Kinetics of Oxidation of Secondary Alcohols by Chloramine T†

By **M. M. Natarajan** and **V. Thiagarajan** * Department of Chemistry, Vivekananda College, Madras 600 004, India.

The kinetics of oxidation by chloramine T (CAT) of secondary alcohols with propan-2-ol as reference compound have been studied in aqueous acidic and aqueous acetic acid media. In the presence of strong mineral acid in aqueous medium the rate law is found to be $-d[CAT]/dt = k[CAT][Alcohol][H^+]^2$ The rate law, a low kinetic isotope effect, and the effect of solvent polarity on the rate are consistent with a mechanism involving a rate determining interaction of either the protonated chloramine T ($CATH_2^+$) or H_2OCl^+ with the secondary alcohol giving alkyl hypochlorite followed by a fast decomposition to ketone. The observed order of 1.5 in [HCl] is interpreted by a simultaneous oxidation by molecular chlorine or HOCl and $CATH_2^+$. At low percentages of acetic acid (10% and 20% v/v) the reaction exhibits a second-order dependence on CAT and first-order in alcohol. Dichloramine T (DCT) formed in a disproportionation step is possibly the active oxidant under these conditions. At 50% HOAc(v/v) a fractional order dependence on [Alcohol] and first-order in [CAT] are observed. Further increase in percentage of acetic acid increases the order in alcohol and a limiting value of 1 is reached in 90% HOAc(v/v). These results are indicative of the formation of a complex, the stability of which is solvent dependent. The concentration dependence on alcohol varies in buffered acetic acid in the presence of chloride and the rate law is rationalised by a concurrent oxidation by DCT and molecular chlorine.

CHLORAMINE T (CAT), the sodium salt of *N*-chlorotoluene-*p*-sulphonamide is a two electron oxidant in both acidic and basic media. The redox potential of chloramine T–toluene-*p*-sulphonamide system is pH dependent,[1] decreases with increasing pH, and has a value of 1.139 V at pH 0.65 and 0.499 V at pH 12. Although only a few kinetic investigations are available, mention may be made of the kinetics of oxidation of α-hydroxy-acids,[2] aliphatic aldehydes,[3] aldoses,[4] and primary alcohols [5] by Mushran *et al.* and recent work by Mahadevappa *et al.* on the oxidation of allyl alcohol.[6] The oxidation of primary alcohols were investigated in the pH range 4.0—5.2 and the oxidation of allyl alcohol was catalysed by hydrochloric acid. The reactions showed first-order dependences on [CAT] and [H^+] and the order with respect to reducing substrate was zero. The results were rationalised by the formation of HOCl in a slow step followed by the interaction of HOCl or $ClOH_2^+$ with the alcohol.

In the present work the kinetics of oxidation of secondary alcohols have been studied both in aqueous acid and buffered media in order to elucidate the nature of the oxidising species and mechanism.

RESULTS

Oxidation in Aqueous Acid Medium.—The oxidation of secondary alcohols by CAT proceeds smoothly at 65° in aqueous acid medium. The reaction is found to be cleanly of first order both with respect to time (as evidenced by good fits of log [CAT] *versus* time plots) and concentration [as evidenced by the time order rate coefficient being independent of initial concentration of CAT (Table 1)]. The effect of variation of initial concentration of propan-2-ol (Table 1) and hydrogen ion (Table 2) shows a first-order dependence on the concentration of the alcohol and second-order on the concentration of hydrogen ion. The rate law under these conditions is: rate $= k[CAT][Alcohol][H^+]^2$. Though the oxidation is sluggish under uncatalysed condition the catalysis is independent of the nature of the acid (Table 2).

Effect of Added Salts.—Addition of a neutral salt such as perchlorate does not result in any pronounced effect on the reaction rate (Table 3). On the contrary addition of

---

† Presented at the Annual Convention of Chemists, Indian Chemical Society, 1974.

[1] A. R. V. Murthy and V. S. Rao, *Proc. Indian Acad. Sci.*, 1952, **35***A*, 69.

[2] S. P. Mushran, M. C. Agrawal, and B. Prasad, *J. Chem. Soc.* (*B*), 1971, 1712.

