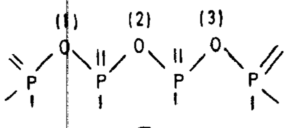

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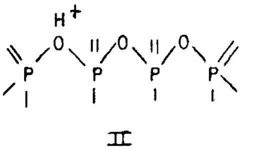

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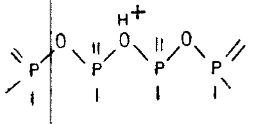

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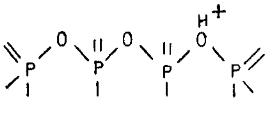

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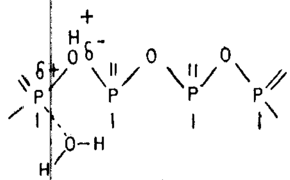

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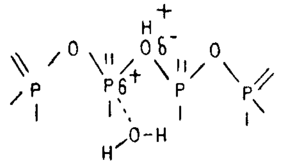

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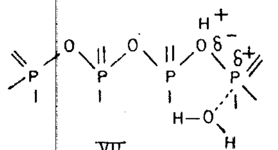

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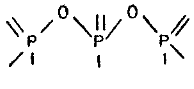

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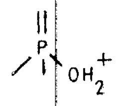

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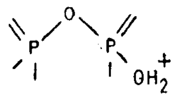

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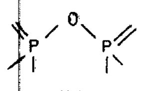

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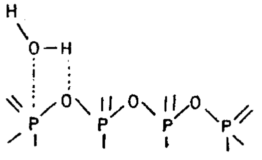

XII

ΔS^{*P}_n will be only a fraction of ΔS_n for the corresponding species as protonation is required only at a fixed site. As has been shown previously[8], ΔS_n for the above reaction is positive and its value increases with the decrease in n. Like ΔS_n, ΔS^{*P}_n will also be positive and its value will increase as n decreases. Thus, ΔS^{*P}_n will accordingly make an increasingly large positive contribution to the overall entropy of activation (ΔS^{*}_n) as the negative charge on the tetraphosphate species increases (or as n decreases). ΔS^{*i}_n will always be negative as the activated complexes V, VI and VII produce a more orderly and highly polar state. However, ΔS^{*i}_n may be assumed to remain constant for all the species. On the whole, the net entropy of activation will become less and less negative as negative charge on the species increases. This is what has been actually observed.

In the case of uncatalysed hydrolysis of tetraphosphates, a given tetraphosphate species is first attacked by a water dipole, but this time, one of the positive ends of the dipole is attacked by one of the common vertical oxygens. Since P atom has a residual positive charge (δ^+), it tends to form a link with the negative oxygen end of the water dipole to form cyclic structure (XII) which decomposes to give one molecule each of orthophosphate and triphosphate.

Some stretching of the bond is necessary to form the activated complex (XII) having cyclic structure. The energy of activation has been found to be of the same order as is expected for a four-centred reaction[9].

References

1. Muss, J., *Z. physik. Chem.*, **A159** (1932), 263.
2. Mitra, R. P., Malhotra, H. C. & Jain, D. V. S., *Trans. Faraday Soc.*, **62** (1966), 173.
3. Mitra, R. P. & Thukral, B. R., *Indian J. Chem.*, **8** (1970), 350.
4. Crowther, J. P. & Westmann, A. E. R., *Can. J. Chem.*, **34** (1956), 969.
5. Smith, M. J., *Can. J. Chem.*, **73** (1959), 1115.
6. Otani, S., Miura, M. & Doi, T., *Kogyo: Kagaku Zasshi*, **66** (1963), 593.
7. Griffith, E. J. & Buxton, R. L., *J. Am. chem. Soc.*, **89** (1967), 2884.
8. Malhotra, H. C. & Thareja, S. K., *Indian J. Chem.*, **14** (1976), 223.
9. Malhotra, H. C. & Thareja, S. K., *Indian J. Chem.*, **14** (1976), 226.

Kinetics of Oxidation of Glycollic Acid by Os(VIII)

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Kinetics of Os(VIII) oxidation of glycollic acid in alkaline medium has been studied. At $[OH^-] \leq 0{\cdot}04M$ the rate is proportional to [Os(VIII)], [glycollate] and $[OH^-]^2$. The positive salt effect and negative $\Delta S^{\ddagger}$ indicate the formation of an ester intermediate involving $OsO_4[(OH)_2]^{2-}$ species in the rate determining step.

