Kinetics & Mechanism of Chloramine-T Oxidation of α-Hydroxy Acids in Perchloric Acid Solution

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The oxidations of glycollic, lactic and α-hydroxybutyric acids by chloramine-T (CAT) in aq. perchloric acid solution have been studied. The reaction rates are found to be of first order with respect to each CAT and the substrate, and are proportional to $[H^+]^2$. The main product of oxidation has been identified as the corresponding aldo or keto acid. The oxidation of glycollic acid exhibits a kinetic isotope effect (k_H/k_D) of 2.73 at 303K. The solvent isotope effect $[k(D_2O)/k(H_2O)]$ is 4.90 at 303K. The rate increases with the introduction of an alkyl group in the organic substrate. A mechanism involving a hydride-ion transfer has been suggested.

WHILE kinetics of chloramine-T oxidation in alkaline media received much attention[1], similar studies in acid solutions are rather scanty. Only the oxidation of some alcohols have been studied[2-4]. There seems to be no report on the oxidation of hydroxy acids in acid solution though the same has been studied in alkaline solution[5]. In this paper are reported the kinetics of chloramine-T (CAT) oxidation of glycollic, lactic and α-hydroxybutyric acids in aq. perchloric acid solution. The mechanistic conclusions are also discussed.

Materials and Methods

Preparation and the specification of the organic compounds have been described earlier[6]. Acetic acid (analar, BDH) was purified by the usual methods before use[7]. Perchloric acid was used as a source of hydrogen ions. D_2O (98%) used was supplied by BARC, Trombay, Bombay. ·All other chemicals used were of AR grade.

Product analysis — The aldo or keto acids formed as the main oxidation products were detected by their characteristic spot tests[8]. Glyoxalic acid as its 2,4-dinitrophenylhydrazone[9] was estimated by the titrimetric method.

Kinetic measurements — The reactions were carried out under pseudo-first order conditions by keeping a large excess of the hydroxy acid over CAT. The temperature was maintained within ±0.1K. The kinetics were followed by estimating the unreacted oxidant iodometrically. The rate constants were evaluated from the plots of log [oxidant] versus time and were reproducible within ±4%. Preliminary experiments showed oxidation to be independent of the ionic strength, hence no attempt was made to keep it constant.

Results and Discussion

Stoichiometry — The excess of CAT was allowed to react with 0.02M glycollic acid at various acidities. In some runs, the glyoxalic acid formed was determined using an excess of glycollic acid.

From the values of CAT and glyoxalic acid consumed and formed the overall reaction corresponded to Eq. (1).

$$CH_2OHCOOH + MeC_6H_4SO_2NCl^- \rightarrow$$
$$CHO.COOH + MeC_6H_4SO_2NH_2 + Cl^- \quad ...(1)$$
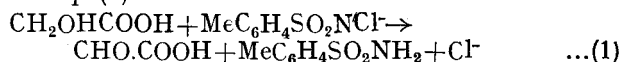
Rate laws — When excess of hydroxy acid was used the rate of disappearance of CAT followed a first order rate law. The reaction followed first order kinetics with respect to [hydroxy acid] (Fig. 1) and was proportional to $[H^+]^2$ (Fig. 2).

