

# Kinetics of Reaction of Isopropyl Alcohol with Aqueous Chlorine

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Kinetics of oxidation of isopropyl alcohol by aqueous solution of chlorine at  $\mu = 0.4M(\text{NaClO}_4)$  are described. The reaction is first order each with respect to isopropyl alcohol and chlorine molecule. The apparent second order rate constant is  $(6.3 \pm 0.1) \times 10^{-2} M^{-1}$  at  $35^\circ$ . Acetone is the primary product of reaction. The metal chlorides increase the rate manifold. In the presence of added chloride or hydrogen ions the chlorination of acetone becomes the side reaction. The activation enthalpy is  $16.8 \pm 0.6$  and  $15.9 \pm 0.02$  kcal mole $^{-1}$ , and activation entropy is  $-10 \pm 2$  and  $-13 \pm 1$  e.u. for the reaction in the absence and presence of added  $[\text{Cl}^-]$  or  $[\text{H}^+]$ , respectively. A mechanism involving isopropyl hypochlorite ester as an intermediate proposed.

EARLIER kinetic investigations on the oxidation of alcohol by chlorine<sup>1-7</sup> have suggested that the reactions are complex. The existence of many species in equilibrium in aqueous solution of chlorine, and rapid interactions between the species themselves also complicates the reactions as suggested by Lichtin and Saxe in the oxidation of glucose with chlorine in aqueous solution. However, they proposed that in aqueous solution of chlorine the principal oxidizing agent is the chlorine molecule<sup>8</sup> and in uncatalysed chlorination the substituting agent is also undissociated chlorine molecule<sup>9</sup>.

It seemed desirable to obtain more information about the role of various oxidizing species in aqueous solution of chlorine. In this paper the results of a kinetic investigation of the reaction of isopropyl alcohol with aqueous solution of chlorine are reported.

## Materials and Methods

All the chemicals used were either of BDH (Analar) or Merck (C.p.) grade or of comparable purity.

Chlorine gas (prepared by treating potassium permanganate with conc. hydrochloric acid) was passed through a bubbler containing  $\text{KMnO}_4$  solution and then into flask filled with conductivity water. The solutions were stored in bottles wrapped in black paper. All the chlorine solutions were standardized iodometrically just before use.

Isopropyl alcohol was distilled, refluxed with calcium for about 8 hr, and then redistilled with adequate protection from moisture.

Perchloric acid solution was titrated against standard sodium hydroxide solution, and the latter was standardized against standard potassium acid phthalate.

Throughout, alkaline permanganate redistilled water was used.

**Kinetic procedure** — The experiments were carried out at  $35^\circ \pm 0.05^\circ$ . After equilibrating the reactants

except chlorine solution, the reactants were mixed and shaken well. The progress of the reaction was followed by estimating iodometrically the unreacted chlorine in 20 ml aliquots of the reaction mixture at regular time intervals.

**Product analysis** — Acetone, identified by its 2,4-DNP derivative<sup>10</sup> was the major product. However, monochloroacetone was also formed as revealed by the analysis of 2,4-DNP derivative<sup>11</sup>. Acetone and monochloroacetone were formed in the ratio 4:1.

## Results

**Rate law** — Although the reaction of isopropyl alcohol with aqueous solution of chlorine proceeds beyond the acetone stage, an attempt has been made to investigate the kinetics of the reaction up to acetone stage by using large excess of alcohol.

In most cases, no simple kinetic law was obeyed and the rate constant could not be determined by the application of an integrated rate equation to the experimental data. Only initial rates,  $k_0$ , were, therefore, considered. A method<sup>12</sup> of finding the initial rate is to plot  $x/t$  against  $x$  ( $x$  being the number of moles per litre of chlorine consumed) and to extrapolate to  $x = 0$ . Satisfactory linear plots were obtained up to 50-60% of the reaction, and the estimated probable errors in  $k_0$  for various runs were within 3%.

