Although epoxides have been reported to have been formed in the oxidation of styrenes by chromic acid(122-124), the occurrence of rearrangements indicated that a positively charged product-determining species may be formed during the reaction. Under the acidic reaction conditions, the initially formed epoxide may rearrange to the observed carbonyl products.

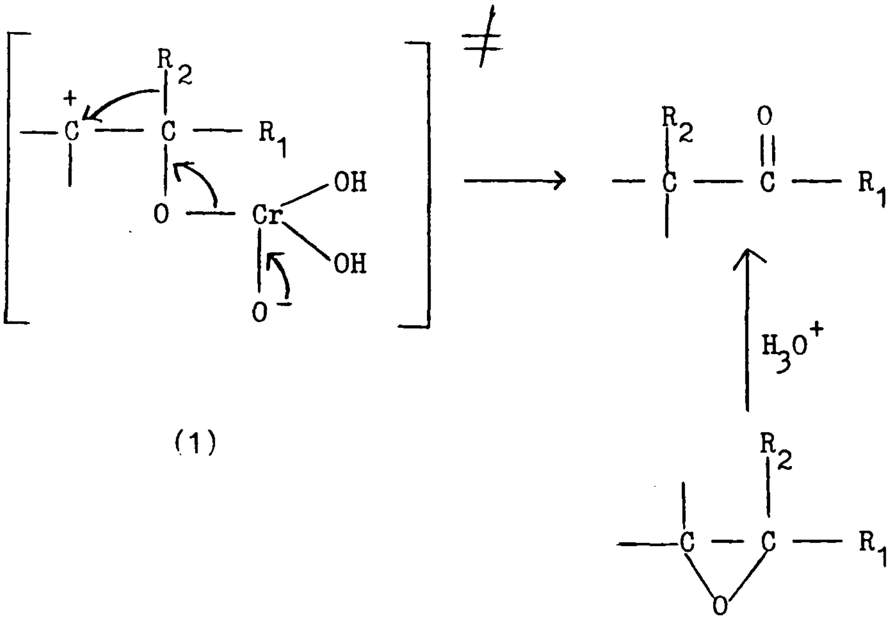
These oxidation reactions can be considered in the light of the Zimmerman treatment of electrocyclic reactions. Several plausible reaction pathways are shown:

I



(1) (2)

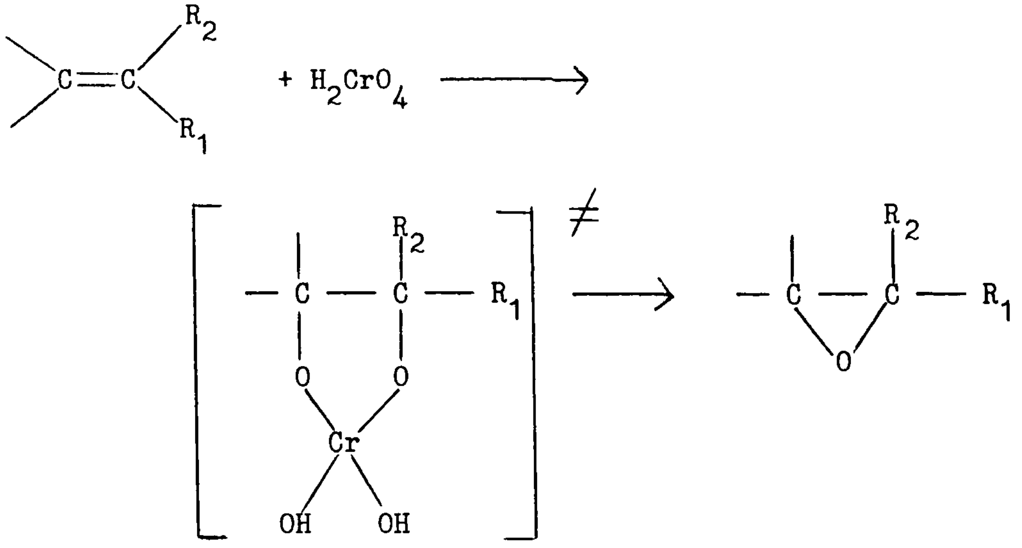
II



(1)

(2)

III



(A)

The Zimmerman treatment suggests that the structure 1 more closely resembles the activated complex than A, for the chromic acid oxidation of styrenes(153,154).

It has been shown that under alkaline conditions, permanganate ion was able to convert olefins to the corresponding diols in good yields(155), while in neutral or slightly basic solution, α-hydroxy ketones were produced(156). These reactions were always accompanied by some amount of carbon-carbon bond cleavage(18), and under acidic conditions, cleavage products were predominantly obtained(19,20). Cyclic manganese esters were formed in the initial step of the reaction(157). For example, it was shown that during the dihydroxylation reaction, the two hydroxy groups were added cis, and that the oxygens were transferred directly from the MnO_4^- ion(158). Subsequently, it was shown that hypomanganate esters were formed as intermediates in the oxidation of alkenes by $KMnO_4$(50). The transition state for the ester formation was one in which the olefinic carbons had acquired substantial sp^3 character with the bond rearrangements nearly complete. Isotope and substitution effects helped to establish that the transition state for the second step (oxidative decomposition of the ester) contained a fairly well developed carbonyl group. Under these conditions, the second step was much slower, and thus controlled the overall rate of the reaction(50).

Permanganate ion was used to oxidize carbon-carbon double bonds to cis-glycols and, depending on the reaction conditions, to hydroxycarbonyl compounds(159-161). A five-membered cyclic activated complex was proposed on the basis of kinetic, stereochemical and ^{18}O studies(159-161). The oxidation of crotonic acid(52,53,158) and cinnamic acid(162) by permanganate ion showed that the reaction pathway involved a cyclic manganese(V) intermediate and other organomanganese intermediates. The kinetic data obtained for these oxidation reactions suggested that manganese(VII) was reduced to tetrahedral hypomanganate, wherein the d electrons were in a d_{z^2} orbital(153). This treatment predicted the cis-hydroxylation of carbon-carbon double bonds, which was consistent with the subsequent formation of the observed oxidation products(52,53,159-162).

The stoichiometric oxidations of organic substrates by oxometal (M=O) reagents such as permanganate(157), chromic acid and chromyl compounds(74), SeO_2(163-166), OsO_4(167), RuO_4(168,169) and MnO_2(170) have been well established. These reagents have played an important role in organic synthesis, owing to their capacity for selective oxygen transfer to a wide variety of substrates under mild conditions. Participation by one or more M=O groups is a key mechanistic feature common to virtually all of these reactions. Oxometal reagents can effect oxidative cleavage of double bonds. A characteristic feature of oxometal reagents that effect the oxidative cleavage of double bonds is the presence of a cis-dioxometal functionality. Reaction with a double bond can produce cleavage via a (4+2 or a 2+2 cycloaddition). Oxidative cleavage of olefins over metal oxide catalysts, at elevated temperatures in the gas phase, almost always results in complete combustion giving CO_2, CO and H_2O, since the cleavage products (aldehydes or ketones) are generally more reactive than the reactant olefins.

