produced during the ozonolysis of unsymmetrical olefins, did not interfere with the measurements. It was found that the *cis/trans* distributions did not depend on the extent of the reaction. The given proportions (Tables V and VI) were calculated from five to seven independent experiments in each case and they are expressed with a 95% confidence limit.

Kinetics and Mechanism of the Osmium Tetroxide Catalyzed Oxidation of Acetone and Ethyl Methyl Ketone by Alkaline Hexacyanoferrate(III) Ion[1]

V. N. Singh, H. S. Singh, and B. B. L. Saxena

Contribution from the Department of Chemistry, University of Allahabad, Allahabad, India. Received June 10, 1968

Abstract: The studies in the kinetics of the osmium tetroxide catalyzed oxidation of acetone and ethyl methyl ketone by aqueous alkaline potassium hexacyanoferrate(III) were made at four temperatures to investigate the way osmium tetroxide participates as catalyst in the oxidation of ketones. The data suggest that the oxidation of these ketones proceeds *via* the formation of an activated complex between the enolate and osmium tetroxide which rapidly decomposes followed by a fast reaction between the reduced osmium species and ferricyanide. The product study has made it possible to give the intermediates and the reactions which occur.

Catalysis of oxidation by hexacyanoferrate(III) ion has been observed with a number of metal salts.[2] Recently, osmium tetroxide has been used as catalyst in analytical procedures with hexacyanoferrate(III) ion.[3] Solymosi[4] has studied a number of oxidations with alkaline hexacyanoferrate(III) ion in presence of osmium tetroxide from an analytical viewpoint. Krishna and Singh[5] were the first to examine kinetic features of this problem, and accordingly, they have studied the osmium tetroxide catalyzed oxidation of methanol and ethanol by hexacyanoferrate(III) ion in aqueous alkaline medium. The study was quite limited and could not account for much except a guidance in this field. Recently an attempt was made by us in the oxidation of mandelate ion,[6] and it has been concluded that there is formation of a mandelate–osmium complex through the hydroxyl group which decomposes with hydroxide ion giving an osmium(VI) species which in turn is rapidly oxidized by hexacyanoferrate(III) ion. However, the exact role of the osmium tetroxide in the oxidation of ketones has not yet been shown, and the present study has been made to obtain definite information concerning the possible participation of osmium tetroxide in the oxidation of methyl ketones by aqueous alkaline hexacyanoferrate(III) ion. Accordingly, the kinetic investigations were carried out with acetone and ethyl methyl ketone at four temperatures. The details of the results are presented.

(1) Part of the work assigned for the Ph.D. degree of V. N. Singh, University of Allahabad, 1968.
(2) L. Rosenthaler, *Chem. Zentr.*, **56**, 441 (1932).
(3) N. Suseela, *Z. Anal. Chem.*, **145**, 175 (1955).
(4) F. A. Solymosi, *et al.*, *Magy. Kem. Folyoirat*, **62**, 318 (1957).
(5) B. Krishna and H. S. Singh, *Z. Phys. Chem.*, **231**, 399 (1966).
(6) M. P. Singh, V. N. Singh, and N. P. Singh, *Australian J. Chem.*, **21**, 2913 (1968).

Results and Discussion

The hexacyanoferrate(III) ion oxidation of these ketones has already been studied by the previous workers in alkaline medium in the absence of osmium tetroxide[7,8] catalyst, so here an attempt has been made to study the reactions in such a condition where there is no appreciable oxidation without the catalyst osmium tetroxide. The details of the kinetic data for the rate of osmium tetroxide catalyzed oxidation of acetone and ethyl methyl ketone are presented in Tables I–VI. The kinetic measurements were carried out in aqueous alkaline buffer solution obtained by carbonate and bicarbonate ions.

The standard zero-order rate constants (k_s) presented in these tables are the average ones obtained from a particular run and are given in terms of the concentration of hexacyanoferrate(II) ion obtained per minute.