Three oxidizing species,  $\text{Cl}_2$ ,  $\text{HOCl}$  or  $\text{OCl}^-$ , and  $\text{Cl}_3^-$ , exist in aqueous solution of chlorine, the relative concentrations of each depend upon the concentration of chlorine solution,  $\text{H}^+$  and  $\text{Cl}^-$  (ref. 13). The initial molar concentration of these species in aqueous solution of chlorine was calculated using a computer programme\*. The method of calculation utilizes the equilibrium constants

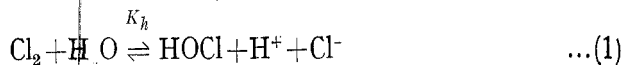
\*The author wishes to thank Mr Robert A. Silverman of the Chemistry Department, University of Maryland, for his help in writing computer programme.

TABLE 1 — DEPENDENCE OF THE OXIDATION RATE ON THE CONCENTRATION OF CHLORINE MOLECULE

{[Isopropyl alcohol] <sub>0</sub> = 0.2000M, $\mu$ = 0.40M}						
[OX] <sub>0</sub> M	10 <sup>3</sup> [Cl <sub>2</sub> ] <sub>0</sub> M	10 <sup>3</sup> [HOCl] <sub>0</sub> M	10 <sup>3</sup> [Cl <sup>-</sup> ] <sub>0</sub> M	10 <sup>5</sup> k <sub>0</sub> M sec <sup>-1</sup>	10 <sup>2</sup> k' <sub>2</sub> M <sup>-1</sup> sec <sup>-1</sup>	10 <sup>2</sup> k <sub>app</sub> M <sup>-1</sup> sec <sup>-1</sup>
0.0248	8.474	16.30	16.28	10.80	2.18	6.4
0.0166	3.953	12.64	12.63	5.00	1.51	6.3
0.0099	1.262	8.636	8.635	1.55	0.783	6.2
0.0083	0.8198	7.479	7.479	1.05	0.633	6.4
0.0066	0.4547	6.145	6.145	0.580	0.439	6.4

Av: 6.3 ± 0.1

for the reactions (1 and 2) at various temperatures<sup>14</sup>.



The input data consist of the molar concentrations of stoichiometric chlorine, chloride, and acid\* and the output data include the molar concentrations of the species Cl<sub>2</sub>, HOCl, Cl<sub>3</sub><sup>-</sup>, H<sup>+</sup>, and Cl<sup>-</sup> in aqueous solution of chlorine.

The reaction is first order each with respect to [oxidant] and [isopropyl alcohol], indicating a second order rate law. The results are summarized in Table 1.

In order to find out the effective oxidizing chlorine species, the value of k<sub>0</sub>/[chlorine species]<sub>0</sub> have been calculated. The constancy of apparent second order rate constant {k<sub>app</sub> = k<sub>0</sub>/[Cl<sub>2</sub>]<sub>0</sub> [isopropyl alcohol]<sub>0</sub>} (Table 1) strongly suggests that chlorine molecule is the principal oxidizing species.

The value of the rate constant k<sub>app</sub>, appropriate to the law (3)

$$-\frac{d[\text{Cl}_2]_0}{dt} = k_{\text{app}} [\text{Isopropyl alcohol}]_0 [\text{Cl}_2]_0 \quad \dots(3)$$

was found to be 6.3 ± 0.1 10<sup>-2</sup>M<sup>-1</sup>sec<sup>-1</sup> at 35°.

Considering that the three oxidizing species in aqueous solution of chlorine are Cl<sub>2</sub>, HOCl and Cl<sub>3</sub><sup>-</sup>, then k'<sub>2</sub> can be written as

$$k'_2 = k_{\text{Cl}_2} \frac{[\text{Cl}_2]_0}{[\text{OX}]_0} + k_{\text{HOCl}} \frac{[\text{HOCl}]_0}{[\text{OX}]_0} + k_{\text{Cl}_3^-} \frac{[\text{Cl}_3^-]_0}{[\text{OX}]_0} \quad \dots(4)$$

Assuming that the ratio of Cl<sub>3</sub><sup>-</sup> to aqueous chlorine, and the [H<sup>+</sup>] remains constant during the reaction, the Eq. (4) reduces to

$$k'_2 \{B + [\text{Cl}^-]_0 + K_3[\text{Cl}^-]_0^2\} = k_{\text{Cl}_2}[\text{Cl}^-]_0 + k_{\text{HOCl}}B + K_{\text{Cl}_3}K_3[\text{Cl}^-]_0^2 \quad \dots(5)$$

where B = K<sub>h</sub>/[H<sup>+</sup>]<sub>0</sub>.

