MECHANISM OF OXIDATIONS BY CHLORINE

THESIS SUBMITTED FOR THE AWARD OF THE
DEGREE OF DOCTOR OF PHILOSOPHY
IN CHEMISTRY

BY

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Certified that the thesis entitled "Mechanism of Oxidations by Chlorine" which is being submitted by Shri Virendra Prakash Kudesia for the award of the Degree of Doctor of Philosophy in Chemistry of the University of Roorkee, is a record of students' own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other Degree.

This is further to certify that he has worked for a period of more than two years (From February 17, 1965 to February 25,1967) for the Ph.D. Degree at this University.

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February 25,1967

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PREFACE

The present investigation on the "Mechanism of Oxidations by Chlorine" has been undertaken under the guidance and supervision of Dr. S.K.Mukherjee, M.Sc.,Ph.D. He pointed out that although chlorine is frequently used for the disinfection of drinking water and waste waters, the detailed mode of its action as oxidizing agent has not been investigated.

The Sanitary Chemists advanced two views to account for the action of chlorine upon bacteria. According to the first view, chlorine on hydrolysis yields HOCl and HCl, and HOCl oxidizes some of the essential constituents of the bacterial cell. The second view is that the destruction of living organisms is brought about by direct chemical combination of chlorine with the protoplasm of the microorganisms. More data thus seems to be necessary in order to arrive at definite conclusions. Dr. Mukherjee suggested that a systematic kinetic study of the reactions of chlorine with simple organic molecules would throw light on the mechanism and with this view a general research scheme was prepared.

Chlorine is a powerful oxidizing agent. Its reversible electrode potential for the two electron reduction to Cl^- is 1.3583 Volts. It is known to hydrolyse in water to yield HOCl,H^+ and Cl^-. Beside these, Cl^+ and Cl_3^- ions have also been detected under different conditions. From a general chemical point of view, it is of prime importance (a) to investigate the causes that lead to the formation of different types of products by action of chlorine, (b) to find out if the oxidation involves the transfer of an oxygen atom from the oxidant molecule or it is a simple case of dehydrogenation of the organic compound, (c) to identify which of the species of chlorine in water, Cl_2, $HOCl$, Cl^+, Cl_3^-, or Cl^-, is the principal effective oxidant, (d) to know if the reaction is of electron-transfer type. If so, whether the reaction takes place by one electron or two electron step.

A complete elucidation of the above research project requires many sided investigations. To start with at the first instance, the kinetic study of the reactions of chlorine with monohydric alcohols and formaldehyde was alloted to the author by Dr.Mukherjee with a view to elucidate the mechanisms of these reactions.

A critical examination of the attempts made by various investigators to postulate the reaction mechanisms with chlorine shows that with aromatic compounds, generally the chlorination of the organic molecule, and with aliphatic compounds, complicated reactions, involving both oxidation and chlorination, take place. For example, Rodd(A) pointed out that chlorine attacks aqueous methyl alcohol quite easily. The dichloro di-methyl ether, $(Cl\,CH_2)_2O$, is first produced as an intermediate, which is

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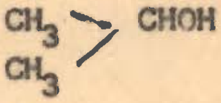
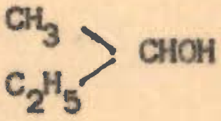
(A) E.H.Rodd," Chemistry of Carbon Compounds," Elsever Publ. Co., Amsterdam (1961), Vol.I, Part A, p.298, 305.

converted by water to formaldehyde and hydrochloric acid. Similarly, ethyl alcohol gets oxidized to acetaldehyde, which forms acetal with excess of alcohol. Further chlorination leads to the formation of mono and dichloroacetal, finally to chloral alcoholate. These complications further aggravate the kinetic investigations.

The following is the brief summary of the present investigation reported in this thesis :

The kinetics of reactions of

	1. Methyl Alcohol	CH_3OH
	2. Ethyl Alcohol	C_2H_5OH
	3. IsoPropyl Alcohol	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$
	4. Sec.Butyl Alcohol	 $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle CHOH$
and	5. Formaldehyde	$HCHO$

with chlorine in aqueous solution has been studied in detail. With all the above compounds the following investigations have been made :

(1) The orders of the reactions with respect to each reactant at various sets of concentrations in absence and in presence of perchloric acid have been determined. This we have done by considering initial rates.

(2) The influence of ionic strength on the reaction rates has been studied.

(3) The catalytic effects of about two dozen metallic salts on the reaction rates have been investigated.

(4) The rates of the reactions have been measured at various temperatures in the range of 25° to 55°C and the various activation parameters have been calculated.

(5) The products of the reactions have been identified and the alkyl hypochlorites have been isolated.

(6) The influence of sodium chloride on the reaction rates has been investigated in detail.

The reactions were found to be very complex. Besides oxidation, chlorination of the methyl group also follows through consecutive reactions. We established that molecular chlorine is the principal effective oxidant and hypochlorous acid plays a minor role in all the cases.

Consistent with the observed facts the mechanism of reactions of monohydric alcohols and formaldehyde with chlorine in aqueous solution have been proposed.

The initial rates of the reactions of seven aliphatic alcohols (Methyl, Ethyl, n-Propyl, Iso-Propyl, n-Butyl , IsoButyl and Sec.Butyl Alcohols) with chlorine in aqueous solution have been measured at 25° and 35°C with a view to find out the effect of structure of organic molecule on the reaction rate. The relative thermodynamic activation parameters, enthalpy, free energy, and entropy of activation, have been calculated and an attempt has been made to interpret the data in a proper way. The orders of the reactions of chlorine in aqueous solution with n-Propyl, n-Butyl and IsoButyl Alcohols with respect to each reactant in absence and in presence of perchloric acid have also been determined.

CHAPTER 1

GENERAL INTRODUCTION

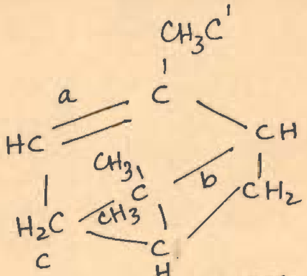
****

SEC. 1.1 ORGANIC OXIDATIONS :

On the basis of electronic theory, the statement that oxidation is equivalent to electron loss, resulting in an increase in the valency, and reduction to electron gain, resulting in a decrease in the valency of the elements, e.g.

$$Fe^{2+} \underset{\text{reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} Fe^{3+} + e$$

is adequate for describing reactions of ionizable substances. By developing this concept, electro chemists compare the oxidizing powers of different ions by reference to redox potentials, which are measures of free energy changes in thermodynamically reversible equilibria. These concepts, however, are not so clearly applicable in organic chemistry, for when carbon compounds are oxidized, their component atoms are very seldom deprived of their surrounding complete electron shells, e.g. no electronic or wave mechanic formulation of the structure of α- pinene can explain why it is attacked at the olefinic bond 'a' by dilute potassium permanganate, although at the C-C bond 'b' by only air and water, and at the allylic methylene group 'C' or 'C′' by selenium dioxide :



α - pinene

The study of the oxidation of organic compounds is an examination of ways by which electrons can be removed from them. The organic compounds are essentially covalent. Moreover, they are mainly composed of a carbon skeleton surrounded by a skin of hydrogen and consequently, have few superficial electrons accessible for direct attack by colliding reagents.

The covalent bond rupture is an essential feature of organic reactions, which can be effected by two different ways, viz. Homolysis, in which the electron - pair bond is broken symmetrically so that each fragment acquires complete control over one of the electrons and thus become a free, uncharged atom or compound radical, and Heterolysis, in which the electron - pair bond is broken unsymmetrically so that the two fragments become oppositely charged ions :

$$A{:}B \longrightarrow A^{*} + {}^{*}B \qquad \text{(Homolysis)}$$

$$A{:}B \longrightarrow A^{+} + ({:}B)^{-} \qquad \text{(Heterolysis)}$$

electron removals by these two ways have clearly distinguishable characteristics.

In Homolytic oxidations, the electrons are removed singly from organic molecules by active atoms or by active free radicals. They usually involve the removal from an organic molecule of one electron together with a hydrogen nucleus, e.g.

$$HO.CMe_2.CMe_2.OH + Mn^{3+} \xrightarrow{slow} {}^{*}O.CMe_2.CMe_2.OH + Mn^{2+} + H^{+}$$

The initial organic product necessarily has an unpaired electron and so must perforce undergo a reaction :(1)

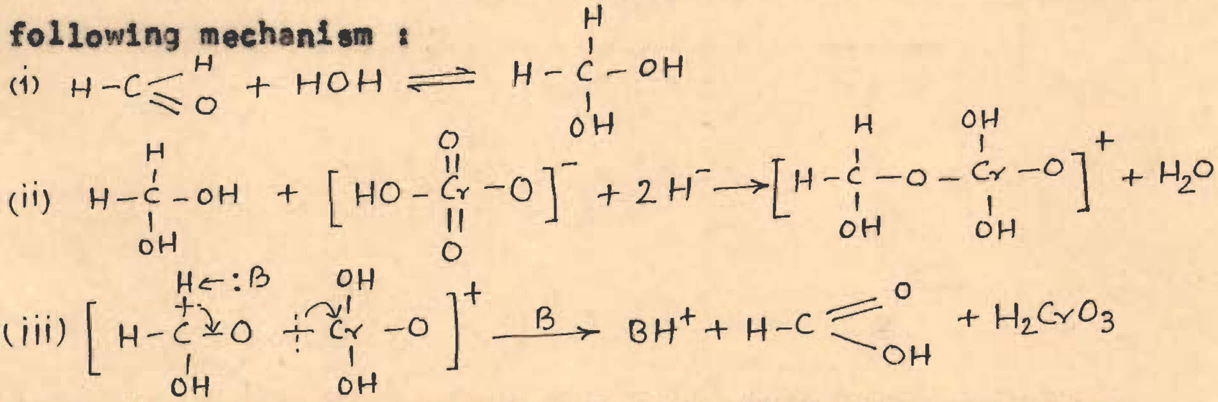
$${}^{*}O.CMe_2\ .\ CMe_2\ .\ OH \xrightarrow{Fast} Me_2\,C{=}O + {}^{*}C\ .\ Me_2\ .OH$$

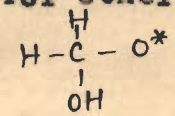
$$Mn^{3+} + {}^{*}C.Me_2\ .\ OH \xrightarrow{Fast} Me_2\,C{=}O + Mn^{2+} + H^{+}$$

$${}^{*}O.CMe_2\ .\ CMe_2\ .OH + Mn^{3+} \longrightarrow {}^{*}O.CMe_2\ .\ CMe_2O^{*} + Mn^{2+} + H^{+}$$

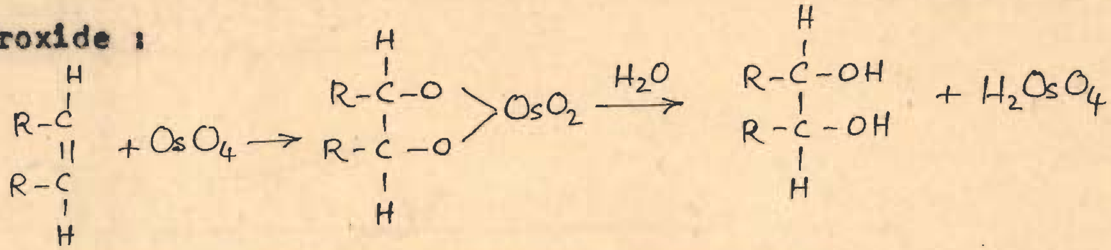
$${}^{*}O.CMe_2\ .\ CMe_2O^{*} \longrightarrow 2\ \ Me_2\,C{=}O$$

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents which can, by a single process, gain control of a further electron pair. Heterolytic oxidants, therefore, attack the exposed electron pairs of atoms such as oxygen, nitrogen or sulphur, or the loosely held π electrons of olefines, rather than the huried electron pairs of C-H, O-H or N-H bonds. A heterolytic oxidant thus approaches an organic molecule towards the region in which its valency electrons are most exposed. Further, heterolytic oxidations often involve sequences of reactions ending with the elimination from an organic complex of the oxidant together with its extra electrons. A simple example of heterolytic reaction is the chromic acid oxidation of formaldehyde. Chatterji and Mukherjee(2,3) suggested the following mechanism :



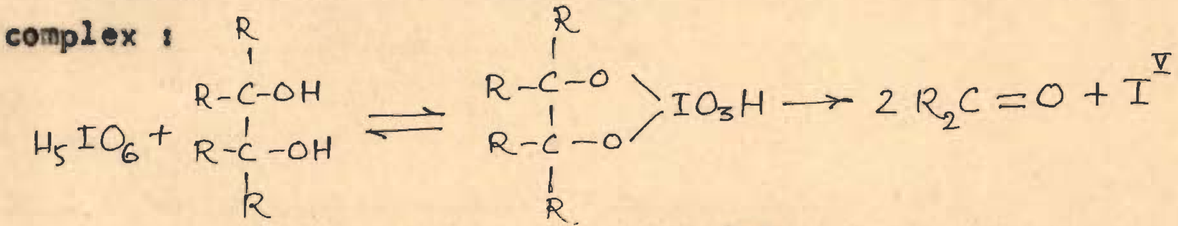
where B is a proton acceptor. In the elimination process (iii), the electron movements involve the C-H, C-O and O-CrO_3H_2 bonds simultaneously, for otherwise transient ions of very high energy content, e.g.  $H-\overset{H}{\underset{OH}{C}}-O^*$, would have to be formed. A count of electrons shows that whereas hydrated formaldehyde has 20 valence electrons in its molecule, formic acid has only 18 electrons. Thus two hydrogen nuclei together with two electrons have been removed by the oxidizer.

Criegee and coworkers(4,5) proposed the following mechanism of oxidation of alkenes to glycols with osmium tetroxide :



The hydrolytic cleavage presumably occurs at the O_s-O bonds in view of the stereospecificity of the reaction. This is a simple example of olefine oxidation.

The stereochemical considerations are of much greater significance in heterolytic than in homolytic reactions. For example, Bulgrin(6) and Buist et al(7) studied the rates of periodate oxidation of cis and trans - cyclopen--tanediol 1:2 and cis - and trans-cyclohexanediol 1:2 and showed that the greater reactivity of the cis - than the trans -isomers was caused, not by a greater ease of complex formation, but by a much more rapid break-down of the cyclic complex :

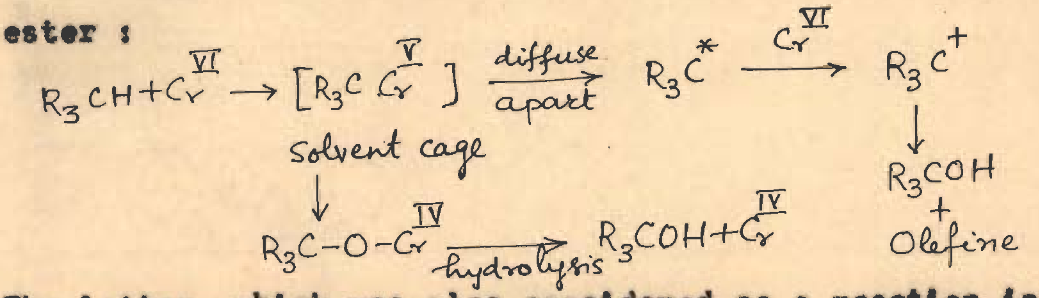


However, Zonis and Pesina(8) observed that there is no significant difference in the manganese tetraacetate oxidation rates of cis- and trans-cyclohexanediol 1:2 either in acetic acid or in tetrachloroethane. Similarly, Waters et al(9) found that cis - 1:2 dimethyl cyclohexanediol 1:2 is oxidized by manganic pyrophosphate much more slowly than its trans-isomer. They pointed out that the stereochemical significance should not be attached to simple measurements of relative rates of oxidation.

The majority of organic oxidations involve the cleavage of C-H or C-C bonds. A C-H bond may be broken homolytically by hydrogen atom abstraction, or heterolytically by either proton or hydride abstraction. The measurement of deuterium isotope effect had proved to be of great significance for elucidating the mechanism of oxidations, involving cleavage of C-H bond(10,11,12). Few examples of C-H bond cleavage are given below :

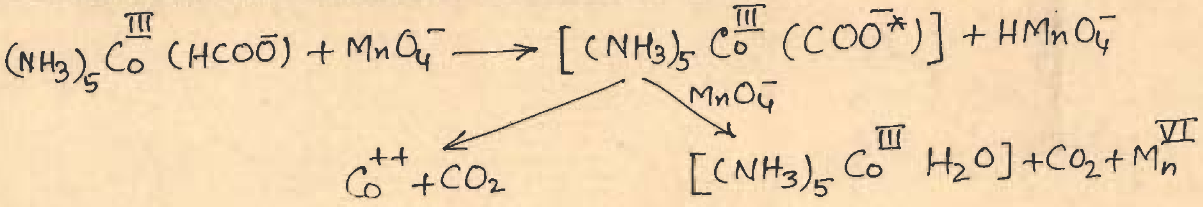
(a) <u>C-H Bond Cleavage by Hydrogen Atom Abstraction</u> :

Wiberg and Foster(13) suggested that in the chromic acid oxidation of hydrocarbons, a hydrogen atom transfer occurs, giving two radicals in a solvent cage, which may then either diffuse apart or combine to give a Cr (IV) ester :



The latter, which was also considered as a reaction intermediate by Slack and Waters(14), can cleave either at the Cr-O bond to give the alcohol with retension of configuration or at the C-O Bond to give partial racemization.

Recently Candlin and Halpern(15) suggested a hydrogen atom transfer mechanism for permanganate oxidation of formate ion complexed to cobalt (III) :

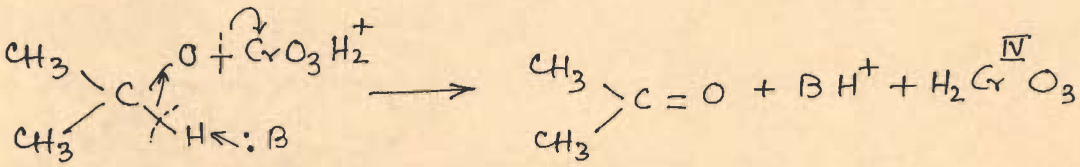


Only two examples of homolytic C-H bond cleavage are given here. The reader is referred to other works for discussion of reactions that proceed by this process(16-20).

(b) <u>C-H Bond Cleavage by Proton Abstraction</u> :

Chromic acid oxidation of isopropyl alcohol is an example in which the rate determining step is the proton abstraction. Westheimer and coworkers(21-23) used the tracer technique for the first time and showed that the rate controlling step in this oxidation involves the cleavage of secondary C-H bond, as indicated by the deuterium isotope effect, k_H/k_D, of 6.7 at 25°C. They suggested a mechanism, in which the chromate ester decomposes by proton loss to any available base with elimination of a Cr^{iv} ion :

$$(CH_3)_2CHOH + HCrO_4^- + 2H^+ \longrightarrow (CH_3)_2CHO\cdot CrO_3H_2^+ + H_2O$$



followed by, $Cr^{iv} + Cr^{vi} \xrightarrow{fast} 2Cr^V$

$$2Cr^V + 2(CH_3)_2CHOH \xrightarrow{fast} 2Cr^{III} + 2(CH_3)_2C{=}O + 4H^+$$

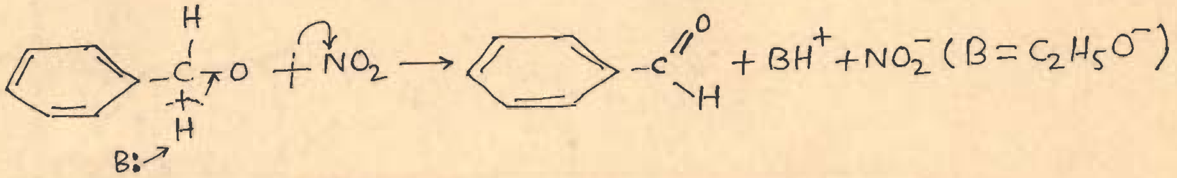
or, in presence of Mn^{++} ions, by

$$Cr^{iv} + Mn^{ii} \longrightarrow Cr^{iii} + Mn^{iii}$$

$$Cr^{iv} + Mn^{iii} \longrightarrow Cr^{iii} + MnO_2$$

Recently Chatterji and Mukherjee(3) concluded that the chromic acid oxidation of alcohols proceed via chromate ester as intermediate, by showing that pyridine, a proton accepter, accelerates the rates of oxidation of alcohols.

Another example of proton abstraction in the rate determining step is the carbonyl elimination reaction that benzyl nitrate undergoes under the influence of base to produce benzaldehyde and nitrite ion(24)

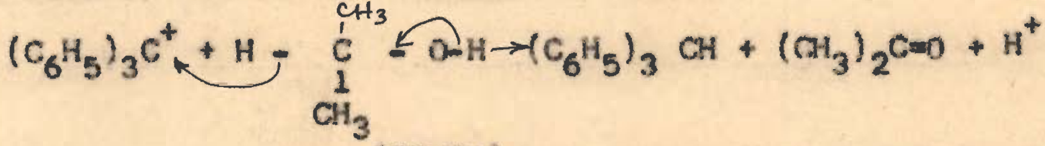


Buncel and Bourns(25) showed that α C-H bond rupture occurs in the rate controlling step, as indicated by isotope effect, k_H/k_D, of 5.04 at 60°C for the reaction of $C_6H_5\,CD_2ONO_2$

(c) C-H Bond Cleavage by Hydride Abstraction :

Hydride transfer now seems to be the general route for the heterolytic oxidation of alcohols by reagents which cannot react by way of esterification. A clear cut example is the oxidation of an alcohol by triaryl carbonium ion, which occurs in mineral acid solution(26);

$$(C_6H_5)_3\,C\text{-}OH + H_3O^+ \rightleftharpoons (C_6H_5)_3C^+ + 2H_2O$$



$$(C_6H_5)_3C^+ + H - \underset{CH_3}{\overset{CH_3}{C}} - O\text{-}H \rightarrow (C_6H_5)_3\,CH + (CH_3)_2C{=}O + H^+$$

Stewart(27,28) suggested a hydride ion transfer mechanism for the oxidation of benzhydrol, $(C_6H_5)_2\cdot CHOH$, by potassium permanganate in neutral and basis solutions:

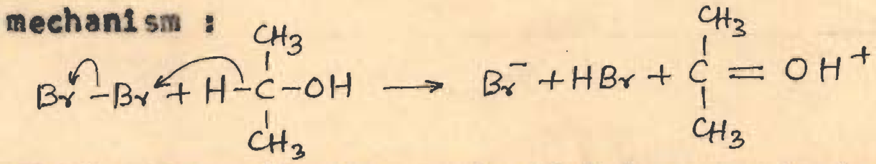
$$(C_6H_5)_2\,CHOH + OH^- \rightleftharpoons (C_6H_5)_2\,CHO^- + H_2O \quad \text{(rapid equilibrium)}$$

$$(C_6H_5)_2\,CHO^- + MnO_4^- \rightarrow (C_6H_5)_2\,C{=}O + HMnO_4^{=} \quad \text{(Slow)}$$

$$HMnO_4^{=} + MnO_4^- + OH^- \rightarrow 2MnO_4^{=} + H_2O \quad \text{(fast)}$$

He also noted an isotope effect, k_H/k_D, of 6.6 at 25°C for the cleavage of secondary C-H Bond.

For the oxidation of isopropyl alcohol by bromine, Swain et al(29) proposed a hydride abstraction mechanism :

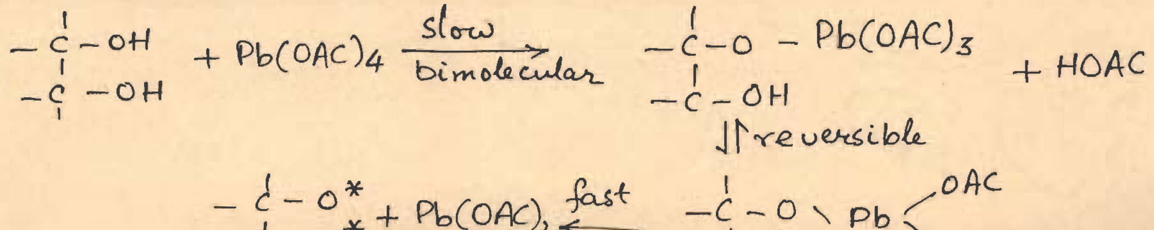


$$Br{-}Br + H{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH \longrightarrow Br^- + HBr + \overset{CH_3}{\underset{CH_3}{C}}{=}OH^+$$

on the theoretical grounds that isopropyl alcohol exhibits C-H and O-H isotope effects of 2.94 and 1.49, whereas 1 - Fluoro - 2 propanol exhibits C-H and O-H isotope effects of 2.83 and 2.06, The constancy of the value for C-H suggests a hydride transfer.

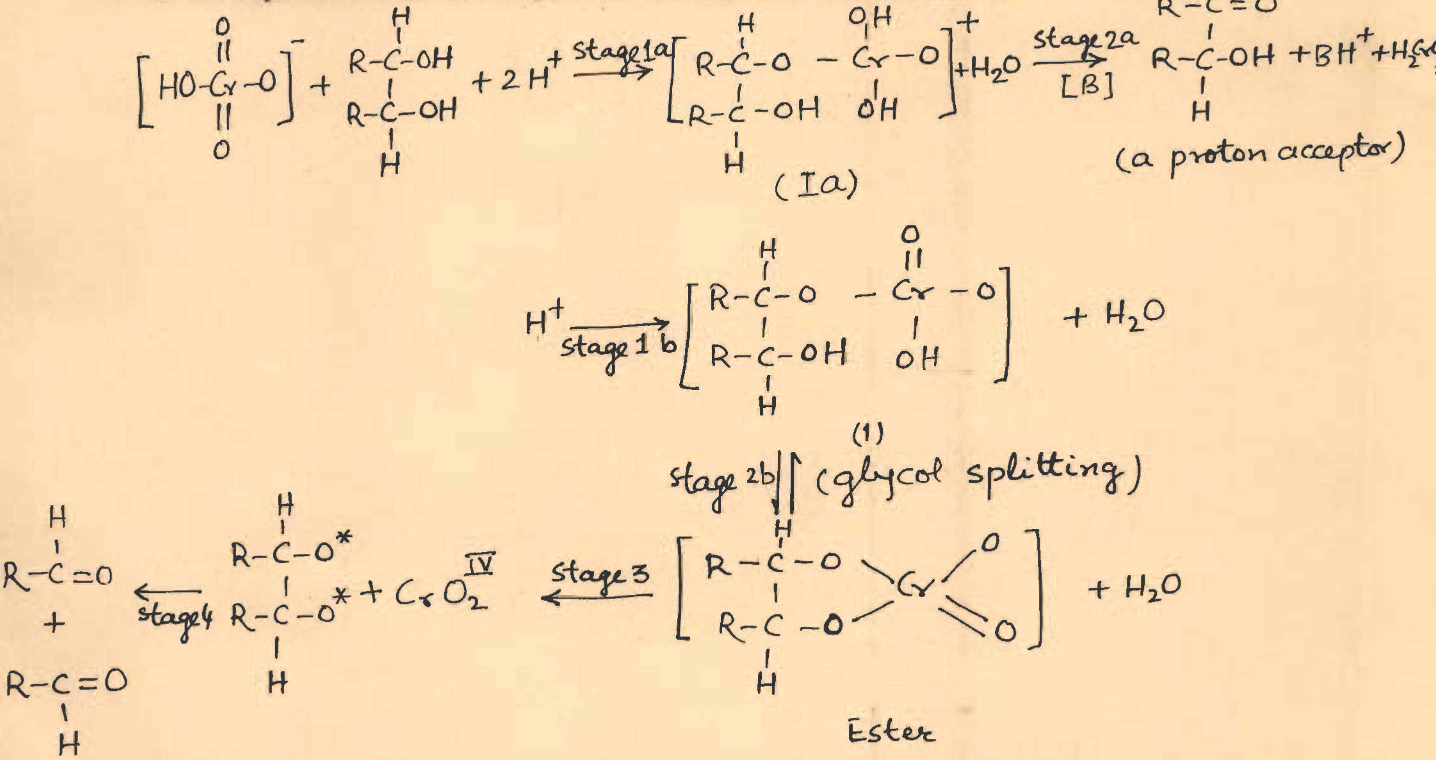
C-C Bond Cleavage :

The cleavage of C-C bond of 1:2 glycols by cold solution of lead tetraacetate in glacial acetic acid was first noticed by Criegee. From a very careful kinetic investigation, Criegee and coworkers(31-33) arrived at the conclusion that the glycol splitting involves a rate determining bimolecular reaction, which they represented as a cyclic heterolytic process, for they found that the cis - glycols of 5- and 6 - membered alicyclic rings were oxidized very much more easily than their trans-isomers :

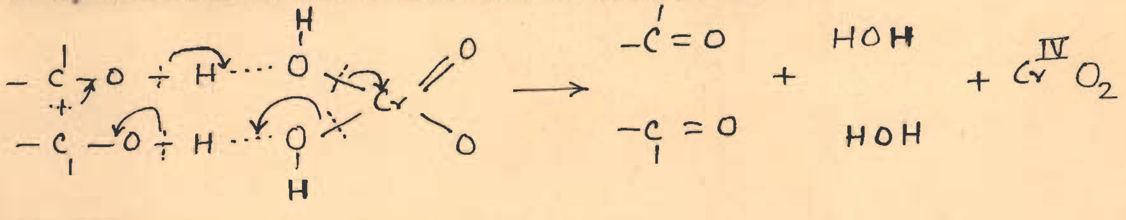


$$\begin{matrix}-\overset{|}{C}-OH\\ -\underset{|}{C}-OH\end{matrix} + Pb(OAC)_4 \xrightarrow[\text{bimolecular}]{\text{slow}} \begin{matrix}-\overset{|}{C}-O-Pb(OAC)_3\\ -\underset{|}{C}-OH\end{matrix} + HOAC$$

Several oxidizing agents, such as periodic acid(34), aryl iodosoacetates(35), manganic pyrophosphate(1) manganese tetraacetate(8), chromyl chloride(36), ceric ions(37), sodium bismuthate(38) etc. can break the C-C bonds of even primary and secondary glycols, e.g. $HO.CH_2.CH_2.OH$, but more recently it has been found that several oxidants of monohydric alcohols can effect C-C bond rupture of di-tertiary alcohols, such as pinacol, though they tend preferably to oxidize primary and secondary 1:2 glycols by C-H bond rupture. For example, Chatterji and Mukherjee(39-41) suggested the following mechanism for chromic acid oxidation of ethylene and methylated ethylene glycols :



They suggested the following mechanism of electron displacement in the activated complex :



Transition state

Rocek and Westheimer(42) found that cis - 1:2 dimethyl cyclopentane 1:2 diol oxidizes 1700 times as fast as its trans - isomer and 47 times as fast as does pinacol. This difference in reaction rates provides the best evidence for the formation of acyclic intermediate compound.

SEC. 1.2 THE HYDROLYSIS OF CHLORINE :

The gaseous chlorine hydrolyses in pure water to yield HOCl, H^+ and Cl^-. Since long there had been disagreement of views regarding the mechanism of the hydrolysis and actual value of hydrolysis constant. Jakowkin(43) measured the hydrolysis constant at various temperatures as early as in 1899. Liebhafsky(44) pointed out that the heat of hydrolysis of chlorine varies with temperature. He interpreted the results of Jakowkin as indicating the existence of hydrated chlorine in equilibrium with non hydrated or less hydrated chlorine, with the equilibrium shifting with temperature.

Shilov and Solodushenkov(45) noticed that the reaction substantially completes in less than a second even at 1°C. Morris(46) found that the rate constant for the reaction is about 5×10^{14}, indicating that reaction occurs at almost every collision. He proposed a mechanism in which the hydroxyl ion reacts with chlorine :

$$Cl_2 + OH^- \rightleftharpoons HO\,Cl + Cl^-$$

He pointed out that the results of Solodushenkov and Shilov can be explained properly by this type mechanism.

Several investigators(45,47,48) determined the hydrolysis constant by different methods but their values vary from 2.09×10^{-4} upto the value close to Jakowkin at 25°C (4.48×10^{-4}). A large number of investigators(46,49-52) recalculated the values of the hydrolysis constant at different temperatures obtained by Jakowkin by making different assumptions. The recalculated values at 25°C were found to be in the range of 4.84 to 3.90 x 10^{-4}.

Recently Connick and Chia(53) repeated the Jakowkin's measurements and determined more accurately the values of hydrolysis constant at various temperatures from 0° to 45°C, using conductivity method. In agreement with the observations of earlier investigators, Connick and Chia found the reaction to have a positive ΔH^o, which changes quickly with temperature, corresponding to a value of ΔC_p^o of approximately - 93 cals. $mole^{-1}$ deg^{-1}. They argued that the properties of Cl_2 (aq) are responsible for this value and discussed the significance of the large heat capacity of this species in terms of plausible models. In calculation, they took into consideration the following :

(i) in addition to the formation of H ClO, H^+ and Cl^-, a minute quantity of Cl_2O which also forms through the volatility of HClO in the preparation of Cl_2, and

$$2\ HClO\ (aq) \longrightarrow Cl_2O(g) + H_2O$$

(ii) the formation of Cl_3^- from Cl_2 and Cl^-:

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^-$$

The equilibrium constant ef this reaction was reported to be 0.18 at 25°C.

The values of the hydrolysis constant K_h $(3.94 + 0.02) \times 10^{-4}$ at 25°C and (5.104 ± 0.021) at 35°, obtained by Connick and Chia(53) agrees well with the values obtained by Zimmerman and Strong(52) by recalculation of Jakowkin's data.

Frank and Evans$^{(54)}$ have proposed that non polar gases dissolved in water cause the formation of ordered arrangements of water around them - "iceberg" - whose "melting" with increasing temperature is a source of large Cp^o. Such configurations might correspond to partially formed gas hydrate structures$^{(55\text{ to }58)}$ for which it is known that the water molecules, while being hydrogen bonded to each other, leave holes for gas molecules which perhaps interact through London forces with the atoms on the inner surface of the holes.

In a series of papers, Lifshitz and Perlmutter Hayman$^{(59)}$ reported data on kinetics and mechanism of hydrolysis of chlorine. They argued that the mechanism (1) is correct and not the (2) originally suggested by Morris$^{(46)}$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{1}$$

$$OH^- + Cl_2 \rightleftharpoons HOCl + Cl^- \tag{2}$$

They discussed two possible schemes of the reaction mechanism :

SCHEME A:

$$Cl_2 + A^- \longrightarrow ACl + Cl^- \tag{a}$$

$$ACl + H_2O \longrightarrow AH + HOCl \tag{b}$$

where A^- is the anion of weak acid, HA.

SCHEME B:

$$H_2O + Cl_2 + A^- \xrightarrow{K_{\bar{A}}} HOCl + Cl^- + HA \tag{c}$$

OR

$$Cl_2 + H_2O + A^- \longrightarrow HOCl_2^- + HA \tag{d}$$

$$HOCl_2^- \longrightarrow HOCl + Cl^- \tag{e}$$

They discarded the scheme C:

$$Cl_2 + H_2O \rightarrow H_2ClO^+ + Cl^- \qquad (f)$$

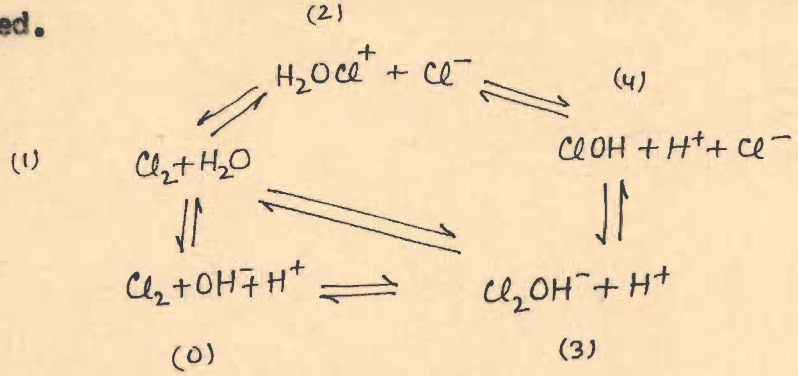
$$H_2ClO^+ + A^- \longrightarrow HA + HOCl \qquad (g)$$

because it does not account for the accelerating influence of A^- unless (f) is a rapid pre-equilibrium. For (a) or(f) to be rapid equilibrium, the rate of reaction would have to be inversely proportional to the concentration of the chloride formed during the reaction, which they had not observed. Their results support the scheme B to represent the mechanism of the reaction.

Independently, Eigen and Kustin$^{(60)}$ also studied the Kinetics of chlorine hydrolysis by the temperature jump relaxation technique. They found the rate constant K_{Cl_2} of the overall reaction mechanism :

$$Cl_2 + H_2O \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} Cl^- + H^+ + HOCl$$

to be 11.0 sec^{-1}. The following possible mechanism were proposed.



but the arguments put forward by them support the view that the hydrolysis occurs via the intermediate $Cl_2 \cdot OH^-$ as was also suggested by Lifshitz and Perlmutter - Hayman (That is, the reaction proceeds via $Cl_2 + H_2O \longrightarrow Cl_2 \cdot OH^- + H^+ \longrightarrow HOCl + H^+ + Cl^-$)

It appears that the hydrolysis constant values now reported by Connick and Chia(53) are accurate, because they took into consideration various factors responsible for influencing the values of K_h at different temperatures.

SEC. 1.3 SURVEY OF LITERATURE ON REACTIONS WITH CHLORINE:

Chlorine is a powerful oxidizing agent. Its reversible electrode potential for the 2 - electron reduction to Cl^- is 1.3583 Volts(61). A survey of the literature reveals that although a large number of oxidizing agents have been used to oxidize organic and inorganic compounds, the detailed mode of action of chlorine as oxidizing agent has not been investigated fully. The probable reason for its being neglected was the difficulty in its handling for kinetic studies, the uncertainty regarding its species taking part in the oxidation - reduction reactions and also the consecutive chlorination, particularly of organic compounds.

Among the earlier studies, one was on the oxidation of aqueous methyl alcohol by Chlorine(62), in which it was demonstrated that the intermediate compound is dichloro dimethyl ether $(ClCH_2)_2O$, which converts by water into formaldehyde and hydrochloric acid. Griffith and coworkers(63) reported the reactivity of HOCl in the oxidation of acid oxalate ion by aqueous chlorine.

Taube(64 and 65) studied the kinetics of the reaction of oxalic acid with chlorine, induced by ferrous (64) and manganic ions(65) over a wide range of conditions and suggested a chain mechanism, involving atomic chlorine :

Chain initiating step(4)

$$Fe^{++} + Cl_2 \longrightarrow Fe^{+++} + Cl_2^- \text{ or } FeCl^{++} + Cl$$

Chain carrying steps

$$H_2C_2O_4 \rightarrow HC_2O_4^- + H^+ \quad \text{(rapid equilibrium)}$$

$$Cl + HC_2O_4^- \xrightarrow{K_2} H^+ + Cl^- + C_2O_4^-$$

$$C_2O_4^- + Cl_2 \xrightarrow{K_3} Cl + Cl^- + 2CO_2$$

Chain breaking steps

$$Cl + C_2O_4^- \xrightarrow{K_4} Cl^- + 2\,CO_2$$

$$Cl + Cl \xrightarrow{K_5} Cl_2$$

In the presence of manganic ion, he(65) observed that (i) the initial rate of reaction is independent of the concentration of chlorine, is first order with respect to catalyst concentration, and varies in a complex manner with the concentration of oxalic acid. The rate follow the equation

$$\frac{-\,d\,(Cl_2)}{dt} = K \left[Mn\ (III)\right]_0$$

(ii) at low oxalic acid concentrations, the rate is decreased because the complex $Mn\ C_2O_4^+$ is appreciably dissociated into a chloro manganic complexion and oxalic acid. Hochhauser and Taube(66) proposed the following mechanism for the direct and ferric ion sensitized photochemical reaction of chlorine with oxalic acid :

Chain initiating steps

$$Fe^{++} + Cl_2 \rightarrow FeCl^{++} + Cl$$

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Fe^{+++} + \text{a nion} \rightarrow Fe^{++} + Cl \text{ or } Fe^{+++} + C_2O_4^-$$

Chain carrying steps

$$H_2C_2O_4 \rightarrow H^+ + HC_2O_4^- \quad \text{(rapid)}$$

$$Cl + HC_2O_4^- \rightarrow H^+ + Cl^- + C_2O_4^-$$

$$C_2O_4^- + Cl_2 \rightarrow 2\ CO_2 + Cl + Cl^-$$

Chain breaking

$$Cl + Cl \rightarrow Cl_2$$

Chapman(67) observed that the oxidation of chloroform with chlorine proceeds without accompanying thermal or chlorination reactions; the products formed are phosgene and hydrogen chloride.

West and Rollefson(68) found that the photochemical reaction of chlorine with formic acid is a chain reaction, which proceeds at least partially through chloroformic acid; the final products are CO_2 and HCl :

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$Cl + HCOOH \rightarrow COOH + HCl$$

$$COOH = CO_2 + H$$

$$COOH + Cl_2 \rightarrow ClCOOH + Cl$$

$$H + Cl_2 \rightarrow HCl + Cl$$

$$ClCOOH = CO_2 + HCl$$

Shilov et al(69,70) as well as Thamsen(71) found that the formic acid is oxidized readily to carbon dioxide by chlorine in aqueous solution. The path involving formate ion is about 10^4 times faster than that involving neutral formic acid. Since a 1 -equivalent reaction between chlorine and formate ion is unlikely, a hydrate transfer appears to be the most satisfactory mechanism in this case :

$$H\,COO^- + Cl_2 \rightarrow CO_2 + HCl + Cl^-$$

In basic solution, chlorine forms ClO^-, which appears to be unable to oxidize formate ion at all. In neutral solution, the presence of a second order term in OCl^- in the rate law suggests that Cl_2O, which is known to be in equilibrium with HOCl is the active oxidant. They demonstrated that chloride ions accelerate the reaction.

The reaction between ethyl alcohol and chlorine was studied under various experimental conditions by several investigators(72 to 77). Lieben(72,73) pointed out that the chlorination of ethyl alcohol yields acetaldehyde as an intermediate. Fritzsch(74) detected the formation of diethyl acetal as an intermediate in the chlorination of ethyl alcohol. Malhotra(77) found that the vapour phase chlorination of ethyl alcohol under silent electric discharge yields chloral and hexachloroethane as the main chlorinated products. He pointed out that the chlorination of acetaldehyde, which is formed during the reaction, proceeds through its polymers to sym, - trichloro paraldehyde and then to monochloroacetaldehyde :

$$\begin{tikzcd}
C_2H_5OH \arrow[r, "Cl_2"] & CH_3\ CHO \arrow[r, "Cl_2"] & CH_2\ Cl\ \ CHO \\
(CH_3CHO)_3 \arrow[ur, shift left, "HCl"] \arrow[r, "Cl_2"] & (Ch_2Cl\ \ CHO)_3 \arrow[from=1-2, to=2-1, shift left] &
\end{tikzcd}$$

The final product of the chlorination of acetaldehyde, paraldehyde and dichloroacetaldehyde was found to be C_2Cl_6

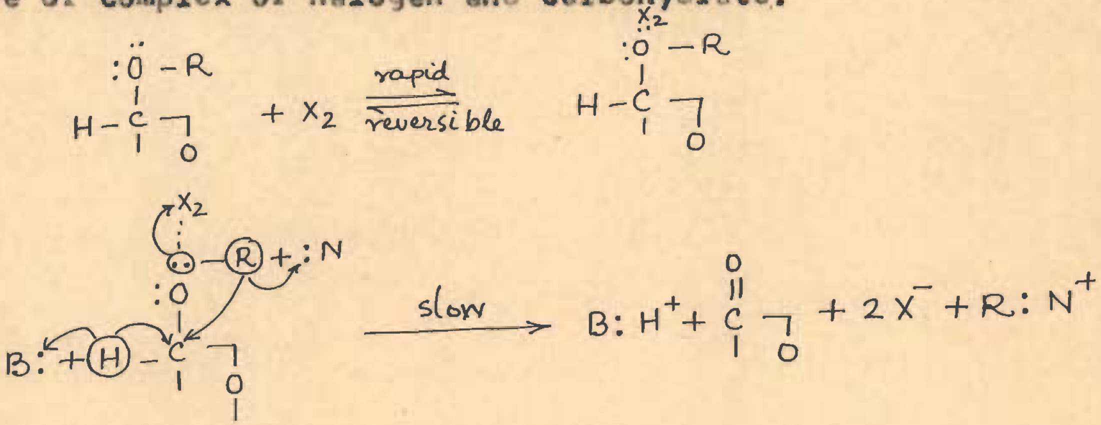
in all the cases.

Shilov and Yasnikov(78) studied the oxidation of glycol aldehyde and D-glucose by active chlorine in aqueous solution. In the range pH 5 to 13.5, the rate was found to increase with pH in a complex manner. They concluded that in the acid medium the active agent is chlorine and in neutral or weakly alkaline medium, it is HOCl.

The oxidation of glucose with chlorine in acid aqueous solution was investigated by Lichtin and Saxe(79), who concluded, from the variation of the specific rate both during the course of the reaction and with change in the initial concentration of the oxidant, added chloride ion and hydrogen ion, that chlorine is much more reactive than HOCl. At pH 2.2, the reaction follows the rate law :

$$v = K_2 \left[Cl_2\right] \quad \left[\text{glucose}\right]$$

They suggested a mechanism, which involves the attack of a base of complex of halogen and carbohydrate.



Here B: and N: represent any base, including water, or for the glycosides N: represents any nucleophilic reagent. R is either hydrogen or alkyl group.

Bognar and Somogyi(80) suggested a new method of isolation of D-fructose and D-mannose from the oxidation of D-mannitol by chlorine.

Kozinenko and Shilov studied the oxidation of m-benzaldehyde sulfonate ion(81), p- and o -benzaldehyde sulfonate ion(82) and m-hydroxy methyl benzene sulfonate ion(83) by active chlorine. They obtained the following rate equation :

(i) In 0.1M HCl, $-\frac{dC}{dt} = K \, [I] \, [Cl_2]$

where $I \mp$ concentration of organic compound.

(ii) At pH 4-13 in presence of buffers,

$$-\frac{dC}{dt} = K_o^A \, [HOCl] + K_o^A \, [HOCl] \, [B] + K_{OH}^{-} \, [A] \, [HOCl] \, a_{OH}^{-}$$

where A = concentration of organic compound,

and B = concentration of buffer ion.

Spence and Wild(84) studied the thermal reaction between formaldehyde and chlorine. The reaction was found to proceed either by an explosion or by a relatively slow process, depending on temperature, pressure and condition of the reaction vessel. They concluded that the slow reaction is preceded by an induction period and that an excess of formaldehyde present is decomposed into carbon monoxide and hydrogen.

Krauskopf and Rollefson(85) noticed that the photochemical reaction between chlorine and formaldehyde is very rapid and the chief products of the reaction are carbon monoxide and hydrogen chloride with the gradual formation of phosgene from carbon monoxide and excess of chlorine. Formaldehyde polymerises during the reaction at 80°. A possibility of the formation of dichloro methyl ether with hydrogen chloride and formaldehyde was also suspected. They preferred the mechanism (c) among the different possibilities of chlorine - formaldehyde reaction :

$$CH_2O + Cl_2 \longrightarrow COCl_2 + H_2 \qquad (a)$$

$$CH_2O + 2Cl_2 \longrightarrow COCl_2 + 2\,HCl \qquad (b)$$

$$CH_2O + Cl_2 \longrightarrow COHCl + HCl \qquad (c)$$

The formation of formyl chloride was detected by the preparation of an asymmetrical form - m - xylidide derivative. They(86) further pointed out that the mechanism proposed to account for the photochemical change is applicable to the thermal process as well.

Kinetic studies on the addition of HClO to olefinic compounds in aqueous solution have been carried out by Schilov and coworkers(87,88) who studied the rates of addition of HOCl to crotonic acid, ethylene(89 to 91) and but -2- ene - 1:4 - diol. Israel and coworkers(92,93) found that the reaction between HOCl and crotonic acid or crotonate ion follow the rate equation :

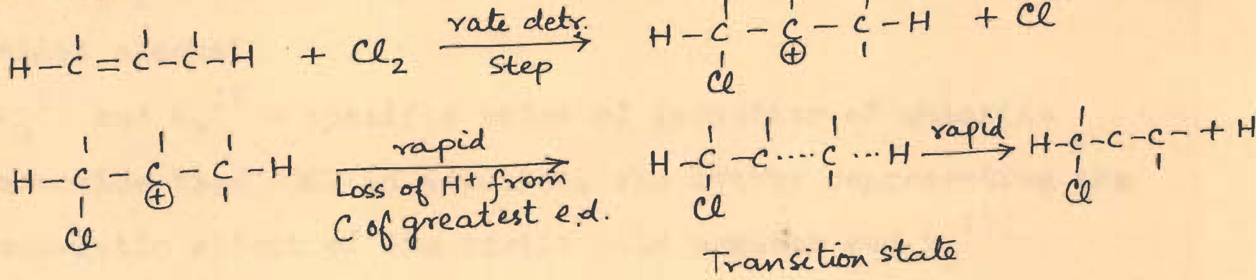
$$v=k_2^{I}\,[HOCl]\,[R.CO_2H] + [R.CO_2^-] + \left(k_2^{II} + k_3^{II}\,[R.CO_2H]\right)(HOCl)^2$$

where $R = CH_3.\ CH{:}\ CH$

k_2^{II} and k_3^{II} are interpreted as being the specific rates of formation of Cl_2O from HClO, the latter being specific rate of formation of catalysed by crotonic acid. The reaction of HClO with ethyl crotonate in aqueous solutions in the presence of sodium acetate acetic acid buffer of pH 4.74 conforms to the velocity equation

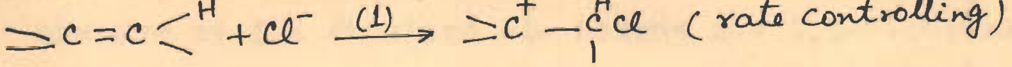
$$V = K_2^{I}\,[HOCl]\,[E_tR] + K_3^{II}\,[HOCl]^2\,[E_tR] + K_3^{III}\,[HOCl]\,[HOAC]\,[E_tR]$$

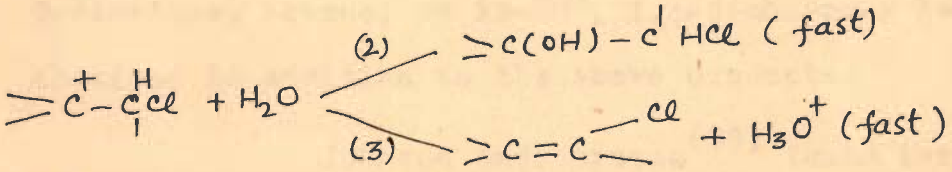
Taft(94) suggested an ionic mechanism for the substitution in the low temperature non activated chlorination of olefins.



$$H^+ + Cl^- \longrightarrow HCl$$

De la Mare, Hughes and Vernon(95) studied the kinetics of the reaction of chlorine with olefins by treating olefins with 0.002M HOCl in the presence of 0.1M $HClO_4$ and $AgClO_4$ at 25°. They proposed the following mechanism :





In aromatic series, step (2) is supposed in favour of (3), giving the reasonable stabilized structure, ArCl.

According to Israel and coworkers$^{(96,97)}$, the addition of HClO to allyl alcohol in aqueous solution and in the presence of sodium acetate - acetic acid buffers conform to the kinetic equations (1) and (2) respectively :

$$v = k_2^{I} \left[HOCl\right] \left[C_3H_5OH\right] + k_2^{II} \left[HOCl\right]^2 \qquad (1)$$

where k_2^{I} and k_2^{II} are interpreted as being the specific rates of two simultaneous reactions, k_2^{I} being that for direct addition of HClO to allyl alcohol, and k_2^{II} that for formation of Cl_2O from HClO in solution, and

$$v=k_2^{I}\left[HOCl\right] \left[C_3H_5OH\right] + \left[k_2^{II}+ k_3^{II}(HOAC)\ (HOCl)^2+ k_3^{III}(HOCl)\cdot(HOAC$$

~~(HOAC)~~

where k_2^{I} = specific rate for direct addition of HClO to allyl alcohol

k_2^{II} and k_3^{II} = specific rates of formation of chlorine monoxide from HOCl in solution, the latter representing the catalytic effect of the acetic acid present and k_3^{III} represents the specific rate of formation of acetyl hypochlorite by the reaction :

$$Ac\ OH + HOCl \longrightarrow Ac\ OCl + H_2O$$

Verbanc and Hennion$^{(98)}$ observed that the chlorination of 1-hexyne in methanol at 0-5^{0} yielded a mixture of 1,2 dichloro -1- hexene and 1,1-dichloro-2, 2-dimethoxy hexane. At 25-30^{0}, 1,1-dichloro-2 hexanone was obtained in addition to the above products.

Johnson and Sprague$^{(99)}$ found that

(i) nitrogen substituted iso thiourea salts interact with chlorine in aqueous solution to form a sulphonyl chloride and cyanamide hydrochloride, (ii) N-alkyl substituted isothioureas yield sulphonyl chloride and the corresponding alkyl cyanamide derivatives.

Baum, Vogt and Hennion(100) isolated the products, methyl chloride, 1-chloro-2 methoxy -1,3-butadiene, 1,1,4 trichloro-2 butanone, and 1,1,4 -trichloro-2, 2-dimethoxy butane of the chlorination of vinyl acetylene in methanol.

Anbar and coworkers(101,102) found that the reaction between t-butyl alcohol and HClO is subject to general acid-base catalysis and that the rate of reaction is independent of alcohol concentration. By use of O^{18} as tracer, they demonstrated that in both the formation of ester and its hydrolytic reactions under alkaline and acid conditions, the bond between tertiary butyl group and the oxygen atom remains intact. They interpreted the kinetics and isotopic reactions in terms of the following generalized mechanism :

$$\left.\begin{array}{l} HOCl + HA \rightleftharpoons ACl + H_2O \\ ACl + Bu\,OH \rightleftharpoons BuOCl + HA \end{array}\right) \quad \text{Acid region}$$

$$\left.\begin{array}{l} HOCl + Cl^- = ACl + OH^- \\ ACl + BuO^- = BuOCl + A^+ \end{array}\right) \quad \text{alkaline region}$$

Jungers and coworkers(103,104) found that the reaction between chlorine and acetic anhydride in presence of ICI, $FeCl_3$ and $SnCl_4$ as catalyst is first order with respect to the catalyst and zero order with respect to chlorine.

A detailed kinetic study of the chlorination of acetone in aqueous solution was made by Bell and Yates,(105) who demonstrated that at higher chlorine concentrations, the reaction is of zero order with respect to chlorine, both in solutions of strong acids and in acetate buffers and at low chlorine concentrations, the velocity in acid solutions becomes proportional to the chlorine concentration. They suggested the following reaction mechanism :

$$SH + H^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} HS + H^+$$

$$HS + Cl_2 \xrightarrow{K_2} SCl + H^+ + Cl^-$$

where SH and HS are keto-and enol-form of acetone, respectively (The formation of the enol- is actually believed to involve the rapid reversible addition of a proton to oxygen, followed by transfer of a proton from carbon to a water molecule).

The kinetic investigations on chlorination of aromatic compounds were made by a number of investigators(106 to 118) in which a simple law

$$-\frac{d\ (Cl_2)}{dt} = K_2\ [ArH]\ [Cl_2]$$

was established for many systems of widely different structures and reactivities. The influence of added electrolytes shows that the electrophile(119 to120) is molecular chlorine. Further, it has been accepted that these reactions are processes of substitution in the aromatic nucleus and that (in the absence of certain recognisable structural complications) the effects of substituents on the rate are independent and additive. It has also been reported that hydrogen chloride generated in the reaction, results in small autocatalysis(110).

