Pt^{IV} inhibition on the rate of chloramine-T oxidation of α-amino acids in alkaline medium

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An inhibition effect of platinum(IV) on the rate of oxidation of α-amino acids (alanine, phenylalanine and valine) by alkaline chloramine-T (CAT) has been observed. The kinetic results may be represented by the following rate law.

$$\frac{d[CAT]}{dt} = \frac{2k[CAT]_T [AA]}{K'[AA]+K''[Pt^{IV}]}$$

where AA represents α-amino acid and k, K' and K'' represent constants.

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Among the platinum group metals, the catalysis by palladium(II) and platinum(IV) (the chemistry of which have some common features) in various redox-reactions is well reported[1-7] in literature. In some cases palladium(II) inhibition has also been observed[8]. In preliminary studies, platinum(IV) showed an inhibition effect like that of palladium(II) on the rate of oxidation of some α-amino acids by sodium salt of N-chlorotoulene-p-sulphonamide (chloramine-T, abbreviated as CAT) which acts[9-11] as a versatile oxidizing agent in acidic, alkaline or in a neutral media. The title reaction, therefore, has been studied in detail in order to observe the role of platinum(IV) in the reaction.

Experimental

The reagents employed were (DL)-alanine, (L)-phenylalanine (Thomas Baker) (DL)-valine (Loba, AR), chloramine-T (Loba, AR) and chloroplatinic acid (Thomas Baker). Other reagents, viz., NaOH, NaClO₄, NaCl etc. used were of AR grade. All solutions were prepared in doubly distilled water. Freshly prepar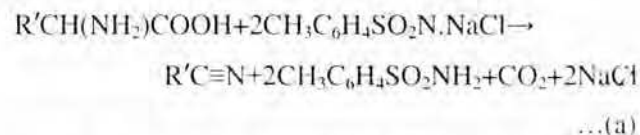ed solution of the substrate was used in the experiments. Stock solution of chloramine-T was standardized iodometrically and stored in dark coloured bottle.

The stock solution of chloroplatinic acid (9.34×10^{-3} mol dm^{-3}) was prepared by dissolving the sample in very dilute HCl (1.0×10^{-3} mol dm^{-3}) and was stored in black coated bottle to prevent photochemical decomposition. The reaction vessels were also coated with black varnish to avoid photochemical effect.

Appropriate quantities of solutions of chloramine-T, NaOH and H_2PtCl_6 were taken in a 100 cm^3 Jena glass vessel. The requisite amount of doubly distilled water was added so the total volume of the reaction mixture was 50 cm^3 after adding the substrate. The reaction mixture was then placed in a thermostatic bath maintained at the desired temperature $\pm 0.1°C$ and was allowed to attain the bath temperature. The reaction was then initiated by adding the requisite amount of amino acid solution, placed separately in the same bath. The progress of the reaction was followed by determining CAT iodometrically in aliquots withdrawn after regular time intervals.

Stoichiometry and reaction products

Different ratios of [Amino acid] to [CAT] were mixed in the presence of [H_2PtCl_6] and [NaOH]. The estimation of the unreacted CAT after 24h showed that one mole of amino acid consumed two moles of CAT, in accordance with Eq. (a).

$$R'CH(NH_2)COOH + 2CH_3C_6H_4SO_2N.NaCl \rightarrow$$
$$R'C{\equiv}N + 2CH_3C_6H_4SO_2NH_2 + CO_2 + 2NaCl$$
$$...(a)$$

where R' represents CH_3, $C_6H_5.CH_2$ and $(CH_3)_2$ CH for alanine, phenylalanine and valine, respectively.

The nitrile as a major product has been reported[9] by various workers in chloramine-T oxidation of amino acids. The presence of nitrile as the main product, in absence as well as presence of platinum(IV) has also been confirmed by the colour reaction with hydroxylamine in polyethylene glycol and iron(III) chloride. The presence of aldehyde has also been confirmed by Schiff's reagent.