When the quantity k'<sub>2</sub>{B + [Cl<sup>-</sup>]<sub>0</sub> + K<sub>3</sub>[Cl<sup>-</sup>]<sub>0</sub><sup>2</sup>} is plotted against [Cl<sup>-</sup>]<sub>0</sub>, a linear plot is obtained which suggests that the contribution of the third term in the Eq. (5) is negligible; i.e. k<sub>Cl<sub>2</sub></sub> ≫ k<sub>Cl<sub>3</sub><sup>-</sup></sub>.

TABLE 2 — INITIAL RATES IN THE PRESENCE OF INORGANIC SALTS

{[Isopropyl alcohol]<sub>0</sub> = 0.0332M; [OX]<sub>0</sub> = 0.0078M;  $\mu$  = 0.40M}

Salt added	[Salt] M	10 <sup>7</sup> k <sub>0</sub> M sec <sup>-1</sup>	Salt added	Salt M	10 <sup>7</sup> k <sub>0</sub> M sec <sup>-1</sup>
—	—	13.3	SrCl <sub>2</sub>	0.050	35.8
NaCl	0.100	42.0	BaCl <sub>2</sub>	0.050	35.1
NaCl	0.210	50.8	ZnCl <sub>2</sub>	0.050	79.8
NaCl	0.320	58.6	CdCl <sub>2</sub>	0.050	24.2
KCl	0.075	54.0	AlCl <sub>3</sub>	0.050	19.4
MgCl <sub>2</sub>	0.050	40.9	NaF	0.100	14.23
CaCl <sub>2</sub>	0.100	70.0	KH <sub>2</sub> PO <sub>4</sub>	0.100	17.54

From the slope of linear plot the value of k<sub>Cl<sub>2</sub></sub> has been found to be 6.28 × 10<sup>-2</sup>M<sup>-1</sup>sec<sup>-1</sup>, which agrees well with the value of k<sub>app</sub> shown in Table 1. The intercept of linear plot indicates that k<sub>HOCl</sub> is 7.8 × 10<sup>-4</sup>M<sup>-1</sup>sec<sup>-1</sup>. Thus k<sub>Cl<sub>2</sub></sub> ≫ k<sub>HOCl</sub>.

**Effect of varying ionic strength** — The effect of varying [sodium perchlorate] on the reaction rate has been studied and the results indicate that the initial rate k<sub>0</sub> is not very sensitive to the changes in ionic strength.

**Effect of added inorganic salts** — The effect of some salts on the reaction rate was also studied at  $\mu$  = 0.4M(NaClO<sub>4</sub>). The data in Table 2 indicate that mono-, di-, and tri-valent metal chlorides in general enhance the rate manifold. Zinc chloride, for example, increases the rate by about six fold. F<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions also accelerate the reaction.

**Effect of chloride ion** — The results of such experiments are given in Table 3.

The plot of k'<sub>2</sub>{B + [Cl<sup>-</sup>]<sub>0</sub> + K<sub>3</sub>[Cl<sup>-</sup>]<sub>0</sub><sup>2</sup>} against [Cl<sup>-</sup>]<sub>0</sub> is linear from which we conclude that Cl<sub>3</sub><sup>-</sup> species is kinetically inactive in this reaction. The slope of the linear plot has been found to be 3.04 × 10<sup>-2</sup>M<sup>-1</sup>sec<sup>-1</sup>. These observations are consistent with the rate law (6).