De la Mare and coworkers(121), while studying the kinetics of the chlorination of phenol and anisole, suggested the importance of chlorine cation in the reaction.

$$Cl^+ + ArH \longrightarrow ArHCl$$

$$ArHCl \longrightarrow ArCl + H^+$$

They further stated that the rates of chlorination are of zero order with respect to the compound substituted and first order with respect to HOCl.

The results of De la Mare and coworkers(121) were criticized by Shilov(122), who interpreted these results in terms of rate controlling production of free chlorine from HOCl and traces of chloride ion.

Derbyshire and Waters(123) studied the kinetics of chlorination of sodium toluene - ω-sulphonate by HOCl in presence of sulphuric or perchloric acid as catalyst. The reaction was found to be second order, involving cations, Cl^+ or $(H_2OCl)^+$.

In a detailed kinetic investigation of anisole with HOCl, De la Mare and others(124) found the rate to be dependent on acidity and independent of the concentration of aromatic compound over the range of 0.004 - 0.01M. The formation of Cl_2 from HClO by the reaction: $ClOH + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$ was prevented by the addition of sufficient silver perchlorate. The following mechanism was suggested by them :

$$ClOH \rightleftharpoons Cl^{+} + OH^{-}$$

$$ClOH + H^{+} \rightleftharpoons Cl\,OH_2^{+}$$

$$Cl^{+}OH_2 \rightleftharpoons Cl^{+} + OH_2$$

$$Cl^{+} + ArH \longrightarrow ArCl + H^{+}$$

The cations react with anions Cl^{-} or OCl^{-} as follows :

$$Cl\,OH_2^{+} + Cl^{-} \longrightarrow Cl_2 + H_2O$$

$$Cl\,OH_2^{+} + OCl^{-} \longrightarrow Cl_2O + H_2O$$

The chlorination of phenol, anisole, methyl p- or m-tolyl ether or mesitylene by HClO in aqueous or aqueous dioxane solution containing excess silver perchlorate at 25° were found to obey the kinetic law(125).

$$-\frac{d\,[HOCl]}{dt} = K\,[HOCl] + K^{1}\,[H^{+}]\,[HOCl] + K^{ii}\,[H^{+}]\,[HOCl]\,[ArH]$$

Stanley and Shorter succeeded(126) in measuring the initial rates for the chlorination by HOCl of p-anisic acid (p-methoxybenzoic acid) in acetic acid. They suggested that the mechanism involves a chlorinating species reacting with an active form of anisic acid produced from unreactive bulk form at a finite rate.

$$\begin{array}{ccccccc} E_b & \underset{K_2}{\overset{K_1}{\rightleftharpoons}} & E_a & & E_a + D & \xrightarrow{K_3} & \text{Product} \\ C_2 & & C_3 & ; & C_3 \quad f_{c_1} & & \end{array}$$

where E_b represents the bulk form and Ea the active form of anisic acid, D is the chlorinating species assumed to be present in concentration proportional to that of HClO and f is a proportionality constant. For reactions of hypochlorous acid in 75 % acetic acid with several p - alkoxy benzoic acids and with p -chloroanisole and methyl anisate, the kinetics and mechanism were found similar to those of anisic acid.

Andrews and Keefer(127) investigated the reaction kinetics of pentamethyl benzene with chlorine in carbon tetrachloride. The disappearance of chlorine from these mixtures was subject to short periods of induction. The effects of increasing hydrogen chloride suggest that reaction is between first and second order in the hydrogen halide.

The reaction of chlorine with ammonia is very important for public health engineers. Noyes and Lyon(128) showed that a considerable amount of nitrogen trichloride may be formed by the action of chlorine on a dilute solution of ammonia. Bray and Dowell(129) found that nitrogen and nitrogen trichloride are formed in independent reactions and NCl_3 can be prepared from ammonia and HOCl. Investigations due to Noyes etal(130,131) have led to the conclusion that (i) anhydrous ammonia and chlorine react to form nitrogen trichloride and ammonium chloride; $4\ NH_3 + 3Cl_2 \rightleftharpoons 3\ NH_4Cl + NCl_3$; (ii) a part of the trichloride always decomposes by intraction between the trichloride and ammonia :

$$NCl_3 + NH_3 = 3\ HCl + N_2 \quad ;$$

(iii) the chlorine reacts primarily with ammonia. It does not react with solid ammonium chloride; (iv) dry HCl converts nitrogen trichloride quantitatively to ammonium chloride; (v) monochloroamine or dichloroamine are also formed together with trichloride when ammonium salts are treated with chlorine.

According to Chapin(132), dichloroamine is produced by chlorination of excess ammonium ions at pH 4.4 to 8.5, being practically the solid ultimate product at pH 4.5 to 5.0, and likewise, by corresponding acidification of monochloroamine solutions. He(133) pointed out that the hydrogen ion induces the formation of ammonium ion from each chloroamine, practically below a characteristic pH 4.0 .

$$NH_2Cl + H^+ + H_2O \longrightarrow NH_4^+ + HClO$$

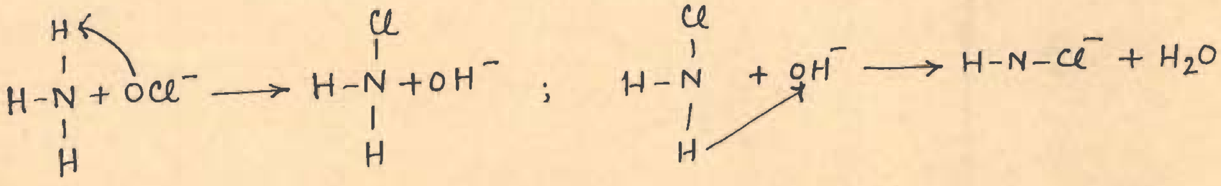
$$NH_2Cl + HClO \longrightarrow NHCl_2 + H_2O$$

the resulting HOCl then reacts to produce a more highly chlorinated derivative. The hydroxyl ion found to induce the formation of chloride ion :

$$2\ NHCl_2 + 4\ OH^- \longrightarrow 3\ Cl^- + ClO^- + 3H_2O + N_2$$

$$2\ NCl_3 + 6\ OH^- \longrightarrow 3\ Cl^- + 3\ ClO^- + 3\ H_2O + N_2$$

A number of workers(134 to 139) discussed the various aspects of the purification of water by adding ammonia and chlorine at different pH values. Mauger and Soper(140) suggested the following mechanism of N- chlorinations :



Fair and coworkers(141) concluded that in the reaction of chlorine and ammonia, hypochlorous acid is responsible for producing mono-, di-, and tri-chloramine in the stepwise process :

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$$

They observed that the rate of reaction is strongly dependent on pH; a maximum rate is observed at about pH 7.5 (where monochloramine is formed) and decreases rapidly at high and low pH values (where dichloramine is formed). They explained the formation of $NHCl_2$ in terms of the equilibrium :

$$2\ NH_2Cl + H^+ \longrightarrow NH_4^+ + NHCl_2$$

Weil and Morris(142) studied the kinetics of the formation of NH_2Cl, CH_3NHCl and $(CH_3)_2NCl$ from HOCl and appropriate amine.

Mattair and Sisler(143) demonstrated the formation of hydrazine by the reaction of chlorine with ammonia. They carried out the reaction in three ways :(i) the reaction of gaseous chlorine with liquid ammonia;(ii) the reaction in a solution of carbon tetrachloride with liquid ammonia; and (iii) the reaction of gaseous chlorine diluted with nitrogen, gaseous ammonia followed by condensation of the gaseous products to the liquid state. The reactions were as follows :

$$Cl_2 + 2NH_3 \longrightarrow NH_2Cl + NH_4Cl$$

$$NH_2Cl + 2\ NH_3 \longrightarrow NH_2NH_2 + NH_4Cl$$

They stated that excess of ammonia functions as a diluent for the chloramine, hydrazine and ammonium ion.

Sisler and coworkers(144,145) concluded that the high yields of chloramine is obtained from the gas phase reaction of ammonia with chlorine :

$$Cl_2(g) + 2NH_3\ (g) \longrightarrow ClNH_2(g) + NH_4Cl\ (s)$$

The side reaction leads to the formation of gaseous nitrogen and ammonium chloride :

$$8NH_3\ (g) + 3Cl_2\ (g) \rightarrow N_2(g) + 6NH_4Cl\ (s)$$

They further demonstrated that the yield of hydrazine increases as the temperature is increased and the initial concentration of chloramine is decreased.

$$2Cl\ NH_2 + N_2H_4 \rightarrow N_2 + 2\ NH_4Cl$$

Ammonium chloride was also found to reduce the yield of hydrazine due to the reaction :

$$N_2\ H_4 + NH_4Cl \longrightarrow N_2H_5Cl + NH_3$$

They(146) studied the same reaction in different solvents. In ethyl alcohol, hydrazine is formed at room temperature and high yield 38 % of hydrazine was also obtained in ethyl cellosolve. They devised(146) several methods for the separation of hydrazine.

Audrieth and coworkers(147) approved the mechanism suggested by Mauger and Soper(140) and proposed two more reactions in alkaline medium.

$$NH_2Cl + OH^- \rightarrow NHCl^- + H_2O$$

$$NHCl^- + B \longrightarrow HNB + Cl^-$$

where B = NH_3, RNH_2, R_2NH, H_2O and ROH (?)

Cahn and Powell$^{(148)}$ proposed the following mechanism between ammonia and alkaline hypochlorite :

$$NH_3 + OCl^- = NH_2Cl + OH^- \quad \text{(fast)}$$

$$NH_2Cl + NH_3 = (N_2H_5Cl) \xrightarrow{OH^{-1}} N_2H_4 + Cl^- + H_2O$$

$$NH_2Cl + N_2H_4 = (N_3H_6Cl) \xrightarrow[NH_2Cl]{2\ OH^-} N_2 + 2NH_3 + 2Cl^- + 2H_2O$$

Drago and Sisler$^{(149)}$ studied the effect of OH^- and NH_4^+ ions on the reaction of chloramine with aqueous ammonia and concluded that ammonium ion lowers the yield of hydrazine while gelatin increases the yield upto 70 %. The following mechanism was suggested :

$$NH_3 + NH_2Cl \rightarrow NH_3NH_2^+ + Cl^-$$

$$N_2H_5^+ + Cl^- + OH^- \longrightarrow H_2O + Cl^- + N_2H_4$$

The investigations of a number of workers$^{(150\ \text{to}\ 166)}$ lead to the conclusion that all the three chloramines are formed at different pH values and primary amine can easily be isolated in alkaline region. Anbar and Yagil$^{(162)}$ prepared chloramine from hypochlorite - ammonia reaction. The formation of hydroxylamine, hydrazine, N_2O, N_2, NH_4Cl and chloride ions was also shown.

The reaction between chlorine and Fe^{2+} was discussed by Taube etal$^{(64, 65, 167)}$, who demonstrated that Fe^{++} reduces chlorine by one electron change to produce atomic chlorine :

$$F_e^{++} + Cl_2 \longrightarrow F_eCl^{++} + Cl$$

A mechanism through chlorine radical was suggested,

$$Fe^{2+} + Cl_3^- \longrightarrow Fe^{3+} + Cl_2^- + Cl^-$$

$$Fe^{2+} + Cl_2 \longrightarrow Fe^{3+} + Cl_2^-$$

$$Fe^{2+} + Cl_2^- \longrightarrow Fe^{3+} + 2Cl^-$$

Scafer and Bayer(168) investigated in detail the chlorine - iron (III) chloride system. The kinetics of the oxidation of iron (II) by aqueous chlorine at an ionic strength of 1.00 was investigated recently by Crabtree and Scaefer(169), who found that the rate constant increases with increasing chloride concentration and the rate is independent of hydrogen ion concentration. They pointed out that both Cl_2 and Cl_3^- are effective as oxidants. The following mechanism was suggested:

$$2\ Fe^{2+} + Cl_3^-\ (\text{or } Cl_2) \longrightarrow 2Fe^{3+} + 3Cl^-\ (\text{or } 2Cl^-)$$

$$Fe^{2+} + Cl_3^- \longrightarrow 3Cl^- + Fe\ (IV)$$

$$Fe^{2+} + Cl_2 \longrightarrow 2Cl^- + Fe\ (IV)$$

$$Fe^{2+} + Fe\ (IV) \longrightarrow 2\ Fe^{3+}$$

The kinetic study of chlorine-nitric oxide reaction shows that the velocity constant of the reaction diminishes. The reaction was found to be influenced by surface conditions, and adsorption of the nitrosyl chloride formed during the reaction.

The reaction between H_2O_2 and chlorine was studied by Connick(171), who proposed that for higher than 1M HCl concentration, the following mechanism operates :

$$H_2O_2 + Cl_2 \longrightarrow H^+ + Cl^- + HOOCl$$

$$HOOCl \longrightarrow O_2 + H^+ + Cl^- \quad \text{(rate determining)}$$

but in the presence of HCl, 10^{-4}M, a change in mechanism was observed:

$$HOCl \; = \; H^{+} + ClO^{-}$$

$$ClO^{-} + H_2O_2 \rightarrow H_2O + O_2 + Cl^{-} \text{ (rate determining)}$$

Taube(167) suggested the following mechanism for the reactions of Mn^{++} and C_u^{+} with chlorine :

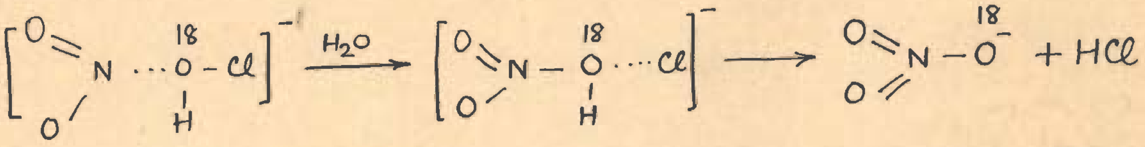
$$M_n^{++} + Cl \longrightarrow Mn^{+++} + Cl^{-}$$

and

$$Cu^{+} + Cl_2 \rightarrow CuCl^{++} + Cl^{-}$$

$$CuCl^{++} + Cu^{+} \longrightarrow 2\,Cu^{++} + Cl^{-}$$

Using O^{18} laveling, Taube(172) demonstrated that atom transfer takes place in the oxidation of $SO_3^{=}$ with ClO^{-}, ClO_2^{-} and ClO_3^{-}, and in the oxidation of NO_2^{-} with HOCl such reactions can be regarded as nucleophilic attacks on oxygen atom acting as a Lewis acid or electrophile, an anion being displaced :



From the detailed kinetic study of the reaction between chlorine and nitrite in water, Anbar and Taube(173) concluded that (i) when HOCl is active oxidant, transfer of oxygen to the reducing agent takes place.

The reactions between metal and non metals with chlorine have been reviewed in brief by Sneed and coauthors(174).

Ardon and Plane(175) have shown that when chromium (II) is treated with chlorine containing oxidizing agents, both mononuclear and polynuclear chromium (III) products are formed. Chlorine dioxide, chlorite ion, hypochlorite ion and chlorine are possible intermediates in the reduction of chlorate ion by Cr (III). The formation of $Cr\ (OH_2)_6^{3+}$ and the $(H_2O)_5\ CrCl^{2+}$ species were detected. The formation of $(H_2O)_5\ CrCl^{2+}$ was found to be small. Thomson and Gordon(176), while studying the stoichiometry and kinetics of the reaction between chromium (II) and the chlorine oxidants in aqueous perchloric acid, noticed that addition of a small amount of chloride ion effects the stoichiometry. The amount of $(H_2O)_5\ CrCl^{2+}$ and $Cr\ (OH_2)_6^{2+}$ increases in the presence of chloride ion in all the reactions. They concluded that the mutual reactions between chlorine containing oxidizing agents may further complicate the reaction of Cr (II) :

$$2HClO_2 + HClO \rightarrow 2ClO_2 + Cl^- + H_2O + H^+$$

$$HClO + ClO_2^- \rightarrow ClO_3^- + Cl^- + H^+$$

$$2\ HClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ Cl^- + H^+$$

The reactions between chlorine containing oxidizing agents and Cr (II) are very complex :

$$Cr\ (II) + ClO_2^- \rightarrow Cr\ (IV) + Cl\ \ (I)$$

$$Cr\ (II) + Cr(IV) \rightarrow \text{Binuclear species.}$$

Recently Gordon and Tewari(177) suggested that the chlorine (III) - chlorine (I), the chlorine (III) - chlorine (0), and the chlorine (I)- chloride reactions(175 to

177) are important in the uranium (IV)- chlorite(176), iron (II)- chlorite(176) and vanadium (II) - chlorite(117) reactions,

$$2\,HClO_2 + HClO \longrightarrow 2ClO_2 + Cl^- + H_2O + H^+$$

$$ClO_2^- + HClO = ClO_3^- + Cl^- + H^+$$

$$2\,HClO_2 + Cl_2 = 2\,ClO_2 + 2Cl^- + 2H^+$$

$$Cl^- + HOCl = Cl_2 + OH^-$$

The oxidation of Pu(III) to Pu(IV) by chlorine in the presence of chloride ions was studied by Ghosh Mazumdar and coworkers(178). The reaction order was found to be first and first with respect to Pu(III) and chlorine respectively. They suggested the following mechanism :

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^-$$

$$P_u^{3+} + Cl_3^- \longrightarrow (P_u....Cl_3)^{2+} \longrightarrow P_u^{3+} + Cl_3^-$$

$$(P_u....Cl_3)^{2+} + Cl_3^- \rightarrow P_u^{3+} + 2Cl_3^-$$

$$(P_u....Cl_3)^{2+} + P_u^{3+} \longrightarrow 2\,P_u^{3+} + Cl_3^-$$

$$(P_u....Cl_3)^{2+} + P_u^{3+} \longrightarrow P_uCl^{3+} + Cl^- \quad \text{(Rate determining)}$$

The reaction of chlorine molecule and potassium iodide has been recently investigated by Harrison et al(179) in which it was noticed that KCl and I_2 are the only products of the reaction. The reaction was found to be zero order.

From the above literature survey, it is clear that the kinetics of oxidations of simple organic molecules by chlorine have not been investigated. Such studies are of prime importance for proper understanding of the mechanism of chlorine oxidations.

SEC. 1.4 HALOGEN CATIONS :

The halogen compounds, in which the element is in the +1 oxidation state, can be divided into two parts : (i) neutral or negatively charged species - the hypohalous acids and their anions and (ii) positively charged species - the protonated hypohalous acids, such as H_2OCl^+, H_2OBr^+ and H_2OI^+, and their halogen cations, Cl^+, Br^+ and I^+. These species are very powerful electrophiles and can exist in media containing only the weakest of nucleophiles and high ionizing power.

In any interacting medium, the configuration of the cations will be more or less perturbed, The situation is closer to that of solvated transition - metal ions than that of ions with a rare gas configuration. Thus, the medium may perturb the energy levels in the cation in such a manner that transition similar to those between the d - levels of transition metal complexes can occur(180).

Noyes and Lyons(128) put forward the idea of the existence of halogen cations for the first time while studying the chlorine - ammonia reaction. Several workers thereafter suggested, on the basis of theoretical considerations that cations exist in solution(106,181 to 184).

De la Mare and coworkers(95,121) indicated the importance of chlorine cation, Cl^+, while studying the chlorination of phenol and anisole, but Israel etal(96) pointed out that the calculated relative potential ease of ionization of chlorine monoxide, Cl_2O, and HClO to give positive chlorine is approximately $4x10^9$, which causes the former to be more reactive than the latter.

Recently Arotsky and Symons(180) discussed critically the formation of halogen cations. They pointed out that the thermodynamic calculations of Bell and Gelles(185) concerning the probable existence of halogen cations in aqueous media are erroneous, because they derived the numerical values for ionic radii and solvation energies of the cations from partly justifiable extrapolations. In Table A, the equilibrium constants for the reactions are presented. The values were estimated by Arotsky and Symons(180) from free energy data computed by means of thermodynamic cycles (Table B).

There are evidences(70,122,125, 186 to 188) that H_2OCl^+ or Cl^+ is an intermediate in the chlorination of organic compounds, but the equilibrium constants established by Bell and Gelles(185) for reaction (3) (Table A) lead to the concentrations of protonated hypohalous acids so small that they could hardly act as important intermediate in the chlorination. The kinetic evidences are so strong(189) that many workers simply assume that chlorine cation is the main chlorinating agent in aqueous acidic media(123,185,190,191).

TABLE (A)

Free Energies and Equilibrium Constants for some Reactions of the Halogens (from Bell and Gelles(185))

$$X_2\ (aq.) \rightleftharpoons X^+\ (aq.) + X^-\ (aq.) \qquad (1)$$

X	Cl	Br	I
ΔG^o(KCal mole^{-1})	84(56)	67(39)	55(27)
K	$10^{-60}(10^{-40})$	$10^{-50}(10^{-30})$	$10^{-40}(10^{-21})$

(The values in parenthesis incorporate Arotsky and Symons(180) approximate ligand field correction of 28 K Cal.mole^{-1})

$$X_2\ (aq.) + H_2O \rightleftharpoons H^+ + HOX + X^- \qquad (2)$$

X	Cl	Br	I
ΔG^o(KCal.mole^{-1})	4.5	11.2	17
K	10^{-3}	10^{-8}	10^{-13}

$$X_2(aq.) + H_2O \rightleftharpoons H_2OX^+ + X^- \qquad (3)$$

X	Cl	Br	I
ΔG^o(KCal.mole^{-1})	42	30	14
K	10^{-30}	10^{-20}	10^{-10}

TABLE (B)

The Born-Haber Cycle for the Determination of the Free Energy

$$X_2\ (aq.) = X^+\ (aq.) + X^-\ (aq.)$$

$$\begin{tikzcd}
X_2\ (gas) \arrow[r] & 2\ x\ (gas) \arrow[r] & X^+\ (gas) \arrow[d] & + & X^-\ (gas) \arrow[d] \\
X_2\ (aq.) \arrow[u] \arrow[rr] & & X^+\ (aq.) & + & X^-\ (aq.)
\end{tikzcd}$$

According to De la Mare and Ridd(189), for relatively unreactive aromatic compounds, the rate of chlorination is given by

$$\frac{-d\ (HOCl)}{dt} = K_1\ [HOCl] + K_2\ [HOCl]\ [H^+]$$

which may be interpreted in terms of a rate determining heterolysis of the oxygen - chlorine bond, followed by a rapid attack of the resulting chlorine cation upon the aromatic compound. In accord with this is the observation that when D_2O is used as solvent, there is large increase in rate(125). This has been accepted as evidence for the transient formation of chlorine cations.

In order to suppress the reaction

$$Cl^- + H_2OCl^+ \rightleftharpoons Cl_2 + H_2O$$

these investigators added excess of silver perchlorate in solutions. The reaction rates were found insensitive to small changes in the concentration of silver perchlorate, from which they concluded that silver ions were not involved in the reaction(125).

Arotsky and Symons(180) pointed out that there are evidences for the formation of $Ag\ I_2^+$, $Ag\ Br_2^+$ and $AgCl_2^+$ and hence the possible participation of $AgCl_2^+$ in the chlorinations studied by De la Mare and coworkers(124) should be considered. They suggested the following alternative mechanism for chlorination in acidified aqueous solution of HClO containing an excess of silver perchlorate and some solid silver chloride :

$$AgCl(Solid) + H_2OCl^+ \underset{}{\overset{K_2O}{\rightleftharpoons}} AgCl_2^+ + H_2O .$$

$$AgCl_2^+ + ArH \longrightarrow ArCl + AgCl\ (Solid) + H^+$$

Recently in the chlorination of aromatic compounds, catalysed by $FeCl_3$ and $AlCl_3$, Olah and coworkers(192) suggested a mechanism involving Cl^+. Bartlett and Tarbell(193), while discussing the mechanism of alcohol - bromine reaction, postulated the existence of Br^+ as an intermediate. It was also shown that Br^+ ions are formed in the bromination of anisole - m - sulphonic acid in water by HBrO(194) through the reaction,

$$HOBr + H^+ \longrightarrow Br\overset{+}{O}H_2 + H_2O$$

but Bradfield and Jones(195) concluded in the case of bromination of phenol ethers that the electrophile reagent is the bromine molecule, and not Br^+ ions. Hinshelwood(196) pointed out that bromine may sometimes react in water after complete dissociation, $Br_2 \rightleftharpoons Br^- + Br^+$, and not merely as an inductively polarized molecule, while Weiss(197) put forward the view that the simple bromine cation may exist in acid solutions of HOBr, as suggested by Shilov and Naniaev(194).

Further researches on bromination of organic compounds(198 to 212) indicated the participation of Br^+ or $H_2O.Br^+$ in the reactions. The presence of bromine cations in acidified solution of HBrO was demonstrated by Gonda - Hunwald et al(201) but the data of Bell and Gelles(185) showed that bare cations cannot exist in appreciable concentrations although solvated cation is much more stable. The aromatic bromination by HBrO[207] in presence of acids may be represented by :

$$H^+ + HOBr \overset{rapid}{\rightleftharpoons} BrOH_2^+$$

$$BrOH_2^+ + ArH \xrightarrow{slow} (ArH \cdot Br)^+ + H_2O$$

$$(ArH \cdot Br)^+ \longrightarrow Ar \cdot Br + H^+$$

Iodine cations have been clearly identified in the gas phase by emission and mass spectroscopy. The spark spectrum of iodine(213) shows lines attributed to electronically excited iodine cations. The I^+ ions were found to stabilize on a resin(204,205). A typical procedure is to pass a solution of 0.5 gm. of iodine in 100 ml of absolute alcohol through Amberlite IR 100H resin.

$$H^+ Res^- + I_2 \longrightarrow I^+ Res^- + HI$$

The amount of I^+ in the resin may be determined by passing a saturated solution of potassium iodide through the exchange column and titrating the liberated iodine with thiosulphate.

$$I^+ Res^- + KI \longrightarrow K^+ Res^- + I_2$$

A number of other evidences have now been advanced for the existence of iodine cations(214 to 218) Aynsley and coworkers(219) concluded from their experiments that each molecule of iodine, I_2 gives rise to 2.5 gm.ions of cation I^+.

From the spectra of the oleum solutions, Symons and coworker(180) estimated a value of about 28 K cals mole^{-1} for the "ligand field stabilization" of the iodine cation due to the oriented field of solvent molecules(220). They pointed out that as a result of this extra solution energy, the iodine cation is sufficiently stable to be a reasonable intermediate in chemical reactions. The participation of chlorine - and bromine - cations, Cl^+ and Br^+, in halogenations still appears doubtful.

CHAPTER 2

REACTIONS OF MONOHYDRIC ALIPHATIC ALCOHOLS WITH CHLORINE IN AQUEOUS SOLUTION

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INTRODUCTION

The kinetics of oxidation of alcohols by a large number of oxidizing agents have been studied in detail. In general, the primary and secondary alcohols were found to oxidize much more readily than the tertiary alcohols, especially by heterolytic oxidants. Recently Waters(221) and Stewart(222) discussed critically the mechanisms of oxidation of alcohols. They pointed out that the rate determining step in the oxidation of primary and secondary alcohols generally involve the breaking of C-H bond. The determination of deuterium isotope effect had proved to be of great value for such oxidations.

One of the earliest studies on the oxidation of alcohols was made by Lieben(72,73), who observed the formation of acetaldehyde from the reaction of ethyl alcohol with chlorine. Chattaway and Backeberg(223) demonstrated that in this reaction ethyl hypochlorite and hydrochloric acid are first produced and the acetaldehyde is formed from the hypochlorite by the elimination of HCl :

$$CH_3.CH_2.OH + Cl_2 \longrightarrow CH_3CH_2OCl + HCl$$

$$CH_3.CH_2.OCl \longrightarrow CH_3CHO + HCl$$

The other reactions of chlorine with alcohols have already been described in the previous chapter(75,77,97,101).

Etard(224) isolated trimethyl ethylene dibromide as a final product in the reaction of bromine with t-amyl alcohol. Later on, Whitmore and coworkers(225) also isolated same products of reaction. Andrews and Keefer(226) studied the kinetics of the reaction between bromine and t-amyl alcohol in carbon tetrachloride. The rate was found to obey second order kinetics. The preliminary studies on the reaction of bromine with methyl alcohol were made by number of workers(227,228). From a detailed study of the reaction, Meinel(229) concluded that methyl hypobromite is the primary product. Bartlett and Tarbell(193) found that the rate follows a second order kinetics and sodium bromide diminishes the rate.

$$Br_2 + CH_3OH \longrightarrow CH_3OBr + H^+ + Br^-$$

They suggested that the initiator of the reaction is molecular bromine, whose concentration decreases by the addition of bromide due to formation of tribromide.

$$Br_2 + Br^- \longrightarrow Br_3^- .$$

The reaction between ethyl alcohol and bromine was studied by Bugarszky(230), which was later on studied in more detail by Perlmutter - Hayman and coworkers(231 to 234). According to them, (i) the reaction between the alcohol of concentration 76 % (by weight) and bromine at concentration 0.05M is of first order with respect to free bromine, (ii) the tribromide ions are inactive, (iii) as bromine concentration is increased, rate also increases and (iv) in dilute alcohol, 1-4% by weight, the following consecutive reactions occur, in which the value of K_2

$$CH_3CH_2OH + Br_2 \xrightarrow{k_1} CH_3CHO + 2HBr$$

$$CH_3CHO + Br_2 + H_2O \xrightarrow{k_2} CH_3\ COOH + 2HBr$$

increases as the oxidation proceeds. They suggested three possible mechanisms and appear to favour mechanism(a)largely on the grounds that alkyl hypochlorites are known to break up into aldehyde and HCl(235).

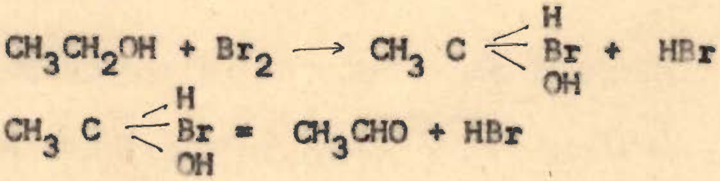
(a) $C_2H_5OH + Br_2 \longrightarrow C_2H_5\ OBr + HBr$ (1) (rate determining)

$C_2H_5\ OBr \longrightarrow C_2H_3\ CHO + HBr$

(b) $CH_3CH_2OH + Br_2 \rightarrow [CH_3\ CHOH]^+ + Br_2H^-$

$[CH_3CHOH]^+ \longrightarrow CH_3CHO + H^+$ (rate determining)

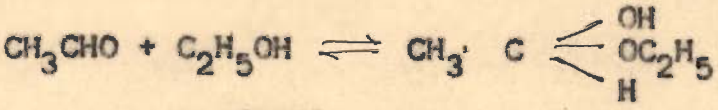
$Br_2H^- = H^+ + 2Br^-$



(c) $CH_3CH_2OH + Br_2 \longrightarrow CH_3\ C\begin{smallmatrix}H\\Br\\OH\end{smallmatrix} + HBr$

$CH_3\ C\begin{smallmatrix}H\\Br\\OH\end{smallmatrix} = CH_3CHO + HBr$

The simultaneous formation of acetic acid and ethyl acetate was explained on the assumption of the formation of hemiacetal:



$$CH_3CHO + C_2H_5OH \rightleftharpoons CH_3\ C\begin{smallmatrix}OH\\OC_2H_5\\H\end{smallmatrix}$$

Farkas and Schachter(232)found that the total yield of oxidation products is more than 90 % in the oxidation of ethyl -, isobutyl-, amyl-, and hexyl- alcohol by bromine in presence of bromate. They also noted that the oxidation rate of secondary alcohols is faster than of primary alcohols and benzyl alcohol gave 10.6% benzyl benzoate, 5.6% benzoic acid and 79 % benzaldehyde as products. They(231) suggested a mechanism for the oxidation of aliphatic alcohols by bromine in presence of bromate, involving two reaction paths :

$$2\ RCH_2OH + 2Br_2 \longrightarrow RCOO\ CH_2R + 4H^+ + 4Br^-$$

$$BrO^-_3 + 6H^+ + 5\ Br^- \longrightarrow 3Br_2 + 3H_2O$$

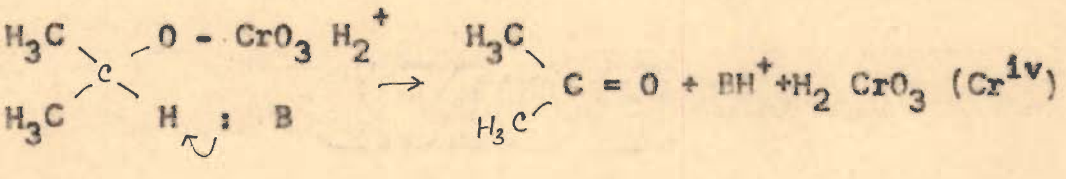
The deuterium isotope effect for the oxidation of CH_3CD_2OH ($k_H/k_D \approx 4$ in acid at 25°) showed that the rate controlling step requires cleavage of C-H bond(236). The variation of oxidation rate with pH indicated that the anions of alcohols are oxidized much more rapidly than are the neutral molecules. The removal of a hydride ion from the anions by molecular bromine appears to be the most satisfactory mechanism for the reaction between ethyl alcohol and bromine(29,236)

$$CH_3CH_2OH + OH^- \longrightarrow CH_3CH_2O^- + H_2O$$

$$CH_3CH_2O^- + Br_2 \longrightarrow CH_3CHO + HBr + Br^-$$

Researches on the oxidation of alcohols by chromic acid(3,21 to 23, 237 to 258) have been extensively carried out. All the facts determined by Westheimer and his coworkers(21,22,242 to 246) on the chromic acid oxidation of isopropyl alcohol may be explained by an ester mechanism in which the chromic acid ester decomposes by proton loss to any available base (proton acceptor) with elimination of a Cr^{iv} ion,

$$(CH_3)_2\ CHOH + HCrO4^- + 2H^+ \longrightarrow (CH_3)_2\ CHOCrO_3H_2^+ + H_2O$$

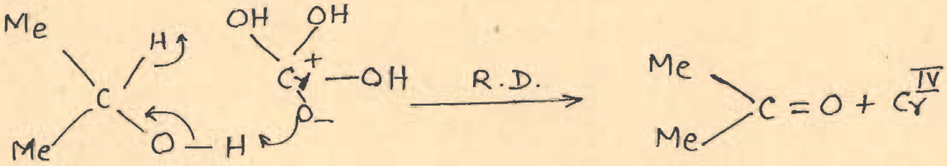


followed by

$$C_r^{iv} + Cr^{vi} \xrightarrow{fast} 2\,Cr^{v}$$

$$2\,C_r^{v} + 2\,(CH_3)_2\,CHOH \xrightarrow{fast} 2\,C_r^{iii} + 2\,(CH_3)_2\,C{=}O + 4H^+$$

Further support to this type of ester mechanism was given by Chatterji and coworkers(3,247 to 251). The suggestion of Rocek and Krupicka(256)



that a direct hydride transfer from alcohol to chromic acid or to its conjugate acid, chromic acidium ion has been finally rejected in the year 1962 by Rocek, Westheimer and coworkers.(23) The chromic acid oxidations of alcohols have also been reviewed by Stewart(222), who supported the ester mechanism.

The behaviour of iodine in some sensitized decompositions of gaseous organic compounds, such as CH_3OH was discussed by Faull and Rollefson(259).

$$CH_3OH + I_2 = HCHO + 2IH;$$

$$HCHO + I_2 = 2HI + CO$$

$$2HI + CH_3OH \rightleftharpoons H_2O + CH_4 + I_2\ ;$$

$$2HI \rightleftharpoons H_2 + I_2$$

The oxidation of alcohols by iodic acid was investigated in detail by Williams and Woods(260).

From a careful investigation of the oxidation of alcohols by potassium permanganate, Stewart etal(27,28,261) suggested a mechanism involving a hydride ion transfer from alcohol to the permanganate :

$$(C_6H_5)_2CHOH + OH^- \underset{}{\overset{K}{\rightleftharpoons}} (C_6H_5)_2CHO^- + H_2O$$

$$MnO_4^- + (C_6H_5)_2CHO^- \xrightarrow{k} \text{Products}$$

Recently Banerjee and Sen Gupta(262) studied the oxidation of methyl and ethyl alcohols by potassium permanganate. They noticed that the rate increases with H^+ but retards by addition of Mn(ii).

While studying the oxidation of cyclohexanol by quin quevalent Vanadium, Waters and coworkers(262 to 265) postulated the existence of cations VO_2^+ and $V(OH)_3^{2+}$ of Vanadium (v) in mineral acids. They proposed the following mechanism :

$$V^{v} + R_2CH(OH) \longrightarrow V^{iii} + R_2C = O + 2H^+ \text{ (heterolytic)}$$

$$V^{iii} + V^{v} \longrightarrow 2V^{iv} \text{ (very rapid)}$$

The oxidation of alcohols by Co^{iii} was found to occur more readily than other transition metal ions(266). The rate of alcohol oxidation is inversely proportional to the hydrogen ion concentration and exhibits a deuterium isotope effect.

The oxidations of alcohols by potassium persulphate were investigated by several workers(267 to 271). Wiberg(267) elucidated a mechanism for the persulphate oxidation of isopropyl alcohol in which a chain process is initiated by the first order decomposition of $S_2O_8^=$ to the sulphate radical anion.

$$S_2O_8^= \xrightarrow{k_1} 2\ SO_4^{-*}$$

$$SO_4^{-*} + H_2O \xrightarrow{k_2} HO^* + HSO_4^-$$

$$HO^* + R_2CHOH \xrightarrow{k_3} H_2O + R_2COH$$

$$R_2COH + S_2O_8^= \xrightarrow{k_4} R_2C=O + HSO_4^- + SO_4^{-*}$$

The catalytic effect of Cu ion on the reaction has been attributed to the action of Cu (iii) produced by a chain reaction(268). Levitt etal(269,271)suggested the following mechanism :

$$R_2CHOH + S_2O_8^- \rightleftharpoons \text{COMPLEX} \longrightarrow R_2CO + 2HSO_4^-$$

The rates of oxidation of variety of phenyl Carbinols by MnO_2 in benzene was determined by Prat and coworkers(272). A mechanism in which the reaction proceeds via free radical intermediates was suggested by them. They also noticed that aliphatic alcohols underwent oxidation much more slowly than did the phenyl carbinols. Konaka and Nakata(273) studied the oxidation of primary and secondary alcohols with nickel peroxide in aqueous alkalihe solution. They detected acids and ketones as products of the reaction. Recently a study of the reaction of methanol vapour with Ag(1) oxide was made by Allen(274), who isolated formaldehyde, formic acid, CO_2 and CO as products.

According to Stevens and Kaman(275), the epoxidation of primary and secondary allylic alcohols by H_2O_2

in the presence of tungstic acids appears to involve the formation of a pertungstate ester followed by a rate determining re-arrangement :

$$H_2WO_4 + H_2O_2 \longrightarrow H_2WO_5 + H_2O$$

$$H_2WO_5 + ROH \xrightarrow{fast} ROWO_3OH + H_2O$$

$$ROWO_3OH \xrightarrow{slow} R'OWO_2OH$$

$$R'OWO_2OH + H_2O \xrightarrow{fast} R'OH + H_2WO_4$$

where R = alkenyl and R' = apoxyalkyl

The oxidation of alcohols by heterolytic oxidants generally takes place by way of esterification or by hydride transfer. In both type of mechanisms, the cleavage of C-H bond involves in the rate determining step as indicated by isotope effect (k_H/k_D). However, the interpretation of magnitude of these kinetic effects is still controversial.

In this Chapter the reactions of methyl-,ethyl-, isobutyl-, isopropyl-, n-butyl-, n-propyl- and sec-butyl - alcohol with aqueous chlorine in the presence as well as in the absence of perchloric acid are discussed. In all the cases besides oxidation to carbonyl compounds, the chlorinated carbonyl compounds due to chlorination by consecutive reactions are also formed. It will not be out of place to mention here that chlorination should also be regarded as an oxidation, e.g. in the reaction

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

the two chlorine atoms are initially associated, in Cl_2, with

14 valency electron and eventually, in

$$CH_3Cl + HCl$$

with 16. Clearly chlorine has been reduced and therefore, methane has been oxidized; the two electrons have in fact been abstracted with the hydrogen nucleus that has been replaced by chlorine(221). Similarly, the reaction

$$CH_3COCH_3 + Cl_2 = CH_3COCH_2Cl + HCl$$

is also an oxidation because chlorine is reduced and therefore, acetone is oxidized.

SEC. 2.1 ORDER OF THE REACTION :

Introduction :- The most important step in elucidation of the mechanism of a reaction is determination of the order of reaction. It can be determined by one of the several methods available(276), provided the reaction is not complicated by consecutive reaction, back reaction, side reaction or other factors which influence the rate.

We started this kinetic investigation with the reaction of isopropyl alcohol with chlorine, and noticed that chlorine in aqueous solution oxidizes isopropyl alcohol to acetone and then a small portion of acetone gets chlorinated into monochloroacetone. This means that it is a consecutive reaction :

$$(CH_3)_2CHOH + Cl_2 \longrightarrow (CH_3)_2C{=}O + 2HCl$$

$$(CH_3)_2C{=}O + Cl_2 \longrightarrow CH_3.CO.CH_2.Cl + HCl$$

A number of methods of handling such complex reactions are available(277). For example, for consecutive reactions involving a common reagent, viz.

$$A + B \xrightarrow{k_i} C$$

$$C + B \xrightarrow{k_{ii}} D$$

often k_i can be measured by working at high concentration of B, whence a pseudo-first order reaction is observed. In addition, the initial rate of disappearance of A or B can provide a measure of k_i(278).

In this investigation throughout we maintained large excess concentrations of alcohols and determined the orders of the reactions by Ostwald's isolation method(279). The pseudo-first order rate constants, k Sec^{-1}, were calculated for each aliquot portion titrated and the arithmetic means of the sets of values were obtained. The variations of the rate constants from the mean did not exceed 5%.

We also considered the initial rates. These can be determined by the following method :

If a is the initial concentration of total oxidant in moles per lit., x is the number of moles of total oxidant per litre consumed in time t, N is the normality of the thiosulphate, v is the volume of aliquot (v = 20 cc.) and c' and c are the number of ml of thiosulphate required after respectively zero time and time t, then

$$x = \frac{(c' - c)\,N}{2\,V}$$

A convenient method of finding initial rate is to plot x/t against x and to extrapolate to x = 0(280,281); where this method has been used, satisfactory linear plots have been obtained. In Fig.1 and 2 typical plots of x/t vs x are shown.

The present section deals with the order of reactions of isopropyl-, sec-butyl-, methyl-, ethyl-, n-propyl-, n-butyl-, and iso-butyl- alcohols with chlorine in the absence and in the presence of perchloric acid.

The initial rates, ko, moles per lit. sec^{-1}, have been determined in the case of methyl-, ethyl-,

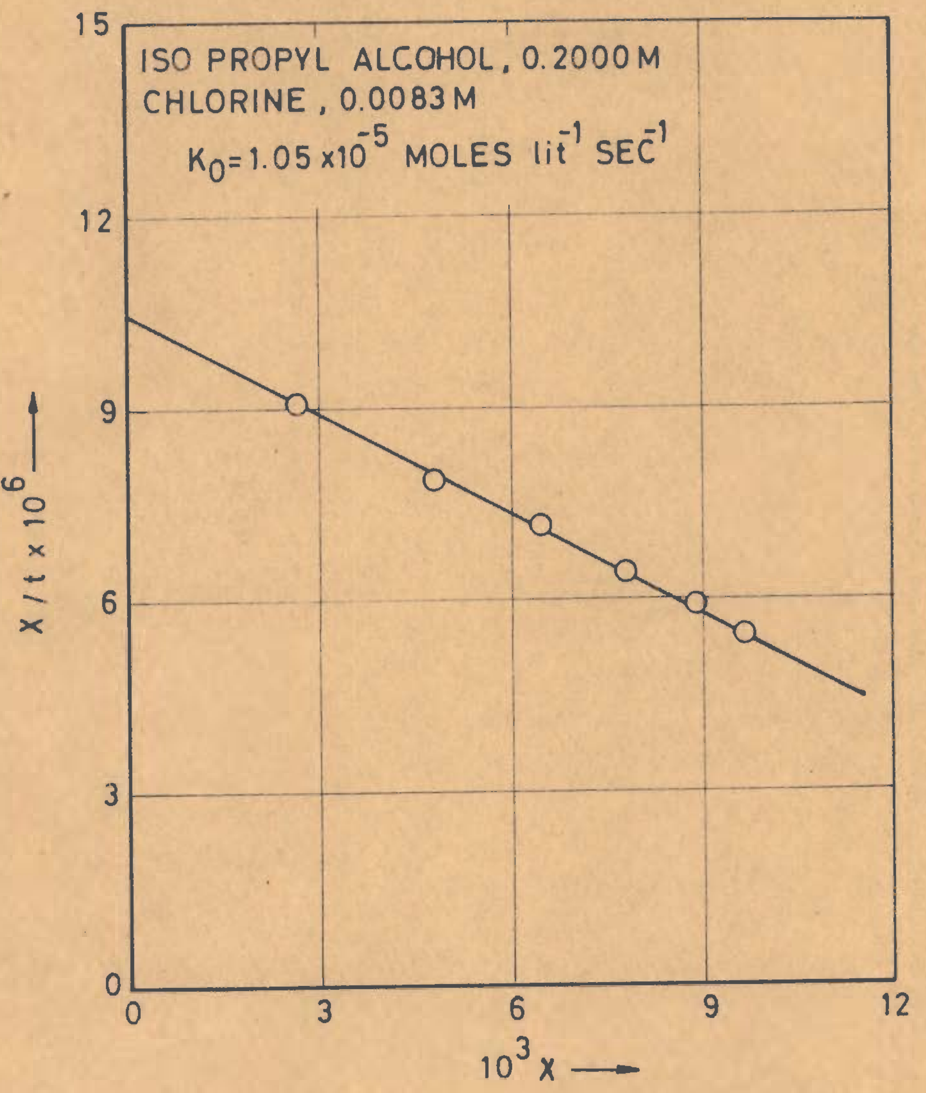


FIG. 1a_ DETERMINATION OF K_0

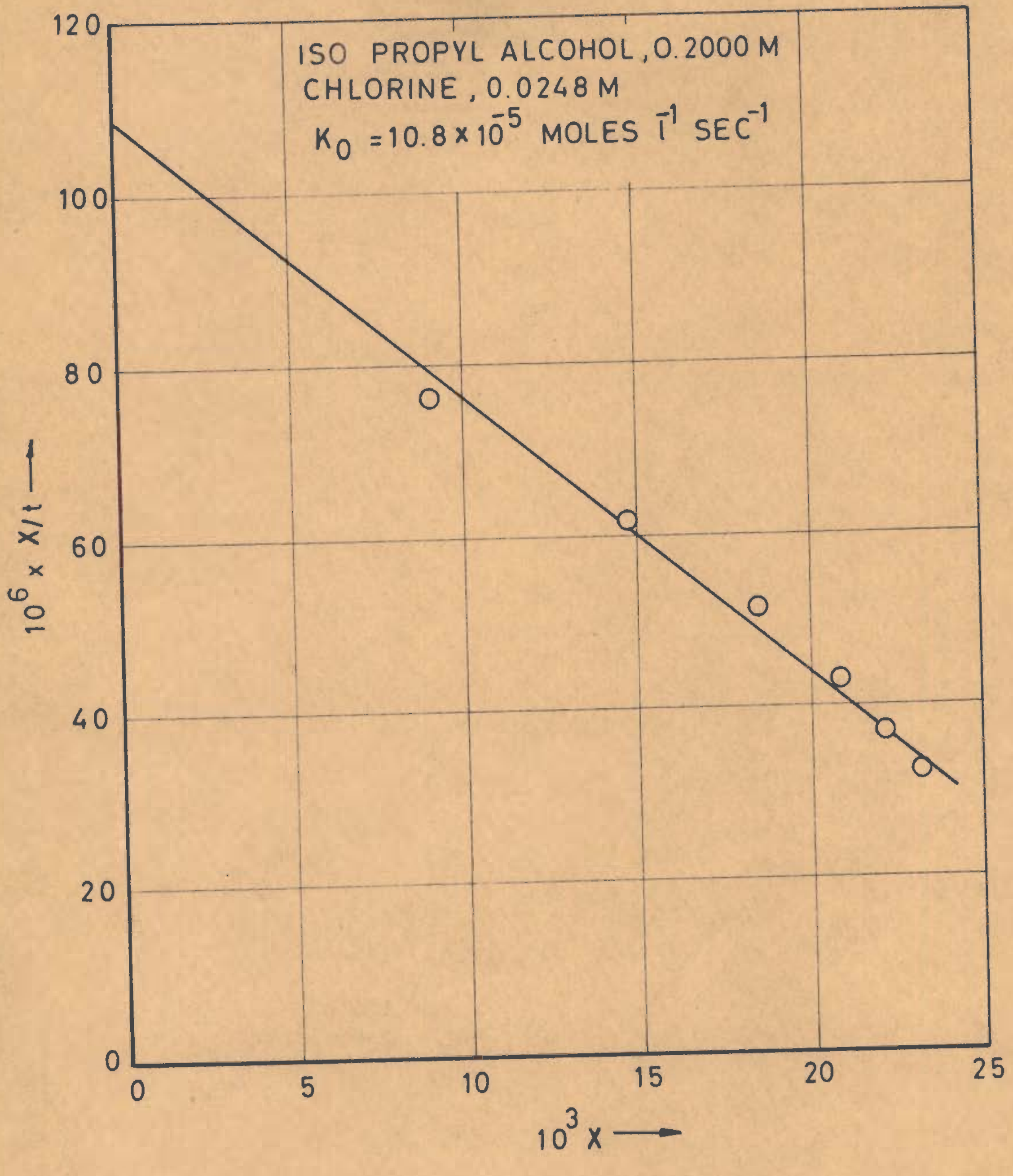


FIG.1b_ DETERMINATION OF K_0

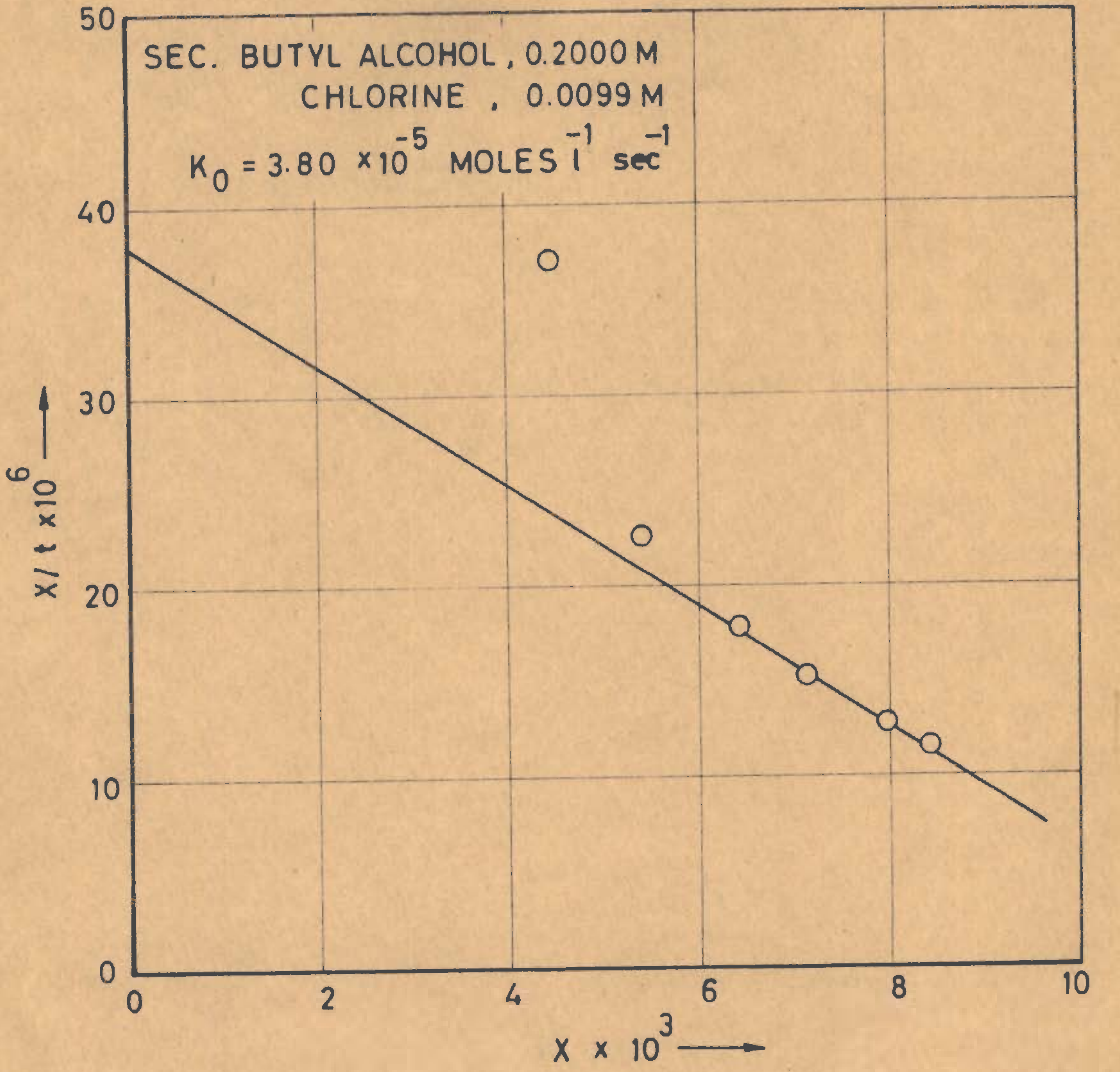


FIG. 2a _ DETERMINATION OF K_0

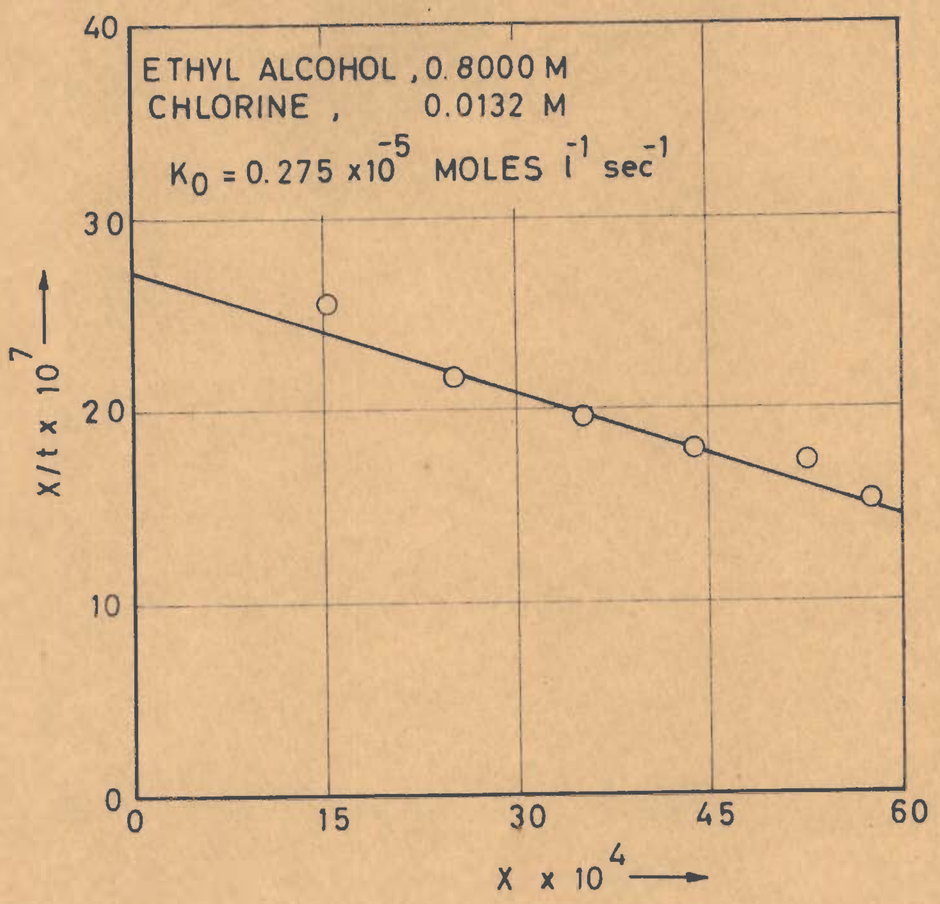


FIG. 2b _ DETERMINATION OF K_0

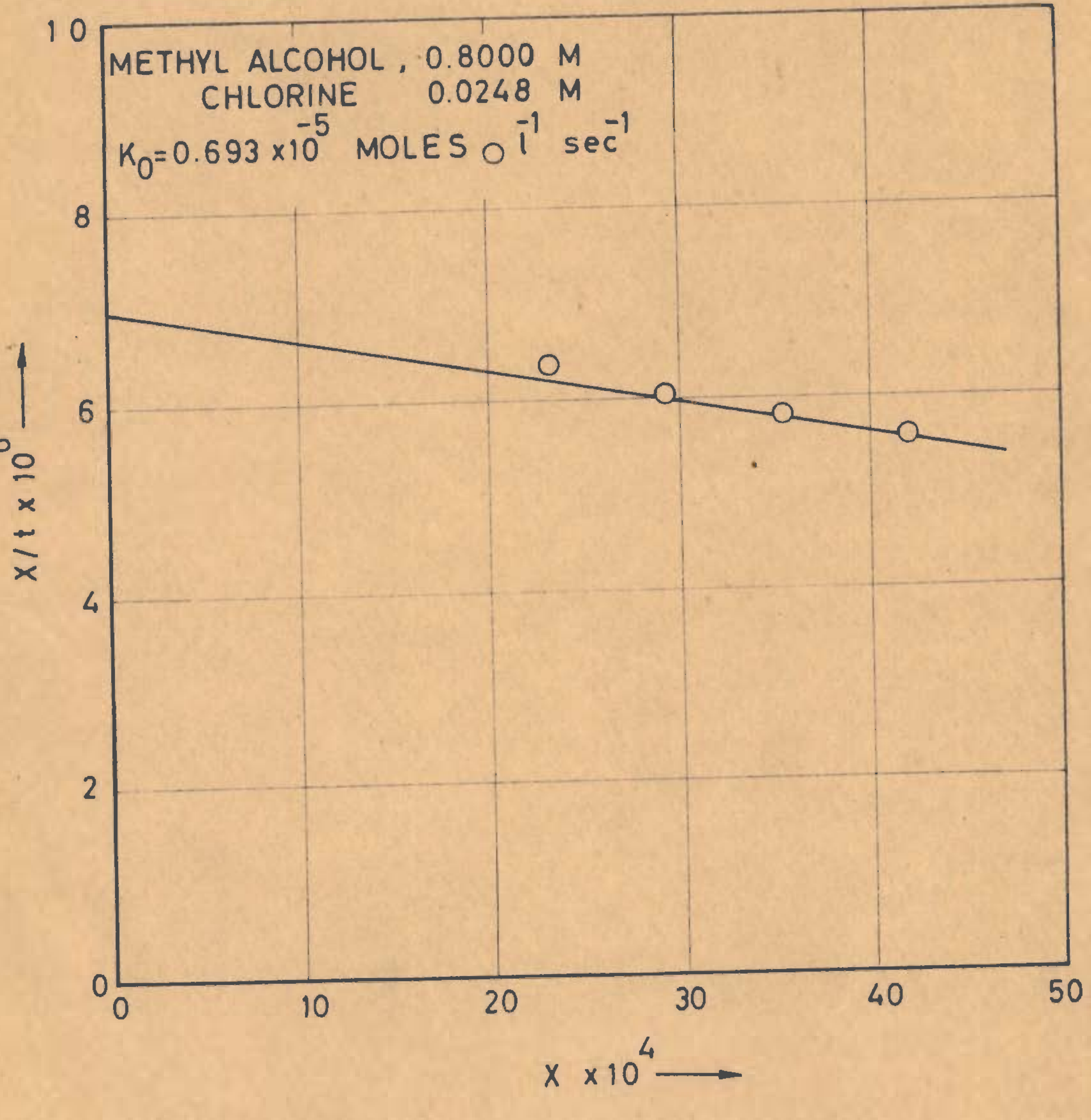


FIG. 2c_ DETERMINATION OF K_0

isopropyl- and sec.butyl- alcohols only as the procedure is time consuming, and the orders have been calculated(279) by using k_0 values as well. In the case of n-propyl-, n-butyl- and iso-butyl alcohols, the initial rates have not been determined.

