Kinetics and Mechanisms of Redox Reactions in Aqueous Solution. Part 8.[1] Osmium(VIII) Catalysed Oxidation of Amino Acids by Alkaline Hexacyanoferrate(III)

Raj N. Mehrotra * and Ramesh C. Kapoor *
Department of Chemistry, University of Jodhpur, Jodhpur 342001, India
Sharad Kumar Vajpai
Department of Chemistry, C.M.D. Post-graduate College, Bilaspur(M.P.), India

Amino acids, in the presence of Os^{VIII} as a catalyst, are oxidised by alkaline hexacyanoferrate(III) to aldehydes. There is a zero-order dependence in $[Fe(CN)_6{}^{3-}]$, an order less than unity in [amino acid], and a first-order dependence in $[Os^{VIII}]$ and $[OH^-]$. The observed zero-order rate constant was independent of $[Fe(CN)_6{}^{4-}]$. The proposed mechanism envisages the formation of a transient $[OsO_4(OH)_2]^{2-}$–amino acid complex prior to its rate-limiting interaction with hydroxide ion. The respective values of the equilibrium and rate-limiting constants are reported. The values of the enthalpy and entropy of activation in each case are also estimated.

A detailed study on the kinetics of the oxidation of amino acids by alkaline $[Fe^{III}(CN)_6]^{3-}$, in the presence of Os^{VIII} as catalyst, has been reported by Upadhyay and Agrawal,[2-4] who reported that the reaction is catalysed by $[Fe(CN)_6]^{4-}$ and that there is a zero-order dependence in [amino acid] and a second-order dependence in $[Fe(CN)_6{}^{3-}]$ in the presence of excess amino acid. At moderate concentrations of amino acids {*i.e.* when [amino acid] > $[Fe(CN)_6{}^{3-}]$} the reaction was stated to have zero-order dependence in $[Fe(CN)_6{}^{3-}]$ and first order in [amino acid]. The following mechanism was proposed [equations (1)—(6)]. Reaction (1)

$$\text{amino acid} + [Fe(CN)_6]^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex X (fast)} \quad (1)$$

$$\text{complex X} + Os^{VIII} \xrightarrow{k_2} Os^{VI} + [Fe(CN)_6]^{4-} + \text{products (slow)} \quad (2)$$

$$2[Fe(CN)_6]^{3-} + Os^{VI} \xrightarrow{k_3} 2[Fe(CN)_6]^{4-} + Os^{VIII} \text{ (fast)} \quad (3)$$

$$\text{amino acid} + Os^{VIII} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{complex Y (slow)} \quad (4)$$

$$\text{complex Y} \xrightarrow{k_5} Os^{VI} + \text{keto acid} + NH_3 \text{ (fast)} \quad (5)$$

$$\text{amino acid} + Os^{VI} \xrightarrow{k_6} Os^{IV} + \text{keto acid} + NH_3 \text{ (slow)} \quad (6)$$

was included apparently to explain the observed autocatalysis by $[Fe(CN)_6]^{4-}$.

This mechanism presented some interesting features which were not explained: (*i*) why the complex formation in (1) is a faster process than the complex formation shown in (4), and (*ii*) does the faster oxidation of Os^{VI} in reaction (3) leave behind enough Os^{VI} to be reduced slowly by amino acid in reaction (6)? Similarly the formation of a keto acid as the oxidation product [3,4] was inconsistent with the reported formation of aldehydes in the oxidation of amino acids by a variety of oxidants [5-15] which included both metal and non-metal oxidants.

Attracted by these anomalies, the reinvestigation of the kinetics of the oxidation of glycine and α-alanine was undertaken. The results presented are inconsistent with those reported by Upadhyay and Agrawal,[2-4] and also suggest a much simpler mechanism.

Experimental

Reagents.—Solutions of glycine (BDH, A.R.), α-alanine (Sigma), and $K_3[Fe(CN)_6]$ (Fluka, puriss) were freshly prepared from samples which were used as received.