[3] S. P. Mushran and M. C. Agrawal, *Z. Naturforsch.*, 1972, **27b**, 401.

[4] S. P. Mushran and M. C. Agrawal, *J.C.S. Perkin II*, 1973, 762.

[5] S. P. Mushran, R. M. Mehrotra, and R. Sanehi, *J. Indian Chem. Soc.*, 1974, **51**, 594.

[6] D. S. Mahadevappa and H. M. K. Naidu, *Austral. J. Chem.*, 1974, **27**, 1203.

chloride enhances the rate of oxidation by a factor of 40—70 and the rate is nearly first order in chloride concentration (Table 3). Simultaneous addition of chloride and hydrogen ion curiously gives an order of 1.5 in the gross concentration of HCl (Table 2). This result is in keeping with an earlier observation in chlorination of phenols.[7]

TABLE 1

Effect of concentration of reactants at 65°

10[Propan-2-ol]/ M	10^3[CAT]/ M	[H_2SO_4]/ M	10^4k_1/ s^{-1}
0.5	3.60	0.2	0.24
1.5	3.60	0.2	0.58
2.5	3.60	0.2	1.06
4.0	3.60	0.2	1.87
5.0	3.60	0.2	2.06
6.0	3.60	0.2	2.50
4.0	3.98	0.1	1.34
4.0	4.87	0.1	1.35
4.0	6.82	0.1	1.32

Solvent HOAc–H_2O (1 : 4 v/v).

TABLE 2

Effect of hydrogen ion concentration at 65°

[H^+]/M	$10^4k_1/s^{-1}$ for catalysis by			
	H_2SO_4 [a]	$HClO_4$ [b]	HNO_3 [c]	HCl [a]
0.1	1.34	1.23		11.74
0.2	1.87			28.75
0.3		1.60	1.87	48.35
0.5	2.30	1.81	2.39	
1.0	3.07			
1.5	4.61			
2.0	7.15			
2.5	11.98			
3.0	17.72			
3.5	20.93			
4.0	27.20			
5.0	52.28			

[a] [CAT] 3.6 × 10^{-3}M. [b] [CAT] 2.4 × 10^{-3}M. [c] [CAT] 3·2 × 10^{-3}M. Solvent HOAc–H_2O (1 : 4 v/v), [Propan-2-ol] 0.4M.

TABLE 3

Effect of added perchlorate and chloride in aqueous acidic media at 65°

[$HClO_4$]/ M	[H_2SO_4]/ M	[$NaClO_4$] [a]/ M	[NaCl] [b]/ M	10^4k_1/ s^{-1}
0.1		0.1		1.66
0.1		0.2		1.84
0.1		0.3		1.92
0.1		0.4		1.97
	1.0		0.3	115.2
	1.0		0.5	150.7
	1.0		0.8	226.9

[a] [CAT] 3.6 × 10^{-3}M. [b] [CAT] 2.2 × 10^{-3}M, [Propan-2-ol] 0.4M.

Kinetic Isotope Effect.—The ratios of oxidation of propan-2-ol and [2-^{2}H]propan-2-ol are found to be nearly the same {10^5k_1 for propan-2-ol and [2-^{2}H]propan-2-ol 2.37 and 1.92 s^{-1} respectively in HOAc–H_2O (1 : 1 v/v) at 65° in 0.2M-H_2SO_4; [substrate]: 0.02M}. Such a low primary kinetic isotope effect is in contrast to the oxidation of alcohols by molecular halogen under similar conditions.[8,9]

Structural Effects.—The introduction of alkyl substituents on the secondary carbon increases the rate of the reaction (Table 4).