The exact nature of the reaction is shown in Figures 1 and 2. Figure 1 shows a typical zero-order plot for the rate of oxidation of acetone and Figure 2 shows the same for the rate of oxidation of ethyl methyl ketone. It is obvious from these plots that the reaction velocity remains constant even up to 98% of the reaction. However, in the case of ethyl methyl ketone, some deviations occur from the above view when the concentration of hexacyanoferrate(III) ion or the catalyst is increased. The zero-order velocity constants begin to increase after some 65–70% of reaction. From these data it has been concluded that this increase in zero-order rate constant values might be due to further oxidation of some intermediate whose rate might appear after a certain interval of time at higher concentrations of hexacyanoferrate(III) ion or the catalyst osmium tetroxide. Table IA and B

(7) V. N. Singh, Ph.D. Thesis, Allahabad University, 1968.
(8) P. T. Speakman and W. A. Waters, *J. Chem. Soc.*, 40 (1955).

Table I

A		B	
Temp, 30° $[(CH_3)_2CO] = 20.00 \times 10^{-2} M$ $[OsO_4] = 3.93 \times 10^{-5} M$ pH 11.05		Temp, 30° $[C_2H_5COCH_3] = 2.50 \times 10^{-2} M$ $[OsO_4] = 1.97 \times 10^{-5} M$ pH 10.50	
$[K_3Fe(CN)_6] \times 10^4$ M	$k_s \times 10^5$ mol $l.^{-1}$ min^{-1}	$[K_3Fe(CN)_6] \times 10^4$ M	$k_s \times 10^5$ mol $l.^{-1}$ min^{-1}
50.00	4.60	30.00	1.98
40.00	4.36	25.00	1.85
30.00	4.18	20.00	1.94
20.00	4.18	12.50	1.59
15.00	3.96	10.00	1.40
10.00	3.18	9.00	1.35

Table II

A			B		
Temp, 30° $[K_3Fe(CN)_6] = 0.20 \times 10^{-2} M$ $[OsO_4] = 3.93 \times 10^{-5} M$ pH 11.05			Temp, 30° $[K_3Fe(CN)_6] = 1.25 \times 10^{-3} M$ $[OsO_4] = 1.97 \times 10^{-5} M$ pH 10.5		
$[(CH_3)_2CO]$ $\times 10^{-2} M$	$k_s \times 10^5$ mol $l.^{-1}$ min^{-1}	$k_s \times 10^4/$ $[(CH_3)_2CO]$, min^{-1}	$[C_2H_5COCH_3]$ $\times 10^{-3} M$	$k_s \times 10^5$ mol $l.^{-1}$ min^{-1}	$k_s \times 10^4/$ $[C_2H_5COCH_3]$, min^{-1}
2.50	0.88	3.52	6.25	0.46	7.36
5.00	1.35	2.70	12.50	0.85	6.80
10.00	2.35	2.35	25.00	1.59	6.34
20.00	4.18	2.09	37.50	2.16	5.75
40.00	7.56	1.89	50.00	2.91	5.82
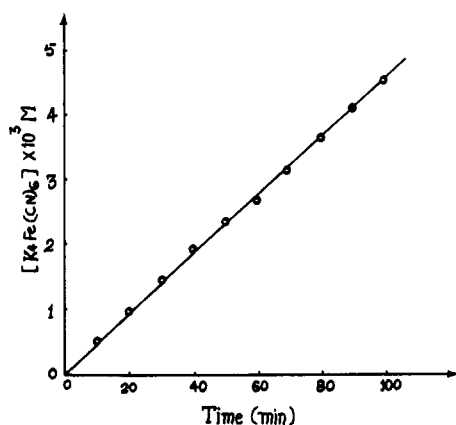
Figure 1. Zero-order plot for the rate of oxidation of acetone at 30°: $[K_3Fe(CN)_6] = 0.50 \times 10^{-2} M$, [acetone] = 20.00 × $10^{-2} M$, $[OsO_4] = 3.93 \times 10^{-5} M$, pH = 11.05.

clearly indicate that the k_s values are almost constant for various initial hexacyanoferrate(III) ion concentration. However, at higher concentrations, they are somewhat greater than that at lower. This increase in zero-order rate constant values might be taken as due to secondary salt effect, and it is valid to assume the zero-order dependence of the reaction rate on hexacyanoferrate(III) ion concentration for both the ketones.

