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Kinetics and mechanism of Ru(III)-catalysed oxidation of amino acids by N-chloro-N-sodio-toluene-*p*-sulphonamide in acid media

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Abstract. The kinetics of Ru(III)-catalysed oxidations of several amino acids (AA) (glycine, alanine, valine, leucine and phenyl alanine) by N-chloro-N-sodio-toluene-*p*-sulphonamide have been studied in aqueous perchloric acid medium under various conditions. Catalysed oxidations of all the amino acids show second-order kinetics in [oxidant], fractional order each in [AA] and Ru(III), and inverse fractional order in $[H^+]$ as compared to the second order dependence in [oxidant], first order in [AA] and inverse first order in $[H^+]$, generally observed for the uncatalysed oxidations. Variation in ionic strength of the medium or the addition of reduced product of the oxidant had no significant effect on the rates of reactions. Decrease in dielectric constant of the medium by changing the solvent composition with methanol decreased the rate in all the cases. A two-pathway mechanism has been considered to explain the observed kinetics and other effects. The rate-controlling steps have been identified in all cases and coefficients of these steps are calculated at different temperatures by varying [AA] at each temperature. Hence the activation parameters associated with the rate-controlling steps have been computed. The rate constants were also predicted from the rate laws as [AA] and [Ru(III)] were varied.

Keywords. Ru(III)-catalysed oxidation; amino acids; chloramine-T; kinetics and mechanism.

1. Introduction

Oxidative decarboxylation of amino acids is of interest both from a pure chemical point of view and from the point of view of its bearing on the mechanism of amino acid metabolism. The free amino acids take part in numerous metabolic reactions. The specific metabolic role of amino acids includes the bio-syntheses of polypeptides and proteins and syntheses of nucleotides etc. Thus the mechanism of analogous non-enzymatic chemical processes of oxidative decarboxylation of amino acids is a potential area for intensive experimentation. Hence the subject matter has been extensively studied using a variety of oxidants including chloramine-T (Kumar *et al* 1975; Sharma *et al* 1980; Gowda and Mahadevappa 1983; Gowda and Rao 1986, 1987, 1988; Gowda and Sherigara 1986; Banerji *et al* 1987). We have recently studied the kinetics of oxidation of amino acids by chloramine-T (CAT) in an attempt to explain the course of the positive chlorine reactions under varying conditions of

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acidity and chloride concentrations (Gowda and Rao 1986, 1987, 1988; Gowda and Sherigara 1986). Metallic ions play a significant role in the oxidative decarboxylation of amino acids. Hence in the present investigations, the role of the Ru(III) catalyst in the oxidative decarboxylation of amino acids by chloramine-T has been studied in aqueous perchloric acid medium.

2. Materials and methods

An aqueous stock solution (0·1 mol dm^{-3}) of chloramine-T (Fluka AG) was standardised by the iodometric method and preserved in dark-coloured bottles. Chromatographically pure glycine (Gly), L-alanine (Ala), L-valine (Val), L-leucine (Leu) and L-phenylalanine (Phe) (Sisco Research Laboratories, India) were used. Aqueous stock solutions of the amino acids (0·20 mol dm^{-3}) were prepared and standardised. All other reagents employed were of analytical grade. Ionic strength of the medium was kept at a high value (0·30 mol dm^{-3}) using the concentrated aqueous solution of sodium perchlorate.

2.1 *Kinetic measurements*

The kinetic studies were made in glass-stoppered pyrex boiling tubes under pseudo-first order conditions with [amino acid] $\gg$ [CAT] (by at least 5–10 times). The reactions were initiated by the rapid addition of known amounts of oxidant solution (0·0005–0·005 mol dm^{-3}), pre-equilibrated at a desired temperature, to mixtures containing the required amounts of amino acid (0·005–0·10 mol dm^{-3}), perchloric acid (0·01–0·20 mol dm^{-3}), $RuCl_3$($0{\cdot}4 \times 10^{-4}$–$1{\cdot}6 \times 10^{-4}$ mol dm^{-3}) solutions and water in the boiling tube, thermostatted at the same temperature. The progress of the reaction was monitored for at least two half-lives by iodometric determination of unreacted oxidant at regular intervals of time. The pseudo first-order rate constants (k_{obs}) were computed by graphical methods and the values are reproducible to within $\pm$ 3%.