Oxidation in Aqueous Acetic Acid.—While the order with respect to CAT is 1 in acid medium we find a curious dependence on CAT in aqueous acetic acid in the presence of sodium acetate. The order with respect to CAT is 2 in 10 and 20% HOAc (v/v), in the presence of 0.2M-sodium acetate. As the proportion of acetic acid is increased the order with respect to CAT changes to one in 50% HOAc (v/v). The dependence on alcohol proportionately changes from 1 in 10% and 20% HOAc (v/v) to 0.5 in 50% HOAc (v/v). Under these conditions a plot of $1/k_{obs}$ against 1/[ROH] gives a straight line with a finite intercept (Figure 1). Increasing proportions of acetic acid converts the concentration dependence on alcohol to 0.75 at 80% HOAc (v/v) and it reaches a limiting value of unity in

TABLE 4

Substituent effects

Substrate	$10^5k_1/s^{-1}$ at				
	45°	50°	55°	60°	65°
Propan-2-ol	0.55	0.97		2.95	3.51
Butan-2-ol	0.64	1.38	2.00	3.55	5.76
Pentan-2-ol		1.71	2.24		5.76
Octan-2-ol	25.6	34.5	53.7	99.7	135.1
1,3-Dichloropropan-2-ol			0.64 *		

[Alcohol] 0.05M, [CAT] 3.4 × 10^{-3}M, solvent HOAc–H_2O (1 : 1 v/v), [H_2SO_4] 0.2M.

* [1,3-Dichloropropan-2-ol] 0.03M, [H_2SO_4] 1.0M

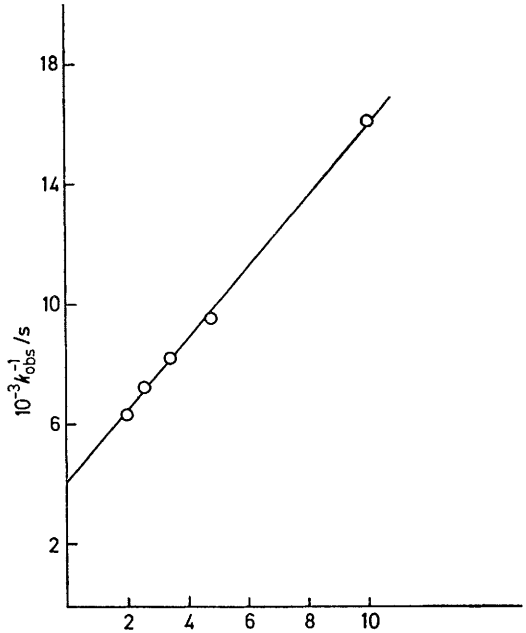

FIGURE 1 Double reciprocal plot of $1/k_{obs}$ against 1/[ROH]: temp. 65°; [NaOAc] 0.2M; solvent HOAc–H_2O (1 : 1 v/v); [ROH] 0.1—0.5M. ROH = Propan-2-ol

---

[7] V. Thiagarajan and V. Balasubramanian, *Internat. J. Chem. Kinetics*, 1975, **7**, 605.

[8] C. G. Swain, R. A. Wiles, and R. F. W. Bader, *J. Amer. Chem. Soc.*, 1961, **83**, 1945.

[9] L. Kaplan, *J. Amer. Chem. Soc.*, 1954, **76**, 4645; 1958, **80**, 2639.

90% HOAc (v/v) (Table 5). Hence the rate law is: $-\mathrm{d}[\mathrm{CAT}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{CAT}]^n[\mathrm{Alcohol}]^{n'}$ where n is either 1 or 2 and $n' = 0.5$—1 depending on the solvent system.

TABLE 5

Effect of variation of propan-2-ol in aqueous acetic acid at 65°

	$10k_2$/l mol^{-1} s^{-1}	10^5k_1/s^{-1}		
[Propan-2-ol]/M	10% HOAc [a]	50% HOAc [b]	80% HOAc [b]	90% HOAc [c]
0.1	1.43	6.15		
0.2	1.91	10.6	2.41	2.08
0.3	2.66	11.9		2.57 *
0.4	4.00	13.7	4.03	4.10
0.5	4.63	15.8	4.60	5.10

[NaOAc] 0.2M.

* [Propan-2-ol] 0.28M.

[a] [CAT] 2.7 × 10^{-3}M. [b] [CAT] 3.4 × 10^{-3}M. [c] [CAT] 3.1 × 10^{-3}M.

Effect of Added Sodium Acetate.—Addition of sodium acetate in the concentration region 0.2—1.6M enhances the rate of oxidation in aqueous acetic acid [90% HOAc (v/v)] where first-order dependences both on CAT and the alcohol are followed. The addition of acetate at very low percentages of acetic acid [10 and 20% HOAc (v/v)] where the order in CAT is 2, does not seem to have any pronounced effect although we observe a slight retardation in rate (Table 6).

