

Kinetics and mechanism of oxidation by metal ions: Part XV¹—Oxidation of glyoxalate ion by alkaline osmium tetroxide

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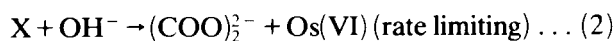
The kinetics of oxidation of glyoxalate ion by alkaline osmium (VIII) is studied with stopped-flow in the presence of excess of glyoxalate ion. A linear correlation between (a) k_{obs}^{-1} and $[\text{OH}^-]$, and (b) k_{obs} and $[\text{CHO.COO}^-]$ is observed where k_{obs} is the observed pseudo-first order rate constant. The rate determining step is the decomposition of, probably, an inner sphere complex $[\text{OsO}_3(\text{OH})_3(\text{OH})_2\text{C.COO}]^{3-}$ formed between $[\text{OsO}_4(\text{OH})_2]^{2-}$ and $(\text{OH})_2\text{CH.COO}^-$. The formation of the complex is inferred by the rapid scanning of the spectrum of the reaction mixture. The kinetically deduced value of the equilibrium constant K_{ha} for the deprotonation of the hydrated glyoxalate ion at 25°C is $3.54 \pm 0.34 \text{ dm}^3\text{mol}^{-1}$. Using this value of K_{ha} , the pK_a value of the gem-diol of glyoxalate ion is calculated to be 13.4 which is in good agreement with the pK_a value of 13.6 for formaldehyde. The thermodynamic parameters and activation enthalpy and entropy values are reported.

Osmium tetroxide is a powerful two-equivalent oxidant² having a redox potential of 0.85V for the couple $\text{Os(VIII)}/\text{Os(VI)}^3$. Its solution in $[\text{OH}^-] \geq 0.5 \text{ mol dm}^{-3}$ is stable⁴ and has found extensive use as a catalyst in the oxidation of organic⁵ and inorganic⁶ compounds by hexacyanoferrate (III) ions. The subject matter has been briefly reviewed⁷. The common mechanism of the catalysed reactions is the formation of an Os(VIII)-substrate complex which decomposes in the rate limiting step to Os(VI) and oxidation products of the substrate. Os(VI) is then oxidized to Os(VIII) by two equivalents of hexacyanoferrate (III) ion in the fast step.

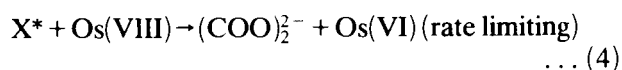
The present study was undertaken to verify the two alternate mechanisms A and B suggested in the osmium (VIII)-catalyzed oxidation of glyoxalate ion (hereafter represented by S) by hexacyanoferrate (III) in alkaline medium⁸ each of these lead to the common rate law, Eq. (5), where k is the composite rate constant. The reactions (2) and (4)

are followed by the reaction (6) which established the catalytic cycle of Os(VIII)/Os(VI).

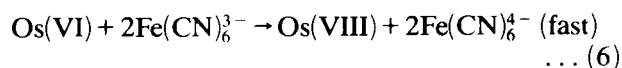
Mechanism A



Mechanism B



$$\frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k[\text{Os(VIII)}][\text{OH}^-][\text{S}] \quad \dots (5)$$



where $[\text{OsO}_4(\text{OH})(\text{OH}_2)]^-$ is the reactive osmium (VIII) species.

The results of this study on the dependence of the observed rate constant on $[\text{OH}^-]$ is contrary to that observed by earlier workers⁸. Hence a different mechanism is proposed and the value of the equilibrium constant K_{ha} for reaction (3) is estimated and the values of the related thermodynamic parameters are estimated. Although the formation of a complex between the reactive species of osmium (VIII) and glyoxalic acid is supported by the rapid scanning of the spectrum of the reaction mixture, the inner-sphere nature of complex is supported by the dependence of k_{obs} on $[\text{OH}^-]$.