A standard osmium tetraoxide solution (G. F. Smith) was suitably diluted with a standard sodium hydroxide solution with due regard for the neutralisation of sulphuric acid present in the sample. Sodium hydroxide solutions were freshly prepared and standardised against potassium hydrogen phthalate solution. Sodium chloride (BDH, A.R.) was used throughout for adjusting the ionic strength. Doubly distilled water, with final distillation from an all-glass still, was used throughout.

Stoicheiometry.—Several reaction mixtures with $[Fe(CN)_6{}^{3-}] \ll$ [amino acid] at a fixed $[Os^{VIII}]$ (same as used in the kinetics) but at different $[OH^-]$ were prepared. After the complete reduction of $[Fe(CN)_6{}^{3-}]$ the reaction mixtures were acidified and treated with 2,4-dinitrophenylhydrazine. The precipitated hydrazones were purified, weighed, and their m.p.s determined. On the basis of the melting points it was concluded that glycine and α-alanine were oxidised to formaldehyde and acetaldehyde respectively. The concentration of the aldehyde was calculated from the weight of the hydrazone recovered. The results shown in Table 1 indicated that $\Delta[Fe(CN)_6{}^{3-}]/\Delta[\text{aldehyde}] = 2.1 \pm 0.2$, which formed the basis for the stoicheiometric equation (7) (R = H or Me).

$$RCH(NH_2)CO_2{}^- + 2[Fe(CN)_6]^{3-} + OH^- \longrightarrow RCHO + CO_2 + NH_3 + 2[Fe(CN)_6]^{4-} \quad (7)$$

Test for Free Radical.—Reaction solutions were degassed with nitrogen before the initiation of the reaction and the addition of acrylonitrile to the partially oxidised reaction mixtures. No polymerisation of the monomer was noted over a considerable period of time. This experiment, however, does not prove that a free radical is not formed. It is possible that the monomer might not be polymerised if the free radical reacts more quickly with one of the species present in solution than with the monomer. However, in the knowledge that Os^{VIII} undergoes a two-electron change in the oxidation of

Table 1. Details of the stoicheiometric investigations in the presence of $10^6[\mathrm{Os^{VIII}}] = 0.5$ mol dm^{-3} (gly = glycine, ala = α-alanine)

$10^4[\mathrm{Fe(CN)_6^{3-}}]$/ mol dm^{-3}	10^3[Amino acid]/ mol dm^{-3}	$[\mathrm{OH^-}]$/mol dm^{-3}	10^2 (Mass hydrazone recovered)/g	10^4[Aldehyde]/ mol dm^{-3}	$\dfrac{\Delta[\mathrm{Fe(CN)_6^{3-}}]}{\Delta[\mathrm{Aldehyde}]}$
8.00	2.0 (gly)	0.1	7.12	3.39 [a]	2.36
6.00	2.0 (ala)	0.2	6.32	2.82 [b]	2.13
6.00	3.2 (gly)	0.25	6.13	2.92 [a]	2.05
4.00	2.0 (ala)	0.50	4.12	1.84 [b]	2.17
4.62	4.5 (ala)	0.40	5.40	2.41 [b]	1.92
5.00	4.5 (gly)	0.32	5.71	2.72 [a]	1.84
					Mean = 2.08 ± 0.19

[a] Aldehyde = HCHO. [b] Aldehyde = $\mathrm{CH_3CHO}$.