TABLE 6

Variation of NaOAc at 65°

[NaOAc]/M	10^5k_1/s^{-1} HOAc–H$_2$O (9 : 1 v/v)	$10k_2$/l mol^{-1} s^{-1} HOAc–H$_2$O (1 : 9 v/v)
0.2	4.10	4.0
0.4	2.74	
0.5		3.57
0.8	4.27	
1.0		3.08
1.2	5.91	
1.5		2.63
1.6	7.42	

[Propan-2-ol] 0.4M. [CAT] 3.0 × 10^{-3}M.

Effect of Added Sodium Chloride.—The addition of chloride in 20% HOAc (v/v) produces a clean second-order dependence on CAT and half-order dependences on both chloride and alcohol. But in 90% HOAc (v/v) the order with respect to CAT is 1 as in the case of added sodium acetate and there is a nearly half-order dependence on the chloride ion concentration. However, the addition of chloride ion increases the rate in both the systems (Table 7).

TABLE 7

Variation of NaCl and TSA at 65°

[NaCl]/M	10^4[TSA]/M	10^3k_1/s^{-1} [a]	$10k_2$/l mol^{-1} s^{-1} [b]
0.2		3.19	2.39
0.25			2.73
0.25	5.85		0.75 *
0.25	11.70		0.50 *
0.3		4.80	2.89
0.4			3.52
0.5			4.00

[a] Solvent HOAc–H$_2$O (9 : 1 v/v). [b] Solvent HOAc–H$_2$O (1 : 4 v/v). [CAT] 3.2 × 10^{-3}M. [Propan-2-ol] 0.4M.

* [CAT] 2.6 × 10^{-3}M.

Effect of Added Toluene-p-*sulphonamide.*—As observed by Higuchi and Hussain [10] in the chlorination of phenols we observe a rate retardation with initially added toluene-p-sulphonamide (TSA) {10^5 k_1 6.19, 3.21, 2.33, and 1.80 s^{-1} for initially added [TSA] of 0, 3.51 × 10^{-4}, 7.02 × 10^{-4}, and 10.53 × 10^{-4}M respectively in HOAc–H$_2$O (1 : 4 v/v) at 65°; [Propan-2-ol] = 0.1M}. Similar rate retardation is noticed when the reaction is conducted in aqueous acetic acid and in the presence of chloride (Table 7).

Effect of Temperature.—The rate data on temperature effects in aqueous acid and aqueous acetic acid media have been studied (Tables 5 and 8). The activation parameters E_a and log A have been calculated from plots of log k_{obs} against $1/T$ and rate coefficients for the total order of the reaction (Table 9).

TABLE 8

Effect of temperature

T/K	$10k_2$/l mol^{-1} s^{-1} [a]	10^5k_1/s^{-1} [b]
318	1.00	1.61
323	1.36	2.79
328	1.82	4.22
333	2.50	6.34
338	4.00	13.65

[a] Solvent HOAc–H$_2$O (1 : 9 v/v). [b] Solvent HOAc–H$_2$O (1 : 1 v/v).
[CAT] 3.4 × 10^{-3}M, [Propan-2-ol] 0.4M, [NaOAc] 0.2M.

TABLE 9

Activation parameters

Substrate	E_a/ kJ mol^{-1}	log A at 65°	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}
Solvent HOAc–H$_2$O (1 : 1 v/v), [H$_2$SO$_4$] 0.2M			
Propan-2-ol	76.9	10.1	−54.6
Butan-2-ol	96.2	13.3	+8.4
Pentan-2-ol	76.9	10.3	−50.4
Octan-2-ol	85.3	13.0	+4.2
Solvent HOAc–H$_2$O (1 : 9 v/v), [NaOAc] 0.2M			
Propan-2-ol	57.5	8.9	−75.6