Results and discussion

The rate of the reaction has been determined at several initial concentrations of the reactants. In alkaline medium, the log [CAT] versus time plots were always found to be linear up to 80% of the reactions and, the pseudo-first order rate constants in CAT (k_{obs}) have been evaluated from the slopes of these plots. The identical value of k_{obs} (Table 1) at various initial concentrations of CAT further confirmed a first order dependence of rate with respect to CAT. A plot of k_{obs} versus [Amino acid] deviates from the linearity at higher [Amino acid], while the plot of $1/k_{obs}$ versus $1/$[Amino acid] (Fig. 1) is linear with a positive intercept. Thus, it appears that the order of reaction in amino acid decreases from unity to zero at higher [Amino acid].

The effect of increasing [Platinum(IV)] leads to a decrease in the observed rate constant. A plot of k_{obs} versus [Platinum(IV)] is linear with a negative slope (Fig. 2), which clearly indicates an inhibition effect of platinum(IV) on the rate of the reaction. The effect of [OH⁻] on the rate of oxidation was studied at a fixed ionic strength ($\mu=4.0\times10^{-3}$ mol dm⁻³) maintained by sodium perchlorate. The amount of NaOH already present in the catalyst was taken into account. A negligible effect of [OH⁻] on the rate of oxidation has been observed. Addition of sodium chloride (up to 6.0×10^{-4} mol dm⁻³) and NaClO₄ (up to 4.0×10^{-3} mol dm⁻³) also showed a negligible effect on k_{obs}.

The rates were also measured at various temperatures, viz., 30, 35, 40, 45°C and the activation parameters have been evaluated (Table 2).

The various oxidizing species in an alkaline solution are CAT itself, RNHCl and hypochlorite ion (OCl⁻).

The kinetics of oxidation of a series of aminoacids by chloramine-T in alkaline medium have been investigated[9] and the mechanism of the reaction has been proposed to proceed via formation of an intermediate between the aminoacid and RNHCl, i.e., the reactive species of chloramine-T in a fast step. The intermediate show form, subsequently interacts with another molecule of RNHCl to give the products. On the basis of the above facts and experimental results in presence of platinum(IV), a general mechanism for the oxidation of α-amino acid by CAT in alkaline medium (Scheme 1) is proposed as follows.

Table 1 — Effect of [Reactants] on the rate constants at 35°C. [OH⁻]= 2.0×10^{-3} mol dm⁻³

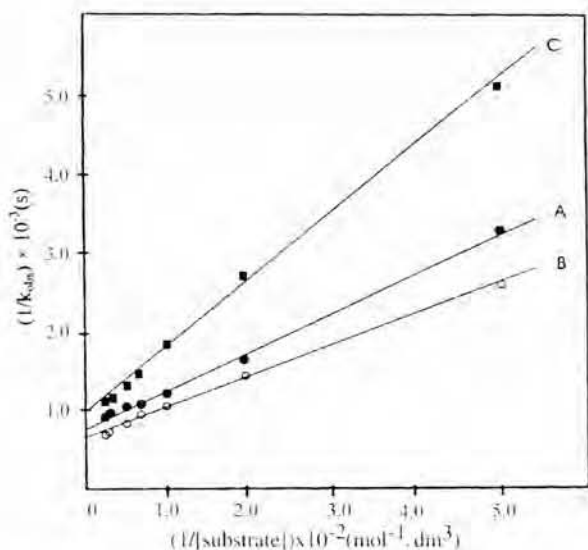| 10^3[CAT] (mol dm⁻³)	10^2[Substrate] (mol dm⁻³)	10^4[Pt^{IV}] (mol dm⁻³)	$10^3 k_{obs}$ (s⁻¹)		
			Alanine(A)	Phenylalanine(B)	Valine(C)
1.0	2.0	0.93	0.95	1.26	0.80
1.5	2.0	0.93	0.95	1.22	0.76
2.0	2.0	0.93	0.95	1.26	0.76
3.0	2.0	0.93	0.95	1.26	0.76
4.0	2.0	0.93	0.95	1.26	0.76
2.0	0.2	0.93	0.30	0.38	0.19
2.0	0.5	0.93	0.61	0.65	0.38
2.0	1.0	0.93	0.80	0.99	0.53
2.0	1.5	0.93	0.92	1.18	0.69
2.0	3.0	0.93	1.03	1.42	0.80
2.0	4.0	0.93	1.07	1.45	0.84
2.0	2.0	Nil	1.15	1.42	0.92
2.0	2.0	0.46	1.07	1.34	0.84
2.0	2.0	1.40	0.88	1.18	0.69
2.0	2.0	1.86	0.80	1.13	0.61
2.0	2.0	2.80	0.65	0.99	0.46
2.0	2.0	3.73	0.49	0.92	0.26