Experimental

The stock solution of sodium glyoxalate was prepared by neutralising glyoxalic acid (Fluka, purum) which was used as received. The stock solutions of potassium hydrogen phthalate (BDH, AnalaR) and sodium chloride (Sarabhai-M, GR) were prepared by dissolution of the respective weighed samples in doubly distilled water. A weighed sample of osmium tetroxide was dissolved in a standardised sodium hydroxide solution and stored in a refrigerator. It was frequently standardised.

Stoichiometry and product study

Several reaction mixtures having different [osmium(VIII)] and [glyoxalate ion] (Os(VIII) was always in excess) were prepared in 0.5 mol dm^{-3} sodium

hydroxide together with corresponding blanks (no glyoxalate ion was present). After a suitable time interval (>10 times of the half-life of the reaction), the excess unreacted $[\text{Os(VIII)}]$ was estimated from the difference in the absorbancies at 400 nm of the blank and the corresponding reaction mixture. $\Delta[\text{Os(VIII)}]/\Delta[\text{OHC.COO}^-] = 2.1 \pm 0.2$ was found at room temperature. This ratio was later confirmed by the spectrophotometric titration of glyoxalate ion. Hence the stoichiometry of the reaction is given in Eq. (7). The reaction of oxalate ion with Os(VIII) at $0.1 \text{ mol dm}^{-3} [\text{OH}^-]$ was found to be slow enough to affect either the rate or the stoichiometry of the reaction.



The product was repeatedly extracted with ether after the reaction was complete and the reaction mixtures were acidified with hydrochloric acid. The ether was evaporated and the liquid left behind was treated with a saturated solution of calcium sulphate to precipitate oxalic acid as calcium oxalate. The precipitate was washed, treated with warm sulphuric acid ($\approx 1 \text{ mol dm}^{-3}$) and filtered. The filtrate was treated with 50% hydrochloric acid and granular zinc to reduce oxalic acid to glycolic acid. The liquid was separated from the unreacted zinc, concentrated and treated with 2,7-dihydroxynaphthalene. The mixture on keeping in boiling water developed the characteristic red to violet-red colour confirming the presence of glycolic acid and thereby that of oxalic acid⁹.

Spectral studies

The UV-visible spectra of the solutions, described below, were recorded on a Shimadzu 240 UV-vis Graphicord spectrophotometer at room temperature ($\approx 30^\circ\text{C}$). These are shown in Fig. 1.

Glyoxalate ion

The spectrum of glyoxalate ion (bottom most) shows a maximum absorbance at 200 nm and then there is no maximum absorbance between 200-400 nm; rather the absorbance beyond 250 nm and onwards is almost near the base line. This means that the absorbance of glyoxalate ion in this range is negligible.

Aqueous osmic acid

OsO_4 has a tetrahedral structure¹⁰. It is moderately soluble in water². The spectrum of aqueous osmic acid has an absorbance maxima at 240 nm, a shoulder at 280 nm and a trough around 220 nm. The absorption spectrum of OsO_4 in water is