2.2 *Stoichiometry and product analysis*

The stoichiometry of each CAT amino acid (AA) oxidation was determined in a perchloric acid medium (0·01–0·10 mol dm^{-3}), in the presence of $RuCl_3$(0·0 1·2 $\times 10^{-4}$ mol dm^{-3}), by equilibrating varying ratios of [CAT] to [AA] at 303 K for different intervals of time. Nitrile was identified as the major product by standard tests (Soloway and Lipschitz 1952), and recording the spectra of the reaction mixtures. The toluene-*p*-sulphonamide (TSA), the reduced product of the oxidant was detected by paper chromatography with benzyl alcohol saturated with water as the solvent and 0·5% vanillin in 1% HCl solution in ether as the spray reagent. The observed stoichiometry may be represented by:

$$RCH(NH_2)COOH + 2ArSO_2NCl^-Na^+ \rightarrow RCN + 2ArSO_2NH_2 + CO_2 + 2Na^+ + 2Cl^-, \quad (1)$$

where

$R = H$(Gly), CH_3(Ala), $(CH_3)_2CH$(Val), $(CH_3)_2CHCH_2$(Leu) and $C_6H_5CH_2$(Phe) and $Ar = CH_3C_6H_4$.

3. Results

Kinetics of Ru(III)-catalysed oxidations of several amino acids (AA), namely, Gly, Ala, Val, Leu and Phe, by CAT have been studied in perchloric acid media under varying conditions. The results are shown in tables 1 4 and figures 1–3.

At constant $[HClO_4]$, [Ru(III)] and $[AA]_0$, plots of 1/[CAT] versus time were linear (figure 1) at least up to 75% completion of reaction with all the five amino acids and the pseudo second-order rate constants (k_{obs}, $dm^3\,mol^{-1}\,s^{-1}$) computed from the plots were insensitive to the variations in $[CAT]_0$, establishing second-order kinetics in [CAT]. At fixed $[CAT]_0$, $[AA]_0$ and [Ru(III)], the rates decreased with increase in $[HClO_4]$ (table 1) and the plots of $\log k_{obs}$ versus $\log[HClO_4]$ were linear with negative fractional slopes indicating inverse fractional order dependence of rate on $[H^+]$ in all the cases, compared to inverse first-order kinetics observed in $[H^+]$ for the uncatalysed oxidations (table 3). The rates increased with increase in $[AA]_0$ and the plots of $\log k_{obs}$ versus $\log[AA]_0$ were linear with fractional slopes showing fractional order kinetics in $[AA]_0$, contrary to first order kinetics observed in the uncatalysed oxidations (table 3). The plots of k_{obs} versus [AA] were also linear (figure 2). The rates also increased with increase in [Ru(III)] with fractional order kinetics for all the oxidations. The plots of k_{obs} versus [Ru(III)] were linear with finite

Table 1. Pseudo second-order rate constants (k_{obs}) for the Ru(III)-catalysed oxidations of amino acids (AA) by chloramine-T (CAT) in aqueous perchloric acid medium at 303 K ($I = 0{\cdot}3\,mol\,dm^{-3}$).
I: ionic strength of the medium.

$10^3[CAT]_0$ ($mol\,dm^{-3}$)	$10^2[AA]_0$ ($mol\,dm^{-3}$)	$10^2[HClO_4]$ ($mol\,dm^{-3}$)	$10^5[RuCl_3]$ ($mol\,dm^{-3}$)	$10k_{obs}$ ($dm^3\,mol^{-1}\,s^{-1}$)				
				Gly	Ala	Val	Phe	Leu
Variation of $[CAT]_0$								
0·5	2·0	5·0	4·0	22·6	4·5	5·7	7·4	9·6
1·0	2·0	5·0	4·0	22·6	4·5	5·7	7·6	9·8
2·0	2·0	5·0	4·0	22·6	4·6	5·7	7·6	9·8
5·0	2·0	5·0	4·0	22·6	4·5	5·7	7·6	9·6
Variation of $[AA]_0$								
1·0	0·5	5·0	4·0	6·5	2·9	3·7	4·2	5·8
1·0	1·0	5·0	4·0	11·5	3·5	4·6	5·7	7·2
1·0	2·0	5·0	4·0	22·6	4·5	5·7	7·6	9·8
1·0	5·0	5·0	4·0	51·3	8·0	8·9	13·7	17·1
1·0	10·0	5·0	4·0	102·4	12·6	14·4	23·8	29·9
Variation of $[HClO_4]$								
1·0	2·0	1·0	4·0	111·3	18·2	20·9	26·2	39·9
1·0	2·0	2·0	4·0	58·3	9·5	11·2	14·6	20·4
1·0	2·0	5·0	4·0	22·6	4·5	5·7	7·6	9·8
1·0	2·0	10·0	4·0	13·4	2·8	3·4	4·8	5·1
Variation of $[RuCl_3]$								
1·0	2·0	5·0	0·0	16·3	1·9	2·2	3·4	5·4
1·0	2·0	5·0	4·0	22·6	4·5	5·7	7·6	9·8
1·0	2·0	5·0	8·0	26·5	6·5	7·1	10·0	12·6
1·0	2·0	5·0	12·0	30·2	7·9	8·3	11·8	14·8
1·0	2·0	5·0	16·0	33·1	8·9	9·5	13·5	16·6