Fig. 1 — Plot of $1/k_{obs}$ versus $1/[$Substrate$]$ at 35°C. {[CAT] = 2.0×10^{-3} mol dm^{-3}; [H$_2$PtCl$_6$] = 0.93×10^{-4} mol dm^{-3}; [OH$^-$] = 2.0×10^{-3} mol dm^{-3}; A, alanine; B, phenylalanine; C, valine}.
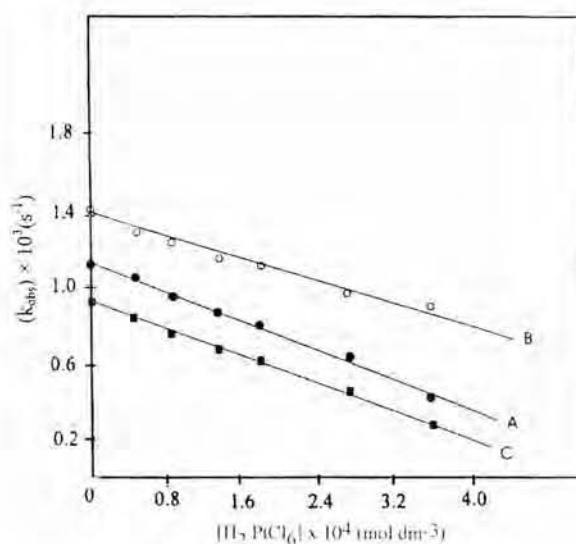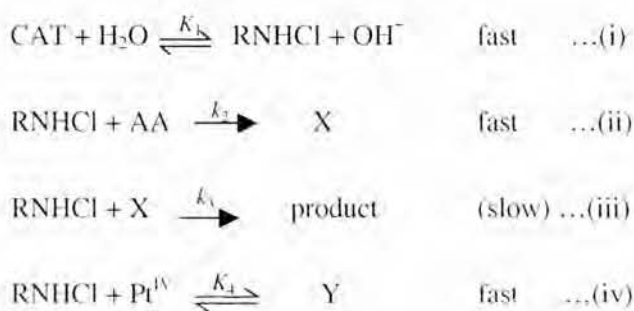

Fig. 2 — Plots of k_{obs} versus [H$_2$PtCl$_6$] at 35°C. {[CAT] = 2.0×10^{-3} mol dm^{-3}; [Substrate] = 2.0×10^{-2} mol dm^{-3}; [OH$^-$] = 2.0×10^{-3} mol dm^{-3}; A, alanine; B, phenylalanine; C, valine}.

Table 2 — Activation parameters for the oxidation of amino acids in presence of Pt^{IV} {[Substrate] = 2.0×10^{-2} mol dm^{-3}, [H$_2$PtCl$_6$] = 0.93×10^{-4} mol dm^{-3}; [OH$^-$] = 2.0×10^{-3} mol dm^{-3}; [CAT] = 2.0×10^{-3} mol dm^{-3}}

Substrate	$\Delta E^{\#}$ (kJ mol^{-1})	log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
Alanine (A)	84.20 ± 0.05	11.28	81.62 ± 0.25	-29.17 ± 0.5	90.68 ± 1.0
Phenylalanine (B)	76.55 ± 0.05	10.11	73.97 ± 0.25	-51.60 ± 0.5	89.98 ± 1.0
Valine (C)	91.86 ± 0.05	12.44	89.28 ± 0.25	-6.97 ± 0.5	91.44 ± 1.0