Table 2. Dependence of the observed pseudo-zero-order rate constant, k_0, on [amino acid]; $10^4[\mathrm{Fe(CN)_6^{3-}}] = 8.0$, $10^5[\mathrm{Os^{VIII}}] = 1.5$, and $I = 1.5$ mol dm^{-3}

	10^7k_0/mol dm^{-3} s^{-1}					10^7k_0/mol dm^{-3} s^{-1}			
[gly] [a]/mol dm^{-3}	25 °C	30 °C	35 °C	40 °C	[ala] [b]/mol dm^{-3}	25 °C	30 °C	35 °C	40 °C
0.0048	3.11	3.37	3.63	4.20	0.005	2.36	2.84	4.02	5.12
0.0096	5.71	6.23	6.70	7.83	0.010	4.56	5.41	7.80	10.0
0.020	10.1	11.1	12.1	14.2	0.020	8.41	10.0	14.7	18.8
0.040	15.7	17.4	19.2	22.8	0.030	11.7	14.2	20.7	26.8
0.060	19.3	21.4	24.0	28.6	0.040	14.7	17.9	26.4	34.2

[a] [NaOH] = 0.2 mol dm^{-3}. [b] [NaOH] = 0.5 mol dm^{-3}.

organic compounds, it might not be erroneous to assume the absence of free radicals during the course of the reaction.

Rate Measurements.—A Spectrochem spectrophotometer fitted with a thermostatted compartment and a recorder was used to follow the disappearance of $[\mathrm{Fe(CN)_6}]^{3-}$ at 420 nm. The temperature was maintained at the desired value to within ±0.1 °C. Reaction mixtures having [amino acid] $\gg$ $[\mathrm{Fe(CN)_6^{3-}}]$ were used for the kinetics. The reaction was initiated by the quick addition of the amino acid solution to a solution containing appropriate concentrations of $[\mathrm{Fe(CN)_6}]^{3-}$, NaOH, NaCl, and $\mathrm{Os^{VIII}}$ (after the solutions had reached thermal equilibrium). The reaction mixture was immediately transferred into the test-tube and returned to the thermostatted compartment as quickly as possible.

The absorbance was recorded until it reached a value which was approximately one-eighth of the initial absorbance. Plots of absorbance against time were linear indicating a zero-order dependence in $[\mathrm{Fe(CN)_6^{3-}}]$. The slopes of these plots were divided by $\varepsilon_{420} = 1\,298$ dm^3 mol^{-1} cm^{-1}, obtained for the test-tube used. The quotient was the value of k_0, the observed pseudo-zero-order rate constant. The ionic strength was kept constant at 1.5 mol dm^{-3}. The k_0 values had a reproducibility $\geqslant 97\%$ and the mean values are reported in the Tables. The zero-order dependence in $[\mathrm{Fe(CN)_6^{3-}}]$ was further confirmed by the observed proportionate increase in $t_{\frac{1}{2}}$ with increasing $[\mathrm{Fe(CN)_6^{3-}}]$.

Results

Dependence on [Amino Acid].—The values of k_0 at different [amino acid] and temperatures are given in Table 2. Plots of k_0 *versus* [amino acid] were found to be strongly curved as were plots of log k_0 *versus* log [amino acid]. This implies k_0 = [amino acid]/f([amino acid]) where f is a polynomial in [amino acid]. Accordingly the plot between k_0^{-1} and [amino acid]$^{-1}$ was attempted and found to be linear at all temperatures. One such plot at 25 °C is shown in the Figure. The intercepts and slopes were obtained statistically for use in the calculations of other constants as described later.

Dependence on $[\mathrm{Os^{VIII}}]$.—The rate measurements over a six-fold variation in the initial $[\mathrm{Os^{VIII}}]$ are given in Table 3. Higher $[\mathrm{Os^{VIII}}]$ could not be used because the rate increased beyond manageable limits. The results in the restricted range did indicate a proportional increase in the rate. The plot of k_0 *versus* $[\mathrm{Os^{VIII}}]$ was found to be linear and passed through the origin. Passage through the origin implied that alkaline $[\mathrm{Fe(CN)_6}]^{3-}$ did not oxidise the amino acid to any appreciable extent in the absence of osmium(VIII).

