Effect of Chloride Ion on Kinetics of Oxidation of Threonine by Chloramine-T in Acid Medium

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Effect of chloride on the kinetics of oxidative decarboxylation and deamination of threonine (Thr) by chloramine-T (CAT) has been studied in $HClO_4$ medium at 303 K. The reaction has been investigated over a wide range of $[H^+]$ (0.001-0.2 mol dm^{-3}) both in the presence and absence of Cl^-. It has been observed that the catalytic effect of Cl^- is $[H^+]$ dependent. The effect is more pronounced at $[H^+] > 0.03$ mol dm^{-3}. The change of either $[H^+]$ or $[Cl^-]$ has no effect on the kinetic order in [CAT]. But the order in [Thr], $[H^+]$ and $[Cl^-]$ change with the $[H^+]$ and $[Cl^-]$. The effects of added reaction product, and variation of ionic strength and dielectric constant of the medium on the rate have been investigated. Activation parameters have also been computed. Rate laws in agreement with the experimental results have been deduced by proposing appropriate mechanistic schemes.

In continuation of our earlier work[1] on the effect of chloride ion on the kinetics of decarboxylation and deamination of histidine by chloramine-T (CAT) in H_2SO_4 medium, we report herein the results of title investigation in $HClO_4$ medium.

Stock solutions of chloramine-T (Fluka, AG) and threonine (Thr) (SRL, India) were prepared in doubly distilled water and standardised by methods reported elsewhere. All other reagents used were of AR grade. Preliminary investigations showed that ionic strength of the medium had no significant effect on the rate.

The kinetic measurements were made under pseudo-first order conditions ([Thr] $\gg$ [CAT]). The progress of the reaction was monitored for two half-lives by iodometric estimation of unreacted oxidant at regular time intervals. The pseudo-first order rate constants were reproducible within $\pm 4\%$.

The stoichiometry of reaction was determined under the conditions [Thr] $\gg$ [CAT] at different $[H^+]$ and $[Cl^-]$. The products were identified to be NH_3, CO_2, RNH_2 ($R = CH_3C_6H_4SO_2$) and the corresponding aldehyde by standard tests. The stoichiometry could be represented by Eq. (1).

$$CH_3CH(OH)\ CH(NH_2)\ COOH + (RNCl)^-Na^+$$
$$+ H_2O$$
$$\rightarrow CH_3CH(OH)CHO + RNH_2 + NH_3 + CO_2$$
$$+ Na^+ + Cl^- \quad ...(1)$$

Kinetics of Thr-CAT reactions were investigated over a wide range of $[H^+]$ (0.001 to 0.2 mol dm^{-3}) and $[Cl^-]$ (0.0 to 0.2 mol dm^{-3}), (Table 1). The orders in $[H^+]$, [S] and $[Cl^-]$ (Table 2) were determined from the log-log plots of k_{obs} versus the concentration of the respective species. The plots of log ($[CAT]_0/[CAT]$) versus time were linear in all the cases showing first order dependence in [CAT]. Addition of the reaction product, PTS, or the variation of ionic strength of the medium had no significant effect on the rate in all ranges of $[H^+]$ and $[Cl^-]$. Decrease in dielectric constant of the medium decreased the rate both in the presence and absence of Cl^-. The activation parameters computed from the Arrhenius plots are given in Table 3.

Our earlier results[1] on the effect of Cl^- on the kinetics of decarboxylation and deamination of histidine by CAT in H_2SO_4 revealed that the reaction orders were the same both in the absence and presence of Cl^- at low $[H^+]$, namely, second order in [CAT], first order in [His] and inverse first order in $[H^+]$. While in the presence of Cl^- at high $[H^+]$ the reaction was first order in [CAT], zero order in [His] and fractional order each in $[H^+]$ and $[Cl^-]$. In the present case the reaction was first order in [CAT], zero order in [Thr] and zero order in $[H^+]$ in the absence of Cl^- at low $[H^+]$. But in the absence of Cl^- at high $[H^+]$ and in the presence of Cl^- at both low and high $[H^+]$ the orders changed to fractional order in [Thr] and inverse fractional order in $[H^+]$ while the order in [CAT] remained the same.