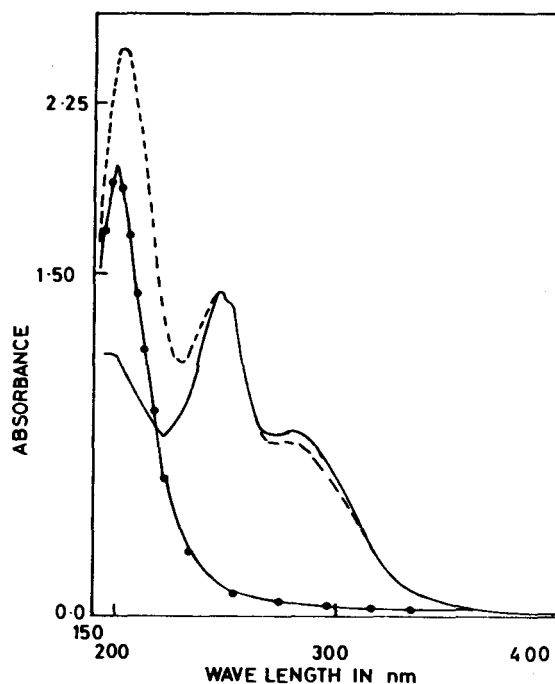


Fig. 1—The UV-visible spectra of aqueous osmic acid, glyoxalate ion, and the mixture of the two at room temperature ($\approx 30^\circ\text{C}$). The spectra of the mixture taken soon after the mixing and some 15 minutes after superimposed indicating that there is no reduction of OsO_4 dissolved in water. $10^4[\text{OsO}_4] = 6.0 \text{ mol dm}^{-3}$; $10^3 [\text{OHC.COO}^-] = 6.0 \text{ mol dm}^{-3}$ (---), and the reaction mixture (----) having the stated concentrations of Os(VIII) and glyoxalate ions

the same as in hexane indicating that it is still tetrahedral².

Aqueous reaction mixture

The spectra of the reaction mixture shows an increase in the height of the trough which is shifted more towards 230 nm and the height of the shoulder is slightly decreased. The spectrum of reaction mixture is taken immediately and some 15 minutes after mixing. Since these two spectra superimposed each other and did not show any change in absorbance over this period of time; it is concluded that osmic acid in aqueous solution does not react with glyoxalate ion.

Perosmate ion

A spectrum of $10^4[\text{OsO}_4] = 3.24 \text{ mol dm}^{-3}$ in different NaOH concentrations shows the characteristic absorbance peak around $320 \pm 5 \text{ nm}$ for solutions $\geq 0.05 \text{ mol dm}^{-3}$ sodium hydroxide. This is consistent with an earlier observation¹¹ that alkaline OsO_4 solutions absorb strongly at 316 nm. The spectra, however, does not show any maximum absorbance at 340 nm as reported by Mohan and Gupta^{6a}. Since these workers recorded

the spectrum beginning from 330 nm and onwards, they probably missed the maximum absorbance at 320 nm.

Rapid scan

Because of the labile nature of the Os(VIII)-glyoxalate complex in alkaline solution, a rapid scan of the spectrum of the reaction mixture was carried out with the Union Giken 401 stopped-flow spectrophotometer attached to RA 415 rapid scan attachment. The rapid scan covers 48 nm on either side of the selected central wavelength which was fixed at 360 nm. The rapid scan of alkaline OsO_4 ($10^4[\text{Os(VIII)}] = 5.5 \text{ mol dm}^{-3}$ in 0.2 mol dm^{-3} NaOH) and those of the reaction mixtures having the same concentrations of sodium hydroxide and OsO_4 are shown in Fig. 2. It is to be noted that the osmium (VIII) solution has maximum absorbance at 325 nm. In the reaction mixture this peak is shifted. The shift, however, cannot be ascribed to the increasing [glyoxalate]. The peak height has, however, decreased with [glyoxalate]. These scans are recorded between 52-102 ms after mixing. The gate time (time taken to scan 96 nm) was fixed at 50 ms and the temperature was kept constant at 6°C .

Rate measurements

The kinetics of the reaction is studied under pseudo-first order conditions ($[\text{glyoxalate}] \gg [\text{OsO}_4]$) at constant ionic strength (1.0 mol dm^{-3} , NaCl). Union Giken RA-401 stopped-flow spectrophotometer, interfaced with RA-451 data acquisition system, is used to follow the reaction at 325 nm. However, few runs are also studied at 400

nm¹². Beers law is obeyed at this wavelength. The rate constant obtained at 400 nm are in agreement with those obtained at 325 nm. The reaction in general is followed for more than three half-lives. For a particular reaction condition at least 7-10 duplicate runs were studied and the mean k_{obs} values with standard deviations are reported in the Tables.