Dependence on $[\mathrm{OH^-}]$.—The k_0 values over a twelve-fold variation in the initial [NaOH] are given in Table 4, a perusal of which indicates that k_0 increases proportionately with increasing [NaOH]. The plot of k_0 *versus* [NaOH] was linear with zero intercept. The zero intercept signified the fact that aqueous osmium tetraoxide solution did not act as a catalyst for the reaction.

Dependence on $[\mathrm{Fe(CN)_6^{4-}}]$.—The dependence of k_0 on the initial $[\mathrm{Fe(CN)_6^{4-}}]$ was investigated in the oxidation of L-leucine. The results given in Table 5 indicated that the initial addition of hexacyanoferrate(II) in concentrations up to 60% of $[\mathrm{Fe(CN)_6}]^{3-}$ present in the reaction mixture did not affect the observed rate. It might be added that Upadhyay and Agrawal [2-4] reported an autocatalysis of the rate by $[\mathrm{Fe(CN)_6}]^{4-}$.

Discussion

This study has shown that the reaction has a zero-order dependence in $[\mathrm{Fe(CN)_6^{3-}}]$, a first-order dependence in $[\mathrm{Os^{VIII}}]$ and $[\mathrm{OH^-}]$, and a fractional order in [amino acid] which decreased from 0.9 at the lowest concentrations to *ca.* 0.5 at the highest.* A total change in the order of the reaction,

---

* We thank a referee for pointing out this fact.

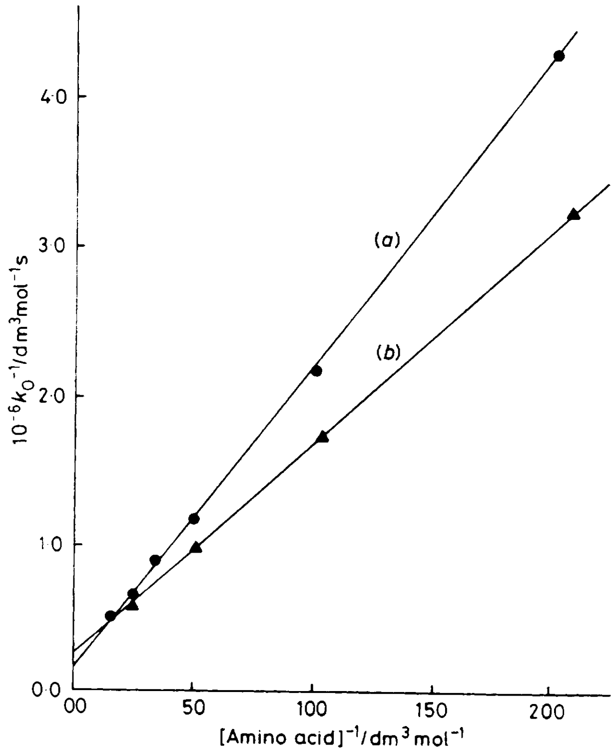


Figure. Representative plot between k_0^{-1} *versus* [amino acid]$^{-1}$ at 25 °C. Similar plots were obtained at other temperatures. Plot (*a*) is for α-alanine and (*b*) for glycine. Experimental conditions are given in Table 2

Table 3. Dependence of the observed pseudo-zero-order rate constant, k_0, on [Os^{VIII}] at 25 °C; 10^4[Fe(CN)$_6^{3-}$] = 8.0, 10^2[amino acid] = 4.0 and I = 1.5 mol dm^{-3}

	10^7k_0/mol dm^{-3} s^{-1}	
10^5[Os^{VIII}]/mol dm^{-3}	Glycine [a]	α-Alanine [b]
0.48	5.22	5.41
1.02	11.7	11.4
1.50	16.0	16.3
2.04	23.1	22.6
2.52	28.9	28.2
3.00	34.2	33.8

[a] [NaOH] = 0.2 mol dm^{-3}. [b] [NaOH] = 0.5 mol dm^{-3}.

i.e. from zero order to second order with respect to [Fe(CN)$_6^{3-}$] and from first order to zero order with respect to [amino acid] in the presence of excess amino acid, reported by Upadhyay and Agrawal,[2-4] was however not encountered although [amino acid] was varied almost in the same range.