EXPERIMENTAL

Reagents : Chlorine water solutions were prepared by treating potassium permanganate (B.D.H., AnalaR) with concentrated hydrochloric acid (AnalaR) in a flask and passing the gas thus produced in water through the bubblers containing $KMnO_4$ solution. The concentrations of chlorine in water were estimated iodometrically immediately before use.

Reagent grade n-propyl-, isopropyl-, n-butyl-, isobutyl-, and sec. butyl- alcohols (B.D.H) were distilled, refluxed with calcium sulphate for about eight hours and then redistilled with adequate protection from the moisture.

Methyl and ethyl alcohols were distilled, dehydrated by adding quick lime and refluxing the mixture for about 8 hours and then redistilled.

AnalaR grade perchloric acid (Merck)solutions were standardised against carbon dioxide free standard sodium hydroxide solution.

Throughout alkaline permanganate redistilled water was used. All other chemicals were either B.D.H.(AnalaR) or Merck (C.P) grade or of comparable purity.

Kinetic Procedure : The thermostat was controlled within ± 0.05°C. Sodium perchlorate was added to the reaction mixture to bring to the ionic strength of 0.4. Before mixing, chlorine solution was thermostated for only 3 to 5 minutes and other solutions for more than half an hour. The progress of the reaction was followed by estimating unreacted chlorine in 20 ml aliquot portions of the reaction mixture at regular intervals. The aliquots were poured into ice cold water containing potassium iodide and then 2 ml of glacial acetic acid was added and the liberated iodine was titrated against standard sodium thiosulphate solution using freshly prepared starch as indicator(282). To avoid photochemical complications, black coloured bottles were used. Prior to each experiment, the bottles were cleaned with strong chromic acid, washed, steamed and then dried in oven. The observations are presented in the following tables. A summary of the data is given in Tables 118 to 138.

TABLE 1

Total Oxidant 0.0248M
IsoPropyl Alcohol 0.2000M

Time mts.	Thio CCS.	$k \times 10^3$ Sec^{-1}
0	146.0	-
2	93.0	3.76
4	59.0	3.77
6	37.0	3.81
8	23.7	3.79
10	15.8	3.70
12	9.7	3.76

Mean $k \times 10^3$ Sec^{-1} = 3.76
$k_o \times 10^5$ =10.8

TABLE 2

Total Oxidant 0.0166M
IsoProphyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	100.0	-
2	73.0	2.62
4	55.0	2.49
6	40.0	2.54
8	30.0	2.51
10	22.0	2.52
12	17.1	2.45

Mean $k \times 10^3$ Sec^{-1} = 2.52
$k_o \times 10^5$ = 5.00

TABLE 3

Total Oxidant 0.0132M
IsoProphyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	77.4	-
2	62.0	1.85
4	51.1	1.73
6	42.2	1.68
8	35.05	1.65
10	27.0	1.75
12	23.0	1.68

Mean $k \times 10^3$ Sec^{-1} = 1.73
$k_o \times 10^5$ = 2.65

TABLE 4

Total Oxidant 0.0099M
IsoProphyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	111.2	-
10	58.9	1.06
20	32.0	1.04
30	16.9	1.05
40	8.5	1.07
50	4.9	1.04
60	2.5	1.05

Mean $k \times 10^3$ Sec^{-1} = 1.05
$k_o \times 10^5$ = 1.50

TABLE 5

Total Oxidant 0.0083M
IsoPropyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k\text{x}10^{3}$ Sec^{-1}
0	92.7	-
10	60.0	0.725
20	39.5	0.711
30	27.0	0.686
40	16.7	0.714
50	10.9	0.714
60	8.4	0.667
Mean $k\text{x}10^{3}$Sec^{-1} =		0.703
$k_{o}\text{x}10^{5}$ =		1.05

TABLE 6

Total Oxidant 0.0066M
IsoPropyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k\text{x}10^{3}$ Sec^{-1}
0	74.15	-
10	54.0	0.528
20	40.3	0.508
30	30.0	0.503
40	21.5	0.516
50	16.1	0.509
60	11.9	0.508
Mean $k\text{x}10^{3}$Sec^{-1} =		0.512
$k_{o}\text{x}10^{5}$ =		0.58

TABLE 7

IsoPropyl Alcohol 0.0740M
Total Oxidant 0.0034M

Time mts.	Thio ccs.	$k\text{x}10^{4}$ Sec^{-1}
0	20.4	-
10	18.3	1.81
20	16.4	1.82
30	14.55	1.88
40	13.1	1.84
50	11.8	1.82
60	10.5	1.84
Mean $k\text{x}10^{4}$Sec^{-1} =		1.83

TABLE 8

IsoPropyl Alcohol 0.0650M
Total Oxidant 0.0034M

Time mts.	Thio ccs.	$k\text{x}10^{4}$ Sec^{-1}
0	20.7	-
10	18.85	1.56
20	17.10	1.59
30	15.45	1.63
40	14.05	1.62
50	12.80	1.60
60	11.6	1.61
Mean $k\text{x}10^{4}$ Sec^{-1} =		1.60

TABLE 9

IsoPropyl Alcohol 0.0510M
Total Oxidant 0.0034M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	19.75	-
10	18.4	1.18
20	17.15	1.18
30	16.0	1.17
40	14.9	1.17
50	13.8	1.19
60	12.9	1.18
Mean $k \times 10^4$ Sec^{-1} =		1.18

TABLE 10

IsoPropyl Alcohol 0.0386M
Total Oxidant 0.0034M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	18.05	-
10	17.1	0.902
20	16.2	0.902
30	15.3	0.918
40	14.5	0.912
50	13.75	0;915
60	12.85	0.944
Mean $k \times 10^4$ Sec^{-1} =		0.910

TABLE 11

IsoPropyl Alcohol 0.0321M
Total Oxidant 0.0034M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	23.45	-
10	22.4	0.763
20	21.4	0.761
30	20.4	0.774
40	19.5	0.768
50	18.6	0.772
60	17.9	0.750
Mean $k \times 10^4$ Sec^{-1} =		0.765

TABLE 12

IsoPropyl Alcohol 0.0257M
Total Oxidant 0.0034M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	17.4	-
10	16.8	0.583
20	16.2	0.595
30	15.6	0.606
40	14.05	0.604
50	14.5	0.606
60	13.9	0.623
Mean $k \times 10^4$ Sec^{-1} =		0.599

TABLE 13

IsoPropyl Alcohol 0.0129M
Total Oxidant 0.0034M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	21.1	-
10	20.75	0.276
20	20.3	0.322
30	20.0	0.298
40	19.55	0.318
50	19.3	0.297
60	19.0	0.291
Mean $k \times 10^4$ Sec^{-1} =		0.296

IsoPropyl Alcohol 0.1066M
Total Oxidant 0.0052M

TABLE 14

Perchloric Acid 0.01M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.45	-
4	41.8	0.614
8	36.1	0.618
12	31.2	0.611
16	27.0	0.609
20	23.2	0.614
24	20.0	0.614
Mean $k \times 10^3$ Sec^{-1} =		0.613
$k_o \times 10^5$ =		0.350

TABLE 15

Perchloric Acid 0.04M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.45	-
4	35.7	1.27
8	26.3	1.27
12	19.4	1.27
16	14.3	1.27
20	10.4	1.28
24	7.85	1.26
Mean $k \times 10^3$ Sec^{-1} =		1.27
$k_o \times 10^5$ =		0.720

TABLE 16

Perchloric Acid 0.12M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.45	-
4	28.0	2.28
8	16.2	2.28
12	9.7	2.23
16	6.1	2.16
20	3.1	2.29
24	1.5	2.41

Mean $k \times 10^3$ Sec^{-1} = 2.25

$k_o \times 10^5$ = 1.30

TABLE 17

Perchloric Acid 0.20M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.45	-
4	24.0	2.93
8	11.45	3.00
12	5.9	2.92
16	2.9	2.93
20	1.45	2.92
24	0.7	2.94

Mean $k \times 10^3$ Sec^{-1} = 2.93

$k_o \times 10^5$ = 2.20

TABLE 18

Perchloric Acid 0.25M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.45	-
2	30.2	3.94
4	19.0	3.90
6	12.0	3.88
8	7.7	3.83
10	5.0	3.78
12	3.0	3.86

Mean $k \times 10^3$ Sec^{-1} = 3.86

$k_o \times 10^5$ = 2.74

TABLE 19

Perchloric Acid 0.30M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.45	-
2	27.75	4.64
4	16.0	4.62
6	9.0	4.67
8	5.1	4.69
10	3.0	4.64
12	1.8	4.57

Mean $k \times 10^3$ Sec^{-1} = 4.64

$k_o \times 10^5$ = 3.40

TABLE 20

Total Oxidant 0.0248M
Sec.Butyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	142.6	-
2	45.5	9.53
4	14.8	9.44
6	4.4	9.67
8	1.45	9.34
10	0.5	9.42
12	-	

Mean $k \times 10^3$ Sec^{-1} = 9.48
$k_o \times 10^5$ = 31.6

TABLE 21

Total Oxidant 0.0166M
Sec.Butyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	95.5	-
2	45.0	6.27
4	22.6	6.00
6	10.5	6.13
8	5.0	6.14
10	2.4	6.14
12	1.15	6.14

Mean $k \times 10^3$ Sec^{-1} = 6.14
$k_o \times 10^5$ = 12.5

TABLE 22

Total Oxidant 0.0132M
Sec.Butyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	75.9	-
2	44.0	4.54
4	26.8	4.34
6	16.6	4.22
8	9.7	4.29
10	5.7	4.31
12	3.2	4.40

Mean $k \times 10^3$ Sec^{-1} = 4.35
$k_o \times 10^5$ = 7.15

TABLE 23

Total Oxidant 0.0099M
Sec.Butyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	56.9	-
2	39.0	3.15
4	28.0	2.95
6	20.2	2.88
8	15.8	2.67
10	11.4	2.68
12	8.2	2.69

Mean $k \times 10^3$ Sec^{-1} = 2.84
$k_o \times 10^5$ = 3.80

TABLE 24

Total Oxidant 0.0066M
Sec.Butyl Alcohol 0.2000M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	40.3	-
5	26.0	1.46
10	16.6	1.48
15	11.0	1.44
20	7.0	1.46
25	4.4	1.48
30	2.9	1.46

Mean $k \times 10^3$ Sec^{-1} = 1.46
$k_o \times 10^5$ = 1.40

TABLE 25

Total Oxidant 0.0059M
Sec.Butyl Alcohol 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	22.6	-
5	16.9	0.969
10	12.6	0.974
15	9.5	0.963
20	7.2	0.953
25	5.3	0.967
30	4.1	0.948

Mean $k \times 10^3$ Sec^{-1} = 0.962
$k_o \times 10^5$ = 0.930

TABLE 26

Sec.Butyl Alcohol 0.1250M
Total Oxidant 0.0025M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	29.0	2.15
20	25.6	2.12
30	22.4	2.15
40	19.7	2.15
50	17.4	2.13
60	15.2	2.15

Mean $k \times 10^4$ Sec^{-1} = 2.14

TABLE 27

Sec.Butyl Alcohol 0.1030M
Total Oxidant 0.0025M

Time mts.	Thio ccs	$k \times 10^4$ Sec-1
0	33.0	-
10	29.8	1.70
20	26.9	1.70
30	24.3	1.70
40	22.0	1.69
50	19.9	1.68
60	18.0	1.68

Mean $k \times 10^4$ Sec^{-1} = 1.69

TABLE 28

Sec.Butyl Alcohol 0.0741M
Total Oxidant 0.0025M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	30.7	1.20
20	28.5	1.22
30	26.5	1.22
40	24.8	1.19
50	23.0	1.20
60	21.3	1.22

Mean $k \times 10^4$ Sec^{-1} = 1.21

TABLE 29

Sec.Butyl Alcohol 0.0644M
Total Oxidant 0.0025M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	31.0	1.04
20	29.1	1.05
30	27.3	1.05
40	25.7	1.04
50	24.1	1.05
60	22.7	1.04

Mean $k \times 10^4$ Sec^{-1} = 1.05

TABLE 30

Sec.Butyl Alcohol 0.0508M
Total Oxidant .0025M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	31.4	0.829
20	29.9	0.822
30	28.45	0.824
40	27.0	0.835
50	25.7	0.834
60	24.5	0.827

Mean $k \times 10^4$ Sec^{-1} = 0.828

TABLE 31

Sec.Butyl Alcohol 0.0390M
Total Oxidant 0.0025M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	31.6	0.668
20	30.4	0.683
30	29.2	0.681
40	28.0	0.684
50	26.9	0.681
60	25.8	0.684

Mean $k \times 10^4$ Sec^{-1} = 0.680

Sec.Butyl alcohol 0.0800M
Total Oxidant 0.0032M

TABLE 32

Perchloric Acid 0.0100M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	30.0	-
10	20.5	6.34
20	14.0	6.35
30	9.5	6.39
40	6.5	6.37
50	4.5	6.32
60	3.1	6.30

Mean $k \times 10^4$ Sec^{-1} = 6.34
$k_o \times 10^5$ = 0.242

TABLE 33

Perchloric Acid 0.0400M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	28.9	-
10	13.7	12.4
20	6.5	12.4
30	3.1	12.4
40	1.45	12.5
50	0.7	12.4
60	-	

Mean $k \times 10^4$ Sec^{-1} = 12.4
$k_o \times 10^5$ = 0.498

TABLE 34

Perchloric Acid 0.1200M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	28.9	-
5	14.2	2.37
10	7.0	2.36
15	3.45	2.36
20	1.7	2.36
25	0.85	2.35
30	-	

Mean $k \times 10^3$ Sec^{-1} = 2.36
$k_o \times 10^5$ = 0.867

TABLE 35

Perchloric Acid 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	56.4	-
2	38.1	3.27
4	25.5	3.31
6	17.4	3.27
8	11.7	3.28
10	7.9	3.28
12	5.3	3.28

Mean $k \times 10^3$ Sec^{-1} = 3.28
$k_o \times 10^5$ = 1.20

TABLE 36

Perchloric Acid 0.2500M

Time mts.	Thio ccs	$Kx10^3$ Sec^{-1}
0	56.4	-
2	34.5	4.10
4	21.0	4.12
6	12.8	4.12
8	7.85	4.11
10	4.8	4.11
12	2.9	4.12

Mean $Kx10^3$ Sec^{-1} = 4.11

$k_o x10^5$ = 1.50

TABLE 37

Perchloric Acid 0.2700M

Time mts.	Thio ccs.	$Kx10^3$ Sec^{-1}
0	56.4	-
2	32.7	4.54
4	19.0	4.53
6	11.0	4.54
8	6.4	4.53
10	3.8	4.50
12	2.15	4.53

Mean $kx10^3$ Sec^{-1} = 4.53

$k_o x10^5$ = 1.63

TABLE 38

Total Oxidant 0.0248M
Methyl Alcohol 0.8000M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	111.1	-
10	98.3	2.04
20	87.8	1.96
30	78.1	1.96
40	69.4	1.96
50	61.7	1.96
60	54.9	1.96

Mean $kx10^4$ Sec^{-1} = 1.96

$k_o x10^5$ = 0.693

TABLE 39

Total Oxidant 0.0166M
Methyl Alcohol 0.8000M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	73.3	-
10	67.8	1.30
20	62.8	1.29
30	58.0	1.30
40	53.8	1.29
50	49.8	1.29
60	46.1	1.29

Mean $kx10^4$ Sec^{-1} = 1.29

$k_o x10^5$ = 0.282

TABLE 40

Total Oxidant 0.0132M
Methyl Alcohol 0.8000M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	55.6	-
10	51.8	1.18
20	48.7	1.10
30	45.0	1.18
40	42.3	1.14
50	39.1	1.17
60	36.4	1.18

Mean kx10^4 Sec^{-1} = 1.16
k_ox10^5 = 0.197

TABLE 41

Total Oxidant 0.0099M
Methyl Alcohol 0.8000M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	35.3	-
10	34.0	0.626
20	33.1	0.537
30	32.2	0.510
40	31.0	0.541
50	30.1	0.531
60	29.1	0.537

Mean kx10^4 Sec^{-1} = 0.531
k_ox10^5 = 0.085

TABLE 42

Total Oxidant 0.0083M
Methyl Alcohol 0.8000M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	40.0	-
10	38.8	0.512
20	37.8	0.472
30	36.6	0.494
40	35.5	0.498
50	34.5	0.494
60	33.5	0.493

Mean kx10^4 Sec^{-1} = 0.494
k_ox10^5 = 0.062

TABLE 43

Methyl Alcohol 0.6205M
Total Oxidant 0.0070M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	15.8	-
10	15.4	0.430
20	15.0	0.434
30	14.6	0.439
40	14.3	0.416
50	13.9	0.428
60	13.55	0.427

Mean kx10^4 Sec^{-1} = 0.429

TABLE 44

Methyl Alcohol 0.5645M
Total Oxidant 0.0070M

Time mts.	Thio ccs.	kx10^{4} Sec^{-1}
0	15.8	-
10	15.35	0.484
20	15.0	0.434
30	14.7	0.402
40	14.3	0.416
50	13.9	0.428
60	13.45	0.448
Mean kx10^{4} Sec^{-1} =		0.426

TABLE 45

Methyl Alcohol 0.4945M
Total Oxidant 0.0070M

Time mts.	Thio ccs.	kx10^{4} Sec^{-1}
0	15.8	-
10	15.45	0.376
20	15.0	0.434
30	14.7	0.402
40	14.3	0.416
50	13.9	0.428
60	13.5	0.438
Mean kx10^{4} Sec^{-1} =		0.416

TABLE 46

Methyl Alcohol 0.4338M
Total Oxidant 0.0070M

Time mts.	Thio ccs.	kx10^{4} Sec^{-1}
0	15.8	-
10	15.4	0.430
20	14.9	0.489
30	14.6	0.439
40	14.35	0.402
50	13.25	0.406
60	13.4	0.458
Mean kx10^{4} Sec^{-1} =		0.437

TABLE 47

Methyl Alcohol 0.3405M
Total Oxidant 0.0070M

Time mts.	Thio ccs.	kx10^{4} Sec^{-1}
0	15.8	-
10	15.4	0.430
20	15.0	0.434
30	14.6	0.439
40	14.35	0.402
50	13.85	0.406
60	13.55	0.427
Mean kx10^{4} Sec^{-1} =		0.423

TABLE 48

Methyl Alcohol 0.2985M
Total Oxidant 0.0070M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	15.8	-
10	15.4	0.430
20	14.9	0.489
30	14.7	0.402
40	14.3	0.416
50	13.8	0.451
60	13.5	0.438
Mean $k \times 10^4$ Sec^{-1} =		0.437

Methyl Alcohol 0.1333M
Total Oxidant 0.006M

TABLE 49

Perchloric Acid 0.0400M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	20.2	-
10	19.2	8.48
20	18.2	8.69
30	17.3	8.62
40	16.4	8.69
50	15.6	8.62
60	14.8	8.64
Mean $k \times 10^5$ Sec^{-1} =		8.63
$k_o \times 10^6$ =		0.910

TABLE 50

Perchloric Acid 0.1000M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	20.2	-
10	18.6	13.8
20	17.1	13.9
30	15.7	14.0
40	14.5	13.8
50	13.3	13.9
60	12.2	14.0
Mean $k \times 10^5$ Sec^{-1} =		13.9
$k_o \times 10^6$ =		1.43

TABLE 51

Perchloric Acid 0.1500M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	20.2	-
10	18.3	16.5
20	16.6	16.4
30	15.0	16.5
40	13.55	16.6
50	12.3	16.5
60	11.1	16.6
Mean $k \times 10^5$ Sec^{-1} =		16.5
$k_o \times 10^6$ =		1.70

TABLE 52

Perchloric Acid 0.2200M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	20.2	-
10	17.35	25.4
20	14.9	25.4
30	12.8	25.4
40	11.1	25.0
50	9.4	25.5
60	8.1	25.4

Mean $k \times 10^5$ Sec^{-1} = 25.3

$k_o \times 10^6$ = 2.50

TABLE 53

Total Oxidant 0.0248M
Ethyl Alcohol 0.8000M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	94.6	-
10	63.5	6.64
20	47.0	5.83
30	32.3	5.97
40	22.6	5.97
50	15.7	5.99
60	11.0	5.98

Mean $k \times 10^4$ Sec^{-1} = 5.95

$k_o \times 10^5$ = 1.30

TABLE 54

Total Oxidant 0.0166M
Ethyl Alcohol 0.8M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	61.8	-
10	47.8	4.30
20	39.9	3.65
30	32.4	3.59
40	25.6	3.67
50	20.6	3.66
60	16.5	3.67

Mean $k \times 10^4$ Sec^{-1} = 3.65

$k_o \times 10^5$ = 0.500

TABLE 55

Total Oxidant 0.0132M
Ethyl Alcohol 0.8000M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	45.0	-
10	38.0	2.82
20	33.5	2.46
30	29.2	2.40
40	25.2	2.42
50	21.8	2.41
60	18.9	2.41

Mean $k \times 10^4$ Sec^{-1} = 2.42

$k_o \times 10^5$ = 0.275

TABLE 56

Total Oxidant 0.0099M
Ethyl Alcohol 0.8000M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	25.2	-
10	23.2	1.38
20	22.0	1.13
30	20.55	1.13
40	19.2	1.13
50	18.0	1.12
60	16.8	1.13

Mean $k \times 10^4$ Sec^{-1} = 1.13
$k_o \times 10^5$ = 0.165

TABLE 57

Total Oxidant 0.0083M
Ethyl Alcohol 0.8000M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	22.0	-
10	20.5	1.17
20	19.6	0.962
30	18.6	0.933
40	17.6	0.930
50	16.7	0.919
60	15.8	0.919

Mean $k \times 10^4$ Sec^{-1} = 0.925
$k_o \times 10^5$ = 0.107

TABLE 58

Total Oxidant 0.0066M
Ethyl Alcohol 0.8000M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	16.3	-
10	15.5	0.840
20	15.0	0.693
30	14.3	0.728
40	13.8	0.694
50	13.2	0.703
60	12.7	0.693

Mean $k \times 10^4$ Sec^{-1} = 0.702
$k_o \times 10^5$ = 0.060

TABLE 59

Ethyl Alcohol 0.8400M
Total Oxidant 0.0065M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	25.8	-
10	24.76	0.795+
20	23.8	0.672
30	22.8	0.687
40	21.8	0.701
50	21.0	0.686
60	20.2	0.679

Mean $k \times 10^4$ Sec^{-1} = 0.685

TABLE 60

Ethyl Alcohol 0.8103M
Total Oxidant 0.0065M

Time mts.	Thio ccs.	$kx10^{4}$ Sec^{-1}
0	25.8	-
10	24.6	0.795
20	23.8	0.672
30	22.8	0.687
40	21.7	0.720
50	21.0	0.686
60	20.2	0.679
Mean $kx10^{4}$ Sec^{-1} =		0.689

TABLE 61

Ethyl Alcohol 0.7445M
Total Oxidant 0.0065M

Time mts.	Thio ccs.	$kx10^{4}$ Sec^{-1}
0	25.8	-
10	24.6	0.795+
20	23.8	0.672
30	22.75	0.699
40	21.8	0.701
50	21.0	0.686
60	20.1	0.693
Mean $kx10^{4}$ Sec^{-1} =		0.690

TABLE 62

Ethyl Alcohol 0.6424M
Total Oxidant 0.0065M

Time mts.	Thio ccs.	$kx10^{4}$ Sec^{-1}
0	25.8	-
10	24.7	0.725
20	23.75	0.691
30	22.7	0.712
40	21.8	0.701
50	21.0	0.686
60	20.2	0.679
Mean $kx10^{4}$ Sec^{-1} =		0.690

TABLE 63

Ethyl Alcohol 0.5732M
Total Oxidant 0.0065M

Time mts.	Thio ccs	$kx10^{4}$ Sec^{-1}
0	25.8	-
10	24.7	0.725
20	23.7	0.708
30	22.7	0.712
40	21.7	0.720
50	20.9	0.702
60	20.2	0.679
Mean $kx10^{4}$ Sec^{-1} =		0.708

TABLE 64

Ethyl Alcohol 0.4345M
Total Oxidant 0.0065M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	25.8	-
10	24.7	0.725
20	23.75	0.691
30	22.8	0.687
40	21.8	0.701
50	21.0	0.686
60	20.0	0.707
Mean $k \times 10^4$ Sec^{-1} =		0.694

Ethyl Alcohol 0.4000M
Total Oxidant 0.0050M

TABLE 65

Perchloric Acid 0.0400M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	20.0	-
10	17.7	2.03
20	15.7	2.02
30	13.9	2.02
40	12.2	2.06
50	10.8	2.05
60	9.6	2.04
Mean $k \times 10^4$ Sec^{-1} =		2.04
$k_o \times 10^6$ =		2.05

TABLE 66

Perchloric Acid 0.1000M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	20.0	-
10	16.2	3.51
20	13.2	3.46
30	10.7	3.47
40	8.8	3.42
50	7.1	3.45
60	5.8	3.44
Mean $k \times 10^4$ Sec^{-1} =		3.46
$k_o \times 10^6$ =		3.52

TABLE 67

Perchloric Acid 0.1500M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	20.0	-
10	14.8	5.02
20	11.8	4.40
30	9.4	4.19
40	7.4	4.14
50	5.6	4.24
60	4.4	4.20

Mean $k\times10^4$ Sec^{-1} = 4.19

$k_o\times10^6$ = 4.30

TABLE 68

Perchloric Acid 0.2300M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	20	-
5	15.7	8.07
10	14.5	5.36
15	12.1	5.58
20	10.6	5.29
25	9.0	5.32
30	7-8	5.23

Mean $k\times10^4$ Sec^{-1} = 5.36

$k_o\times10^6$ = 6.60

TABLE 69

Perchloric Acid 0.2500M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	16.2	-
2	14.7	8.10
4	14.1	5.80
6	13.2	5.68
8	12.25	5.82
10	11.55	5.65
12	10.80	5.63

Mean $k\times10^4$ Sec^{-1} = 5.72

$k_o\times10^6$ = 7.10

TABLE 70

Perchloric Acid 0.3000M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	17.20	-
2	15.6	8.14
4	14.75	6.40
6	13.55	6.63
8	12.25	7.07
10	11.25	7.10
12	10.35	7.05

Mean $k\times10^4$ Sec^{-1} = 6.85

$k_o\times10^6$ = 8.40

TABLE 71

Total Oxidant 0.0110M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs.	$kx10^5$ Sec^{-1}
0	33.8	-
10	31.5	11.7
20	29.5	11.3
30	27.6	11.3
40	25.5	11.7
50	23.9	11.5
60	22.2	11.7

Mean $kx10^5$ Sec^{-1} = 11.5

TABLE 72

Total Oxidant 0.0090M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs.	$kx10^5$ Sec^{-1}
0	27.9	-
10	26.6	7.95
20	25.4	7.83
30	24.3	7.50
40	23.1	7.82
50	22.0	7.92
60	20.95	7.96

Mean $kx10^5$ Sec^{-1} = 7.84

TABLE 73

Total Oxidant 0.0075M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs.	$kx10^5$ Sec^{-1}
0	21.3	-
10	20.45	6.79
20	19.6	6.93
30	18.8	6.93
40	18.05	6.89
50	17.2	7.13
60	16.6	6.93

Mean $kx10^{-5}$ Sec^{-1} = 6.94

TABLE 74

Total Oxidant 0.0060M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs	$kx10^5$ Sec^{-1}
0	22.5	-
10	21.7	6.03
20	21.0	5.76
30	20.2	5.99
40	19.5	5.97
50	18.7	6.17
60	18.1	6.04

Mean $kx10^5$ Sec^{-1} = 5.99

TABLE 75

Total Oxidant 0.0055M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	33.8	-
10	32.9	4.49
20	32.1	4.30
30	31.15	4.53
40	30.3	4.56
50	29.5	4.54
60	28.7	4.54
Mean $k \times 10^5$ Sec^{-1} =		4.49

TABLE 76

n-Propyl Alcohol 0.2560M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	27.0	-
10	25.2	11.5
20	23.5	11.6
30	21.95	11.5
40	20.5	11.5
50	19.1	11.5
60	17.8	11.6
Mean $k \times 10^5$ Sec^{-1} =		11.5

TABLE 77

n-Propyl Alcohol 0.2180M
Total Oxidant 0.0060M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	27.0	-
10	25.45	9.87
20	24.0	9.83
30	22.6	9.89
40	21.3	9.88
50	20.1	9.84
60	18.95	9.84
Mean $k \times 10^5$ Sec^{-1} =		9.86

TABLE 78

n-Propyl Alcohol 0.1950M
Total Oxidant 0.0060M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	27.0	-
10	25.6	8.91
20	24.3	8.79
30	23.1	8.67
40	21.9	8.73
50	20.8	8.70
60	19.75	8.68
Mean $k \times 10^5$ Sec^{-1} =		8.75

TABLE 79

n-Propyl Alcohol 0.1780
Total Oxidant 0.0060M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	27.0	-
10	25.7	8.25
20	24.55	7.93
30	23.4	7.96
40	22.3	7.97
50	21.3	7.90
60	20.3	7.93
Mean $k \times 10^5$ Sec^{-1} =		7.99

TABLE 80

n-Propyl Alcohol 0.1333M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	22.5	-
10	21.7	6.03
20	21.0	5.76
30	20.2	5.99
40	19.5	5.97
50	18.7	6.17
60	18.1	6.04
Mean $k \times 10^5$ Sec^{-1} =		5.99

TABLE 81

n-Propyl Alcohol 0.1000M
Total Oxidant 0.0060M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	33.8	-
10	32.9	4.49
20	32.1	4.30
30	31.15	4.53
40	30.3	4.56
50	29.5	4.54
60	28.7	4.54
Mean $k \times 10^5$ Sec^{-1} =		4.49

n-Propyl Alcohol 0.1333M
Total Oxidant 0.0060M

TABLE 82

Perchloric Acid 0.0250M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	18.7	-
10	17.9	7.25
20	17.2	6.97
30	16.5	6.95
40	15.8	7.01
50	15.2	6.91
60	14.6	6.87
Mean $k \times 10^5$ Sec^{-1} =		6.99

TABLE 83

Perchloric Acid 0.0400M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	18.7	-
10	17.7	9.13
20	16.7	9.42
30	15.8	9.35
40	15.0	9.18
50	14.2	9.17
60	13.4	9.26
Mean $k \times 10^5$ Sec^{-1} =		9.25

TABLE 84

Perchloric Acid 0.0650M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	14.8	-
10	13.8	11.7
20	12.85	11.8
30	12.05	11.4
40	11.15	11.8
50	10.4	11.8
60	9.75	11.6
Mean $k \times 10^5$ Sec^{-1} =		11.7

TABLE 85

Perchloric Acid 0.1000M

Time mts	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	17.0	-
10	15.6	14.3
20	14.3	14.4
30	13.1	14.5
40	12.0	14.5
50	11.0	14.5
60	10.1	14.5
Mean $k \times 10^5$ Sec^{-1} =		14.4

TABLE 86

Perchloric Acid 0.1500M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	17.0	-
10	15.3	17.5
20	13.9	16.8
30	12.5	17.1
40	11.3	17.0
50	10.3	16.7
60	9.3	16.7
Mean $K \times 10^5$ Sec^{-1} =		17.0

TABLE 87

Total Oxidant 0.0095M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	34.8	-
10	32.6	10.9
20	30.5	11.0
30	28.65	10.8
40	26.7	11.0
50	25.1	10.9
60	23.5	10.9
Mean $K \times 10^5$ Sec^{-1} =		10.9

TABLE 88

Total Oxidant 0.0090M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs	$K \times 10^5$ Sec^{-1}
0	29.7	-
10	28.1	9.25
20	26.7	8.89
30	25.3	8.92
40	24.0	8.88
50	22.8	8.82
60	21.6	8.85
Mean $K \times 10^5$ Sec^{-1} =		8.93

TABLE 89

Total Oxidant 0.0075M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs	$K \times 10^5$ Sec^{-1}
0	23.8	-
10	22.8	7.18
20	21.8	7.31
30	20.9	7.23
40	20.0	7.25
50	19.3	6.98
60	18.4	7.15
Mean $K \times 10^5$ Sec^{-1} =		7.18

TABLE 90

Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	21.0	-
10	20.2	6.45
20	19.5	6.18
30	18.9	5.85
40	18.2	5.96
50	17.7	5.69
60	17.0	5.87
Mean $K \times 10^5$ Sec^{-1} =		6.00

TABLE 91

Total Oxidant 0.0049M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	28.0	-
10	27.2	4.84
20	26.4	4.91
30	25.6	4.99
40	25.0	4.73
50	24.1	5.00
60	23.5	4.87
Mean $K \times 10^5$ Sec^{-1} =		4.89

TABLE 92

n-Butyl Alcohol 0.2700M
Total Oxidant 0.0060M

Time mts.	Thio ccs	$K \times 10^5$ Sec^{-1}
0	17.3	-
10	16.1	13.1
20	15.0	11.9
30	14.0	11.8
40	13.0	11.9
50	12.0	12.2
60	11.2	12.1
Mean $K \times 10^5$ Sec^{-1} =		12.2

TABLE 93

n-Butyl Alcohol 0.2300M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	17.3	-
10	16.2	10.9
20	15.3	10.2
30	14.4	10.2
40	13.5	10.3
50	12.7	10.3
60	12.0	10.1
Mean $K \times 10^5$ Sec^{-1} =		10.4

TABLE 94

n-Butyl Alcohol 0.2170M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	17.3	-
10	16.3	9.90
20	15.4	9.69
30	14.5	9.80
40	13.6	10.02
50	12.9	9.78
60	12.2	9.70
Mean $k \times 10^5$ Sec^{-1} =		9.82

TABLE 95

n-Butyl Alcohol 0.1750M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	28.0	-
10	26.7	7.95
20	25.5	7.81
30	24.3	7.88
40	23.1	8.02
50	22.0	8.05
60	21.1	7.86
Mean $k \times 10^5$ Sec^{-1} =		7.93

TABLE 96

n-Butyl Alcohol 0.1595M
Total Oxidant 0.0060M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	23.8	-
10	22.8	7.18
20	21.8	7.31
30	20.9	7.23
40	20.0	7.25
50	19.3	6.98
60	18.4	7.15
Mean $k \times 10^5$ Sec^{-1} =		7.18

TABLE 97

n-Butyl Alcohol 0.1088M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	28.0	-
10	27.2	4.84
20	26.4	4.91
30	25.6	4.99
40	25.0	4.73
50	24.1	5.00
60	23.5	4.87
Mean $k \times 10^5$ Sec^{-1} =		4.89

n-Butyl Alcohol 0.1333M
Total Oxidant 0.0060M

TABLE 98

Perchloric Acid 0.0600M

Time mts.	Thio ccs	kx10^4 Sec^{-1}
0	29.3	-
10	27.0	1.36
20	24.9	1.36
30	23.0	1.35
40	21.3	1.33
50	19.6	1.34
60	18.1	1.34
Mean kx10^4 Sec^{-1} =		1.35

TABLE 99

Perchloric Acid 0.1000M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	21.2	-
10	19.0	1.82
20	17.1	1.79
30	15.4	1.78
40	13.8	1.79
50	12.4	1.79
60	11.1	1.80
Mean kx10^4 Sec^{-1} =		1.79

TABLE 100

Perchloric Acid 0.1300M

Time mts.	Thio Ccs	kx10^4 Sec^{-1}
0	29.3	-
10	25.9	2.06
20	22.9	2.06
30	20.2	2.07
40	17.8	2.08
50	15.7	2.08
60	13.8	2.09
Mean kx10^4 Sec^{-1} =		2.07

TABLE 101

Perchloric Acid 0.2000M

Time mts.	Thio ccs	kx10^4 Sec^{-1}
0	29.3	-
10	24.8	2.78
20	21.4	2.62
30	18.2	2.64
40	15.5	2.65
50	13.4	2.61
60	11.6	2.57
Mean kx10^4 Sec^{-1} =		2.62

TABLE 102

Total Oxidant 0.0110M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	27.0	-
10	25.0	1.28
20	23.15	1.28
30	21.4	1.29
40	19.85	1.28
50	18.35	1.29
60	17.0	1.28
Mean $k \times 10^4$ Sec^{-1} =		1.28

TABLE 103

Total Oxidant 0.0090M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	61.0	-
10	57.2	1.07
20	53.5	1.09
30	50.15	1.09
40	47.0	1.09
50	44.0	1.08
60	41.3	1.08
Mean $k \times 10^4$ Sec^{-1} =		1.08

TABLE 104

Total Oxidant 0.0075M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	52.0	-
10	49.1	0.956
20	46.4	0.950
30	43.9	0.940
40	41.5	0.940
50	39.2	0.942
60	37.2	0.931
Mean $k \times 10^4$ Sec^{-1} =		0.943

TABLE 105

Total Oxidant 0.0060M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	47.0	-
10	44.8	0.798
20	42.7	0.800
30	40.6	0.810
40	38.7	0.810
50	36.9	0.807
60	35.0	0.819
Mean $k \times 10^4$ Sec^{-1} =		0.807

TABLE 106

Total Oxidant 0.0055M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	36.7	-
10	35.2	0.699
20	33.8	0.687
30	32.5	0.675
40	31.2	0.677
50	29.8	0.695
60	28.6	0.693
Mean $k\times10^4$ Sec^{-1} =		0.688

TABLE 107

IsoButyl Alcohol 0.2330M
Total Oxidant 0.0055M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	60.7	-
10	56.5	11.98
20	52.6	11.94
30	49.0	11.90
40	45.2	12.29
50	42.7	11.72
60	39.9	11.66
Mean $k\times10^5$ Sec^{-1} =		11.9

TABLE 108

IsoButyl Alcohol 0.1970M
Total Oxidant 0.0055M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	25.3	-
10	23.7	10.09
20	22.2	10.09
30	20.8	10.09
40	19.5	10.08
50	18.2	10.10
60	17.1	10.09
Mean $k\times10^5$ Sec^{-1} =		10.09

TABLE 109

IsoButyl Alcohol 0.1810M
Total Oxidant 0.0055M

Time mts.	Thio ccs	$k\times10^5$ Sec^{-1}
0	51.5	-
10	48.8	8.98
20	45.7	9.96
30	43.5	9.38
40	41.4	9.10
50	39.1	9.18
60	37.0	9.18
Mean $k\times10^5$ Sec^{-1} =		9.30

TABLE 110

IsoButyl Alcohol 0.1333M
Total Oxidant 0.0055M

Time mts.	Thio ccs.	$k \times 10^{5}$ Sec^{-1}
0	36.7	-
10	35.2	6.99
20	33.8	6.87
30	32.5	6.75
40	31.2	6.77
50	29.8	6.95
60	28.6	6.93

Mean $k \times 10^{4}$ Sec^{-1} = 6.88

TABLE 111

IsoButyl Alcohol 0.1218M
Total Oxidant 0.0055M

Time mts.	Thio ccs.	$k \times 10^{5}$ Sec^{-1}
0	37.5	-
10	36.1	6.33
20	34.7	6.47
30	33.6	6.10
40	32.2	6.34
50	31.2	6.12
60	30.0	6.20

Mean $k \times 10^{5}$ Sec^{-1} = 6.26

IsoButyl Alcohol 0.1333M
Total Oxidant 0.0060M

TABLE 112

Perchloric Acid 0.0500M

Time mts.	Thio ccs.	$k \times 10^{4}$ Sec^{-1}
0	22.6	-
10	18.9	2.98
20	15.7	3.04
30	13.1	3.03
40	10.9	3.04
50	9.1	3.03
60	7.5	3.06

Mean $k \times 10^{4}$ Sec^{-1} = 3.03

TABLE 113

Perchloric Acid 0.1000M

Time mts.	Thio ccs.	$k \times 10^{4}$ Sec^{-1}
0	22.6	-
10	17.3	4.46
20	13.2	4.48
30	10.2	4.43
40	7.6	4.54
50	6.0	4.42
60	4.8	4.31

Mean $k \times 10^{4}$ Sec^{-1} = 4.44

TABLE 114

Perchloric Acid 0.1500M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	22.6	-
10	16.3	5.44
20	11.7	5.49
30	8.4	5.50
40	6.0	5.53
50	4.3	5.53
60	3.1	5.52

Mean $kx10^4$ Sec^{-1} = 5.50

TABLE 115

Perchloric Acid 0.2000M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	22.6	-
5	18.6	6.49
10	15.4	6.39
15	12.0	6.40
20	10.5	6.39
25	8.7	6.37
30	7.3	6.28

Mean $kx10^4$ Sec^{-1} = 6.39

TABLE 116

Perchloric Acid 0.2500M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	22.6	-
5	17.7	8.14
10	13.9	8.10
15	11.0	8.00
20	8.7	7.96
25	6.7	8.14
30	5.30	8.06

Mean $kx10^4$ Sec^{-1} = 8.07

TABLE 117

Perchloric Acid 0.3000M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	22.6	-
5	16.9	9.69
10	12.6	9.74
15	9.5	9.63
20	7.1	9.65
25	5.3	9.67
30	4.0	9.62

Mean $kx10^4$ Sec^{-1} = 9.67

TABLE (C)

The Fraction of Total Oxidant Present at Zero Time as Molecular chlorine and Hypochlorous Acid in the Absence of Sodium chloride.

$(OX)_o$, M	pH	$a_{H^+} \times 10^3$	γCl^-	α_o	$(1-\alpha_o)$	B	$(Cl_2)_o \times 10^4$, M	$(HClO)_o \times 10^2$ M	$(B+Cl^-)_o$
0.0248	1.8	15.85	0.664	0.7282	0.2718	0.0485	67.42	1.806	0.0666
0.0166	2.05	8.913	0.664	0.8554	0.1446	0.0862	24.00	1.420	0.1004
0.0132	2.1	7.944	0.664	0.8903	0.1097	0.0967	14.48	1.175	0.1084
0.0099	2.15	7.080	0.664	0.9193	0.0807	0.1080	7.990	0.9100	0.1171
0.0083	2.2	6.310	0.664	0.9337	0.0663	0.1220	5.503	0.7750	0.1297
0.0066	2.25	5.624	0.664	0.9547	0.0453	0.1370	2.990	0.6300	0.1433

TABLE (D)

The Fraction of Total Oxidant Present at Zero Time as Molecular Chlorine and Hypochlorous Acid in the Presence of Sodium Chloride.

$(OX)_o$, M	pH	$a_H \times 10^3$	γCl^-	NaCl, M	α_o	$(1-\alpha_o)$	B	$(Cl^-)_o \times 10^2$ M	$(Cl_2) \times 10^3$ M	$(B+Cl^-)_o$	$K_3(Cl^-)_o^2$ $\times 10^3$
0.0066	2.25	5.624	.664	.050	.7120	.2880	0.1370	2.735	1.90	.1643	.1347
				.150	.4772	.5228		7.657	3.45	.2136	1.055
				.200	.3940	.6060		10.13	4.00	.2383	1.846
0.0099	2.15	7.080	.664	.004	.8940	.1060	0.1080	.6425	1.05	.1144	.0074
				.010	.8535	.1465		.9225	1.45	.1172	.0153
				.020	.7930	.2070		1.392	2.05	.1219	.0349
				.030	.7475	.2525		1.969	2.50	.1277	.0698
				.040	.6970	.3030		2.345	3.00	.1314	.0990
				.050	.6565	.3435		2.825	3.40	.1362	.1437
				.100	.5050	.4950		5.250	4.90	.1605	.4962
				.150	.4091	.5909		7.702	5.85	.1850	1.068
				.200	.3535	.6465		10.17	6.40	.2097	1.861
				.250	.3031	.6969		12.65	6.90	.2345	2.880
				.300	.2626	.7374		15.13	7.30	.2593	4.120

TABLE 118

Dependence of Oxidation Rate on the Concentration of Chlorine at 35°C (IsoPropyl Alcohol) = 0.2000M, $\mu = 0.4$

Total Oxidant $(OX)_{o}$, M	$k \times 10^3$ Sec^{-1}	$k_o \times 10^5$ mole. lit^{-1} Sec^{-1}	$\frac{k_o \times 10^3}{(ox)_o}$ Sec^{-1}	$\frac{k_o \times 10^3}{(HClO)}$ Sec^{-1}	$\frac{k_o \times 10^2}{(Cl_2)_o}$ Sec^{-1}
0.0248	3.76	10.8	4.35	5.98	1.60
.0166	2.52	5.00	3.01	3.52	2.08
.0132	1.73	2.65	2.01	2.25	1.83
.0099	1.05	1.50	1.51	1.65	1.88
.0083	.703	1.05	1.26	1.35	1.91
.0066	.512	.580	.879	.921	1.94

Mean $k_o/(Cl_2)_o$ = 1.87×10^{-2} Sec^{-1}

TABLE 119

Rate Constants as the Function of Isopropyl Alcohol Concentration at 35°C.

$(OX)_o = 0.0034M$

(Alcohol) M	0.0129	.0257	.0321	.0386	.0510	.0650	.0740
$10^4 k$, Sec^{-1}	0.296	.599	.765	.910	1.18	1.60	1.83
Order	-	1.03	1.10	.94	.93	1.25	1.04
$10^3 k$/(Alcohol)	2.30	2.33	2.38	2.36	2.32	2.46	2.47

Average $10^3 k$/ (Alcohol) = 2.37 litre $mole^{-1}$ Sec^{-1}

TABLE 120

Rate Constants as the Function of Perchloric Acid Concentration at 35°

(IsoPropyl Alcohol) = 0.1066M, $(OX)_o$ = 0.0052M, μ = 0.4

$(HClO_4)$,M	0.01	.04	.12	.20	.25	.30
$10^6 k_o$	3.50	7.20	13.0	22.0	27.4	34.0
Order	-	.52	.54	1.03	.98	1.18
$10^5 k_o/(H^+)^{1/2}$	3.50	3.60	3.75	-	-	-
$10^4 k_o/(H^+)$	-	-	1.08	1.10	1.10	1.13

TABLE 121

Dependence of Oxidation Rate on the Concentration of Chlorine at 35°C

(Sec. Butyl Alcohol) = 0.2000M, μ = 0.4

$(OX)_{o1}$M	k $\times 10^3$ Sec^{-1}	$k_o \times 10^5$ $mole.lit^{-1}$ Sec^{-1}	$\frac{k_o}{(HClO)_o} \times 10^3$ Sec^{-1}	$\frac{k_o}{(OX)_o} \times 10^3$ Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^2$ Sec^{-1}
0.0248	9.48	31.6	17.5	12.7	4.69
.0166	6.14	12.5	9.80	7.53	5.21
.0132	4.35	7.15	6.08	5.42	4.94
.0099	2.84	3.8	4.18	3.84	4.76
.0066	1.46	1.4	2.22	2.12	4.68

Mean $\frac{k_o}{(Cl_2)_o}$ = 4.86

TABLE 122

Rate Constants as the Function of Secondary Butyl Alcohol Concentration at 35°C

$(OX)_o$ = 0.0025M

(Alcohol) M	0.0390	.0508	.0644	.0741	.1030	.1250
10^4k, Sec^{-1}	0.680	.828	1.05	1.21	1.70	2.14
Order	-	0.74	1.00	1.00	1.04	1.19
10^3k/(Alcohol)	1.74	1.63	1.63	1.63	1.65	1.71

Average 10^3k/(Alcohol) = 1.66 litre $mole^{-1}$ Sec^{-1}

TABLE 123

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

(Sec.Butyl Alcohol) = 0.0800M, $(OX)_o$ = 0.0032M, μ = 0.4

$[HClO_4]$ M	0.01	.04	.12	.20	.25	.27
10^5k_o	.260	.498	.867	1.20	1.50	1.63
Order	-	.47	.50	.64	1.00	1.00
$10^5k_o/(H^+)^{1/2}$	2.32	2.49	2.50	2.68	-	-
$10^5k_o/(H^+)$	-	-	-	6.00	6.00	6.04

TABLE 124

Dependence of Oxidation Rate on the Concentration of Chlorine at 35°C

(Methyl Alcohol) = 0.8000M, $\mu = 0.4$

$(OX)_o$, M	Kint.$\times 10^4$ Sec^{-1}	$k_o \times 10^5$ mole lit^{-1} Sec^{-1}	$\frac{k_o}{(OX)_o} \times 10^3$ Sec^{-1}	$\frac{k_o}{(HClO)_o} \times 10^3$ Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^2$ Sec^{-1}
0.0248	1.96	.693	.279	.383	.103
.0166	1.29	.282	.170	.199	.117
.0132	1.16	.197	.150	.168	.136
.0099	.531	.085	.086	.093	.106
.0083	.494	.062	.075	.081	.114

$$\text{Mean } \frac{k_o}{(Cl_2)_o} = 0.115 \times 10^{-2}\ Sec^{-1}$$

TABLE 125

Rate Constants as the Function of Methyl Alcohol Concentration at 35°C

$(OX)_o = 0.0070$

(Alcohol),M	.2985	.3405	.4338	.4945	.5645	.6205	.6800
$10^4 k$	.437	.423	.437	.416	.426	.429	.429
Order	-	0	0	0	0	0	0

TABLE 126

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

(Methyl Alcohol) = 0.1333M, $(OX)_o$ = 0.0060, μ = 0.4

$(HClO_4)$, M	.04	.10	.15	.22
$k_o \times 10^6$	.910	1.43	1.70	2.50
Order	-	.49	.43	1.01
$10^6 k_o/(H^+)^{1/2}$	4.55	4.52	4.39	5.33
$10^6 k_o/(H^+)$	-	-	-	11.4

TABLE 127

Dependence of Oxidation Rate on the Concentration of Chlorine at 35°C

(Ethyl Alcohol) = 0.2000M, μ = 0.4

$(OX)_o$, M	$k \times 10^4$ Sec^{-1}	$k_o \times 10^5$ mole lit^{-1} Sec^{-1}	$\frac{k_o \times 10^3}{(OX)_o}$ Sec^{-1}	$\frac{k_o \times 10^3}{(HClO)_o}$ Sec^{-1}	$\frac{k_o \times 10^2}{(Cl_2)_o}$ Sec^{-1}
0.0248	5.95	1.30	.523	.718	.193
.0166	3.65	.500	.301	.352	.208
.0132	2.42	.275	.208	.234	.190
.0099	1.13	.165	.167	.181	.206
.0083	.925	.107	.129	.138	.195
.0066	.702	.060	.091	.095	.201

$$\text{Mean } \frac{k_o}{(Cl_2)_o} = 0.199 \times 10^{-2} \text{ Sec}^{-1}$$

TABLE 128

Rate Constants as the Function of Ethyl Alcohol Concentration at 35°C

$(OX)_o$ = 0.0065M

(Alcohol),M	.4345	.5732	.6424	.7445	.8103	.8400
10^4k, Sec^{-1}	.694	.708	.690	.690	.689	.685
Order	-	0	0	0	0	0

TABLE 129

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

(Ethyl Alcohol) =0.4000M, $(OX)_o$ = 0.0050M, μ = 0.4

($HClO_4$),M	.04	.10	.15	.23	.25	.30
10^6k_o	2.05	3.52	4.30	6.60	7.10	8.40
Order	-	.59	.49	1.00	.88	.92
$10^5k_o/(H^+)^{1/2}$	1.02	1.11	1.11	-	-	-
$10^5k_o/(H^+)$	-	-	-	2.87	2.84	2.80

TABLE 130

Rate Constants as the Function of Total Oxidant at 35°C

(n-Propyl Alcohol) = 0.1333M

(Total Oxidant),M	0.0110	.0090	.0075	.0060	.0055
10^5k, Sec^{-1}	11.5	7.84	6.94	5.99	4.49
Order	1	1	1	1	1

TABLE 131

Rate Constants as the Function of n-Propyl Alcohol Concentration at 35°C

$(OX)_o$ = 0.0060M

(Alcohol),M	0.1000	.1333	.1780	.1950	.2180	.2560
10^5k, Sec^{-1}	4.49	5.99	7.99	8.75	9.86	11.5
Order	-	1.00	1.00	1.00	1.08	.94
10^4k/(Alcohol)	4.49	4.50	4.48	4.48	4.52	4.48

Average 10^4k/(Alcohol) = 4.49 litre mole^{-1}Sec^{-1}

TABLE 132

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

(n-Propyl Alcohol) =0.1333M, $(OX)_o$ = 0.0060M, μ= 0.4

($HClO_4$),M	0.025	.040	.065	.100	.150
10^5k, Sec^{-1}	6.99	9.25	11.7	14.4	17.0
Order	-	.60	.49	.48	.41
$10^4k/(H^+)^{1/2}$	.830	1.39	2.24	3.42	4.95

TABLE 133

Rate Constants as the Function of Total Oxidant at 35°C

(n- Butyl Alcohol) = 0.1333M

(Total Oxidant), M	0.0095	.0090	.0075	.0060	.0049
10^5k, Sec^{-1}	10.9	8.93	7.18	6.00	4.89
Order	1	1	1	1	1

TABLE 134

Rate Constants as the Function of n-Butyl Alcohol Concentration at 35°C

$(OX)_o$ = 0.0060M

(Alcohol), M	0.1088	.1595	.1750	.2170	.2300	.2700
10^5k, Sec^{-1}	4.89	7.18	7.93	9.82	10.4	12.2
Order	-	1.00	1.07	.99	1.00	1.00
10^5k/(Alcohol)	4.50	4.50	4.53	4.52	4.52	4.52

Average 10^5k/(Alcohol) = 4.51 litre mole^{-1}Sec^{-1}

TABLE 135

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

(n-Butyl Alcohol) = 0.1333M, $(OX)_o$ = 0.0060M, μ = 0.4

$(HClO_4)$, M	.06	.10	.13	.20
10^4k, Sec^{-1}	1.35	1.79	2.07	2.62
Order	-	.55	.55	.55
$10^4k/(H^+)^{1/2}$	2.48	4.25	5.60	8.78

TABLE 136

Rate Constants as the Function of Total Oxidant at 35°C

(IsoButyl Alcohol) = 0.1333M

(Total Oxidant), M	0.0110	.0090	.0075	.0060	.0055
10^4k, Sec^{-1}	1.28	1.08	.943	.807	.688
Order	1	1	1	1	1

TABLE 137

Rate Constants as the Function of IsoButyl Alcohol Concentration at 35°C

$(OX)_o = 0.0055M$

(Alcohol),M	0.1218	.1333	.1810	.1970	.2330
10^5k, Sec^{-1}	6.26	6.88	9.30	10.09	11.9
Order	-	1.04	.99	.97	.99
$10^5k/$(Alcohol)	51.4	51.7	51.4	51.2	51.1

Average $10^5k/$(Alcohol) = 51.3 litre mole^{-1}Sec^{-1}

TABLE 138

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

(IsoButyl Alcohol) = 0.1333M, $(OX)_o = 0.0060M$, $\mu = 0.4$

$(HClO_4)$,M	0.05	.10	.15	.20	.25
10^4k, Sec^{-1}	3.03	4.44	5.50	6.39	8.07
Order	-	.55	.53	.52	1.04
$10^4k/\ H^{+\frac{1}{2}}$	5.10	1.05	1.59	2.14	-
$10^3k/\ H^+$	-	-	-	4.80	6.02

Results and Discussion : The orders of the reactions have been determined by Ostwald's isolation method(279). We observed that for the system : oxidant and alcohol, the order is first and first, with respect to both oxidant and alcohol in the case of isopropyl, sec.butyl, n-propyl, n-butyl, and iso-butyl alcohols, whereas in the case of methyl and ethyl alcohols, the order is first and zero, with respect to oxidant and alcohol respectively. Thus, for the system : oxidant and alcohol, the total order is second in the case of isopropyl, sec.butyl, n-propyl, n-butyl, and iso-butyl alcohols, and in the case of methyl and ethyl alcohols, the total order is first.

