KINETICS AND MECHANISM OF OXIDATION OF ALLYL AND CROTYL ALCOHOLS BY SODIUM N-CHLOROBENZENE-SULPHONAMIDE IN HYDROCHLORIC ACID MEDIUM

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The kinetics of oxidation of allyl and crotyl alcohols by sodium N-chlorobenzenesulphonamide or chloramine B (CAB) in presence of hydrochloric acid (0·06—0·26M) has been studied at 0°C. The rate of reaction is first order in [CAB], independent of substrate concentration and is first order with respect to the gross concentration of HCl (0·06—0·12M), which changes to second order at higher acidities (0·15—0·26M). Chloride ion catalyses the oxidation in accordance with the mixed rate laws

$$-\frac{d[CAB]}{dt} = k'[CAB][H^+]^{0.5} + k''[CAB][Cl^-]^{0.5}$$

and

$$-\frac{d[CAB]}{dt} = k'''[CAB][H^+]^{1.6} + k^{\prime v}[CAB][Cl^-]^{0.4}$$

at lower and higher acidities respectively. Ionic strength and addition of the reaction product, benzenesulphonamide, have negligible influence on the rate. The effect of changes in dielectric constant of the medium on the reaction rate has been studied. Activation parameters for the reaction have been calculated. Plausible mechanisms have been proposed for the observed kinetics.

Organic haloamines are well known as mild oxidants and are employed as analytical reagents in the estimation of variety of reductants. The prominent member of this class is chloramine T, (sodium N-chloro-4-methylbenzenesulphonamide, CAT). The other member is chloramine-B (sodium N-chlorobenzenesulphonamide, CAB). The N—Cl bond in CAT and CAB is highly polar and hence these two compounds are fairly strong electrophiles, since chlorine leaves as Cl^+ in reactions. Although the oxidation mechanisms of many chloraminometric reactions have been kinetically investigated, almost no information is available in literature about the oxidative behavior of CAB. It was, therefore, found to be of interest to investigate the mechanism of oxidations of compounds such as unsaturated alcohols by this oxidant. The present communication reports the kinetics of oxidation of allyl and crotyl alcohols by CAB in HCl medium.

EXPERIMENTAL

Materials and Methods

All solutions were prepared in triply distilled water. Allyl alcohol (E. Merck, corrected b.p. 97·1°C, n_D 1·412) and crotyl alcohol (Fluka, b.p. 125°C, n_D 1·424) were used without further purification. The purity of the compounds was checked by phthalation with phthalic anhydride in pyridine[1]. The requisite amount of alcohols was accurately weighed and dissolved in water to get an approximately 0·5M solution. Chloramine B was prepared by passing pure chlorine through benzenesulphonamide[2] dissolved in NaOH solution (4M) over a period of one hour at 70°C. The mass obtained was filtered, dried and crystallised from water. The purity of the compound was checked by estimating the amount of active chlorine present in the compound. An aqueous solution of CAB was prepared and standardised by the iodometric method. The ionic strength was kept constant at a high value using a concentrated solution of sodium perchlorate.

The reaction was carried out in a glass stoppered pyrex tube. Requisite amounts of alcohol, hydrochloric acid, sodium perchlorate solutions and water to keep the total volume constant for all runs were taken in the tube and were thermostated in an ice bath maintained at 0°C. A measured volume of CAB solution, which was also cooled to 0°C, was added to the mixture in the tube. The progress of the reaction was followed by iodometric estimation of CAB in a measured aliquot of the reaction mixture at various intervals of time.

Conductance measurements were made at room temperature (26°C) using a Philips PR 9 500 conductivity bridge and a dip type conductivity cell. Potentiometric titrations were carried out on an Elico model Li-10 pH meter.

Stoichiometry[3]

Reaction mixtures containing excess of CAB over the alcohol were kept at room temperature (26°C) in presence of hydrochloric acid over-all concentration (0·06—0·5M) for 24 h. Iodometric estimation of unchanged CAB showed that one mol of alcohol consumed one mol of CAB

$$\mathrm{R'CHCH_2OH + RNClNa \rightarrow R'CHCHO + RNH_2 + NaCl},$$

where R′ is CH_2 for allyl and CH_3CH for crotyl alcohol and $R = C_6H_5SO_2$.