In acid solutions of CAT (RNClNa, where R $= CH_3C_6H_4SO_2$), $RNHCl$, $RNCl_2$, HOCl and H_2OCl^+ are the probable oxidising species[2-5] in the absence of Cl^- and Cl_2 in the presence of Cl^-. Threonine $[CH_3CHOHCH(NH_2)COOH, S]$ exists in cationic form (SH^+)[6] in strong acid solutions.

The observed kinetics (Table 2) in the absence of Cl^- at low $[H^+]$ (< 0.03 mol dm^{-3}) may be explained by a mechanism shown in Scheme 1. The hypochlorous acid formed in a slow step interacts with the substrate in a fast step to give the products.

$$RNHCl + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNH_2 + HOCl$$
$$k_1 \text{ reaction being slow}$$

$$HOCl + S \overset{k_2}{\rightarrow} S' + H_2O \quad (fast)$$

$$S' + H_2O \overset{k_3}{\rightarrow} Products \quad (fast)$$

Scheme 1

Table 1—Effect of [Reactant] on the Rate in the Presence and Absence of Cl⁻ at Different [Acid] (Temp: 303 K)

[Cl⁻] (mol dm⁻³)	10^2[Thr] (mol dm⁻³)	$10^4 k_{obs}$, s⁻¹ at [HClO₄] (mol dm⁻³)			10^3[CAT] (mol dm⁻³)	$10^4 k_{obs}$, s⁻¹ at [HClO₄] (mol dm⁻³)		
		0.005	0.05	0.1		0.005	0.05	0.1
0.0					0.5	4.7		
	1.0	4.8	1.69	1.52	1.0	4.8	2.4	2.1
	2.0	4.8	2.63	2.1	2.0	4.8	2.63	2.1
	5.0	4.6	3.84	2.63	3.0	4.8	2.7	2.3
	7.5	4.6	4.21	2.70	4.0	4.8	2.6	2.4
	10.0	4.7	4.65	2.75	5.0	4.9	2.7	2.4
0.05	1.0	10.5	3.5	3.45	0.5	12.0	5.0	5.1
	2.0	12.6	5.4	5.3	1.0	12.8	5.4	5.2
	5.0	15.2	8.7	6.6	2.0	12.6	5.4	5.3
	7.5	15.9	10.1	8.3	3.0	12.2	5.6	5.3
	10.0	16.6	11.8	8.8	4.0	12.6	5.6	5.3
					5.0	12.3	5.6	5.5
0.1	1.0	11.9	—	4.55	0.5	15.0	6.9	6.8
	2.0	15.5	7.5	7.3	1.0	15.3	7.4	7.3
	5.0	19.5	9.6	10.9	2.0	15.5	7.5	7.3
	7.5	21.7	13.5	12.5	3.0	15.6	7.5	7.4
	10.0	22.2	15.4	13.1	4.0	15.7	7.4	7.5
					5.0	15.6	7.6	7.5
0.2	1.0	12.5	7.7	5.5	0.5	15.8	10.4	8.6
	2.0	16.0	10.7	8.7	1.0	15.7	10.8	8.6
	5.0	20.0	14.5	13.8	2.0	16.0	10.7	8.7
	7.5	22.7	17.4	16.6	3.0	15.9	10.82	8.7
	10.0	25.0	19.5	18.3	4.0	16.0	11.0	9.0
					5.0	16.2	11.2	9.0

Table 2—Kinetic Data for the Oxidation of Threonine (Thr) by Chloramine T[a] under Varying Conditions of Acidity and [Cl⁻]

[Cl⁻] (mol dm⁻³)	Orders observed in						
	[H⁺]		[Thr] at [H⁺] (mol dm⁻³)			[Cl⁻] at	
	0.004-0.03 (mol dm⁻³)	0.03-0.2 (mol dm⁻³)	0.005	0.05	0.1	[H⁺] (mol dm⁻³)	Order
0.0	0	−0.51	0	0.45	0.27	0.005	0.12
0.05	−0.25	−0.06	0.19	0.42	0.34	0.05	0.38
0.1	−0.37	−0.12	0.27	0.44	0.35	0.10	0.38
0.2	−0.20	−0.20	0.31	0.42	0.39	0.20	0.35

[a]rate showed first order kinetics in [CAT]

