Kinetics of Alkaline Chloramine-T Oxidation of Arginine Monohydrochloride With and Without Catalytic Action of Cu(II) Ion

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The kinetics of uncatalysed and Cu(II) catalysed oxidation of arginine monohydrochloride was investigated. Both reactions follow a singular order dependence each in oxidant and substrate. An inverse order dependence is reported with the alkali concentration. A plot of observed rate constant versus Cu(II) concentrations Cu(II) $\leq 2.0 \times 10^{-5} M$ is linear; from the intercept the rate constant for the uncatalysed pathway was calculated. However, at high copper ion concentrations i.e. Cu(II) $> 2.0 \times 10^{-5} M$ a fixed value of rate constant was found for all catalyst concentrations. Added neutral salts show an insignificant effect on the reaction rate. Mechanisms were proposed for both cases and rate expressions were derived by applying steady state assumptions.

(Keywords: Arginine; Catalysis; Kinetics; Mechanism; Oxidation)

Die Kinetik der alkalischen Chloramin-T-Oxidation von Arginin-monohydrochlorid mit und ohne Cu(II) *als Katalysator*

Die Oxidation erfolgt sowohl mit als auch ohne Cu(II)-Katalysator in erster Ordnung bezüglich des Oxidationsmittels und des Substrats; inverse Ordnung wird bezüglich der Alkalikonzentration beobachtet. Bis zu einer Cu(II)-Konzentration von $\leq 2 \times 10^{-5} M$ ist die Geschwindigkeitskonstante der Katalysatorkonzentration proportional; darüber wird eine konstantbleibende Geschwindigkeit beobachtet, die nun von der Cu(II)-Konzentration unabhängig ist. Neutralsalze haben keinen Effekt auf die Geschwindigkeitskonstante. Es wird für den katalysierten und unkatalysierten Reaktionsablauf ein Mechanismus vorgeschlagen und ein mathematischer Ansatz präsentiert.

Introduction

Mechanism for the oxidation of aminoacids by alkaline chloramine-T have been proposed by *Dakin*[1], and *Mushran* et al.[2,3]. Recently *Yadav* et al. employed Cu(II) ion as catalyst[4] for such reactions. Their

findings led us to investigate the oxidation mechanisms of arginine monohydrochloride by alkaline chloramine-T in the absence and presence of Cu(II) ion as catalyst.

Experimental

Chloramine-T (E. Merck, G.R.) solution was prepared freshly for each kinetic run by dissolving the weighted amount of it in the desired volume of doubly distilled water and the strength checked by iodometric method[5]. Exact weight of arginine-monohydrochloride (AR, BDH) was dissolved in bidistilled water and the strength checked by *Sorensen* formal method. Other standard solutions viz., copper sulphate, sodium hydroxide, sodium nitrate etc. were prepared from A. R. BDH samples. Reaction stills were blackened from outside in order to exclude photo chemical effects[6].

Reactants were brought to thermostatic temperature ($\pm$ 0.1°) and the reaction initiated by adding the appropriate amount of chloramine-T. The progress of the reaction was followed by estimating unconsumed chloramine-T.

Results

(i) Chloramine-T Dependence

The order of reaction with respect to chloramine-T was determined by carrying out the oxidation at eight different initial concentrations of oxidant. It follows a pseudo first order disappearance at all the concentrations of chloramine-T. First order rate constants are depicted in Tab. 1 a.

Table 1 a. *[Arginine·HCl]* = 1.0 × 10^{-2}M; [NaOH] = 5.0 × 10^{-2}M; *Temp.* 37 °C

[Chloramine-T] × 10^3M	0.6	0.8	1.0	1.2	1.4	1.6	1.8	1.9
k × 10^3 min^{-1}	2.4	2.7	2.5	2.6	2.6	2.7	2.4	2.6

The runs were repeated in Cu(II) and the findings enlisted in Tab. 1 b.

Table 1 b. *[Arginine·HCl]* = 1.0 × 10^{-2}M; [NaOH] = 5.0 × 10^{-2}M; [Cu(II)] = 1.0 × 10^{-5}M; *Temp.* = 37 °C

[Chloramine-T] × 10^3M	0.6	0.8	1.0	1.2	1.6
k' × 10^3M min^{-1}	4.3	4.2	4.1	3.9	3.8

A comparision of rate constants—Tab. 1 a and 1 b—indicates that the rate is enhanced in presence of copper ion.

(ii) Arginine-Monohydrochloride Dependence

Tab. 2 enlists the results obtained with varying concentrations of substrate in the absence and presence of Cu(II) ion as catalyst. From columns 3 and 5 it is obvious that the oxidation follows a first order dependence in substrate concentration for both the cases.