One example of a selective cleavage, namely, the oxidation of ethylene to formaldehyde carried out over an iron-molybdate catalyst at 350-400°C, had resulted in 76% selectivity(171). Ruthenium tetroxide in CCl_4(172) was found to be an extremely powerful oxidant that could cleave double bonds at ambient temperatures(168). Ruthenium tetroxide was used in catalytic amounts, in conjunction with sodium hypochlorite as the primary oxidant, to oxidatively cleave olefins to ketones or carboxylic acids(173,174).

The direct interaction of strong metal oxidants with organic substrates have sometimes led to the production of radical intermediates. Thus, electron transfer processes (involving radical intermediates) as well as electrophilic mechanisms (involving organometallic intermediates) are possible(175). Any reasonable mechanism must account for two important experimental observations, in that many of these reactions:

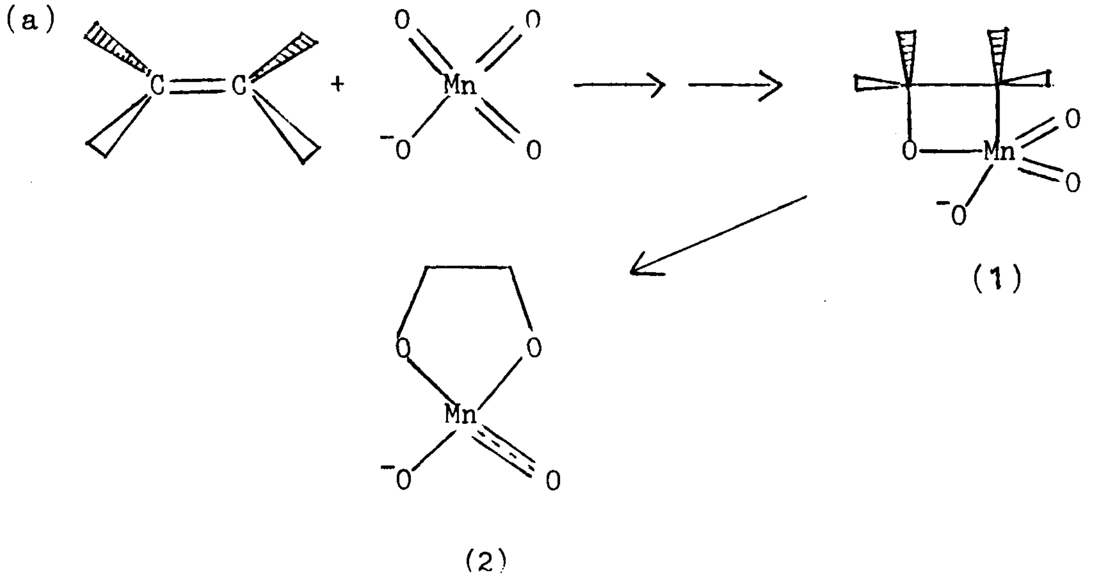
(a) exhibit substantial deuterium kinetic isotope effect; and (b) proceed with partial retention of configuration (74,157,176,177). In an electron transfer mechanism, this would require the C-H bond-breaking step to be rate-limiting. With regard to electrophilic attack, the mechanistic possibility seemed to be an attack of the nucleophile on the positive metal centre(175), in analogy with the nucleophilic additions to carbonyl groups. Organometallic species are a direct consequence of this hypothesis, and had not generally been considered to be viable intermediates in the reactions of oxometal reagents.

The interaction of olefins with oxometal reagents, as with other oxidants, could involve reaction either at the double bond or at the allylic C-H bond. Parallels were noted for both allylic oxidations and those involving an overall reaction at the double bond. The basic underlying feature of all these reactions was the participation of the oxometal groups(178-180). In general, it appears that allylic oxidation stems from moderately strong oxidants (electrophiles) such as Se^{IV} and Mo^{VI}, whereas reaction at the double bond occurs with the very strong oxidants such as Cr^{VI}, Mn^{VII}, Ru^{VIII} and V^{V}. Although reagents such as SeO_2 react with olefins at the labile allylic C-H bonds (ene reactions), high valent oxometal compounds such as O=Cr(VI) or O=Os(VIII) effect reaction at the double bond (1,2-addition). It has been suggested that the mode of attack depends on: (a) the degree of covalency or polarisation of the M=O bond; and (b) the presence of non-bonding electrons on the metal(181). For oxometal reagents, the hard reagents such as O=Cr(VI) and O=Os(VIII) are expected to effect electron transfer since their oxidation potentials are sufficient to accept an electron from olefins. For example, in the reaction between an olefin and chromyl chloride, the initial electron transfer would be followed by the solvent cage combination of the cation radical with the oxo anion.

A novel aspect of the oxidation of olefins was the possibility of the formation of a metallocycle intermediate (175), which could decompose to form a carbonyl compound, or an epoxide, or the precursor to a chlorohydrin. Each of these products has been experimentally observed in the oxidation of alkenes by chromyl chloride(175,182,183). The energetics for the oxidation of ethylene by chromyl chloride(184) confirmed the earlier observation that the metallocyclooxetane was a likely precursor for all the observed oxygen containing products. It also excluded the possibility of a direct addition reaction, characteristic of oxidations by osmium tetroxide.

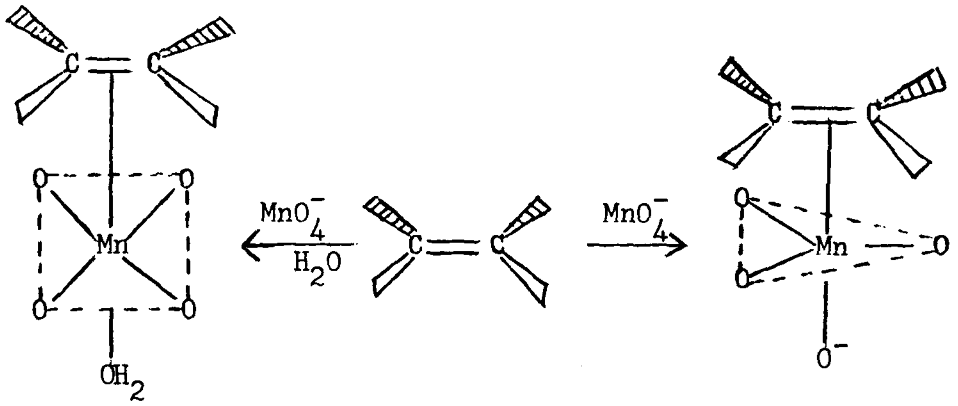
It was significant that the chromyl chloride oxidation of olefins did not result in the formation of diols. This was in contrast to the oxidation of olefins by potassium permanganate(185,186) and osmium tetroxide(167,187), wherein significant amounts of the diols were formed. This differential reactivity was explained in terms of stabilization due to spectator oxo groups resulting from the differing number of valence electrons present.

For the reaction of permanganate ion with carbon-carbon double bonds, theoretical calculations(184,188) suggested the formation of a metallocyclooxetane, 1, which could rearrange to the five-membered cyclic hypomanganate diester, 2.