The slope and intercept values of the linear plots together with respective standard deviations were computed by using a single linear regression (SLR) computer program based on the method of least squares. In general the value of $r \geq 0.997$ was obtained in most cases.

Results and discussion

The kinetic results can be summarised as follows:

(i) The invariance of pseudo-first order rate constant k_{obs} ($41.7 \pm 0.3 \text{ s}^{-1}$) over a twenty-fold variation in the initial $[\text{OsO}_4]$ (3.9×10^{-4} – 7.8×10^{-3}) at $[\text{OH}^-] = 0.1 \text{ mol dm}^{-3}$ at 25°C is indicative of a first order dependence of the reaction in $[\text{Os(VIII)}]$.

(ii) Effect of $[\text{OH}^-]$ on k_{obs} is studied at various temperatures over a tenfold variation in its initial concentration. The results, Table 1, indicate that k_{obs} decreases with increase in $[\text{OH}^-]$ and the plot between k_{obs}^{-1} and $[\text{OH}^-]$, is linear with an intercept on the rate ordinate. The respective values of the intercepts and slopes at different temperatures are in Table 1.

(iii) The linear plot between k_{obs} and $[\text{OHC.COO}^-]$ with zero intercept indicated that the order in glyoxalate ion is one. The values of

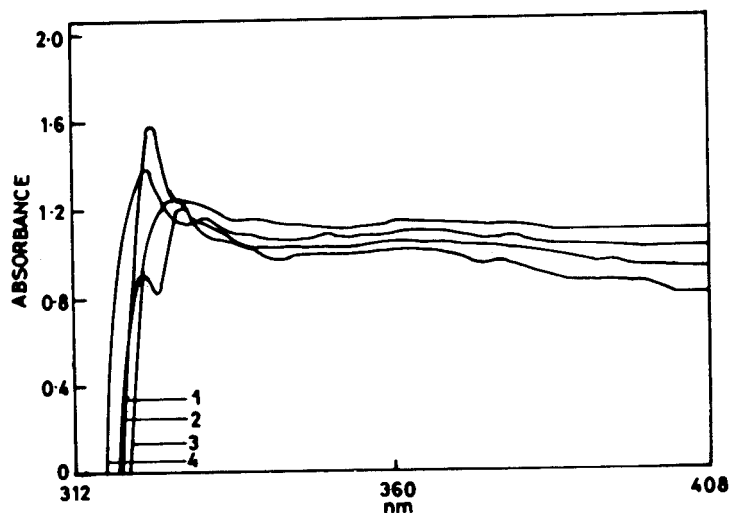


Fig. 2—Rapid scan spectra of $[\text{Os(VIII)}]$ and the reaction mixture in 0.2 mol dm^{-3} NaOH at 6°C . The spectrum of the reaction mixture was recorded between 52-102 ms after mixing. $10^4 [\text{Os(VIII)}] = 5.5 \text{ mol dm}^{-3}$ (spectrum 1) and reaction mixtures having $10^4 [\text{Os(VIII)}] = 5.5 \text{ mol dm}^{-3}$ and $10^3 [\text{OHC.COO}^-] = 5.0$ (spectrum 2), 10.0 (spectrum 3) and 20.0 mol dm^{-3} (spectrum 4)

Table 1—Dependence of k_{obs} on the initial $[\text{OH}^-]$ at different temperature. $10^3[\text{Os(VIII)}]=1.56$, $[\text{OHC.COO}^-]=0.1$ and $I=1.0 \text{ mol dm}^{-3}$