$$-\frac{1}{2} \frac{d[\text{Cl}_2]_0}{dt} = k'_{\text{app}} [\text{isopropyl alcohol}]_0 [\text{Cl}_2]_0 \quad \dots(6)$$

TABLE 3 — DEPENDENCE OF THE RATE ON THE CONCENTRATION OF ADDED [Cl<sup>-</sup>]

{[Isopropyl alcohol]<sub>0</sub> = 0.2000M; [OX]<sub>0</sub> = 0.0099M;  $\mu$  = 0.40M}

[NaCl] M	10 <sup>3</sup> [Cl <sub>2</sub> ] <sub>0</sub> M	10 <sup>3</sup> [HOCl] <sub>0</sub> M	10 <sup>3</sup> [Cl <sup>-</sup> ] <sub>0</sub> M	10 <sup>5</sup> k <sub>0</sub> M sec <sup>-1</sup>	10 <sup>2</sup> k' <sub>2</sub> M <sup>-1</sup> sec <sup>-1</sup>	10 <sup>2</sup> k' M <sup>-1</sup> sec <sup>-1</sup>
0.004	1.638	8.259	1.226	0.905	4.57	2.8
0.010	2.110	7.783	1.778	1.20	6.06	2.9
0.020	2.727	7.160	2.715	1.50	7.58	2.8
0.030	3.202	6.677	3.666	1.85	9.34	2.9
0.050	3.897	5.963	5.592	2.32	11.72	3.0

Av: 2.9 ± 0.1

\*For the system in which no chloride or acid was added, the concentration of chloride and acid are taken to be 1.0 × 10<sup>-6</sup>M.

TABLE 4 — INITIAL RATE AS A FUNCTION OF [SILVER NITRATE]

{[Isopropyl alcohol]<sub>0</sub> = 0.0332M; [OX]<sub>0</sub> = 0.0078M;  
μ = 0.40M}

[AgNO <sub>3</sub> ], M	0.000	0.002	0.004	0.008	0.010
10 <sup>7</sup> k <sub>0</sub> , M sec <sup>-1</sup>	13.3	13.4	14.2	15.2	18.1

**Effect of silver nitrate** — In order to reduce the [Cl<sup>-</sup>], kinetic experiments were carried out in the presence of varying [AgNO<sub>3</sub>] and the results are summarized in Table 4.

Although de la Mare and coworkers<sup>15</sup> conducted their experiments in the presence of an excess silver perchlorate to minimize the [Cl<sup>-</sup>], Shilov *et al.*<sup>16</sup> stated that dissolved AgCl actually acts like chloride ion, and hence is a source of Cl<sup>-</sup> for the formation of Cl<sub>2</sub>.

If the reaction in the presence of silver nitrate is due to dissolved AgCl, which is probably completely dissociated<sup>17</sup>, the rate should vary with the [Ag<sup>+</sup>]. The results show that the initial rate varies directly with [Ag<sup>+</sup>] until the concentration of AgNO<sub>3</sub> and total oxidant are nearly equal. Thereafter, there is a sharp increase in the rate. These observations also support the view that the reaction actually involves chlorine molecule.

**Effect of varying [H<sup>+</sup>]** — The results of such kinetic experiments are summarized in Table 5. k<sub>app</sub> is independent of [H<sup>+</sup>] at lower acid concentrations, but varies directly with [H<sup>+</sup>] at higher [acid].

**Isolation of isopropyl hypochlorite** — Several investigators isolated the hypochlorites of primary, secondary and tertiary alcohols<sup>18-20</sup>. We observed that when concentrated chlorine water and isopropyl alcohol were shaken in the presence as well as in the absence of catalyst with carbon tetrachloride, or benzene in a separating funnel, the solvent layer became yellow at once, and the colour deepened as the shaking continued for about 1 min. Prior to these experiments, when the chlorine solution was shaken with the solvent alone, the solvent layers changed to faint yellow but in the presence of alcohol the colour deepened.