It was further suggested that the formation of the cyclic manganate ester would be enhanced by the simultaneous formation of a triply bonded spectator oxo group, which would be formed when the d orbitals were available for bonding to a single oxygen(184). The oxidation of carbon-carbon double bonds by permanganate ion in phosphate buffered solutions indicated that the relative reactivities of α,β-unsaturated acids were influenced by steric factors(189) These results were consistent with those obtained earlier in the permanganate oxidation of alkenes(190), and of maleic and fumaric acids(191). The kinetic data thus obtained suggested that the oxidation of olefins by permanganate ion involved an initial interaction between the double bond and the metal to give an octahedral (A) or a trigonal

(b)



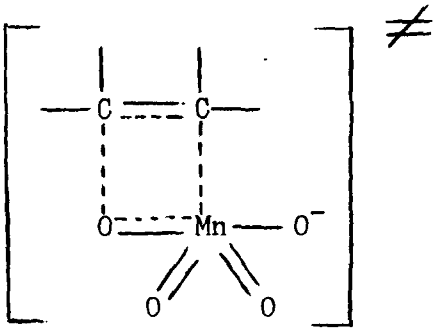
(A)

(B)

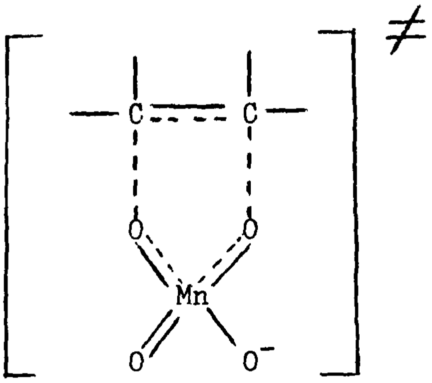
bypyramidal (B) organo metallic complex. These could undergo rearrangement to a metallocyclooxetane, 1, or to a five-membered cyclic manganate(V) diester, 2 (189). It is pertinent to observe that organometallic intermediates were involved in the oxidation of olefins by oxo metals(175) The structure-activity relationship observed in the permanganate ion oxidations of double bonds(189) was similar to those observed for the Pd(II) catalyzed oxidation of olefins, and for the stabilities of Ag^+-olefin complexes (192-195). The Ag^+ and Pd(II) reactions proceeded via metal complexation with the carbon-carbon double bond(192-195).

The kinetics of oxidation of substituted α,β-unsaturated carboxylate ions by permanganate ion in phosphate-buffered solutions was investigated, in order to determine the influence of substituents on these reactions(196). Low sensitivity of permanganate ion to electronic effects and small ρ values for the oxidation of cinnamic acid(50,52,162, 189,197) were observed. The inverse secondary deuterium kinetic isotope effects(50,52,162,189,197,198), the ^{18}O studies(158), the low enthalpy of activation and the large negative entropy of activation all suggested that there was a cycloaddition of the permanganate ion with the carbon-carbon double bond to yield a metallocyclooxetane, 1 (via C), or cyclic manganate(V)diester, 2(via D), in the rate-determining step of the reaction(154,184).

(c)



(C)



(D)

The kinetics of oxidation of (E)-3-(2-thienyl)-2-propenoates and (E)-3-(3-thienyl)-2-propenoates by permanganate ion was studied, and the kinetic data obtained were consistent with the formation of a metallocyclooxetane, 1, or a cyclic manganate(V)diester, 2 (199).

Under phase transfer conditions, olefins have been converted to aldehydes(200-202). However the cleavage of double bonds to aldehydes in aqueous organic mixtures had not been studied. A simple method was developed using THF-water mixtures for the oxidation of olefins by $KMnO_4$ (203). In these reactions it was observed that the solvent mixtures (THF:Water) acted as quenching reagents, resulting in the conversion of olefins to aldehydes in good yields(203).

The oxidation of cinnamic acid by tetrabutylammonium permanganate in dichloromethane solutions containing quarternary ammonium salts was observed to proceed via the initial formation of an organometallic complex, in which the double bond became a η^2 ligand on manganese(175,189). This complex underwent a rearrangement to form a reactive manganate(V) cyclic diester, which then was rapidly reduced to a manganese(III) species(66).

The use of permanganate, with silica as a solid support, was used for the cleavage of double bonds(204), as also to carry out allylic oxidation reactions(205). When moist alumina was used as a solid support and dichloromethane as the solvent, permanganate became reactive enough to readily cleave carbon-carbon double bonds, giving good yield of the aldehydes(65). Using these reaction conditions, cinnamic acid and 4-nitrocinnamic acid were converted to benzaldehyde and 4-nitrobenzaldehyde respectively, in very good yields(65). The mechanistic pathway involved the initial formation of an alkene/MnO_4 complex which was then transformed to a metallooxetane and then to a cyclic manganate(V) ester(175,206).

Based on the stoichiometries of the oxidation reactions, and the observed experimental data, the mechanistic pathways for the oxidation of the unsaturated compounds (styrene, cinnamic and crotonic acids, and maleic and fumaric acids) by quinolinium dichromate(QDC) in acid medium, using dimethylformamide(DMF), has to be rationalized. While suggesting mechanistic pathways for these oxidation reactions, the following kinetic observations have to be taken into consideration:

(1) The rates of the reactions were dependent on the first powers of the concentrations of each —— substrate and oxidant (Tables 2-5). This kinetic behaviour was consistent with a mechanism involving a rate-determining reaction between the substrate and oxidant.

(2) The rates of the reactions were dependent on the first powers of the concentrations of the acid (Tables 6-7). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated chromium(VI) species in the rate-determining step of the reaction.

(3) The rates of the reactions were decreased, with an increase in the polarity of the medium, using DMF-water mixtures (Table 8). Plots of log k_1 against the reciprocal of the dielectric constants (Figs. 3-4) were linear, with positive slopes. This indicated an interaction between a positive ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated chromium(VI) species.

(4) The rates of the oxidation reactions showed an increase, with an increase in temperature (Tables 9-10). The negative entropies of activation suggested that

the transition state formed was considerably rigid, resulting in a decrease in the degrees of freedom of the molecules. The similarity in $\Delta G^{\neq}$ values (Tables 11-12) for all the substrates were due to changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, and suggested that all the oxidation reactions involved similar rate-determining steps.

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

(6) The effect of substituents on the rates of oxidation was studied. It was observed that electron-releasing substituents accelerated the oxidation process, and electron-withdrawing groups retarded the process (Tables 9-10). Plots of log k_1 versus the σ values of the substituents were linear (Figs. 9-10), and gave values of the reaction constant ρ as -4.0 for both, styrenes and cinnamic acids. This suggested that the transition state possessed considerable carbonium ion character, resulting from a large amount of positive charge developing at the carbon atom adjacent to the benzene ring (α-carbon atom).

(7) The kinetic isotope effects observed were as follows (vide Table 14):

Substrate	k_H/k_D
α-Deuteriostyrene	0.98
β,β-Dideuteriostyrene	0.80
Cinnamic acid-α-d	0.99
Cinnamic acid-β-d	0.78

Since the oxidation of styrene (and of cinnamic acid) exhibited an inverse secondary deuterium isotope effect only at the β-carbon atom (Table 14), this suggested that the rate-determining step of the reaction produced a carbonium ion in which the α-carbon remained sp^2 in character. This implied that there was negligible C_α-O bond formation, but substantial C_β-O bond formation, in the transition state.