The rate laws obtained in this investigation differed from those reported for the oxidation of primary alcohols[2] (in the pH range 4.0-5.2) and allyl alcohol[3].
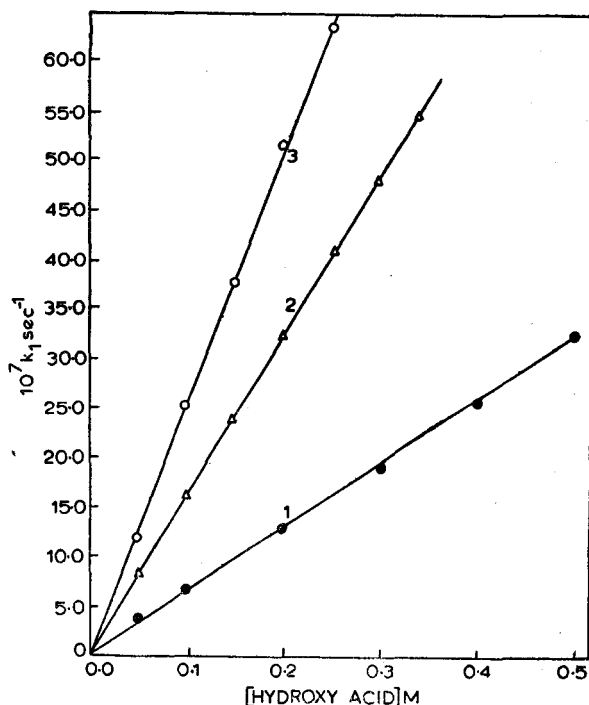
Fig. 1 — Effect of varying [substrate] on the reaction rate at 303K [Curve (1): [CAT] = 0.01M; [H+] = 1.0M; curves (2) and (3): [CAT] = 0.01M; [H+] = 0.5M]
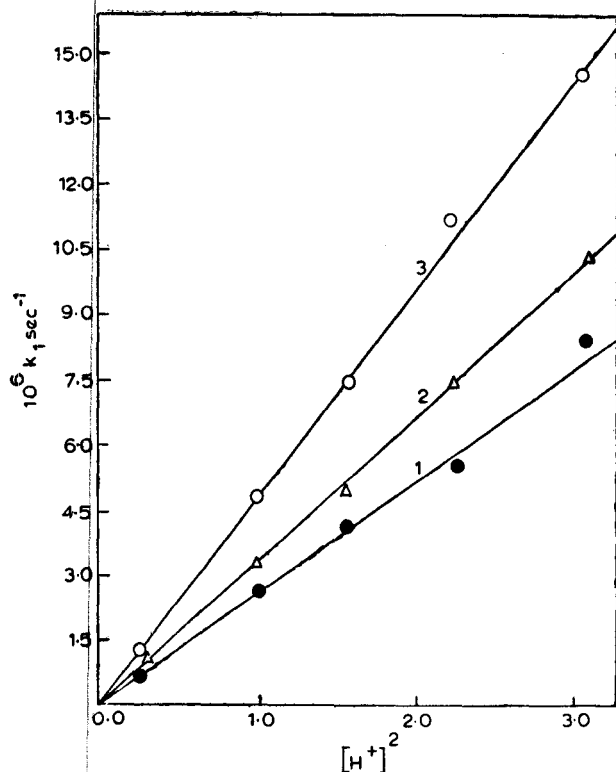
Fig. 2 — Effect of varying [H+] on the reaction rate at 303K [Curve (1): [Glycollic acid] = $0.20M$; [CAT] = $0.01M$; curve (2): [lactic acid] = $0.05M$; [CAT] = $0.01M$; curve (3): [α-hydroxybutyric acid] = $0.05M$; [CAT] = $0.01M$]

TABLE 1 — EFFECT OF TEMPERATURE ON THE OXIDATION OF HYDROXY ACIDS

Acid	$10^6 k$ litre³ mole⁻³ sec⁻¹ at different temperatures (K)				
	298	303	308	313	318
Glycollic	4·35	6·40	9·10	12·8	18·5
Lactic	47·7	65·0	87·0	115·0	155·0
α-Hydroxy- butyric	70·5	95·0	125·0	165·0	218·0

TABLE 2 — OXIDATION OF METHOXYACETIC ACID BY CAT AT 303K

[CAT], M	[Substrate], M	[H+], M	$10^7 k_1$ sec⁻¹
0·01	0·1	1·0	3·50
0·01	0·2	1·0	6·80
0·02	0·4	1·0	14·1
0·02	0·2	0·5	1·75
0·02	0·2	2·0	28·0

$10^6 k = 3.54 \pm 0.08$ litre³ mole⁻³ sec⁻¹.

and those of $-\Delta S^{\ddagger}$ were 152, 176 and 181 J mole⁻¹ K⁻¹ respectively for glycollic, lactic and α-hydroxybutyric acids.

Mechanism — Chloramine-T being a strong electrolyte dissociates[10] into ions in aq. solutions as shown in Eq. (2).

$$RNClNa \rightleftharpoons (RNCl)^- + Na^+ \qquad ...(2)$$

where R = p-MeC₆H₄SO₂. The anion (RNCl)⁻ gets protonated in acid solution to give the free acid. The free acid could not be isolated as it undergoes hydrolysis[3] (Eqs. 3 and 4).