CAT + H$_2$O $\underset{}{\overset{K_1}{\rightleftharpoons}}$ RNHCl + OH$^-$ fast ...(i)

RNHCl + AA $\xrightarrow{k_2}$ X   fast ...(ii)

RNHCl + X $\xrightarrow{k_3}$ product   (slow) ...(iii)

RNHCl + Pt^{IV} $\underset{}{\overset{K_4}{\rightleftharpoons}}$ Y   fast ...(iv)

Scheme 1

A complex of CAT with other platinum group metal-ion viz. osmium(VIII) is also reported in the literature.

According to Scheme 1, the rate of disappearance of [CAT] may be obtained as.

$$-\frac{d[CAT]}{dt} = k_2[RNHCl][AA] + k_3[RNHCl][X] \quad ...(1)$$

$$= 2k_2[RNHCl][AA] \quad ...(2)$$

Considering the total concentration of CAT as.

$$[CAT]_T = [CAT] + [RNHCl] + [X] + [Y] \quad ...(3)$$

Again, taking

$$[RNHCl] = K_1[CAT][H_2O]/[OH^-] \quad ...(4)$$

$$[X] = k_2[RNHCl][AA], \text{ and} \quad ...(5)$$

$$[Y] = K_4[RNHCl][Pt^{IV}] \quad ...(6)$$

with the help of Eqs (3), (4), (5) and (6), the value of [RNHCl] in terms of [CAT]$_T$ may be given as.

$$[RNHCl] = \frac{K_1[CAT]_T[H_2O]}{[OH^-]+K_1[H_2O]\{k_2[AA]+K_4[Pt^{IV}]\}} \quad ...(7)$$

And, therefore, the rate law (2) becomes,

$$\frac{d[CAT]}{dt} = \frac{2k_2K_1[CAT]_T[H_2O][AA]}{[OH^-]+K_1[H_2O]\{k_2[AA]+K_4[Pt^{IV}]\}} \quad ...(8)$$

Neglecting [OH⁻] is the denominator in comparison to other terms, the rate law (8) is converted to,

$$\frac{d[CAT]}{dt} = \frac{2k_2[CAT]_T[AA]}{k_2[AA]+K_4[Pt^{IV}]} \quad ...(9)$$

The above rate law (9) explains all the experimental results i.e. first order dependence of rate with respect to CAT, negligible effect of [OH⁻] on the rate, inhibition effect of [Pt^{IV}] and a decrease in order of reaction in amino acid from unity to zero at higher [Aminoacid].

References

1. Singh A K, Chopra D, Rahmani S & Singh B. *Carbohydr Res*, 3-4 (1998) 157.

2. Grover N, Kambo N & Upadhyay S K, *Indian J Chem*, 41A (2002) 2482.

3. Kambo N & Upadhyay S K, *Oxid Commun*, 24 (2001) 547.

4. Grover N, Kambo N & Upadhyay S K, *Int J Chem Kinet*, 34 (2002) 603.

5. Mallamma, Anand S, Rangaswamy & Gowda NMM, *Oxid Commun*, 26 (2003) 603.

6. Kondarasaiah M H, Ananda S, Puttaswamy & Gowda N M M, *Synth React Inorg Metal Org Chem*, 33 (2003) 1145.

7. Kambo N & Upadhyay S K, *Indian J Chem*, 43A (2004) 1210.

8. Shukla A, Gupta S & Upadhyay S K, *Int J Chem Kinet*, 23 (1991) 279.

9. (a) Agrawal M C & Upadhyay S K, *J Scient Ind Res*, 49 (1990) 13 and references therein; (b) Banerji K K, Jayaram B & Mahadevappa D S, *J Scient Ind Res*, 46 (1987) 65 and references therein.

10. Grover N & Upadhyay S K, *Bull Chem Ind*, 74 (2003) 67.

11. Kambo N, Upadhyay S K & Jain A K, *Oxid Commun*, 26 (2003) 502.