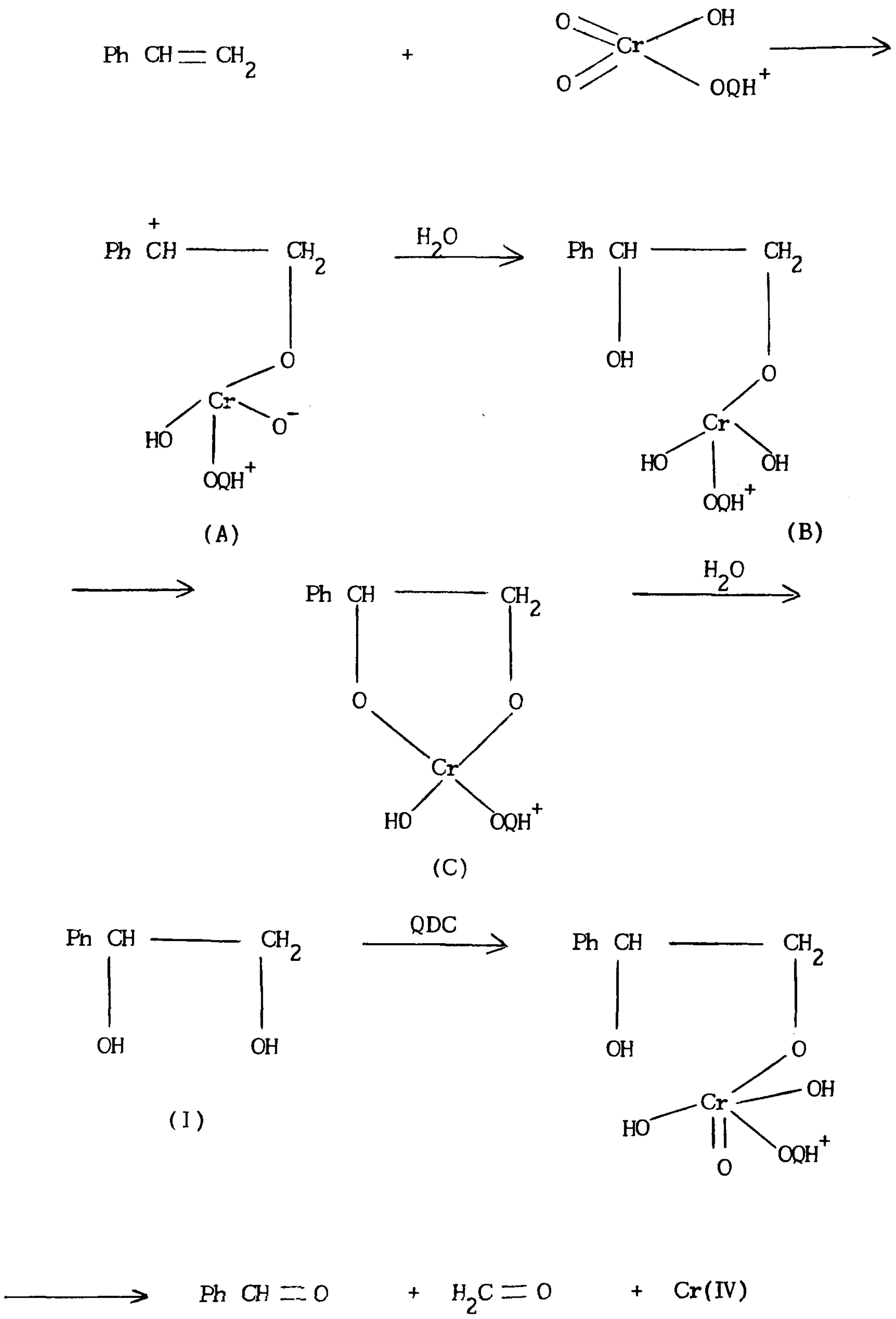
A hydrogen abstraction mechanism was unlikely, in view of the failure to induce the polymerization of acrylonitrile or the reduction of mercuric chloride.

In the present investigation, the large negative values of the reaction constant ($\rho = -4.0$ for styrenes and cinnamic acids), together with the values of the kinetic isotope effects (Table 14), would suggest considerable carbonium ion character in the transition state.

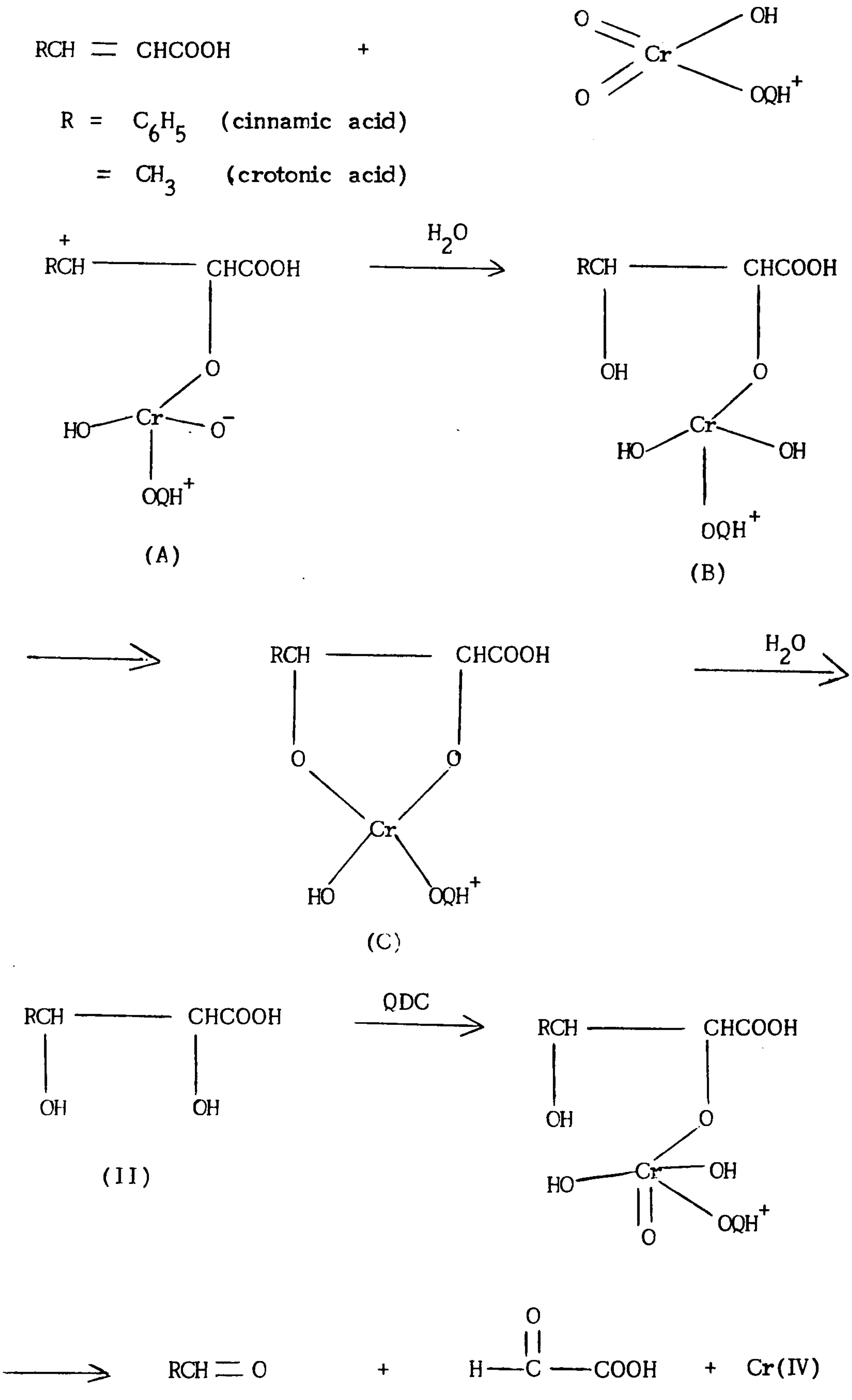
The sequence of reactions is shown in Scheme 1 (styrene) and Scheme 2 (cinnamic and crotonic acid). The kinetic data suggested the compatibility of an electrophilic attack of the protonated form of the oxidant(QDC) on the double bond of the substrate, to form a carbonium ion, A (Schemes 1 and 2). This carbonium ion could be stabilized by the phenyl group. The intermediate formed reacts with a nucleophile (water) in the reaction mixture to form an intermediate, B, which could be converted to the cyclic chromate ester, C. This ester could then be cleaved to give the observed products.