| $[\text{OH}^-]$ (mol dm^{-3}) | Temp. ($^\circ\text{C}$) | | | |
|---|----------------------------|----------|----------|----------|
| | 20 | 25 | 30 | 35 |
| | k_{obs} | | | |
| 0.1 | 32.7±0.1 | 41.6±0.2 | 58.6±0.6 | 71.0±0.7 |
| 0.2 | 27.8±0.1 | 37.0±0.3 | 44.7±0.2 | 56.1±0.5 |
| 0.4 | 20.5±0.3 | 23.9±0.1 | 30.5±0.1 | 39.5±0.1 |
| 0.6 | 16.4±0.2 | 16.6±0.4 | 23.4±0.1 | 29.1±0.1 |
| 0.8 | 13.4±0.5 | 15.6±0.2 | 18.5±0.3 | 23.6±0.1 |
| 1.0 | 12.0±0.2 | 12.6±0.1 | 15.5±0.2 | 19.3±0.3 |
| 10^3 (intc) | 24.7±2.9 | 17.3±2.4 | 11.4±0.5 | 9.3±0.8 |
| 10^3 (slope) | 61.8±5.8 | 60.7±2.6 | 53.0±0.9 | 41.8±1.4 |

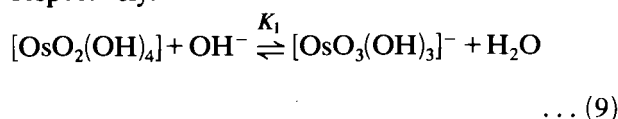
$k_{\text{obs}}/[\text{OHC.COO}^-]$ are almost constant ($422 \pm 16 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C).

(iv) Under the conditions $10^3 [\text{Os(VIII)}]=1.56$, $[\text{OH}^-]=0.1$ and $[\text{OHC.COO}^-]=0.1 \text{ mol dm}^{-3}$ at 25°C , k_{obs} increases from 14.4 ± 0.2 to $41.6 \pm 0.3 \text{ s}^{-1}$ when μ is increased from 0.2 to 1.0 mol dm^{-3} . Effect of ionic strength on k_{obs} is given by Eq. (8) due to Davies¹³.

$$\log k_{\text{obs}} = \log k_0 + 2A z_a z_b \sqrt{\mu} / (1 + \sqrt{\mu}) \quad \dots (8)$$

The slope value, 2.35 ± 0.04 , of the linear plot between $\log k_{\text{obs}}$ and $\sqrt{\mu}/(1 + \sqrt{\mu})$ indicates that the reactants are similarly charged, and probably one of these carried two units of charges and the other has an unit charge.

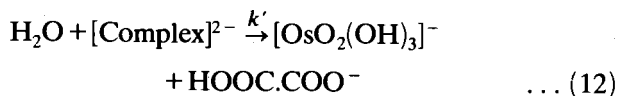
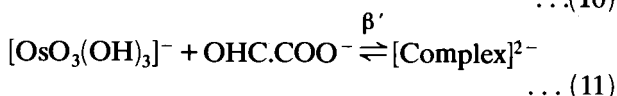
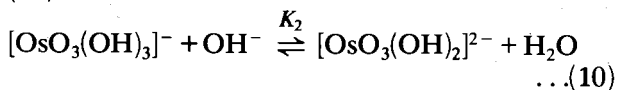
In an alkaline solution, there exist two equilibria (9) and (10) with equilibrium constants K_1 and K_2 respectively.



The value of K_1 determined by kinetic method¹⁴ is $302 \text{ dm}^3 \text{ mol}^{-1}$. Hence equilibrium (9) is completely shifted to the right in alkali solutions used here and therefore any free concentration of OsO_4 is negligible. The spectrophotometric estimation of K_2 has resulted in the values 24 ± 4 , (ref. 6a) and $19.5 \pm 3 \text{ dm}^3 \text{ mol}^{-1}$ (ref. 15) in solutions of 1 mol dm^{-3} ionic strength at 25°C .

Further, it has been pointed out that the heights of the successive waves in polarogram of Os(VIII) in both dilute and concentrated sodium hydroxide (0.3 to 10 mol dm^{-3}) solutions¹⁶ are in the ratio of 2:2:1 which is in conformity with the reduction scheme: $\text{Os(VIII)} \rightarrow \text{Os(VI)} \rightarrow \text{Os(IV)} \rightarrow \text{Os(III)}$ proposed earlier¹⁷.