Similarly the autocatalysis of the rate by [Fe(CN)$_6$]$^{4-}$, reported previously,[2-4] was also not observed. The fact that k_0 was independent of [Fe(CN)$_6^{4-}$], added from outside, ruled out the possibility of the existence of equilibrium (1).

The spectrophotometric determination of the dissociation of osmic acid in KOH solution (I = 1 mol dm^{-3}) at 25 °C showed the first (K_{1a}) and second (K_{2a}) dissociation constants to be 1×10^{-2} and 3×10^{-15} mol dm^{-3} respectively.[16] Further, osmium tetraoxide gives complexes such as *trans*-[OsO$_4$(OH)(H$_2$O)]$^-$ and *trans*-[OsO$_4$(OH)$_2$]$^{2-}$ with alkalis.[17,18] The two possible equilibria are therefore as given by equations (8) and (9).

Table 4. Dependence of k_0 on [NaOH] at 25 °C and I = 1.5 mol dm^{-3}; 10^4[Fe(CN)$_6^{3-}$] = 8.0, 10^5[Os^{VIII}] = 1.5, and 10^2[amino acid] = 4.0 mol dm^{-3}

	10^7k_0/mol dm^{-3} s^{-1}	
[NaOH]/mol dm^{-3}	Glycine	α-Alanine
0.12	8	—
0.20	16	7
0.40	27	12
0.60	40	19
0.80	53	26
1.00	67	32
1.20	—	38

Table 5. Dependence of k_0 on [Fe(CN)$_6^{4-}$]; 10^3[Fe(CN)$_6^{3-}$] = 1.0, 10^6[Os^{VIII}] = 4.6; 10^2[L-leucine] = 1.0, [NaOH] = 0.3, and I = 1.0 mol dm^{-3} at 33 °C

10^3[Fe(CN)$_6^{4-}$]/mol dm^{-3}	0.0	0.1	0.4	0.6
10^8k_0/ mol dm^{-3} s^{-1}	8.20	8.17	8.24	8.16

$$[OsO_4(H_2O)_2] + OH^- \overset{K_1}{\rightleftharpoons} [OsO_4(OH)(H_2O)]^- + H_2O \quad (8)$$

$$[OsO_4(OH)(H_2O)]^- + OH^- \overset{K_2}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \quad (9)$$

The values of K_1 and K_2 can be calculated from the known values of K_{1a} and K_{2a} respectively ($K_n = K_{na}[H_2O]/K_w$). Thus the value of K_1 was 5.55×10^{13} which meant that almost all of the [OsO$_4$(H$_2$O)$_2$] existed as [OsO$_4$(OH)(H$_2$O)]$^-$ even in dilute alkaline solution. Similarly the value of K_2 was 16.6 which is in fair agreement with the value of 24 ± 4 reported recently.[19] It is thus obvious that equilibrium (9) is the only equilibrium that needs consideration in the mechanisms of redox reactions involving the use of osmium tetraoxide in alkaline medium.

Amino acids exist as zwitterions in aqueous solution. In alkaline solutions, the zwitterion is quantitatively converted to RCH(NH$_2$)CO$_2^-$ which is the obvious reactive species under the present experimental conditions.

A zero-order dependence in [Fe(CN)$_6^{3-}$] excludes any possibility of its appearance in any mechanistic step preceding the rate-limiting step.

A first-order dependence in [Os^{VIII}] and the linearity of the plot between k_0^{-1} and [amino acid]$^{-1}$ (Figure) is considered to suggest the possible formation of a transient complex between Os^{VIII} and the amino acid similar to that assumed to form between an enzyme and substrate in the well known Michaelis and Menten [20] mechanism for enzyme–substrate reactions. This assumption might not be erroneous because the intermediacy of Os^{VIII}–amino acid complexes has been proposed [21,22] earlier although their existence has not been demonstrated.