The presence of allyl aldehyde and crotyl aldehyde in the reaction mixture was shown by spot tests[4]. Further, the aldehydes were isolated as their 2,4-dinitrophenylhydrazones[5] (m.p. 165° and 189°C respectively for the hydrazones of allyl- and crotylaldehydes). The presence of benzene sulphonamide among the reaction products was detected by TLC. A mixture of light petroleum, $CHCl_3$ and n-butanol (1 : 1 : 0·5 v/v) was used as the solvent with iodine as the developing reagent (R_F 0·88).

RESULTS

Effect of reagents: The kinetics of oxidation of alcohols by CAB were investigated at several initial concentrations of the reactants. When the alcohols are in large excess, plots of log[CAB] against time are found to be linear (Fig. 1) indicating first order dependence on [CAB]. The pseudo first order rate constants in CAB at different initial concentrations of the reactants are found to be independent of the substrate concentrations (Table I). Hence the reaction is zero order with respect to alcohols.

Effect of [HCl]: The kinetics of the reaction were studied at different overall concentrations of HCl. The rate of reaction increased with increase in [HCl] (Table II). The order with respect to [HCl] was found to be unity for allyl and crotyl alcohols in the acid range of 0·06 to 0·12M and a second order dependence on [HCl] was noticed above 0·12M (between 0·15 and 0·26M). This was also verified by plotting log k_{obs} *vs* log [HCl] for the alcohols (Fig. 2).

TABLE I

Effect of concentrations of the reactants on the reaction rate $\mu = 0.5$ mol l^{-1}; temperature 0°C

$[CAB]_0$ mol l^{-1}	$[Alcohol]_0$ M	$k_{obs} \cdot 10^4$ s^{-1} allyl alcohol	$k_{obs} \cdot 10^4$ s^{-1} crotyl alcohol
	[HCl] = 0·1 mol l^{-1}		
0·005	0·10	0·96	0·97
0·005	0·15	0·99	0·96
0·005	0·20	0·99	0·99
0·005	0·25	0·99	0·99
0·005	0·30	0·99	0·99
0·003	0·10	0·96	0·96
0·004	0·10	0·94	0·95
0·006	0·10	0·98	0·99
0·007	0·10	0·96	0·98
0·005[a]	0·10	0·98	0·99
0·005[b]	0·10	0·98	0·96
	[HCl] = 0·2 mol l^{-1}		
0·005	0·05	2·92	3·03
0·005	0·10	2·92	2·99
0·005	0·15	2·92	3·07
0·005	0·20	2·92	3·20
0·005	0·25	2·99	2·99
0·003	0·10	2·92	3·03
0·004	0·10	2·96	3·03
0·006	0·10	2·96	3·03
0·007	0·10	2·84	3·03
0·005[a]	0·10	2·99	3·07
0·005[b]	0·10	2·92	3·07

[a] At ionic strength of 1·0 mol l^{-1}; [b] in presence of excess of benzenesulphonamide.

TABLE II

Effect of HCl concentration on the reaction rate $[CAB]_0 = 0{\cdot}005 \text{ mol l}^{-1}$ $[\text{alcohol}]_0 = 0{\cdot}1 \text{ mol l}^{-1}$; $\mu = 0{\cdot}5 \text{ mol l}^{-1}$; temperature 0°C

[HCl] mol l^{-1}	Allyl alcohol			Crotyl alcohol		
	$10^4 k_{obs}$ s^{-1}	$\frac{10^4 k_{obs}}{[HCl]}$	$\frac{10^3 k_{obs}}{[HCl]^2}$	$10^4 k_{obs}$ s^{-1}	$\frac{10^4 k_{obs}}{[HCl]}$	$\frac{10^3 k_{obs}}{[HCl]^2}$
0·06	0·58	9·66	—	0·58	9·66	—
0·08	0·77	9·62	—	0·75	9·37	—
0·10	0·96	9·60	—	0·97	9·70	—
0·12	1·16	9·66	—	1·19	9·90	—
0·15	1·73	—	7·70	1·71	—	7·60
0·17	2·30	—	7·96	2·24	—	7·75
0·20	2·92	—	7·30	2·99	—	7·48
0·23	4·07	—	7·70	3·91	—	7·39
0·26	4·95	—	7·32	5·22	—	7·72

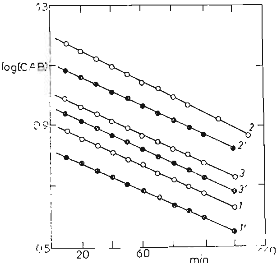


FIG. 1

Plot of log [CAB] *vs* time (min). [HCl] = = 0·1M; [alcohol] = 0·1M; μ = 0·5M; Temp. 0°C [CAB] = 0·004M *1*, 0·005M *2* allyl alcohol ○ 0·006M *3*; [CAB] = 0·005M *1'*, 0·006M *2'*, crotyl alcohol ●, 0·007M *3'*