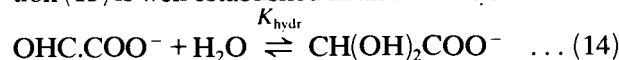
In view of the simple kinetics and the observation that k_{obs} decreased with increase in $[\text{OH}^-]$, a simple mechanism consisting of the reactions (10)–(12) comes to the mind. The rate law based on these reactions, with the assumption that $(1 + K_2[\text{OH}^-]) \gg \beta'[\text{OHC.COO}^-]$ dictated by the first-order dependence in glyoxalate ion, is in the Eq. (13).



$$k_{\text{obs}} = \frac{k' \beta' [\text{OHC.COO}^-]}{1 + K_2 [\text{OH}^-]} \quad \dots (13)$$

Equation (13) is consistent with the linearity of the k_{obs} versus $[\text{OHC.COO}^-]$ and k_{obs}^{-1} versus $[\text{OH}^-]$ plots and the value of K_2 could be obtained by the ratio slope/intercept of the later plot. The evaluated value of K_2 was found to be much less than the experimentally determined values^{6a} at each temperature. This indicated that some equilibrium other than that in (10) is needed.

Glyoxalic acid forms a *gem*-diol on hydration¹⁸, and so does the glyoxalate ion¹⁹. Values of 16.5 ± 2.5 (ref. 20) and $15.1 \text{ dm}^3 \text{ mol}^{-1}$ (ref. 21) have been determined for the hydration constant, K_{hydr} as in reaction (14). Hence it is assumed that the glyoxalate ion present in solution is almost completely hydrated. The dianion can be formed either by loss of a proton from the *gem*-diol or addition of hydroxide to the aldehyde²². Hence reaction (15) is well established in an alkaline solution.

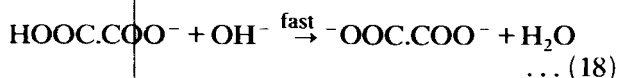
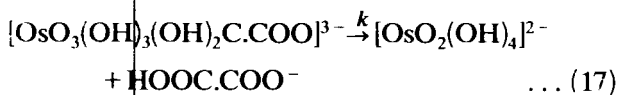
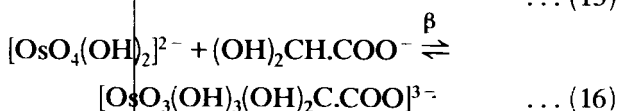
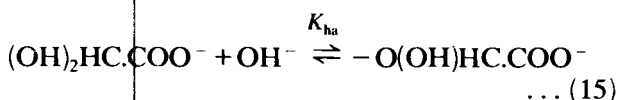


Now, there are two equilibria, (10) and (15), that are affected by OH^- . The consideration of both the equilibria and that one of the reactants is doubly charged, predicted by the effect of ionic strength on the rate, requires the consideration of the probability of the reaction between two pair, viz., (i) $[\text{OsO}_3(\text{OH})_3]^-$, and $^- \text{O}(\text{OH}).\text{HC.COO}^-$, or (ii) $[\text{OsO}_4(\text{OH})_2]^{2-}$ and $(\text{OH})_2\text{CH.COO}^-$. The consideration of either of the pair should not result in the pronounced effect of $[\text{OH}^-]$, as observed, due to the compensatory effect of OH^- on the rate because the equilibrium reactions involving the formation of the respective species are affected by the OH^- in the opposite directions. Hence equi-

libria (10) and (15) cannot be considered together in the mechanism.