Table 2. Effect of varying ionic strength (I) and solvent composition of the medium, and addition of the reduced product of the oxidant (TSA) on the rates of Ru(III)-catalysed oxidation of amino acids by chloramine-T in aqueous perchloric acid medium at 303 K.

I (mol dm^{-3})	$10k_{obs}$ (dm^3 mol^{-1} s^{-1})				
	Gly	Ala	Val	Phe	Leu
0·1	22·6	4·5	5·7	7·5	9·6
0·3	22·6	4·5	5·7	7·6	9·8
0·4	22·6	4·6	5·8	7·8	9·9
0·5	22·7	4·6	5·8	7·8	9·9
% Methanol					
10	14·5	3·5	4·6	6·1	7·9
20	9·7	2·8	3·6	4·7	6·3
30	6·7	2·0	2·8	3·8	5·4
40	3·7	1·7	2·2	2·9	4·4
10^3[TSA](mol dm^{-3})					
1·0	22·7	4·6	5·7	7·5	9·9
2·0	22·7	4·6	5·7	7·5	9·9
3·0	22·7	4·6	5·7	7·5	9·8
5·0	22·6	4·7	5·6	7·4	9·8

* $10^3[CAT]_0 = 50[AA]_0 = 20[H^+] = 1{\cdot}0$ mol dm^{-3}, 10^5[Ru(III)] = 4·0 mol dm^{-3}), $I = 0{\cdot}30$ mol dm^{-3} (except during its variation).

Table 3. Kinetic data for the Ru(III)-catalysed, uncatalysed and chloride-catalysed oxidations of amino acids by chloramine-T in aqueous perchloric acid media.

Orders observed in	Gly	Ala	Val	Phe	Leu
Ru(III)-catalysed oxidations					
[CAT]	2·0	2·0	2·0	2·0	2·0
[AA]	0·86	0·46	0·31	0·40	0·52
[H^+]	−0·90	−0·70	−0·83	−0·73	−0·86
[Ru(III)]	0·28	0·45	0·34	0·38	0·41
Uncatalysed oxidations					
[CAT]	2·0	2·0	2·0	2·0	
[AA]	1·0	1·0	1·0	1·0	
[H^+]	−1·0	−1·0	−1·0	−1·0	
Chloride-catalysed oxidations					
[CAT]	1·0	2·0	2·0	2·0	
[AA]	0·59	1·0	1·0	0·9	
[H^+]	−0·62	−1·0	−1·0	−1·0	
[Cl^-]	0·22	0·40	0·64	0·30	

Table 4. Activation parameters associated with schemes 1 and 2 represented by the coefficients K_2k_3 and K_4k_5 [vide(14)].

	Gly	Ala	Val	Phe	Leu
From (K_2k_3)					
E_a(kJ mol^{-1})	35·9	35·0	43·9	43·3	59·8
log A	8·0	7·0	8·6	8·8	11·7
ΔH^*(kJ mol^{-1})	35·1	33·1	41·6	42·8	56·7
ΔS^*(JK^{-1} mol^{-1})	−92·1	−116·8	−88·4	−79·0	−32·3
ΔG^*(kJ mol^{-1})	62·8	68·5	68·4	66·8	66·5
From K_4k_5					
E_a(kJ mol^{-1})	105·1	23·6	19·5	27·2	14·3
log A	21·7	7·8	7·3	8·6	6·5
ΔH^*(kJ mol^{-1})	103·5	20·5	16·8	25·2	12·6
ΔS^*(JK^{-1} mol^{-1})	+166·1	−95·4	−114·7	−86·7	−125·3
ΔG^*(kJ mol^{-1})	53·2	49·4	51·5	51·5	50·6

