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-tetrabutylammonium 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), \((\text{C}_9\text{H}_7\text{NH}^+\text{)}_2\text{Cr}_2\text{O}_7^{2-}\). 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-H₂O) 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-$\text{H}_2\text{O}$ 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$_2$O) 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, $\Delta[QDC]/\Delta[Substrate]$, 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 $\Delta H^\#$ against $\Delta S^\#$, was 498K. Although current views do not attach much physical significance to isokinetic temperatures, a linear correlation between $\Delta H^\#$ and $\Delta S^\#$ 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 ($\Delta G^\#$) 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.

This order of reactivity was rationalized on the basis of a change in ring strain involved, in passing from the initial state (sp³) to the transition state (sp²). 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 $\text{CHOH} \rightarrow \text{C}=\text{O}$. 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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\text{Scheme Image}
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+ Cr(IV)
SCHEME 2

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\text{[Reaction Diagram]}
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\[
\text{[Intermediate Structure]}
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\[
\text{[Final Product]}
\]

\[
\text{H} + \text{OH} \rightarrow \text{OH} \quad \text{Cr(IV)}
\]

\[
\text{[Intermediate Structure]} \rightarrow \text{[Final Product]}
\]

\[
\text{[Final Product]} + \text{Cr(IV)}
\]
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$_2$O) 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, $\Delta[QDC]/\Delta[Substrate]$, 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 $\Delta H^\ddagger$ and $\Delta G^\ddagger$, which suggested that the transition state was highly solvated. The negative entropies of activation ($\Delta S^\ddagger$) 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 $\sigma$ 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 (a carbon atom). Earlier studies had shown that $\rho$ 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 sp² to the sp³ 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-deuterio-styrene 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 sp² in character (attack being at the β carbon). For the oxidation of β,β-dideuterio-styrene 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 sp² towards sp³ 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 $\beta$ carbon atom, this suggested that the rate-determining step of the reaction produced a carbonium ion in which the $\alpha$ carbon atom remained $sp^2$ in character. The implication of this kinetic observation was that there was negligible $C_\alpha-O$ bond formation, but substantial $C_\beta-O$ 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 $\beta$-carbon, suggesting that the rate-determining step of the reaction produced a carbonium ion in which the $\alpha$-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-$\beta$-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 $\beta$ carbon atom suggested the formation of a carbonium ion wherein the $\alpha$ 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

\[
\begin{align*}
&\text{COOH} \\
&\text{H--C--} \\
&\text{H--C--} \\
&\text{COOH} \\
&+ \\
&\text{O} \equiv \text{Cr} \equiv \text{OH} \\
&\text{O} \equiv \text{Cr} \equiv \text{O} \text{O} \text{H}^+ \\
\rightarrow \\
&\text{HOOC}--\text{C--C--COOH} \\
&\text{OH} \\
&\text{O} \equiv \text{Cr} \equiv \text{OH} \\
&\text{O} \equiv \text{Cr} \equiv \text{O} \text{O} \text{H}^+ \\
\rightarrow \\
&\text{H--C--H} + \text{H--C--H} + 2\text{CO}_2 + \text{Cr(IV)}
\end{align*}
\]
SCHEME 1

\[
\text{Ph CH} = \text{CH}_2 + \text{O} \quad \text{Cr} \quad \text{OH} \quad \text{OQH}^+ \quad \rightarrow
\]

\[
\text{Ph CH} \quad \text{CH}_2 \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Ph CH} \quad \text{CH}_2 \quad \xrightarrow{\text{H}_2\text{O}}
\]

\[
\text{Ph CH} \quad \text{CH}_2 \quad \xrightarrow{\text{QDC}} \quad \text{Ph CH} \quad \text{CH}_2
\]

\[
\text{Ph CH} = \text{O} \quad + \quad \text{H}_2\text{C} = \text{O} \quad + \quad \text{Cr(IV)}
\]
SCHEME 2

\[
RCH = CHCOOH + \quad \xrightarrow{H_2O} \quad \xrightarrow{H_2O} \quad \xrightarrow{QDC} \quad \xrightarrow{H_2O} \quad \xrightarrow{Cr(IV)}
\]

- \( R = C_6H_5 \) (cinnamic acid)
- \( = CH_3 \) (crotonic acid)
REFERENCES