Hence the equilibria (10) and (11) should be a fast process instead of a slow process [equation (4)] as had been assumed by Upadhyay and Agrawal.[2-4] The proposed mechanism of the oxidation is considered to include the reactions (9)—(16) (R = H or Me), in view of the discussion above, wherein reactions (12) and (13) are rate limiting.

The rate law given by equation (20) is derived on the assumption that equations (17) and (18) hold.

$$[OsO_4(OH)(H_2O)]^- + OH^- \overset{K_2}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \quad (9)$$

$$[OsO_4(OH)(H_2O)]^- + RCH(NH_2)CO_2^- \overset{\beta_1}{\rightleftharpoons} [OsO_4(OH)\{RCH(NH_2)CO_2\}]^{2-} + H_2O \quad (10)$$

$$[OsO_4(OH)_2]^{2-} + RCH(NH_2)CO_2^- \overset{\beta_2}{\rightleftharpoons} [OsO_4(OH)_2\{RCH(NH_2)CO_2\}]^{3-} \quad (11)$$

$$[OsO_4(OH)\{RCH(NH_2)CO_2\}]^{2-} + OH^- \xrightarrow{k_1} [OsO_4(OH)]^{3-} + RCHNH + CO_2 + H_2O \quad (12)$$

$$[OsO_4(OH)_2\{RCH(NH_2)CO_2\}]^{3-} + OH^- \xrightarrow{k_2} [OsO_4(OH)_2]^{4-} + RCHNH + CO_2 + H_2O \quad (13)$$

$$RCHNH + H_2O \xrightarrow{\text{fast}} RCHO + NH_3 \quad (14)$$

$$[OsO_4(OH)]^{3-} + 2[Fe(CN)_6]^{3-} + H_2O \xrightarrow{\text{fast}} [OsO_4(OH)(H_2O)]^- + 2[Fe(CN)_6]^{4-} \quad (15)$$

$$[OsO_4(OH)_2]^{4-} + 2[Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} [OsO_4(OH)_2]^{2-} + 2[Fe(CN)_6]^{4-} \quad (16)$$

$$[Os^{VIII}]_0 = [OsO_4(OH)(H_2O)^-] + [OsO_4(OH)_2{}^{2-}] + [OsO_4(OH)\{RCH(NH_2)CO_2\}^{2-}] + [OsO_4(OH)_2\{RCH(NH_2)CO_2\}^{3-}] \quad (17)$$

$$[OsO_4(OH)(H_2O)^-] = [Os^{VIII}]_0/\{1 + \beta_1[RCH(NH_2)CO_2^-] + K_2[OH^-](1 + \beta_2[RCH(NH_2)CO_2^-]\} \quad (18)$$

$$-d[Fe(CN)_6{}^{3-}]/dt = 2(k_1\beta_1 + k_2\beta_2K_2[OH^-])\text{-}[OsO_4(OH)(H_2O)^-][RCH(NH_2)CO_2^-][OH^-] \quad (19)$$

Substitution of the value of $[OsO_4(OH)(H_2O)^-]$ from (18) into (19) gives equation (20).

$$\frac{-d[Fe(CN)_6{}^{3-}]}{dt} = \frac{2(k_1\beta_1 + k_2\beta_2K_2[OH^-])[Os^{VIII}]_0[RCH(NH_2)CO_2^-][OH^-]}{K_2[OH^-]\,(1 + \beta_2[RCH(NH_2)CO_2^-]) + 1 + \beta_1[RCH(NH_2)CO_2^-]} \quad (20)$$

Now, in view of the high value of K_2, an assumption can be made, that $K_2[OH^-](1 + \beta_2[RCH(NH_2)CO_2^-]) \gg 1 + \beta_1[RCH(NH_2)CO_2^-]$ whence equation (20) can be reduced to equation (21) which is the desired rate law.