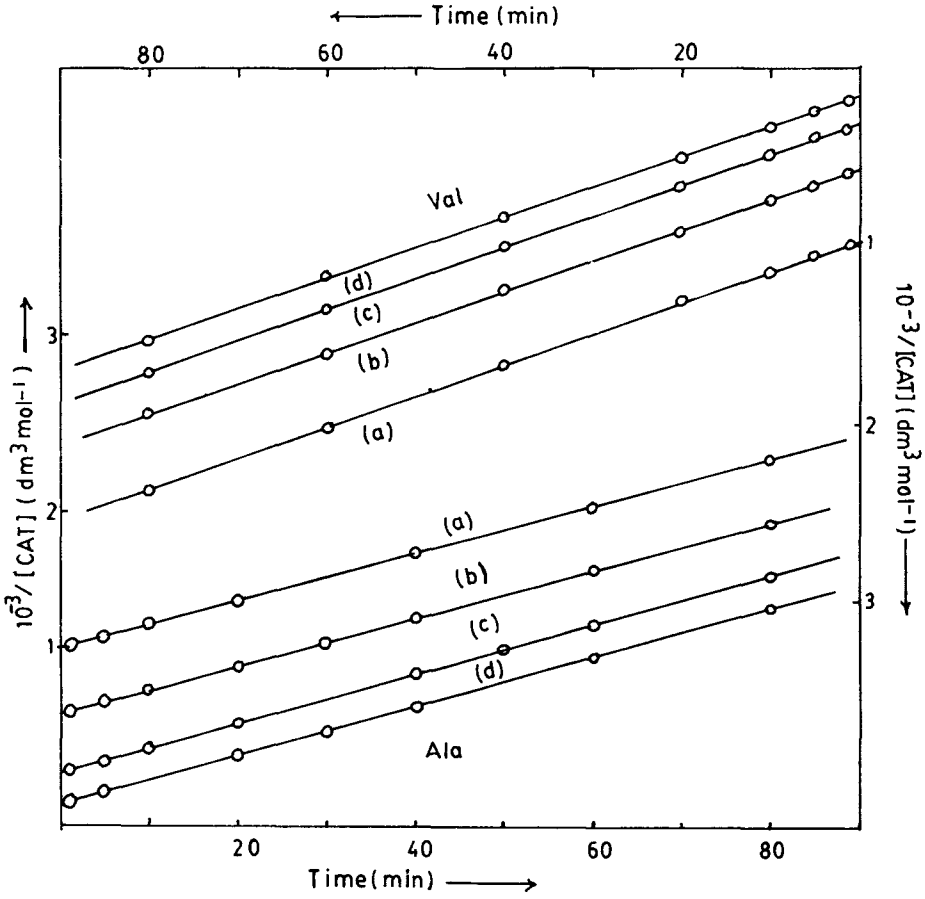


Figure 1. Plot of 1/[CAT] versus time; $50[AA]_0 = 20[HClO_4] = 1{\cdot}0$ mol dm^{-3}; $10^5[Ru(III)] = 4{\cdot}0$ mol dm^{-3}; $I = 0{\cdot}30$ mol dm^{-3}; Temp. 303 K. $10^3[CAT]_0 = 0{\cdot}5$(a), 1·0(b), 2·0(c), and 5·0(d) mol dm^{-3}.