Table IIA and B contains the average standard zero-order rate constants for different concentrations of ketones. The last column of this table contains the first-order rate constant values obtained by dividing the standard zero-order rate constant values by the corre-

sponding ketone concentration and it is evident that as the concentration of ketones is increased, these values go on decreasing showing that the reaction velocity is retarded with increasing concentration of these ketones. For this retardation effect we have considered the effect of the dielectric constant of the medium upon the reaction velocity. In present case the dielectric of the medium is changed due to change of ketone concentration. By increasing the concentration of ketones, the dielectric of the medium is decreased which subsequently affects the reaction velocity. This effect is further discussed in subsequent pages. Assuming this to be true, it is justifiable to take the first-order dependence of the reaction rate on ketone concentration.

Table IIIA and B contains the average k_s values at different concentrations of osmium tetroxide and from the last column of this table it is quite obvious that the k_s values obtained for the molar concentration of osmium tetroxide go on decreasing with increasing concentration of the catalyst osmium tetroxide. The change is clearly apparent in case of ethyl methyl ketone and only 10% with acetone. However to the first approximation the direct proportionality of the reaction rate on low catalyst concentration might be assumed.

Further Table IVA and B contains the average k_s values at different pH, obtained for acetone and ethyl methyl ketone, respectively. From this table it is apparent that as the pH of the solution is increased the k_s values also go on increasing. A more clear picture is shown in Table VA and B. This table contains the k_s values for different hydroxyl ion concentrations calculated from the corresponding pH values. The third column of this table shows the $k_s/[OH^-]$ practically the same indicating the

Table III

A — Temp, 30° $[(CH_3)_2CO] = 20.00 \times 10^{-2}\, M$ $[K_3Fe(CN)_6] = 0.20 \times 10^{-2}\, M$ pH 11.05			B — Temp, 30° $[C_2H_5COCH_3] = 2.50 \times 10^{-2}\, M$ $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}\, M$ pH 10.50		
$[OsO_4] \times 10^5$ M	$k_s \times 10^5$ mol $1.^{-1}\,min^{-1}$	$k_s/[OsO_4]$, min^{-1}	$[OsO_4] \times 10^5$ M	$k_s \times 10^5$ mol $1.^{-1}\,min^{-1}$	$k_s/[OsO_4]$, min^{-1}
0.98	1.10	1.12	0.39	0.60	1.54
1.97	2.18	1.10	0.79	0.94	1.19
3.93	4.18	1.06	1.18	1.19	1.00
8.90	6.12	1.04	1.97	1.59	0.80
7.86	7.99	1.01	3.93	2.31	0.58

Table IV

A — Temp, 30° $[(CH_3)_2CO] = 20.00 \times 10^{-2}\, M$ $[K_3Fe(CN)_6] = 0.20 \times 10^{-3}\, M$ $[OsO_4] = 3.93 \times 10^{-5}\, M$		B — Temp, 30° $[C_2H_5COCH_3] = 2.50 \times 10^{-2}\, M$ $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}\, M$ $[OsO_4] = 1.97 \times 10^{-5}\, M$	
pH	$k_s \times 10^5$ mol $1.^{-1}$ min^{-1}	pH	$k_s \times 10^5$ mol $1.^{-1}$ min^{-1}
11.05	4.18	10.75	2.89
10.95	3.71	10.55	1.78
10.75	2.20	10.50	1.59
10.50	1.34	10.30	1.12
10.35	0.25	10.20	0.80