Further, the calculation of $[\text{OsO}_4(\text{OH})_2]^{2-}$ at different $[\text{OH}^-]$ in a 1.56×10^{-3} mol dm $^{-3}$ solution of OsO_4 indicated that there is not a pronounced change in $[\text{OsO}_4(\text{OH})_2]^{2-}$ between 0.1 and 1.0 mol dm $^{-3}$ sodium hydroxide which changed from 1.10×10^{-3} to 1.50×10^{-3} mol dm $^{-3}$. Hence $[\text{OsO}_4(\text{OH})_2]^{2-} \approx [\text{OsO}_4]$ and to a greater extent could be considered as independent of $[\text{OH}^-]$. For a similar change in sodium hydroxide the change in $[-\text{O}(\text{OH})\text{CH}_2\text{COO}^-]$ is from 0.02 to 0.07 mol dm $^{-3}$ in a 0.1 mol dm $^{-3}$ glyoxalate solution which is significant. Hence, the equilibrium (10) is not considered, justified by the fact that $K_2 \gg K_{\text{ha}}$, and the equilibrium (15) has the mechanistic significance.

The following reactions are therefore considered to represent the most plausible mechanism of the reaction.



The rate of disappearance of $[\text{Os(VIII)}]$ in terms of reactions (15)-(18) is given by Eq. (19).

$$\begin{aligned} & -\frac{d[\text{Os(VIII)}]}{dt} \\ & = k\beta[\text{OsO}_4(\text{OH})_2]^{2-} [(\text{OH})_2\text{HC.COO}^-] \dots (19) \end{aligned}$$

Equation (19) could be written as Eq. (20) where the concentrations are the initial analytical concentrations.

$$\begin{aligned} -\frac{d[\text{Os(VIII)}]}{dt} & = \frac{k\beta[\text{OHC.COO}^-][\text{Os(VIII)}]}{1 + K_{\text{ha}}[\text{OH}^-] + \beta[\text{OHC.COO}^-]} \quad \dots (20) \end{aligned}$$

Now, in view of the simple relation between k_{obs}^{-1} and $[\text{OH}^-]$ and the linearity of the plot between k_{obs}^{-1} and $[\text{OHC.COO}^-]$, which passes through the origin, an assumption that

$(1 + K_{\text{ha}}[\text{OH}^-]) \gg \beta[\text{OHC.COO}^-]$ could be easily made. With this inequality Eq. (20) is reduced to Eq. (21). Equation (22) is the reciprocal of Eq. (21). The slope and intercept values (Table 1) of the linear plots between k_{obs}^{-1} and $[\text{OH}^-]$ are given by Eqs (23) and (24) respectively.

$$k_{\text{obs}} = \frac{k\beta[\text{OHC.COO}^-]}{1 + K_{\text{ha}}[\text{OH}^-]} \quad \dots (21)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k\beta[\text{OHC.COO}^-]} + \frac{K_{\text{ha}}[\text{OH}^-]}{k\beta[\text{OHC.COO}^-]} \quad \dots (22)$$

$$\text{Slope} = \frac{K_{\text{ha}}}{k\beta[\text{OHC.COO}^-]} \quad \dots (23)$$

$$\text{Intercept} = \frac{1}{k\beta[\text{OHC.COO}^-]} \quad \dots (24)$$

From Eqs (23) and (24), one could obtain the values of K_{ha} at 20, 25, 30 and 35°C which are 2.52 ± 0.06 , 3.54 ± 0.34 , 4.65 ± 0.12 and 4.51 ± 0.23 dm 3 mol $^{-1}$ respectively and the corresponding $\Delta H^\circ = 31 \pm 3$ kJ mol $^{-1}$ and $\Delta S^\circ = 112 \pm 4$ JK $^{-1}$ mol $^{-1}$. The positive value of the entropy is consistent with the fact that the transition state has smaller number of charges than the reactants. This results in freeing of water molecules from the hydration sphere of OH^- and $(\text{HO})_2\text{CH.COO}^-$ ions.