Efforts to isolate the intermediates I and II (Schemes 1 and 2) during the course of the reactions were not successful. Independent kinetic experiments performed in this laboratory have shown that styrene glycol (I) and 2,3-dihydroxy-3-phenyl propionic acid (II), underwent rapid reactions with QDC in acid medium under a nitrogen atmosphere, to give benzaldehyde and formaldehyde (products from the oxidation of I), and benzaldehyde and glyoxylic acid (products from the oxidation of II), respectively. The rate constants

SCHEME 1



SCHEME 2


RCH = CHCOOH
+
R = C6H5 (cinnamic acid)
= CH3 (crotonic acid)
O
O
Cr
OH
OQH+
+
RCH
CHCOOH
O
HO
Cr
O−
OQH+
(A)
H2O
RCH
CHCOOH
OH
O
HO
Cr
OH
OQH+
(B)
RCH
CHCOOH
O
O
Cr
HO
OQH+
(C)
H2O
RCH
CHCOOH
OH
OH
(II)
QDC
RCH
CHCOOH
OH
O
HO
Cr
OH
O
OQH+
RCH = O
+
O
H—C—COOH
+
Cr(IV)

obtained were as follows (Tables 15-16).

Table 15. Rate Data for the Oxidation of Styrene and Styrene Glycol ([QDC]=0.001M; [H_2SO_4]=1.5M; T=313K).

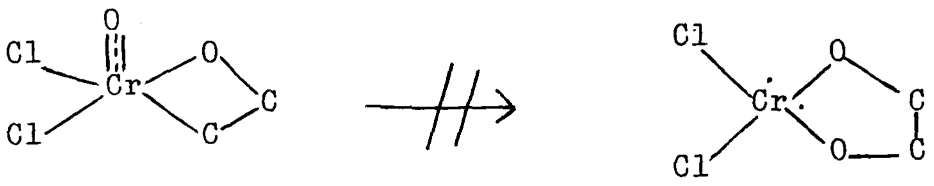
[Substrate] (M)	Styrene	Styrene Glycol
	(10^4k_1, s^{-1})	
0.01	1.46	21.9
0.10	14.8	225

Table 16. Rate Data for the Oxidation of Cinnamic Acid and 2,3-Dihydroxy-3-Phenyl Propionic acid.
([QDC]=0.001M; [H_2SO_4]=1.5M; T=313K).

[Substrate] (M)	Cinnamic Acid	2,3-Dihydroxy-3-Phenyl Propionic Acid
	(10^4k_1, s^{-1})	
0.01	1.49	22.0
0.10	15.3	228

Thus, styrene glycol (I) and 2,3-dihydroxy-3-phenyl propionic acid (II), when formed during the reaction, would be rapidly converted by QDC, in acid medium, to yield benzaldehyde and formaldehyde (products from the oxidation of I), and benzaldehyde and glyoxylic acid (products from the oxidation of II), respectively. These products have been isolated from the respective reaction mixtures, and have been characterized by spectral methods. The formation of these products would substantiate the mechanism of the oxidation reaction, wherein there was a cleavage of the carbon-carbon bond in the final step of the reaction. The oxidative cleavage of the 1,2-glycols to yield aldehydes has been established in earlier investigations(207-210).

In the oxidation of olefins by chromyl chloride, it had been shown that the reaction proceeded via a metallocycle intermediate(175). Ab initio calculations on the energetics of these reactions had confirmed the intermediacy of the metallocyclooxetane for the observed oxygen-containing products. This implied that for CrO_2Cl_2, the shift involved reaction with a strong metal-oxo triple bond, preventing the formation of a five-membered cyclic transition state, that is:



For other metal oxides such as $KMnO_4$ and OsO_4, the reactions were with an oxo double bond, leading to the conversion of a spectator oxo into an oxo triple bond.

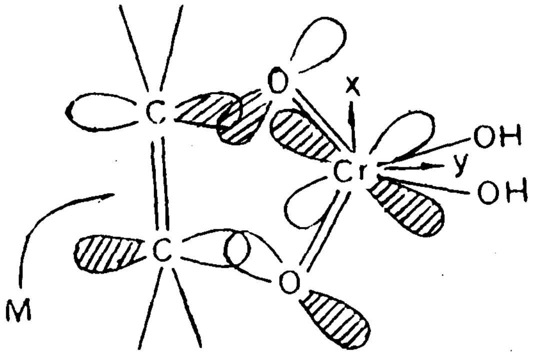
For the oxidation of olefins by Cr(VI) compounds, the second oxo group would be intimately involved in the reaction sequence. Such spectator oxo groups were observed to play a central role in stabilizing critical intermediates in these reactions of metal oxides such as MnO_4^{2-}, OsO_4, RuO_4, and supported transition metal oxides(184).

In the present investigation, the reaction of unsaturated compounds (styrene and cinnamic acid) with quinolinium dichromate (QDC) could be suggested to proceed via an intermediate wherein a spectator oxo group could be converted into an oxo triple bond, similar to the type of intermediate suggested for the oxidation of olefins by $KMnO_4$ and OsO_4 (184).

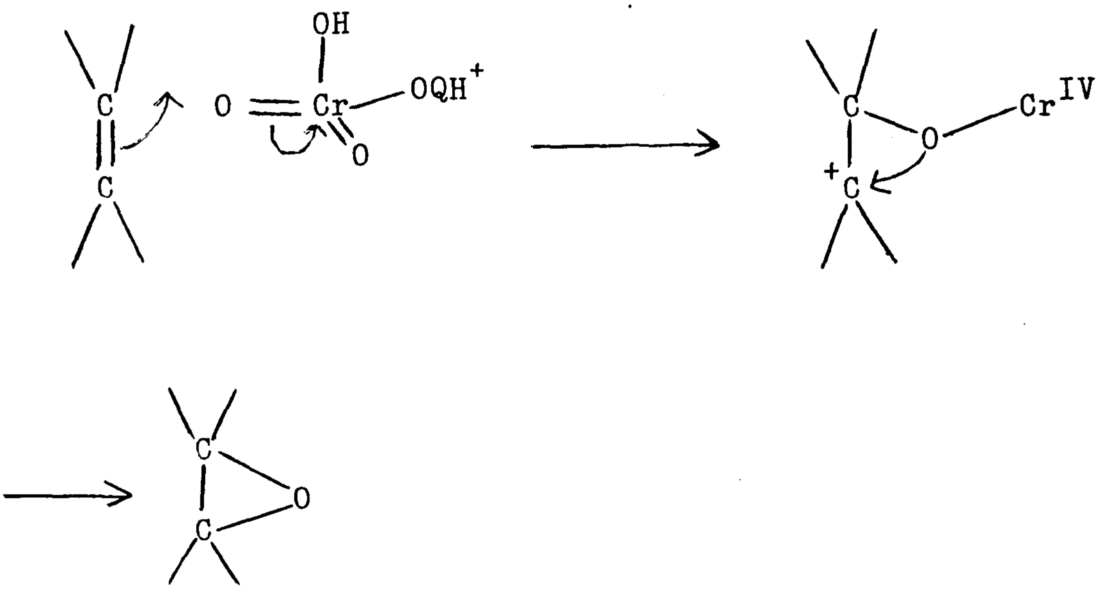
Using the topographical approach to the orbital levels of the transition state(153), it is possible to determine whether the transition state is of the "Hückel-type" (all overlapping pairs of reacting orbitals are bonding) or of the "Möbius-type" (one or an odd number of antibonding overlaps must occur).