Table V

A — Temp, 30° $[(CH_3)_2CO] = 20.00 \times 10^{-2}\, M$ $[K_3Fe(CN)_6] = 0.20 \times 10^{-3}\, M$ $[OsO_4] = 3.93 \times 10^{-5}\, M$			B — Temp, 30° $[C_2H_5COCH_3] = 2.5 \times 10^{-2}\, M$ $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}\, M$ $[OsO_4] = 1.97 \times 10^{-5}\, M$		
$[OH^-] \times 10^4$ M	$k_s \times 10^5$ mol $1.^{-1}\,min^{-1}$	$k_s \times 10^2/$ $[OH^-], min^{-1}$	$[OH^-] \times 10^4$ M	$k_s \times 10^5$ mol $1.^{-1}\,min^{-1}$	$k_s \times 10^2/$ $[OH^-], min^{-1}$
11.22	4.18	3.72	5.62	2.89	5.14
8.91	3.71	4.16	3.55	1.78	5.01
5.62	2.20	3.91	3.16	1.59	5.03
3.16	1.34	4.24	2.00	1.12	5.60
2.24	0.95	4.24	1.58	0.80	5.06

first-order dependence of the reaction rate on hydroxyl ion concentration.

Now on the basis of the experimental results it is worth to assume the first-order dependence of the reaction rate on catalyst, ketone, and hydroxyl ion at their lower concentrations and zero order on hexacyanoferrate(III) ion. Thus under these conditions a probable rate law might be given as

$$-\frac{d[Fey]}{dt} = k[\text{ketone}][OH^-][OsO_4] \qquad (1)$$

where Fey = $Fe(CN)_6^{3-}$. Under these conditions the value of k at 25° comes out to be 44.9 mol^{-2} l.^{2} sec^{-1} and 11.11 × 10^2 mol^{-2} l.^{2} sec^{-1} for acetone and ethyl methyl ketone, respectively. However, these values are given for a particular set of conditions and change in other conditions.
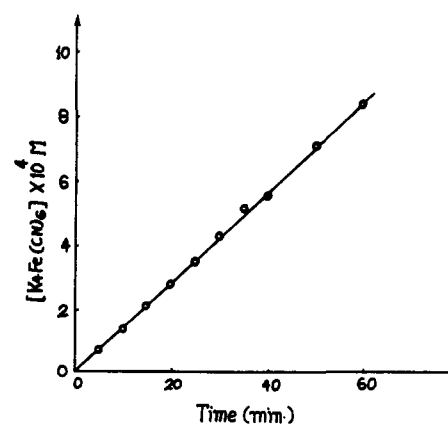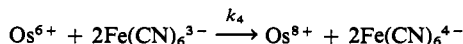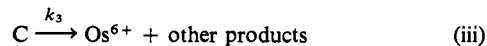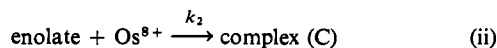

Figure 2. Zero-order plot for the rate of oxidation of ethyl methyl ketone at 30°: $[K_3Fe(CN)_6] = 0.10 \times 10^{-2}\, M$, $[C_2H_5COCH_3] = 2.50 \times 10^{-2}\, M$, $[OsO_4] = 1.97 \times 10^{-5}\, M$, pH = 10.5.

In certain cases the rate of oxidation of ethyl methyl ketone was found to be more than 20 times faster than that of acetone. Paper chromatographic analysis reveals that the oxalic acid is the very common product of oxidation of these ketones.

One thing is interesting to note that if only the acetone or ethyl methyl ketone and OsO_4 are taken in alkaline medium the color of the osmium immediately disappears and if it is acidified and titrated against a standard solution of ceric sulfate; then 2 mol of ceric are used for 1 mol of OsO_4. This leads to the conclusion that it is the reduced osmium which is fast oxidized to its original octavalent state by alkaline hexacyanoferrate(III) ion. It has already been observed that the oxidation of these ketones with ceric sulfate is not appreciable under these conditions and hence it is possibly the Os^{6+} which reacts rapidly with $Fe(CN)_6^{3-}$.