Osmium(VIII) has been widely used as a catalyst in the oxidation of variety of organic[1-5] and inorganic compounds, but its capability as an independent oxidizing agent has been least explored. The present report deals with the results on the kinetics of oxidation of glycollic acid by Os(VIII).

OsO_4 (Johnson & Matthey) and glycollic acid (Riedel) were used. All other chemicals were of AR grade. The solution of oxidant was prepared by disolving a known weight of OsO_4 in KOH solution ($0{\cdot}01M$).

The reaction was started by mixing a known volume of oxidant to requisite quantities of glycollic acid and NaOH, maintained at constant temperature ±0·1°. The ionic strength was kept constant ($1{\cdot}5M$) by the addition of KCl. Aliquots were drawn a regular time intervals and analysed for unconsumed Os(VIII) spectrophotometrically using Klett-Summerson photoelectric colorimeter. Beer's law is obeyed for [Os(VIII)] ranging from $3{\cdot}0 \times 10^{-5}$ to $1{\cdot}5 \times 10^{-3}M$.

Table 1 — Variation of Rate with [Oxidant]

[[Glycollate] = $5{\cdot}0 \times 10^{-3}M$; $[OH^-] = 0{\cdot}012M$; temp. 35°]

$[OsO_4] \times 10^4 M$	5·0	4·0	3·0	2·0	1·0
$K_1 \times 10^4$ (sec^{-1})	3·22	2·83	2·45	2·16	1·90

TABLE 2 — DEPENDENCE OF RATE ON [GLYCOLLATE] AND [OH]

{[Os(VIII)] = $5{\cdot}0 \times 10^{-4}M$; $\mu = 1{\cdot}5$; temp. 35°}

$[OH]^* \times 10^{-2}$ M	$K_1 \times 10^4$ sec^{-1}	[Glycollate] $\times 10^3$ M	$K_1 \times 10^4$ sec^{-1}
1·6	5·6	1·0	0·64
2·0	8·8	2·0	1·30
3·0	17·5	3·0	1·89
4·0	18·1	4·0	2·56
6·0	18·0	5·0	3·22

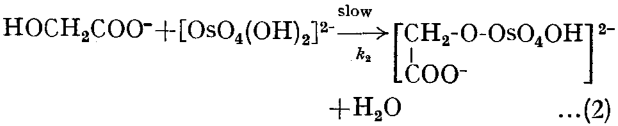
*[Glycollate] = $5{\cdot}0 \times 10^{-3}M$.
†[OH] = $1{\cdot}2 \times 10^{-2}M$.

The results, summarized in Tables 1 and 2, show dependence of the rate on [OsVIII], [glycollate] and $[OH^-]^2$.

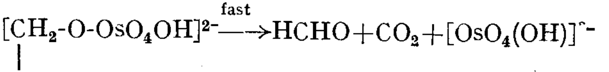
As the ionic strength of the medium has considerable effect on the reaction rate, it was kept constant (1·5) by the addition of KCl.

At $[OH^-] \leqslant 0{\cdot}04M$ the rate of reaction is found to be proportional to [OsVIII], [glycollate], $[OH^-]^2$. Addition of acrylonitrile does not affect the rate, this excludes the possibility of the reaction involving a free radical mechanism. Since OsO_4 in alkaline solution exists as osmate ion[6], it is suggested that oxidation involves formation of an ester intermediate, and then the cleavage of this intermediate.

$$OsO_4 + 2OH^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [OsO_4(OH)_2]^{2-} \quad \ldots(1)$$



$$HOCH_2COO^- + [OsO_4(OH)_2]^{2-} \xrightarrow[k_2]{\text{slow}} \left[\begin{array}{l} CH_2\text{-}O\text{-}OsO_4OH \\ | \\ COO^- \end{array}\right]^{2-} + H_2O \quad \ldots(2)$$



$$\left[\begin{array}{l} CH_2\text{-}O\text{-}OsO_4OH \\ | \\ COO^- \end{array}\right]^{2-} \xrightarrow{\text{fast}} HCHO + CO_2 + [OsO_4(OH)]^{-} \quad \ldots(3)$$

$$[OsO_4OH]^{3-} + 2H_2O \xrightarrow{\text{fast}} [OsO_2(OH)_4]^{2-} + OH^- \quad \ldots(4)$$