Table 2. $[Chloramine\text{-}T] = 1.0 \times 10^{-3} M$; $[NaOH] = 5 \times 10^{-2} M$; *Temp.* 37 °C

[Arginine · HCl] × 10^2 M	$k \times 10^3$ min^{-1}	$\dfrac{k}{[\text{Arginine} \cdot \text{HCl}]}$	$k' \times 10^3$ min^{-1}	$\dfrac{k}{[\text{Arginine} \cdot \text{HCl}]}$
0.8	2.3	0.28	3.1	0.39
1.0	2.5	0.25	4.2	0.42
1.2	2.9	0.24	4.7	0.39
1.4	3.2	0.23	—	—
1.6	3.9	0.25	5.8	0.36
1.8	4.4	0.24	—	—
2.0	5.0	0.25	6.6	0.33
2.2	5.6	0.25	7.9	0.36

k' = First order rate constants in presence of $1.0 \times 10^{-5} M$ [Cu(II)]

(iii) NaOH Dependence

NaOH dependence was studied by taking fixed concentrations of oxidant and substrate and varying the concentration of alkali over the range 2.8-6.0 × $10^{-2} M$. Findings are listed in Tab. 3.

Table 3. $[Chloramine\text{-}T] = 1.0 \times 10^{-3} M$, $[Arginine \cdot HCl] = 1 \times 10^{-2} M$; *Temp.* 37°

[NaOH] × $10^2 M$	2.8	3.2	3.6	4.0	5.0	5.4	6.0
$k \times 10^3$ min^{-1}	4.1	3.8	2.9	2.7	2.5	2.3	2.1
k[NaOH] × 10^6 mol min^{-1}	1.2	1.2	1.1	1.1	1.2	1.2	1.3

The product of NaOH concentrations and first order specific reaction rate is constant for all the concentrations of NaOH, which suggests an inverse (— 1) order in sodium hydroxide.

(iv) Copper Sulphate Dependence

First order rate constants obtained over a wide range of Cu(II) concentration (0.2-4.0 × $10^{-5} M$) were plotted against copper sulphate concentrations (Fig. 1) At lower ʺconcentrations i.e.

$Cu(II) \leq 2.0 \times 10^{-5} M$ the observed rate constants increase in a linear manner with the increase in catalyst concentrations. However, at all concentrations higher than $2.0 \times 10^{-5} M$ no further increase in rate constant value was seen. Further, extrapolation of the curve to zero copper concentration cuts an intercept on the rate constant axis, which corresponds to the value of uncatalysed oxidation. Thus it is concluded
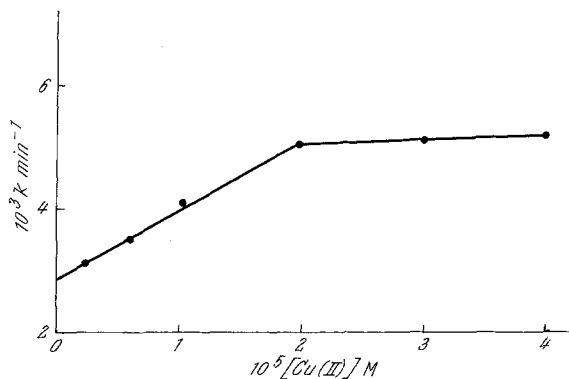

Fig. 1. Plot showing the effect of Cu(II) on observed rate constant. [Chloramine-T] = $1.0 \times 10^{-3} M$; [Arginine·HCl] = $1.0 \times 10^{-2} M$; [NaOH] = $5.0 \times 10^{-2} M$; Temperature = 37 °C

that the observed rate constant is made up of two terms and can be given by the expression.

$$k' = k \text{ uncat} + k \text{ cat } Cu(II)$$

Evidently the rate of disappearance of chloramine-T follows

$$-\frac{d}{dt}[\text{Chloramine-}T] = \frac{k\,\text{uncat [Chloramine-}T]\,[\text{Arginine}]}{[\text{NaOH}]} +$$
$$+ \frac{k\,\text{cat [Chloramine-}T]\,[\text{Arginine}]\,[Cu(II)]}{[\text{NaOH}]}$$

Actually the catalytic action of copper ion is due to the formation of copper complexes of amino acids[7], which is a slow and reversible process.

$$Cu(II) + \text{Arginine} \rightleftharpoons Cu \text{ Arigine complex}$$
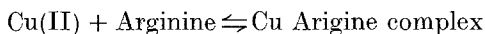
(v) Temperature Dependence

The reaction was carried out at four different temperatures viz., 32, 37, 43 and 47 °C with varying concentrations of Cu(II) ion, and the results are shown in Tab. 4.