Thus on the experimental evidences, the following schemes of oxidation of these ketones might be described.

Scheme I

$$\text{ketone} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{enolate} + H_2O \qquad \text{(i)}$$

$$\text{enolate} + Os^{8+} \xrightarrow{k_2} \text{complex (C)} \qquad \text{(ii)}$$

$$C \xrightarrow{k_3} Os^{6+} + \text{other products} \qquad \text{(iii)}$$

$$Os^{6+} + 2Fe(CN)_6^{3-} \xrightarrow{k_4} Os^{8+} + 2Fe(CN)_6^{4-}$$
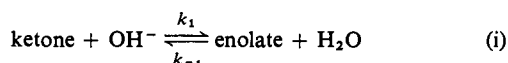
The first product might undergo fast oxidation taking more of Os^{8+} and $Fe(CN)_6^{3-}$. It is evident from the scheme that the enolate anion forms an activated complex (C) which decomposes rapidly and gives the reduced osmium species Os^{6+}. From the above scheme, if one considers the steady-state conditions for the concentration of enolate, and Os^{6+}, a rate law directly comes out to be

$$v = -\frac{d[Fey]}{dt} = \frac{k_1 k_2 [\text{ketone}][OH^-][Os^{8+}]}{k_{-1}[H_2O] + k_2[Os^{8+}]} \qquad (1)$$
$$= k_s$$

If the numerator and denominator is divided by k_{-1} and taking $K = k_1/k_{-1}$, then eq 1 becomes

$$v = -\frac{d[Fey]}{dt} = \frac{Kk_2[\text{ketone}][OH^-][Os^{8+}]}{[H_2O] + (k_2/k_{-1})[Os^{8+}]} \qquad (2)$$
$$= k_s$$

In eq 2 it is quite possible to assume the approximations as $[H_2O] \gg (k_2/k_{-1})[Os^{8+}]$ and $[H_2O] \ll (k_2/k_{-1})[Os^{8+}]$ depending upon the values of k_2 and k_{-1}. If we take the first inequality, then the eq 2 reduces to

$$v = -\frac{d[Fey]}{dt} = \frac{Kk_2}{[H_2O]}[\text{ketone}][OH^-][Os^{8+}] \qquad (3)$$

and explains well the experimental results obtained at low catalyst concentrations. If the value of k_2 is sufficiently large, then at higher catalyst concentrations, the approximation would lie well toward the second inequality and eq 2 becomes eq 4. This equation shows no catalysis of

$$v = -\frac{d[Fey]}{dt} = k_1[\text{ketone}][OH^-] \qquad (4)$$

osmium tetroxide. This region could not be obtained for acetone but is apparent for ethyl methyl ketone
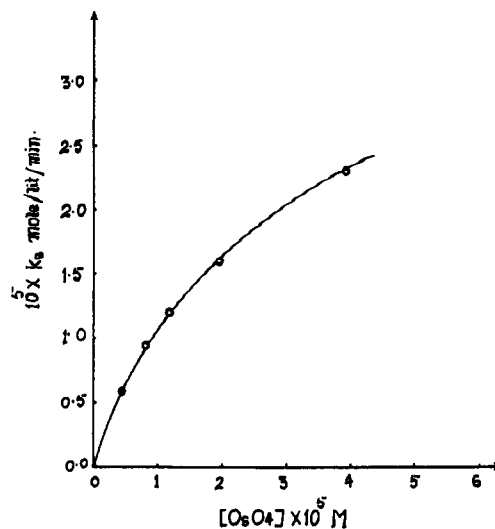
Figure 3. Effect of variation of osmium tetroxide on the reaction rate at 30°: $[C_2H_5COCH_3] = 2.50 \times 10^{-2} M$, $[K_3Fe(CN)_6] = 1.25 \times 10^{-3} M$, pH 10.5.

beyond catalyst concentrations $3.93 \times 10^{-5} M$ (Figure 3). Under these conditions the value of k_1 for ethyl methyl ketone could be calculated as $3.00 \text{ mol}^{-1} \text{ l. min}^{-1}$ at 30° when $[C_2H_5COCH_3] = 2.5 \times 10^{-2} M$.