$$(RNCl)^- + H_3O^+ \rightleftharpoons RNHCl + H_2O \qquad ...(3)$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \qquad ...(4)$$
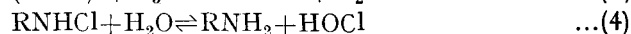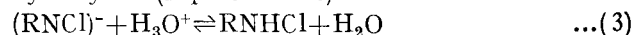
However, the second order dependence on acidity and the magnitude of the solvent isotope effect suggest that a protonated species is involved in the rate-determining step. Thus Eq. (4) is followed by further protonation of HOCl (Eq. 5).
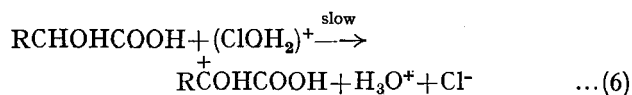
$$HOCl + H_3O^+ \rightleftharpoons (ClOH_2)^+ + H_2O \qquad ...(5)$$
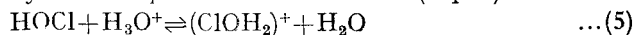
This accords well with the suggestions of earlier workers[3,4] that in the oxidations by CAT in acid solutions, the active oxidizing species is (ClOH₂)⁺. Natarajan and Thiagarajan[4] suggested an alternate mechanism involving (RNH₂Cl)⁺ as the oxidizing species. This is, however, contrary to the observation of Pryde and Soper[11] that the reactions of RNHCl are much slower as compared to those of HOCl. Moreover, the sulphonamido group is not sufficiently basic to accept another proton.

The value of kinetic isotope effect ($k_H/k_D = 2.73$) is close to that obtained earlier in the oxidation of glycollic acid by bromine[6], thereby confirming that the rate-determining step involves the cleavage of C—H bond from the carbon atom bearing the functional group. The marked deuterium isotope effect observed in the present study is at variance from the observation of Natarajan and Thiagarajan[4] who reported $k_H/k_D = 1.23$ in the oxidation of propanol-2 by CAT acid solution.

However, they agreed well with the results of Natarajan and Thiagarajan[4] in the oxidation of propanol-2.

The values of k for the oxidation of glycollic acid and α,α-dideuterioglycollic acid (CD₂OHCOOH) at 303K were 6·40 and 2.35×10^{-7} mole⁻³ litre³ sec⁻¹ respectively. The kinetic isotope effect (k_H/k_D) was found to be 2·73 at 303K.

Glycollic acid was oxidized in 95% D₂O and the value of k was 31.4×10^{-7} litre³ mole⁻³ sec⁻¹ at 303K. The rate constant under similar conditions in water was 6.40×10^{-7} litre³ mole⁻³ sec⁻¹. The solvent isotope effect $[k(D_2O)/k(H_2O)]$ was found to be 4·90.

It is worth noting that oxidation of the hydroxy acids under nitrogen atmosphere failed to induce polymerization of acrylonitrile. Thus a mechanism involving hydrogen abstraction, giving rise to free radicals, is unlikely. In control experiments, with the hydroxy acid being absent, acrylonitrile was not oxidized by CAT.

Solvent effect — It was found that the value of k increased with increasing proportion of acetic acid though the effect was not pronounced. The value of log k did not vary linearly with $1/D$. The rate enhancement was more sharp at lower concentration of the acetic acid than at higher concentration.

Effect of temperature — The oxidation of glycollic, lactic and α-hydroxybutyric acids by CAT was studied at different temperatures (Table 1). The values of $\Delta H^{\ddagger}$ were 56·7, 46·2 and 44·0 kJ mole⁻¹

The comparable ease of oxidation of the glycollic acid and its methyl ether (Table 2) rules out the possibility of a hypochlorite ester intermediate in the present reaction. In chromic acid oxidation, where a chromate ester is initially formed, di-isopropyl ether[12] is oxidized at only fifteen hundredth the rate of propanol-2. An increase in the amount of acetic acid in the solvent brings about a moderate increase in the oxidation rate, and this effect is characteristic of reactions involving positive ion-dipole interactions.

Although the present data are inadequate to evaluate the polar reaction constant, it does show that the rate increases with the introduction of an alkyl group (Table 1). Thus electron-donating groups increase the reaction rate and suggest the formation of an electron-deficient carbon centre in the transition state. The above results support a mechanism involving the transfer of a hydride ion from the hydroxy acid to the oxidant as shown in Eqs. (6) and (7).

$$RCHOHCOOH + (ClOH_2)^+ \xrightarrow{slow}$$
$$\overset{+}{R}COHCOOH + H_3O^+ + Cl^- \qquad \ldots(6)$$

$$\overset{+}{R}COHCOOH \xrightarrow{fast} RCOCOOH + H^+ \qquad \ldots(7)$$

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