Table 3—Activation Parameters for the Oxidation of Threonine by Chloramine-T at Different [H⁺] and [Cl⁻]

[H⁺] (mol dm⁻³)	0.005	0.05	0.05	0.05	0.1
[Cl⁻] (mol dm⁻³)	0.0	0.0	0.1	0.2	0.1
Parameter					
E_a (kJ mol⁻¹)	75.4	56.6	70.2	68.1	74.5
log A	9.68	6.06	8.94	8.76	9.7
ΔS‡ (JK⁻¹)	−68.1	−137.4	−82.2	−85.6	−65.5
ΔH‡ (kJ mol⁻¹)	72.9	52.7	66.1	67.0	72.4
ΔG‡ (kJ mol⁻¹)	93.5	94.3	91.0	92.9	92.2

The rate law in accordance with Scheme 1 is given by Eq. (2).

$$-\frac{d[CAT]}{dt} = k_1[CAT][H_2O] \qquad ...(2)$$

Scheme 2 and rate law (3) account for the first order in [CAT], fractional order in [S] and inverse fractional order in [H⁺] observed in the absence of Cl⁻ at high [H⁺].

$$SH^+ \overset{K_4}{\rightleftharpoons} S + H^+ \text{ (fast)}$$

$$S + RNHCl \overset{K_5}{\rightleftharpoons} X \text{ (fast)}$$

$$X \overset{k_6}{\rightarrow} S' + RNH_2 \text{ (slow)}$$

$$S' + H_2O \overset{k_7}{\rightarrow} \text{Products (fast)}$$
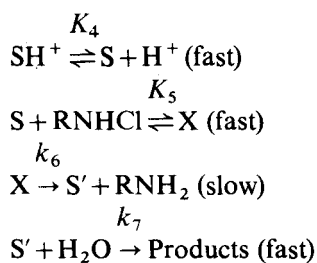
Scheme 2

$$-\frac{d[CAT]}{dt} = \frac{K_5 k_6 [CAT]_0 [S]}{1 + K_5 [S]} \qquad \ldots(3)$$

or

$$k_{obs} = \frac{K_5 k_6 [S]}{1 + K_5 [S]} = \frac{K_4 K_5 k_6 [SH^+]}{[H^+] + K_4 K_5 [SH^+]} \qquad \ldots(4)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{K_5 k_6 [S]} + \frac{1}{k_6} = \frac{[H^+]}{K_4 K_5 k_6 [SH^+]} + \frac{1}{k_6} \qquad \ldots(5)$$

The plots of $1/k_{obs}$ versus $1/[S]$ and $1/k_{obs}$ versus $[H^+]$ were linear with intercepts on the ordinate (Fig. 1) in accordance with the rate law (5) and Scheme 2. The formation equilibrium constant, $K_5(= 40.8$ dm^3 mol^{-1}) and decomposition constant of the complex k_6 $(= 5.9 \times 10^{-4}$ s$^{-1})$ were calculated from the former plot.

The first order in [CAT], fractional order in [S] and slight inverse dependence of rate on $[H^+]$ observed in the presence of Cl$^-$ at low $[H^+]$ can be interpreted on the basis of the mechanism given in Scheme 3. In Scheme 3 step (ii) is relatively a fast step than step (iv), in contrast to the corresponding rates in Scheme 1. This is supported by the fact that the rate constants under these conditions are 3-4 times the rate constants in the absence of Cl$^-$.

$$SH^+ \overset{K_4}{\rightleftharpoons} S + H^+ \text{ (fast)} \qquad \ldots(i)$$

$$RNHCl + Cl^- \overset{K_8}{\rightleftharpoons} Y \text{ (fast)} \qquad \ldots(ii)$$

$$Y + H_2O \overset{k_9}{\rightarrow} RNH_2 + HOCl + Cl^- \text{ (fast)} \qquad \ldots(iii)$$

$$HOCl + S \overset{K_{10}}{\rightleftharpoons} Y' \text{ (fast)} \qquad \ldots(iv)$$