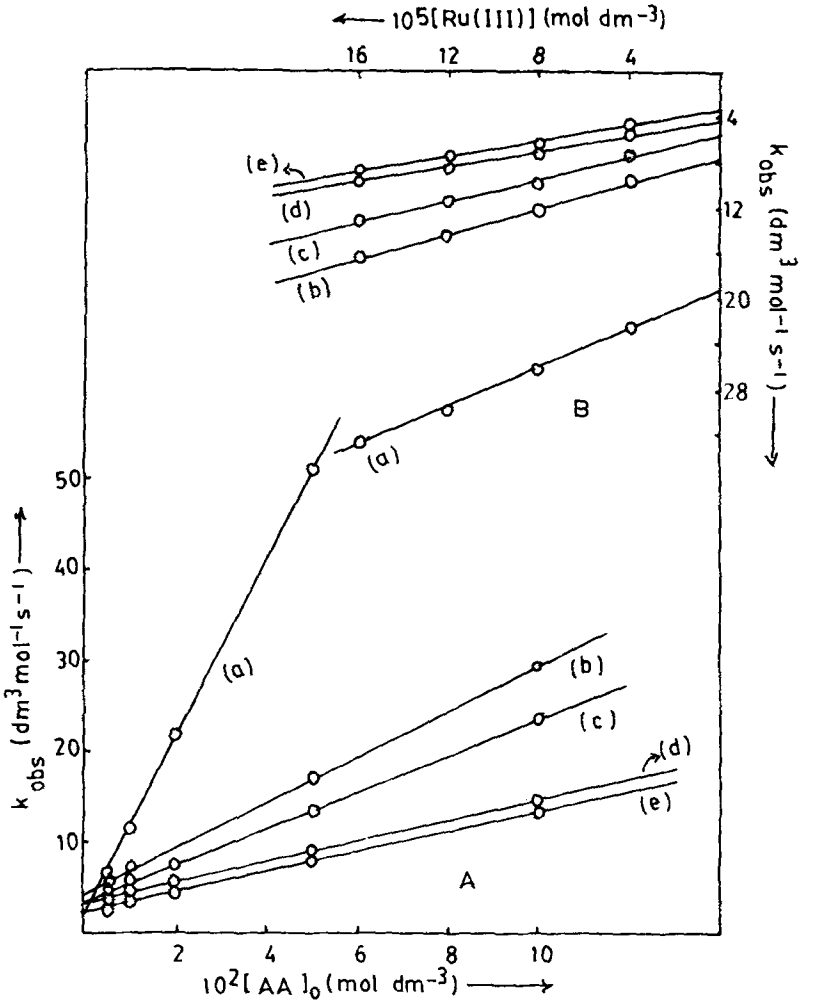


Figure 2. (A) Plots of k_{obs} versus $[AA]_0$; $10^3[CAT]_0 = 20[HClO_4] = 1{\cdot}0\,mol\,dm^{-3}$; $10^5[Ru(III)] = 4{\cdot}0\,mol\,dm^{-3}$; $I = 0{\cdot}30\,mol\,dm^{-3}$; Temp. 303 K. (B) Plots of k_{obs} versus $[Ru(III)]$; $10^3[CAT]_0 = 50[AA]_0 = 20[HClO_4] = 1{\cdot}0\,mol\,dm^{-3}$; $I = 0{\cdot}30\,mol\,dm^{-3}$; Temp. 303 K. Gly(a), Leu(b), Phe(c), Val(d) and Ala(e).

intercepts on k_{obs} axes (figure 2). Addition of the reduced product of the oxidant, TSA and variations in ionic strength of the medium had no significant effect on the rates of oxidations (table 2) of all the amino acids. The rates decreased with decrease in dielectric constant of medium by changing the solvent composition with methanol and the plots of $\log k_{obs}$ versus % methanol were linear with negative slopes (figure 3).

The rates were measured at different temperatures by varying [AA] at each temperature and the coefficients of the rate controlling steps have been calculated at each temperature for all the amino acids as described under discussion. The latter constants were used to compute the activation parameters from the Arrhenius plots (table 4).