DISCUSSION

Mechanism of Oxidation in Aqueous Acid Media.—CAT being a strong electrolyte dissociates in aqueous solution to its anion ($p\text{-MeC}_6\text{H}_4\text{SO}_2\bar{\text{N}}\text{Cl}$) which can be protonated by mineral acid. Hydrolysis of protonated CAT yields HOCl in neutral solution. Pryde and Soper [11] have established that HOCl interaction with p-cresol is very fast while CAT itself reacts very slowly. Higuchi and Hussain have already demonstrated that in the pH range 6.35—6.85 the formation of dichloramine T (DCT) is more significant than the formation of HOCl in the chlorination of p-cresol. They propose a slow rate-determining formation of DCT followed by a fast chlorination to account for second-order dependence on [CAT] and a zero order dependence on [p-Cresol]. The observation of a second-order dependence on the hydrogen ion in the present work is in contrast to a first-order dependence on [HCl] in allyl alcohol oxidation.[6] While a zero-order dependence is found in both allyl alcohol and primary alcohols our results show that the reaction has a first-order dependence on the alcohol.

The low primary kinetic isotope effect probably indicates that C–H cleavage in the alcohol oxidation is

---

[10] T. Higuchi and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 549.

[11] L. R. Pryde and F. G. Soper, *J. Chem. Soc.*, 1931, 1510.

not involved in the rate-determining step or has made little progress in the transition state. Increasing proportions of acetic acid increases the rate though the effect is not pronounced. A variation of 10—12% increment in rate for every 10% increment in acetic acid up to 50% aqueous acetic acid and a further increase of another 45% increment in rate for an additional 10% acetic acid are observed and this effect on rate is characteristic of reactions involving ions and dipoles. The results on high acidity when subject to a Bunnett plot[12] of $\log k + H_0$ against $\log a_{\text{H}_2\text{O}}$ gives +4.2 for ω indicating that water functions only as a proton transfer agent and not as a nucleophile.

Based on our observations the kinetically indistinguishable Schemes 1 and 2 for the oxidation of secondary alcohols may be formulated. It is well known that alkyl hypochlorites decompose to ketones by a very fast process.[13-16] The curious 1.5 order in [HCl] may be rationalised by involving a direct interaction of chloride with CAT to generate molecular chlorine which would oxidise the alcohol giving an overall rate expression (1)

$$\underset{(\text{CAT}^-)}{p\text{-MeC}_6\text{H}_4\text{SO}_2\overset{-}{\text{N}}\text{Cl}} + 2\text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(\text{CATH}_2^+)}{p\text{-MeC}_6\text{H}_4\text{SO}_2\overset{+}{\text{N}}\text{H}_2\text{Cl}}$$

$$\text{CATH}_2^+ + {>}\text{CHOH} \xrightarrow[k_2]{\text{slow}} {>}\text{CHOCl} + \text{TSAH}^+$$

$${>}\text{CHOCl} \xrightarrow[k_3]{\text{fast}} {>}\text{C=O} + \text{HCl}$$

SCHEME 1

$$\text{CAT}^- + 2\text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{CATH}_2^+$$

$$\text{CATH}_2^+ + \text{H}_2\text{O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{H}_2\text{OCl}^+ + \text{TSA}$$

$$\text{H}_2\text{OCl}^+ + {>}\text{CHOH} \xrightarrow[k_3]{\text{slow}} {>}\text{CHOCl} + \text{H}_3\text{O}^+$$

$${>}\text{CH–OCl} \xrightarrow[k_4]{\text{fast}} {>}\text{C=O} + \text{HCl}$$

SCHEME 2

$$\text{rate} = k_{\text{obs}}[\text{CAT}] = (k''[\text{H}^+]^2 + k'''[\text{Cl}^-])[\text{CAT}][\text{Alcohol}] \quad (1)$$

$$k_{\text{obs}} = k[\text{HCl}]^2 + k'[\text{HCl}] \quad (2)$$

leading to (2) and (3) where $k = k''$ [alcohol] and $k' = k'''$ [alcohol].