$$Y' \overset{k_{11}}{\rightarrow} S' + H_2O \text{ (slow)} \qquad \ldots(v)$$

$$S' + H_2O \overset{k_{12}}{\rightarrow} \text{Products (fast)} \qquad \ldots(vi)$$
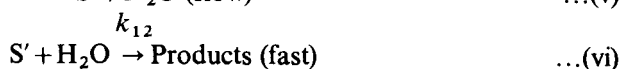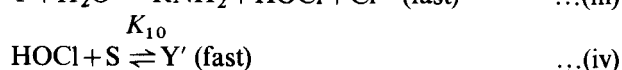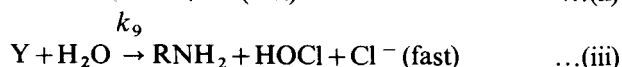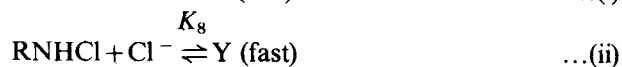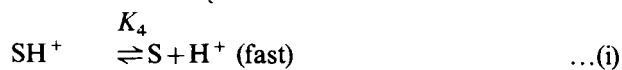
Scheme 3

The rate law (6), compatible with Scheme 3, has been deduced by applying steady state approximation to the intermediates Y and Y'.

$$-\frac{d[CAT]}{dt} = \frac{K_8 K_{10} k_9 k_{11} [CAT][S][Cl^-][H_2O]}{1 + K_8[Cl^-] + K_{10}[S] + K_8 K_{10}[S][Cl^-]} \qquad \ldots(6)$$

or

$$k_{obs} = \frac{K_8 K_{10} k_9 k'_{11} [S][Cl^-]}{1 + K_8[Cl^-] + K_{10}[S] + K_8 K_{10}[S][Cl^-]}$$

$$= \frac{K_4 K_8 K_{10} k_9 k'_{11} [SH^+][Cl^-]}{\{[H^+] + K_8[Cl^-][H^+] + K_4 K_{10}[SH^+]}$$

$$+ K_4 K_8 K_{10}[SH^+][Cl^-]\} \qquad \ldots(7)$$

(where $k'_{11} = k_{11}[H_2O]$)

or

$$\frac{1}{k_{obs}} = \left\{ \frac{1}{K_{10} k_9 k'_{11}} + \frac{1}{K_8 K_{10} k_9 k'_{11} [Cl^-]} \right\} \frac{1}{[S]}$$

$$+ \frac{1}{K_8 k_9 k'_{11} [Cl^-]} + \frac{1}{k_9 k'_{11}} \qquad \ldots(8)$$

The plot of $1/k_{obs}$ versus $1/[S]$ was linear with an intercept on the ordinate (Fig. 1) and the equilibrium constant K_{10} (= Intercept/slope) was calculated to be 142.5, 92.6 and 78.1 dm^3 mol^{-1} at $[Cl^-] = 0.05$, 0.1 and 0.2 mol dm^{-3} respectively.

For $[Cl^-]$ dependence rate law (7) becomes

$$\frac{1}{k_{obs}} = \left\{ \frac{1}{K_8 k_9 k'_{11}} + \frac{1}{K_8 K_{10} k_9 k'_{11} [S]} \right\} \frac{1}{[Cl^-]}$$

$$+ \frac{1}{K_{10} k_9 k'_{11} [S]} + \frac{1}{k_9 k'_{11}} \qquad \ldots(9)$$

The plot of $1/k_{obs}$ versus $1/[Cl^-]$ was also linear (Fig. 1) with $K_8 = 335$ dm^3 mol^{-1}.