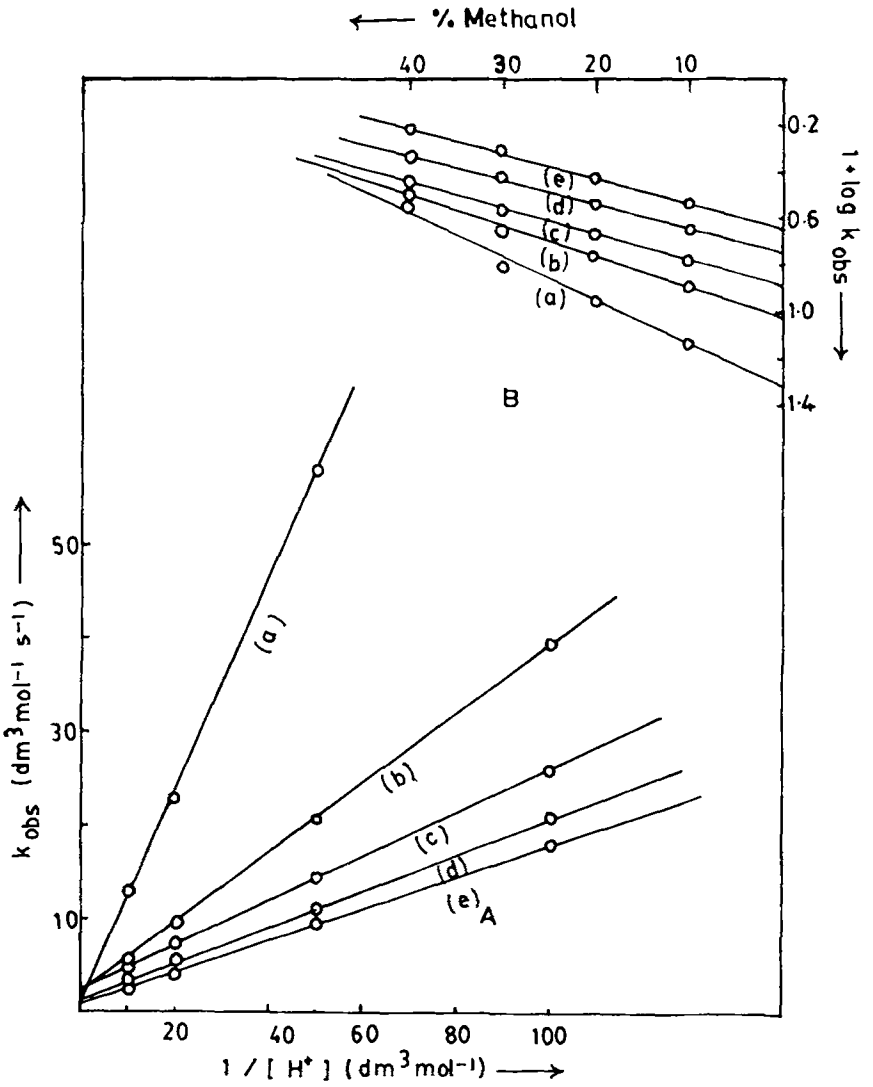


Figure 3. (A) Plots of k_{obs} versus $1/[H^+]$; $10^3[CAT]_0 = 50[AA]_0 = 1{\cdot}0\,mol\,dm^{-3}$; $10^5[Ru(III)] = 4{\cdot}0\,mol\,dm^{-3}$; $I = 0{\cdot}30\,mol\,dm^{-3}$; Temp. 303 K. (B) Plots of $\log k_{obs}$ versus % methanol; $10^3[CAT]_0 = 50[AA]_0 = 20[HClO_4] = 1{\cdot}0\,mol\,dm^{-3}$; $10^5[Ru(III)] = 4{\cdot}0\,mol\,dm^{-3}$; $I = 0{\cdot}30\,mol\,dm^{-3}$; Temp. 303 K. Gly(a), Leu(b), Phe(c), Val(d) and Ala(e).

4. Discussion

In acid solutions amino acids exist in the following protonation equilibrium (Jakubke and Jeschkeit 1977).

$$\underset{(SH^+)}{RCH(\overset{+}{N}H_3)COOH} \rightleftharpoons \underset{(S)}{RCH(\overset{+}{N}H_3)COO^-} + H^+, \qquad (2)$$

where R is an alkyl or aryl moiety as already indicated.

Chloramine-T ($ArSO_2NClNa$, where $Ar = CH_3C_6H_4$) is a strong electrolyte in aqueous solution and depending upon pH of the medium it furnishes different types of oxidising species (Morris *et al* 1948; Bishop and Jennings 1958; Campbell and Johnson 1978; Gowda and Mahadevappa 1983). The following equilibria exist in its aqueous solutions:

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+, \tag{3}$$

$$ArSO_2NCl^- + H^+ \overset{K_a}{\rightleftharpoons} ArSO_2NHCl (K_a = 2{\cdot}82 \times 10^{-5} \text{ at } 25^\circ C), \tag{4}$$

$$2ArSO_2NHCl \overset{K_d}{\rightleftharpoons} ArSO_2NCl_2 + ArSO_2NH_2 (K_d = 0{\cdot}058 \text{ at } 25^\circ C), \tag{5}$$

$$ArSO_2NCl_2 + H_2O \overset{K_h}{\rightleftharpoons} ArSO_2NHCl + HOCl (K_h = 8{\cdot}0 \times 10^{-7} \text{ at } 25^\circ C), \tag{6}$$

$$ArSO_2NHCl + H_2O \overset{K_h'}{\rightleftharpoons} ArSO_2NH_2 + HOCl (K_h' = 4{\cdot}88 \times 10^{-8} \text{ at } 25^\circ C), \tag{7}$$

$$ArSO_2NHCl + H^+ \rightleftharpoons ArSO_2NH_2Cl^+, \tag{8}$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+. \tag{9}$$

Therefore the probable reactive species in acid solutions of CAT are $ArSO_2NHCl$, $ArSO_2NCl_2$, HOCl and possibly $ArSO_2NH_2Cl^+$ and H_2OCl^+.

5. Mechanism of oxidation

The kinetics for the Ru(III)-catalysed oxidations of amino acids show second-order kinetics in [CAT], fractional orders in both [AA] and [Ru(III)] and inverse fractional order in $[H^+]$. Further, the plots of k_{obs} versus [AA], k_{obs} versus [Ru(III)] and k_{obs} versus $1/[H^+]$ were linear with finite intercepts (figures 2 and 3), whereas the corresponding double reciprocal plots were non-linear (figures not shown). Variation in ionic strength of the medium or addition of the reduced product of the oxidant had no significant effect on the rates of oxidations. Hence the observed results may be explained by a two-pathway mechanism (schemes 1 and 2). The electronic spectra of the reaction mixtures showed the formation of a complex between the oxidant and Ru(III) (λ_{max} around 330–370 nm) under the present experimental conditions.