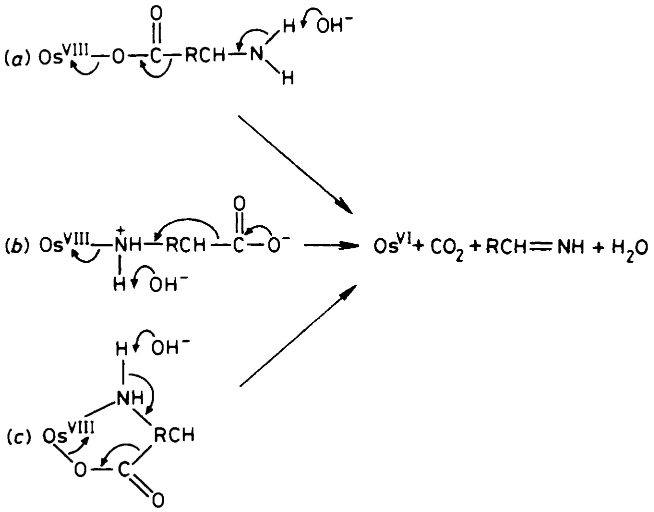
$$k_0 = \frac{2k_2\beta_2[OH^-][Os^{VIII}]_0[RCH(NH_2)CO_2^-]}{1 + \beta_2[RCH(NH_2)CO_2^-]} \quad (21)$$

The rate law (21) can be interpreted to mean that the transient complex $[OsO_4(OH)\{RCH(NH_2)CO_2\}]^{2-}$ is either inert or its contribution to the observed rate is insignificant ($k_1\beta_1/K_2 \ll k_2\beta_2[OH^-]$) in comparison to the contribution by $[OsO_4(OH)_2\{RCH(NH_2)CO_2\}]^{3-}$. A consideration of the co-ordination number and the geometrical structure of the two transient complexes helps to explain their reactivity. The stable octahedral structure and the co-ordination number of six in $[OsO_4(OH)(H_2O)]^-$ and $[OsO_4(OH)_2]^{2-}$ is retained in $[OsO_4(OH)\{RCH(NH_2)CO_2\}]^{2-}$ which explains its stability or lesser reactivity. The octahedral structure changes in $[OsO_4(OH)_2\{RCH(NH_2)CO_2\}]^{3-}$ because of an increase in the co-ordination number from six to seven. The change in the geometrical structure combined with the presence of a higher charge makes this transient complex more labile and therefore more reactive. The amino acid has been considered to be a univalent ligand.

Table 6. Values of k_2/dm³ mol⁻¹ s⁻¹ and β_2/dm³ mol⁻¹ at different temperatures and the respective values of the enthalpy (kJ mol⁻¹) and entropy of activation (J K⁻¹ mol⁻¹)

θ_c/°C	$k_{2(\text{gly})}$	$k_{2(\text{ala})}$		$\beta_{2(\text{gly})}$	$\beta_{2(\text{ala})}$
25	1.18	0.76		20.0	8.6
30	1.33	1.03		19.2	7.5
35	1.56	1.67		17.5	6.7
40	1.94	2.42		16.2	5.8
$\Delta H^\ddagger$	23 ± 4	58 ± 7	$\Delta H^\ominus$	8 ± 3	17 ± 6
$\Delta S^\ddagger$	−167 ± 12	−50 ± 8	$\Delta S^\ominus$	−12 ± 5	−46 ± 9

The probable modes of electron transfer within the transient complex could be represented by the processes shown below,*



each of which lead to the formation of an imine, Os^{VI}, CO_2, and water.

The value of k_2 was evaluated from the intercept of the linear plots between k_0^{-1} and [amino acid]$^{-1}$. The quotient of the intercept/slope was equated to the value of β_2. Plots between log k_2 or log β_2 and T^{-1} were linear and the values of the entropy and enthalpy corresponding to these two parameters are reported in Table 6.