System : Oxidant and Alcohol

Alcohol	Order with respect to		Total order
	Oxidant	Alcohol	
Methyl	1	0	1
Ethyl	1	0	1
n-Propyl	1	1	2
Iso-Propyl	1	1	2
n-Butyl	1	1	2
Iso-Butyl	1	1	2
Sec-Butyl	1	1	2

In presence of perchloric acid, i.e. for the system : oxidant, alcohol, and hydrogen ions, the order with respect to hydrogen ions is half and first, at lower and higher concentrations of perchloric acid respectively, for all the alcohols.

From summary of the data it is clear that the value of pseudo first order rate constant increases in all cases with increasing initial stoichiometric concentration of oxidant, which is contrary to the expected trend if HOCl, produced by the hydrolysis of chlorine, is the active oxidant.

Consideration of the hydrolytic equilibrium of chlorine :

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

provides an explanation of the observed variation in the pseudo first order rates with initial stoichiometric concentration of oxidant. Assuming that hydrolysis is the sole source of initially present chloride ions, it is clear that the fraction of the total oxidant present initially as molecular chlorine increases with increasing initial stoichiometric concentration of oxidant. Our observations thus indicate that in all the cases studied, the rate of oxidation is proportional to the molecular chlorine concentration. This is confirmed by calculating $k_o/(Cl_2)_o$ (where k_o is the initial rate and $(Cl_2)_o$ is the initial concentration of molecular chlorine) which has been found to be constant for all the initial stoichiometric concentration of oxidant.

For reaction (i), the hydrolysis constant is given by

$$K_h = \frac{a_{HOCl} . a_{H^+} . a_{Cl^-}}{a_{Cl_2} . a_{H_2O}} = \frac{(HOCl)\ (H^+)\ (Cl^-)}{(Cl_2)} . \frac{\gamma_{HOCl} . \gamma_{Cl^-} \gamma_{H^+}}{\gamma_{Cl_2}} \quad ..(ii)$$

Assuming that $\gamma_{HOCl}/\gamma_{Cl_2}$ becomes unity even at 0.4 molar ionic strength, the equation (ii) at constant pH can be written as

$$\frac{K_h}{(H^+)\ \gamma_{Cl^-} \cdot \gamma_{H^+}} = \frac{(HOCl)\ (Cl^-)}{(Cl_2)}$$

or,

$$\frac{K_h}{\frac{a_{H^+}}{\gamma_{H^+}} \cdot \gamma_{Cl^-} \cdot \gamma_{H^+}} = \frac{(HOCl)\ (Cl^-)}{(Cl_2)}$$

where $(H^+) = \frac{a_{H^+}}{\gamma_{H^+}}$ and $pH = -\log_{10} a_{H^+}$.

or $$B = \frac{K_h}{a_{H^+} \cdot \gamma_{Cl^-}} = \frac{(HOCl)\ (Cl^-)}{(Cl_2)} \quad \ldots\ldots\ldots\ldots \quad (iii)$$

B can be calculated by substituting in values of K_h, a_{H^+} and γ_{Cl^-}

Connick and Chia(53) reported the value of K_h at 35°C as equal to 5.10×10^{-4}. The value of a_{H^+} has been determined by measuring the pH of the solution with the help of a pH meter (Beckmann Zeromatic, No.175) using glass electrode and calomel half cell. The value of γ_{Cl^-} in KCl solution has been calculated by extrapolation of the values reported by Harned and Owen(283), which comes out to be 0.664 at 35°C.

The value of γ_{H^+} can easily be estimated by assuming(284) that $\gamma_{K^+} = \gamma_{Cl^-}$ in 0.4 molar solutions of of KCl. Thus,

$$\gamma^2_{KCl} = \gamma_{Cl^-} \cdot \gamma_{Cl^-} \quad \text{and} \quad \gamma^2_{HCl} = \gamma_{H^+} \cdot \gamma_{Cl^-}$$

so that $$\frac{\gamma^2_{KCl}}{\gamma^2_{HCl}} = \frac{\gamma_{Cl^-} \cdot \gamma_{Cl^-}}{\gamma_{H^+} \cdot \gamma_{Cl^-}} = \frac{\gamma_{Cl^-}}{\gamma_{H^+}}$$

or, $$\gamma_{H^+} = \frac{\gamma_{Cl^-} \cdot \gamma^2_{HCl}}{\gamma^2_{KCl}} \qquad \text{................} \quad (iv)$$

the values of γ_{Cl^-}, γ^2_{HCl} and γ^2_{KCl} are available in literature$^{(283)}$.

For reaction (i), the degree of hydrolysis at zero time can be written as

$$\alpha_o = \frac{(HOCl)o}{(OX)o} \quad \text{and} \quad (1-\alpha_o) = \frac{(Cl_2)o}{(OX)o}$$

and $(Cl^-)o = (HOCl)o = \alpha_o\,(OX)o$

where (OX)o is the initial stoichiometric concentration of the oxidant.

From equation (iii), thus we have at zero time,

$$B = \frac{(HOCl)\,(Cl^-)}{(Cl_2)} = \frac{\alpha_o(OX)o\;\alpha_o(OX)o}{(1-\alpha_o)\,(OX)o} = \frac{\alpha_o^2(OX)o}{(1-\alpha_o)}$$

or $\alpha_o^2\,(OX)_o + B\alpha_o - B = 0$

or $$\alpha_o = \frac{-B + \sqrt{B^2 + 4B\,(OX)_o}}{2\,(OX)_o} \qquad \text{..............} \quad (v)$$

We calculated the value of α_o for various initial stoichiometric concentration of oxidant. In Table C various data obtained by using the above equations are shown.

The specific first order rate constants, k_{Cl_2} and k_{HOCl}, for molecular chlorine and hypochlorus acid can easily be calculated by knowing the values of k_o and α_o

because

$$k_{Cl_2} = \frac{ko}{(Cl_2)_o} \text{ and } k_{HOCl} = \frac{ko}{(HOCl)o}$$

The constancy of $k_o/(Cl_2)o$ at different initial concentration of total oxidant is an evidence that molecular chlorine is the principal effective oxidant for the oxidation of alcohols and HOCl is playing a negligible role.

It will not be out of place to mention here that as the calculations of k_o and other data are time consuming and tedious, we calculated $ko/(Cl_2)_o$ in the case of isopropyl, sec.butyl, methyl and ethyl alcohols only. In the case of n-propyl, n-butyl and iso-butyl alcohols we have not calculated $ko/(Cl_2)_o$, but similar trend of data indicates that in these cases as well, molecular chlorine is the principal effective oxidant.

SEC. 2.2 IDENTIFICATION OF PRODUCTS OF THE REACTIONS

Introduction :- The starting point for any reaction mechanism is the identification of all possible products of the reaction in question. In this section, products of the reactions of alcohols with aqueous chlorine have been isolated and identified.

In general, the primary alcohols were found to oxidize to their corresponding aldehydes and secondary alcohols to their corresponding ketones by chlorine in aqueous solution and then the alkyl groups of the carbonyl compounds get chlorinated through consecutive reactions. In order to know the peculiar behaviour of aqueous chlorine, the identifications, specially of the reaction of isopropyl alcohol with chlorine have been made under different conditions.

EXPERIMENTAL

(i) Analysis of the Products of the Reaction of Isopropyl Alcohol:

Chlorine in aqueous solution oxidizes isopropyl alcohol into acetone and then a small portion of acetone gets chlorinated into monochloroacetone. The reaction products were analysed as follows:-

In a typical experiment, 11.72 gms of isopropyl alcohol and 120 ml of 0.029M chlorine water were taken in a conical flask. The solution was allowed to stand at room temperature for two days and then the products of the reaction were precipitated as 2:4 - dinitro phenyl hydrazone derivative(285). Yield of derivative, 1.0278 gm; m.p.121-122°C (m.p. of pure 2:4 -di - nitro phenyl hydrazone of acetone is 125-126°C).

In a portion of the above derivative, the quantity of monochloroacetone was estimated by Stephnow's method(285). We found that the derivative contains acetone and monochloroacetone in the ratio of 4:1.

Similarly, we also precipitated the 2:4-dinitro phenyl hydrazones of the products of the reaction of aqueous chlorine with isopropyl alcohol in the presence of (i) perchloric acid (m.p 122-123°C), (ii) sodium chloride (m.p123-124°C) and (iii) zinc chloride (m.p.119-120°C). The preliminary estimations reveal that beside acetone, a small portion of monochloro-, dichloro-, and trichloro - acetones are formed in the presence of perchloric acid, sodium chloride and zinc chloride respectively. It may be mentioned here that the estimations of exact amount of chloro derivatives in this reaction by ordinary organic estimation methods are difficult. Rodd(286) reported that the chlorine gas, however, converts pure isopropyl alcohol into 1:1:1:3 tetrachloro acetone(286).

(ii) Identification of the Products of the Reaction of Other Primary and Secondary Alcohols :

In the case of methyl-, ethyl-, n-propyl-, n-butyl-, isobutyl- and secondary butyl alcohols, as described above, the reaction mixtures, (i) 2 gms of alcohol + 40 ml of 0.035M total oxidant and (ii) 2 gms of alcohol + 40 ml of 0.035M total oxidant + 2 ml of 2M perchloric acid, were allowed to stand for two days at room temperature and the products of the reactions were precipitated as 2:4 dinitrophenyl hydrazone derivative. In Table 139, the m.p.of the derivatives and the m.p of pure 2:4 dinitro phenyl hydrazone of the carbonyl compounds(287)are given.

TABLE 139

Identification of the Products of the Reactions of Alcohols with Aq. Chlorine.

Alcohol	Expected Oxidation Product	m.p.of pure 2:4 dinitrophenyl hydrazone of the carbonyl compound in °C	Observed m.p.of the derivative		Colour of the derivative
			in absence of $HClO_4$ °C	in presence of $HClO_4$ °C	
Methyl	Formaldehyde	166°	134°-135°	132°-133°	Orange-Yellow
Ethyl	Acetaldehyde	147°,168°	138°-139°	137°-138°	Orange-Yellow
n-Propyl	n-Propionaldehyde	155°	137°-138°	134°-135°	Orange
IsoPropyl	Acetone	126°	121°-122°	122°-123°	Yellow
n-Butyl	n-Butyraldehyde	126°	131°-132°	128°-129°	Orange
IsoButyl	Iso-Butyraldehyde	187°	171°-172°	170°-171°	Yellow
Sec-Butyl	Methyl-ethyl ketone	115°	106°-107°	105°-106°	Orange

SEC. 2.3 INFLUENCE OF IONIC STRENGTH ON THE REACTION RATE

According to Lewis and Randall(288), the ionic strength is a measure of the intensity of electric field due to the ions in solutions. They defined the ionic strength μ of a solution by the equation.

$$\mu = \frac{1}{2} \Sigma Ci\ Zi^2$$

where c_i is the actual concentration (or molality) of each ion and Z_i its valence.

Ionic strength of the medium plays an important role in the reactions occurring in solution between ions. It was found that the velocity of the reaction 'v' may be given by the equation

$$v = KC_aC_b\ 10^{Z_aZ_b\sqrt{\mu}}$$

where Ca and C_b are the concentrations and Za and Z_b the valency of the each ion(289) respectively.

This expression clearly indicates that if the product Za Zb is positive, i.e., when the reacting ions are of the same sign (either positive or negative), the velocity of the reaction will increase with increasing ionic strength; and when the reacting ions are of the opposite sign, the velocity will decrease with increasing ionic strength. In a case when either one or both the reactants are uncharged, the velocity will be independent of the ionic strength.

Bronsted(290,291) suggested that for ionic reactions in solution, it is necessary to keep the total ionic strength of the solution constant throughout for a comparative study. In such cases the primary and secondary salt effects influence the velocity of the reaction when experiments are performed in solutions of varying ionic strength. The primary salt effect is concerned with the effect of salts on the activity coefficients of the reactants and the activated complex formed as an intermediate in the reaction(292 to 294), while the secondary salt effect is concerned with the influence of ionic strength of the medium on the concentration of catalytic active ions(294,295).

In this section the influence of ionic strength on the rates of the reactions have been studied in the case of isopropyl and sec. butyl alcohols only by varying the amounts of sodium perchlorate. The results are recorded in the following tables.

TABLE 140

Temperature 35°C
IsoPropyl Alcohol 0.0674M
Total Oxidant 0.0042M

1. Sodium Perchlorate 0.0000M

Time mts	Thio ccs	$k \times 10^4$ Sec^{-1}
0	21.2	-
10	19.6	1.30
20	18.15	1.29
30	16.8	1.29
40	15.55	1.29
50	14.4	1.29
60	13.2	1.31
Mean $k \times 10^4$ Sec^{-1} =		1.29

2. Sodium Perchlorate 0.2000M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	29.0	-
10	27.0	1.19
20	25.15	1.18
30	23.35	1.20
40	21.75	1.20
50	20.25	1.20
60	18.85	1.20
Mean $k \times 10^4$ Sec^{-1} =		1.19

3. Sodium Perchlorate 0.2700M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	29.0	-
10	27.0	1.19
20	25.1	1.20
30	23.4	1.19
40	21.75	1.20
50	20.25	1.20
60	18.85	1.20
Mean $k \times 10^4$ Sec^{-1} =		1.20

4. Sodium Perchlorate 0.3300M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	21.2	-
10	19.85	1.09
20	18.6	1.09
30	17.4	1.10
40	16.3	1.09
50	15.25	1.10
60	14.3	1.09
Mean $k \times 10^4$ Sec^{-1} =		1.09

5. Sodium Perchlorate 0.3600M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	21.2	-
10	19.9	1.05
20	18.65	1.07
30	17.5	1.06
40	16.45	1.06
50	15.4	1.07
60	14.5	1.05

Mean kx10^4 Sec^{-1} = 1.06

6. Sodium Perchlorate 0.3800M

Time mts.	Thio ccs	kx10^4 Sec^{-1}
0	21.2	-
10	19.9	1.05
20	18.65	1.07
30	17.5	1.06
40	16.5	1.05
50	15.4	1.06
60	14.5	1.05

Mean kx10^4 Sec^{-1} = 1.06

TABLE 141

Temperature 35°C
IsoPropyl Alcohol 0.0663M
Total Oxidant 0.0088M
Perchloric Acid 0.0245M

1. No Catalyst

Time mts.	Thio ccs	kx10^4 Sec^{-1}
0	54.25	-
10	33.3	8.14
20	20.4	8.15
30	12.5	8.15
40	7.7	8.14
50	4.7	8.14
60	2.9	8.12

Mean kx10^4 Sec^{-1} = 8.14

2. Sodium Perchlorate 0.0200M

Time mts.	Thio ccs	kx10^4 Sec^{-1}
0	54.25	-
10	33.3	8.14
20	20.5	8.11
30	12.6	8.11
40	7.8	8.08
50	4.7	8.14
60	2.9	8.12

Mean kx10^4 Sec^{-1} = 8.12

3. Sodium Perchlorate 0.0400M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	54.25	-
10	33.35	8.11
20	20.5	8.11
30	12.6	8.11
40	7.75	8.11
50	4.7	8.14
60	2.9	8.12
Mean $k \times 10^4$ Sec^{-1} =		8.12

4. Sodium Perchlorate 0.0600M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	54.25	-
10	33.55	8.02
20	20.7	8.03
30	12.8	8.04
40	7.85	8.06
50	4.7	8.14
60	2.9	8.12
Mean $k \times 10^4$ Sec^{-1} =		8.07

5. Sodium Perchlorate 0.0800M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	54.25	-
10	33.4	8.09
20	20.55	8.09
30	10.65	8.09
40	7.85	8.06
50	4.7	8.14
60	2.9	8.12
Mean $k \times 10^4$ Sec^{-1} =		8.10

6. Sodium Perchlorate 0.1000M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	54.25	-
10	33.3	8.14
20	20.5	8.11
30	12.6	8.11
40	7.8	8.08
50	4.7	8.14
60	3.25	7.78
Mean $k \times 10^4$ Sec^{-1} =		8.07

7. Sodium Perchlorate 0.1500M

Time mts.	Thio ccs.	kx10^{4} Sec^{-1}
0	54.25	-
10	33.4	8.09
20	20.7	8.03
30	12.8	8.03
40	7.85	8.06
50	4.7	8.14
60	3.4	7.69

Mean kx10^{4} Sec^{-1} = 8.00

8. Sodium Perchlorate 0.2000M

Time mts.	Thio ccs.	kx10^{4} Sec^{-1}
0	54.25	-
10	33.4	8.09
20	20.7	8.03
30	12.8	8.03
40	7.85	8.06
50	4.7	8.14
60	3.25	7.78

Mean kx10^{4} Sec^{-1} = 8.02

TABLE 142

Temperature 35°C

Sec.Butyl Alcohol	0.0800M
Total Oxidant	0.0030M
Perchloric Acid	0.0533M

1. Sodium Perchlorate 0.0000M

Time mts.	Thio ccs.	kx10^{3} Sec^{-1}
0	46.4	-
4	32.8	1.44
8	23.2	1.44
12	16.5	1.44
16	11.7	1.43
20	8.4	1.42
24	5.9	1.43

Mean kx10^{3} Sec^{-1} = 1.44

2. Sodium Perchlorate 0.2060M

Time mts.	Thio ccs.	kx10^{3} Sec^{-1}
0	46.4	-
4	31.0	1.68
8	21.2	1.63
12	14.3	1.63
16	9.9	1.61
20	6.9	1.59
24	4.4	1.63

Mean kx10^{3} Sec^{-1} = 1.63

3. Sodium Perchlorate 0.3090M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	46.4	-
4	30.2	1.79
8	21.1	1.64
12	14.0	1.66
16	9.5	1.65
20	6.5	1.64
24	4.3	1.65
Mean $k \times 10^3$ Sec^{-1} =		1.67

4. Sodium Perchlorate 0.4120M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	46.4	-
4	30.0	1.82
8	19.9	1.76
12	13.2	1.75
16	9.8	1.62
20	5.7	1.75
24	3.7	1.57
Mean $k \times 10^3$ Sec^{-1} =		1.71

5. Sodium Perchlorate 0.5150M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	46.4	-
4	29.0	1.96
8	19.05	1.85
12	11.40	1.95
16	7.8	1.86
20	5.0	1.86
24	3.2	1.86
Mean $k \times 10^3$ Sec^{-1} =		1.89

6. Sodium Perchlorate 0.5803M

Time mts.	Thio ccs	$K \times 10^3$ Sec^{-1}
0	46.4	-
4	28.7	2.00
8	17.8	2.00
12	11.0	2.00
16	6.8	2.00
20	4.3	1.98
24	2.7	1.97
Mean $k \times 10^3$ Sec^{-1} =		1.99

TABLE 143

Effect of Change in Ionic Strength on the Rate of Oxidation of Isopropyl Alcohol with Total Oxidant at 35°C

(a) (Isopropyl Alcohol) = 0.0674M, $(OX)_o$ = 0.0042M, $(HClO_4)$ = 0.00M

NaClO4 ,M	0.00	0.20	0.27	0.33	0.36	0.38
10^4k, Sec^{-1}	1.29	1.19	1.20	1.09	1.06	1.06

(b) (Alcohol) = 0.0663M, $(OX)_o$ = 0.0088M, (HClO4) = 0.0245M

NaClO4 ,M	0.00	0.02	0.04	0.06	0.08	0.10	0.15	0.20
10^4k, Sec^{-1}	8.14	8.12	8.12	8.07	8.10	8.07	8.00	8.02

TABLE 144

Effect of Change in Ionic Strength on the Rate of Oxidation of Secondary Butyl Alcohol with Total Oxidant at 35°C

(Alcohol) = 0.0800M, $(OX)_o$ = 0.0029M, (HClO4) = 0.0533M

NaClO4 ,M	0.00	0.21	0.31	0.41	0.51	0.58
10^3k, Sec^{-1}	1.44	1.63	1.67	1.71	1.89	1.99

Results and Discussion : The effect of adding different concentrations of sodium perchlorate solution on the reaction rate was studied at 35°C. The data presented in Tables 143,144 indicate that there is no significant influence of ionic strength on the reaction rates; for the system : isopropyl alcohol, total oxidant and perchloric acid, the variation of the rate constants being within 1 %, whereas for the systems : isopropyl alcohol and total oxidant; sec. butyl alcohol, total oxidant and perchloric acid, the variation is within 6 % and 4 % respectively. This indicates that the reactions are not ionic in nature.

SEC.2.4 EFFECT OF SOME INORGANIC SALTS ON THE REACTION RATE:

Since long it has been observed that the rate of a chemical reaction is altered in presence of a substance (catalyst) which remains unaltered at the end of the reaction. There are indications that the catalyst does undergo a chemical change temporafily by forming transient intermediates with the reactant (or reactants) but in the end the catalyst is regenerated. A catalyst may be thought of as a substance which makes it possible for a reaction to take place by lowering the energy of activation or the free energy of activation requirement of the process.

The mechanism by which a catalyst functions depends upon the type of the reactions in which it takes part. The mode of action of the catalyst may largely be chemical or the catalyst may have a purely physical effect and in some cases both the types of influence may be exerted.

Very little is available about the influence of inorganic salts on the reactions with chlorine. While studying the reactions of chlorine with acetic anhydride,(103,104) aromatic compounds(110,127,192) and glucose(79), the scientists reported that the chloride ions accelerate the rate of the reactions. Saxe and Lichtin(79) observed that in the oxidation of glucose by chlorine, besides sodium chloride, potassium perchlorate also enhances the rate, while sodium sulphate has only a negligible effect. Recently Crabtree and Schaefer(169) reported that chloride ions increases the rate of oxidation of Fe(ii)by chlorine.

In this section the oxidations of methyl, ethyl, isopropyl and sec. butyl alcohols by chlorine water have been studied in the presence of some inorganic salts at constant ionic strength of 0.4. The difference in the rate of the reaction in the presence of a salt from that of the reaction in the absence of the salt shows the effect of the salt used and this difference is assumed to be proportional to the catalysing influence of the salt.

Throughout we maintained the concentrations of alcohols in large excess. The pseudo first order rate constants were calculated for each aliquot portion titrated and the arithmetic mean of the set of values were obtained and compared.

EXPERIMENTAL

All the chemicals were B.D.H (AnalaR) or Merck(c.p) grade or of comparable purity.

The progress of the reaction was studied iodometrically at 35°C according to the method explained in Sec.2.1.

The effects of only those salts have been studied which do not interfere with iodometric titrations. Several mono, di, and trivalent metal chlorides have been used. The concentrations of the salts and the values of pseudo first order rate constants are shown in the following tables. A summary of data is given in Tables 149 to 152.

TABLE 145

IsoPropyl Alcohol 0.0332M
Total Oxidant 0.0078M
Temp. 35°C; μ = 0.4

1. NoCatalyst

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	32.7	-
10	31.9	4.11
20	31.05	4.30
30	30.3	4.25
40	29.5	4.29
50	28.75	4.28
60	28.0	4.30

Mean $k \times 10^5$ Sec^{-1} = 4.28

2. Silver Nitrate 0.0020M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	15.1	-
5	14.9	4.45
10	14.7	4.48
15	14.5	4.50
20	14.3	4.53
25	14.05	4.93
30	13.8	5.00

Mean $k \times 10^5$ Sec^{-1} = 4.75

3. Silver Nitrate 0.0040M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	17.05	-
10	16.5	5.41
20	16.0	5.28
30	15.5	5.28
40	15.0	5.32
50	14.55	5.27
60	14.10	5.27

Mean $k \times 10^5$ Sec^{-1} = 5.28

4. Silver Nitrate 0.0080M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	11.5	-
10	11.05	6.68
20	10.6	6.79
30	10.2	6.67
40	9.8	6.67
50	9.4	6.72
60	9.05	6.66

Mean $k \times 10^5$ Sec^{-1} = 6.70

5. Silver Nitrate 0.0100M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	11.5	-
10	10.8	10.5
20	10.15	10.4
30	9.55	10.3
40	8.95	10.4
50	8.4	10.5
60	7.9	10.4
Mean $k\times10^5$ Sec^{-1} =		10.4

6. Sodium Nitrate 0.3200M

Time mts.	Thio ccs	$k\times10^5$ Sec^{-1}
0	25.95	-
10	25.10	5.56
20	24.25	5.65
30	23.45	5.62
40	22.7	5.58
50	21.9	5.66
60	21.2	5.62
Mean $k\times10^5$ Sec^{-1} =		5.61

7. Cobalt Nitrate 0.0250M

Time mts.	Thio ccs	$k\times10^5$ Sec^{-1}
0	18.55	-
10	18.1	4.11
20	17.7	3.95
30	17.25	4.04
40	16.85	4.01
50	16.45	4.01
60	16.05	4.03
Mean $k\times10^5$ Sec^{-1} =		4.04

8. Zirconium Nitrate 0.0240M

Time mts.	Thio ccs	$k\times10^5$ Sec^{-1}
0	25.95	-
10	23.9	13.7
20	22.0	13.8
30	20.25	13.8
40	18.65	13.8
50	17.15	13.8
60	15.8	13.8
Mean $k\times10^5$ Sec^{-1} =		13.8

9. Cerous Nitrate 0.0130M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	25.9	-
10	24.65	8.24
20	23.5	8.10
30	22.4	8.07
40	21.3	8.15
50	20.3	8.12
60	19.35	8.10

Mean $k \times 10^5$ Sec^{-1} = 8.10

10. Sodium Chloride 0.1000M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	23.15	-
10	17.05	51.0
20	12.6	50.7
30	9.3	50.7
40	6.85	50.7
50	5.05	50.7
60	3.75	50.6

Mean $k \times 10^5$ Sec^{-1} = 50.7

11. Sodium Chloride 0.2100M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	27.3	-
10	19.0	6.04
20	13.25	6.02
30	9.2	6.04
40	6.4	6.04
50	4.45	6.05
60	3.2	5.96

Mean $k \times 10^4$ Sec^{-1} = 6.04

12. Sodium Chloride 0.3200M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	27.3	-
10	18.1	6.85
20	12.0	6.85
30	7.95	6.85
40	5.25	6.85
50	3.5	6.85
60	2.3	6.87

Mean $k \times 10^4$ Sec^{-1} = 6.86

13.Potassium Chloride 0.0750M

Time mts.	Thio ccs	$Kx10^4$ Sec^{-1}
0	25.95	-
10	17.7	6.38
20	12.05	6.39
30	8.2	6.40
40	5.6	6.39
50	3.8	6.40
60	2.6	6.39

Mean $Kx10^4$ Sec^{-1} = 6.39

14.Calcium Chloride 0.1000M

Time mts.	Thio ccs.	$Kx10^4$ Sec^{-1}
0	18.55	-
10	11.4	8.12
20	7.0	8.12
30	4.3	8.12
40	2.65	8.12
50	1.6	8.12
60	-	

Mean $Kx10^4$ Sec^{-1} = 8.12

15.Magnesium Chloride 0.0500M

Time mts.	Thio ccs.	$Kx10^4$ Sec^{-1}
0	15.1	-
10	11.2	5.00
20	8.35	4.94
30	6.2	4.95
40	4.6	4.95
50	3.45	4.92
60	2.55	4.94

Mean $Kx10^4$ Sec^{-1} = 4.95

16.Strontium Chloride 0.0500M

Time mts.	Thio ccs.	$Kx10^4$ Sec^{-1}
0	15.1	-
10	11.6	4.39
20	8.9	4.41
30	6.85	4.39
40	5.25	4.40
50	4.0	4.43
60	3.1	4.40

Mean $Kx10^4$ Sec^{-1} = 4.40

17. Barium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	15.1	-
10	11.65	4.32
20	9.0	4.31
30	7.0	4.27
40	5.35	4.32
50	4.15	4.31
60	3.2	4.31

Mean $k \times 10^4$ Sec^{-1} = 4.31

18. Zinc Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	15.1	-
10	8.85	8.91
20	5.2	8.89
30	3.05	8.89
40	1.8	8.86
50	1.05	8.90
60	0.6	8.95

Mean $k \times 10^4$ Sec^{-1} = 8.90

19. Cadmium Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	15.1	-
10	12.6	3.02
20	10.45	3.07
30	8.7	3.06
40	7.2	3.09
50	6.05	3.05
60	5.00	3.07

Mean $k \times 10^4$ Sec^{-1} = 3.06

20. Aluminium Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	23.15	-
10	20.0	2.44
20	17.25	2.45
30	14.9	2.45
40	12.85	2.45
50	11.10	2.45
60	9.8	2.39

Mean $k \times 10^4$ Sec^{-1} = 2.43

21. Magnesium Sulphate 0.0500M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	23.15	-
10	22.75	2.88
20	22.3	3.11
30	21.9	3.08
40	21.5	3.08
50	21.1	3.08
60	20.7	3.10

Mean $k \times 10^5$ Sec^{-1} = 3.09

22. Manganous Sulphate 0.0500M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	32.7	-
10	32.2	2.53
20	31.7	2.57
30	31.2	2.60
40	30.7	2.63
50	30.25	2.59
60	29.75	2.62

Mean $k \times 10^5$ Sec^{-1} = 2.59

23. Beryllium Sulphate 0.0250M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	25.9	-
10	25.2	4.57
20	24.5	4.63
30	23.85	4.58
40	23.2	4.59
50	22.6	4.54
60	21.95	4.60

Mean $k \times 10^5$ Sec^{-1} = 4.58

24. Zinc Sulphate 0.0500M

Time mts.	Thio ccs	$k \times 10^5$ Sec^{-1}
0	17.05	-
10	16.85	1.92
20	16.65	1.96
30	16.45	1.98
40	16.3	1.86
50	16.1	1.90
60	15.9	1.93

Mean $k \times 10^5$ Sec^{-1} = 1.92

25. Sodium Fluoride 0.1000M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	17.05	-
10	16.5	5.41
20	16.0	5.28
30	15.5	5.28
40	15.0	5.32
50	14.55	5.27
60	14.10	5.27

Mean $k \times 10^5$ Sec^{-1} = 5.28

26. Potassium Dihydrogen Phosphate 0.1000M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	17.05	-
10	16.1	9.52
20	15.15	9.83
30	14.3	9.76
40	13.5	9.72
50	12.7	9.80
60	12.0	9.73

Mean $k \times 10^5$ Sec^{-1} = 9.77

27. Boric Acid 0.0500M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	23.15	-
10	22.5	4.72
20	21.75	5.18
30	21.25	4.76
40	20.65	4.74
50	20.05	4.79
60	19.5	4.77

Mean $k \times 10^5$ Sec^{-1} = 4.75

TABLE 146

Sec.Butyl Alcohol 0.0822M
Total Oxidant 0.0028M
Temp. 35°C , $\mu = 0.4$

1. No Catalyst

Time mts.	Thio ccs.	Kx10^5 Sec^{-1}
0	33.0	-
10	31.4	8.29
20	29.8	8.50
30	28.4	8.34
40	27.0	8.36
50	25.7	8.34
60	24.4	8.38

Mean Kx10^5 Sec^{-1} = 8.37

2. Silver Nitrate 0.0070M

Time mts.	Thio ccs.	Kx10^5 Sec^{-1}
0	26.35	-
10	24.9	9.44
20	23.5	9.54
30	22.2	9.52
40	21.0	9.46
50	19.4	9.44
60	18.8	9.38

Mean Kx10^5 Sec^{-1} = 9.46

3. Potassium Nitrate 0.0500M

Time mts.	Thio ccs.	Kx10^5 Sec^{-1}
0	22.0	-
10	21.0	7.75
20	20.0	7.95
30	19.1	7.86
40	18.3	7.66
50	17.4	7.82
60	16.5	7.99

Mean Kx10^5 Sec^{-1} = 7.84

4. Cobalt Nitrate 0.0500M

Time mts.	Thio ccs.	Kx10^5 Sec^{-1}
0	26.35	-
10	24.5	12.1
20	22.8	12.2
30	21.2	12.1
40	19.7	12.1
50	18.3	12.1
60	17.0	12.2

Mean Kx10^5 Sec^{-1} = 12.1

5.Magnesium Sulphate 0.0500M

Time mts.	Thio ccs.	$k \times 10^{5}$ Sec^{-1}
0	33.0	-
10	31.8	6.18
20	30.65	6.16
30	29.5	6.23
40	28.45	6.18
50	27.4	6.19
60	26.3	6.30

Mean $k \times 10^{5}$ Sec^{-1} = 6.21

6.Zinc Sulphate 0.0500M

Time mts.	Thio ccs.	$k \times 10^{5}$ Sec^{-1}
0	22.0	-
10	21.3	5.37
20	20.65	5.26
30	20.05	5.15
40	19.4	5.24
50	18.8	5.24
60	18.2	5.26

Mean $k \times 10^{5}$ Sec^{-1} = 5.25

7.Nickel Sulphate 0.0500M

Time mts.	Thio ccs.	$k \times 10^{5}$ Sec^{-1}
0	22.0	-
10	21.2	6.18
20	20.5	5.87
30	19.9	5.68
40	19.1	5.89
50	18.4	5.96
60	17.8	5.88

Mean $k \times 10^{5}$ Sec^{-1} = 5.91

8.Alum = 0.0500M

Time mts.	Thio ccs.	$k \times 10^{5}$ Sec^{-1}
0	21.6	-
10	20.5	8.71
20	19.4	8.96
30	18.4	8.92
40	17.4	9.02
50	16.6	8.78
60	15.6	9.04

Mean $k \times 10^{5}$ Sec^{-1} = 8.90

9. Boric Acid 0.0500M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	33.0	-
10	31.25	9.06
20	29.6	9.06
30	28.15	8.83
40	26.55	9.07
50	25.2	8.99
60	23.9	8.96

Mean $K \times 10^5$ Sec^{-1} = 8.99

10. Potassium Dihydrogen Phosphate 0.0600M

Time mts.	Thio ccs.	$K \times 10^5$ Sec^{-1}
0	15.5	-
10	14.7	8.83
20	13.95	8.77
30	13.2	8.92
40	12.55	8.80
50	11.9	8.82
60	11.3	8.78

Mean $K \times 10^5$ Sec^{-1} = 8.81

11. Sodium Fluoride 0.0500M

Time mts.	Thio ccs	$K \times 10^5$ Sec^{-1}
0	33.0	-
10	31.25	9.06
20	29.6	9.06
30	28.1	8.93
40	26.55	9.07
50	25.2	8.99
60	23.9	8.96

Mean $K \times 10^5$ Sec^{-1} = 9.01

12. Sodium Chloride 0.0500M

Time mts.	Thio ccs.	$K \times 10^3$ Sec^{-1}
0	37.6	-
5	27.3	1.07
10	19.9	1.06
15	14.5	1.06
20	10.5	1.06
25	7.6	1.07
30	5.6	1.06

Mean $K \times 10^3$ Sec^{-1} = 1.06

13.Potassium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	37.6	-
5	23.9	1.51
10	15.2	1.51
15	9.6	1.52
20	6.3	1.49
25	3.9	1.51
30	2.5	1.51

Mean $k \times 10^3$ Sec^{-1} = 1.51

14.Strontium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	37.6	-
5	22.2	1.76
10	13.0	1.77
15	7.6	1.78
20	4.4	1.79
25	2.7	1.76
30	1.75	1.70

Mean $k \times 10^3$ Sec^{-1} = 1.76

15.Barium Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	37.6	-
5	22.3	1.74
10	13.2	1.74
15	7.8	1.75
20	4.45	1.78
25	2.75	1.74
30	1.8	1.69

Mean $k \times 10^3$ Sec^{-1} = 1.74

16.Calcium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	37.6	-
5	22.2	1.76
10	13.0	1.77
15	7.6	1.78
20	4.4	1.79
25	2.5	1.81
30	1.5	1.79

Mean $k \times 10^3$ Sec^{-1} = 1.78

17. Magnesium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^3 Sec^{-1}
0	37.6	-
10	12.7	1.81
20	3.9	1.81
30	1.1	1.81
40	0.7	1.87
50	0.3	1.81
60	0.1	1.83

Mean kx10^3 Sec^{-1} = 1.82

18. Nickel Chloride 0.0500M

Time mts.	Thio ccs.	kx10^3 Sec^{-1}
0	37.6	-
5	19.5	2.19
10	10.1	2.19
15	5.2	2.20
20	2.9	2.19
25	1.4	2.19
30	0.7	2.21

Mean kx10^3 Sec^{-1} = 2.20

19. Zinc Chloride 0.1170M

Time mts.	Thio ccs.	kx10^3 Sec^{-1}
0	38.0	-
5	23.0	1.67
10	14.0	1.66
15	8.4	1.68
20	5.0	1.69
25	3.2	1.65
30	2.0	1.63

Mean Kx10^3 Sec^{-1} = 1.66

20. Zirconium Oxychloride 0.0500M

Time mts.	Thio ccs.	kx10^3 Sec^{-1}
0	38.0	-
2	18.4	6.04
4	8.8	6.10
6	4.4	5.99
8	2.05	6.08
10	1.0	6.06
12	0.5	6.02

Mean Kx10^3 Sec^{-1} = 6.05

21. Aluminium Chloride 0.0500M

Time mts.	Thio ccs.	$kx10^3$ Sec^{-1}
0	38.0	-
5	22.0	1.82
10	13.3	1.75
15	7.4	1.82
20	4.3	1.82
25	2.45	1.83
30	1.4	1.83
	Mean $kx10^3$ Sec^{-1} =	1.81

TABLE 147

Methyl Alcohol 0.4000M
Total Oxidant 0.0050M
Temp. 35°C , μ = 0.4

1. No Catalyst

Time mts.	Thio ccs.	$kx10^3$ Sec^{-1}
0	38.7	-
10	38.0	3.20
20	37.2	3.30
30	36.5	3.25
40	35.7	3.36
50	35.0	3.35
60	34.4	3.27
	Mean $kx10^3$ Sec^{-1} =	3.29

2. Sodium Chloride 0.0500M

Time mts.	Thio ccs.	$kx10^4$ Sec^{-1}
0	35.0	-
10	28.2	3.60
20	26.5	2.32
30	25.0	1.87
40	23.0	1.75
50	21.2	1.67
60	19.1	1.68
	Mean $kx10^4$ Sec^{-1} =	1.74

3. Potassium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	35.0	-
10	27.2	4.20
20	25.6	2.61
30	24.1	2.07
40	22.2	1.90
50	20.2	1.83
60	18.4	1.79

Mean kx10^4 Sec^{-1} = 1.90

4. Barium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	35.0	-
10	24.9	5.68
20	24.0	3.14
30	22.8	2.38
40	20.8	2.17
50	19.7	1.92
60	17.8	1.88

Mean kx10^4 Sec^{-1} = 2.09

5. Strontium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	35.0	-
10	23.5	6.64
20	21.5	4.06
30	19.7	3.19
40	18.2	2.72
50	16.7	2.35
60	14.8	2.39

Mean kx10^4 Sec^{-1} = 2.61

6. Calcium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	35.0	-
10	24.9	5.68
20	24.0	3.14
30	22.8	2.38
40	18.2	2.72
50	16.7	2.35
60	14.7	2.41

Mean kx10^4 Sec^{-1} = 2.46

7.Zinc Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	25.0	-
10	18.1	5.38
20	17.0	3.21
30	16.5	2.31
40	15.6	1.96
50	14.1	1.91
60	12.5	1.92

Mean kx10^4 Sec^{-1} = 1.93

8.Nickel Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	33.8	-
10	22.6	6.71
20	21.9	3.62
30	20.6	2.75
40	19.3	2.33
50	18.0	2.10
60	17.0	1.91

Mean kx10^4 Sec^{-1} = 2.27

9.Magnesium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	25.0	-
10	18.1	5.38
20	17.0	3.21
30	16.5	2.31
40	15.6	1.96
50	14.1	1.91
60	12.5	1.92

Mean kx10^4 Sec^{-1} = 1.93

10.Sodium Fluoride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	33.8	-
10	28.9	2.61
20	29.0	1.28
30	27.0	1.08
40	25.6	1.16
50	24.0	1.14
60	22.5	1.13

Mean kx10^4 Sec^{-1} = 1.13

11. Potassium Dihydrogen Phosphate 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	33.8	-
10	28.9	2.61
20	29.1	1.25
30	27.4	1.16
40	26.0	1.09
50	25.0	1.00
60	24.0	0.952

Mean kx10^4 Sec^{-1} = 1.09

12. Silver Nitrate 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	35.0	-
10	23.0	7.00
20	16.0	6.52
30	11.0	6.43
40	7.8	6.25
50	6.5	5.61
60	5.1	5.35

Mean kx10^4 Sec^{-1} = 6.03

TABLE 148

Ethyl Alcohol 0.4000M
Total Oxidant 0.0050M
Temp. 35°C , μ= 0.4

1. No Catalyst

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	18.55	-
10	18.0	0.503
20	17.7	0.393
30	17.25	0.404
40	16.85	0.401
50	16.45	0.401
60	16.05	0.403

Mean kx10^4 Sec^{-1} = 0.402

2. Sodium Chloride 0.0500M

Time mts.	Thio ccs.	kx10^4 Sec^{-1}
0	27.3	-
10	20.8	4.53
20	18.9	3.07
30	16.6	2.76
40	14.1	2.75
50	12.3	2.66
60	10.5	2.65

Mean kx10^4 Sec^{-1} = 2.71

3. Potassium Chloride 0.0500M

Time mts.	Thio ccs.	Kx10^{4} Sec^{-1}
0	27.3	-
10	20.1	5.10
20	17.1	3.90
30	14.5	3.52
40	11.7	3.53
50	9.6	3.48
60	7.9	3.45

Mean Kx10^{4} Sec^{-1} = 3.50

4. Barium Chloride 0.0500M

Time mts.	Thio ccs.	Kx10^{4} Sec^{-1}
0	27.3	-
10	18.8	6.22
20	15.9	4.51
30	13.7	3.83
40	11.0	3.79
50	8.8	3.78
60	7.0	3.78

Mean Kx10^{4} Sec^{-1} = 3.79

5. Strontium Chloride 0.0500M

Time mts.	Thio ccs.	Kx10^{4} Sec^{-1}
0	27.3	-
10	17.9	7.04
20	15.8	4.56
30	14.0	3.71
40	11.4	3.64
50	9.5	3.52
60	7.6	3.55

Mean Kx10^{4} Sec^{-1} = 3.61

6. Calcium Chloride 0.0500M

Time mts.	Thio ccs.	Kx10^{4} Sec^{-1}
0	27.3	-
10	18.8	6.22
20	15.9	4.51
30	13.7	3.83
40	11.0	3.79
50	8.8	3.78
60	7.1	3.74

Mean Kx10^{4} Sec^{-1} = 3.78

7. Zinc Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	16.65	-
2	15.8	4.36
4	15.35	3.38
6	14.75	3.38
8	14.05	3.53
10	13.50	3.50
12	12.80	3.65

Mean $k \times 10^4$ Sec^{-1} = 3.47

8. Nickel Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	33.8	-
10	22.3	6.93
20	18.7	4.93
30	15.6	4.29
40	12.4	4.18
50	9.8	4.13
60	7.9	4.04

Mean $k \times 10^4$ Sec^{-1} = 4.16

9. Cobalt Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	20.4	-
10	14.0	6.27
20	12.3	4.22
30	9.5	4.25
40	7.4	4.23
50	5.7	4.25
60	4.6	4.14

Mean $k \times 10^4$ Sec^{-1} = 4.21

10. Magnesium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	27.3	-
10	18.0	6.94
20	15.7	4.61
30	14.0	3.71
40	11.4	3.64
50	9.5	3.52
60	7.5	3.59

Mean $k \times 10^4$ Sec^{-1} = 3.61

11. Sodium Fluoride 0.0500M

Time mts.	Thio ccs.	$k \times 10^{4}$ Sec^{-1}
0	33.8	-
10	32.5	0.652
20	32.0	0.457
30	31.3	0.427
40	30.5	0.428
50	29.7	0.431
60	29.0	0.425

Mean $k \times 10^{4}$ Sec^{-1} = 0.428

12. Potassium Dihydrogen Phosphate 0.0500M

Time mts.	Thio ccs.	$k \times 10^{4}$ Sec^{-1}
0	33.8	-
10	31.7	1.07
20	31.2	0.666
30	30.5	0.571
40	29.5	0.567
50	28.5	0.569
60	27.5	0.573

Mean $k \times 10^{4}$ Sec^{-1} = 0.570

13. Silver Nitrate 0.0500M

Time mts.	Thio ccs.	$k \times 10^{4}$ Sec^{-1}
0	18.20	-
5	14.0	8.75
10	11.05	8.32
15	8.55	8.34
20	6.60	8.35
25	5.05	8.55
30	3.90	8.43

Mean $k \times 10^{4}$ Sec^{-1} = 8.40

TABLE 149

Pseudo-First Order Rate Constants for the Reaction of Isopropyl Alcohol with Total Oxidant in the Presence of Different Salts at 35°C

$(\text{Alcohol}) = 0.0332\text{M}, (\text{OX})_o = 0.0078\text{M}, \mu = 0.4$

Salt added, M		$10^5 k$ Sec^{-1}
-		4.28
$AgNO_3$	0.002	4.75
$AgNO_3$	.004	5.28
$AgNO_3$	.008	6.70
$AgNO_3$	.010	10.4
$NaNO_3$	.320	5.61
$Co(NO_3)_2$	.025	4.04
$Zr(NO_3)_2$	.024	13.8
$Ce(NO_3)_3$	.013	8.10
$NaCl$	.100	50.7
$NaCl$	.210	60.4
$NaCl$	.320	68.6
KCl	.075	63.9
$MgCl_2$	.050	49.5
$CaCl_2$	.100	81.2
$SrCl_2$	.050	44.0
$BaCl_2$	.050	43.1
$ZnCl_2$	.050	89.0
$CdCl_2$	.050	30.6
$AlCl_2$	.050	24.3
$MgSO_4$	.050	3.09
$MnSO_4$	.050	2.59
$BeSO_4$	.025	4.58
$ZnSO_4$	.050	1.92
NaF	.100	5.28
KH_2PO_4	.100	9.77
H_3BO_3	.050	4.75

TABLE 150

Pseudo -First Order Rate Constants for the Reaction of Secondary Butyl Alcohol with Total Oxidant in the Presence of Salts at 35°C

(Alcohol) = 0.0822M, $(OX)_o$ = 0.0028M, μ = 0.4

Salt Added	M	$10^4 k$ Sec^{-1}
-	-	0.837
$AgNO_3$	0.007	.946
KNO_3	.050	.784
$C_o(NO_3)_2$	.050	1.21
$MgSO_4$	.050	.621
$ZnSO_4$	.050	.525
$NiSO_4$	.050	.591
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	.050	.890
H_3BO_3	.050	.899
KH_2PO_4	.060	.881
NaF	.050	.901
NaCl	.050	1.06
KCl	.050	1.51
$SrCl_2$	.050	1.76
$BaCl_2$	.050	1.74
$CaCl_2$	.050	1.78
$MgCl_2$	.050	1.82
$NiCl_2$	.050	2.20
$ZnCl_2$	.117	1.66
$ZrOCl_2$	.050	6.05
$AlCl_3$	.050	1.81

TABLE 151

Pseudo First Order Rate Constants for the Reaction of Methyl Alcohol with Total Oxidant in the Presence of Different Salts at 35°C

(Alcohol) = 0.4000M $(OX)_o$ = 0.0050M μ = 0.4

Salt = 0.050M

Salt added	$10^4 k$, Sec^{-1}
-	0.329
NaCl	1.74
KCl	1.90
$BaCl_2$	2.09
$SrCl_2$	2.61
$CaCl_2$	2.46
$ZnCl_2$	1.93
$NiCl_2$	2.27
$MgCl_2$	1.93
NaF	1.13
KH_2PO_4	1.09
$AgNO_3$	6.03

TABLE 152

Pseudo First Order Rate Constants for the Reaction of Ethyl Alcohol with Total Oxidant in the Presence of Different Salts at 35°C

(Alcohol) = 0.4000M, $(OX)_o$ = 0.0050M, μ = 0.4

Salt = 0.050M

Salt added	$10^4 k$, Sec^{-1}
-	0.402
NaCl	2.71
KCl	3.50
$BaCl_2$	3.79
$SrCl_2$	3.61
$CaCl_2$	3.78
$ZnCl_2$	3.47
$NiCl_2$	4.16
$CoCl_2$	4.21
$MgCl_2$	3.61
NaF	0.428
KH_2PO_4	0.570
$AgNO_3$	8.40

Results and Discussion : An examination of the data indicates that whereas in the case of isopropyl and sec-butyl alcohols, the pseudo first order rate constant for each aliquot portion titrated is constant within experimental error for all the runs, but in the case of methyl and ethyl alcohols, for all the runs, the pseudo first order rate constant varies for each aliquot portion titrated; during first 10 to 20 minutes the rate constant is 30 to 50 % higher, then decreases and becomes constant within experimental error. Similar trend was also noticed by Stanley and Shorter(126) in other cases, who argued that such erratic results should be obtained if the reaction also involves chlorination and if molecular chlorine is the chlorinating species.

For isopropyl alcohol - chlorine reaction, we noticed that (i) silver, zirconium and cerous nitrates accelerate the reaction, (ii) mono, di and trivalent metal chlorides, in general, accelerate the reaction many fold. Zinc chloride, for example, increases the rate by about twenty fold (In presence of 0.1M $ZnCl_2$ the reaction mixture turns yellow after few minutes of mixing of reactants and keeping it overnight as such, red particles appear), (iii) sulphates have a general tendency to retard the rate (BeSO4 increases the rate), and (iv) F^- and $H_2PO_4^-$ ions accelerate the reaction rate.

In the case of secondary butyl alcohol, the result given in Table 150 shows that (i) silver and cobalt nitrate accelerate the reaction, (ii) mono, di and trivalent metal chlorides, in general, accelerate the reaction many fold. Nickel chloride, for example, increases the rate by about 25 folds, (iii) the sulphates have a general tendency to retard the reaction and (iv) F^- and $H_2PO_4^-$ ions accelerate the rate slightly.

From Table 151 and 152 it is clear that in the case of methyl and ethyl alcohols, (i) mono- and di- valent metal chlorides, in general, accelerate the reactions (ii) F^-, $H_2PO^-_4$ and silver nitrate also enhances the rate.

Thus, as already stated above, chloride ions accelerate all the reactions many fold. In the case of sec. butyl alcohol we kept the concentrations of the salts as 0.05M, with a view to find out if there is any correlation between reaction rate and ionic radii of the cations. A comparison of pseudo first order rate constants, particularly in the presence of divalent metal chlorides, reveals that as the ionic radii of the cations increases, the rate decreases; the rate follows the order :

$$NiCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$$

and the ionic radii of cations follow the order :

$$Ni^{++} < Mg^{++} < Ca^{++} < Sr^{++} < Ba^{++}$$

The significance of these results will be considered in the General Discussion.