The oxidation of olefins by permanganate, for example, clearly involves an electrocyclic process involving six electrons(157). An examination of the orbital overlap picture shows that bonding interaction is possible all round the ring, whether the d_{z^2} orbital is parallel or perpendicular to the double bond. Hence, this is a Hückel-type system satisfying the 4n+2 rule, and is an allowed reaction. The oxidation of olefins by OsO_4 can be accounted for in a similar manner.

If chromium(VI) were to react with olefins by a similar mechanism (as for $KMnO_4$ and OsO_4), the orbital overlap picture would indicate that not all overlapping orbitals are bonding. That is, it is a "Möbius-type" system (154). As it does not satisfy the 4n rule, it is a forbidden reaction (diagram). Hence, the reaction must find an alternative route. This it does by an acylic mechanism which



is not subject to selection rules. The acyclic sequence would be as shown:



In the present investigation, all the kinetic data and experimental evidence for the oxidation of the olefinic substrates (styrene, cinnamic acid and crotonic acid) by quinolinium dichromate (QDC) in acid medium support a reaction pathway involving an acyclic mechanism. The oxidation of all these substrates exhibited an isotope effect only at the β carbon atom (Table 14), which suggested that the rate-determining step of the reaction yielded a carbonium ion in which the α-carbon atom remained sp^2 in character. This was further supported by the value of the reaction constant $\rho = -4.0$ for both, styrenes and cinnamic acids (Figs. 9-10). The thermodynamic parameters obtained for these oxidation reactions (Tables 11-12), also support the proposed mechanism involving an acyclic transition state. Energy considerations have established that an acyclic mechanism would be an allowed process for the oxidation of these substrates by quinolinium dichromate (QDC). The reaction pathways for the oxidation of these substrates by quinolinium dichromate (QDC) in acid medium, have been shown in Scheme 1 (styrene) and Scheme 2 (cinnamic acid and crotonic acid).

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SUMMARY

SUMMARY

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 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 substances 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 oxodiperoxo chromium(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);

Chaudhuri's reagent-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(TBACC); tetramethyl 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); chlorotrimethylsilane - chromium 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-carboxy pyridinium 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); cyano pyridinium 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) and chromium trioxide in the presence of wet aluminium oxide taken in hexane(37).

The most recent chromium(VI) reagent which has been introduced for the oxidation of organic substrates has been quinolinium fluorochromate(QFC), used in chloroform as solvent(38). This reagent has been used for the oxidation of alcohols, polycyclic arenes and diphenyl sulfide, and the yields reported have been excellent(38).

The reagent employed in the present investigation has been quinolinium dichromate (QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$. This reagent was first reported to have been used for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, and for the oxidation of aldehydes to acids(39). This reagent has now emerged as a very useful and versatile oxidant, and has been used for the oxidation of a variety of organic substrates. When taken in dimethylformamide or in dimethylformamide - water mixtures, in the presence of an acid, quinolinium dichromate(QDC) was found to be very efficient for the oxidation of benzyl alcohols(40), aryl alkanes(41), diphenylamines(42), polynuclear aromatic hydrocarbons(43,44), toluene and substituted toluenes(44,45), fluorene(46), amino acids(47) and benzoin(48).

The present investigation focuses attention on the kinetic features pertaining to the oxidation of various organic substrates by quinolinium dichromate(QDC) in acid medium, using dimethylformamide(DMF) and dimethylformamide - water (DMF-H_2O) mixtures as the solvent, 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 acid 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 DMF and DMF-H_2O mixtures, have included the following:

1. Alcohols - Chapter 1

(a) Cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol).

(b) Bicyclic alcohols (borneol and isoborneol).

(c) Allylic alcohols (geraniol and farnesol).

2. Unsaturated Compounds - Chapter 2.

(a) Styrene and substituted styrenes.

(b) Cinnamic acid and substituted cinnamic acids and crotonic acid.

(c) Maleic acid and fumaric acid.

Chapter 1 - Kinetics of Oxidation of Alcohols.

The kinetics of oxidation of alcohols (cyclic alcohols, bicyclic alcohols and allylic primary alcohols) by quinolinium dichromate(QDC) has been studied in acid medium, using dimethylformamide(DMF) and dimethylformamide-water(DMF-H_2O) mixtures as the solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440nm. For all the alcohols studied, stoichiometric ratios, Δ[QDC]/Δ[Substrate], in the range 0.61-0.73 were obtained. The rate of the reaction was found to be dependent on the first powers of the concentration of each reactant (substrate, oxidant and acid). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated chromium(VI) species in the rate-determining step.

The reaction has been found to be fastest in those solvent mixtures that contained the largest proportions of dimethylformamide. Plots of log k_1 (the pseudo-first-order rate constant) against the reciprocal of the dielectric constant were linear, with positive slopes. This indicated an interaction between a positive ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated chromium(VI) species.

The reactions were studied over a range of temperatures, 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 thus 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 498K. Although current views do not attach much physical significance to isokinetic temperatures, a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. It was further found that the values for the free energies of activation($\Delta G^{\neq}$) were nearly constant, indicating that the same mechanism operated for the oxidation of all the alcohols 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.

It has been earlier established that the kinetic rates of oxidation for cyclic compounds could be rationalized on the basis of the difference in strain energy between the ground state and the transition state. In cyclic systems, changes in bond hybridization had resulted in concomitant changes in angle strain, bond opposition strain or transannular strain. In the present investigation, the order of reactivity for the oxidation of cyclic alcohols by quinolinium dichromate (QDC) was observed to be:

Cyclooctanol >	cycloheptanol >	cyclopentanol >	cyclohexanol.
(8-)	(7-)	(5-)	(6-)

This order of reactivity was rationalized on the basis of a change in ring strain involved, in passing from the initial state (sp^3) to the transition state (sp^2). The major source of strain for the 5-, 7- and 8- membered ring systems arose as a result of non-bonded interactions. Such interactions would be absent in the ground state of the 6-membered ring system. The net result would be that reactions leading to the easing of some of these non-bonded interactions in 5-, 7- and 8- membered ring systems would be facilitated. The nature of the transition state would be such that this strain relief could occur, enabling the formation of a product-like transition state. For the 6- membered ring system, any deviation from the staggered conformation would be unfavourable, since this would result in a higher energy of activation. This would account for the slowness in the rate of oxidation of cyclohexanol, and would thus explain the observed order of reactivity for the cyclic alcohols (8>7>5>6).