The proposed mechanism leads to the rate law

$$\frac{-d[Os(VIII)]}{dt} = K_2[\text{glycollate}][Os(VIII)] \quad \ldots(5)$$

The rate equation explains first order kinetics in [glycollate] and [Os(VIII)]. The concentration of the reactive species as given by Eq. (1) would depend on $[OH^-]^2$ up to a certain limit, beyond which the whole of OsO_4 will exist as $[OsO_4(OH)_4]^{2-}$. This explains second and zero order dependence on [OH].

The activation parameters ΔE, PZ, ΔS^* were evaluated from the plot of log K_2 versus 1/T and found to be 12·8 kcal, $6{\cdot}0 \times 10^7$ sec^{-1} —24·0 e.u. respectively. As expected, aggregation should greatly reduce the entropy, —ve values of ΔS^* and +ve salt effect lend additional support to rate determining step (2).

References

1. AGARWAL, M. C. & MUSHRAN, S. P., *J. phys. Chem.*, **72** (1968), 1497.
2. COTTON, F. A. & WILKINSON, G., *Adv. inorg. Chem.*, (1962), 830.
3. MUSHRAN, S. P., *Can. J. Chem.*, **48** (1970), 1148.
4. SINGH, V. N. & SINGH, M. P., *Aust. J. Chem.*, **21** (1968), 2913.
5. SINGH, V. N. & SINGH, M. P., *Aust. J. Chem.*, **23** (1970), 921.
6. SONI, G. C. & MENGHANI, G. D., *Tetrahedron*, **28** (1972), 5567.
7. SONI, G. C. & MENGHANI, G. D., *Z. Naturf.*, **276** (1972), 908.

Kinetics of Substitution of *cis*-Bis(oxalato)-diaquochromate(III) by Orthophosphoric Acid

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The substitution of *cis*-bis(oxalato)diaquochromate(III) by orthophosphoric acid has been investigated spectrophotometrically and the rate law

$$\text{Rate} = \frac{kK[\text{Complex}][H_2PO_4^-]^2h_0}{[Ox^{2-}]}$$

has been poposed.

THE complexation of hexaaquochromium(III) ion by orthophosphoric acid has been studied by Lahiri[1]. The rate of substitution of anionic oxalato complexes of chromium(III) is relatively faster[2]. As such an attempt has been made to study the substitution of *cis*-bis(oxalato) diaquochromate(III) by orthophosphoric acid and the results are presented in this note.

Potassium *cis*-bis(oxalato)diaquochromate(III) was prepared by the method described in literature[3]. Its purity was confirmed by analysis[4]. All the other reagents used were of reagent grade.

The rate of the reaction was followed spectrophotometrically at 420 nm by measuring the absorbance of the complex, $Cr(Ox)_2(H_2O)_2^-$ with a Unicam SP600 spectrophotometer. The kinetic runs were followed employing requisite quantities of metal complex, orthophosphoric acid and added oxalate and also by varying the ionic strength using sodium nitrate. Duplicate runs were performed and the rate constants were found to be reproducible (±5%).

To verify the effect of products on the reaction rate, the time order (n_t) and the concentration order (n_c) were evaluated as described by Laidler[5]. It was found that n_t equals n_c. As such the pseudo-first order rate constants were evaluated by plotting log $(A_t - A_\infty)$ vs t (where A_∞ and A_t represent the absorbance at infinite time and at time t respectively). The plot of log $[(A_{t_1} - A_\infty)/(A_{t_2} - A_\infty)]$ versus $(t_2 - t_1)$ was linear passing through the origin indicating that the rate is first order with respect to bis-oxalato complex. This was further confirmed by changing the initial concentration of the metal complex when there was no significant change in the observed rate constant (k_{obs}). A plot of k_{obs} vs the molarity of orthophosphoric acid was not linear. However, a plot of log k_{obs} versus $-H_0$, where H_0 is the acidity function obtained by using the data of Long and Paul[6] for phosphoric acid medium, was linear with unit slope. In view of the fact that the data of H_- function is not available in the literature for phosphoric acid