

Kinetics & Mechanism of Chloride Ion Catalysed Oxidation of Arginine by Chloramine-T

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Kinetics of chloride ion catalysed oxidation of arginine by chloramine-T has been investigated in perchloric acid medium at 303 K. Due to the participation of different reactive species of the oxidant in the rate-determining steps the kinetics of chloride ion catalysed oxidations are different from those of uncatalysed oxidations.

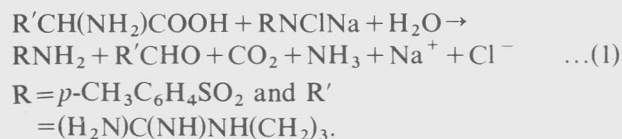
As a part of our kinetic and mechanistic investigations on the reactions of N-halo-N-metallo reagents with a variety of organic reductants, in general, and those involving amino acids, in particular¹⁻⁶, we report herein the results of chloride ion catalysed oxidation of L-arginine (Arg) by chloramine-T (CAT) in perchloric acid medium at 303 K. We have observed that the reaction orders in the presence of and absence of chloride ion are different due to the participation of Cl^+ of the oxidant in different forms under different reaction conditions. Hence determination of orders of reaction with respect to $[\text{CAT}]$, $[\text{substrate}]$ and $[\text{H}^+]$ in the absence of Cl^- to explain the kinetic data in the presence of Cl^- is not justified.

Materials and Methods

Chloramine-T (Fluka AG) was purified by standard method and its aqueous solution was standardised by the iodometric method and stored in dark-coloured bottles. Chromatographically pure L-arginine (Sisco Research Laboratories, India) was assayed by the acetous perchloric acid method⁷. An aqueous solution of this substrate (0.2 mol dm^{-3}) was prepared. Triply distilled water was used throughout the investigations. All other reagents used were of AR grade.

The reactions were carried out in glass stoppered pyrex boiling tubes. A measured amount of CAT solution, thermally equilibrated at the required temperature, was added to a mixture of appropriate amounts of arginine, acid and perchlorate, pre-equilibrated at the same temperature. The progress of the reaction was monitored for two half-lives by iodometric estimation of unreacted CAT at regular intervals of time. The pseudo-first order rate constants were reproducible within $\pm 3\%$.

Stoichiometric runs with varying ratios of CAT to arginine in the presence of $0.01\text{-}0.3 \text{ mol dm}^{-3} \text{ HClO}_4$ and $0.1 \text{ mol dm}^{-3} \text{ NaCl}$ were equilibrated at 303 K for 24 hr. The products were identified to be ammonia, CO_2 , *p*-toluenesulphonamide and the respective aldehyde. The observed stoichiometry can be represented by Eq. (1).



Ammonia and CO_2 were quantitatively estimated by standard methods.

Results

At constant $[\text{HClO}_4]$ and $[\text{chloride}]$ with several fold excess of arginine, plots of $\log ([\text{CAT}]_0/[\text{CAT}])$ versus time were linear at least upto 75% of the reaction (Table 1). At constant $[\text{CAT}]$ and $[\text{Arg}]$ an increase in $[\text{H}^+]$ upto 0.05 mol dm^{-3} had no effect on the rate (Table 1). The rate increased with increase in $[\text{H}^+]$ in the range $0.05\text{-}0.15 \text{ mol dm}^{-3}$ and remained constant thereafter (Table 1). Plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ in the concentration range $0.05\text{-}0.15 \text{ mol dm}^{-3}$ was linear with unit slope showing a first order dependence on $[\text{H}^+]$.

The rate was independent of $[\text{Arg}]$ both at low and high acid concentration ranges (Table 1). At low $[\text{acid}]$ the rate was independent of $[\text{Cl}^-]$ but the rate increased at high $[\text{acid}]$ (Table 1). The plot of $\log k_{\text{obs}}$ versus $\log [\text{Cl}^-]$ was linear with a slope of 0.82 showing a fractional order dependence of rate on $[\text{Cl}^-]$.

Table 1—Effect of Varying [H⁺], [Oxidant], [Substrate] and [Cl⁻] on Chloride Ion Catalysed Oxidation of Arginine by CAT at 303 K.