A perusal of Table 6 indicates that $\beta_{\text{gly}} > \beta_{\text{ala}}$, and $k_{2(\text{gly})} \sim k_{2(\text{ala})}$ which explains why $k_{0(\text{gly})} > k_{0(\text{ala})}$. It seems that the presence of a bulky group attached to the carbon atom α to the NH_2 and CO_2^- groups in the amino acid sterically hinders their approach to the oxy groups of Os^{VIII}. The decrease in the value of k_0 with increasing size of the substituent group is thus explained. This correlation was further tested against the results of Upadhyay and Agrawal[4] and was consistent.

---

* We thank one of the referees for this suggestion. However, process (*c*) in which the amino acid is shown as a divalent ligand is not consistent with our earlier argument concerning the relative reactivity of the two transient complexes wherein the amino acid was considered to behave as a univalent ligand as is shown in processes (*a*) and (*b*).

Acknowledgements

We thank the University Grants Commission, New Delhi, for financial assistance and the award of a junior research fellowship (to S. K. V.), and Miss P. Chaudhary for the rate measurements in Table 5.

References

1 Part 7, R. N. Mehrotra, *J. Chem. Soc., Dalton Trans.*, 1981, 897.
2 S. K. Upadhyay and M. C. Agrawal, *Indian J. Chem., Sect. A*, 1977, **15**, 416.
3 S. K. Upadhyay and M. C. Agrawal, *Indian J. Chem., Sect. A*, 1977, **15**, 709.
4 S. K. Upadhyay and M. C. Agrawal, *Indian J. Chem., Sect. A*, 1978, **16**, 39.
5 G. Chandra and S. N. Srivastava, *Indian J. Chem.*, 1973, **11**, 773.
6 R. S. Varma, M. J. Reddy, and V. R. Shastry, *J. Chem. Soc., Perkin Trans. 2*, 1976, 469.
7 M. Bhargava, B. Sethuram, and T. N. Rao, *Indian J. Chem., Sect. A*, 1976, **14**, 770.
8 M. G. R. Reddy, B. Sethuram, and T. N. Rao, *Indian J. Chem., Sect. A*, 1978, **16**, 31.
9 M. G. R. Reddy, B. Sethuram, and T. N. Rao, *Indian J. Chem., Sect. A*, 1978, **16**, 591.
10 Kamaluddin, *Indian J. Chem., Sect. A*, 1980, **19**, 431.
11 P. Manikyamba and E. V. Sundaram, *Indian J. Chem., Sect. A*, 1980, **19**, 1122.
12 M. A. Beg and Kamaluddin, *Indian J. Chem.*, 1975, **13**, 1167.
13 Y. R. Sarma and P. K. Saiprakash, *Indian J. Chem., Sect. A*, 1980, **19**, 1175.
14 K. B. Reddy, B. Sethuram, and T. N. Rao, *Indian J. Chem., Sect. A*, 1981, **20**, 395.
15 L. M. Bharadwaj and P. C. Nigam, *Indian J. Chem., Sect. A*, 1981, **20**, 793.
16 R. D. Sauerbrum and E. B. Sandell, *J. Am. Chem. Soc.*, 1953, **75**, 4170.
17 F. Krauss and D. Wilken, *Z. Anorg. Allg. Chem.*, 1925, **145**, 166.
18 W. P. Griffith, *J. Chem. Soc.*, 1964, 245.
19 D. Mohan and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 1977, 1085.
20 M. L. Michaelis and M. L. Menten, *Biochem. Z.*, 1913, **49**, 333.
21 J. Nyilasi and P. Somogyi, *Magy. Kem. Foly.*, 1972, **78**, 407.
22 J. Nyilasi and P. Somogyi, *Acta Chim. Acad. Sci. Hung.*, 1973, **75**, 405.

Received 6th *January* 1983; *Paper* 3/032