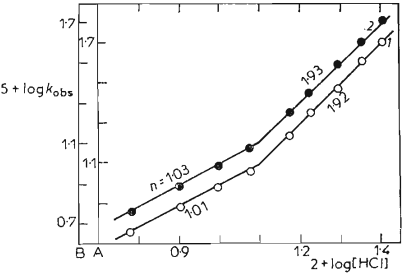


FIG. 2

Plot of log k_{obs} *vs* log [HCl], [CAB] = = 0·005M; [Alcohol] = 0·1M μ = 0·5M; Temp. 0°C. Scale: A for allyl alcohol — *1*, B for crotyl alcohol — 2

Effect of chloride ion: Addition of sodium chloride increases the rate of reaction (Table III). A plot of log k_{obs} *vs* log $[Cl^-]$ gives a straight line in both the acid ranges, the slopes being 0·47 and 0·35 for allyl alcohol, 0·45 and 0·35 for crotyl alcohol in the two ranges.

Effect of $[H^+]$: Since chloride ion was found to catalyse the reaction, $[Cl^-]$ in solution was kept constant by the addition of NaCl and $[H^+]$ was varied. The rate increased with increase in $[H^+]$ (Table IV). Plots of log k_{obs} *vs* log $[H^+]$ gave straight lines of slope 0·5 and 1·6 at lower and higher acidities respectively.

Effect of ionic strength and benzenesulphonamide: Variation of ionic strength of the medium (0·5 – 1·0M) and addition of the reaction product have no significant effect on the rate of reaction (Table I).

Effect of changing solvent composition: The effect of changing solvent composition on the rate was studied by adding methanol to the reaction mixture. Addition of methanol at low acid concentrations had no marked effect on the rate, but at $[H^+] > 0{\cdot}2$M, the rate of reaction increased with methanol concentration (Table V). However, no linear relationship between log k_{obs} and $1/D$ where D is the dielectric constant of the methanol–water mixtures[6], was noticed.

Effect of temperature: The reactions were carried out at different temperatures (0 – 16°C) and the activation parameters have been evaluated (Tables VI and VII).

TABLE III

Effect of $[Cl^-]$ on the reaction rate $[CAB]_0 = 0{\cdot}005$ mol l^{-1}; $[alcohol]_0 = 0{\cdot}1$ mol l^{-1}; $\mu = 0{\cdot}5$ mol l^{-1}; temperature 0°C

[HCl] mol l^{-1}	$[Cl^-]$ mol l^{-1}	$k_{obs} \cdot 10^4$ s^{-1}	
		allyl alcohol	crotyl alcohol
0·10	0·025	1·08	1·04
0·10	0·06	1·29	1·32
0·10	0·10	1·57	1·61
0·10	0·15	1·88	1·94
0·10	0·20	2·19	2·21
0·20	0·025	3·26	3·42
0·20	0·06	3·68	3·79
0·20	0·10	4·32	4·53
0·20	0·15	5·12	5·22
0·20	0·18	5·30	5·41

DISCUSSION

The overall rate laws for the oxidation of allyl and crotyl alcohols by CAB in presence of HCl are of the form:

$$-\frac{d[CAB]}{dt} = k'[CAB][HCl] \qquad (1)$$

and

$$-\frac{d[CAB]}{dt} = k''[CAB][HCl]^2 \qquad (2)$$

at low and high acid concentrations respectively.

Although the equilibria present in acidified CAT solutions have been clearly established by the work of Bishop and Jennings[7], Morris and coworkers[8] and Higuchi and coworkers[9], no detailed information is available about the species present in acidified CAB solutions in literature. Zilberg[10] has shown that acidification of CAB with HCl, acetic acid or H_2SO_4 gives dichloramine B ($RNCl_2$) and benzenesulphonamide (RNH_2). Mogilevskii and coworkers[11] have reported the presence of hypochlorous acid in acidified CAB solutions. It is likely that equilibria[7-9] similar to those of CAT exist in acidified CAB solutions.