The kinetic results observed in the presence of Cl$^-$ at high $[H^+]$ (> 0.03 mol dm^{-3}) can be explained by a mechanism resulting from the replacement of RNHCl and HOCl in Scheme 3 by RNH$_2$Cl and Cl$_2$ respectively. The resulting rate laws are similar to Eqs 6-9. The $1/k_{obs}$ versus $1/[S]$ and $1/k_{obs}$ versus $1/[Cl^-]$ plots were linear (Fig. 1) even under these conditions. From the slopes and intercepts of these plots the equilibrium constants K_8 and K_{10} were calculated to be: $K'_{10} = 33.1$, 32.6 and 39.0 ($[H^+] = 0.05$ mol dm^{-3}) and 48.4, 34.5 and 28.4 dm^3 mol^{-1} ($[H^+] = 0.1$ mol dm^{-3}) at $[Cl^-] = 0.05$, 0.1 and 0.2 mol dm^{-3}
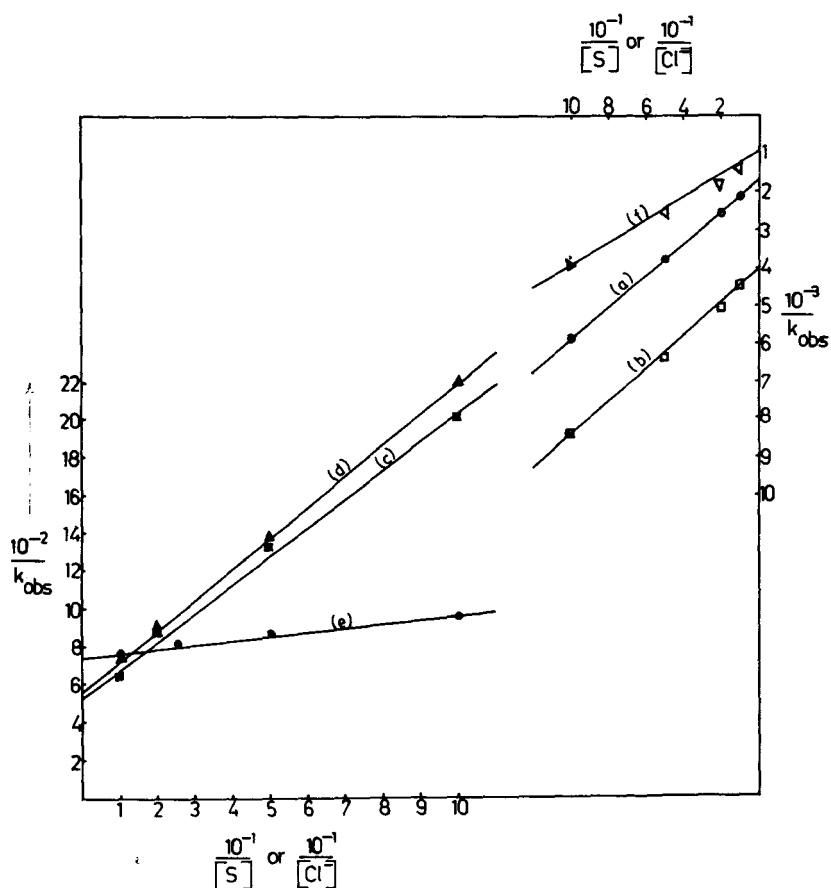
Fig. 1—Plots of $1/k_{obs}$ versus $1/[S]$, $10^3[CAT]_0 = 2.0$ mol dm^{-3}, 10^2 [Thr]$_0 = 2.0$ mol dm^{-3}, Temp $= 303$ K; (a) [H$^+$] $= 0.05$ mol dm^{-3}, [Cl$^-$] $= 0.0$; (b) [H$^+$] $= 0.005$ mol dm^{-3}, [Cl$^-$] $= 0.1$ mol dm^{-3}; (c) [H$^+$] $= 0.05$ mol dm^{-3}, [Cl$^-$] $= 0.1$ mol dm^{-3}; (d) [H$^+$] $= 0.1$ mol dm^{-3}, [Cl$^-$] $= 0.1$ mol dm^{-3} and plots of $1/k_{obs}$ versus $1/[Cl^-]$, $10^3[CAT]_0 = 2.0$ mol dm^{-3}, $10^2[Thr]_0 = 2.0$ mol dm^{-3}, Temp $= 303$ K; (e) [H$^+$] $= 0.005$ mol dm^{-3}; (f) [H$^+$] $= 0.1$ mol dm^{-3}

respectively; $K'_8 = 37.2$, 32.3 and 53.8 dm^3 mol^{-1} at [H$^+$] $= 0.05$, 0.1 and 0.2 mol dm^{-3} respectively.

The observed negligible effect of added reaction product, PTS and of varying ionic strength of the medium on the rate[7-9] are in agreement with proposed reaction schemes. The observed decrease of rate with decrease in dielectric constant of the medium both in the presence and absence of [Cl$^-$] at low and high [H$^+$] are in conformity with Amis' and other theories[7-9].

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