Again eq 2 might be written as eq 5, which shows that a

$$\frac{1}{v} = \frac{[H_2O]}{Kk_2[\text{ketone}][OH^-][Os^{8+}]} + \frac{1}{k_1[\text{ketone}][OH^-]}$$
$$= \frac{1}{k_s} \qquad (5)$$

plot of the reciprocal of the reaction velocity against the reciprocal of the osmium tetroxide concentration should give a straight line. Such a plot is shown in Figure 4. This shows that about a linear proportionality is observed and substantiates the validity of the rate law. The intercept of the line gives the value of k_1 as $4.00 \text{ mol}^{-1} \text{ l.} \text{ min}^{-1}$. This degree of agreement in k_1 value obtained from two different methods (from eq 4 and 5) further indicates the validity of the rate law and the corresponding mechanism.

In spite of this agreement in the rate law and experimental results, some doubt is created when one compares the k_1 value of this ketone with that obtained by Cullis and Hashmi.[9] These workers have reported the value of k_1 as $5.4 \text{ mol}^{-1} \text{ l. min}^{-1}$ at 25° when $[C_2H_5COCH_3] = 2.5 \times 10^{-3} M$. In present case the ketone concentration was kept about ten times higher than that used by the previous workers. Since it has already been shown that the higher ketone concentration retards the reaction rate (medium effect), this scheme of oxidation appears to be quite probable.

In the above analysis, it was assumed that the osmium tetroxide reacted with enolate anion. Another possibility is that it reacts with the enol which is in equilibrium with the enolate ion. The steps then would be as those shown in Scheme II. Applying the steady-state condi-

(9) C. F. Cullis and M. H. Hashmi, *J. Chem. Soc.*, 3080 (1957).

Table VI. Effect of Variation of Temperature upon the Reaction Rate

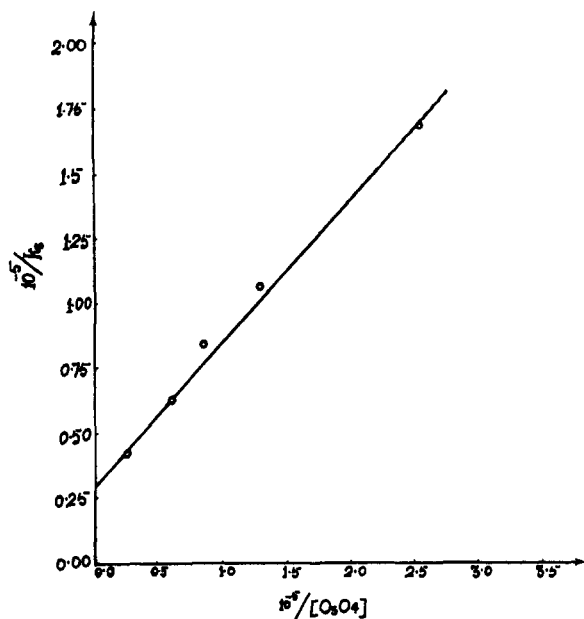|	A $[K_3Fe(CN)_6] = 0.25 \times 10^{-2}\ M$ $[OsO_4] = 3.93 \times 10^{-5}\ M$ pH 11			B $[C_2H_5COCH_3] = 6.25 \times 10^{-3}\ M$ $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}\ M$ $[OsO_4] = 1.97 \times 10^{-5}\ M$ pH 10.5		
$[(CH_3)_2CO] \times 10^2$ M	Temp, °C	$k \times 10^5$ mol l.$^{-1}$ min^{-1}	E_a, kcal/mol	Temp, °C	$k_s \times 10^5$ mol l.$^{-1}$ min^{-1}	E_a, kcal/mol
10.00	25	0.97		25	0.26	
	30	2.12	23.7			
	35	4.01		30	0.46	22.8
	40	7.25				
7.50	25	0.47		35	0.89	
	30	1.64	23.3			
	35	3.11		45		
	40	5.59				
5.00	25	0.53				
	30	0.15	22.9			
	35	2.12				
	40	3.74				