SEC. 2.5 EFFECT OF SODIUM CHLORIDE ON THE REACTION RATE

Introduction : We reported in the previous section that the chloride ions accelerate the rates many fold. In order to find out the role of chloride ions, the rates of the reactions of isopropyl, sec.butyl, methyl and ethyl alcohols with chlorine in water have been measured in presence of varying concentrations of sodium chloride at constant ionic strength of 0.4. The observations are reported in this section.

EXPERIMENTAL

The experimental procedure is same as applied in the previous section.

We calculated the initial rates, k_0 moles lit^{-1} Sec^{-1}, by extrapolating to $x = 0$ of the plots of x/t against x, (where x is the number of moles of total oxidant consumed in time t) as well as the pseudo first order rate constants for all the cases. The results are presented in the following tables.

Table No. 153

IsoPropyl Alcohol 0.2000M
Total Oxidant 0.0099M
Temp. 35°C; μ = 0.4

1. Sodium Chloride 0.05M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	41.2	-
2	31.3	2.29
4	21.9	2.63
6	14.7	2.86
8	9.6	3.03
10	6.1	3.18
12	4.1	3.20

Mean $k \times 10^3$ Sec^{-1} = 2.86
$k_o \times 10^6$ = 25.2

2. Sodium Chloride 0.03M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	41.2	-
2	32.7	1.93
4	25.9	1.93
6	19.5	2.08
8	13.7	2.29
10	10.0	2.36
12	7.0	2.46

Mean $k \times 10^3$ Sec^{-1} = 2.17
$k_o \times 10^6$ = 18.5

3. Sodium Chloride 0.02M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	41.2	-
2	34.5	1.47
4	27.9	1.62
6	21.7	1.82
8	16.7	1.88
10	12.6	1.97
12	9.6	2.02

Mean $k \times 10^3$ Sec^{-1} = 1.92
$k_o \times 10^6$ = 15.0

4. Sodium Chloride 0.01M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	41.2	-
2	35.1	1.33
4	29.7	1.36
6	25.5	1.35
8	21.7	1.33
10	18.5	1.33
12	15.7	1.34

Mean $k \times 10^3$ Sec^{-1} = 1.34
$k_o \times 10^6$ = 12.0

5. Sodium Chloride 0.004M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	41.2	-
2	36.5	1.01
4	32.6	.976
6	29.0	.975
8	25.6	.987
10	22.8	.986
12	20.0	1.00

Mean $k \times 10^3$ Sec^{-1} = 0.989
$k_o \times 10^6$ = 9.00

Table No. 154

Sec. Butyl Alcohol 0.2000M
Total Oxidant 0.0066M
Temp. 35°C; $\mu = 0.4$

1. Sodium Chloride 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	26.4	-
2	7.1	10.9
4	2.1	10.5
6	0.6	10.5
8	0.15	10.8

Mean $k \times 10^3$ Sec^{-1} = 10.7
$k_o \times 10^5$ = 9.75

2. Sodium Chloride 0.1500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	26.4	-
2	10.2	7.93
4	4.2	7.66
6	1.7	7.62
8	0.7	7.56
10	0.25	7.77

Mean $k \times 10^3$ Sec^{-1} = 7.71
$k_o \times 10^5$ = 7.80

3. Sodium Chloride 0.05M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	26.4	-
2	13.4	5.65
4	7.3	5.36
6	3.9	5.31
8	2.0	5.37
10	1.1	5.30
12	0.6	5.25

Mean $k \times 10^3$ Sec^{-1} = 5.37

$k_o \times 10^5$ = 4.2

Table No. 155

Methyl Alcohol	0.8000M
Total Oxidant	0.0099M

Temp. 35°C; $\mu = 0.4$

1. Sodium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	42.4	-
10	38.7	1.52
20	38.2	0.869
30	37.3	0.713
40	36.8	0.591
50	36.3	0.518
60	35.5	0.493

Mean $k \times 10^4$ Sec^{-1} = 0.534

$k_o \times 10^6$ = 1.50

2. Sodium Chloride 0.100M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	42.4	-
10	38.1	1.78
20	37.1	1.11
30	35.8	0.940
40	34.6	0.847
50	33.2	0.816
60	31.8	0.800

Mean $k \times 10^4$ Sec^{-1} = 0.821

$k_o \times 10^6$ = 2.10

3. Sodium Chloride 0.2000M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	42.4	-
10	37.5	2.05
20	36.0	1.36
30	34.8	1.26
40	33.1	1.03
50	31.8	0.954
60	30.1	0.952

Mean $k \times 10^4$ Sec^{-1} = 0.979
$k_o \times 10^6$ = 2.90

4. Sodium Chloride 0.2500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	42.4	-
4	40.5	1.91
8	38.9	1.80
12	36.8	1.97
16	35.0	2.00
20	33.5	1.96
24	32.5	1.85

Mean $k \times 10^4$ Sec^{-1} = 1.90
$k_o \times 10^6$ = 3.50

5. Sodium Chloride 0.30M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	42.4	-
5	38.7	3.05
10	35.8	2.82
15	34.2	2.39
20	32.9	2.11
25	31.4	2.00
30	30.2	1.88

Mean $k \times 10^4$ Sec^{-1} = 2.00
$k_o \times 10^6$ = 3.82

Table No. 156

Ethyl Alcohol 0.8000M
TotalOxidant 0.0099M
Temp.35°C ; μ= 0.4

1. Sodium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	38.4	-
10	32.8	2.62
20	23.5	4.09
30	17.0	4.58
40	11.5	5.02
50	8.0	5.23
60	5.8	5.25

Mean $k \times 10^4$ Sec^{-1} = 5.17
$k_o \times 10^6$ = 3.75

2. Sodium Chloride 0.10M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	38.4	-
10	29.0	4.68
20	19.0	5.87
30	12.0	6.47
40	7.1	7.03
50	4.5	7.15
60	3.0	7.08

Mean $k \times 10^4$ Sec^{-1} = 7.09
$k_o \times 10^6$ = 5.00

3. Sodium Chloride 0.15M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	38.4	-
10	25.2	7.02
20	15.4	7.62
30	8.8	8.18
40	5.5	8.10
50	3.2	8.28
60	-	

Mean $k \times 10^4$ Sec^{-1} = 8.19
$k_o \times 10^6$ = 6.80

4. Sodium Chloride 0.20M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	38.4	-
2	34.2	9.65
4	31.0	8.91
6	27.5	9.27
8	24.6	9.26
10	22.0	9.28
12	19.5	9.41

Mean $k \times 10^4$ Sec^{-1} = 9.29
$k_o \times 10^6$ = 8.70

5. Sodium Chloride 0.25M

Time mts.	Thio ccs.	$K \times 10^3$ Sec^{-1}
0	38.4	-
2	31.2	1.78
4	28.1	1.30
6	25.2	1.17
8	23.0	1.07
10	19.8	1.10
12	17.3	1.10

Mean $k \times 10^3$ Sec^{-1} = 1.11

$k_o \times 10^6$ = 12.0

6. Sodium Chloride 0.30M

Time mts.	Thio ccs.	$K \times 10^3$ Sec^{-1}
0	38.4	-
2	28.9	2.37
4	25.9	1.64
6	23.3	1.39
8	20.8	1.28
10	18.0	1.26
12	15.8	1.23

Mean $k \times 10^3$ Sec^{-1}=1.26

$k_o \times 10^6$ = 14.6

Table No.157

Dependence of Oxidation Rate on the Concentration of Sodium Chloride at 35° C, $\mu = 0.4$

1. (Isopropyl Alcohol) = 0.2000M, $(OX)_o$ = 0.0099M

NaCl,M	$(Cl_2)_o \times 10^3$, M	$k \times 10^3$ Sec^{-1}	$k_o \times 10^6$ mole lit^{-1} Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^3$, Sec^{-1}
0.004	1.05	.989	9.00	8.58
.01	1.45	1.34	12.0	8.28
.02	2.05	1.92	15.0	7.32
.03	2.50	2.17	18.5	7.40
.05	3.40	2.86	25.2	7.43

Mean $k_o/(Cl_2)_o = 7.80 \pm 0.57 \times 10^{-3}$ Sec^{-1}

2. (Sec.Butyl Alcohol) = 0.2000M, $(OX)_o$ = 0.0066M

NaCl,M	$(Cl_2)_o \times 10^3$, M	$k \times 10^3$ Sec^{-1}	$k_o \times 10^6$ mole lit^{-1} Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^3$, Sec^{-1}
0.05	1.90	5.37	42.0	22.1
.15	3.45	7.71	78.0	22.6
.20	4.00	10.7	97.5	24.4

Mean $k_o/(Cl_2)_o = 23.0 \pm 1.2 \times 10^{-3}$ Sec^{-1}

3. (Methyl Alcohol) = 0.8000M, $(OX)_o$ = 0.0099M

NaCl,M	$(Cl_2)_o \times 10^3$, M	$k \times 10^4$ Sec^{-1}	$k_o \times 10^6$ mole lit^{-1} Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^3$, Sec^{-1}
0.05	3.40	.534	1.50	.441
.10	4.90	.821	2.10	.429
.20	6.40	.979	2.90	.453
.25	6.90	1.90	3.50	.507
.30	7.30	2.00	3.82	.523

Mean $k_o/(Cl_2)_o = 0.471 \pm 0.04 \times 10^{-3}$ Sec^{-1}

4. (Ethyl Alcohol) = 0.8000M, $(OX)_o$ = 0.0099M

NaCl M	$(Cl_2)_o \times 10^3$ M	$k \times 10^4$ Sec^{-1}	$k_o \times 10^6$ mole lit^{-1} Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^3$ Sec^{-1}
0.05	3.40	5.17	3.75	1.10
.10	4.90	7.09	5.00	1.02
.15	5.85	8.19	6.80	1.16
.20	6.40	9.29	8.70	1.36
.25	6.90	11.1	12.0	1.74
.30	7.30	12.6	14.6	2.00

Mean $k_o/(Cl_2)_o = 1.28 \pm 0.28 \times 10^{-3}$ Sec^{-1}

Results and Discussion :

A perusal of the data reveals that during the course of a run, the pseudo first order rate constant varies in different cases as follows :

(a) Isopropyl Alcohol : in presence of 0.004M to 0.01M NaCl, within experimental error, the rate constant remains almost unaltered, but in presence of 0.02M, 0.03M and 0.05M NaCl, the rate constant increases with time.

(b) Sec.Butyl Alcohol : in presence of 0.05M, 0.15M and 0.20M NaCl, within experimental error, the rate constant remains unaltered. The reaction is so fast that we failed to measure the rates at higher concentrations of NaCl.

(c) Methyl Alcohol : in this case entirely different trend has been found; in presence of 0.05M to 0.30M NaCl, the rate constant decreases sharply.

(d) Ethyl Alcohol : in presence of 0.05M to 0.15M NaCl, the rate constant increases, but in presence of 0.20M to 0.30M NaCl, there is a decreasing tendency.

The increasing trend of the pseudo first order rates indicates that more and more Cl_2 is formed during the reaction, which is responsible for this increase in rate. The decreasing trend indicates that chlorine substitution takes place at fast rate; the rate decreases because chlorine substitution consumes molecular chlorine.

We found that as the concentration of sodium chloride is increased, the rate constant increases in all the cases. This fact may be correlated with the hydrolytic equilirbium of chlorine,

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad \ldots\ldots\ldots\ldots\ldots \quad (i)$$

At zero time, in presence of sodium chloride.

$$\alpha_o = \frac{[HOCl]}{(OX)_o} \quad , \quad (1-\alpha_o) = \frac{[Cl_2]_o}{(OX)_o}$$

and $[Cl^-]_o = [HOCl]_o + m$, where m is the concentration of added chloride. Then

$$B = \frac{K_h}{aH^+ \gamma Cl^-} = \frac{[HOCl]\ [Cl^-]}{[Cl_2]}$$

$$\text{or,}\quad B = \frac{\alpha_o [OX]_o \{\alpha_o [OX]_o + m\}}{[1-\alpha_o]\ [OX]_o}$$

$$\text{or}\quad \alpha_o^2\ [OX]_o + [B+m]\alpha_o - B = 0$$

$$\therefore\quad \alpha_o = -\frac{(B+m) + \sqrt{(B+m)^2 + 4B\,[OX]_o}}{2\,[OX]_o} \quad \ldots\ldots\ldots\ldots\ldots (vi)$$

Assuming that the added chloride do not convert a significant fraction of the oxidant to trichloride ion, Cl_3^-, (the formation constant of Cl_3^- is 0.180 at 25°C)(296) we calculated the values of α_o for various initial concentrations of sodium chloride by using equation (vi). In Table D (p.89) the fraction of total oxidant present at zero time as Cl_2 and HOCl in presence of sodium chloride is shown. In column 9,11 and 12 (Table D), the concentration of chloride ion has been calculated by assuming that

$$[Cl^-] = \frac{[HOCl]_o + m}{2}$$

The constancy of ko/ $[Cl_2]_o$ for various initial concentration of sodium chloride in all the cases, as shown in Table 157, is an evidence that molecular chlorine is the principal oxidant. However, the values of ko/$[Cl_2]_o$ in presence of NaCl are 40-50 % lower than that in absence of NaCl (See Sec.2.1). Perhaps some molecular chlorine is consumed by chloride ion for the formation of Cl_3^-,which we have not considered in our calculations.

Lichtin and Saxe(79) also showed that Cl_2 is much more reactive than HOCl in the oxidation of glucose and the fraction of the total oxidant present as Cl_2 increases during the course of the reaction, because

$$[Cl^-]_t = 2\left[[OX]_o - [OX]_t + [HOCl] + m\right]$$

and thus during the run more chloride is formed which displaces the hydrolytic equilibrium to the right. This in turn increases the pseudo first order rate during the course of a run.

SEC. 2.6 ISOLATION OF HYPOCHLORITE OF ALCOHOLS

Introduction : It is now recognised that aqueous chlorine forms hypochlorite ester with alcohols. Ethyl hypochlorite was the first ester to be prepared by Sandmeyer.(297) Chattaway and Backeberg(235) prepared methyl, ethyl, n- and isopropyl, primary, secondary and tertiary butyl and tert. amyl hypochlorites. They also studied the decomposition products of the above alcohols and found that the hypochlorites of tertiary alcohols are much more stable than those of primary and secondary alcohols. Taylor and coworkers(298) reinvestigated the formation and decomposition of the hypochlorites of several alcohols and obtained esters as yellow, unstable oils with propyl, isopropyl, isobutyl, sec. butyl, ter.butyl, isoamyl, sec.amyl, tert.amyl, ethyl and methyl alcohols. They concluded that secondary hypochlorites are unstable, iso and n-primary hypochlorites are more stable and tertiary hypochlorites are very stable. Other workers have also postulated the existence of alkyl hypochlorites in the oxidation of alcohols(101,102). With an object to find out if the oxidation involves the hypochlorite ester as an intermediate, an attempt has been made to isolate the esters under various conditions. The observations are reported in this section.

Table No.158

Formation of Hypochlorites of Alcohols under various Conditions

System	Colour of Carbontetrachloride or Benzene layer						
	Methyl	Ethyl	n-Propyl	Isopropyl	n-Butyl	Isobutyl	Sec.butyl
Alcohol -aq. Cl_2	Yellow	bright yellow	Yellow	light yellow	yellow	light yellow	light yellow
Alcohol -aq.Cl_2-$HClO_4$	bright yellow	bright yellow	bright yellow	bright yellow	bright yellow	yellow	light yellow
Alcohol-aq.Cl_2-$AgNO_3$	yellow	bright yellow	yellow	bright yellow	yellow	light yellow	light yellow
Alcohol-aq.Cl_2-NaCl	bright yellow	bright yellow	bright yellow	yellow	yellow	light yellow	light yellow
Alcohol-aq.Cl_2-$ZnCl_2$	bright yellow	bright yellow	yellow	yellow	yellow	light yellow	light yellow
Alcohol-aq.Cl_2-$NaHCO_3$	yellow	very light yellow	no colour	light yellow	no colour	no colour	no colour
Alcohol-aq.Cl_2-$NaHCO_3$+ $HClO_4$	yellow	yellow	very light yellow	bright yellow	very light yellow	light yellow	no colour
Alcohol-aq.Cl_2-$NaHCO_3$+ $AgNO_3$	yellow	very light yellow	no colour	bright yellow	no colour	light yellow	no colour

Results and Discussion :

We have isolated the alkyl hypochlorites in carbon tetrachloride and benzene layers by solvent extraction technique at room temperature. Concentrated solutions of chlorine in water and alcohol in the presence as well as in the absence of catalyst were shaken with carbon tetrachloride or benzene in a separating funnel. The solvent layer became yellow at once and the yellow layer deepened as the shaking continued for about two minutes. Prior to these experiments, when chlorine solution was shakened with the solvent alone, the colour of the layer changed to faint yellow but in the presence of alcohol the colour deepened.

We observed that methyl and ethyl hypochlorites are relatively stable than the other hypochlorites in the presence as well as in the absence of catalyst. Sec. butyl hypochlorite has been found to be the least stable. This may be due to fast decomposition of the hypochlorite to ketone. The relative stability of methyl hypochlorite suggest that perhaps its rate of decomposition is lowest.

In the section 2.5 we pointed out that chloride ions accelerate the rates because they increase the initial concentration of molecular chlorine. From Table 158 it is clear that in presence of catalysts, deeper colours of solvent layers have been noticed for all the alcohols.

In a typical experiment we removed free chlorine by shaking with sodium bicarbonate. Then we added perchloric acid or sodium chloride. In shaking again, bright yellow colour of the solvent layers has been noticed. All these observations indicate that Cl_2 is responsible for hypochlorite formation. The contribution of HOCl towards the hypochlorite formation, however, cannot be ruled out because other investigators noticed that hypochlorite is also formed by reaction with hypochlorous acid (102,298).

SEC. 2.7 ACTIVATION PARAMETERS

Introduction : The determination of activation parameters of chemical reactions is very important because it throws light on the mechanism of chemical change. It is known since long that the rise in temperature accelerates the rates of chemical,reactions and in some cases the acceleration in the velocity is great. So, for the sake of convenience, one considers the increase of reaction velocity for a rise of 10°C. The ratio of the velocity constants at two temperatures differ by 10°C, e.g. k_{35^o}/k_{25^o}, is known as the temperature coefficient of the reaction.

Though several investigators suggested relation between temperature and velocity constant of reactions, the most satisfactory relation was that proposed by Arrhenius(299); he proposed the relation

$$k = A\, e^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

where k is the specific rate constant, A is the Arrhenius frequency factor, E is the energy of activation and the other quantities have their usual significance. The equation (i) can be written as

$$\log k = \log A - \frac{E}{2.303RT} \quad \ldots\ldots\ldots\ldots\ldots \quad (ii)$$

Thus, a plot of logk against 1/T will be a straight line, the slope and intercept of which is equal to $-E/2.303R$ and log A, respectively, ($R = 1.987$ cals/o_C).

In the absolute rate theory, developed by

Eyring(300), the species at the top of the potential energy barrier, known as the activated complex, is considered in most respects an ordinary chemical species which is in equilirbium with the reactants. This permits the problem to be divided into two parts - the calculation of the equilibrium constant for the reaction forming the activated complex and the calculation of the rate at which the activated complex decomposes to form the products of the reaction. Thus, for a simple bimolecular reaction :

$$\underset{\text{reactants}}{A + B} \overset{K^{\neq}}{\rightleftharpoons} \underset{\substack{\text{activated}\\ \text{complex}}}{(AB)^{\neq}} \xrightarrow{k^{*}} \text{products}$$

the ordinary rate constant is given by

$$k_{obs} = \kappa \; K^{\neq} \; k^{*} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(iii)$$

where κ is the transmission coefficient or the fraction of activated complexes which give products; the rest return to reactants, and k_{obs} is the specific rate constant of the reaction. It can be shown(301) that

$$k^{*} = \frac{(\kappa T/2\pi m)^{1/2}}{\delta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(iv)$$

and $K^{\neq}$, in terms of partition function, is given by

$$K = \frac{(2\pi m \; \kappa T)^{1/2}}{h} \cdot \delta \cdot \frac{Q_{AB}}{Q_A \cdot Q_B} \cdot e^{-\Delta E_0/RT} \ldots\ldots(v)$$

By substituting the values of K^{*} and $K^{\neq}$ from equations (iv) and (v) in equation (iii), the observed specific rate constant will be given by

$$k_{obs} = \chi \cdot \frac{(\kappa T)}{h} \cdot \frac{Q_{AB}^{\neq}}{Q_A \cdot Q_B} \cdot e^{-\Delta E_o/RT} \text{.......(vi)}$$

or, in terms of "classical" activation energy,

$$K_{obs} = \chi \frac{(\kappa T)}{h} \cdot \frac{QAB^{\neq}}{Q_A \cdot Q_B} \prod_{i}^{3n^{\neq}-7} e^{-\frac{u_i}{2}} \prod_{i}^{3n-6} e^{\frac{1}{2}u_i} e^{-\Delta E\, class/RT} \text{.....(vii)}$$

where $u_i = h\upsilon i/\kappa T$

Since, $-\Delta G^{\neq} = RT \log_e K^{\neq}$ and $\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq}$, from equation (iii) we get

$$k_{obs} = \frac{\kappa T}{h} e^{-\Delta G^{\neq}/RT} \text{..................(viii)}$$

and also $$k_{obs} = \frac{\kappa T}{h} e^{-\Delta H^{\neq}/RT} \cdot e^{\Delta S^{\neq}/R} \text{...........(ix)}$$

where $\Delta G^{\neq}$ is the free energy of activation, $\Delta S^{\neq}$ is the entropy of activation, and $\Delta H^{\neq}$ is the heat of activation, a quantity that is closely related to the experimental energy of activation(302). The transmission coefficient being omitted for the sake of simplicity.

The thermodynamic activation parameters may be calculated by using the equations (viii) and (ix). From equation (ix) we have

$$\log \frac{k_{obs}}{T} = \frac{-\Delta H^{\neq}}{2.303RT} + \left(\frac{\Delta S^{\neq}}{2.303R} - \log \frac{h}{K}\right) \text{..(x)}$$

A plot of log $\frac{k_{obs}}{T}$ against $\frac{1}{T}$ will be a straight line, the slope and intercept of which is equal to $-\frac{\Delta H^{\neq}}{2.303R}$

and $\frac{\Delta S^{\neq}}{2.303R} - \log \frac{h}{k}$, respectively ($h=6.624\times10^{-27}$ erg sec; $k = 1.380\times10^{-16}$ erg/mole-deg.)

In this section a general study on the temperature coefficient of the reactions of isopropyl, sec.butyl, methyl, and ethyl alcohols with aqueous chlorine in absence and in presence of catalysts at constant ionic strength of 0.4, with special reference to the effect of variation of concentrations of the reactants, has been made. The rates have been measured at 25°,35°,45° and 55°C and the initial rates, k_o moles lit^{-1} Sec^{-1}, have been determined in all the cases. Various activation parameters have been calculated by using k_o values and given in the following Tables.

EXPERIMENTAL

All the chemicals were of B.D.H. (AnalaR) or Merck (Cp) grade or of comparable purity.

The thermostat was controlled within ± 0.05°C. The kinetics of the reactions were studied at various temperatures according to the method explained in Sec.2.1.

Table 159

Temp. 25°C θ.

Total Oxidant 0.0066M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	40.0	-
10	36.0	1.76
20	32.4	1.76
30	29.3	1.73
40	26.4	1.73
50	23.8	1.73
60	21.4	1.74

Mean $k \times 10^4$ Sec^{-1} = 1.74
$k_o \times 10^5$ = 0.196

Table 160

Temp. 35°C

Total Oxidant 0.0066M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	74.15	-
10	54.0	5.28
20	40.3	5.08
30	30.0	5.03
40	21.5	5.16
50	16.1	5.09
60	11.9	5.08

Mean $k \times 10^4$ Sec^{-1} = 5.12
$k_o \times 10^5$ = 0.58

Table 161

Temp. 45°C

Total Oxidant 0.0066M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	51.4	-
10	26.2	1.12
20	13.2	1.13
30	7.5	1.07
40	4.0	1.06
50	2.1	1.07
60	-	

Mean $k \times 10^3$ Sec^{-1} = 1.09
$k_o \times 10^5$ = 1.33

Table 162

Temp. 55°C

Total Oxidant 0.0066M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.6	-
2	13.0	2.03
4	10.45	1.93
6	8.35	1.90
8	6.70	1.88
10	5.4	1.87
12	4.35	1.87

Mean $k \times 10^3$ Sec^{-1} = 1.90
$k_o \times 10^5$ = 2.68

Table 163

Temp. 25°C

Total Oxidant 0.0083M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	48.0	-
10	41.7	2.34
20	36.2	2.35
30	31.3	2.38
40	27.6	2.30
50	23.9	2.32
60	20.5	2.36

Mean $k \times 10^4$ Sec^{-1} = 2.34
$k_o \times 10^5$ = 0.382

Table 164

Temp. 35°C

Total Oxidant 0.0083M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	92.7	-
10	60.0	7.25
20	39.5	7.11
30	27.0	6.86
40	16.7	7.14
50	10.9	7.14
60	8.4	6.67

Mean $k \times 10^4$ Sec^{-1} = 7.03
$k_o \times 10^5$ = 1.05

Table 165

Temp. 45°C

Total Oxidant 0.0083M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	37.6	-
5	24.3	1.45
10	15.5	1.48
15	9.6	1.52
20	6.3	1.49
25	3.9	1.51
30	2.5	1.51

Mean $k \times 10^3$ Sec^{-1} = 1.49
$k_o \times 10^5$ = 2.40

Table 166

Temp. 55°C

Total Oxidant 0.0083M
IsoPropyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	70.0	-
2	48.0	3.14
4	32.6	3.18
6	22.2	3.19
8	15.1	3.20
10	10.1	3.23
12	6.7	3.26

Mean $k \times 10^3$ Sec^{-1} = 3.20
$k_o \times 10^5$ = 4.83

Table 167

Temp.25°C

Perchloric Acid 0.1500M
IsoPropyl Alcohol 0.0845M
TotalOxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	35.0	-
10	22.5	0.736
20	14.4	0.740
30	9.2	0.744
40	6.0	0.735
50	3.8	0.741
60	2.4	0.744

Mean $k \times 10^3$ Sec^{-1} = 0.740
$k_o \times 10^5$ = 0.423

Table 168

Temp.35°C

Perchloric Acid 0.1500M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	24.0	-
5	14.2	1.75
10	8.75	1.68
15	5.3	1.68
20	3.2	1.68
25	1.95	1.67
30	1.05	1.74

Mean $k \times 10^3$ Sec^{-1} = 1.70
$k_o \times 10^5$ = 0.965

Table 169

Temp.45°C

Perchloric Acid 0.1500M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	34.6	-
5	10.85	3.87
10	3.4	3.84
15	1.0	3.94
20	0.35	3.83
25		

Mean $k \times 10^3$ Sec^{-1} = 3.87
$k_o \times 10^5$ = 2.10

Table 170

Temp.55°C

Perchloric Acid 0.1500M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	97.5	-
2	36.85	8.11
4	13.7	8.12
6	5.25	8.11
8	1.95	8.15
10	0.75	8.11
12	-	

Mean $k \times 10^3$ Sec^{-1} = 8.12
$k_o \times 10^5$ = 4.50

Table 171

Temp.25°C

Perchloric Acid 0.1000M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	40.0	-
10	26.8	0.606
20	19.4	0.604
30	13.5	0.604
40	9.3	0.607
50	6.4	0.610
60	4.4	0.611

Mean $k \times 10^3$ Sec^{-1} = 0.607
$k_o \times 10^5$ = 0.351

Table 172

Temp.35°C

Perchloric Acid 0.1000M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	27.85	-
5	18.6	1.34
10	12 .5	1.33
15	8.25	1.35
20	5.6	1.34
25	3.75	1.34
30	2.5	1.34

Mean $k \times 10^3$ Sec^{-1} = 1.34
$k_o \times 10^5$ = 0.800

Table 173

Temp.45°C

Perchloric Acid 0.1000M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	34.6	-
5	14.5	2.90
10	5.85	2.96
15	2.6	2.88
20	1.1	2.87
25	0.45	2.97
30	-	

Mean $k \times 10^3$ Sec^{-1} = 2.92
$k_o \times 10^5$ = 1.60

Table 174

Temp.55°C

Perchloric Acid 0.1000M
IsoPropyl Alcohol 0.0845M
Total Oxidant 0.0050M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	32.6	-
2	15.5	6.20
4	7.7	6.01
6	3.3	6.36
8	1.6	6.28
10	0.8	6.14

Mean $k \times 10^3$ Sec^{-1} = 6.20
$k_o \times 10^5$ = 3.30

Table 175

Temp.25°C

Sodium Chloride	0.2000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	38.0	-
10	24.0	0.766
20	15.1	0.769
30	9.5	0.770
40	6.0	0.770
50	3.7	0.777
60	2.4	0.768

Mean $k \times 10^3$ Sec^{-1} = 0.770

$k_o \times 10^3$ = 0.421

Table 176

Temp.35°C

Sodium Chloride	0.2000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	18.8	-
5	10.75	1.86
10	6.15	1.86
15	3.55	1.85
20	2.0	1.87
25	1.15	1.86
30	0.65	1.87

Mean $k \times 10^3$ Sec^{-1} = 1.86

$k_o \times 10^5$ = 1.00

Table 177

Temp.45°C

Sodium Chloride	0.2000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.7	-
2	10.1	4.20
4	5.8	4.41
6	3.7	4.18
8	2.2	4.22
10	1.3	4.25
12	0.75	4.30

Mean $k \times 10^3$ Sec^{-1} = 4.26

$k_o \times 10^5$ = 2.25

Table 178

Temp.55°C

Sodium Chloride	0.2000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	29.7	-
2	11.7	7.77
4	4.9	7.51
6	1.7	7.94
8	0.7	7.81

Mean $k \times 10^3$ Sec^{-1} = 7.76

$k_o \times 10^5$ = 4.40

Table 179

Temp. 25°C

Sodium Chloride	0.1000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	40.0	-
10	30.8	0.435
20	23.6	0.440
30	18.2	0.438
40	13.9	0.440
50	10.6	0.443
60	8.1	0.444

Mean $k \times 10^3$ Sec^{-1} = 0.440

$k_o \times 10^5$ = 0.297

Table 180

Temp. 35°C

Sodium Chloride	0.1000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	24.0	-
5	16.85	1.18
10	11.85	1.18
15	8.3	1.18
20	5.85	1.18
25	4.1	1.18
30	2.9	1.17

Mean $k \times 10^3$ Sec^{-1} = 1.18

$k_o \times 10^5$ = 0.700

Table 181

Temp. 45°C

Sodium Chloride	0.1000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	34.6	-
5	14.55	2.89
10	5.85	2.96
15	2.65	2.85
20	1.1	2.87
25	0.45	2.96

Mean $k \times 10^3$ Sec^{-1} = 2.91

$k_o \times 10^5$ = 1.59

Table 182

Temp. 55°C

Sodium Chloride	0.1000M
IsoPropyl Alcohol	0.0845M
Total Oxidant	0.0050M

$\mu = 0.4$

Time mts.	Thio ccs.	$K \times 10^3$ Sec^{-1}
0	29.7	-
2	14.8	5.80
4	7.4	5.79
6	3.7	5.79
8	1.9	5.78
10	0.9	5.83

Mean $K \times 10^3$ Sec^{-1} = 5.79

$k_o \times 10^5$ = 3.15

Table 183

Temp.25°C

Total Oxidant 0.0066M
Sec.Butyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	63.0	-
10	46.3	5.13
20	34.0	5.14
30	25.0	5.13
40	18.4	5.13
50	13.5	5.13
60	9.9	5.14

Mean $k\times10^4 Sec^{-1}$ = 5.13
$k_o\times10^5$ = 0.451

Table 184

Temp.35°C

Total Oxidant 0.0066M
Sec.Butyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	40.3	-
5	26.0	1.46
10	16.6	1.48
15	11.0	1.44
20	7.0	1.46
25	4.4	1.48
30	2.9	1.46

Mean $k\times10^3 Sec^{-1}$ = 1.46
$k_o\times10^5$ = 1.40

Table 185

Temp. 45°C

Total Oxidant 0.0066M
Sec. Butyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	16.7	-
2	10.75	3.67
4	7.25	3.48
6	4.80	3.47
8	3.2	3.45
10	2.05	3.48
12	1.35	3.48

Mean $k\times10^3 Sec^{-1}$ = 3.47
$k_o\times10^5$ = 3.08

Table 186

Temp. 55°C

Total Oxidant 0.0066M
Sec.Butyl Alcohol 0.2000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	40.0	-
2	18.65	6.35
4	8.65	6.37
6	4.0	6.38
8	1.85	6.40
10	0.80	6.50

Mean $k\times10^3 Sec^{-1}$ = 6.40
$k_o\times10^5$ = 6.20

Table 187

Temp. 25°C

Total Oxidant 0.0059M
Sec. Butyl Alcohol 0.2000M
μ = 0.4

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	22.6	-
10	18.9	2.98
20	15.7	3.04
30	13.1	3.03
40	10.9	3.04
50	9.1	3.03
60	7.5	3.06

Mean $k \times 10^4$ Sec^{-1} = 3.03
$k_o \times 10^5$ = 0.295

Table 188

Temp. 35°C

TotalOxidant 0.0059M
Sec.Butyl Alcohol 0.2000M
μ = 0.4

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	22.6	-
5	16.9	0.969
10	12.6	0.974
15	9.5	0.963
20	7.2	0.953
25	5.3	0.967
30	4.1	0.948

Mean $k \times 10^3$ Sec^{-1} = 0.962
$k_o \times 10^5$ = 0.930

Table 189

Temp. 45°C

Total Oxidant 0.0059M
Sec.Butyl Alcohol 0.2000M
μ = 0.4

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	70.0	-
2	54.8	2.04
4	42.8	2.05
6	33.4	2.06
8	26.1	2.06
10	20.2	2.07
12	15.7	2.08

Mean $k \times 10^3$ Sec^{-1} = 2.06
$k_o \times 10^5$ = 2.05

Table 190

Temp. 55°C

Total Oxidant 0.0059M
Sec.Butyl Alcohol 0.2000M
μ = 0.4

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	80.0	-
2	50.0	3.92
4	30.6	4.00
6	18.0	4.14
8	10.8	4.17
10	6.5	4.18
12	3.9	4.19

Mean $k \times 10^3$ Sec^{-1} = 4.10
$k_o \times 10^5$ = 4.12

Table 191

Temp. 25°C

Perchloric Acid	0.1500M
Total Oxidant	0.0035M
Sec.Butyl Alcohol	0.0825M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	32.5	-
5	22.2	1.27
10	15.2	1.27
15	10.45	1.26
20	7.1	1.27
25	4.85	1.27
30	3.3	1.27

Mean $k \times 10^3$ Sec^{-1} = 1.27

$k_o \times 10^5$ = 0.500

Table 192

Temp. 35°C

Perchloric Acid	0.1500M
Total Oxidant	0.0035M
Sec.Butyl Alcohol	0.0825M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	33.9	-
5	13.2	3.14
10	5.4	3.06
15	2.0	3.14
20	0.8	3.12
25	0.35	3.05
30	-	

Mean $k \times 10^3$ Sec^{-1} = 3.10

$k_o \times 10^5$ = 1.30

Table 193

Temp. 45°C

Perchloric Acid	0.1500M
Total Oxidant	0.0035M
Sec.Butyl Alcohol	0.0825M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	42.8	-
2	21.7	5.66
4	11.0	5.66
6	5.5	5.70
8	2.8	5.68
10	1.4	5.70
12	0.7	5.71

Mean $k \times 10^3$ Sec^{-1} = 5.69

$k_o \times 10^5$ = 2.70

Table 194

Temp. 55°C

Perchloric Acid	0.1500M
Sec.Butyl Alcohol	0.0825M
Total Oxidant	0.0035M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	65.0	-
2	17.9	10.7
4	5.0	10.7
6	1.4	10.7
8	0.4	10.6

Mean $k \times 10^3$ Sec^{-1} = 10.7

$k_o \times 10^5$ = 5.30

Table 195

Temp. 25°C

Perchloric Acid 0.1000M
Total Oxidant 0.0035M
Sec.Butyl Alcohol 0.0825M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	32.5	-
5	23.9	1.02
10	17.6	1.02
15	13.0	1.02
20	9.5	1.02
25	7.0	1.02
30	5.15	1.02

Mean $k \times 10^3$ Sec^{-1} = 1.02
$k_o \times 10^5$ = 0.350

Table 196

Temp. 35°C

Perchloric Acid 0.1000M
Total Oxidant 0.0035M
Sec.Butyl Alcohol 0.0825M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	33.9	-
5	15.8	2.54
10	7.35	2.55
15	3.45	2.54
20	1.7	2.49
25	0.75	2.54
30	-	

Mean $k \times 10^3$ Sec^{-1} = 2.53
$k_o \times 10^5$ = 0.880

Table 197

Temp.45°C

Perchloric Acid 0.1000M
Total Oxidant 0.0035M
Sec.Butyl Alcohol 0.0825M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	42.8	-
2	25.8	4.22
4	15.5	4.23
6	9.3	4.24
8	5.7	4.20
10	3.4	4.22
12	2.2	4.12

Mean $k \times 10^3$ Sec^{-1} = 4.20
$k_o \times 10^5$ = 1.80

Table 198

Temp. 55°C

Perchloric Acid 0.1000M
Sec.Butyl Alcohol 0.0825M
Total Oxidant 0.0035M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	65.0	-
2	22.9	8.70
4	8.0	8.68
6	2.9	8.64
8	1.0	8.70
10	0.35	8.71

Mean $k \times 10^3$ Sec^{-1} = 8.68
$k_o \times 10^5$ = 3.60

Table 199

Temp. 25°C

Zirconium Oxychloride 0.0100M
Sec. Butyl Alcohol 0.0825M
Total Oxidant 0.0035M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	32.5	-
5	25.0	0.875
10	19.4	0.860
15	14.9	0.867
20	11.5	0.866
25	8.85	0.867
30	6.8	0.870

Mean $k\times10^3$ Sec^{-1} = 0.868
$k_o\times10^5$ = 0.330

Table 200

Temp. 35°C

Zirconium Oxychloride 0.0100M
Sec.Butyl Alcohol 0.0825M
Total Oxidant 0.0035M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	33.9	-
5	17.8	2.15
10	10.7	1.92
15	6.4	1.85
20	3.3	1.94
25	1.9	1.92

Mean $k\times10^3$ Sec^{-1} = 1.91
$k_o\times10^5$ = 0.850

Table 201

Temp. 45°C

Zirconium Oxychloride 0.0100M
Sec. Butyl Alcohol 0.0825M
Total Oxidant 0.0035M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	42.8	-
2	23.9	4.85
4	13.6	4.78
6	7.6	4.80
8	4.2	4.83
10	2.4	4.80
12	1.3	4.85

Mean $k\times10^3$ Sec^{-1} = 4.82
$k_o\times10^5$ = 1.80

Table 202

Temp. 55°C

Zirconium Oxychloride 0.0100M
Sec.Butyl Alcohol 0.0825M
Total Oxidant 0.0035M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	65.0	-
2	21.7	9.14
4	7.25	9.14
6	2.4	9.16
8	0.7	9.44

Mean $k\times10^3$ Sec^{-1} = 9.22
$k_o\times10^5$ = 3.70

Table 203

Temp. 25°C

Zirconium Oxychloride	0.0150M
Sec.Butyl Alcohol	0.0825M
Total Oxidant	0.0035M

$\mu = 0.4$

U

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	32.5	-
5	22.15	1.28
10	14.1	1.39
15	10.3	1.28
20	7.7	1.20
25	4.9	1.28
30	3.25	1.28

Mean $k \times 10^3$ Sec^{-1} = 1.28

$k_o \times 10^5$ = 0.470

Table 204

Temp. 35°C

Zirconium Oxychloride	0.0150M
Sec.Butyl Alcohol	0.0825M
Total Oxidant	0.0035M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	33.9	-
5	14.0	2.95
10	5.8	2.94
15	2.4	2.92
20	1.0	2.93
25	0.3	3.15

Mean $k \times 10^3$ Sec^{-1} = 2.93

$K_o \times 10^5$ = 1.23

Table 205

Temp. 45°C

Zirconium Oxychloride	0.0150M
Sec. Butyl Alcohol	0.0825M
Total Oxidant	0.0035M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	42.8	-
2	18.95	6.79
4	8.4	6.78
6	3.7	6.80
8	1.6	6.85
10	0.7	6.86
12	-	

Mean $k \times 10^3$ Sec^{-1} = 5.69

$k_o \times 10^5$ = 2.52

Table 206

Temp. 55°C

Zirconium Oxychloride	0.0150M
Sec.Butyl Alcohol	0.0825M
Total Oxidant	0.0035M

$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	65.0	-
2	12.3	13.9
4	2.3	13.9
6	0.45	13.8
8		

Mean $k \times 10^3$ Sec^{-1} = 13.9

$k_o \times 10^5$ = 5.15

Table 207

Temp. 25°C

Total Oxidant 0.0132M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	39.0	-
10	38.4	2.61
20	37.7	2.84
30	37.1	2.78
40	36.5	2.76
50	35.6	3.05
60	35.4	2.69

Mean $k \times 10^5$ Sec^{-1} = 2.79
$k_o \times 10^5$ = 0.051

Table 208

Temp. 35°C

Total Oxidant 0.0132M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	55.6	-
10	51.8	1.18
20	48.7	1.10
30	45.0	1.18
40	42.3	1.14
50	39.1	1.17
60	36.4	1.18

Mean $k \times 10^4$ Sec^{-1} = 1.16
$k_o \times 10^5$ = 0.197

Table 209

Temp. 45°C

Total Oxidant 0.0132M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	28.65	-
10	22.5	4.03
20	19.3	3.29
30	15.9	3.27
40	12.7	3.39
50	10.4	3.38
60	8.5	3.37

Mean $k \times 10^4$ Sec^{-1} = 3.34
$k_o \times 10^5$ = 0.550

Table 210

Temp. 55°C

Total Oxidant 0.0132M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$K \times 10^4$ Sec^{-1}
0	18.0	-
2	15.9	10.3
4	14.3	9.60
6	13.3	8.40
8	12.0	8.45
10	10.9	8.36
12	9.8	8.45

Mean $k \times 10^4$ Sec^{-1} = 8.41
$k_o \times 10^5$ = 1.37

Table 211

Temp. 25°C

Total Oxidant 0.0248M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	52.0	-
10	50.4	5.22
20	49.0	4.95
30	47.4	5.14
40	46.0	5.10
50	45.0	4.82
60	43.7	4.83

Mean $k \times 10^5$ Sec^{-1} = 4.97
$k_o \times 10^5$ = 0.175

Table 212

Temp. 35°C

Total Oxidant 0.0248M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	111.1	-
10	98.3	2.04
20	87.8	1.96
30	78.1	1.96
40	69.4	1.96
50	61.7	1.96
60	54.9	1.96

Mean $k \times 10^4$ Sec^{-1} = 1.96
$k_o \times 10^5$ = 0.693

Table 213

Temp. 45°C

Total Oxidant 0.0248M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	60.0	-
5	50.0	6.08
10	43.25	5.46
15	37.15	5.33
20	31.3	5.43
25	26.9	5.36
30	22.75	5.40

Mean $k \times 10^4$ Sec^{-1} = 5.39
$k_o \times 10^5$ = 1.92

Table 214

Temp. 55°C

Total Oxidant 0.0248M
Methyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	12.9	-
5	8.0	1.59
10	5.2	1.51
15	3.4	1.48
20	2.4	1.40
25	1.6	1.39
30	1.0	1.37

Mean $k \times 10^3$ Sec^{-1} = 1.38
$k_o \times 10^5$ = 4.79

Table 215

Temp. 25°C

Total Oxidant 0.0099M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	47.0	-
10	46.0	3.57
20	45.2	3.26
30	44.5	3.03
40	43.5	3.22
50	42.7	3.20
60	41.9	3.19

Mean $k\times10^5$ Sec^{-1} = 3.18
$k_o\times10^5$ = 0.042

Table 216

Temp. 35°C

Total Oxidant 0.0099M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	25.2	-
10	23.2	1.38
20	22.0	1.13
30	20.55	1.13
40	19.2	1.13
50	18.0	1.12
60	16.8	1.13

Mean $k\times10^4$ Sec^{-1} = 1.13
$k_o\times10^5$ = 0.165

Table 217

Temp. 45°C

Total Oxidant 0.0099M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	23.0	-
10	17.5	4.56
20	13.9	4.20
30	11.8	3.71
40	9.6	3.64
50	8.0	3.52
60	7.0	3.30

Mean $k\times10^4$ Sec^{-1} = 3.54
$k_o\times10^5$ = 0.460

Table 218

Temp. 55°C

Total Oxidant 0.0099M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	32.5	-
5	23.7	10.5
10	18.8	9.12
15	14.5	8.97
20	11.5	8.66
25	8.85	8.67
30	6.8	8.70

Mean $k\times10^4$ Sec^{-1} = 8.77
$k_o\times10^5$ = 1.14

Table 219

Temp. 25°C

Total Oxidant 0.0132M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	50.0	-
10	48.0	6.83
20	46.6	5.87
30	45.0	5.86
40	43.3	6.00
50	41.6	6.13
60	40.1	6.13

Mean $k \times 10^5$ = 6.16
$k_o \times 10^5$ Sec^{-1} = 0.070

Table 220

Temp. 35°C

Total Oxidant 0.0132M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	45.0	-
10	38.0	2.82
20	33.5	2.46
30	29.2	2.40
40	25.2	2.42
50	21.8	2.41
60	18.9	2.41

Mean $k \times 10^4$ Sec^{-1} = 2.42
$k_o \times 10^5$ = 0.275

Table 221

Temp. 45°C

Total Oxidant 0.0132M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	29.0	-
5	22.6	8.33
10	18.1	7.85
15	14.75	7.52
20	12.25	7.20
25	9.9	7.20
30	8.2	7.03

Mean $k \times 10^4$ Sec^{-1} = 7.36
$k_o \times 10^5$ = 0.770

Table 222

Temp. 55°C

Total Oxidant 0.0132M
Ethyl Alcohol 0.8000M
$\mu = 0.4$

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	78.0	-
5	20.7	2.02
10	12.2	1.89
15	7.0	1.88
20	4.3	1.82
25	2.45	1.83
30	1.4	1.83

Mean $k \times 10^3$ Sec^{-1} = 1.85
$k_o \times 10^5$ = 1.94

Table 223

Rate Constants and Thermodynamic Activation Parameters for the Reaction of Isopropyl Alcohol with Chlorine under different conditions, $\mu = 0.4$

Conc.	Temp. °C	$10^5 k_o$ moles lit^{-1} Sec^{-1}	$\frac{k_o \times 10^5}{(\text{Alcohol})}$	$\frac{k_{inte} \times 10^5}{(\text{Alcohol})}$	Temp. Coef.	E_A KCals	A Sec^{-1}	ΔH KCals	$-\Delta S$ e.u	ΔG	
a	25°	0.382	1.91	1.71		16.60 ± .11	1.72×10^7	15.86 ± .11	27.1	23.9	a-(Alcohol)=0.2000 M, (OX)=0.0083M.
a	35°	1.05	5.25	4.15	2.75						
a	45°	2.40	12.0	9.81	2.29						
a	55°	4.83	24.1	21.6	2.01						
b	25°	0.196	0.980	1.14		16.48 ± .09	2.68×10^7	16.08 ± .09	27.0	24.1	b-(Alcohol) = 0.2000M, (OX)= 0.0066M.
b	35°	0.580	2.90	3.15	2.96						
b	45°	1.33	6.65	7.29	2.29						
b	55°	2.68	13.4	16.4	2.01						
c	25°	0.423	5.00	5.00		15.81 ± .01	1.73×10^7	14.64 ± .01	29.1	23.3	c-(Alcohol) = 0.0845M, (OX) = 0.0050M ($HClO_4$)= 0.1500M.
c	35°	0.965	11.4	11.5	2.28						
c	45°	2.10	24.8	24.9	2.18						
c	55°	4.50	53.2	52.5	2.14						
d	25°	0.351	4.15	4.22		14.51 ± .01	1.73×10^6	13.70 ± .01	32.6	23.4	d-(Alcohol) = 0.0845M, (OX) = 0.0050M ($HClO_4$)= 0.1000M
d	35°	0.800	9.47	9.17	2.28						
d	45°	1.61	18.9	19.0	2.12						
d	55°	3.30	39.0	38.2	2.05						
e	25°	0.421	4.98	5.17		15.47 ± .02	9.22×10^6	14.55 ± .02	29.3	23.3	e-(Alcohol) = 0.0845M, (OX) = 1.0050M (NaCl)= 0.2000M
e	35°	1.00	11.8	11.9	2.38						
e	45°	2.25	26.6	26.0	2.25						
e	55°	4.40	52.1	54.0	1.96						
f	25°	0.297	3.51	3.63		15.43 ± .02	6.90×10^6	14.57 ± .02	30.0	23.5	f-(Alcohol) = 0.0845M, (OX) = 0.0050M (NaCl)= 0.1000M
f	35°	0.700	8.28	8.21	2.36						
f	45°	1.59	18.8	18.1	2.27						
f	55°	3.15	37.3	37.3	2.06						

Table 224

Rate Constants and Thermodynamic Activation Parameters for the Reaction of Sec.Butyl Alcohol with Chlorine under Different Conditions, $\mu = 0.4$

Conc.	Temp. °C	$10^5 k_o$ moles lit^{-1} Sec^{-1}	$10^5 K_o$ moles lit^{-1} Sec^{-1}	Temp. Coeff.	E_{Arr} KCals	A moles lit^{-1} Sec^{-1}	ΔH KCals	-ΔS e.u.	ΔG KCals
a	25°	0.451	0.502						
a	35°	1.40	1.27	3.10					
a	45°	3.08	2.94	2.20	16.79±.05	8.60×10^6	16.19±.05	28.5	24.7
a	55°	6.20	6.79	2.01					
b	25°	0.295	0.320						
b	35°	0.930	0.812	3.15					
b	45°	2.05	1.97	2.20	16.84±.05	6.97×10^6	16.32±.05	28.9	24.9
b	55°	4.12	4.44	2.01					
c	25°	0.500	0.535						
c	35°	1.30	1.21	2.60					
c	45°	2.70	2.67	2.07	15.29±.03	8.76×10^5	14.57±.03	33.8	24.6
c	55°	5.30	5.50	1.96					
D	25°	0.350	0.360						
D	35°	0.880	0.814	2.51					
D	45°	1.80	1.77	2.05	15.16±.03	3.24×10^5	14.37±.03	35.2	24.9
D	55°	3.60	3.67	2.00					
e	25°	0.470	0.444						
e	35°	1.23	1.03	2.62					
e	45°	2.52	2.27	2.05	14.44±.07	8.51×10^5	14.74±.07	33.6	24.7
e	55°	5.15	4.78	2.04					
f	25°	0.330	.300						
f	35°	0.850	.727	2.58					
f	45°	1.80	1.61	2.12	12.98±.07	2.47×10^4	14.94±.07	33.6	24.9
f	55°	3.70	3.46	2.05					

a-(Alcohol)=0.2000M, (OX)=0.0066M.

b-(Alcohol)=0.2000M, (OX)=0.0059M

c-(Alcohol)=0.0825M, (OX)=0.0035M $(HClO_4)$= 0.1500M.

d-(Alcohol)=0.0825M, (OX)=0.0035M $(HClO_4)$=0.1000M

e-(Alcohol)=0.0825M, (OX)=0.0035M (ZrOCl)=0.0150M

f-(Alcohol)=0.0825M, (OX)=0.0035M (ZrOCl)=0.0100M

Table 225

Rate Constants and Thermodynamic Activation Parameters for the Reaction of Methyl Alcohol with Chlorine.

Conc.	Temp. °C	$10^5 k_o$ moles lit^{-1} Sec^{-1}	Temp. Coff.	$10^5 k_o$ moles lit^{-1} Sec^{-1}	E_{Arr} KCals	A moles lit^{-1} Sec^{-1}	ΔH KCals	$-\Delta S$ e.u	ΔG KCals
a	25°	0.175		.180					
a	35°	.693	3.96	.589	21.23±.06	6.82×10^9	20.69±.06	15.4	25.3
a	45°	1.92	2.77	1.71					
a	55°	4.79	2.49	4.87					
b	25°	.051	3.86	.051					
b	35°	.197	3.86	.166	21.23±.07	1.82×10^9	20.59±.07	18.2	26.0
b	45°	.550	2.79	.482					
b	55°	1.37	2.49	1.34					

A - $(CH_3OH) = 0.8000M, (OX)_o = 0.0248M, \mu = 0.4$

B - $(CH_3OH) = 0.8000M, (OX)_o = 0.0132M$ $\mu = 0.4$

Table 226

Rate Constants and Thermodynamic Activation Parameters for the Reaction of Ethyl Alcohol with Chlorine

Conc.	Temp. °C	$10^5 k_o$ moles lit^{-1} Sec^{-1}	Temp. Coeff.	$10^5 k_{int}$ moles lit^{-1} Sec^{-1}	E_{Arr} KCals	A moles lit^{-1} Sec^{-1}	ΔH KCals	-ΔS e.u	ΔG KCals
a	25°	0.070		0.067	21.21±.08	5.62×10^9	20.78±.08	17.0	25.9
a	35°	.275	3.93	.221					
a	45°	.770	2.80	.657					
a	55°	1.94	2.52	1.87					
b	25°	.042		.050	21.18±.07	3.21×10^9	20.65±.07	18.3	26.1
b	35°	.165	3.93	.165					
b	45°	.460	2.79	.482					
b	55°	1.14	2.48	1.34					

a- $(C_2H_5OH) = 0.8000M$, $(OX)_o = 0.0132M$, $\mu = 0.4$

b- $(C_2H_2OH) = 0.8000M$, $(OX)_o = 0.0099M$, $\mu = 0.4$

Results and Discussion :

In Tables 223 to 226, the values of initial rates, k_o, at different temperatures together with the values of k_{int}, temperature coefficient and various activation parameters with their standard deviation are presented. The energy of activation, E_{Arr}, and the frequency factor, A, of the Arrhenius equation have been calculated from the straight line plot of log k_o versus 1/T, and the enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, of activation have been calculated from the straight line plot of log ko/T versus 1/T, by method of least squares$^{(303)}$ (If the straight line equation is $y = mx + c$, then by least squares method,

$$m = \frac{(n)\sum x_i y_i - \sum x_i \; y_i}{(n)\sum x_i^2 - (\sum x_i)^2}$$

$$c = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i \; y_i}{(n)\sum x_i^2 - (\sum x_i)^2}$$

where n is the number of observations). The free energy, $\Delta G^{\neq}$, of activation has been calculated at 25°C from the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The rate constants, k_{int}, have been calculated by using the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ from equation (x). We calculated the standard deviation, r.m., by using the formula$^{(304)}$.

$$\text{r.m.} = \sqrt{\frac{\sum (\log \ K_{exp}/K_{int})^2 \times n}{(n-2)\left[(\sum 1/T)^2 - n \sum 1/T^2\right]}}$$

where n is the number of experimental points and T is the absolute temperature.

Researches on the temperature coefficient of thermal and photochemical reactions had been carried out extensively(40,249,305 to 310). Dhar(306) found that there exists a relation between order and temperature coefficient of a reaction. He reported the following average values of temperature coefficient (between 25° and 35°C) for chemical reactions. Zero order . 4.40, Unimolecular : 4.15; Pseudo unimolecular: 3.84; Bimolecular: 3.02; Termolecular: 202; Quadrimolecular: 1.79; complex reactions : 1.78. von Halban had also corroborated this(310).