Table 4. $[Chloramine\text{-}T] = 1 \times 10^{-3} M$; $[Arginine \cdot \text{HCl}] = 1.0 \times 10^{-2} M$; $[\text{NaOH}] = 5.0 \times 10^{-2} M$

Temp. °C	Cu(II) $\times 10^{-5} M$	$k \times 10^3 \text{ min}^{-1}$			
		0.2	0.6	1.0	2.0
32		1.8	2.0	2.4	2.8
37		3.1	3.4	4.2	5.1
43		5.1	5.7	6.7	7.9
47		7.1	8.1	9.1	11.7

Linear plots of rate constant versus Cu(II) concentrations are obtained. The extrapolation of these curves do not pass through origin and cut the intercepts on the rate constant axis. This indicates that catalysed and uncatalysed oxidations are taking place side by side. In Tab. 5 the rate constant values for uncatalysed pathways calculated from the intercepts are enlisted. Experimental values for uncatalysed reaction are also given which are in good agreement with the calculated values.

Table 5. $[Chloramine\text{-}T] = 1.0 \times 10^{-3} M$; $[Arginine \cdot \text{HCl}] = 1.0 \times 10^{-2} M$; $[\text{NaOH}] = 5 \times 10^{-2} M$

Temp./°C	$k \times 10^3 \text{ min}^{-1}$ (Experimental)	$k_{\text{uncat}} \times 10^3 \text{ min}^{-1}$ (Calculated)
32	1.7	1.7
37	2.6	2.9
43	4.6	4.8
47	6.6	6.6

Energies of activation for uncatalysed and catalysed pathways are 18.5 and 17.0 kcal/mol respectively. This suggests that the rate of Cu(II) catalysed reaction path is a bit faster than the uncatalysed pathways.

(vi) Salt Effect

Uncatalysed and Cu(II) catalysed oxidations were carried out in presence of different neutral salts, viz., KNO_3, Na_2SO_4 and $Ba(NO_3)_2$ for concentrations of $2.0\text{-}6.0 \times 10^3 M$. The rate was completely independent of the ionic strength of the reaction mixture.

(vii) Stoichiometry

Reaction mixtures containing varying ratios of chloramine-*T* to arginine monohydrochloride were allowed to equilibrate at 32 °C for 48

hours in presence of $5.0 \times 10^{-2}M$-NaOH. From the results given in Tab. 6, it is evident that one mole of arginine-monohydrochloride consumes two moles of chloramine-T.

<div align="center">Table 6</div>

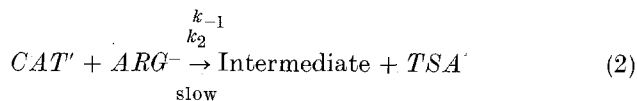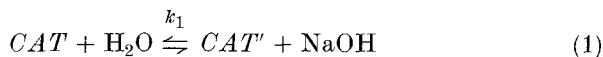| 10^3 [Chloramine-T]	10^3 [Arginine · HCl]	10^3 [Chloramine-T]	Stoichio-metric ratio [Chloramine-T]: [Substrate]
1.0	0.5	0.0	2:1
2.0	0.5	1.0	2:1
2.5	0.5	1.5	2:1
3.0	0.5	2.0	2:1
3.5	0.5	2.5	2:1
0.5	—	0.5	

Discussion

Uncatalysed oxidation of arginine monohydrochloride followed a first order dependence each in chloramine-T and reducing substrate. A negative single order dependence was reported in alkali.

A mechanism is proposed in which the initial step is the hydrolysis of chloramine-T[8].

$$CH_3C_6H_4SO_2N \cdot NaCl + H_2O \rightleftharpoons CH_3C_6H_4SO_2N \cdot HCl + NaOH$$
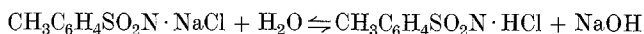
The essential reaction sequences thus involved are:

$$CAT + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CAT' + NaOH \tag{1}$$

$$CAT' + ARG^- \overset{k_2}{\underset{\text{slow}}{\rightarrow}} \text{Intermediate} + TSA \tag{2}$$

$$\text{Intermediate} + CAT' \overset{k_3}{\rightarrow} \text{Products} + TSA \tag{3}$$

Thus the rate of disappearance of chloramine-T

$$\frac{-\mathrm{d}}{\mathrm{d}t}[CAT] = k_2[CAT'][ARG^-] + k_3 \text{[Intermediate]}[CAT'] \tag{A}$$

Applying steady state assumptions followed by the approximation $k_{-1} \text{ NaOH} \gg 2k_2 [ARG^-]$ the rate law obtained as

$$\frac{-\mathrm{d}}{\mathrm{d}t}[\text{Chloramine-}T] = \frac{2k_1k_2}{k_{-1}}\frac{[CAT][ARG^-]}{[\text{NaOH}]} \tag{B}$$
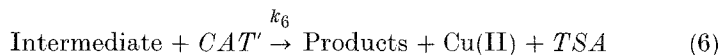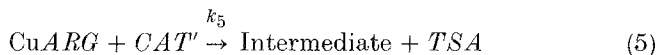
This expression is consistent with the experimental data. Stoichiometric studies also support the mechanism as it explains the consumption of two moles of chloramine-T by one mole of arginine-monohydrochloride.