$$k_{\text{obs}}/[\text{HCl}] = k[\text{HCl}] + k' \quad (3)$$

A dual mechanism of this type is supported by the fact that the plot of k_{obs}/[HCl] *versus* [HCl] gives a straight line with a finite intercept (Figure 2). The electron releasing substituents present in the alcohol such as ethyl, n-propyl, butyl *etc.*, increase the rate of oxidation, while two chlorine substituents in 1,3-dichloropropan-2-ol retard the reaction considerably. The effect may be attributed to the influence of these substituents on the availability of the lone pair of electrons on the oxygen of the alcohol for the attack by positive chlorine. However the enhanced reactivity of octan-2-ol is very difficult to explain on the basis of the mechanism proposed. A similar apparently anomalous reactivity of octan-2-ol in the oxidation by bromine was accounted for by release of steric strain on the alcohol in passing to the ketone.[17]

Mechanism of Oxidation in Aqueous Buffered Media.— In aqueous acetate buffer it is known that CAT dimerises to form dichloramine T[10] a more potent oxidising agent than the parent compound. In 10 and 20% HOAc (v/v) in the presence of 0.2M sodium acetate the probable mechanism is given by equations (4) and (5). This mechanistic scheme is consistent with the observed first order in alcohol, second order in CAT, and retardation by TSA.

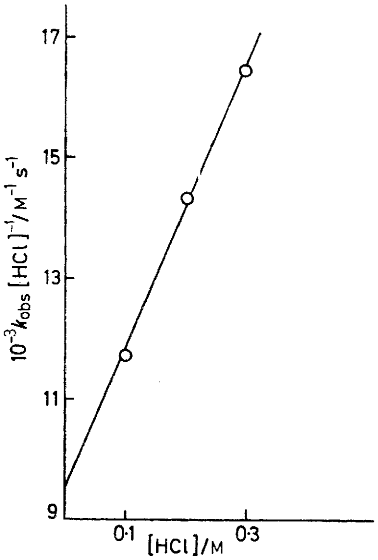

FIGURE 2 Mixed order plot in HCl: temp. 65°; solvent HOAc–H_2O (1 : 4 v/v); [Propan-2-ol] 0.4M; [CAT] 3.6×10^{-3}M

$$2\ \text{CAT} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{DCT} + \text{TSA} \quad (4)$$

$$\text{DCT} + {>}\text{CHOH} \xrightarrow[k_2]{\text{slow}} {>}\text{C=O} + \text{CAT} + \text{HCl} \quad (5)$$

In 50% HOAc (v/v) the fractional order in alcohol and the linearity of $1/k_{\text{obs}}$ *versus* 1/[alcohol] point to a complexation between CAT and alcohol. The stability of the complex decreases with decrease in dielectric constant of the medium. It is reasonable to consider

---

[12] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

[13] F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, 1923, **123**, 3000.

[14] F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, 1924, **125**, 1097.

[15] L. S. Levitt, *J. Org. Chem.*, 1955, **20**, 1297.

[16] L. S. Levitt and E. R. Malinowski, *J. Amer. Chem. Soc.*, 1955, **77**, 4517.

[17] V. Thiagarajan and N. Venkatasubramanian, *Indian J. Chem.*, 1970, **8**, 149.

AcOCl as most potent oxidising agent[18] at 90% HOAc (v/v). This assumption is supported by the fact that increasing concentration of acetate ions increases the rate under such conditions.

The fractional order dependence on chloride and alcohol in 20% HOAc(v/v) may be rationalised by a mixed mechanism involving DCT oxidation of alcohol and oxidation of alcohol by molecular chlorine generated by interaction with chloride ion *in situ*.[19] The rate equation (6) is in accord with the experimental findings.

$$\text{rate} = k'\,[\text{CAT}]^2[\text{Cl}^-] + k''[\text{CAT}]^2[\text{Alcohol}] \quad (6)$$

The probable mechanistic scheme may be represented by (7)—(10).

$$2\ \text{CAT} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{DCT} + \text{TSA} \quad (7)$$

$$\text{DCT} + \text{alcohol} \xrightarrow[k_2]{\text{slow}} \text{ketone} + \text{CAT} + \text{HCl} \quad (8)$$

$$\text{DCT} + \text{Cl}^- \underset{k_{-3}}{\overset{\text{slow}\ k_3}{\rightleftharpoons}} \text{Cl}_2 + \text{CAT}^- \quad (9)$$

$$\text{Cl}_2 + \rangle\text{CHOH} \xrightarrow[k_4]{\text{fast}} \text{products} \quad (10)$$