Using the estimated value of K_{ha} at 25°C, the pK_a ($K_a = K_{\text{ha}}K_w$) of the *gem*-diol of glyoxalate ion is estimated to be 13.4 and considering that it is obtained from the ratio of slope/intercept, it is in fair agreement with the value 13 obtained spectroscopically and 13.05 estimated kinetically. The value is also in fair agreement with the pK_a of 13.57 for acetaldehyde 22 , and 13.6 for formaldehyde 23 .

The oxidation of glyoxalate ion in alkaline solution by deprotonated-amine Cu(III)-peptide complex 19 and Os(VIII) differ from each other both in the kinetics and final oxidation product. The observed rate in Cu(III)-peptide complex oxidation first increased up to 0.1 mol dm $^{-3}$ of OH^- and then decreased. This is ascribed to the operation of two acid-base pre-equilibria. One is the amine deprotonation of Cu(III)-peptide and the other involved the formation of glyoxalate dianion. The unhydrated glyoxalate ion is assumed to be the reactive species.

The mechanism of the present redox reaction also involved two acid-base pre-equilibria, represented by reactions (15) and (16), yet it differs from Cu(III)-peptide complex oxidation in the de-

Table 2—The estimated values of $k\beta$ ($\text{dm}^3\text{mol}^{-1}$) from Eqs (23) and (24) at different temperatures ($\pm 0.1^\circ\text{C}$) and the related thermodynamic parameters

| Temp. ($^\circ\text{C}$) | $10^{-3} k\beta$ (from Eq. 23) | $10^{-3} k\beta$ (from Eq. 24) | $10^{-3} k\beta$ (Mean value) |
|----------------------------|--------------------------------|--------------------------------|-------------------------------|
| 20 | 3.25 ± 0.31 | 3.27 ± 0.34 | 3.26 ± 0.29 |
| 25 | 3.96 ± 0.17 | 4.15 ± 0.61 | 4.05 ± 0.41 |
| 30 | 5.09 ± 0.39 | 5.10 ± 0.22 | 5.10 ± 0.15 |
| 35 | 7.18 ± 0.24 | 7.24 ± 0.66 | 7.21 ± 0.44 |

$\Delta H = 39 \pm 2 \text{ kJ mol}^{-1}$ $\Delta S = -112 \pm 7 \text{ JK}^{-1}\text{mol}^{-1}$

pendence of the observed rate on $[\text{OH}^-]$. The rate decreased with increasing $[\text{OH}^-]$. This is because glyoxalate hydrated anion is the reactive species in the present case and the formation of an inner-sphere complex between the osmium species $[\text{OsO}_4(\text{OH})_2]^{2-}$ and glyoxalate anion. The complex is considered 'inner-sphere' because H atom of glyoxalate anion has formed a hydroxyl group with the oxygen atom of tetraoxodihydroxyosmium (VI-II) species. Equilibrium (16) helps to establish that $\Delta z^2 = 2$ as required by the slope value of the linear plot based on the Davies equation where $\Delta z^2 = \{\sum z_i^2 (\text{products}) - \sum z_i^2 (\text{reactants})\}$. This criteria has been discussed by Espenson²⁴, and is equally applicable to the mechanism based on the assumption of the inner-sphere complex. Thus the salt effect is a property of the rate law and not of the reaction mechanism²⁴.

The transfer of hydride ion as a result of C–H fission in the glyoxalate ion to the oxidant species in the rate determining step reduces the perosmate ion to $[\text{OsO}_2(\text{OH})_4]^{2-}$ and oxidises glyoxalate ion to oxalic acid which is instantly converted to oxalate ion in alkaline medium. The fact that the oxidation of oxalate ion (devoid of the presence of any C–H bond) is very slow, no change in the absorbance was observed in the first few minutes when solutions of Os(VIII) and oxalate ions were mixed, supports the proposed C–H fission and thereby hydride transfer.

The values of $k\beta$, calculated using Eq. (24) at different temperatures together with the mean value, used for the calculation of enthalpy and entropy values, are in Table 2.

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