Scheme II

$$\text{ketone} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{enolate} + H_2O$$

$$\text{enolate} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{enol} + HO^-$$

$$\text{enol} + Os^{8+} \xrightarrow{k_3} \text{complex (C)}$$

$$\text{(C)} + OH^- \xrightarrow[\text{fast}]{k_4} Os^{6+} + \text{other products}$$

$$Os^{6+} + 2Fe(CN)_6{}^{3-} \xrightarrow[\text{fast}]{k_5} Os^{8+} + 2Fe(CN)_6{}^{4-}$$

tions, the rate law for this sequence of steps becomes

$$-\frac{d[\text{Fey}]}{dt} = \frac{k_1 k_2 k_3[\text{ketone}][OH^-][Os^{8+}]}{k_{-1}k_{-2}[OH^-] + (k_{-1} + k_2)k_3[Os^{8+}]} \quad (6)$$

Seeing this rate law (6) it can obviously be stated that Scheme II is ruled out because it is inconsistent with a linear plot of $1/v$ against $1/[OsO_4]$, and a linear dependence on hydroxide concentration in the region where there is a linear dependence of the rate on OsO_4 concentration.

In the derivation of the above two rate laws (eq 1 and 6) it is also assumed that the concentration of the complex is negligible in comparison to total osmium. However, if ketone directly forms complex with osmium(VIII) and then it decomposes with hydroxide ion, one may take that much of the osmium(VIII) forms the complex. In this case the law must be given in terms of the total osmium. The scheme of oxidation would be as shown in Scheme III.

Scheme III

$$\text{ketone} + OsO_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex (C)}$$

$$C + OH^- \xrightarrow{k_2} Os^{6+} + \text{other products}$$

$$Os^{6+} + 2Fe(CN)_6{}^{3-} \xrightarrow[\text{fast}]{k_3} Os^{8+} + 2Fe(CN)_6{}^{4-}$$

Under steady-state conditions, this gives the rate law in terms of the total osmium as shown in eq 7.

$$-\frac{d[\text{Fey}]}{dt} = \frac{k_1 k_2[\text{ketone}][Os O_4]_0[OH^-]}{k_{-1} + k_2[OH^-] + k_1[\text{ketone}]} \quad (7)$$

Since this rate law (7) cannot account for a linear plot of $1/k_s$ against $1/[OsO_4]$, mechanism 3 is also ruled out.

The good first-order hydroxide ion, the retarding effect of the osmium and that of the medium indicates the possibility of the first scheme of oxidation and the full sequence of steps would be

$$\underset{\substack{\text{O} \\ \parallel}}{RCCH_3} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\substack{\text{O}^- \\ \vert}}{RC}{=}CH_2 + H_2O$$

$$\underset{\substack{\text{O}^- \\ \vert}}{RC}{=}CH_2 + OsO_4 \xrightarrow{k_2} \left[\begin{array}{c} \text{O}^- \quad \text{O} \\ \vert \quad \diagup \\ RCO{-}Os \\ \parallel \quad \diagdown \\ CH_2 \quad \text{O} \quad \text{O} \end{array} \right]$$