The temperature coefficient, k_{35^o}/k_{25^o}, of the reactions of methyl and ethyl alcohols with aqueous chlorine has been found to be 3.92 and 3.93 respectively, which correspond well with the value for pseudo unimolecular reaction. In the case of isopropyl and sec.butyl alcohols, the temperature coefficient has been found to 2.96 and 3.12 respectively, which correspond well with the value for bimolecular reaction(306). These results further support the accuracy in the determination of order of reaction.

The activation in a reaction is brought about by increasing the temperature or by adding a positive catalyst. The effect of temperature is less important in presence of a positive catalyst because major portion of the activation takes place at lower temperature. The temperature coefficient of positively catalysed reaction should, therefore, be lower than that of either uncatalysed or negatively catalysed reaction. According to Dhar(308,311), a positve catalyst diminishes the temperature coefficient of a reaction, the decrease being greater the higher the concentration of the catalyst. Data presented in Table 223 to 226 supports this view.

The energy of activation, in the absence of catalyst, has been found to be of the order of 21.2, 21.2, 16.5 and 16.8 kcals respectively for methyl, ethyl, isopropyl and sec.butyl alcohols, i.e. for methyl and ethyl alcohols the values are higher than for isopropyl and sec.butyl alcohols. Perhaps the mechanism of reactionsof methyl and ethyl alcohols are different from that of iso-propyl and sec.butyl alcohols, because we found that the total order of reaction for methyl and ethyl alcohols is first, whereas second for isopropyl and sec.butyl alcohols.

Chatterji and coworkers(247 to 249, 250,251) reported that for chromic acid oxidations of aliphatic monohydric alcohols, the energy of activation is about 11.0 to 13.0 k cals, which is lower than that observed for chlorine oxidations.

Comparing the values of Arrhenius frequency factor, it is seen that the frequency factor, A sec^{-1}, is of the order of 10^9, 10^9, 10^7 and 10^6 respectively, for methyl, ethyl, isopropyl and sec.butyl alcohols.

The entropy of activation, in the absence of catalyst, has been found to be of the order of -17, -18, -27,-29 cals/oC respectively, for methyl, ethyl, isopropyl and sec.butyl alcohols i.e. the values for primary alcohols are different from that of secondary alcohols. The increase in reactivity with the substitution of CH_3 group for H may be attributed to an entropy effect. The free energy of activation values are also different for primary and secondary alcohols.

GENERAL DISCUSSION

The reactions of chlorine with monohydric alcohols in water have been found to be very complex. In most of the cases we noticed that besides oxidation to their corresponding carbonyl compound, viz. $H - \overset{|}{\underset{|}{C}} - OH \rightarrow \overset{|}{\underset{|}{C}} = O$, chlorination of the alkyl groups of the carbonyl compound follows through consecutive reactions. This complicates the problem and we realised after working for more than one year that the consideration of pseudo first order rate constants only would not lead to any conclusion.

One of the methods of dealing such complicated reactions is to find out the initial rates by plotting x/t versus x, and extrapolating to x = 0, where x is the number of moles of total oxidant per litre consumed in time t(280,281). We arrived at most of the conclusions already mentioned in various sections mainly by considering k_o values.

For any mechanistic study, it is of prime importance to find out which of the species is principal effective oxidant, Cl_2, HOCl, Cl^+ or Cl_3^-? In Sec.2.1 we demonstrated by showing the constant values of $ko/(Cl_2)_o$ that molecular chlorine is the principal oxidant and other species play a negligible role. This conclusion may also be arrived at by dealing with the problem in another way :

(a) <u>In absence of chloride ions</u> :

If the initial stoichiometric concentration of chlorine is represented by $[\Sigma Cl_2]_o$ then, considering that the two oxidizing species to be Cl_2 and HOCl,

$$[\Sigma Cl_2]_o = [Cl_2]_o + [HOCL]_o$$

$$= [Cl_2]_o + \frac{B\,[Cl_2]_o}{[Cl^-]_o} = [Cl_2]_o \left\{1 + \frac{B}{[Cl^-]_o}\right\}$$

where $B = \dfrac{[HOCl]_o\,[Cl^-]_o}{[Cl_2]_o} = \dfrac{K_h}{a_{H^+}\cdot\gamma_{Cl^-}}$

Also, $(\Sigma Cl_2)_o = (Cl_2)_o + (HOCl)_o = \dfrac{(HOCl)_o\,(Cl^-)_o}{B} + (HOCl)_o$

$$= (HOCl)_o \left\{1 + \frac{(Cl^-)_o}{B}\right\}$$

Therefore,

$$\frac{k_o}{(OX)_o} = k_{Cl_2}\frac{(Cl_2)_o}{(\Sigma Cl_2)_o} + k_{HOCl}\frac{(HOCl)_o}{(\Sigma Cl_2)_o}$$

$$= \frac{k_{Cl_2}\,(Cl_2)_o}{(Cl_2)_o\left\{1 + \frac{B}{(Cl^-)}\right\}} + \frac{k_{HOCl}\,(HOCl)_o}{(HOCl)_o\left\{1 + \frac{(Cl^-)_o}{B}\right\}}$$

$$= \frac{k_{Cl_2}\,(Cl^-)_o}{B + (Cl^-)_o} + \frac{k_{HOCl}\,.\,B}{B + (Cl^-)_o}$$

or, $\left\{B + (Cl^-)_o\right\}\dfrac{ko}{(OX)_o} = k_{Cl_2}\,(Cl^-)_o + k_{HOCl}.\,B$ ...... (1)

A plot of $\left\{B + (Cl^-)_o\right\}\dfrac{k_o}{(OX)_o}$ versus $(Cl^-)_o$ will be a straight line, the slope and intercept being equal to k_{Cl_2} and $k_{HOCl}\cdot B$, respectively.

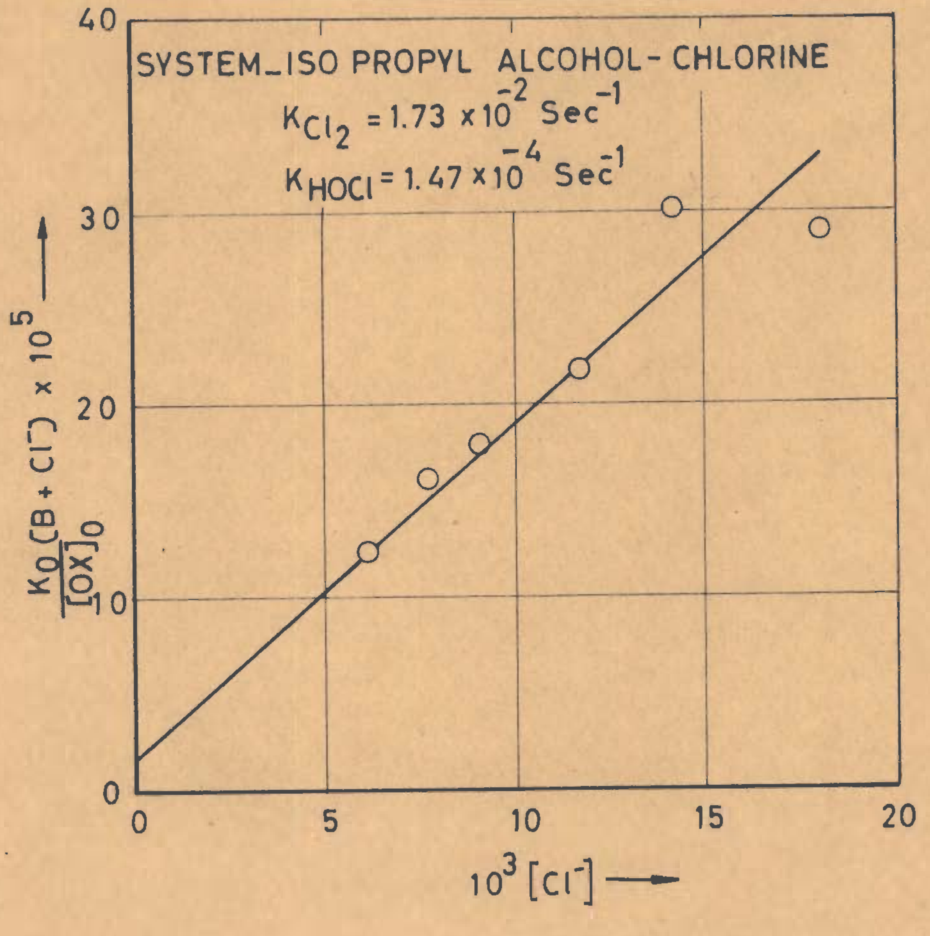


FIG. 3 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

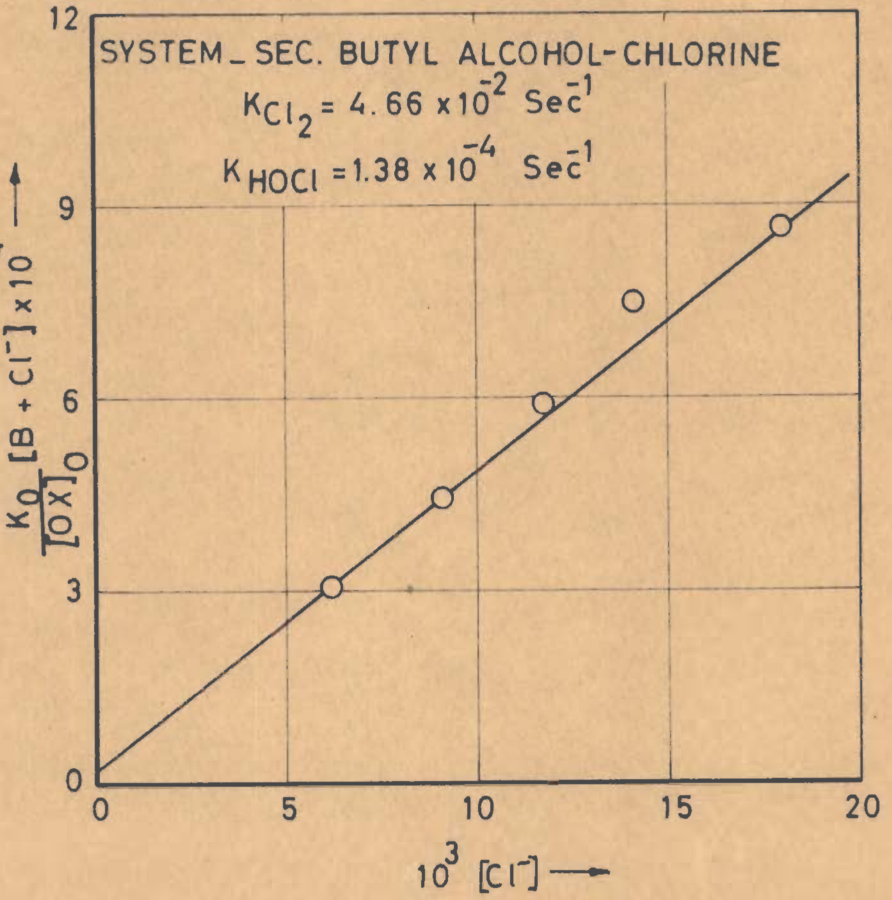


FIG. 4 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

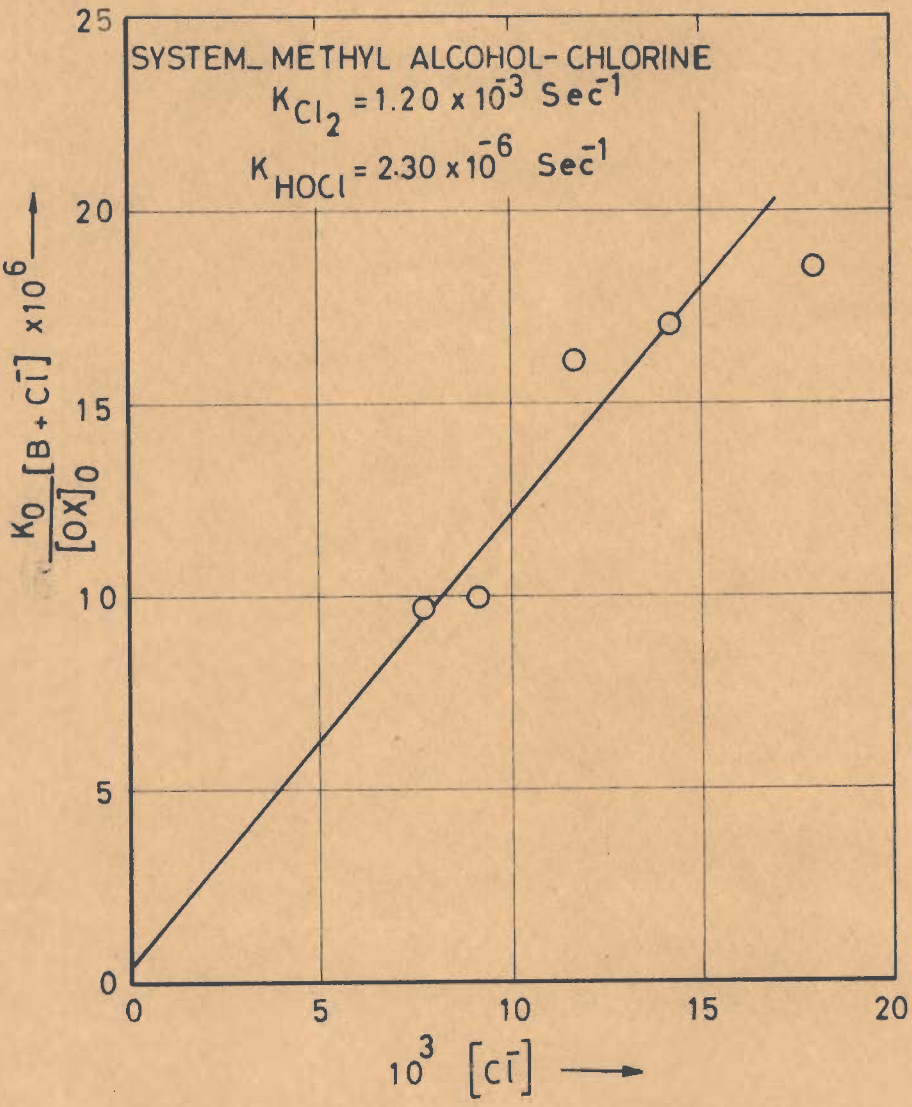


FIG. 5 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

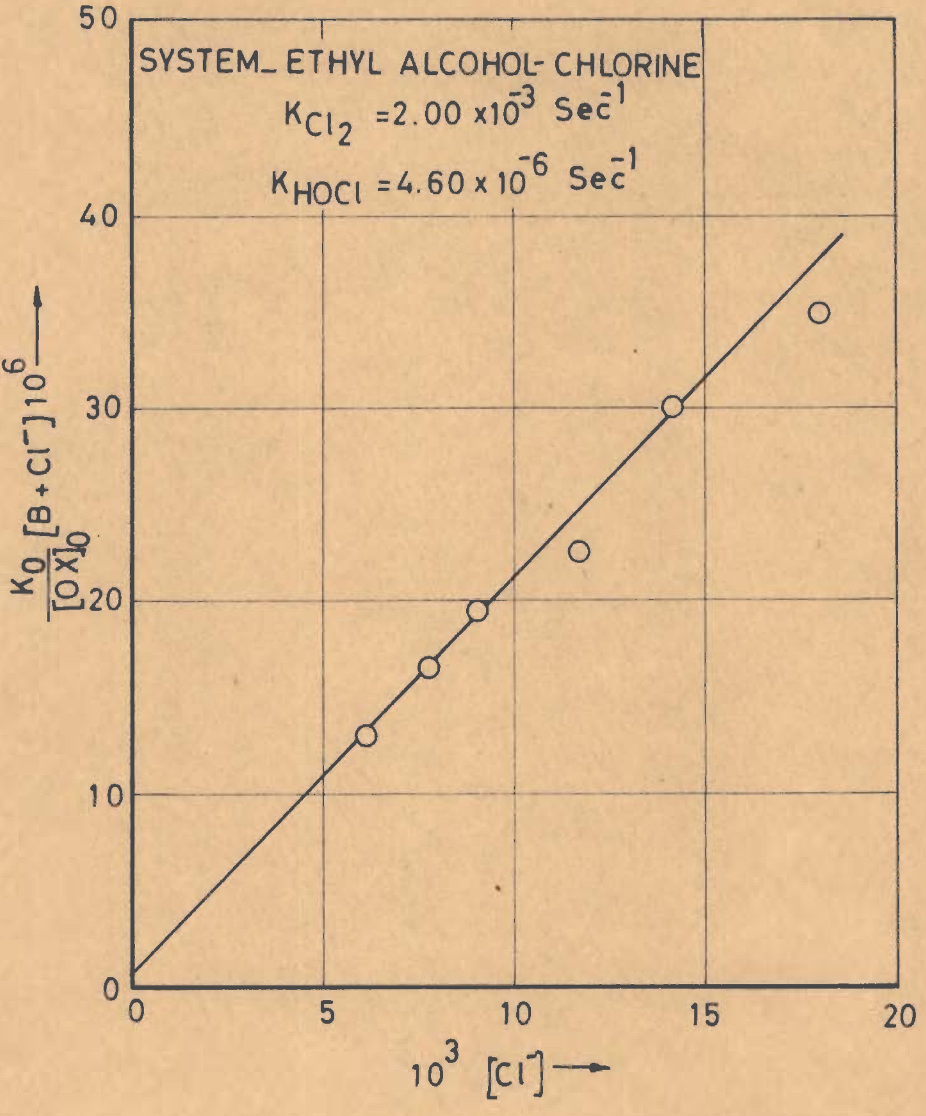


FIG. 6 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

In Fig. 3 to 6, the plots of $\left\{B + (Cl^-)_o\right\} \frac{ko}{(OX)_o}$ versus $(Cl^-)_o$ for the reactions of oxidant with isopropyl, sec.butyl, methyl and ethyl alcohols are shown. The values of $\left\{B + (Cl^-)_o\right\}$, $(Cl^-)_o$ etc. are given Table C (P.88). From slope and intercept, the mean values of k_{Cl_2} and k_{HOCl} have been found to be :

Alcohol	k_{Cl_2}, Sec^{-1}	k_{HOCl}, Sec^{-1}
Isopropyl Alcohol	1.73×10^{-2}	1.47×10^{-4}
Sec.Butyl Alcohol	4.66×10^{-2}	1.38×10^{-4}
Methyl Alcohol	1.20×10^{-3}	2.30×10^{-6}
Ethyl Alcohol	2.00×10^{-3}	4.60×10^{-6}

For calculating k_{HOCl} from intercept, the mean value of B has been considered. The above data shows that in all the cases, $k_{Cl_2} \gg k_{HOCl}$. The agreement of $k_{Cl_2} \left(= k_o/(Cl_2)_o\right)$ values reported in Sec.2.1 with the above k_{Cl_2} values (graphical) is within about 4% in all the cases.

(b) <u>In presence of Chloride ions</u> :

In presence of chloride ions, Cl^-_3 is formed by the reaction,

$$Cl_2 + Cl^- \rightleftharpoons Cl^-_3$$

Therefore, $K_3 = \dfrac{(Cl^-_3)}{(Cl_2)\,(Cl^-)}$, where K_3 is the formation constant of Cl^-_3.

If we consider the three oxidizing species to be Cl_2, HOCl and $Cl^-{}_3$, then

$$[\Sigma Cl_2]_o = (Cl_2)_o + (HOCl)_o + (Cl^-{}_3)_o$$

$$= (Cl_2)_o + B\,\frac{(Cl_2)_o}{(Cl^-)_o} + K3\,(Cl_2)_o\,(Cl^-)_o$$

$$= \frac{(Cl_2)_o}{(Cl^-)}\left\{B + (Cl^-)_o + K_3\,(Cl^-)_o{}^2\right\}$$

also, $(\Sigma Cl_2)_o = \dfrac{(HOCl)_o\,(Cl^-)_o}{B} + (HOCl)_o + K_3\dfrac{(HOCl)_o(Cl^-)_o{}^2}{B}$

$$= \frac{(HOCl)_o}{B}\left\{B + (Cl^-)_o + K_3\,(Cl^-)_o{}^2\right\}$$

Therefore,

$$\frac{k_o}{(OX)_o} = k_{Cl_2}\,\frac{(Cl_2)_o}{(\Sigma Cl_2)_o} + k_{HOCl}\cdot\frac{(HOCl)_o}{(\Sigma Cl_2)_o} + k_{Cl^-{}_3}\frac{(Cl^-{}_3)_o}{(\Sigma Cl_2)_o}$$

$$= \frac{k_{Cl_2}\,(Cl^-)_o}{B+(Cl^-)_o + K3\,(Cl^-)_o{}^2} + \frac{k_{HOCl.}\,B}{B+(Cl^-)_o + K_3(Cl^-)_o{}^2}$$

$$+ \frac{k_{Cl_3^-}\,.\,K3\,(Cl^-)_o{}^2}{B + (Cl^-)_o + K_3\,(Cl^-)}$$

or $\dfrac{k_o}{(OX)_o}\left\{B + (Cl^-)_o + K_3\,(Cl^-)_o{}^2\right\} = k_{Cl_2}.(Cl^-)_o + k_{HOCl}.$

$$B + k_{Cl^-{}_3}.\,K_3\,(Cl^-)_o{}^2 \quad \ldots\ldots \text{(ii)}$$

This is a parabolic equation, but if Cl_3^- species is not effective as oxidant, then the third term of the equation may be neglected. It then reduces to

$$\frac{k_o}{(OX)_o}\left\{B + (Cl^-)_o + K_3\,(Cl^-)_o{}^2\right\} = k_{Cl_2}.\,(Cl^-)_o + k_{HOCl}.B \ldots \text{(iii)}$$

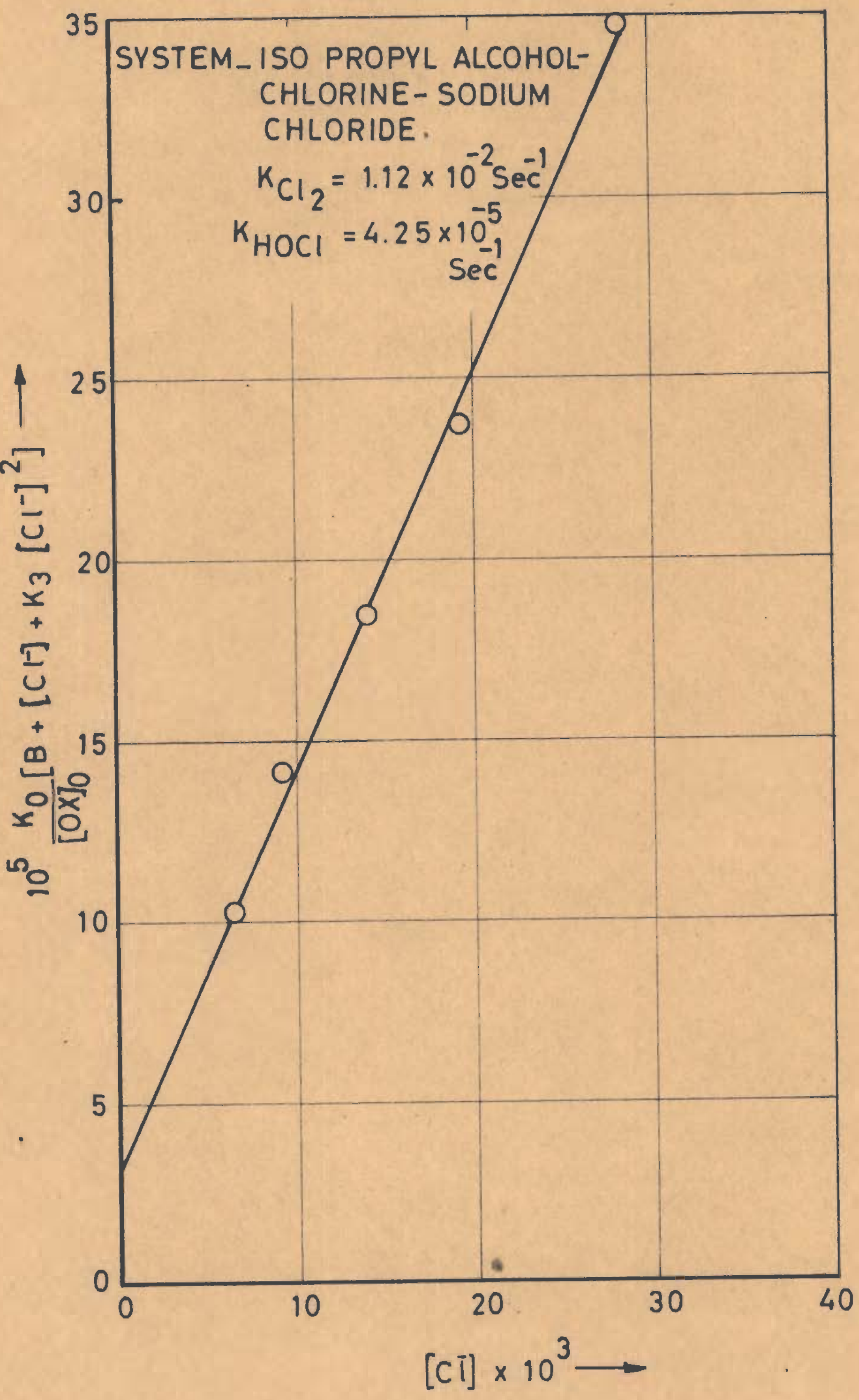


FIG. 7 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

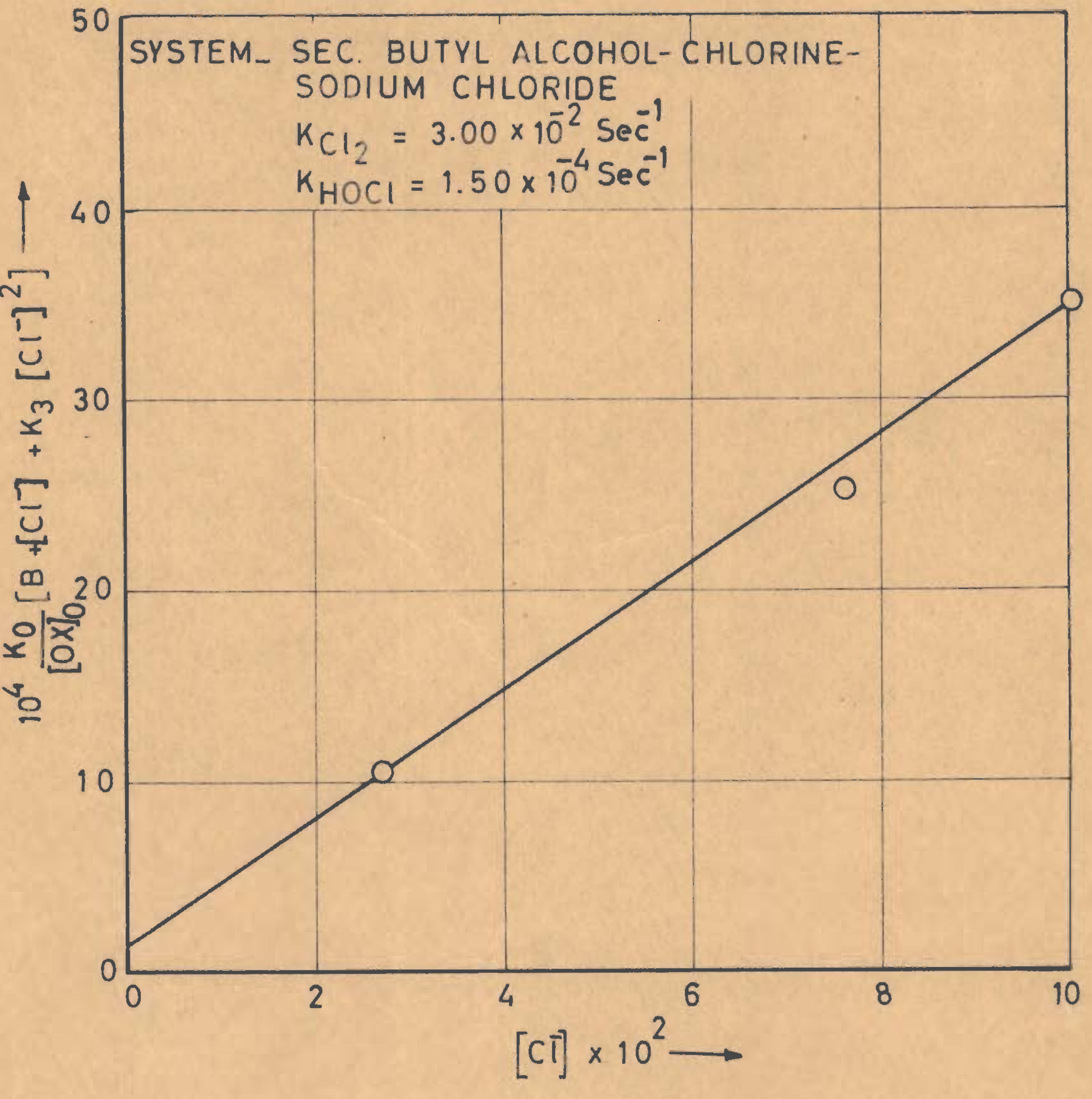


FIG. 8_ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

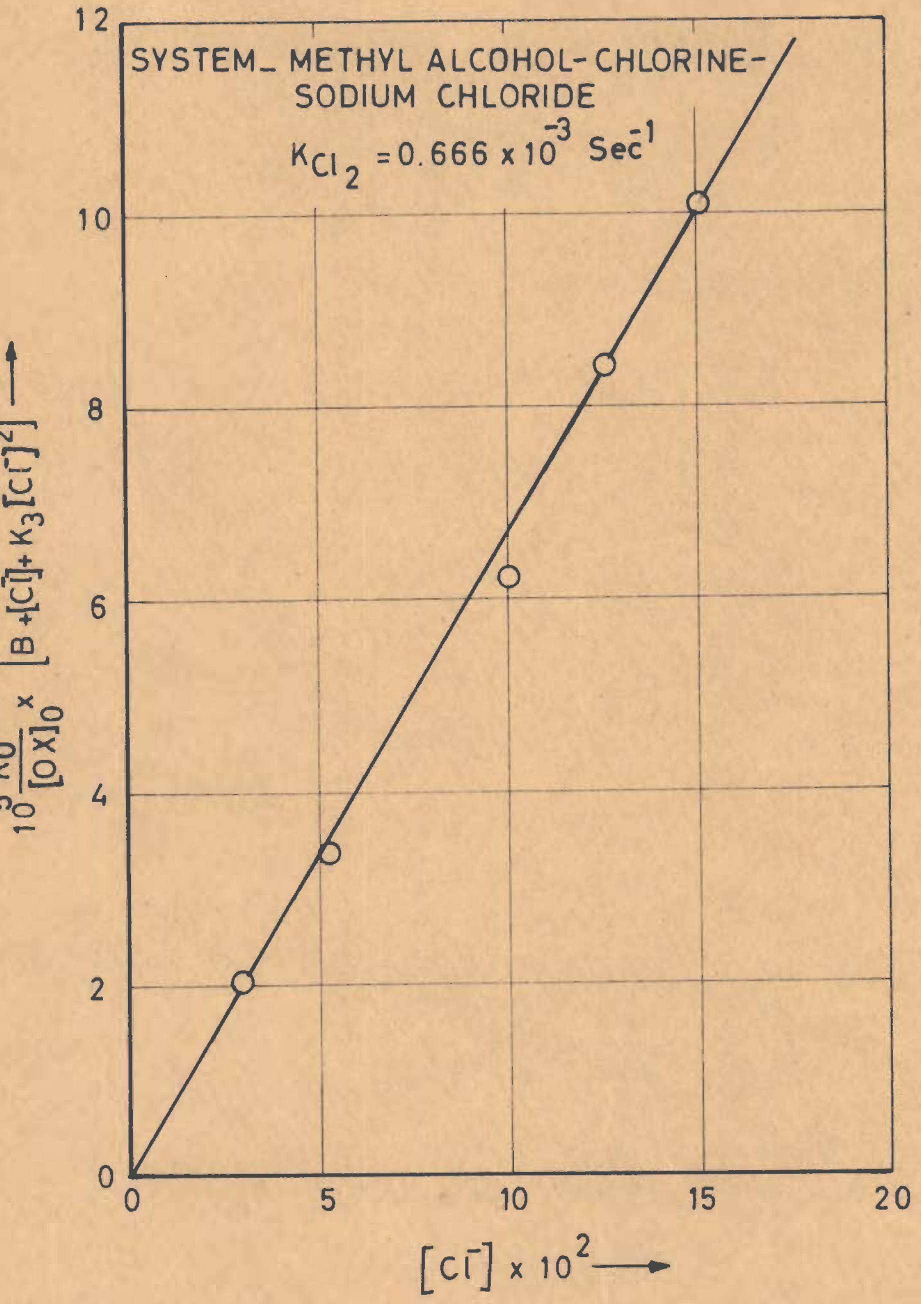


FIG. 9 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

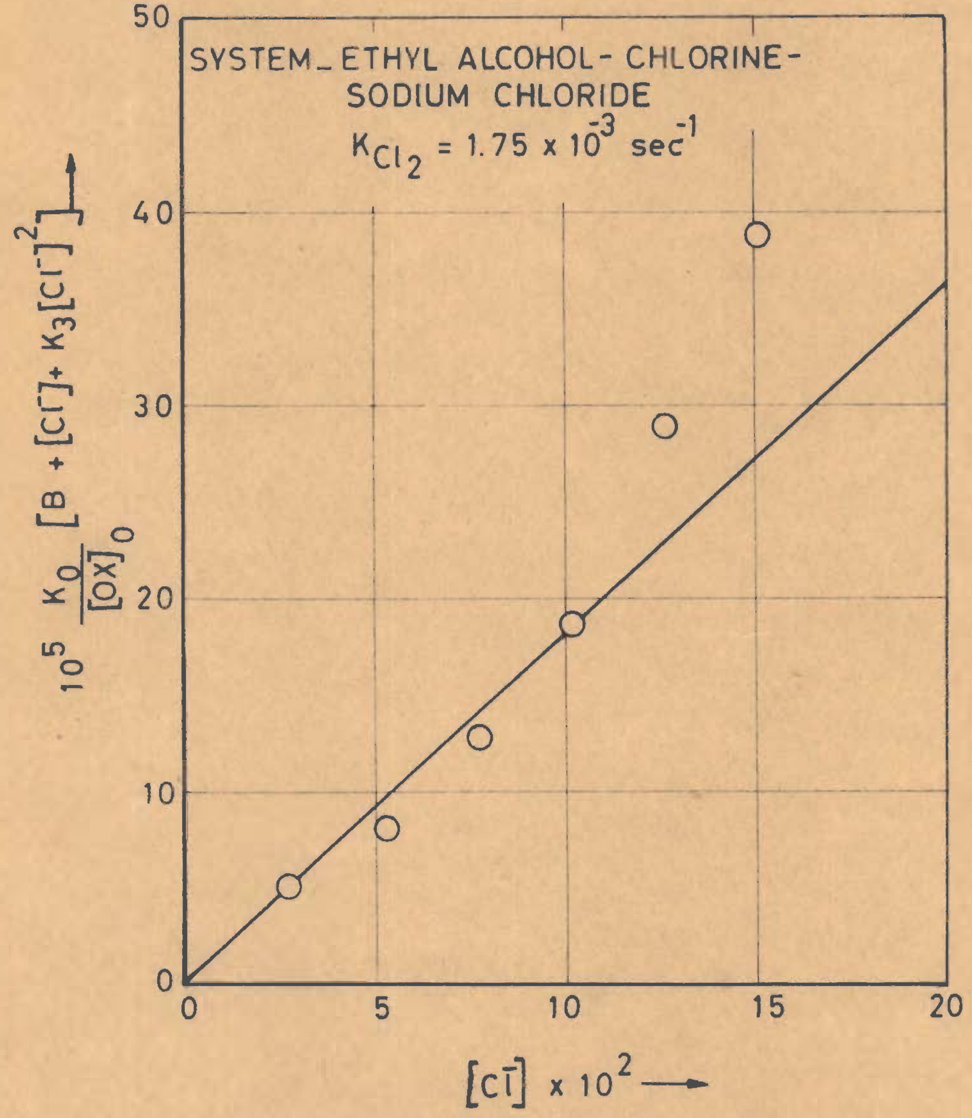


FIG.10 _ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

which is a straight line equation.

In Fig.7 to 10, the plots of $\frac{k_o}{(OX)_o}\left\{B+(Cl^-)_o + K_3 (Cl^-)_o^2\right\}$ versus (Cl^-) for the reactions of oxidant with isopropyl, sec. butyl, methyl, and ethyl alcohols in presence of varying concentrations of sodium chloride are shown (for K_3, we took the value of 0.180$^{(52,296)}$, and for $(Cl^-)_o$, its mean value, viz., $(Cl^-)_o = \frac{\alpha o(OX)_o + m}{2}$ during each run, taking trichloride formation into account). From the fact that straight lines have been obtained, we conclude the contribution of the third term in equation (2) to be negligible; furthermore, the fact that the straight lines passes through very near to the origin shows that

$$k_{Cl_2} \gg k_{HOCl} \gg k_{Cl_3^-}$$

However, the mean values of k_{Cl_2} in presence of chloride is about 30-40% lower than that obtained in absence of chloride. This is perhaps due to several uncertain assumptions.

We, thus, conclude that in chlorine water, molecular chlorine, Cl_2, is the principal effective oxidizing agent.

The mean value of the pseudo first order rate constants has been found to be higher than $k_o/(Cl_2)_o$ value for each run. This difference in the rate accounts for the rate of chlorination of the carbonyl compound.

Oxidation of Alcohols with Aqueous Chlorine.

In order to assign the mechanism of oxidation of alcohols to their corresponding carbonyl compound, as well as the chlorination of alkyl group of the carbonyl compounds, the following experimental facts must be taken into consideration.

(A) In the case of methyl and ethyl alcohols, the reaction kinetics accord the equation,

$$-\frac{d\,(Cl_2)}{dt} = k_{obs}\,(Cl_2)$$

and in presence of perchloric acid,

$$-\frac{d\,(Cl_2)}{dt} = k'_{obs}\,(Cl_2)\,(H^+)^n$$

where $n = 1/2$ or 1. (In the case of methyl alcohol, $n = 1/2$). The reaction kinetics for isopropyl and sec. butyl alcohols accord the equation.

$$-\frac{d\,(Cl_2)}{dt} = k_{obs}\,(Cl_2)\,(\text{Alcohol})$$

and in presence of perchloric acid,

$$-\frac{d\,(Cl_2)}{dt} = k'_{obs}\,(Cl_2)\,(\text{Alcohol})\,(H^+)^n$$

where $n = 1/2$ or 1.

(B) The products of the reaction in the case of methyl and ethyl alcohols are formaldehyde and chloroformaldehyde, and acetaldehyde and chloro substituted acetaldehyde, respectively.

In the case of isopropyl and secondary butyl alcohols, the products are acetone and monochloro acetone, and butanone-2 and 3-chlorobutanone-2, $CH_3.\ CHCl.\ COCH_3$, respectively.

(C) The influence of ionic strength on the reaction rates is insignificant.

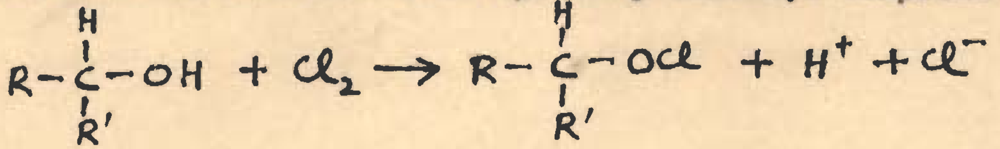
(D) Chloride ions, in general, accelerate the reaction rates, because these ions displace the hydrolytic equilibrium of chlorine to the left and, in turn, produces more chlorine.

(E) Silver nitrate, fluoride and dihydrogen phosphate ions also enhance the rates.

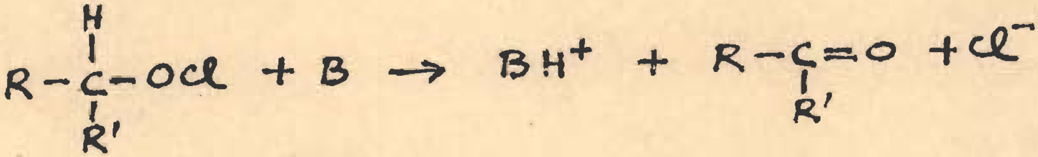
(F) The formation of alkyl hypochlorites has been detected. This suggests that hypochlorite ester is an essential intermediate in these reactions.

(G) The energy of activation has been found to be of the order of 21.2, 21.2, 16.6 and 16.8 Kilo Cals respectively in the case of methyl, ethyl, isopropyl and sec.butyl alcohols.

Consistent with all the facts, the following mechanisms may be ascribed to the chlorine oxidation of alcohols in water to corresponding carbonyl compound :



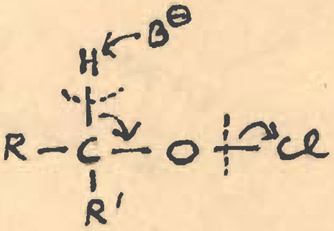
$$R-\overset{H}{\underset{R'}{C}}-OH + Cl_2 \rightarrow R-\overset{H}{\underset{R'}{C}}-OCl + H^+ + Cl^- \qquad (i)$$



$$R-\overset{H}{\underset{R'}{C}}-OCl + B \rightarrow BH^+ + R-\underset{R'}{C}=O + Cl^- \qquad (ii)$$

where B is a base.

The contribution of HOCl towards the alkyl hypochlorites formation, however, cannot be ruled out. However, the rate of reaction with HOCl is very slow in comparison to the rate with chlorine molecule. Here the rate controlling step involves the abstraction of proton from the C-H bond by a base (e.g. water). The mechanism of electron movements in the elimination process (ii) may be represented as follows :

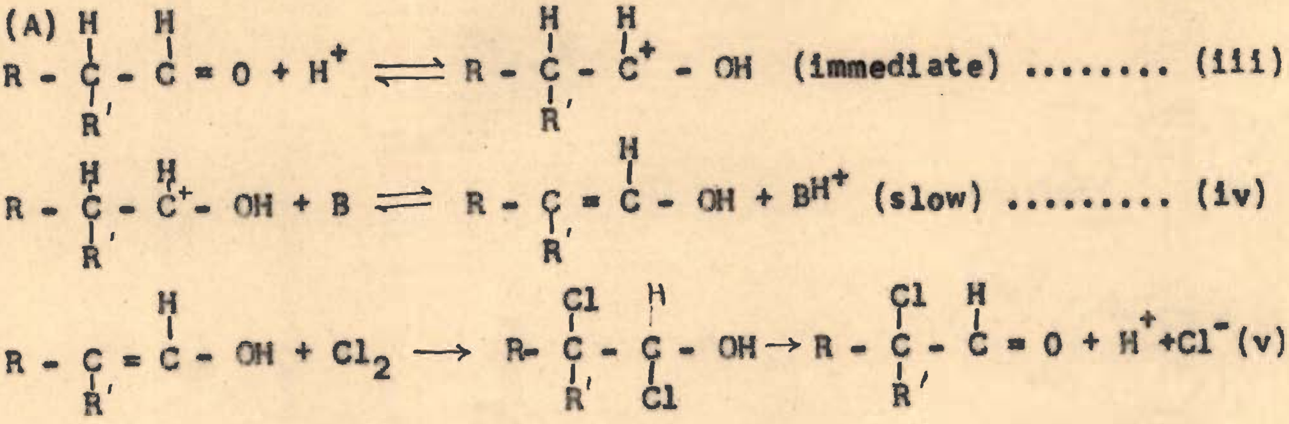


The electron movements involve the C-H, C-O and O-Cl bonds simultaneously, for otherwise transient ion, R - C - O$^+$, of very high energy content would have to be formed.

Chlorine is a heterolytic oxidant. The oxidation of alcohols by heterolytic oxidants generally takes place by way of esterification or by hydride transfer. We favour ester mechanism in this case.

It is generally believed that the oxidations of ketones occur via enols, if they are acid or base catalysed reaction, which proceed at the enolization rate(312). Actually the chlorination of a ketone or aldehyde should be regarded as oxidation.

The chlorination of aldehydes or ketones may be regarded as occuring by the initial enolization of aldehyde(221) or ketone, followed by addition of chlorine and the splitting out of a molecule of HCl :

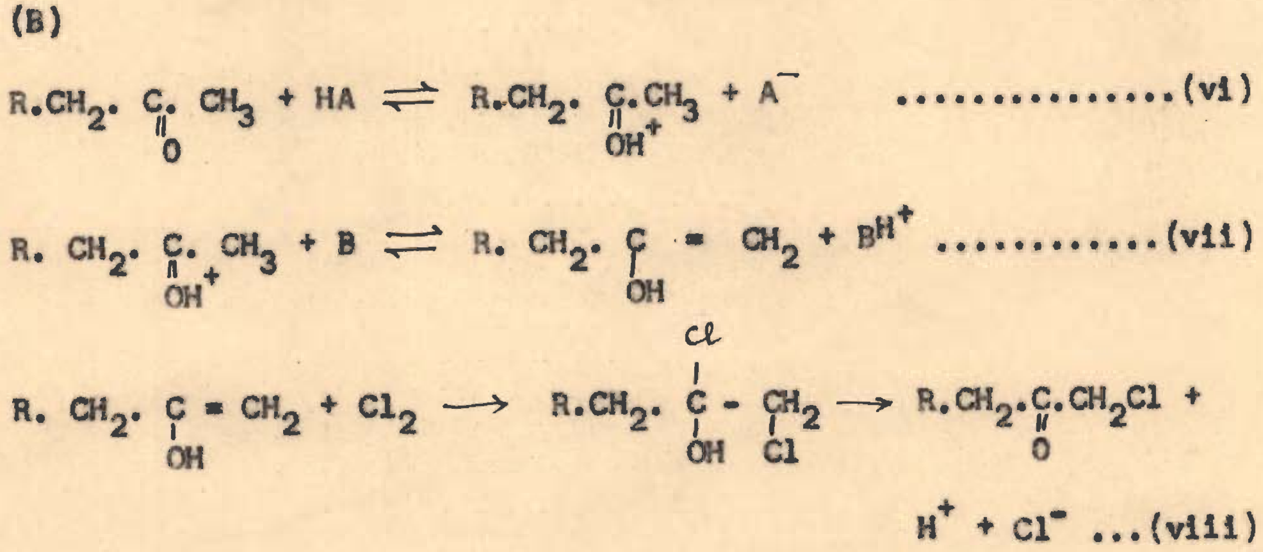


(A)

$$R-\overset{H}{\underset{R'}{C}}-\overset{H}{C}=O+H^{+} \rightleftharpoons R-\overset{H}{\underset{R'}{C}}-\overset{H}{C^{+}}-OH \quad \text{(immediate) .... (iii)}$$

$$R-\overset{H}{\underset{R'}{C}}-\overset{H}{C^{+}}-OH+B \rightleftharpoons R-\underset{R'}{C}=\overset{H}{C}-OH+BH^{+} \quad \text{(slow) .... (iv)}$$

$$R-\underset{R'}{C}=\overset{H}{C}-OH+Cl_2 \longrightarrow R-\overset{Cl}{\underset{R'}{C}}-\overset{H}{\underset{Cl}{C}}-OH \rightarrow R-\overset{Cl}{\underset{R'}{C}}-\overset{H}{C}=O+H^{+}+Cl^{-} \text{(v)}$$



(B)

$$R.CH_2.\underset{\overset{\|}{O}}{C}.CH_3+HA \rightleftharpoons R.CH_2.\underset{\overset{\|}{OH^{+}}}{C}.CH_3+A^{-} \quad \text{...............(vi)}$$

$$R.\ CH_2.\underset{\overset{\|}{OH^{+}}}{C}.CH_3+B \rightleftharpoons R.\ CH_2.\underset{OH}{C}=CH_2+BH^{+} \quad \text{............(vii)}$$

$$R.\ CH_2.\underset{OH}{C}=CH_2+Cl_2 \longrightarrow R.CH_2.\overset{Cl}{\underset{OH}{C}}-\underset{Cl}{CH_2} \longrightarrow R.CH_2.\underset{\overset{\|}{O}}{C}.CH_2Cl+H^{+}+Cl^{-} \text{...(viii)}$$

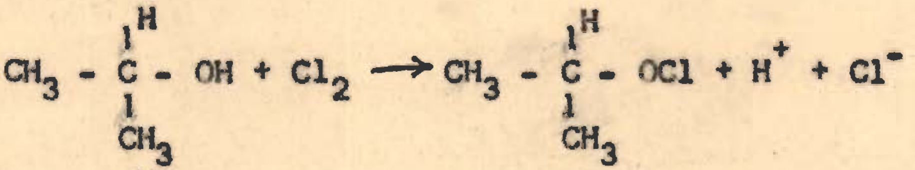
The effect of adding the proton to the carbonyl group is to increase its attraction for electrons and hence make it easier for the alpha - hydrogen to leave as proton. Since chlorine also is electron-attracting, a second hydrogen atom is replaced still more readily than the first hydrogen atom and the symmetrical polysubstitution results.

The rate of chlorination will, therefore, be equal to the rate of enolization, which is, therefore, rate controlling step, the subsequent addition of chlorine being rapid.

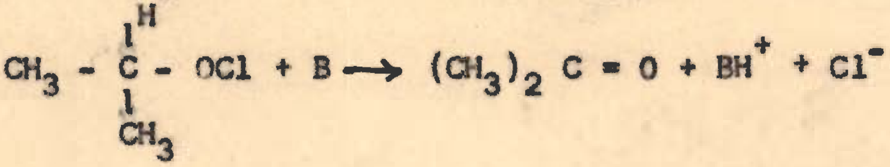
Smith(313) pointed out that the aldehydes and ketones which have hydrogens on the carbon alpha to the carbonyl group react rapidly with halogen to produce the corresponding α- halo - substituted carbonyl compounds. If other hydrogens are available, they too will be substituted until no more α - hydrogen remains.

$$R\text{-}CH_2.CHO + X_2 \longrightarrow R.CHX.\ CHO + HX$$

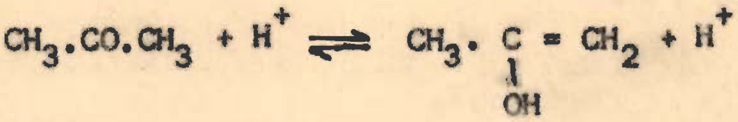
The overall reaction mechanism, e.g. for the reaction of isopropyl alcohol with chlorine, maybe written as follows :



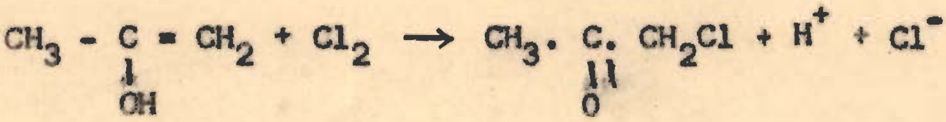
$$CH_3 - \overset{H}{\underset{CH_3}{C}} - OH + Cl_2 \longrightarrow CH_3 - \overset{H}{\underset{CH_3}{C}} - OCl + H^+ + Cl^- \qquad (ix)$$



$$CH_3 - \overset{H}{\underset{CH_3}{C}} - OCl + B \longrightarrow (CH_3)_2\ C = O + BH^+ + Cl^- \qquad (x)$$



$$CH_3.CO.CH_3 + H^+ \rightleftharpoons CH_3.\ \underset{OH}{C} = CH_2 + H^+ \qquad (xi)$$



$$CH_3 - \underset{OH}{C} = CH_2 + Cl_2 \longrightarrow CH_3.\ \underset{O}{\underset{\|}{C}}.\ CH_2Cl + H^+ + Cl^- \qquad (xii)$$

The hydrogen ions produced in step (ix) are utilised for enolization in step (xi). Thus the pH of the reaction mixture remains almost constant during a run. This we have seen by measuring the pH of the reaction mixture with the help of a pH meter during the progress of the reaction upto about one hour.

The following arguments may be advanced in support of the ester mechanism :

(a) The chromic acid oxidations of alcohols have now been shown to proceed via chromic acid ester of alcohol as intermediate(3,22,23,41). Such ester mechanisms of oxidation of alcohols by a large number of oxidizing agents have gained maximum support(222,314).

(b) Chattaway and Backeberg(235) observed that alkyl hypochlorites are unstable and they decomposes quietly, yielding as primary prdducts, aldehydes or ketones :

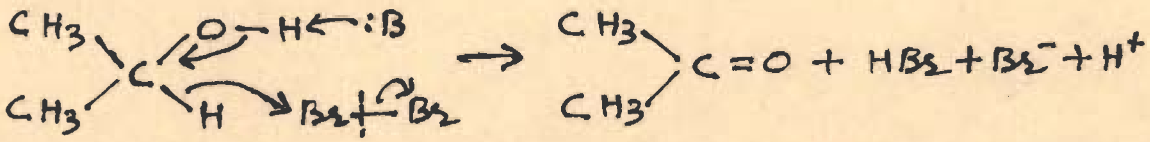
$$RCH_2OCl \longrightarrow R.CHO + HCl$$

$$R_2CHOCl \longrightarrow R_2\,CO + HCl$$

(c) Alkyl hypochlorites usually oxidize alcohols to the corresponding carbonyl compounds. Pyridine, a proton acceptor, catalyzes such reaction(102).

(d) The rate determining step in the oxidation of alcohols usually involve the cleavage of C-H bond as indicated by C-H kinetic isotope effect(10,21,29,236).

(e) Although Swain et al(29) suggested that the oxidation of isopropyl alcohol by bromine proceeds via hydride transfer, viz.



this does not appear to be applicable for chlorine oxidation, because the basic difference in the chlorine and bromine oxidations are : (i) the chlorine oxidation does involve the alkyl hypochlorite ester formation, the bromine oxidation does not; whereas alkyl hypochlorites have been isolated, the alkyl hypobromites have not been isolated so far by any investigator, (ii) whereas chloride ion enhances the rate of chlorine oxidation, the bromide ion inhibits the rate of bromine oxidation, (iii) the rates increase with increasing pH in bromine oxidation(233), but the rates decrease with increasing pH in chlorine oxidation.

While discussing the mechanism of electrophilic chlorination, Robertson and coworkers(111) pointed out that chlorine reacts directly in molecular form, the rate determining step being the formation of an intermediate ($ArH.Cl_2$) with aromatic compounds. Soper et al(315) have clearly stated that trichloride ion, Cl_3^- is not an effective chlorinating agent.

Although many workers(122 to 126) believe that chlorine cation, Cl^+ or $Cl^+.H_2O$ is the main chlorinating agent in aqueous acidic media, Arotsky and Symons(180) showed that the concentration of these ions in aqueous acidic media are so small that they could hardly act as important intermediate in chlorination. Harvey and Norman(191) mentioned that in acidic solutions, the attacking species is Cl^+ ions, whereas in non acidic conditions the molecular chlorine is the principal species.

The influence of chloride ions clearly shows that the chlorination with Cl^+ ions does not appear to be possible, because the equilibrium $Cl^+ + Cl^- \rightleftharpoons Cl_2$ would be displaced almost completely to the right and hence the concentration of Cl^+ ions in the reaction mixture must be virtually zero. Moreover, according to Bell and Gelles(185), the concentration of Cl^+ ions is so small in solution that it is unlikely to be effective chlorinating agent. Further, the possibility that there might be initially exceedingly small concentration of Cl^+ ions may also be excluded because in that case the HCl formed in the substitution reaction would immediately destroy the reactive species.