The rates of oxidation of bicyclic alcohols have been observed to be influenced both by steric and electronic factors. The rate data on the oxidation of bicyclic alcohols by quinolinium dichromate (QDC) have been interpreted in terms of the differences in the relative stability of the alcohols and the transition states. The present data on the oxidation of bicyclic alcohols by QDC suggested that, if the strain-induced instability of the chromate ester were to determine the relative rates of oxidation, then there would be an acceleration of the rate resulting from the relief of steric strain in the chromate ester. The effect of the strain-relief factor on the relative rates of oxidation of bicyclic alcohols by QDC have thus been examined. The kinetic data showed that borneol, with an axial hydroxyl group, was more stable than the isomeric equatorial isoborneol. In isoborneol, since the chromate ester group was in the exo configuration and was more strained due to the presence of the bridged gem-dimethyl groups, there would be the distinct possibility of the hydroxyl group suffering a non-bonded repulsion from the gem-dimethyl group at C-7. This effect would be diminished when the transition state was formed. In the transition state, therefore, there would be a rate-enhancing relief of steric strain. This resulted in isoborneol being oxidized more rapidly than borneol by a factor of 2.63, thus indicating a difference in the ease of ester decomposition.

Mechanistic pathways for the oxidation of alcohols have very often been established using kinetic isotope effects. In the present investigation, kinetic isotope effects have been used to establish the structure of the transition state and the nature of bond cleavage in the rate-determining step of the reaction. The kinetic isotope effects, k_H/k_D were observed to be in the range 5.6-6.3 for the oxidation of the different alcohols studied. The high values of the kinetic isotope effects observed would suggest a cyclic transition state, with a rate-determining cleavage of the carbon-hydrogen bond. The observed k_H/k_D values obtained for the oxidation of the various alcohols (cyclohexanol, isoborneol, geraniol and farnesol) corresponded to a substantial loss of zero point energy in the transition state (4.7-5.3 kJ mol^{-1}). This indicated that the C-H bond was considerably stretched in the transition state. Thus, the high values of k_H/k_D and the high zero point energy values would establish a rate-determining cleavage of the C-H bond.

All the kinetic evidence obtained for the oxidation of alcohols by quinolinium dichromate (QDC), in acid medium, would establish that the oxidation proceeded via a mechanism which involved the formation of a cyclic chromate ester, followed by the decomposition of the ester involving the slow rupture of the C-H bond. A cyclic transition state could be postulated on the basis of the relative rates of oxidation of the cyclic alcohols studied. A conversion of the cyclic alcohols to the corresponding ketones was observed, and this process involved a change $>\mathrm{CHOH} \longrightarrow >\mathrm{C{=}O}$. The reaction intermediate could be visualized as having a cyclic structure, which would explain all the kinetic features of the oxidation reactions. The negative entropies of activation would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The decomposition of the ester could be visualized, wherein the hydrogen was bonded in the transition state to both, the alcoholic carbon atom and the oxygen atom attached to chromium. In a cyclic transition state, the electron flow could be considered for the conversion of the ester to the transition state. This could be rationalized if the chromium were to be coordinated through the alcohol O-H group. The process of electron transfer could then take place through the carbon-oxygen-chromium bond. This not only would help to facilitate the formation of the chromate ester, but would also enhance the ease of conversion to the ketone. The kinetic isotope effects observed for this process had established a cleavage of the C-H bond in the rate-determining step of the reaction. The proton was removed in the cyclic transition state (coplanarity of all the atoms being involved), the centre of which resides on an electron-dense oxygen in the chromate ester. The transition state thus postulated would envisage the transfer of electrons towards the chromium occurring by the formation of the carbon-oxygen-hydrogen bonds as well as carbon-oxygen-chromium bonds.

The Zimmerman treatment of electrocyclic reactions was also used to support the mechanism of these oxidation reactions. Using this topological approach to the orbital levels of the transition state, 4n+2 electrons would form a closed shell giving it stability (Hückel transition state), resulting in the reaction being an allowed process. In the present investigation, the oxidation of alcohols (cyclic, bicyclic and allylic primary alcohols) by quinolinium dichromate (QDC), in acid medium, involved the formation of a cyclic chromate ester. The second step of the reaction would involve the transfer of two electrons in a cyclic system. The electrocyclic mechanism for the oxidation of alcohols by quinolinium dichromate(QDC) clearly involved six electrons. Since this would be a Hückel-type system (4n+2), this would be an allowed process.

Under the experimental conditions employed in the present investigation, cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol) were oxidized by quinolinium dichromate (QDC) in acid medium, to the corresponding cyclic ketones in each case. The products (the respective cyclic ketones), obtained in good yields, were characterized by IR analysis, and by their respective 2,4-dinitrophenylhydrazone derivatives.

Under the experimental conditions employed in the present investigation, bicyclic alcohols (borneol and isoborneol) were oxidized by quinolinium dichromate(QDC) in acid medium to the corresponding ketone (camphor) in each case. The product (camphor), obtained in good yield, was characterized by its melting point, IR analysis and by its 2,4-dinitrophenylhydrazone derivative.

Under the experimental conditions employed in the present investigation, allylic alcohols (geraniol and farnesol) were oxidized by quinolinium dichromate (QDC) in acid medium to the corresponding aldehydes (geranial and farnesal). The products (geranial and farnesal), obtained in good yields, were characterized by IR analysis and by their respective 2,4-dinitrophenylhydrazone derivatives.

Chapter 2 - Kinetics of Oxidation of Unsaturated Compounds.

The oxidation of carbon-carbon double bonds by various oxidants is an important and well-known reaction. The periodate-permanganate cleavage of alkenes has been used as a means of determining the position of double bonds in unsaturated compounds(49). Earlier work on the oxidation of styrenes have been reported wherein oxidants such as thallic ions(50-52), chromyl chloride(53,54), lead tetraacetate(55), ceric ions(56) cobaltic ions(57-59), peracetic acid(60) and acidic hexacyanoferrate(111) ions(61) have been employed. The oxidation of cinnamic acid by permanganate had resulted in a cleavage of the carbon-carbon double bond to yield benzaldehyde(62,63).

The present work is a detailed kinetic investigation of the oxidation of unsaturated compounds (styrenes, cinnamic acids, crotonic acid, maleic acid and fumaric acid) by quinolinium dichromate (QDC), in acid medium, using dimethylformamide(DMF) and dimethylformamide-water (DMF-H_2O) mixtures as the solvent, under a nitrogen atmosphere. The course of the reactions was monitored by observing the disappearance of chromium(VI) at 440nm, spectrophotometrically. The stoichiometric ratios, Δ[QDC]/Δ[Substrate], were in the range 1.30-1.38. 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 protonated chromium(VI) species would be a reactive electrophile, and hence sufficiently reactive to attack the double bond of the unsaturated compounds and bring about the oxidative cleavage of the carbon-carbon double bond.