$$\Big\downarrow OH^-$$

$$\underset{\substack{\text{O} \\ \parallel}}{RC}{-}CO_2{}^- \leftarrow \underset{\substack{\text{O} \\ \parallel}}{RC}CHO \leftarrow \underset{\substack{\text{O} \\ \parallel}}{RC}CH_2OH + OsO_4{}^-$$

$$\Big\downarrow \qquad\qquad\qquad\qquad \text{fast} \Big| 2Fe(CN)_6{}^{3-}$$

$$\underset{\substack{\vert \\ CO_2{}^-}}{CO_2{}^-} + \text{other reaction products} \qquad OsO_4 + 2Fe(CN)_6{}^{4-}$$

The keto acid formed in this case would be pyruvic acid for acetone, and its products of oxidation are reported to be oxalic (80%) and acetic (20%) acids with alkaline permanganate.[10] The intermediates are only supposed on the basis of the final products. The study was extended at four temperatures and the summarized results are given in Table VIA and B, respectively.

In case of acetone the energy of activation was calculated for three sets of acetone concentration and it has been found that the E_a (energy of activation) value increases with increasing concentration of acetone. Thus it is apparent that it is the energy of activation of the system which is affected by the acetone concentration or by the dielectric constant of the medium in such a way as to retard the reaction velocity. However, it is possible to

(10) W. L. Evans and E. J. Witzemann, J. Am. Chem. Soc., 34, 1096 (1912).

Figure 4. Plot of $1/k_s$ against $1/[OsO_4]$.

consider the retarding effect of these ketones as due to the effect of dielectric constant of the medium upon the hydrolysis of the weak electrolyte (the CO_3^{2-}). However, in the concentration range of ketones, there is not much change in the dielectric constant of the medium and apparently there was no change in pH of the system with these ketones. Further, to test this possibility one may employ the Winstein–Grunwald equation[11] to evaluate the magnitude of deviation from first-order dependence due to the effect of polarity on the dissociation of sodium carbonate. The value of "m" is found to be 4.5 which is

(11) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948); 78, 2770 (1956).

unusually large and casts considerable doubt on this statement. Thus it is the energy content of the system which is actually responsible for the deviation from the first-order dependence.

Experimental Section

The Analar (BDH) grade samples of acetone and ethyl methyl ketone were employed and were redistilled before use. The solutions were estimated by hydroxylamine hydrochloride method and also by bisulfite titration. The solution of osmium tetroxide was prepared by disolving the sample (Johnson Mattey & Co., Ltd.) in the solution of potassium hydroxide. The final strength of KOH and that of OsO_4 was kept $5.00 \times 10^{-2} M$ and $3.93 \times 10^{-3} M$, respectively. The samples of Na_2CO_3 and $NaHCO_3$ were of AR (BDH) grade but that of potassium hexacyanoferrate(III) was of GR (S. Merck) grade.

The initiation of the reaction was carried out by mixing the requisite quantity of the ketone solution maintained at a constant temperature into the solution of $K_3Fe(CN)_6$, Na_2CO_3, $NaHCO_3$, and OsO_4 kept in a reaction bottle at the same temperature. The temperature of the reaction mixture was kept constant with the help of an electrically operated thermostat with an accuracy of $\pm 0.1°$.

The progress of the reaction was followed by estimating the amount of hexacyanoferrate(II) ion produced after definite intervals of time with the help of a standard solution of ceric sulfate using ferroin as a redox indicator. The method gave always reproducible results.

However, ceric sulfate has been used as an oxidant for these ketones by Hinshelwood and coworkers[12] but in this study it was found that the estimation of $Fe(CN)_6^{4-}$ in presence of these ketones is not affected. Further, the oxidation of these ketones by ceric sulfate has been carried out at 70° and in present study there was no possibility of interference of these substances in the estimation of $Fe(CN)_6^{4-}$.

(12) C. N. Hinshelwood and J. Shorter, *J. Chem. Soc.*, 3276 (1950).