Oxidation of Alcohols with Aqueous Chlorine in Presence of Perchloric Acid

Perchloric acid functions in two ways :

(i) it suppresses the hydrolysis of chlorine, which, in turn, increases the concentration of Cl_2 and (ii) it increases the rate of enolization of carbonyl compound. That is why the reaction rates are faster in presence of perchloric acid than in absence of it. We observed that in the case of isopropyl alcohol oxidation, the percentage of monochloroacetone increases in presence of perchloric acid. This is a clear evidence that perchloric acid increases the enolization rate.

Catalytic effect of Salts

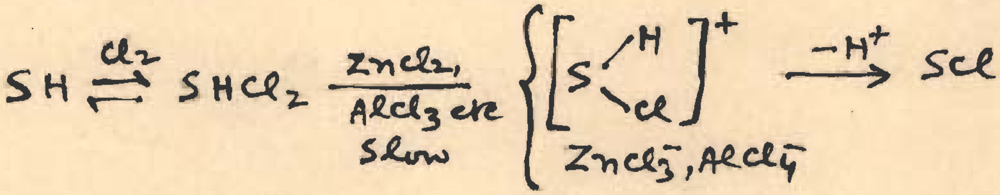
The chloride ions enhance the reaction rates because they displace the hydrolytic equilibrium of chlorine to the left. In section 2.4 it has been shown that the reaction rates are faster in presence of tri or divalent metal chlorides than in presence of monovalent metal chlorides.

$AlCl_3$, $NiCl_2$, $ZnCl_2$, $MgCl_2$ etc. for example, enhance the rate many fold. Two reaction mechanisms seem to be possible (i) these salts have tendency to hydrolyse in water :

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + HCl$$

$$MCl_2 + 2H_2O \rightleftharpoons M(OH)_2 + 2HCl$$

HCl produced by hydrolysis of salt is perhaps responsible for acceleration in rates; the acid may act in two ways : (a) it increases the concentration of molecular chlorine by suppressing the chlorine hydrolysis (b) it increases the rates of enolization. This may be one of the reasons why the reaction rates in presence of $AlCl_3$, $NiCl_2$, $ZnCl_2$, $MgCl_2$ etc. are higher than in presence of $CaCl_2$, $SrCl_2$, $BaCl_2$ etc. The acceleration in rate and the formation of trichloroacetone for the reaction of chlorine with isopropyl alcohol in presence of $ZnCl_2$ seems to be best explained in this manner. (ii) the chlorine molecule forms a complex with the substrate and then the Lewis acid, $ZnCl_2$, $AlCl_3$ etc, assist in breaking of the bond between chlorine atoms :



The rate determining step is a simultaneous nucleophilic 'push' by the substrate and an electrophilic 'pull' by the catalyst on opposite ends of the chlorine molecule, with heterolytic cleavage of Cl-Cl bond.

The $H_2PO_4^-$ and F^- ions are known to act as base (proton acceptor). The catalytic effect of these ions is perhaps due to their participation as base in the removal of H from the C-H Bond of the alkyl hypochlorite in the rate determining step :

$$R_2\text{-}CHOCl + H_2PO^-_4 \longrightarrow R_2C = O + H_3PO_4 + Cl^-$$

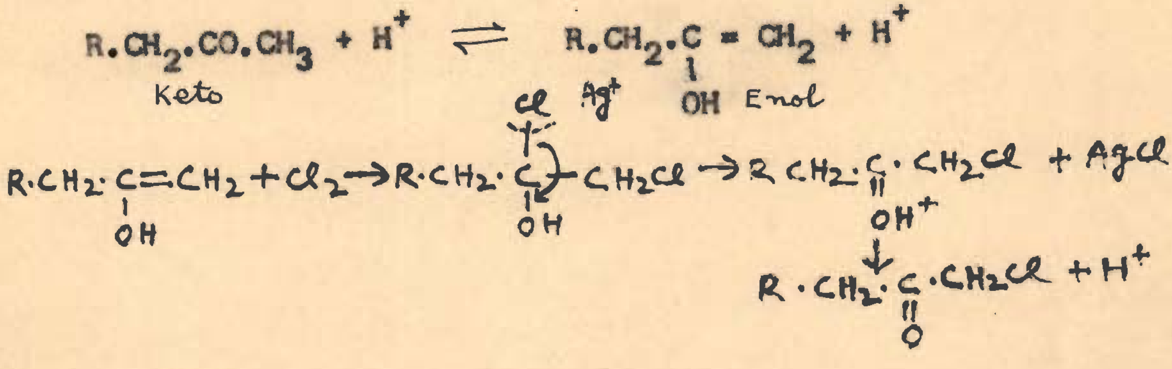
$$R_2CHOCl + F^- \longrightarrow R_2C = O + HF + Cl^-$$

De la Mare and Ridd(189) found that for relatively unreactive aromatic compound, the reaction rates are insensitive to small changes in concentration of $AgClO_4$, but we notice that for the reaction of alcohols with chlorine, the reaction rate increases with increasing concentration of silver nitrate. Arotsky and Symons(180) pointed out that there are evidences for the formation of $AgCl_2^+$ and hence the possible participation of $AgCl_2^+$ in the chlorination should be considered.

$$AgCl\ (Solid) + H_2OCl^+ \underset{}{\overset{K_2O}{\rightleftharpoons}} AgCl_2^+ + H_2O$$

$$AgCl_2^+ + ArH \xrightarrow{K_2} ArCl + AgCl\ (Solid) + H^+$$

Perhaps silver ion helps in displacing chlorine atom from the hydroxy alkyl halide :



$$\underset{\text{Keto}}{R.CH_2.CO.CH_3} + H^+ \rightleftharpoons \underset{\text{Enol}}{R.CH_2.\underset{OH}{\underset{|}{C}} = CH_2} + H^+$$

$$R\cdot CH_2\cdot \underset{OH}{\underset{|}{C}}{=}CH_2 + Cl_2 \rightarrow R\cdot CH_2\cdot \overset{Cl\ \ Ag^+}{\underset{OH}{\underset{|}{C}}} - CH_2Cl \rightarrow R\,CH_2\cdot \underset{OH^+}{\underset{\|}{C}}\cdot CH_2Cl + AgCl$$

$$\downarrow$$

$$R\cdot CH_2\cdot \underset{O}{\underset{\|}{C}}\cdot CH_2Cl + H^+$$

This is only a tentative suggestion.

The chlorination of oxidation product of methyl alcohol, formaldehyde, will be considered in more detail in the next Chapter. In the case of n-propyl, n-butyl, and iso-butyl alcohols, we have determined the orders of the reactions only, which follow the same pattern as we have seen in the case of isopropyl and sec.butyl alcohols. These alcohols also appear to follow the same mechanism.

CHAPTER 3

REACTION OF FORMALDEHYDE WITH CHLORINE IN AQUEOUS SOLUTION

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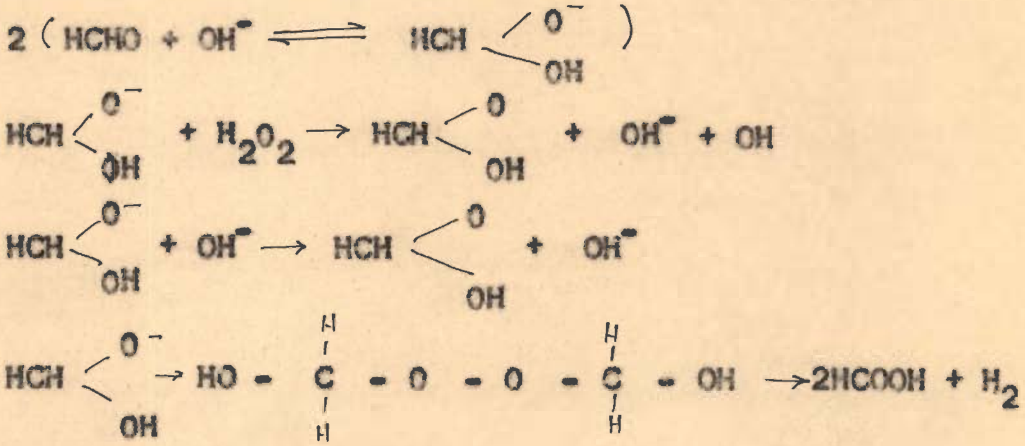
INTRODUCTION

The kinetics of oxidation of aliphatic and aromatic aldehydes by various oxidizing agents have been extensively investigated, but little information is available concerning the mechanism of their oxidation by chlorine.

Kastle and Lovenhart(316) found that the reaction between formaldehyde and hydrogen peroxide obey the second order kinetics. The product of the reaction was found to be dimethylol peroxide(317), $H_2 (HO) CO_2$. Various investigators(318 to 322) studied the reaction in more detail. Abel(322) suggested the following mechanism for the oxidation of formaldehyde by alkaline hydrogen peroxide solution :



$$2\left(HCHO + OH^- \rightleftharpoons HCH\left<{}^{O^-}_{OH}\right.\right)$$

$$HCH\left<{}^{O^-}_{OH}\right. + H_2O_2 \rightarrow HCH\left<{}^{O}_{OH}\right. + OH^- + OH$$

$$HCH\left<{}^{O^-}_{OH}\right. + OH^- \rightarrow HCH\left<{}^{O}_{OH}\right. + OH^-$$

$$HCH\left<{}^{O^-}_{OH}\right. \rightarrow HO-\overset{H}{\underset{H}{C}}-O-O-\overset{H}{\underset{H}{C}}-OH \rightarrow 2HCOOH + H_2$$

Wieland(323) put forward the view that the oxidations of aldehydes are in reality dehydrogention of aldehyde hydrate:

$$R.CH\ (OH)_2 + O \longrightarrow RCOOH + 2H^+$$

He(323) suggested the following mechanism for the oxidation of aldehydes by molecular oxygen in autoxidation :

$$R.CHO + O_2 \longrightarrow R.C(:O)\ O.OH$$

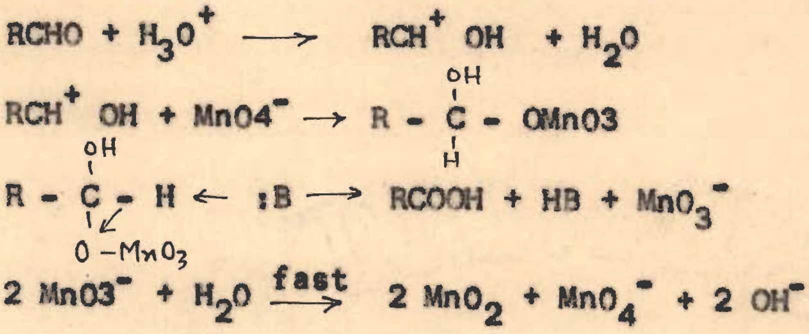
$$R.C(:O)O.OH + RCHO \longrightarrow 2\ RCOOH$$

$$R.CHO + HO.OC\ (:O)R \longrightarrow RCH(OH)OC(:O)R + 2RCOOH$$

or, $$RCH(OH)_2 + R\ CO_3H \longrightarrow 2\ RCOOH + H_2O$$

Conant and coworkers(324) studied the kinetics of oxidation of formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde and isobutyraldehyde at 80° in different media by ceric sulphate, ferricyanide, tungsticyanide and molybdicyanide.

The potassium permanganate oxidation of aldehydes were studied by several investigators(325 to 329). Wiberg and Stewart(329) observed that the rates of oxidations of eight aromatic aldehydes are proportional to the first powers of permanganate and the aldehyde concentrations. They concluded from the magnitude of kinetic isotope effect that the rate determining step involve the cleavage of aldehyde C-H Bond, and the oxygen introduced into the aldehyde was derived mainly from the oxidant. They suggested the following mechanism for acid catalysed reaction :



$$RCHO + H_3O^+ \longrightarrow RCH^+OH + H_2O$$

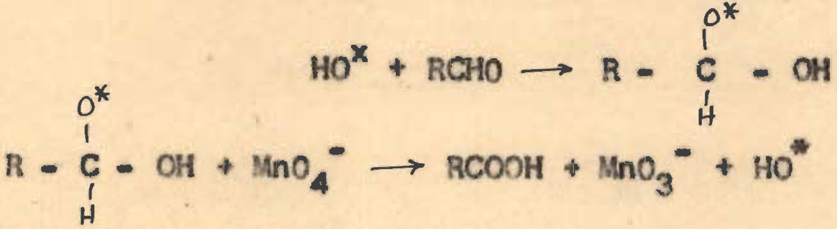
$$RCH^+OH + MnO4^- \longrightarrow R - \overset{OH}{\underset{H}{C}} - OMnO3$$

$$R - \overset{OH}{\underset{O-MnO_3}{C}} - H \leftarrow :B \longrightarrow RCOOH + HB + MnO_3^-$$

$$2\ MnO3^- + H_2O \xrightarrow{fast} 2\ MnO_2 + MnO_4^- + 2\ OH^-$$

A free radical mechanism was proposed by them for the reaction in basic solution :

Initiation: $MnO4^- + OH^- \longrightarrow MnO_4^= + OH^*$



$$HO^x + RCHO \longrightarrow R-\underset{H}{\overset{O^*}{C}}-OH$$

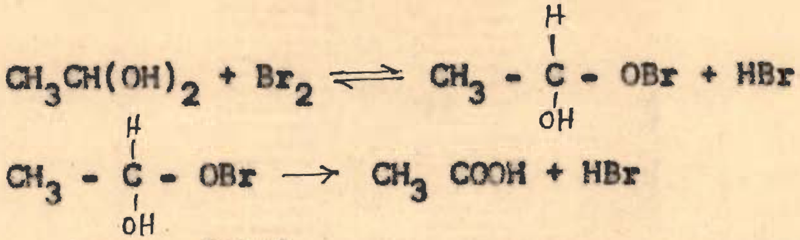
$$R-\underset{H}{\overset{O^*}{C}}-OH + MnO_4^- \longrightarrow RCOOH + MnO_3^- + HO^*$$

Termination : $2\,HO^* \longrightarrow H_2O_2$

$$H_2O_2 + MnO_4^- \longrightarrow O_2 + HMnO_4^=$$

Ladbury and Cullis(330) reviewed in detail the kinetics and mechanism of potassium permanganate oxidations. The great reactivity of potassium permanganate was reflected in its ability to follow different reaction paths, depending upon the structure of organic compound, and pH of the solution.

Bugarszky(230) found that the order of the reaction of acetaldehyde with bromine is first with respect to both the reactants. Various investigators(231,233,236,331) obtained similar results and pointed out that the rate by molecular bromine is faster than the rate by hypobromous acid. Perlmutter-Hayman and coworkers(233) supported Kaplan's(236) view, who claimed that the similarity of deuterium isotope effect ($k_H/k_D = 3.9$) in the acetaldehyde oxidation to that in ethanol oxidation by bromine was in accord with the idea(231) that these reactions have similar mechanism. Perlmutter-Hayman et al proposed the following mechanism :



$$CH_3CH(OH)_2 + Br_2 \rightleftharpoons CH_3 - \overset{H}{\underset{OH}{C}} - OBr + HBr$$

$$CH_3 - \overset{H}{\underset{OH}{C}} - OBr \longrightarrow CH_3\ COOH + HBr$$

Cox and Mc Tigue(332) proposed a hydride abstraction mechanism for number of aliphatic aldehydes.

$$R(CH)OH_2 + OH^- \overset{slow}{\rightleftharpoons} RCH\ (O^-)\ OH + H_2O$$

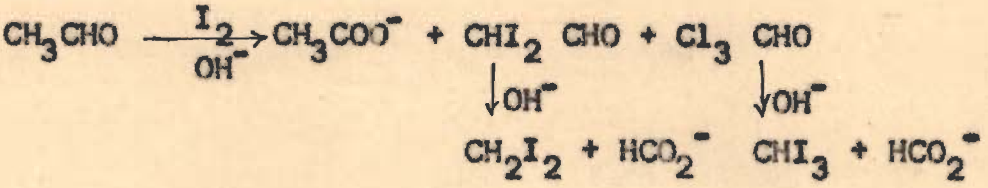
$$RCH(O^-)\ OH + Br_2 \longrightarrow RCOOH + HBr_2^-$$

$$HBr_2^- \xrightarrow{fast} H^+ + 2\ Br^-$$

Hatcher and coworkers(333) noticed that the rate of oxidation of acetaldehyde by oxygen is proportional to the aldehyde concentration and independent of oxygen concentration. Recently Norrish (334) detected the product, H_2O_2, of the reaction between formaldehyde and oxygen.

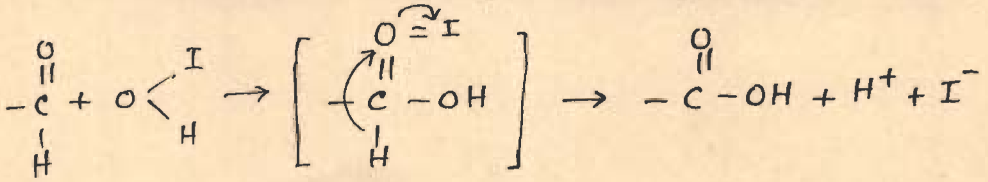
The researches of Spence and Wild(84) concludes that the reaction between chlorine and formaldehyde proceeds either by an explosion or by a slow process, preceded by an induction period. These results are in accord with the photochemical reaction studied by Krauskopf and Rollefson.(85,86)

Faull and Rollefson(259) observed that hydrogen iodide and carbon monoxide are the final products of the reaction of gaseous formaldehyde with iodine. The reactions of aldehydes with iodic acid(260) or iodine(335 to 337) have also been studied. The oxidations were found to proceed rapidly in base and competes with iodination, which is followed by hydrolytic cleavage(335,336). The rate controlling step of the iodination process is base - catalyzed enolization :



$$\begin{array}{llll} CH_3CHO \xrightarrow[OH^-]{I_2} CH_3COO^- + & CHI_2\ CHO & + & Cl_3\ CHO \\ & \downarrow OH^- & & \downarrow OH^- \\ & CH_2I_2 + HCO_2^- & & CHI_3 + HCO_2^- \end{array}$$

Cullis and Swain(336) suggested the following mechanism for the reaction of aldehyde with hypoiodous acid :



According to Bawn and Williamson(338), the uncatalyzed and the tracer metal catalyzed oxidation of acetaldehyde in solution proceeds in two well defined stages : (a) the oxidation of the aldehyde to peracetic acid, (b) the reaction of peracetic acid with acetaldehyde to give a peroxide. They further noticed that the oxidation of acetaldehyde in acetic acid solution is strongly catalyzed by small amounts of cobalt salts.

Melnikov and Rokitskaya(339) studied the kinetics of the oxidation of aldehydes by selenium dioxide and selenic acid and found that the velocity of the reaction with selenic acid decreases with increasing molecular weight, with the exception of acetaldehyde.

The kinetics of halogen addition to $\alpha\beta$ - olefinic aldehydes in acetic acid solution was studied by De la Mare and Robertson(340), who proposed the following mechanism :

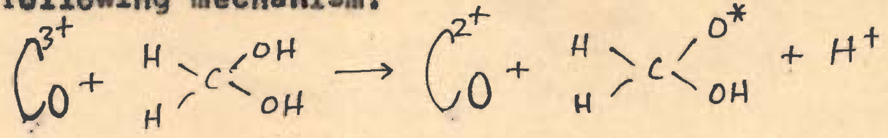
$$A + H^+ \underset{2}{\overset{1}{\rightleftharpoons}} AH^+$$

$$AH^+ + Br_2 \underset{4}{\overset{3}{\rightleftharpoons}} ABr_2 + H^+$$

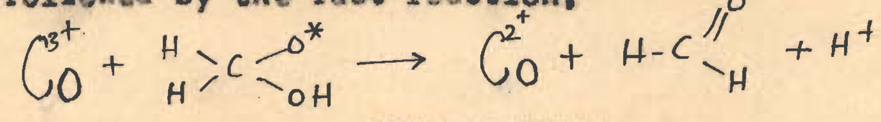
$$ABr_2 \xrightarrow{5} ABrBr$$

The reaction of aliphatic aldehydes with nitrogen dioxide was studied by many workers(341 to 343) in which different products were detected. It was found that the slow reaction between formaldehyde and NO_2 becomes explosive in the region of 180°C and this explosive reaction becomes thermal in nature. Barton(344) proposed a chain mechanism involving hydrogen abstraction for the gas phase oxidation of formaldehyde by NO_2.

Bawn and White(345) investigated the oxidation of formaldehyde by cobaltic ions, From a detailed study of the reaction, Hargreaves and Sutcliffe(346) proposed the following mechanism:



followed by the fast reaction,



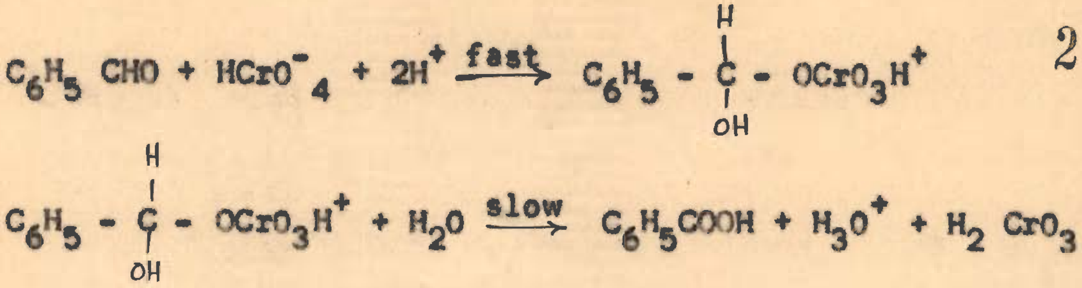
Water and coworkers(347 to 349) studied the kinetics of oxidations of propionaldehyde, n -butyraldehyde, acraldehyde and formaldehyde by manganic (111) ions and found that the rates are zero, first and first orders, respectively, with respect to tetravalent manganese, aldehyde and hydrogen ions, with the exception of HCHO, where rate of oxidation was found to be first order with respect to both the oxidant and the formaldehyde, but independent of acid concentration.

The air oxidation of aliphatic aldehydes was also studied in detail(350 to 353).

According to Wiberg and Lepse(354), the reaction between aromatic aldehydes and chromyl acetate follows the second order kinetics, showing a kinetic isotope effect and involve oxygen transfer from the oxidant to the aldehyde.

Lucchi(355 to 357) investigated the oxidation of substituted aromatic aldehydes by chromic acid in acetic acid - sulphuric acid solution. He found that generally the reactions are bimolecular, but failed to detect the active ion of chromium responsible for oxidation.

Wiberg and coworkers(358,359) reported that the rate determining step involves the cleavage of aldehyde C-H Bond in the oxidation of benzaldehyde by chromic acid, as indicated by isotope effect k_H/k_D of 4.3 at 25°C. They suggested that a mechanism which is analogous to that for the permanganate oxidation of aldehydes may be operative. Graham and Westheimer(360) found that the rate of the chromic acid oxidation of benzaldehyde in water at 80°C increases with the first power of both the concentration of benzaldehyde and acid-chromate ion, and with a more complicated function of the concentration of acid. They suggested that the reaction proceeds by way of the chromic acid ester of hydrated benzaldehyde as intermediate (similar to that of isopropyl alcohol oxidation).



$$C_6H_5CHO + HCrO_4^- + 2H^+ \xrightarrow{fast} C_6H_5-\overset{H}{\underset{OH}{C}}-OCrO_3H^+$$

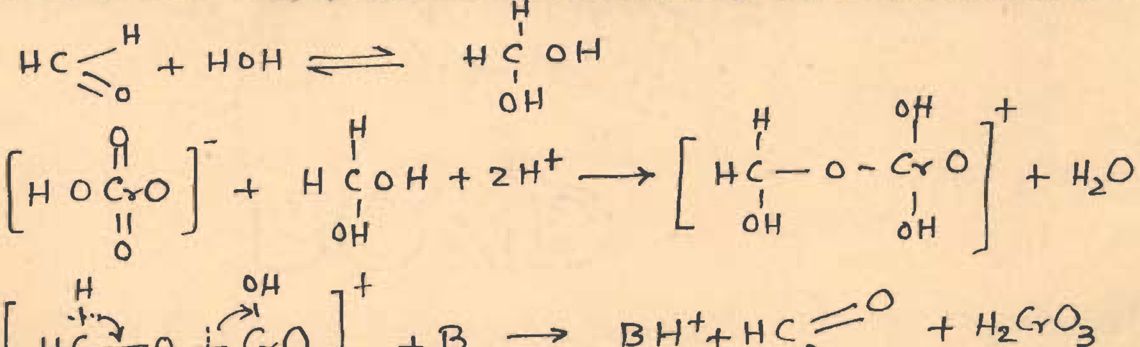
$$C_6H_5-\overset{H}{\underset{OH}{C}}-OCrO_3H^+ + H_2O \xrightarrow{slow} C_6H_5COOH + H_3O^+ + H_2CrO_3$$

$$Cr^{iv} + Cr^{iv} \xrightarrow{fast} 2Cr^{v}$$

$$Cr^{v} + C_6H_5CHO \xrightarrow{fast} C_6H_5COOH + Cr^{iii}$$

The formation of an aldehyde - chromate complex of the type AcH-$HCrO_4^-$ was detected by Klanning(361).

Chatterji and Antony(249,362) investigated the kinetics of chromic acid oxidation of acetaldehyde, n - butyraldehyde and isobutyraldehyde. The oxidation of other aldehydes by chromic acid was investigated in detail by various investigators(363 to 365). From a detailed kinetic investigation of the chromic acid oxidation of formaldehyde. Chatterji and Mukherjee(3,366) concluded that (i) the order with respect to formaldehyde, chromic acid and H^+ ions is first, first and second, at all hydrogen ion concentrations, (ii) the induction factor for the induced oxidation of manganous sulfate to manganese dioxide is 0.5; (iii) the energy of activation is 9.1 K cals and (iv) pyridine accelerates the reaction in pyridine - pyridinium ion buffers indicating a base initiated break down of the chromic acid ester. They proposed the following ester mechanism :



$$HC\overset{H}{\lessgtr}_{O} + HOH \rightleftharpoons H\overset{H}{\underset{OH}{C}}OH$$

$$\left[HO\overset{O}{\underset{O}{Cr}}O\right]^- + H\overset{H}{\underset{OH}{C}}OH + 2H^+ \longrightarrow \left[H\overset{H}{\underset{OH}{C}}-O-\overset{OH}{\underset{OH}{Cr}}O\right]^+ + H_2O$$

$$\ldots + B \longrightarrow BH^+ + HC=O + H_2CrO_3$$

A perusal of the literature reveals that the oxidation mechanisms of monohydric alcohols and aldehydes bear a formal resemblance in many cases. The aldehydes react in the form of their hydrate. The similarity of the deuterium isotope effect(10) in the aldehyde oxidations to that in alcohol oxidations is in accord with the view that perhaps these reactions have similar mechanisms; in both the cases, the rate controlling step is the rupture of C-H bond.

In the present chapter the reaction of formaldehyde with chlorine is discussed. An attempt has been made to find out if there is any similarity in the mechanisms of reactions of alcohols and aldehydes with chlorine.

SEC.3.1 ORDER OF THE REACTION

Introduction : The order of the reaction of formaldehyde with chlorine in water, in absence and in presence of perchloric acid, has been determined at constant ionic strength of 0.4. The initial rates, k_o moles litre^{-1} Sec^{-1}, have been determined graphically in all the cases. The orders with respect to chlorine, formaldehyde and hydrogen ions have been calculated by the same method as applied in the case of alcohols$^{(279)}$. The values of pseudo first order rate constants have also been calculated by using the equation

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

EXPERIMENTAL

All the chemicals used were either B.D.H. (AnalaR) or Merck (Cp.) grade and were further purified if necessary.

Since A.R.formaldehyde is not suitable for kinetic work as it contains methyl alcohol which was found to be reactive with aqueous chlorine, the fresh formaldehyde solutions were prepared for each experiment by decomposing paraformaldehyde (Merck Cp) by heating and collecting the gas in ice cold conductivity water. The concentrations of formaldehyde solutions were then estimated by iodine titration$^{(367)}$.

The progress of the reaction was studied iodometrically at 35°C. Throughout we maintained large excess concentration of formaldehyde. The results are tabulated in the following Tables.

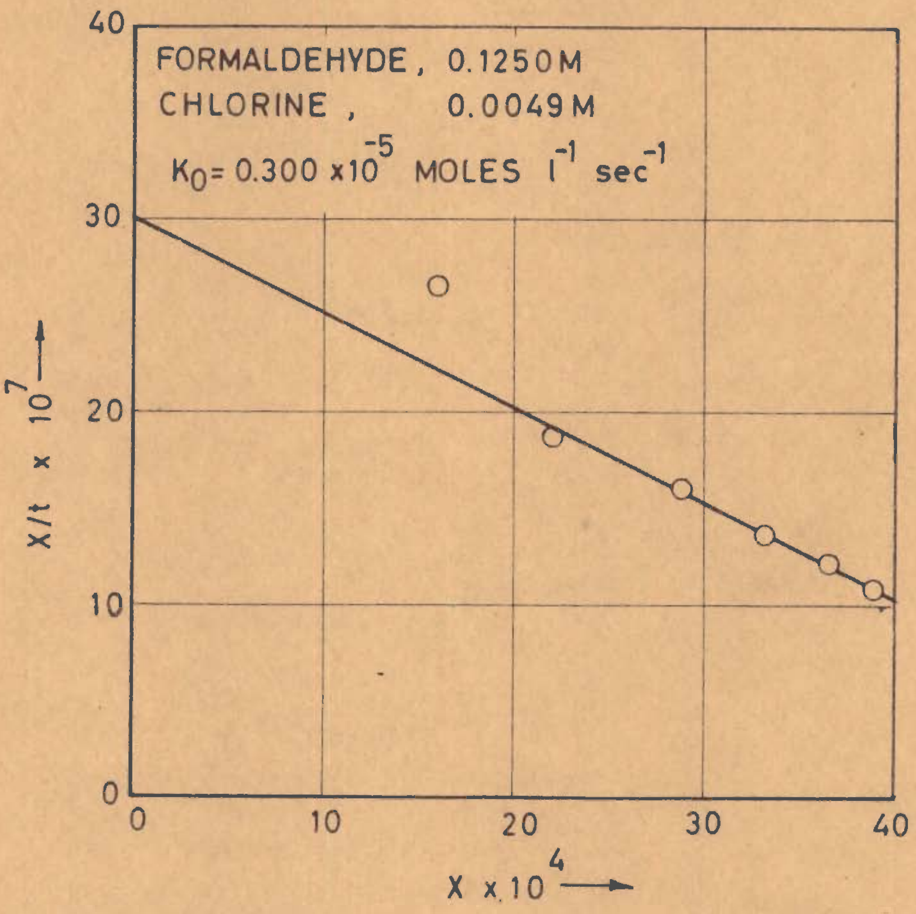


FIG. 11 _ DETERMINATION OF K_0

Table 227

Total Oxidant 0.0166M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	65	-
2	40	8.09
4	21.0	4.71
6	12.0	4.69
8	8.3	4.29
10	5.0	4.27
12	3.0	4.27

Mean $k \times 10^3$ Sec^{-1} = 4.45
$k_o \times 10^5$ = 5-30

Table 228

Total Oxidant 0.0132M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	54	-
2	35	3.61
4	27	2.89
6	20.0	2.76
8	15.5	2.60
10	12.0	2.51
12	8.3	2.60

Mean $k \times 10^3$ Sec^{-1} = 2.67
$k_o \times 10^5$ = 3.20

Table 229

Total Oxidant 0.0066M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	48.2	-
10	23.6	1.19
20	16.7	0.883
30	10.0	0.874
40	6.0	0.868
50	3.5	0.874
60	2.3	0.845

Mean $k \times 10^3$ Sec^{-1} = 0.869
$k_o \times 10^5$ = 0.700

Table 230

Total Oxidant 0.0059M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	50.2	-
10	28.4	9.50
20	19.0	0.810
30	18.8	0.814
40	7.1	0.815
50	4.4	0.812
60	2.7	0.812

Mean $k \times 10^3$ Sec^{-1} = .813
$k_o \times 10^5$ = 0.430

Table 231

Total Oxidant 0.0049M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	33.45	-
10	22.8	0.639
20	17.35	0.547
30	12.25	0.558
40	8.7	0.561
50	6.1	0.567
60	4.5	0.557

Mean $k \times 10^3$ Sec^{-1} = 0.558
$k_o \times 10^5$ = 0.300

Table 232

Formaldehyde 0.2130M
Total Oxidant 0.0045M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	26.4	0.825
20	17.4	0.760
30	11.1	0.756
40	7.1	0.753
50	4.6	0.747
60	3.0	0.742

Mean $k \times 10^3$ Sec^{-1} = 0.752
$k_o \times 10^5$ = 0.410

Table 233

Formaldehyde 0.1870M
Total Oxidant0.0045M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	27.0	0.787
20	19.0	0.687
30	12.8	0.677
40	8.4	0.683
50	5.7	0.676
60	3.9	0.668

Mean $k \times 10^3$ Sec^{-1} = 0.678
$k_o \times 10^5$ = 0.360

Table 234

Formaldehyde 0.1520M
Total Oxidant 0.0045M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	28.0	0.727
20	22.0	0.564
30	15.7	0.564
40	11.3	0.560
50	8.2	0.555
60	6.0	0.549

Mean $k \times 10^3$ Sec^{-1} = 0.558
$k_o \times 10^5$ = 0.300

Table 235

Formaldehyde 0.1320M
Total Oxidant 0.0045M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	31.8	0.525
20	24.55	0.473
30	18.6	0.470
40	13.05	0.500
50	9.8	0.495
60	7.4	0.491

Mean $k \times 10^3 \text{Sec}^{-1}$ = .486
$k_o \times 10^5$ = 0.245

Table 236

Formaldehyde 0.1150M
Total Oxidant 0.0045M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	29.2	0.657
20	24.55	0.473
30	19.5	0.443
40	15.3	0.433
50	12.2	0.422
60	8.9	0.439

Mean $k \times 10^3$ Sec^{-1} = .442
$k_o \times 10^5$ = 0.245

Table 237

Formaldehyde 0.1000M
Total Oxidant 0.0045M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	30.7	0.573
20	24.55	0.473
30	19.3	0.449
40	14.8	0.447
50	11.4	0.445
60	9.1	0.433

Mean $k \times 10^3$ Sec^{-1} = .449
$k_o \times 10^5$ =0.245

Table 238

Formaldehyde 0.0885M
Total Oxidant 0.0045M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	30.7	0.573
20	24.55	0.473
30	19.3	0.449
40	14.8	0.447
50	11.3	0.448
60	9.0	0.436

Mean $k \times 10^3$ Sec^{-1} = .451
$k_o \times 10^5$ = 0.245

Table 239

Formaldehyde 0.0634M
Total Oxidant 0.0045M

Time mts.	Thio ccs.	$kx10^3$ Sec^{-1}
0	43.3	-
10	30.5	0.584
20	24.55	0.473
30	19.3	0.449
40	14.9	0.444
50	11.4	0.445
60	8.8	0.443

Mean $kx10^3$ Sec^{-1} = .451
$k_o x10^5$ = 0.245

Formaldehyde 0.1914M
Total Oxidant 0.0060M

Table 240

Perchloric Acid 0.0500M

Time mts.	Thio ccs.	$kx10^3$ Sec^{-1}
0	22.4	-
2	18.2	1.73
4	15.5	1.53
6	13.5	1.41
8	11.3	1.42
10	9.6	1.41
12	8.1	1.41

Mean $kx10^3$ Sec^{-1} = 1.412
$k_o x10^5$ = 1.13

Table 241

Perchloric Acid 0.1000M

Time mts.	Thio ccs	$kx10^3$ sec^{-1}
0	22.4	-
2	17.7	1.96
4	15-2	1.62
6	13.5	1.41
8	11.15	1.45
10	9.7	1.39
12	8.25	1.39

Mean $kx10^3$ Sec^{-1} = 1.41
$k_o x10^5$ = 1.11

Table 242

Perchloric Acid 0.1500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	22.4	-
2	17.5	2.06
4	15.0	1.67
6	13.4	1.43
8	11.2	1.44
10	9.5	1.43
12	8.0	1.43

Mean $k \times 10^3$ Sec^{-1} = 1.43

$k_o \times 10^5$ = 1.12

Table 243

Perchloric Acid 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	22.4	-
2	17.3	2.15
4	14.9	1.70
6	13.55	1.40
8	11.3	1.42
10	9.65	1.40
12	8.1	1.41

Mean $k \times 10^3$ Sec^{-1} = 1.41

$k_o \times 10^5$ = 1.12

Table 244

Perchloric Acid 0.2500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.2	-
2	13.2	1.71
4	10.9	1.65
6	9.65	1.44
8	8.15	1.43
10	6.95	1.41
12	5.90	1.40

Mean $k \times 10^3$ Sec^{-1} = 1.42

$k_o \times 10^5$ = 1.13

Table 245

Perchloric Acid 0.2800M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.2	-
2	13.0	1.83
4	11.1	1.57
6	9.7	1.42
8	8.15	1.43
10	6.95	1.41
12	5.90	1.40

Mean $k \times 10^3$ Sec^{-1} = 1.41

$k_o \times 10^5$ = 1.12

TABLE (E)

The Fraction of Total Oxidant Present at Zero Time as Molecular Chlorine and Hypochlorous Acid in the Absence of Sodium Chloride.

$(OX)_o$,M	pH	$a_{H^+}\times10^3$	γ_{Cl^-}	B	$(B+Cl^-)$	α_o	$(1-\alpha_o)$	$(Cl_2)_o\times10^4$ M	$(HClO)_o\times10^2$ M
0.0166	2.05	8.913	0.664	0.0862	0.1004	0.8554	0.1446	24.00	1.420
0.0132	2.10	7.944	0.664	0.0967	0.1084	0.8903	0.1097	14.48	1.175
0.0066	2.25	5.624	0.664	0.1370	0.1433	0.9547	0.0453	2.990	0.6300
0.0059	2.30	5.012	0.664	0.1532	0.1589	0.9660	0.0340	2.006	0.5700
0.0049	2.35	4.467	0.664	0.1720	0.1767	0.9695	0.0305	1.494	0.4750

Table 246

Dependence of Oxidation rate of Formaldehyde on the Concentration of Chlorine at 35°C

$(HCHO) = 0.1250M$, $\mu = 0.4$

Total Oxidant $(OX)_o$, M	$k \times 10^3$ Sec^{-1}	$k_o \times 10^5$ moles lit^{-1} Sec^{-1}	$\frac{k_o}{(OX)_o} \times 10^3$ Sec^{-1}	$\frac{k_o}{(HClO)_o} \times 10^3$ Sec^{-1}	$\frac{k_o}{(Cl_2)_o} \times 10^2$ Sec^{-1}
0.0166	4.45	5.30	3.19	3.73	2.21
0.0132	2.67	3.20	2.42	2.72	2.21
.0066	0.869	0.700	1.06	1.11	2.34
.0059	0.813	0.430	0.728	0.754	2.14
.0049	0.558	0.300	0.612	0.632	2.01

Mean $\frac{k_o}{(Cl_2)_o} = 2.18 \times 10^{-2}\ Sec^{-1}$

Table 247

Rate Constants as the Function of Formaldehyde Concentration at 35°C

$(OX)_o = 0.0045M$, $\mu = 0.4$

(HCHO),M	0.0634	0.0885	0.1000	0.1150	0.1320	0.1520	0.1870	0.2130
$10^3 k$, Sec^{-1}	0.451	0.451	0.449	0.442	0.486	0.558	0.678	0.752
$10^5 k_o$, moles lit^{-1} Sec^{-1}	0.245	0.245	0.245	0.245	0.245	0.300	0.360	0.410
Order	-	0	0	0	0	1.43	0.88	1.00
$10^5 k_o/(HCHO)$	-	-	-	-	-	1.97	1.92	1.92

Table 248

Rate Constants as the Function of Perchloric Acid Concentration at 35°C

$(HCHO) = 0.1914M$, $(OX)_o = 0.0060M$, $\mu = 0.4$

$(HClO_4)$, M	0.05	0.10	0.15	0.20	0.25	0.28
$10^3 k$, Sec^{-1}	1.41	1.41	1.43	1.41	1.42	1.41
$10^5 k_o$ moles lit^{-1} Sec^{-1}	1.13	1.11	1.12	1.12	1.13	1.12
Order	-	0	0	0	0	0

Results and Discussion :

The order of the reaction has been determined by Ostwald's isolation method(279). We found that for the system :oxidant and formaldehyde, the order is first with respect chlorine, and zero with respect to formaldehyde at lower concentrations of formaldehyde (0.06 to 0.13M) and first at higher concentrations of formaldehyde (0.15 to 0.21M). Thus the total order is either first or second, depending upon the concentration of formaldehyde.

In presence of perchloric acid i.e. for the system : oxidant, formaldehyde and perchloric acid, the order with respect to hydrogen ions is zero at all hydrogen ion concentrations (0.05 to 0.28M).

As the initial stoichiometric concentration of the oxidant is increased, the pseudo first order rate or initial rate, k_o, also increases. This fact may be correlated with the hydrolytic equilibrium of chlorine,

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

It is obvious that the fraction of the total oxidant present initially as molecular chlorine increases with increasing initial stoichiometric concentration of the oxidant. Our observations thus clearly indicate that the rate of oxidation of formaldehyde is proportional to the molecular chlorine concentration. This is confirmed by calculating $k_o/[Cl_2]_o$, which has been found to be constant for all the initial stoichiometric concentration of oxidant. It is, therefore, evident that molecular chlorine is the principal effective oxidant and HOCl is playing a negligible role. We calculated the values of $[Cl_2]_o$ by the same method as explained in Sec.2.1. In Tables 246 to 248, the data obtained by applying the equations of Sec.2.1 are shown.

IDENTIFICATION OF THE PRODUCTS OF THE REACTION

SEC. 3.2 INTRODUCTION :

The products of the reactions of chlorine with formaldehyde in aqueous solution have been identified.

The main product is chloroformaldehyde, ClCHO. A portion of the chloroformaldehyde has been found to get oxidized to chloroformic acid, which has been detected by chromotropic acid reaction(368).

EXPERIMENTAL

(i) Identification of Chloroformaldehyde : In a typical experiment, chlorine, solution was taken in excess (130 cc of 0.0420M aqueous chlorine, 14cc of 0.0119M formaldehyde) and after an hour, two hours and four hours, the reaction products were precipitated as 2:4 dinitro-phenyl hydrazone derivative(285). The m.p. of all the three derivatives have been found to be 158-159°C.

A portion of the derivative was fused with metallic sodium and then tested for presence of chlorine in the derivative, which gave positive test. It is obvious that in this case the only possible chloro 2:4 dinitrophenyl hydrazone derivative is of chloroformaldehyde.

In another experiment the aqueous chlorine solution was again taken in excess (130 cc of 0.0385M aqueous chlorine and 5 cc of 0.0110M formaldehyde) and the reaction mixture was kept for two days at room temperature. It was then distilled (b.p.99°C). The distillate was found to have no smell, 2:4 dinitrophenyl -hydrazone derivative was prepared by reacting with the distillate (m.p.158-159°C).

(ii) Detection of chloroformic acid : In an experiment formaldehyde was taken in large excess (25 cc of 0.01M and 5 cc of 0.01M of aqueous chlorine) and the reaction mixture was distilled after four hours (b.p.99-100°C). The distillate was found to have no smell. It was shakened with carbon tetrachlode in a separating funnel and the carbon tetrachloride layer was separated. The solvent layer was then shakened with distilled water so that chloroformic acid might be extracted in the water layer.

In a portion of the water layer, chromotropic acid and sulphuric acid solutions were added and then heated on a water bath for 45 minutes, which gave no colour. In another portion of the water layer, magnesium metal and hydrochloric acid was added to reduce chloroformic acid to chloroformaldehyde. Chromotropic acid solution and sulphuric acid was added and the mixture was heated on a water bath for about 45 minutes, which gave a deep violet colour. This indicates the formation of chloroformic acid.

SEC. 3.3 INFLUENCE OF IONIC STRENGTH ON THE REACTION RATE

Introduction : The effect of ionic strength in the rate of the reaction of formaldehyde with chlorine in presence and in absence of perchloric acid, has been studied at 35°c in this section. The ionic strength of the solution has been varied by the addition of sodium perchlorate. The difference in the rate constants of the reaction in the presence of sodium perchlorate from that in the absence shows the effect of ionic strength. The results are recorded in the following Table.

Table 249

Formaldehyde 0.1003M
Total Oxidant 0.0044M

1. Sodium Perchlorate 0.0000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	19.7	-
10	15.6	0.534
20	14.3	0.267
30	12.3	0.262
40	10.5	0.262
50	8.8	0.269
60	7.5	0.268

Mean $k \times 10^3$ Sec^{-1} = 0.266
$k_o \times 10^5$ = 0.122

2. Sodium Perchlorate 0.1000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	19.7	-
10	16.2	0.326
20	14.45	0.258
30	13.1	0.227
40	11.45	0.226
50	9.9	0.229
60	8.8	0.224

Mean $k \times 10^3$ Sec^{-1} = 0.226
$k_o \times 10^5$ = 0.105

3. Sodium Perchlorate 0.2000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	19.7	-
10	14.85	0.472
20	13.6	0.309
30	13.0	0.231
40	11.5	0.224
50	9.9	0.229
60	8.9	0.221

Mean $k \times 10^3$ Sec^{-1} = 0.226
$k_o \times 10^5$ = 0.105

4. Sodium Perchlorate 0.3000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	19.7	-
10	14.3	0.534
20	13.2	0.334
30	12.0	0.275
40	10.2	0.274
50	8.5	0.280
60	7.3	0.275

Mean $k \times 10^3$ Sec^{-1} = 0.276
$k_o \times 10^5$ = 0.125

5. Sodium Perchlorate 0.340 M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	28.65	-
10	22.5	0.403
20	19.3	0.329
30	15.9	0.327
40	12.7	0.339
50	10.4	0.338
60	8.5	0.337

Mean $k \times 10^3 Sec^{-1}$ = 0.334
$k_o \times 10^5$ = 0.152

6. Sodium Perchlorate 0.4000M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	43.3	-
10	30.7	0.573
20	24.55	0.473
30	19.3	0.449
40	14.8	0.447
50	11.4	0.445
60	9.1	0.433

Mean $k \times 10^3$ Sec^{-1} = .449
$k_o \times 10^5$ = 0.223

Table 250

Formaldehyde 0.1000M
Total Oxidant 0.0049M
Perchloric Acid 0.1000M

1. Sodium Perchlorate 0.0000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	29.6	-
5	18.6	1.55
10	12.1	1.49
15	9.0	1.32
20	7.0	1.20
25	5.0	1.18
30	3.4	1.20

Mean $k \times 10^3$ Sec^{-1} = 1.23
$k_o \times 10^5$ = 0.740

2. Sodium Perchlorate 0.1000M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.5	-
5	10.7	1.44
10	6.8	1.48
15	5.7	1.18
20	4.3	1.12
25	3.1	1.11
30	2.2	1.12

Mean $k \times 10^3$ Sec^{-1} = 1.13
$k_o \times 10^5$ = 0.720

3. Sodium Perchlorate 0.2000M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	16.5	-
5	10.7	1.44
10	8.2	1.16
15	5.6	1.20
20	4.0	1.18
25	3.0	1.14
30	2.6	1.17

Mean $k\times10^3$ Sec^{-1} = 1.17
$k_o\times10^5$ = 0.725

4. Sodium Perchlorate 0.3000M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	29.6	-
5	19.7	1.36
10	13.9	1.26
15	9.4	1.27
20	7.3	1.17
25	5.2	1.16
30	3.9	1.13

Mean $k\times10^3$ Sec^{-1} = 1.20
$k_o\times10^5$ = 0.735

5. Sodium Perchlorate 0.4000M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	29.6	-
5	19.7	1.36
10	12.9	1.38
15	9.4	1.27
20	6.5	1.26
25	5.2	1.16
30	4.2	1.14

Mean $k\times10^3$ Sec^{-1} = 1.25
$k_o\times10^5$ = 0.742

6. Sodium Perchlorate 0.5000M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	29.6	-
5	18.9	1.49
10	12.7	1.41
15	8.7	1.36
20	6.2	1.30
25	4.1	1.32
30	2.7	1.33

Mean $k\times10^3$ Sec^{-1} = 1.34
$k_o\times10^5$ = 0.840

7. Sodium Perchlorate 0.6000M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	29.6	-
5	18.9	1.49
10	12.7	1.41
15	8.7	1.36
20	6.1	1.32
25	4.1	1.32
30	2.7	1.33
	Mean $k \times 10^3$ Sec^{-1} =	1.35
	$k_o \times 10^5$ =	0.840

Table 251

Effect of Change in Ionic Strength on the Rate of Oxidation of Formaldehyde with Chlorine at 35°C

(a) (HCHO) = 0.1003M, $(OX)_o$ = 0.0044M, $(HClO_4)$ = 0.0000M

$(NaClO_4)$, M	0.00	0.10	0.20	0.30	0.34	0.40
10^3 k Sec^{-1}	0.266	0.226	0.226	0.276	0.334	0.449
10^5 k_o moles lit^{-1}Sec^{-1}	0.122	0.105	0.105	0.125	0.152	0.223

(b) (HCHO) = 0.1000M, $(HClO_4)$ = 0.1000M, $(OX)_o$ = 0.0049M

$(NaClO_4)$, M	0.00	0.10	0.20	0.30	0.40	0.50	0.60
10^3k, Sec^{-1}	1.23	1.13	1.17	1.20	1.25	1.34	0.840
$10^5$$k_o$ moles lit^{-1}Sec^{-1}	0.740	0.725	0.725	0.735	0.742	0.840	0.840

Results and Discussion :

The effect of adding different concentrations of sodium perchlorate solution on the rate of reaction of formaldehyde with chlorine has been investigated at 35°C. The data given in Table 251 reveals that in absence of perchloric acid, there is no significant influence of ionic strength on the reaction rate upto $\mu = 0.30$, but the rate increases with ionic strength from $\mu = 0.34$ to 0.40. In presence of perchloric acid also the effect of variation of ionic strength on reaction rate is insignificant upto $\mu = 0.4$, but the rate increases with ionic strength from $\mu = 0.5$ to 0.6.

The observed increase in rate may be due to Salt effect(369). Perhaps the higher concentrations of sodium perchlorate alter the factor $\frac{\gamma_{HOCl} \cdot \gamma_{Cl^-} \gamma_{H^+}}{\gamma_{Cl_2}}$ of the hydrolysis equilibrium constant,

$$[Cl_2] = \frac{1}{K_h} [HOCl]\,[H^+]\,[Cl^-]\,\frac{\gamma_{HOCl} \cdot \gamma_{Cl^-} \cdot \gamma_{H^+}}{\gamma_{Cl_2}}$$

This results in the increase in concentration of Cl_2, which in turn enhances the rate.

SEC. 3.4 EFFECT OF SOME INORGANIC SALTS

Introduction : In this section the formaldehyde - chlorine reaction has been studied in presence of small quantities of inorganic salts at constant ionic strength of 0.4 at 35°C. This study was undertaken in aneffort to find out the difference in the behaviour of metallic salts in the reactions of alcohols and aldehyde with aqueous chlorine.

The difference of the rate inpresence of the salt from that in absence of the salt shows the effect of the used.

EXPERIMENTAL

All the chemicals used were of Merck (C.p) or B.D.H. (AnalaR) grade and were further purified, if necessary. Formaldehyde was prepared by decomposing paraformaldehyde. Generally 0.05M concentration of salts were used. Those salts have been avoided which affect the iodometric titrations.

Table 252

Temp.35°C

Formaldehyde 0.1250M
Total Oxidant 0.0049M
μ= 0.4

1. No Catalyst

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	33.45	-
10	22.8	0.639
20	17.35	0.547
30	12.25	0.558
40	8.7	0.561
50	6.1	0.567
60	4.5	0.557

Mean $k \times 10^3$ Sec^{-1}= 0.558
$k_o \times 10^5$ = 0.300

2. Lithium Chloride 0.500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	31.6	-
5	22.0	1.21
10	17.0	1.03
15	12.4	1.04
20	9.5	1.00
25	7.2	0.986
30	5.2	1.00

Mean $k \times 10^3$ Sec^{-1} = 1.01
$k_o \times 10^5$ = 0.560

3. Sodium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	14.0	-
5	9.8	1.19
10	6.4	1.30
15	4.3	1.31
20	2.6	1.40
25	1.9	1.33
30	-	

Mean $k \times 10^3$ Sec^{-1} = 1.31
$k_o \times 10^5$ = 0.660

4. Potassium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	14.0	-
5	8.0	1.86
10	4.5	1.89
15	1.9	2.11
20		
25		
30		

Mean $k \times 10^3$ Sec^{-1} = 1.95
$k_o \times 10^5$ = 0.860

5. Barium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.0	-
10	7.6	1.24
20	3.5	1.27
30	1.6	1.28
40	0.75	1.27
50	-	
60	-	

Mean $k \times 10^3$ Sec^{-1} = 1.26

$k_o \times 10^5$ = 0.665

6. Strontium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.0	-
10	9.2	0.922
20	4.5	0.969
30	2.9	0.949
40	1.7	0.934
50	1.0	0.924
60	-	

Mean $k \times 10^3$ Sec^{-1} = 0.940

$k_o \times 10^5$ = 0.650

7. Calcium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	20.8	-
5	14.2	1.27
10	9.6	1.29
15	6.6	1.27
20	4.5	1.28
25	3.1	1.27
30	2.0	1.30

Mean $k \times 10^3$ Sec^{-1} = 1.28

$k_o \times 10^5$ = 0.665

8. Nickel Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	14.0	-
5	8.4	1.70
10	4.4	1.93
15	2.5	1.91
20	1.4	1.92
25	0.3	2.00
30		

Mean $k \times 10^3$ Sec^{-1} = 1.89

$k_o \times 10^5$ = 0.970

9. Manganese Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	20.8	-
5	14.3	1.25
10	10.2	1.22
15	6.95	1.22
20	4.8	1.22
25	3.35	1.22
30	2.3	1.22

Mean $k \times 10^3$ Sec^{-1} = 1.22

$k_o \times 10^5$ = 0.620

10. Zinc Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	18.0	-
2	16.3	0.827
4	14.7	0.844
6	13.3	0.840
8	12.0	0.845
10	10.9	0.836
12	9.8	0.845

Mean $k \times 10^3$ Sec^{-1} = 0.840

$k_o \times 10^5$ = 0.405

11. Magnesium Chloride 0.0500M

Time mts.	Thio ccs	$k \times 10^3$ Sec^{-1}
0	12.9	-
5	8.5	1.39
10	5.6	1.39
15	3.7	1.39
20	2.4	1.40
25	1.6	1.39
30	1.0	1.37

Mean $k \times 10^3$ Sec^{-1} = 1.39

$k_o \times 10^5$ = 0.810

12. Aluminium Chloride 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	27.7	-
5	13.1	2.50
10	6.3	2.47
15	3.1	2.43
20	1.4	2.49
25	-	
30	-	

Mean $k \times 10^3$ Sec^{-1} = 2.47

$k_o \times 10^5$ = 1.78

13. Disodium Hydrogen Phosphate 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	11.8	-
10	8.3	0.586
20	5.75	0.599
30	4.1	0.588
40	2.9	0.585
50	2.0	0.592
60	1.4	0.592

Mean $k \times 10^3$ Sec^{-1} = 0.590

$k_o \times 10^5$ = 0.340

14. Beryllium Sulphate 0.0500M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	14.5	-
10	13.6	1.07
20	12.75	1.07
30	12.0	1.05
40	11.2	1.08
50	10.5	1.08
60	9.8	1.09

Mean $k \times 10^4$ Sec^{-1} = 1.07

$k_o \times 10^5$ = 0.052

15. Sodium Fluoride 0.1500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	22.6	-
5	16.8	0.989
10	12.6	0.974
15	9.5	0.963
20	7.2	0.953
25	5.3	0.967
30	4.1	0.948

Mean $k \times 10^3$ Sec^{-1} = 0.961

$k_o \times 10^5$ = 0.500

16. Silver Nitrate 0.0500M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	24.3	-
5	16.1	1.37
10	11.5	1.25
15	7.9	1.25
20	5.4	1.25
25	3.8	1.24
30	2.8	1.20

Mean $k \times 10^3$ Sec^{-1} = 1.24

$k_o \times 10^5$ = 0.840

Table 253

Rate Constants for the Reaction of Formaldehyde with Chlorine in the Presence of Different Salts at 35°C

$(HCHO) = 0.1250M$, $(OX)_o = 0.0049M$, $\mu = 0.4$

Salt added,	M	$k \times 10^3$ Sec^{-1}	$k_o \times 10^5$ moles lit^{-1} Sec^{-1}	$\frac{k_o \times 10^5}{(HCHO)}$
-		0.558	0.300	2.40
LiCl	0.05	1.01	.560	4.48
NaCl	.05	1.31	.660	5.28
KCl	.05	1.95	.860	6.88
$BaCl_2$	.05	1.26	.665	5.32
$SrCl_2$	.05	0.940	.650	5.20
$CaCl_2$	.05	1.28	.665	5.32
$NiCl_2$	.05	1.89	.970	7.76
$MnCl_2$	.05	1.22	.620	4.96
$ZnCl_2$	.05	0.840	.405	3.24
$MgCl_2$	.05	1.39	.810	6.48
$AlCl_3$	.05	2.47	1.78	14.2
Na_2HPO_4	.05	0.590	.340	2.72
$BeSO_4$	.05	0.107	.052	0.416
NaF	.15	0.961	.500	4.00
$AgNO_3$	.05	1.24	.840	6.72

Results and Discussion :

An examination of the data reveals that the pseudo first order rate constant for each aliquot portion titrated during a run is unaltered within experimental error, for all the runs. To calculate the pseudo first order constant from the integrated rate expression, it is necessary to evaluate the initial stoichiometric concentration of chlorine. This was accomplished by extrapolation of log (OX) to zero time. We calculated the initial rates as well for all the runs. Comparison of either initial rates or pseudo first order rate constants for various runs indicates that chloride ion, in general, enhances the rate. We kept the concentrations of the salts as equal to 0.05M with a view to find out if there is any correlation between reaction rate and ionic radii or charge density of the cations. In presence of divalent metal chlorides, the rate follow the order :

$$NiCl_2 > MgCl_2 > CaCl_2 \geqslant BaCl_2 > SrCl_2 > MnCl_2 > ZnCl_2$$

and the ionic radii of cations follow the order

$$Mi^{++} < Mg^{++} < Ca^{++} < Ba^{++} < Sr^{++}$$

However, the transition metals (That is, 3d structure) do not seem to obey above correlation. In presence of monovalent metal chlorides, the rate follow the order

$$KCl > NaCl > LiCl$$

whereas the ionic radii follow the order

$$Li^{+} < Na^{+} < K^{+}$$

The maximum rate has been found with $AlCl_3$.