In presence of Cu(II) a liner dependence in catalyst concentration was observed at concentrations Cu(II) $\leq 2.0 \times 10^{-5}M$. To explain this aspect the complex formation and its reaction with chloramine-T is suggested.

Arginine anion reacts with copper ion reversibly and slowly generate copper complex arginine (CuARG) as follows:

$$\mathrm{Cu(II)} + ARG^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{Cu}ARG \tag{4}$$
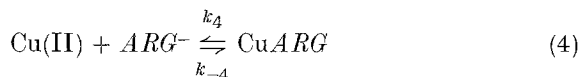
Now along with reaction sequences (2) and (3) following steps also occur simultaneously:

$$\mathrm{Cu}ARG + CAT' \overset{k_5}{\rightarrow} \text{Intermediate} + TSA \tag{5}$$

$$\text{Intermediate} + CAT' \overset{k_6}{\rightarrow} \text{Products} + \mathrm{Cu(II)} + TSA \tag{6}$$

Applying steady state treatment to the steps (1), (2), (3), (5), and (6) the rate expression obtained is

$$\frac{-\mathrm{d}}{\mathrm{d}t}[\text{Chloramine-}T] = \frac{2k_1 k_2}{k_{-1}}\frac{[CAT][ARG^-]}{[\text{NaOH}]} + \frac{2k_1 k_5}{k_{-1}}\frac{[CAT][\mathrm{Cu}ARG]}{[\text{NaOH}]} \tag{C}$$

From equation (4) the concentration of copper complex can be given as

$$[\mathrm{Cu}ARG] = \frac{k_4}{k_{-4}}[\mathrm{Cu(II)}][ARG^-] \tag{D}$$

The value is fed into expression C to get the equation

$$\frac{-\mathrm{d}}{\mathrm{d}t}[\text{Chloramine-}T] = \frac{2k_1}{k_{-1}}\frac{[CAT][ARG^-]}{[\text{NaOH}]}\left\{k_2 + \frac{k_4 k_5}{k_{-4}}[\mathrm{Cu(II)}]\right\}$$

$$k' = \frac{2k_1 k_2}{k_{-1}} + \frac{2k_1 k_4 k_5 [\mathrm{Cu(II)}]}{k_{-1} k_{-4}} \tag{E}$$

This explains a linear dependence of observed specific reaction rate k' on Cu(II) concentration.

At high copper concentration i.e. Cu(II) $> 2.0 \times 10^{-5}M$, the whole of the arginine is oxidised by reaction sequences (5) and (6) and (2) and (3)

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are completely abolished. The rate of reaction can be given by the expression

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\text{Chloramine-}T] = \frac{k_1 k_5}{k_{-1}} \frac{[CAT][\text{Cu}ARG]}{[\text{NaOH}]}$$

Here $[\text{Cu}ARG] = [ARG]$ and thus an optimum value of rate constant was observed at high catalyst concentration.

References

[1] *H. D. Dakin*, J. biol. Chem. **C 4**, 237 (1908); Biochem. J. **10**, 319 (1916); Proc. Roy. Soc. **B 89**, 232 (1916).

[2] *A. K. Bose, R. M. Mehrotra*, and *S. P. Mushran*, Ind. J. Chem. **11**, 896 (1973).

[3] *A. Kumar, A. K. Bose*, and *S. P. Mushran*, Mh. Chem. **106**, 13 (1975).

[4] *B. S. Yadav, D. R. Singh*, and *G. Chandra*, J. Inorg. Nucl. Chem., in press; Balwant-Vidyapeeth Journal of Agricul. and Sci. Res. **15**, 129 (1973).

[5] *K. Böttger* and *W. Böttger*, Z. Anal. Chem. **70**, 225 (1927).

[6] *W. Poethke* and *F. Wolf*, Z. anorg. allgem. Chem. **268**, 244 (1952).

[7] *I. L. Finar*, Organic Chemistry, Vol. 2, 3rd ed., p. 469. Longmans Green & Co. Ltd. 1965.

[8] *R. Dietzel* and *K. Taufel*, Apotheker-Ztg. **44**, 989 (1929).