The related rate law is

$$-\frac{d[CAT]}{dt} = K_2k_3[CAT]^2[S] = \frac{K_1K_2k_3[CAT]^2[SH^+]}{[H^+]}, \tag{10}$$

but we have

$$-\frac{1}{[CAT]^2}\cdot\frac{d[CAT]}{dt} = \frac{d\{1/[CAT]\}}{dt} = k_{obs},$$

$$SH^{+} \underset{}{\overset{K_1}{\rightleftharpoons}} S + H^{+} \quad \text{(fast)}$$

$$S + ArSO_2NHCl \underset{}{\overset{K_2}{\rightleftharpoons}} \underset{(X)}{\text{Intermediate}} \quad \text{(fast)}$$

$$X + ArSO_2NHCl \xrightarrow{k_3} \text{Products} \quad \text{(Slow)}$$

Scheme 1.

$$ArSO_2NHCl + Ru(III) \underset{}{\overset{K_4}{\rightleftharpoons}} \underset{(Y)}{(\text{adduct})_1^{+3}} \quad \text{(fast)}$$

$$ArSO_2NHCl + Y \xrightarrow{k_5} (\text{adduct})_2^{+3} \quad \text{(Slow)}$$

$$(\text{Adduct})_2^{+3} + H_2O \longrightarrow HOCl + ArSO_2NH_2 + Ru(III) \quad \text{(fast)}$$

$$HOCl + S \longrightarrow \text{Products} \quad \text{(fast)}$$

Scheme 2.

and hence the rate law (10) becomes

$$k_{obs} = K_2k_3[S] = \frac{K_1K_2k_3[SH^+]}{[H^+]}. \tag{11}$$

The following rate laws are in accordance with scheme 2

$$-\frac{d[CAT]}{dt} = K_4k_5[CAT]^2[Ru(III)] \tag{12}$$

or

$$k_{obs} = K_4k_5[Ru(III)]. \tag{13}$$

The combined rate laws below explain the observed kinetics.

$$K_{obs} = K_2k_3[S] + K_4k_5[Ru(III)] \tag{14}$$

or

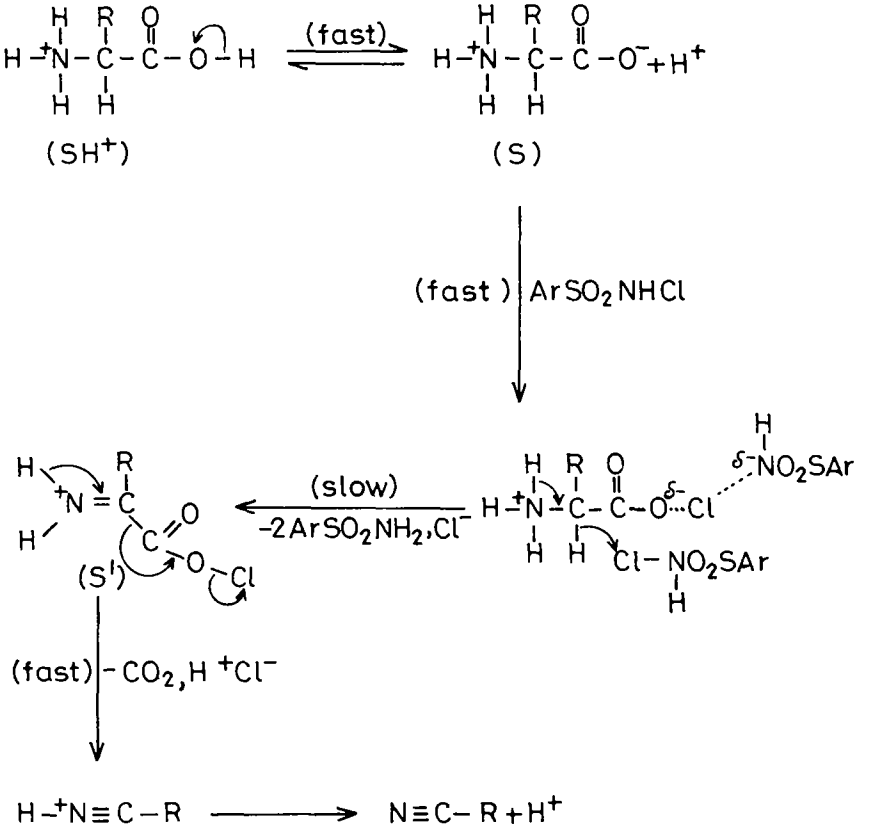
$$K_{obs} = K_1K_2k_3\frac{[SH^+]}{[H^+]} + K_4k_5[Ru(III)]. \tag{15}$$