$AgNO_3$, NaF, HPO_4^{-} enhances whereas $BeSO_4$ inhibits the rate.

The significance of these results will be considered in the General Discussion.

SEC. 3.5 ACTIVATION PARAMETERS

Introduction : A general study of the temperature Coefficient of the reaction of formaldehyde with chlorine at constant ionic strength of 0.4 has been made. The velocities have been measured at 25°, 35°, 45° and 55°C. The initial rates, ko moles lit.^{-1} Sec^{-1}, and the activation parameters have been calculated. The thermostat was controlled within ± 0.05°C. The results are shown in Table 266.

Table 254

Temp.25°

Total Oxidant 0.0059M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	10.5	-
10	8.9	2.75
20	7.75	2.53
30	6.6	2.58
40	5.75	2.51
50	4.90	2.54
60	4.2	2.55

Mean $k\times10^4$ Sec^{-1} = 2.54
$k_o\times10^5$ = 0.122

Table 255

Temp.35°

Total Oxidant 0.0059M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	50.2	-
10	28.4	9.50
20	19.0	8.10
30	18.8	8.14
40	7.1	8.15
50	4.4	8.12
60	2.7	8.12

Mean $k\times10^4$ Sec^{-1} = 8.13
$k_o\times10^5$ = 0.430

Table 256

Temp.45°

Total Oxidant 0.0059M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	16.6	-
2	12.9	21.0
4	10.3	19.9
6	8.3	19.2
8	6.70	18.8
10	5.40	18.7
12	4.35	18.7

Mean $k\times10^4$ Sec^{-1} = 19.1
$k_o\times10^5$ = 1.03

Table 257

Temp.55°

Total Oxidant 0.0059M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	16.65	-
2	10.2	4.08
4	6.6	3.85
6	4.1	3.89
8	2.8	3.72
10	1.8	3.72
12	1.20	3.65

Mean $k\times10^3$ Sec^{-1} = 3.77
$k_o\times10^5$ = 2.05

Table 258

Temp.25°
Total Oxidant 0.0049M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	20.4	-
10	17.25	2.79
20	16.3	1.87
30	14.55	1.88
40	13.1	1.84
50	11.8	1.82
60	10.5	1.84

Mean $k\times10^4$ Sec^{-1} = 1.85
$k_o\times10^5$ = 0.085

Table 259

Temp. 35°
Total Oxidant 0.0049M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	33.45	-
10	22.8	6.39
20	17.35	5.47
30	12.25	5.58
40	8.7	5.61
50	6.1	5.67
60	4.5	5.57

Mean $k\times10^4$ Sec^{-1} = 5.58
$k_o\times10^5$ = 0.300

Table 260

Temp.45°
Total Oxidant 0.0049M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	22.55	-
2	19.0	1.43
4	17.0	1.18
6	14.7	1.19
8	12.6	1.21
10	10.7	1.24
12	9.2	1.24

Mean $k\times10^3$ Sec^{-1} = 1.21
$k_o\times10^5$ = 0.710

Table 261

Temp.55°
Total Oxidant 0.0049M
Formaldehyde 0.1250M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	22.55	-
2	14.7	3.57
4	12.0	2.63
6	9.2	2.48
8	6.7	2.53
10	4.9	2.55
12	3.5	2.58

Mean $k\times10^3$ Sec^{-1} = 2.55
$k_o\times10^5$ = 1.53

Table 262

Temp.25°

Perchloric Acid	0.1000M
Formaldehyde	0.1250M
Total Oxidant	0.0049M

Time mts.	Thio ccs	$k\times10^4$ Sec^{-1}
0	20.4	-
10	14.6	5.57
20	12.3	4.22
30	9.5	4.25
40	7.4	4.23
50	5.7	4.25
60	4.6	4.14

Mean $k\times10^4$ Sec^{-1} = 4.22

$k_o\times10^5$ = 0.230

Table 263

Temp.35°

Perchloric Acid	0.1000M
Formaldehyde	0.1250M
Total Oxidant	0.0049M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	29.6	-
5	18.9	1.49
10	12.7	1.41
15	8.7	1.36
20	6.2	1.30
25	4.1	1.32
30	2.7	1.33

Mean $k\times10^3$ Sec^{-1} = 1.34

$k_o\times10^5$ = 0.800

Table 264

Temp.45°

Perchloric Acid	0.1000M
Formaldehyde	0.1250M
Total Oxidant	0.0049M

Time mts.	Thio ccs.	$k\times10^3$ Sec^{-1}
0	15.25	-
2	9.5	3.94
4	6.8	3.37
6	4.85	3.18
8	3.25	3.25
10	2.15	3.27
12	1.55	3.18

Mean $k\times10^3$ Sec^{-1}=3.25

$k_o\times10^5$ =1.90

Table 265

Temp.55°

Perchloric Acid	0.1000M
Formaldehyde	0.1250M
Total Oxidant	0.0049M

Time mts.	Thio ccs	$k\times10^3$ Sec^{-1}
0	25.0	-
2	10.0	7.63
4	5.4	6.38
6	2.4	6.51
8	1.1	6.50
10	0.6	6.22
12	0.3	6.14

Mean $k\times10^3$ Sec^{-1} = 6.35

$k_o\times10^5$ = 4.05

Table 266

Rate Constants and Thermodynamic Activation Parameters for the Reaction of Formaldehyde with Chlorine Under Different conditions, $\mu = 0.4$

Conc.	Temp. °C	$10^5 k_o$ moles lit^{-1} Sec^{-1}	Temp. Coeff.	$10^5 k_{o\,int}$ moles lit^{-1} Sec^{-1}	E_{Arr} KCals	A, moles lit^{-1} Sec^{-1}	ΔH KCals	−ΔS e.u	ΔG KCals	
a	25°	0.122		0.136						a-(Aldehyde)= 0.1250M, $(OX)_o$=0.0059M
a	35°	0.430	3.52	0.370	18.45±.07	5.41×10^7	17.58±.07	26.4	25.4	
a	45°	1.03	2.39	0.939						
a	55°	2.05	1.99	2.27						
b	25°	0.085		0.091						b-(Aldehyde)= 0.1250M, $(OX)_o$=0.0049M
b	35°	0.300	3.53	0.255	18.57±.06	6.04×10^7	17.94±.06	25.9	25.7	
b	45°	0.710	2.37	0.707						
b	55°	1.53	2.15	1.63						
c	25°	0.230		0.235						c-(Aldehyde)= 0.1250M, $(OX)_o$=0.0049M $(HClO_4)$ = 0.1000M
c	35°	0.800	3.48	0.654	18.39±.07	8.41×10^7	17.82±.07	24.5	25.1	
c	45°	1.90	2.36	1.66						
c	55°	4.05	2.13	4.10						

Results and Discussion :

In Table 266 the values of initial rate, k_o, at different temperatures together with the values of K_{int}, temperature coefficient and various activation parameters with their standard deviation are given. All these values have been calculated by the method already explained in Sec.2.7.

The temperature coefficient, k_{35^o}/k_{25^o}, of the reaction has been found to be 3.52, which corresponds well with the value for pseudo unimolecular reaction. The results further support the accuracy in the determination of order of reaction.

The energy of activation, in the absence of perchloric acid, has been found to be of the order of 18.5 kcals and the Arrhenius frequency factor, A moles $litre^{-1}$ Sec^{-1}, is of the order of 10^7. The value of energy of activation is lower than that observed for primary alcohols but greater than that observed for secondary alcohols. Chatterji and Mukherjee(366) found that for chromic acid oxidation of formaldehyde, the energy of activation is about 9.1 Kcals, which is lower than that observed for chlorine oxidation.

The entropy of activation has been found to be of the order of 26 Cals/°C, which is again, higher than for primary alcohols but lower than that for secondary alcohols.

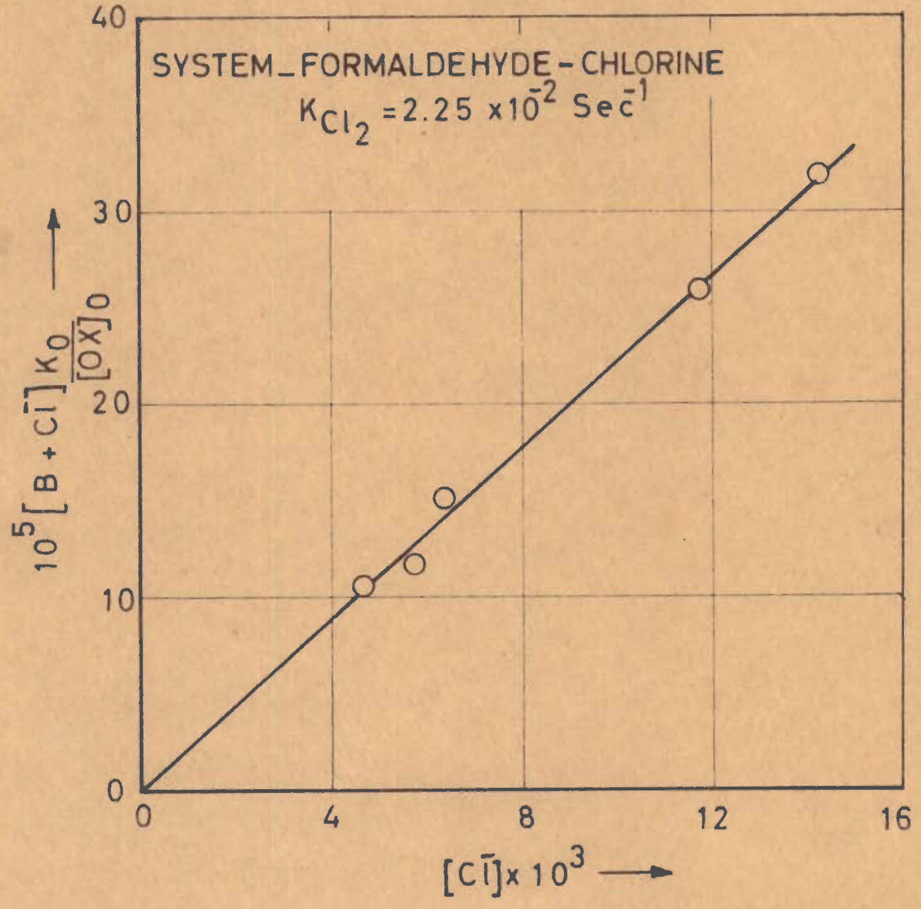


FIG.12_ GRAPHICAL CALCULATION OF K_{Cl_2} AND K_{HOCl}

GENERAL DISCUSSION

The reaction of chlorine with formaldehyde has also been found to be very complex, because both chlorination and oxidation takes place. We tried to arrive at the conclusions by considering mainly k_o values, which we have calculated throughout in this case.

In Section 3.1, it has been shown that molecular chlorine is the principal effective species and HOCl plays a negligible role in this reaction. In Fig.12, the plot of $\left\{B + (Cl^-)\right\} \dfrac{k_o}{(OX)_o}$ versus (Cl^-) is shown. The fact that the straight line passes through the origin shows that k_{HOCl} is almost zero. From the slope, k_{Cl_2} has been found to be 2.25×10^{-2} Sec^{-1} and the mean value of $k_{Cl_2}\left(= \dfrac{k_o}{(Cl_2)_o}\right)$ has been found to be 2.18×10^{-2} Sec^{-1}. These values agree very well. It can be concluded that molecular chlorine is the main reactive species in chlorine water.

The present investigation provides sufficient data which contribute towards an understanding of the mechanism of the reaction of formaldehyde with aqueous chlorine. The main results achieved in this study are :

(A) The reaction kinetics follow the equation

$$\frac{-d(Cl_2)}{dt} = k_{obs}\,(Cl_2),$$ at lower concentrations of HCHO

$$\frac{-d(Cl_2)}{dt} = k'_{obs}\,(Cl_2)\,(HCHO),$$ at higher concentrations of HCHO.

$$\frac{-d(Cl_2)}{dt} = k''_{obs}\,(Cl_2)\,(HCHO)$$

in presence of perchloric acid, when concentration of formaldehyde is high.

(B) The products of the reaction are chloroformaldehyde, ClCHO, and chloroformic acid, ClCOOH.

(C) There is no significant influence of ionic strength on the reaction rate in absence of perchloric acid upto μ=0.30, but the rate increases with ionic strength from μ=0.34 to 0.40. In presence of perchloric acid also, the effect of variation of ionic strength is insignificant upto μ= 0.4, but the rate increases with ionic strength from μ= 0.5 to 0.6.

(D) Chloride ion enhances the reaction rate but the acceleration in presence of chloride ion is less than that observed in the case of monohydric alcohols.

(E) Silver nitrate and fluoride ion also accelerate the reaction rate.

(F) The temperature coefficient, energy of activation and entropy of activation in absence of perchloric acid are 3.52, 18.5 Kcals and 26 e.u., respectively, and in presence of perchloric acid the temperature coefficient, energy of activation and entropy of activation are respectively 3.48, 18.4 Kcals. and 24.5 e.u. This indicates that perchloric acid plays a minor role in this reaction.

It may be mentioned here that there is a dissimilarity in the observed kinetics of reactions of formaldehyde and monohydric alcohols with chlorine.

While studying the kinetics of chlorination of phenol and anisole, De la Mare and coworkers(121) found that the chlorination rate is zero order with respect to the organic compound substituted and first order with respect to HOCl. Schilov(122) criticized their explanation and argued that the rate controlling step of these reactions is production of free Cl_2 from HOCl and traces of Cl^- ion. The reaction of chlorine with formaldehyde has been found to follow the above pattern. This suggests that chlorination is the main reaction and the oxidation follows, in the case of formaldehyde.

West and Rollefson(68) noticed that the photochemical reaction of chlorine with formic acid is a chain reaction, which proceeds partially through chloroformic acid to the final products, CO_2 and HCl :

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$

$$Cl + HCOOH \longrightarrow COOH + HCl$$

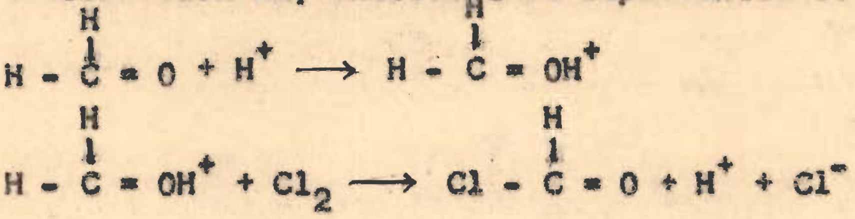
$$COOH \longrightarrow CO + H$$

$$COOH + Cl_2 \longrightarrow ClCOOH + Cl$$

$$H + Cl_2 \longrightarrow HCl + Cl$$

$$ClCOOH \longrightarrow CO_2 + HCl$$

As we have already pointed out ih the previous chapter, the chlorination of carbonyl compounds follow through enolization, but formaldehyde cannot form enol of normal type. Even then it is easily chlorinated to chloroformaldehyde. When looking for the mechanism of chlorination of formaldehyde, it should be taken into consideration that the rate controlling step is independent of formaldehyde concentration. Thus the mechanism of chlorination may therefore be represented as :



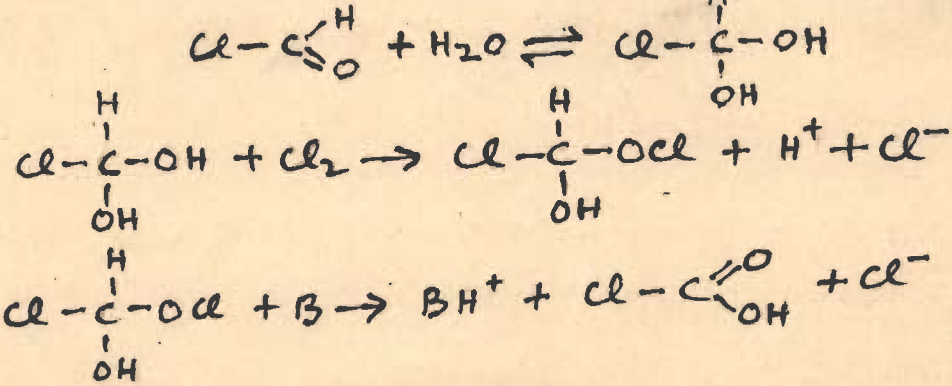
$$H-\overset{H}{\overset{|}{C}}=O + H^{+} \longrightarrow H-\overset{H}{\overset{|}{C}}=OH^{+} \tag{i}$$

$$H-\overset{H}{\overset{|}{C}}=OH^{+} + Cl_2 \longrightarrow Cl-\overset{H}{\overset{|}{C}}=O + H^{+} + Cl^{-} \tag{ii}$$

(The H^+ ions formed in step (ii) appear to be utilized in step (i)

The influence of adding the proton to the carbonyl group is to increase its attraction for electrons and hence makes it easy for the hydrogen to leave as proton.

We observed that a small percentage of Chloroformaldehyde gets oxidized to chloroformic acid. The kinetic studies have shown that the reactions of formaldehyde are typically those of an alcohol. Bieber and Trümpler(370) demonstrated that aqueous formaldehyde solution in concentrations less than 1M consist almost entirely(99.99%) of $CH_2(OH)_2$. With all the reagents as yet examined, the isotope molecule, $CD_2(OH)_2$, was found to oxidize more slowly than does $CH_2(OH)_2$(221). The reaction mechanism for the oxidation of chloroformaldehyde may thus be represented as



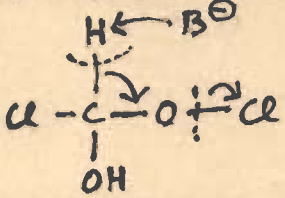
$$Cl-C{\scriptstyle\begin{matrix}H\\ =O\end{matrix}} + H_2O \rightleftharpoons Cl-\overset{H}{\underset{OH}{C}}-OH \tag{iii}$$

$$Cl-\overset{H}{\underset{OH}{C}}-OH + Cl_2 \rightarrow Cl-\overset{H}{\underset{OH}{C}}-OCl + H^{+} + Cl^{-} \tag{iv}$$

$$Cl-\overset{H}{\underset{OH}{C}}-OCl + B \rightarrow BH^{+} + Cl-C{\scriptstyle\begin{matrix}=O\\ OH\end{matrix}} + Cl^{-} \tag{v}$$

(where B is a base, e.g. water).

The mechanism of electron movement in the elimination process (v) may be represented by



in which the C-H, C-O and O-Cl bonds involve simultaneously.

This type of reaction mechanism bears a formal resemblance with the mechanism of chromic acid oxidation of formaldehyde, suggested by Chatterji and Mukherjee$^{(2)}$.

Although order with respect to perchloric acid has been found to be zero at all concentrations, the rate constants appear to be slightly higher than in the absence of perchloric acid. The role of perchloric acid is perhaps the addition of proton to the carbonyl group as proposed in step (i).

The metal chlorides enhance the reaction rate, but the magnitude of acceleration is not so high as observed in the case of reactions of chlorine with monohydric alcohols. We suggested two alternative mechanisms for the catalysing action of chloride in the previous chapter. The hydrolysis view appears to be more reasonable because formaldehyde cannot form enol of normal type. That is why the rates in presence of di- and trivalent metal chlorides for formaldehyde reaction are not so high as observed for monohydric alcohols.

The role of silver nitrate and fluoride ions appears to be similar to that already mentioned in the previous chapter.

CHAPTER 4

EFFECT OF STRUCTURE ON REACTIVITY

" The Reactions of Chlorine with Monohydric Aliphatic Alcohols in Aqueous Solution : Relative Activation Parameters "

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SEC. 4.1 EFFECT OF STRUCTURE OF ORGANIC MOLECULE ON THE REACTION RATE

Introduction : It is now well known for several reactions that the introduction of substituents into the parent molecule produces definite changes in the reaction velocity, which can frequently be correlated with the electronic properties of the substituent group; a substituent alters the availability of electrons at the seat of the reaction. Such studies have been made in the oxidation of glycols by chromic acid(40), lead tetracetate(371) and periodic acid(372 to 374); oxidation of substituted toluenes(280) and substituted benzaldehydes(375) by potassium permanganate; oxidation of olefines by perbenzoic acid(376), oxidation of substituted benzaldehydes(355 to 357), aliphatic monohydric alcohols(249,377) and aliphatic aldehydes(249) by chromic acid.

An idea of the properties of activated complex is essential for knowing the effect of substituent in reactivity. The activated complex is to be regarded as an ordinary molecule possessing all the usual thermodynamic properties. The free energy, heat, and entropy of activation is related to the potential energy and probability changes(378).

Price and Hammett(379,380) and Fitzpatrick and Gettler(381) have studied the formation of semicarbazones and oximes of several carbonyl compounds. They calculated the relative entropies, enthalpies and free energies of activation related to that of acetone by using the following equations :

$$\Delta S^{\ddagger} - \Delta S_s^{\ddagger} = \frac{\partial}{\partial T} (RT \ln k/k_s) \text{ .... (i)}$$

$$\Delta H^{\ddagger} - \Delta H_s^{\ddagger} = RT^2 \frac{\partial}{\partial T} (\ln \frac{k}{k_s}) \text{ ....(ii)}$$

$$\Delta G^{\ddagger} - \Delta G_s^{\ddagger} = - RT \ln \frac{k}{k_s} \text{ ....(iii)}$$

In all these equations symbols with subscript s refer to the standard substance, those without subscript to the carbonyl compound in question.

Hammett(382,383) noticed that a linear relationship of the form

$$\log k - \log k_s = \rho\sigma$$

holds for many reactions involving side chains of benzene derivatives; here ρ is a constant depending on the reaction series, σ is a constant depending on the substituents, and k and k_s are the rate constants of the substituted and unsubstituted reactants. This equation had been tested for a large number of aromatic reactions.

In this Chapter the relative thermodynamic activation parameters for the reactions of aliphatic monohydric alcohols with aqueous chlorine in absence and in presence of perchloric acid, relative to that of methyl alcohol, bave been calculated. An attempt has been made to establish a correlation between the stfucture of organic molecule and reaction rate.

EXPERIMENTAL

All the chemicals were either Merck (C.P) or B.D.H (AnalaR) grade.

The kinetics of the reactions of methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl and sec.butyl alcohols with aqueous chlorine in absence and in presence of perchloric acid at various concentrations of the reactants have been studied at 25° and 35°C according to the method explained in Sec.2.1.

The initial rates, k_0 moles lit^{-1} sec^{-1}, have been calculated from the plots of x/t versus x by extrapolating to $x = 0$.

The relative thermodynamic activation parameters have been calculated by using the equations(384)

$$\Delta\Delta G^{\ddagger} = -2.303RT \log (k/k_s)$$

$$\Delta\Delta H^{\ddagger} = -2.303R \left[\frac{\log (k/k_s)_{T_2} - \log (k/k_s)_{T_1}}{1/T_2 - 1/T_1} \right]$$

$$\Delta\Delta S^{\ddagger} = \frac{2.303\, R \left[T_2 \log (k/k_s)_{T_2} - T_1 \log (k/k_s)_{T_1} \right]}{T_2 - T_1}$$

These equations have been obtained from the equations (i) to (iii). A summary of the data is given in Tables 322,323.

Table 267

Temp.25°C

Total Oxidant 0.0075M
IsoPropyl Alcohol 0.1333M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	23.8	-
10	22.0	1.31
20	20.3	1.33
30	18.8	1.31
40	17.35	1.32
50	16.05	1.31
60	14.9	1.30

Mean $k \times 10^4$ Sec^{-1} = 1.31
$k_o \times 10^6$ = 1.34

Table 268

Temp.35°C

Total Oxidant 0.0075M
IsoPropyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	30.0	-
10	23.5	4.07
20	18.5	4.03
30	14.6	4.00
40	11.5	3.99
50	9.0	4.01
60	7.1	4.00

Mean $k \times 10^4$ Sec^{-1} = 4.02
$k_o \times 10^6$ = 4.10

Table 269

Temp.25°C

Total Oxidant 0.0060M
IsoPropyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	35.2	-
10	33.2	0.975
20	31.2	1.00
30	29.4	1.00
40	27.7	0.998
50	26.1	0.997
60	24.5	1.01

Mean $k \times 10^4$ Sec^{-1} = 0.997
$k_o \times 10^6$ = 0.988

Table 270

Temp.35°C

Total Oxidant 0.0060M
IsoPropyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	27.7	-
5	25.2	3.15
10	22.8	3.25
15	20.6	3.29
20	18.7	3.27
25	17.0	3.26
30	15.4	3.26

Mean $k \times 10^4$ Sec^{-1} = 3.25
$k_o \times 10^6$ = 3.29

Table 271

Temp.25°C

Perchloric Acid	0.1500M
Total Oxidant	0.0060M
IsoPropyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	35.2	-
5	24.0	1.28
10	17.3	1.18
15	12.4	1.16
20	8.5	1.18
25	5.95	1.18
30	4.2	1.18

Mean $k \times 10^3$ Sec^{-1} = 1.19

$k_o \times 10^5$ = 1.30

Table 272

Temp.35°C

Perchloric Acid	0.1500M
IsoPropyl Alcohol	0.1333M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	33.9	-
5	13.2	3.14
10	5.4	3.06
15	2.0	3.14
20	0.8	3.12
25	0.35	3.05
30	-	

Mean $k \times 10^3$ Sec^{-1} = 3.10

$k_o \times 10^5$ = 3.40

6

Table 273

Temp.25°C

Perchloric Acid	0.1000M
IsoPropyl Alcohol	0.1333M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	16.0	-
10	9.2	0.922
20	5.0	0.969
30	2.9	0.949
40	1.7	0.934
50	1.0	0.924

Mean $k \times 10^3$ Sec^{-1} = 0.940

$k_o \times 10^5$ Sec^{-1} = 1.24

Table 274

Temp.35°C

Perchloric Acid	0.1000M
IsoPropyl Alcohol	0.1333M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	33.9	-
5	15.8	2.54
10	7.35	2.55
15	3.45	2.54
20	1.7	2.49
25	0.75	2.54
30	-	

Mean $k \times 10^3$ Sec^{-1} = 2.53

$k_o \times 10^5$ = 2.90

Table 275

Temp. 25°C

Total Oxidant 0.0075M
Sec.Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	22.6	-
10	18.9	2.98
20	15.7	3.04
30	13.1	3.03
40	10.9	3.04
50	9.1	3.03
60	7.5	3.06

Mean $k\times10^4$ Sec^{-1} = 3.03
$k_o\times10^6$ = 3.18

Table 276

Temp.35° C

Total Oxidant 0.0075M
Sec.Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	32.5	-
5	25.0	8.75
10	19.4	8.60
15	14.9	8.67
20	11.5	8.66
25	8.85	8.67
30	6.8	8.70

Mean $k\times10^4$ Sec^{-1} = 8.68
$k_o\times10^6$ = 8.92

Table 277

Temp.25°C

Total Oxidant 0.0060M
Sec.Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	35.8	-
10	30.6	2.62
20	26.1	2.63
30	22.3	2.63
40	19.0	2.64
50	16.4	2.60
60	14.0	2.61

Mean $k\times10^4$ Sec^{-1} = 2.62
$k_o\times10^6$ = 2.75

Table 278

Temp.35° C

Total Oxidant 0.0060M
Sec.Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	27.7	-
5	22.3	7.23
10	18.0	7.18
15	14.5	7.19
20	11.7	7.18
25	9.4	7.21
30	7.6	7.19

Mean $k\times10^4$ Sec^{-1} = 7.20
$k_o\times10^6$ = 7.37

Table 279

Temp. 25°C

Perchloric Acid	0.1500M
Total Oxidant	0.0060M
Sec.Butyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	35.2	-
5	16.8	2.47
10	8.0	2.47
15	3.7	2.50
20	1.8	2.48
25	0.9	2.44
30	-	

Mean $k \times 10^3$ Sec^{-1} = 2.47

$k_o \times 10^5$ = 2.98

Table 280

Temp. 35°C

Perchloric Acid	0.1000M
Total Oxidant	0.0060M
Sec.Butyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	27.7	-
2	15.2	5.00
4	8.3	5.02
6	4.6	4.99
8	2.5	5.01
10	1.3	5.10
12	0.75	5.01

Mean $k \times 10^3$ Sec^{-1} = 5.02

$k_o \times 10^5$ = 5.88

Table 281

Temp. 25°C

Perchloric Acid	0.1000M
TotalOxidant	0.0060M
Sec.Butyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	46.4	-
4	28.7	2.00
8	17.8	2.00
12	11.0	2.00
16	6.8	2.00
20	4.3	2.00
24	2.7	1.97

Mean $k \times 10^3$ Sec^{-1} = 1.99

$k_o \times 10^5$ = 2.35

Table 282

Temp. 35°C

Perchloric Acid	0.1500M
Total Oxidant	0.0060M
Sec.Butyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^3$ Sec^{-1}
0	42.8	-
2	18.95	6.79
4	8.4	6.78
6	3.7	6.80
8	1.7	6.72
10	0.8	6.63
12	-	

Mean $k \times 10^3$ Sec^{-1} = 6.74

$k_o \times 10^5$ = 7.68

Table 283

Temp. 25°C

Total Oxidant 0.0075M
Methyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	40.0	-
35	39.0	0.121
70	38.2	0.110
105	37.1	0.119
140	36.2	0.119
175	35.2	0.122
210	34.2	0.124

Mean $k\times10^4$ Sec^{-1} = 0.119
$k_o\times10^6$ = 0.120

Table 284

Temp. 35°C

Total Oxidant 0.0075M
Methyl Alcohol 0.1333M

Time mts.	Thio ccs	$k\times10^4$ Sec^{-1}
0	33.8	-
10	32.9	0.449
20	32.1	0.430
30	31.15	0.453
40	30.3	0.456
50	29.5	0.454
60	28.7	0.454

Mean $k\times10^4$ Sec^{-1} = 0.449
$k_o\times10^6$ = 0.578

Table 285

Temp. 25°C

Total Oxidant 0.0060M
Methyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	40.0	-
35	39.2	0.965
70	38.3	1.04
105	37.3	1.11
140	36.45	1.11
175	35.6	1.11
210	34.7	1.13

Mean $k\times10^5$ Sec^{-1} = 1.08
$k_o\times10^6$ = 0.110

Table 286

Temp. 35°C

Total Oxidant 0.0060M
Methyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	38.7	-
10	37.8	0.391
20	36.9	0.397
30	36.1	0.353
40	35.2	0.397
50	34.5	0.383
60	33.6	0.393

Mean $k\times10^4$ Sec^{-1} = 0.391
$k_o\times10^6$ = 0.487

Table 287

Temp.25°C

Perchloric Acid	0.1500M
Total Oxidant	0.0060M
Methyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	15.9	-
10	15.3	6.41
20	14.8	5.97
30	14.3	5.90
40	13.8	5.90
50	13.3	5.95
60	12.85	5.92

Mean $k\times10^5$ Sec^{-1} = 5.93

$k_o\times10^6$ = 0.594

Table 288

Temp.35°C

Perchloric Acid	0.1500M
Methyl Alcohol	0.1333M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	20.2	-
10	18.3	16.5
20	16.6	16.4
30	15.0	16.5
40	13.55	16.6
50	12.3	16.5
60	11.1	16.6

Mean $k\times10^5$ Sec^{-1} = 16.5

$k_o\times10^6$ = 1.70

Table 289

Temp.25°C

Perchloric Acid	0.1000M
Total Oxidant	0.0060M
Methyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	15.3	-
10	14.85	4.95
20	14.45	4.76
30	14.0	4.94
40	13.6	4.91
50	13.2	4.92
60	12.8	4.96

Mean $k\times10^5$ Sec^{-1} = 4.91

$k_o\times10^6$ = 0.492

Table 290

Temp.35°C

Perchloric Acid	0.1000M
Methyl Alcohol	0.1333M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	20.2	-
10	18.6	13.8
20	17.1	13.9
30	15.7	14.0
40	14.5	13.8
50	13.3	13.9
60	12.2	14.0

Mean $k\times10^5$ Sec^{-1} = 13.9

$k_o\times10^6$ = 1.43

Table 291

Temp.25°C

Total Oxidant 0.0075M
Ethyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	21.6	-
10	21.3	0.234
20	21.1	0.196
30	20.9	0.184
40	20.6	0.198
50	20.3	0.207
60	20.1	0.200

Mean $k\times10^4\,\mathrm{Sec}^{-1}$ = 0.203
$k_o\times10^6$ = 0.212

Table 292

Temp.35°C

Total Oxidant 0.0075M
Ethyl Alcohol 0.1333M

Time mts.	Thio ccs	$k\times10^4$ Sec^{-1}
0	21.0	-
10	19.9	0.894
20	19.3	0.702
30	18.4	0.734
40	17.6	0.736
50	16.9	0.724
60	16.2	0.721

Mean $k\times10^4\,\mathrm{Sec}^{-1}$ = 0.723
$k_o\times10^6$ = 0.735

Table 293

Temp.25°C

Perchloric Acid 0.1500M
Ethyl Alcohol 0.1333M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	37.4	-
10	33.9	1.74
20	30.9	1.59
30	28.0	1.61
40	25.4	1.61
50	23.1	1.61
60	20.9	1.62

Mean $k\times10^4\,\mathrm{Sec}^{-1}$ = 1.61
$k_o\times10^6$ = 1.64

Table 294

Temp.35°C

Perchloric Acid 0.1500M
Ethyl Alcohol 0.1333M
Total Oxidant 0.0060M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	20.0	-
10	14.8	5.02
20	11.8	4.40
30	9.4	4.19
40	7.4	4.14
50	5.6	4.24
60	4.4	4.20

Mean $k\times10^4\,\mathrm{Sec}^{-1}$ = 4.23
$k_o\times10^6$ = 4.32

Table 295

Temp.25°C

Perchloric Acid	0.1000M
Ethyl Alcohol	0.1333M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	23.8	-
10	21.8	1.46
20	20.3	1.33
30	18.8	1.31
40	17.35	1.32
50	16.05	1.31
60	14.9	1.30

Mean $k\times10^4$ Sec^{-1} = 1.31

$k_o\times10^6$ = 1.34

Table 296

Temp.35°C

Perchloric Acid	0.1000M
Ethyl Alcohol	0.133M
Total Oxidant	0.0060M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	20.0	-
10	16.2	3.51
20	13.2	3.46
30	10.7	3.47
40	8.8	3.42
50	7.1	3.45
60	5.8	3.44

Mean $k\times10^4$ Sec^{-1} = 3.46

$k_o\times10^6$ = 3.53

Table 297

Temp.25°C

Total Oxidant	0.0075M
IsoButyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	10.2	-
10	10.0	0.330
20	9.8	0.334
30	9.6	0.336
40	9.4	0.341
50	9.2	0.344
60	9.0	0.348

Mean $k\times10^4$ Sec^{-1} = 0.339

$k_o\times10^6$ = 0.340

Table 298

Temp.35°C

Total Oxidant	0.0075M
IsoButyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	52.0	-
10	49.1	0.956
20	46.4	0.950
30	43.9	0.940
40	41.5	0.940
50	39.2	0.942
60	37.2	0.931

Mean $k\times10^4$ Sec^{-1} = 0.943

$k_o\times10^6$ = 0.952

Table 299

Temp. 25°C

Total Oxidant 0.0060M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	38.7	-
10	38.1	0.261
20	37.5	0.263
30	36.9	0.265
40	36.3	0.267
50	35.7	0.269
60	35.1	0.271

Mean $k\times10^4$ Sec^{-1} = 0.266
$k_o\times10^6$ = 0.265

Table 300

Temp. 35°C

Total Oxidant 0.0060M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	47.0	-
10	44.8	0.798
20	42.7	0.800
30	40.6	0.810
40	38.7	0.810
50	36.9	0.807
60	35.0	0.819

Mean $k\times10^4$ Sec^{-1} = 0.807
$k_o\times10^6$ = 0.809

Table 301

Temp. 25°C

Perchloric Acid 0.1000M
Total Oxidant 0.0060M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	33.0	-
10	29.8	1.70
20	26.9	1.70
30	24.3	1.70
40	22.0	1.69
50	19.9	1.68
60	18.0	1.68

Mean $k\times10^4$ Sec^{-1} = 1.69
$k_o\times10^6$ = 1.73

Table 302

Temp. 35°C

Perchloric Acid 0.1000M
Total Oxidant 0.0060M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k\times10^4$ Sec^{-1}
0	22.6	-
10	17.3	4.46
20	13.2	4.48
30	10.2	4.43
40	7.6	4.54
50	6.0	4.42
60	4.8	4.31

Mean $k\times10^4$ Sec^{-1} = 4.44
$k_o\times10^6$ = 4.56

Table 303

Temp. 25°C

Perchloric Acid 0.1500M
Total Oxidant 0.0060M
IsoButyl Alcohol 0.1333M

Time mts.	Thio ccs	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	29.0	2.15
20	25.6	2.12
30	22.4	2.15
40	19.7	2.15
50	17.4	2.13
60	15.2	2.15

Mean $k \times 10^4$ Sec^{-1} = 2.14

$k_o \times 10^6$ = 2.19

Table 304

Temp. 35°C

Perchloric Acid 0.1500M
Total Oxidant 0.0060M
IsoPropyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	22.6	-
10	16.3	5.44
20	11.7	5.49
30	8.4	5.50
40	6.0	5.53
50	4.3	5.53
60	3.1	5.52

Mean $k \times 10^4$ Sec^{-1} = 5.50

$k_o \times 10^6$ = 5.63

Table 305

Temp. 25°C

Total Oxidant 0.0075M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	51.7	-
10	51.0	2.26
20	50.5	1.96
30	49.6	2.30
40	48.9	2.32
50	48.3	2.27
60	47.6	2.30

Mean $k \times 10^5$ Sec^{-1} = 2.23

$k_o \times 10^7$ = 2.22

Table 306

Temp. 35°C

Total Oxidant 0.0075M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	23.8	-
10	22.8	7.18
20	21.8	7.31
30	20.9	7.23
40	20.0	7.25
50	19.3	6.98
60	18.4	7.15

Mean $k \times 10^5$ Sec^{-1} = 7.18

$k_o \times 10^6$ = 0.720

Table 307

Temp.25°C

Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	16.8	-
10	16.6	2.00
20	16.4	2.01
30	16.2	2.02
40	16.0	2.03
50	15.8	2.04
60	15.6	2.06

Mean $k \times 10^5$ Sec^{-1} = 2.03
$k_o \times 10^7$ = 2.02

Table 308

Temp.35°C

Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	21.0	-
10	20.2	6.45
20	19.5	6.18
30	18.9	5.85
40	18.2	5.96
50	17.7	5.69
60	17.0	5.87

Mean $k \times 10^5$ Sec^{-1} = 6.00
$k_o \times 10^6$ = 0.617

Table 309

Temp.25°C

Perchloric Acid 0.1500M
Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	47.0	-
10	44.8	0.798
20	42.7	0.800
30	40.6	0.810
40	38.7	0.810
50	36.9	0.807
60	35.0	0.819

Mean $k \times 10^4$ Sec^{-1} = 0.807
$k_o \times 10^6$ = 0.910

Table 310

Temp.35°C

Perchloric Acid 0.1500M
Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	34.7	-
10	30.5	2.10
20	26.6	2.21
30	23.5	2.16
40	20.5	2.19
50	18.1	2.17
60	15.9	2.17

Mean $k \times 10^4$ Sec^{-1} = 2.17
$k_o \times 10^6$ = 2.29

Table 311

Temp. 25°C

Perchloric Acid 0.1000M
Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	33.0	-
10	31.6	0.668
20	30.5	0.656
30	29.2	0.679
40	28.2	0.655
50	26.9	0.681
60	26.1	0.652

Mean $k \times 10^4$ Sec^{-1} = 0.665
$k_o \times 10^6$ = 0.754

Table 312

Temp. 35°C

Perchloric Acid 0.1000M
Total Oxidant 0.0060M
n-Butyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^4$ Sec^{-1}
0	21.2	-
10	19.0	1.82
20	17.1	1.79
30	15.4	1.78
40	13.8	1.79
50	12.4	1.79
60	11.1	1.80

Mean $k \times 10^4$ Sec^{-1} = 1.79
$k_o \times 10^6$ = 1.88

Table 313

Temp. 25°C

Total Oxidant 0.0075M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	51.7	-
10	51.1	1.96
20	50.5	1.96
30	49.6	2.30
40	48.9	2.32
50	48.3	2.27
60	47.6	2.30

Mean $k \times 10^5$ Sec^{-1} = 2.18
$k_o \times 10^6$ = 0.220

Table 314

Temp. 35°C

Total Oxidant 0.0075M
n-Propyl Alcohol 0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	21.3	-
10	20.45	6.79
20	19.6	6.93
30	18.8	6.93
40	18.05	6.89
50	17.2	7.13
60	16.6	6.93

Mean $k \times 10^5$ Sec^{-1} = 6.94
$k_o \times 10^6$ = 0.697

Table 315

Temp.25°C

Total Oxidant	0.0060M
n-Propyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	16.8	-
10	16.6	2.00
20	16.4	2.01
30	16.2	2.02
40	16.0	2.03
50	15.8	2.04
60	15.6	1.88

Mean $k \times 10^5 Sec^{-1}$ = 2.00

$k_o \times 10^6$ = 0.201

Table 316

Temp.35° C

Total Oxidant	0.0060M
n-Propyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	22.5	-
10	21.7	6.03
20	21.0	5.76
30	20.2	5.99
40	19.5	5.97
50	18.7	6.17
60	18.1	6.04

Mean $k \times 10^5$ Sec^{-1} = 5.99

$k_o \times 10^6$ = 0.601

Table 317

Temp.25°C

Perchloric Acid	0.1500M
Total Oxidant	0.0060M
n-Propyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	15.9	-
10	15.3	6.41
20	14.8	5.97
30	14.3	5.90
40	13.6	5.90
50	13.3	5.95
60	12.8	6.03

Mean $k \times 10^5 Sec^{-1}$ = 5.95

$k_o \times 10^6$ = 0.603

Table 318

Temp.35°C

Perchloric Acid	0.1500M
Total Oxidant	0.0060M
n-Propyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k \times 10^5$ Sec^{-1}
0	17.0	-
10	15.3	17.5
20	13.9	16.8
30	12.5	17.1
40	11.3	17.0
50	10.3	16.7
60	9.3	16.7

Mean $k \times 10^5$ Sec^{-1} = 17.0

$k_o \times 10^6$ = 1.72

Table 319

Temp. 25°C

Perchloric Acid	0.1000M
Total Oxidant	0.0060M
n-Propyl Alcohol	0.1333M

Time mts.	Thio ccs	$k\times10^5$ Sec^{-1}
0	15.3	-
10	14.85	4.95
20	14.4	5.05
30	14.0	4.94
40	13.6	4.91
50	13.2	4.92
60	12.8	4.96

Mean $k\times10^5$ Sec^{-1} = 4.95

$k_o\times10^6$ = 0.502

Table 320

Temp. 35°C

Perchloric Acid	0.1000M
Total Oxidant	0.0060M
n-Propyl Alcohol	0.1333M

Time mts.	Thio ccs.	$k\times10^5$ Sec^{-1}
0	17.0	-
10	15.6	14.3
20	14.3	14.4
30	13.1	14.5
40	12.0	14.5
50	11.0	14.5
60	10.1	14.5

Mean $k\times10^5$ Sec^{-1} = 14.4

$k_o\times10^6$ = 1.45

Table 321

Initial Rates $K_o \times 10^6$ moles $litre^{-1}$ Sec^{-1} of various Alcohols at 25°C & 35°C

Concentration	a		b		c		d	
Temp. °C	25	35	25	35	25	35	25	35
Methyl Alcohol	0.120	0.578	0.110	0.487	0.594	1.70	0.492	1.43
Ethyl Alcohol	0.212	0.735	-	-	1.64	4.32	1.34	3.53
n-Propyl Alcohol	0.220	0.697	0.201	0.601	0.603	1.72	0.502	1.45
IsoPropyl Alcohol	1.34	4.30	1.10	3.29	13.0	34.0	12.4	32.8
n-Butyl Alcohol	0.222	0.720	0.202	0.617	0.910	2.29	0.754	1.88
IsoButyl Alcohol	0.340	0.952	0.265	0.809	2.19	5.63	1.73	4.56
Sec.Butyl Alcohol	3.18	8.92	2.75	7.37	29.8	76.8	23.5	58.8

a-(Alcohol)=0.1333M, $(OX)_o$= 0.0075M

b-(Alcohol)=0.1333M, $(OX)_o$=0.0060M

c-(Alcohol)=0.1333M, $(OX)_o$=0.0060M, $(HClO_4)$= 0.1500M

d-(Alcohol)=0.1333M, $(OX)_o$=0.0060M, $(HClO_4)$=0.1000M

TABLE 322

Reaction of Monohydric Alcohols with Aqueous Chlorine in Absence of Perchloric Acid : Energy of Activation, Frequency Factor; Relative Entropy, Enthalpy and Free Energy of Activation at 30^{o}C.

Alcohol	Conc.a	Conc.b	Conc.a	Conc.b	Conc.a	Conc.b	Conc.a	Conc.b	Conc.a	Conc.
	E_{Arr} Kcals		log A moles lit.$^{-1}$Sec^{-1}		$\Delta S^{\ddagger} - \Delta S^{\ddagger}_{s}$ Cal/^{o}C		$\Delta H^{\ddagger} - \Delta H^{\ddagger}_{s}$ KCal.		$\Delta G^{\ddagger} - \Delta G^{\ddagger}_{s}$ Cal.	
Methyl	28.7	27.2	14.105	12.944	0	0	0	0	0	0
Ethyl	22.5	-	9.826	-	-18.9	-	-6.0	-	-250	-
n-Propyl	21.0	20.0	8.738	7.966	-24.4	-22.7	-7.6	-7.0	-240	-240
Iso Propyl	21.2	20.0	9.675	8.704	-20.1	-19.4	-7.4	-7.2	-1330	-1270
n-Butyl	21.4	20.4	9.037	8.263	-22.9	-21.5	-7.2	-6.8	-250	-250
Iso Butyl	18.8	20.3	7.300	8.305	-32.5	-21.0	-9.9	-6.8	-460	-420
Sec.Butyl	18.8	18.0	8.271	7.638	-21.2	-24.4	-9.8	-9.2	-1800	-1790

Conc. a : - (Alcohol) = 0.1333M, $(OX)_o$ = 0.0075M, μ = 0.4

Conc. b : - (Alcohol) = 0.1333M, $(OX)_o$ = 0.0060M, μ = 0.4

TABLE 323

Reaction of Monohydric Alcohols with Aqueous Chlorine in Presence of Perchloric Acid : Energy of Activation, Frequency Factor; Relative Entropy, Enthalpy and Free Energy of Activation at 30°C

Alcohol	Conc.c	Conc.d	Conc.c	Conc.d	Conc.c	Conc.d	Conc.c	Conc.d	Conc.c	Conc.d
	$E_{Arr.}$, KCals		log A, moles lit.$^{-1}$ Sec^{-1}		$\Delta S^{\ddagger} - \Delta S^{\ddagger}_{s}$ Cals/^{o}C		$\Delta H^{\ddagger} - \Delta H^{\ddagger}_{s}$ Kcals.		$\Delta G^{\ddagger} - \Delta G^{\ddagger}_{s}$ Cal.	
Methyl	19.2	19.5	7.852	7.998	0	0	0	0	0	0
Ethyl	17.7	17.7	7.195	7.107	-2.9	-4.1	-1.5	-1.8	-590	-570
n-Propyl	19.1	19.4	7.788	7.926	-0.2	-0.3	-0.1	-0.1	-8.0	-10.2
IsoPropyl	17.5	17.8	7.943	8.145	+0.5	+0.7	-1.6	-1.7	-1830	-1920
n-Butyl	16.8	16.7	6.279	6.121	-7.0	-8.5	-2.3	-2.8	-220	-210
IsoButyl	17.3	18.1	7.035	7.503	-3.8	-3.5	-1.9	-1.8	-750	-730
Sec.Butyl	17.3	16.8	8.169	7.690	+1.4	-1.4	-1.9	-2.7	-2320	-2280

Conc.c : - (Alcohol) = 0.1333M; $(OX)_o$ = 0.0060M, $(HClO_4)$ = 0.1500M, μ = 0.4

Conc.d : - (Alcohol) = 0.1333M; $(OX)_o$ = 0.0060M, $(HClO_4)$ = 0.1000M, μ = 0.4

RESULTS AND DISCUSSION

In alcohol molecules, $R - \overset{\overset{H}{|}}{\overset{+\delta}{C}} - \overset{-\delta}{O} - \overset{+\delta}{H}$, both the C-O and O-H bonds are polarised with negative end of the bond dipoles at oxygen. Moreover, the oxygen has two unshared pairs of electrons. It is these features that determine the chemical reactions of the unsaturated alcohols(385).

In Table 321, the values of initial rates under different conditions are given. We measured the initial rates of the reactions by keeping the concentrations of the reactants fixed in all the cases. The data indicates that in absence of perchloric acid, the rate of reaction increases regularly with the substitution of methyl group for hydrogen, i.e., the reaction rate of methyl < ethyl ⩽ n propyl ⩽ n butyl < isobutyl < isopropyl < sec.butyl, whereas in presence of perchloric acid, the reaction rate of methyl < n-propyl < n-butyl < ethyl < isobutyl < isopropyl < sec.butyl. This is the expected order for electron release at the C-H bond of the carbinol group, since the methyl group will tend to increase the electron density at the carbon atom by their general inductive effect, $\overset{+}{CH_3} \overset{\longrightarrow}{—\!—} \underset{|}{C}HOH$. The polarizability of the molecule increases as the number of electrons in the molecule increases and as their distance from the nucleus increases. Thus by increasing hydrocarbon chain length, the attractive forces resulting from the polarizability of the molecule increases. Since chlorine is electron attracting, the increase in chain length facilitates the formation of alkyl hypochlorite, which, in turn, increase the rates of reactions. However, the reactions of ethyl and isopropyl alcohols have been found to deviate from the above trend.

It appears that dielectric constant of the alcohols also play a role on the rates of reactions, because the increasing order of dielectric constant is methyl > ethyl > n-propyl ≥ isobutyl ≥ isopropyl > n-butyl sec.butyl.

In Tables 322 and 323, the data in absence and in presence of perchloric acid on energy of activation, frequency factor and relative thermodynamic activation parameters are shown.

The enthalpy may be considered to reside in the bond energies. A decrease in enthalpy is a driving force for a reaction. In absence of perchloric acid, the enthalpy decreases significantly, but in presence of perchloric acid, the decrease in enthalpy is not much. Sometimes it is found that the substituents exert their effect primarily on the enthalpy of activation. The changes in the entropy of activation or the frequency factor being rather incidental. It appears that enthalpy is a rate controlling factor in absence of perchloric acid.

Entropy is a measure of the probability for the existence of a given state. The ability of a process to take place with an increase in entropy is a driving force that causes the process to take place. In absence of perchloric acid the negative entropy increases with substitution of methyl group significantly, whereas in presence of perchloric acid, the negative entropy shows an erratic trend. The direction and extent of a reaction are determined by two driving forces, (i) the tendency to react in a state of lowest enthalpy, (ii) the tendency to reach a state of highest entropy. Perhaps both entropy and enthalpy of activation are the main rate controlling factors.

The free energy of activation represents the reactivity. The more reactive one will have a lower free energy of activation. The observed rate data shows a fairly good parallelism.

A factor that influences the activation energy is the steric condition in the transition state. Any structural feature that lead to greater crowding in the transition state, that is, greater repulsion among the electrons of the bonding orbitals increases the activation energy, whereas reduction of repulsive forces decreases activation energy. The observed decreasing trend in the activation energy seems to be explained in this manner.

Arrhenius' Frequency Factor :

Many reactions have been found to take place very much slowly than that would be expected from the simple collision theory, and in order to overcome the difficulty raised by the existence of slow reactions, the collision theory equation, $k = Ze^{-E/RT}$, was modified by the introduction of a factor P, that is, $k = PZe^{-E/RT}$, where P is referred to as the 'probability' or 'steric' factor. The value of P is a measure of the deviation of an actual reaction from the 'ideal' behaviour of the simple collision theory.

The data presented in column 2 of Tables 322 and 323 indicates that these reactions are characterised by low values of the frequency factor and negative entropies of activation. This is because of a conversion of a rotational degree of freedom into vibrational in the activated complex. In absence of perchloric acid, the frequency factor is rather high in the case of methyl alcohol, which indicates that perhaps it follows a different reaction path at lower concentrations of methyl alcohol. Other reactions have similar values of frequency factor. In presence of perchloric acid, the values of frequency factor agree fairly well. On the basis of the collision theory these reactions require an assignment of a probability factor of about 10^{-1} or 10^{-2}.

It is not clear to us at this stage why in absence of perchloric acid, the values of energy of activation at lower concentrations of alcohols are higher than at higher concentrations of alcohol. Perhaps the consecutive reactions aggravate the problem and so the above trend has been noticed.

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