The role of the solvent in these oxidation reactions was investigated. It was observed that the rate of oxidation was slowest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of dimethylformamide resulted in an increase in the rate of oxidation. Plots of log k_1 (pseudo-first-order rate constant) against the reciprocal of the dielectric constant were linear, with positive slopes, indicating an ion-dipole type of reaction.

The effect of changes in temperature on the rate of the reaction was studied, and the Arrhenius equation was found to be valid. The activation energies and the other activation parameters were evaluated. The reactions were characterized by fairly high positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$, which suggested that the transition state was highly solvated. 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 isokinetic temperature, obtained from the plots of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, were 313K (for styrenes) and 333K (for cinnamic acids). The similarity 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.

Structure-reactivity correlations were used to establish the nature of the transition state, and hence to deduce the mechanistic pathway of these reactions. It was observed that electron-releasing substituents accelerated the oxidation process, and electron-withdrawing groups retarded the process. Hence, a linear free energy relationship of the Hammett equation type was used to correlate the reactivity with the Hammett substituent constants. Plots of log k_1 against the σ substituent constants gave values of $\rho = -4.0$ for both, styrenes and cinnamic acids. A hydrogen abstraction mechanism was unlikely, in view of the failure to induce the polymerization of acrylonitrile and the reduction of mercuric chloride. In most hydrogen abstraction reactions, the reaction constants have small magnitudes. In the present investigation, the values obtained for the reaction constant were $\rho = -4.0$. This suggested that the transition state possessed a large degree of carbonium ion character, resulting from a large amount of positive charge developing at the carbon atom adjacent to the benzene ring (α carbon atom). Earlier studies had shown that ρ values larger than -3 suggested a fairly large degree of carbonium ion character in the transition state(64,65).

The rate data showed that cinnamic acid was oxidized at a faster rate by quinolinium dichromate(QDC), as compared to crotonic acid. In cinnamic acid, the phenyl group exerted an electron-releasing effect which counteracted, in part, the electron-attracting effect of the carboxyl group. In crotonic acid, the reaction proceeded at a slower rate because the electron-attracting properties of the carboxyl group reduced the nucleophilic properties of the double bond. The reasonable conclusion from these data was that the electron-releasing effect of the phenyl group seemed to be greater than that of the alkyl group.

In the present investigation, the kinetic data obtained revealed that maleic acid reacted marginally faster than fumaric acid. This order of reactivity was explained on the basis of steric factors. The cis-attack of the two oxygen atoms of quinolinium dichromate(QDC) resulted in the formation of a cyclic intermediate, accompanied by a change in the hybridization of the olefinic carbon atom from the sp^2 to the sp^3 state. The cis-approach of the oxidant imposed an eclipsed conformation on the maleate species. The carboxylate groups were thus brought into closer proximity to each other, before the staggered conformation in the cyclic intermediate was obtained. This resulted in the reaction taking place at a marginally faster rate for the oxidation of maleic acid than that for the oxidation of fumaric acid.

The kinetic isotope effect showed a clear distinction between the α and β carbon atoms of styrenes (and cinnamic acids) in the transition state. For the oxidation of α-deuteriostyrene and cinnamic acid -α-d, the k_H/k_D values were 0.98 and 0.99, respectively. These values were reasonable, since the benzylic carbon atom (α carbon), in going from an olefinic centre to a carbonium ion-like character, during the process of electron abstraction, would remain sp^2 in character (attack being at the β carbon). For the oxidation of β,β-dideuteriostyrene and cinnamic acid -β-d, the k_H/k_D values were 0.80 and 0.78, respectively. These values indicated that, in the rate-determining step, the oxygen atom of quinolinium dichromate(QDC) attacked the terminal carbon atom (β carbon), and the change in the state of hybridization progressed from sp^2 towards sp^3 as the new bond was being formed. The hybridization of the benzylic carbon atom (α carbon) would remain essentially sp^2 in character, since it was going from an olefinic centre to a carbonium ion-like character. Since the oxidation of styrene (and of cinnamic acid) exhibited an inverse secondary deuterium kinetic isotope effect only at the β carbon atom, this suggested that the rate-determining step of the reaction produced a carbonium ion in which the α carbon atom remained sp^2 in character. The implication of this kinetic observation was that there was negligible C_α-O bond formation, but substantial C_β-O bond formation in the transition state.

The oxidation of alkenes by chromium(VI) reagents had often led to a variety of products. In some cases, allylic oxidation predominated, while in other cases, the oxidation had resulted in the formation of epoxides, ketols, acids or ketones. It had been suggested that the oxidation of alkenes by chromic acid involved an electrophilic attack of chromium(VI) at the double bond, with the formation of a cationic intermediate in the rate-determining step. It had also been shown that the oxidation of styrene by chromyl chloride exhibited an isotope effect only at the β-carbon, suggesting that the rate-determining step of the reaction produced a carbonium ion in which the α-carbon remained sp^2 in character(66).

The reaction pathway involved an acyclic process in the rate-determining step. The formation of the carbonium ion implied substantial C_β-O bond formation, an observation which was supported by the value of $\rho = -4.0$ (for styrenes and cinnamic acids), and by the kinetic isotope effects. The acyclic mechanism was further supported by earlier ab initio calculations on the energetics of such reactions, wherein the formation of a five-membered cyclic transition state was not favoured(67). In the present investigation, the application of the topological approach to the orbital levels of the transition state indicated that not all overlapping orbitals were bonding. Since such an orbital overlap picture did not satisfy the 4n rule, it was considered to be a Möbius-type system, and hence was a forbidden process. This implied that the reaction pathway involved an alternative route. Thus, the reaction route involved an acyclic mechanism which was not subject to selection rules.

In the present investigation, all the kinetic data and experimental evidence for the oxidation of the olefinic substrates (styrene, cinnamic acid and crotonic acid) by quinolinium dichromate(QDC), in acid medium, supported a reaction pathway involving an acyclic mechanism. The observation of an isotope effect only at the β carbon atom suggested the formation of a carbonium ion wherein the α carbon atom remained sp^2 in character. This was further supported by the value of the reaction constant, $\rho = -4.0$ for both, styrenes and cinnamic acids. The thermodynamic parameters obtained also supported an acyclic transition state. Energy considerations have established that an acyclic mechanism would be an allowed process for the oxidation of these substrates by quinolinium dichromate(QDC).

For the oxidation of the substrates under consideration (styrenes, cinnamic acids and crotonic acid), the kinetic data suggested the compatibility of an electrophilic attack of the protonated form of the oxidant(QDC) on the double bond of the substrate to give a carbonium ion. The carbonium ions thus formed, from the oxidation of styrene (and cinnamic and crotonic acid), were stabilized by the phenyl group. The intermediate thus formed reacted with a nucleophile (water), in the reaction mixture, to form a second unstable intermediate. In the presence of water and excess QDC, this intermediate was converted to the cyclic chromate ester, which was cleaved to give the observed products. The products formed, from the oxidation of styrene, were benzaldehyde and formaldehyde, which were characterized by spectral methods. The products obtained, from the oxidation of cinnamic acid, were benzaldehyde and glyoxylic acid, which were characterized by spectral methods. The products obtained, from the oxidation of crotonic acid, were acetaldehyde and glyoxylic acid, which were characterized by spectral methods. The formation of these products substantiated the mechanism of the oxidation reactions, wherein there was a cleavage of the carbon-carbon bond in the final step of the reaction.

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