The plots of k_{obs} versus [AA], k_{obs} versus [Ru(III)] and k_{obs} versus $1/[H^+]$ were linear with finite intercepts on the ordinates (figures 2 and 3) in accordance with rate laws. The constants (K_2k_3), (K_4k_5) and K_1 were computed from the above plots $10^3K_1(\text{mol dm}^{-3}) = 2{\cdot}3$ (Gly), 3·4 (Ala), 3·8 (Val), 4·7 (Phe) and 7·5 (Leu). Further, the constants computed from the plots of k_{obs} versus [S] were used to predict the rate constants from the rate law (14) as [Ru(III)] was varied and vice versa. The predicted constants compared with the experimental values are shown in table 5. There is a reasonable agreement between the predicted values and the experimental rate constants.

[AA] were also varied at different temperatures and the constants K_2k_3 and K_4k_5 were calculated at each temperature. These constants were employed to compute two sets of activation parameters from the Arrhenius plots (table 4).

Table 5. Comparison of predicted and experimental rate constants $10k_{obs}(dm^3 mol^{-1} s^{-1})$ for the Ru(III)-catalysed oxidation of amino acids (AA) by chloramine-T as [AA] and [Ru(III)] were varied. Numbers in parentheses are predicted values.

10^2[AA]	Gly	Ala	Val	Phe	Leu
0·5	6·5(8·3)	2·9(2·3)	3·7(2·5)	4·2(3·4)	5·8(4·5)
1·0	11·3(13·0)	3·5(3·0)	4·6(3·7)	5·7(4·8)	7·2(6·2)
2·0	22·6(22·4)	4·5(4·5)	5·7(5·7)	7·6(7·6)	9·8(9·8)
5·0	51·3(50·6)	8·0(8·0)	8·9(18·3)	13·7(16·0)	17·1(20·9)
10·0	102·4(97·6)	12·6(15·6)	14·4(23·2)	23·8(30·0)	29·9(39·4)
10^5[Ru(III)](mol dm^{-3})					
4·0	22·6(21·9)	4·5(4·5)	5·7(5·6)	7·6(7·5)	9·8(9·6)
8·0	27·5(23·4)	7·5(7·0)	7·1(9·0)	10·0(10·9)	12·6(14·6)
12·0	30·2(24·5)	7·9(9·5)	8·3(12·4)	11·8(14·3)	14·8(19·4)
16·0	33·1(26·4)	8·9(12·0)	9·5(15·8)	13·5(17·7)	16·6(24·2)



Scheme 3.

Scheme 2 is an [AA] independent path. Hence one would expect the same intercept for the k_{obs} versus [AA] plots, (14). But as can be seen from figure 2 intercepts do vary to some extent. The deviation is maximum with glycine, the parent amino acid. This is

also reflected in the magnitudes of fractional orders observed in [AA] (table 3). It is evident from these that although all the amino acids follow similar mechanisms the extent to which a reaction follow a particular mechanism and its specific velocity is characteristic of the amino acid. This kind of behaviour has also been observed earlier and a small variation in structure causes significant variation in the characteristic properties or relative rates of reaction (Gopalakrishnan and Hogg 1985).

Comparison of kinetic data (table 3) for the uncatalysed, Ru(III)-catalysed and chloride-catalysed oxidations of amino acids by chloramine-T establishes the significant role of Ru(III) in the oxidative decarboxylation of amino acids. Chloride generally enhances the rates of oxidations without significantly altering the kinetic orders, whereas Ru(III) under identical acid conditions not only increases the rates of oxidations markedly but also changes the rate dependencies on [AA] and $[H^+]$. A typical detailed mechanism of oxidation of amino acids by CAT is shown in scheme 3.

Free energies of activation are almost the same for all the oxidations showing the operation of similar mechanisms in all cases. Relatively large negative values of entropy of activation may indicate the formation of more ordered activated complexes.

The observed decrease of rates with decrease in dielectric constant of the medium (figure 3) is in conformity with the proposed mechanisms and the Amis concept (Amis 1966; Zuman and Patel 1984; Laidler 1987).

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