10 ² [H ⁺] ^a (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)	10 ³ [CAT] ₀ (mol dm ⁻³)	10 ² [Arg] ₀ (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)		10 ² [Cl ⁻] (mol dm ⁻³)		10 ⁴ k _{obs} (s ⁻¹)	
				at [H ⁺] ^b	(mol dm ⁻³)	at [H ⁺] ^c	(mol dm ⁻³)		
				0.01	0.05			0.01	0.05
0.20	7.01	2.0	1.0	5.83	7.57	1.0		7.38	—
0.50	7.10	2.0	1.5	—	7.65	2.0		—	2.56
0.75	7.31	2.0	2.0	7.11	7.22	2.5		7.16	—
1.00	7.11	2.0	2.5	—	7.36	5.0		7.05	4.64
2.00	7.68	2.0	3.0	7.34	7.67	7.5		7.11	6.41
5.00	7.22	2.0	3.5	—	7.58	10.0		7.11	7.22
6.00	8.45	2.0	4.0	7.46	7.44	15.0		7.22	11.70
8.00	11.17	2.0	5.0	7.23	—	20.0		7.18	14.13
10.00	13.35	2.0	10.0	7.53	—	—		7.18	—
15.00	14.10	1.0	2.0	7.68	7.28				
20.00	13.90	2.0	2.0	7.20	7.22				
—	—	2.5	2.0	—	7.25				
—	—	3.0	2.0	7.43	7.41				
—	—	3.5	2.0	—	7.38				
—	—	4.0	2.0	7.31	7.91				
—	—	5.0	2.0	6.98	—				

(a) 10³[CAT]₀=2.0 mol dm⁻³, 10²[Arg]₀=2.0 mol dm⁻³, [Cl⁻]=0.1 mol dm⁻³, μ=0.5 mol dm⁻³. (b) [Cl⁻]=0.1 mol dm⁻³, μ=0.5 mol dm⁻³; and (c) 10³[CAT]₀=2.0 mol dm⁻³, 10²[Arg]₀=2.0 mol dm⁻³, μ=0.5 mol dm⁻³.

Table 2—Effect of Varying Ionic Strength, *p*-Toluenesulphonamide Concentration, Dielectric Constant and Temperature on Chloride Ion Catalysed Oxidation of Arginine by CAT^a

μ ^b (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)		Temp ^c (K)	10 ⁴ k _{obs} (s ⁻¹)		10 ³ [RNH ₂] ^d (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)		%	D ^d	10 ⁴ k _{obs} (s ⁻¹)	
	at [H ⁺]	(mol dm ⁻³)		at [H ⁺]	(mol dm ⁻³)		at [H ⁺]	(mol dm ⁻³)			Methanol	at [H ⁺]
	0.01	0.05		0.01	0.05		0.01	0.05			0.01	0.05
0.3	7.01	7.10	293	1.48	3.16	0.0	7.11	7.20	0	76.58	7.11	7.20
0.5	7.10	7.10	303	7.11	7.22	2.0	7.16	7.22	10	72.09	8.30	6.43
0.8	7.10	7.12	308	15.35	10.75	3.0	7.04	7.28	20	67.60	10.37	5.82
0.9	7.11	7.22	313	30.71	16.79	5.0	7.01	7.31	30	63.10	13.16	5.48
1.15	7.20	7.24	318	61.41	23.20				35	60.86	17.06	5.12
1.40	7.57	7.10										

(a) 10³[CAT]₀=2.0 mol dm⁻³, 10²[Arg]₀=2.0 mol dm⁻³, [Cl⁻]=0.1 mol dm⁻³; (b) temp.=303 K; (c) μ=0.5 mol dm⁻³; and (d) temp.=303 K; μ=0.5 mol dm⁻³.

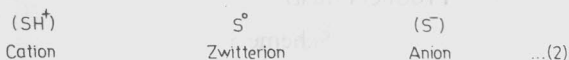
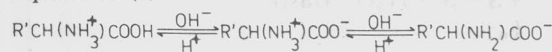
Table 3—Kinetic and Thermodynamic Parameters for Oxidation of L-Arginine by CAT in HClO₄ Medium

Order (n) in	[H ⁺] (mol dm ⁻³)		Thermodynamic parameter	[H ⁺] (mol dm ⁻³)	
	0.01	0.05		0.01	0.05
[CAT] ₀	1.0	1.0	Log <i>A</i>	16.87	7.90
[Arg] ₀	0.0	0.0	<i>E</i> _a (kJ mol ⁻¹)	115.50	63.80
[H ⁺]	0.0	1.0	Δ <i>H</i> [‡] (kJ mol ⁻¹)	108.20	61.30
[Cl ⁻]	0.0	0.82	Δ <i>S</i> [‡] (JK ⁻¹)	+75.90	-94.60
			Δ <i>G</i> [‡] (kJ mol ⁻¹)	85.20	89.90

The rate was unaffected by the change in ionic strength or the addition of the reaction product, *p*-toluenesulphonamide (Table 2). Decrease in dielectric constant of the medium increased the rate at low [acid] while it decreased at high [acid] (Table 2). The reactions were studied at different temperatures and the activation parameters were computed in both [H⁺] ranges (Table 3).

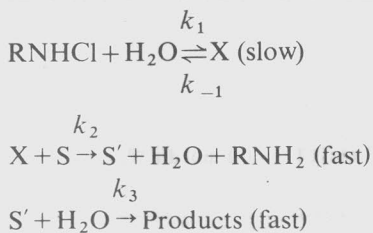
Discussion

Arginine exists in different forms as the medium is changed from acidic to alkaline, in accordance with the equilibria (2).