To confirm this hypothesis, conductometric and potentiometric titrations between aqueous solutions of CAB and HCl were performed. The conductometric behaviour

TABLE IV
Effect of $[H^+]$ on the reaction rate $[CAB] = 0{\cdot}005$ mol l^{-1} $[alcohol]_0 = 0{\cdot}1$ mol l^{-1}; $\mu = 0{\cdot}5$ mol l^{-1}; temperature 0°C

$[Cl^-]$ mol l^{-1}	$[H^+]$ mol l^{-1}	$k_{obs} \cdot 10^4$ s^{-1} allyl alcohol	$k_{obs} \cdot 10^4$ s^{-1} crotyl alcohol
0·12	0·06	0·79	0·79
0·12	0·08	0·86	0·84
0·12	0·10	1·02	1·02
0·12	0·12	1·16	1·19
0·26	0·15	2·24	2·25
0·26	0·17	2·63	2·60
0·26	0·20	3·35	3·37
0·26	0·23	4·17	4·12
0·26	0·26	4·95	5·22

of CAB solution is identical[12-14] with that of CAT while the pH titraton curves observed were similar to those noted by Morris and coworkers[8] and Mahadevappa and Rangaswamy[13] in CAT–HCl titrations. Further, pH measurements on aqueous solutions of CAB showed that a 0·05M-CAB solution has a pH of 7·7 at 25°C. Hence, a similar set of equilibria can be expected in CAB solutions. The work of Mukherji and coworkers[15] also indicates a similar set of equilibria.

The possible equilibria in aqueous CAB solutions are:

$$\mathrm{RNCl^{(-)} + H^{(+)} \rightleftharpoons RNHCl} \tag{A}$$

$$\mathrm{2\,RNHCl \rightleftharpoons RNH_2 + RNCl_2} \tag{B}$$

$$\mathrm{RNCl_2 + H_2O \rightleftharpoons RNH_2 + HOCl} \tag{C}$$

$$\mathrm{RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl}\,. \tag{D}$$

The possible oxidizing species in acidified CAB solutions are RNHCl, $RNCl_2$ and HOCl. If $RNCl_2$ were to be the active species, the rate law predicts a second order dependence of rate on [CAB] as seen from equation (*B*), which is contrary to experimental observations. In the case of CAT solutions, Pryde and Soper[16] have shown that the direct interaction of RNHCl with the substrates could be slow while HOC

TABLE V

Effect of dielectric constant on the reaction rate $[\mathrm{CAB}]_0 = 0{\cdot}005\ \mathrm{mol\,l^{-1}}$ $[\mathrm{alcohol}]_0 = 0{\cdot}1\ \mathrm{mol\,.\,l^{-1}}$; $\mu = 0{\cdot}5\ \mathrm{mol\,l^{-1}}$; Temperature 0°C

[HCl] mol l^{-1}	$[\mathrm{MeOH}]_0$ %	$k_{obs}\,.\,10^4\ s^{-1}$	
		allyl alcohol	crotyl alcohol
0·1	0	0·96	0·97
0·1	10	1·06	1·07
0·1	20	1·27	1·28
0·1	40	1·36	1·34
0·1	50	1·40	1·38
0·2	0	2·92	2·99
0·2	10	3·53	3·61
0·2	20	4·37	4·30
0·2	40	5·18	5·22
0·2	50	5·60	5·60

formed by hydrolysis of RNHCl and $RNCl_2$ would attack at a faster rate. It is likely that HOCl is the reactive species in the oxidation of unsaturated alcohols with CAB. This is further supported by the fact that equations (*B*), (*C*) and (*D*) would result in a net reaction involving the hydrolysis of the free acid RNHCl.

TABLE VI

Effect of temperature on the reaction rate $[CAB]_0 = 0{\cdot}005\ mol\ l^{-1}$; $[alcohol]_0 = 0{\cdot}1\ mol\ l^{-1}$; $\mu = 0{\cdot}5\ mol\ l^{-1}$

Allyl alcohol				Crotyl alcohol			
[HCl] = 0·1 mol l^{-1}		[HCl] = 0·2 mol l^{-1}		[HCl] = 0·1 mol l^{-1}		[HCl] = 0·2 mol l^{-1}	
K	$k_{obs} \cdot 10^4\ s^{-1}$	K	$k_{obs} \cdot 10^4\ s^{-1}$	K	$k_{obs} \cdot 10^4\ s^{-1}$	K	$k_{obs} \cdot 10^4\ s^{-1}$
273·0	0·96	273·0	2·92	273·0	0·97	273·0	2·99
277·0	1·31	277·5	4·38	280·8	2·02	277·9	4·72
281·0	1·92	280·5	6·03	284·0	2·72	280·5	6·33
285·0	2·88	283·5	8·06	287·0	3·68	282·5	7·68
289·0	4·18	286·5	10·49	289·9	4·90	284·9	9·60