To conclude, the mechanism of oxidation of alcohols by CAT is likely to proceed through protonated CAT or H_2OCl^+ in acid medium interacting in a slow step with the alcohol to give the alkyl hypochlorite which decomposes in a fast step and by a mixed protonated CAT and molecular chlorine oxidation in the presence of HCl. The oxidising species differ in aqueous acetic acid media and the nature of the oxidant is dependent on the percentage of acetic acid, DCT at low percentages and AcOCl at high percentages of acetic acid are probably more important oxidising species. At intermediate percentages of acetic acid the oxidising species complexes with the alcohol before undergoing decomposition in a slow step. The addition of Cl^- in aqueous acetic acid follows a mixed order rate law indicating simultaneous oxidation by molecular chlorine or HOCl or ClOAc and by DCT.

EXPERIMENTAL

Chloramine T (Societé des usines Chimiques Rhône) was used as such. Liquids were purified by distillation from an all glass apparatus, fractions distilling at the literature b.p.s. being collected. AnalaR grade acetic acid was used after purifying by the usual procedure.[20] Conductivity water was purified by the usual procedure. All the inorganic chemicals used were of AnalaR grade.

Solutions of secondary alcohols were prepared in acetic acid–water mixtures in the presence of suitable concentrations of H_2SO_4, $HClO_4$, HNO_3, or HCl or NaOAc, NaCl, or $NaClO_4$. Both alcohol and CAT solutions were thermostatted for 2 h before each run and 50 ml of each solution were mixed. Portions (5 ml) of the reaction mixture were pipetted out at regular intervals and quenched in 5% KI solution (5 ml). 2N-H_2SO_4 (10 ml) was added and the liberated iodine was titrated against standard thiosulphate to a starch end point.[21] The reactions were carried out under pseudo-first-order conditions. The first-order rate coefficients were evaluated by a numerical method using the integrated rate expression. The rate constants were reproducible to within ± 3%. In the evaluation of rate coefficients the kinetics were followed to nearly three half-lives and the reactions were found to be smooth. Where-ever a second order dependence on CAT was observed the rate coefficients were evaluated from a plot of 1/[CAT] *versus* time, the slope giving the rate constant.

The stoicheiometry (11) of the reaction was obtained by taking a known excess of CAT over alcohol at 65 °C in 1M-H_2SO_4. Acetone was estimated as its 2,4-dinitrophenylhydrazone derivative.

$$\text{Me}_2\text{CHOH} + \text{CAT}^- \longrightarrow \text{TSA} + \text{Me}_2\text{CO} + \text{Cl}^- \quad (11)$$

Preparation of [2-^{2}H]*Propan*-2-*ol*.—[2-^{2}H]Propan-2-ol was prepared by the catalytic reduction of acetone with deuterium obtained by electrolysis of D_2O in a U shaped vessel with nickel electrodes. The reaction flask containing Raney nickel catalyst and acetone was connected to the U shaped vessel with sealed joints. After 12 h g.l.c. analysis of the contents of the flask showed 54% conversion. The mixture was taken out, centrifuged, and the acetone was removed using a Podbeilniak spinning band column. The isotopic purity was checked with n.m.r., i.r., and mass spectra.

We thank Dr. N. Venkatasubramanian, Principal and Head of the Department of Chemistry, Vivekananda College, for permission to work in the laboratory, for providing facilities, and for guidance and discussions. We thank Professor C. N. Pillai, Department of Chemistry, Indian Institute of Technology, Madras for allowing us to prepare [2-^{2}H]propan-2-ol in his laboratory.

[5/132 *Received*, 21*st January*, 1975]

---

[18] C. G. Swain and D. R. Crist, *J. Amer. Chem. Soc.*, 1972, **94**, 3195.

[19] N. S. Srinivasan and N. Venkatasubramanian, *Tetrahedron*, 1974, **30**, 419.

[20] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 1924, 960; 1927, 983.

[21] A. Berka, J. Zyka, and J. Vulterin, ' Newer Redox Titrants, Pergamon Press, New York, 1965, p. 43.