Chloramine-T (RNClNa where R = *p*-CH₃C₆H₄SO₂) behaves as a strong electrolyte⁸ in aqueous solutions and depending upon the pH of the medium it furnishes different types of reactive species¹. The probable oxidising species in acidified CAT solutions are RNHCl, RNCl₂, HOCl and possibly H₂OCl⁺ in the absence of Cl⁻ and Cl₂ in the presence of Cl⁻.

The following mechanisms (Schemes 1-3) are proposed to account for the observed kinetics (Table 3) of chloride ion catalysed oxidation of arginine in perchloric acid medium. At low [acid] the rate law is independent of [Arg], [H⁺] and [Cl⁻]. This indicates the participation of only the oxidant in the rate-determining step. Under these conditions, the reaction follows the mechanism shown in Scheme 1.

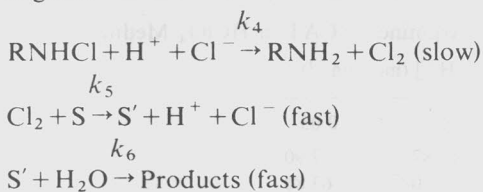


Scheme 1

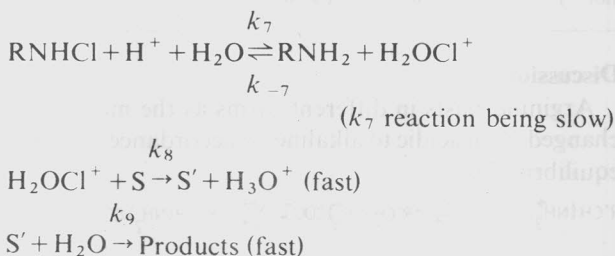
The rate law in accordance with Scheme 1 is given by Eq. (3)

$$-\frac{d[\text{CAT}]}{dt} = k_1[\text{CAT}][\text{H}_2\text{O}] = k'_1[\text{CAT}] \quad \dots(3)$$

At high [HClO₄] the observed kinetics of first order each in [CAT] and [H⁺] and fractional order in [Cl⁻] can be explained by considering the reaction to follow the pathways, shown in Schemes 2 and 3, to varying degrees.



Scheme 2



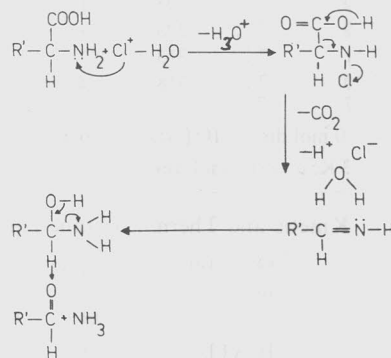
Scheme 3

The combined rate law in accordance with Schemes 2 and 3 is given by Eq. (4).

$$\begin{aligned} -\frac{d[\text{CAT}]}{dt} &= k_4[\text{CAT}][\text{H}^+][\text{Cl}^-] \\ &+ k_7[\text{CAT}][\text{H}^+][\text{H}_2\text{O}] \\ k_{\text{obs}} &= -\frac{d \ln[\text{CAT}]}{dt} = [\text{H}^+] \{k_4[\text{Cl}^-] + k_7[\text{H}_2\text{O}]\} \quad \dots(4) \end{aligned}$$

The plot of *k*_{obs} versus [Cl⁻] is linear with an intercept on the ordinate supporting the combined rate law and the assumption that the reaction proceeds by two pathways represented by Schemes 2 and 3. From the slope and intercept, the rate constants *k*₄ and *k*₇ were calculated at constant [H⁺] { [H₂O] = $\frac{1000}{18} = 55.56$ mol dm⁻³ } The computed *k*₄ and *k*₇ values were used to predict the rate constants at different [H⁺] (Table 4). There is good agreement between the predicted and observed values supporting the proposed mechanisms (Schemes 2 and 3).

The detailed mechanism of chloride ion catalysed oxidation of arginine by CAT is shown in Scheme 4. The N-chloro intermediate (S') formed⁹⁻¹¹ by electrophilic attack by Cl₂ or RNHCl or H₂OCl⁺ on the nitrogen atom of the amino acid undergoes decarboxylation and elimination processes in fast steps to give the reaction products.



Scheme 4

Table 4—Comparison of Calculated and Observed Values of Rate Constants on Varying [H⁺]

[H ⁺] (mol dm ⁻³)	10 ⁴ <i>k</i> _{obs} (s ⁻¹)	10 ⁴ <i>k</i> _{calc} ^a (s ⁻¹)
0.05	7.22	7.61
0.06	8.45	9.14
0.08	11.17	12.19
0.10	13.35	15.24

^aFrom Eq. (4).

In most cases the effect of dielectric constant on the rate of reaction¹²⁻¹⁴ is in conformity with the Amis' theory¹², i.e. for the limiting case of zero angle of approach between two dipoles or an ion-dipole system, a plot of log k_{obs} versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or between two dipoles.

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