TABLE VII

Activation parameters for the oxidation of allyl and crotyl alcohol by chloramine B

[HCl] mol l^{-1}	A s^{-1}	E_a kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ JK^{-1}	$\Delta G^{\ddagger}$ kJ mol^{-1}
			Allyl alcohol		
0·1	$2{\cdot}19 \cdot 10^8$ $\pm 0{\cdot}081$	59·36	$57{\cdot}02 \pm 0{\cdot}013$	$-89{\cdot}12 \pm 0{\cdot}074$	$82{\cdot}65 \pm 0{\cdot}120$
0·2	$4{\cdot}03 \cdot 10^9$ $\pm 0{\cdot}074$	61·32	$58{\cdot}98 \pm 0{\cdot}012$	$-64{\cdot}92 \pm 0{\cdot}039$	$77{\cdot}20 \pm 0{\cdot}067$
			Crotyl alcohol		
0·1	$2{\cdot}36 \cdot 10^9$ $\pm 0{\cdot}069$	64·79	$62{\cdot}45 \pm 0{\cdot}015$	$-69{\cdot}39 \pm 0{\cdot}058$	$82{\cdot}05 \pm 0{\cdot}110$
0·2	$1{\cdot}22 \cdot 10^{10}$ $\pm 0{\cdot}020$	63·79	$61{\cdot}45 \pm 0{\cdot}013$	$-55{\cdot}76 \pm 0{\cdot}033$	$77{\cdot}04 \pm 0{\cdot}048$

Addition of benzenesulphonamide and ionic strength of the medium has no effect on the rate indicating that neutral species are involved in the rate determining step. Since the rate is independent of alcohol concentration, the disappearance of the alcohol probably takes place by a fast reaction with HOCl. So, Scheme 1 is proposed for explaining the observed kinetics at low acid concentrations.

$$\mathrm{RNHCl} + \mathrm{H_2O} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{RNCl^{(-)}} + \mathrm{H_3O^+} \qquad (i)$$

slow and forward reaction is rate determining

$$\mathrm{RNCl^{(-)}} + \mathrm{H^{(+)}} + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{RNH_2} + \mathrm{HOCl} \qquad (ii)$$

$$\mathrm{HOCl} + \text{alcohol} \xrightarrow{k_3} \text{Products} \qquad (iii)$$

fast

SCHEME 1

The rate law (*1*) can be derived in the form

$$-\frac{\mathrm{d}[\mathrm{CAB}]}{\mathrm{d}t} = \frac{k_1[\mathrm{H_2O}]\,[\mathrm{CAB}]\,[\mathrm{H_3O^+}]}{k_1[\mathrm{H_2O}]/k_{-1} + [\mathrm{H_3O^+}]}\,. \qquad (3)$$

At higher [HCl], a second order dependence on [HCl] is noted while the rate is still independent of substrate concentrations. Scheme 2 explains the observed kinetics under high acid concentrations.

$$\mathrm{RNCl^{(-)}} + \mathrm{H^{(+)}} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{RNHCl} \qquad (i)$$

$$\mathrm{RNHCl} + \mathrm{H^{(+)}} \xrightarrow{k_2'} \mathrm{RNH_2} + \mathrm{Cl^{(+)}} \qquad (ii)$$

slow and rate determining

$$\mathrm{Cl^{(+)}} + \mathrm{H_2O} \xrightarrow{k_3'} \mathrm{H_2OCl^{(+)}} \qquad (iii)$$

$$\mathrm{H_2OCl^{(+)}} + \text{alcohol} \xrightarrow{k_4'} \text{products} \qquad (iv)$$

fast

SCHEME 2

The presence of chlorinium ion in HOCl solutions has been speculated by Swain and Crist[17] but it is proposed that the ion is not highly reactive and is rapidly converted[18] into $\mathrm{H_2OCl^{(+)}}$ which then attacks the substrate in a fast step.