In some experiments the chlorine solution was shaken with NaHCO<sub>3</sub> in presence of CCl<sub>4</sub> or benzene, and then isopropyl alcohol and perchloric acid, or silver nitrate, or sodium chloride was added.

On shaking, the solvent layers develop bright yellow colour. The colour stays for a longer time at low pH. All these observations suggest that the oxidation of isopropyl alcohol proceeds via hypochlorite ester, and the chlorine molecule is responsible for hypochlorite formation. However, the contribution of HOCl cannot be ruled out, because other investigators observed the hypochlorite ester formation with HOCl<sup>19</sup>.

**Activation parameters** — The activation parameters were calculated using Eyring's absolute reaction rate theory (Eq. 7) using a non-linear least

$$k_{app} = k_b T/h \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R) \quad \dots(7)$$

squares computer programme\*. The value of ΔH<sup>‡</sup> is 16.9 ± 0.6 and 15.5 ± 0.2 kcal mole<sup>-1</sup>, and of ΔS<sup>‡</sup> is -10 ± 2 and -13 ± 1 e.u., respectively for the reaction in the absence of added Cl<sup>-</sup> or H<sup>+</sup>, and in the presence of added Cl<sup>-</sup> or H<sup>+</sup>.

## Discussion

Although the present kinetic experiments were carried out with excess of alcohol, it is suspected that the chlorination of the primary product, acetone is still appreciable because the rate of chlorination of acetone is about 10<sup>7</sup> times faster than the rate of reaction of chlorine with isopropyl alcohol. In the presence of added chloride or perchloric acid the chlorination of the primary product, acetone becomes a serious side reaction. Due to these complications the rate constants could not be determined by the application of an integrated second order rate equation to the experimental data.

Our data strongly suggest that chlorine molecule is the principal oxidizing species in this reaction. Similar conclusion was reached by Bell and Yates<sup>21</sup> while studying the kinetics of reaction of acetone with chlorine. Similar observations were also made for the oxidations of glucose<sup>8</sup>, ferrous ion<sup>22</sup>, and tris-(1,10-phenanthroline) iron(II) ion<sup>23</sup> by aqueous chlorine.

**Mechanism** — While discussing the mechanism of oxidation of alcohols, Waters<sup>24</sup> and Stewart<sup>25</sup> pointed out that with heterolytic oxidants, the oxidation generally proceeds via esterification or by hydride transfer. In both the mechanisms the rate determining step involves the cleavage of C-H bond. Consistent with the results of present investigation we propose an ester mechanism (steps a and b) similar

TABLE 5 — RATE CONSTANT AS THE FUNCTION OF [PERCHLORIC ACID]

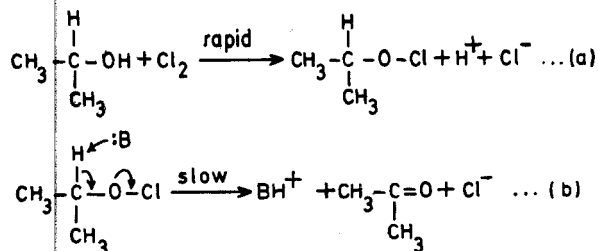
{[Isopropyl alcohol]<sub>0</sub> = 0.1066M; [OX]<sub>0</sub> = 0.0052M; μ = 0.40M}

[HClO <sub>4</sub> ] <sub>0</sub> × M	0.01	0.04	0.12	0.20	0.25	0.30
10 <sup>6</sup> k <sub>0</sub> , M sec <sup>-1</sup>	0.350	0.725	1.30	2.20	2.74	3.40
10 <sup>6</sup> k <sub>0</sub> <sup>(a)</sup> , M sec <sup>-1</sup>	0.324	0.700	1.38	1.89	2.31	2.80
	±0.001	±0.009	±0.03	±0.09	±0.05	±0.09
10 <sup>6</sup> [H <sup>+</sup> ] <sub>0</sub> , M	1.460	4.389	12.30	20.26	25.24	30.22
10 <sup>6</sup> [Cl <sub>2</sub> ] <sub>0</sub> , M	0.604	1.304	2.187	2.626	2.813	2.962
10 <sup>3</sup> k <sub>app</sub> , M <sup>-1</sup> sec <sup>-1</sup>	5.4	5.2	5.6	7.9	9.1	10.8

(a), computer value.