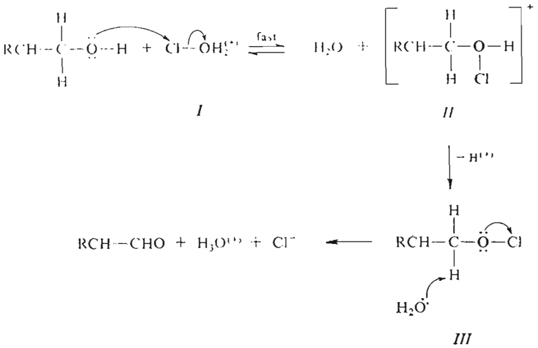
The rate law (*2*) can be derived in the form

$$-\frac{d[\mathrm{CAB}]}{dt} = \frac{k_1 k_2'[\mathrm{CAB}][\mathrm{H}^+]^2}{k_{-1} + k_2'[\mathrm{H}^+]} \qquad (4)$$

Equations (*3*) and (*4*) explain the fractional order dependence on $[\mathrm{H}^+]$ at lower and higher acidities respectively.

Scheme2 is supported by the negligible influence of ionic strength and RNH_2 on the reaction rate. The rate increases with the decrease in dielectric constant of the medium. The positive methanol effect supports Scheme 2 where the rate determining step involves a positive ion and a dipole[19].

A detailed mechanism of oxidation of allyl and crotyl alcohols by CAB is given in Scheme 3. The protonated species $H_2OCl^{(+)}$ (*I*) interacts with the alcohols forming a chloronium ion complex (*II*). The complex loses a proton giving a hypochlorite (*III*).



R is CH_2 for allyl alcohol and CH_3—CH for crotyl alcohol.

SCHEME 3

Proton abstraction from this species in presence of the solvent is promoted by the π-electron cloud in the alcohol to form the conjugated oxidation products, namely, allyl and crotyl aldehydes. The low energy of activation and highly negative entropy value support the formation of the highly solvated chloronium complex (*II*) in a fast step.

Effect of Chloride Ion

Addition of chloride ion increases the rate of reaction and a fractional order dependence on $[Cl^-]$ is observed. Such behaviour has been noted in the Orton rearrangement[20] involving N-haloamides. Scheme 4 can be proposed for explaining the observations:

$$RNCl^{(-)} + H^{(+)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RNHCl \tag{i}$$

$$RNHCl + Cl^{(-)} \xrightarrow{k_2''} RNH^{(-)} + Cl_2 \tag{ii}$$

slow and rate determining

$$Cl_2 + H_2O \xrightarrow{k_3''} HOCl + H^{(+)} + Cl^{(-)} \tag{iii}$$

$$HOCl + H^{(+)} \xrightarrow{k_4''} H_2OCl^{(+)} \tag{iv}$$

$$H_2OCl^{(+)} + \text{alcohol} \xrightarrow{k_5''} \text{products} \tag{v}$$

$$RNH^{(-)} + H^{(+)} \xrightarrow{k_6''} RNH_2 \tag{vi}$$

SCHEME 4

Assuming steady state conditions for RNHCl, the rate law,

$$-\frac{d[CAB]}{dt} = \frac{k_1 k_2''[CAB][H^+][Cl^-]}{k_{-1} + k_2''[Cl^-]} \tag{5}$$

can be derived in agreement with the fractional order noted with respect to $[Cl^-]$.

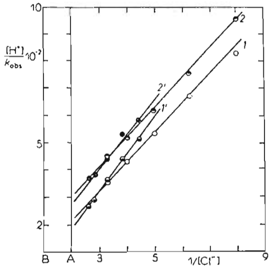


FIG. 3

Plot of $[H^+]/k_{obs}$ *vs* $1/[Cl]^-$. [CAB] = = 0·005M; [alcohol] = 0·1M; μ = 0·5M; temp. 0°C. Scale: A allyl alcohol *1* and *1'*; *B* crotyl alcohol 2 and *2'*; *1* and 2; lower acid concentration *1'* and *2'* higher acid concentration

Equation (*5*) can be transformed into equations (*6*) and (*7*).

$$k_{\text{obs}} = \frac{k_1 k_2''[\text{H}^+][\text{Cl}^-]}{k_{-1} + k_2''[\text{Cl}^-]} \qquad (6)$$

$$\frac{[\text{H}^+]}{k_{\text{obs}}} = \frac{k_{-1}}{k_1 k_2''[\text{Cl}^-]} + \frac{1}{k_1} = \frac{K}{k_2''[\text{Cl}^-]} + \frac{1}{k_1}, \qquad (7)$$

where $K = k_{-1}/k_1$ is the equilibrium constant for reaction (*i*) in Scheme 4.

A plot of $[\text{H}^+]/k_{\text{obs}}$ *vs* $1/[\text{Cl}]^-$ gives a straight line (Fig. 3). From the values of slope and intercept K/k_2'' and k_1 were calculated.

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