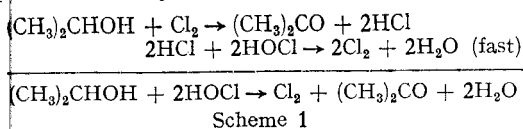
\*A detailed description of the programme be obtained from Prof. Gilbert Gordon, Department of Chemistry, Iowa City, Iowa 52240.

to that reported for chromic acid oxidation<sup>26,27</sup>.



where B is a proton acceptor. Here the rate determining step (b) involves the abstraction of proton from the secondary C-H bond by a base. In the oxidation of alcohol and ethers by aqueous bromine, Deno and Potter<sup>28,29</sup> have suggested the formation of ester as an intermediate.

In the absence of added  $[\text{Cl}^-]$  or perchloric acid, small percentage of monochloroacetone is formed because the  $[\text{H}^+]$  produced in step (a) are utilized for enolization of acetone. Further, the aqueous solution of chlorine which initially contains both chlorine and hypochlorous acid helps the reaction to proceed chiefly according to Scheme 1.



Only a small percentage of isopropyl alcohol is oxidized by hypochlorous acid directly. Under these conditions oxidation of the primary product acetone then proceeds to give monochloroacetone.

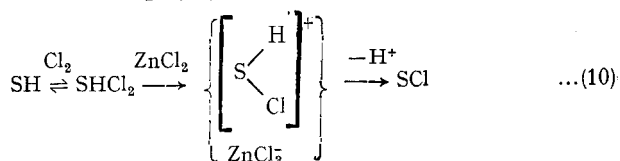
Experiments carried out under such conditions have the advantage that as long as hypochlorous acid is present, no  $\text{Cl}^-$  or  $\text{H}^+$  accumulates during the reaction. This has been verified by measuring the pH of the reaction mixture, which remains constant during a run.

Kinetic evidence for the existence and participation in chlorination of  $\text{H}_2\text{OCl}^+$  or  $\text{Cl}^+$  has been provided by Bell and Gelles<sup>30</sup> who concluded that the equilibrium constant for the cation  $\text{Cl}^+$  (aq) is too small for the species to exist in appreciable concentrations in water. The corrected values of the equilibrium constant as given by Arotsky and Symons<sup>31</sup> also lead to the same conclusion. Apparently, the participation of  $\text{Cl}^+$  as kinetic intermediate is unlikely.

Perchloric acid functions in two ways in this reaction: (a) it suppresses the hydrolysis of chlorine which in turn increases the concentration of chlorine molecule, and (b) it increases the enolization rate of acetone. In the presence of higher concentrations of perchloric acid the reaction of acetone with chlorine is appreciable.

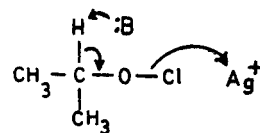
The chloride ions enhance the rate because they displace the hydrolytic equilibrium of chlorine to the left. We notice that zinc chloride enhances the initial rate manyfold. This salt has a tendency to hydrolyse. One possible explanation for the increase in rate is that the  $[\text{H}^+]$  produced by hydrolysis enolize acetone, which in turn increases the percentage of acetone. Another possibility is that the chlorine molecule forms complex with the substrate, and then the Lewis acid ( $\text{ZnCl}_2$ ) assist

in breaking the bond between chlorine atoms as shown in Eq. (10).



A linear plot has been obtained by plotting a double reciprocal plot of  $1/\text{rate}$  versus  $1/\text{ZnCl}_2$ , confirming the above mechanism.

The sharp increase in rate in the presence of  $\text{Ag}^+$  ions may perhaps be due to the affinity of  $\text{Ag}^+$ .



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