

## Kinetics of Os(VIII)-catalysed Oxidation of Neutralized Glyoxylic & Pyruvic Acids by Alkaline Hexacyanoferrate(III)

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Received 17 June 1975; accepted 22 January 1976

In the reactions between alkaline hexacyanoferrate(III) and some  $\alpha$ -keto carboxylate catalysed by Os(VIII) at  $[\text{OH}^-] < 10^{-3}M$ , the rate of reaction has been found to be proportional to the [substrate] but independent of the initial [Oxidant]. The rate is also directly proportional to the  $[\text{OH}^-]$  and  $[\text{Os(VIII)}]$ . The reactions have been studied at different temperatures and activation parameters evaluated. Tentative reaction mechanism has been proposed.

**K**INETICS of Os(VIII)-catalysed oxidation of various inorganic<sup>1,2</sup> and organic compounds<sup>3-7</sup>, by alkaline hexacyanoferrate(III) have been studied. Some of the results have indicated that unless catalyst is employed, the reactions are either extremely slow or do not occur, especially when the alkali concentration is very low. It has earlier been shown<sup>8</sup> that the oxidation of glyoxylic and pyruvic acids by hexacyanoferrate(III) do not proceed at  $[\text{OH}^-] < 10^{-3}M$ . However, the addition of a catalyst like Os(VIII) enhanced the rate of oxidation even at low  $[\text{OH}^-]$ . The present report, therefore, deals with the Os(VIII)-catalysed oxidation of the glyoxylic and pyruvic acids by alkaline hexacyanoferrate(III) at low [alkali].

### Materials and Methods

All inorganic chemicals were either of BDH (Analar) or E. Merck (GR) grades and used without further purification. Neutralized glyoxylic and pyruvic acids were always used for studying reactions. The chemicals employed and the procedure adopted were described in a previous paper<sup>8</sup>.

The solution of osmium tetroxide (Johnson & Matthey) was prepared by dissolving the sample in potassium hydroxide solution. Freshly prepared sodium carbonate-sodium bicarbonate buffer was used throughout during kinetic runs.

**Procedure**—The rate of disappearance of hexacyanoferrate(III) was followed spectrophotometrically as mentioned earlier<sup>8</sup>. The extinction coefficient ( $\epsilon$ ) of ferricyanide ions at 420 nm is  $1060 \pm 10M^{-1} \text{ cm}^{-1}$ . The initiation of the reaction was carried out by adding the requisite quantity of substrate maintained at a constant temperatures, to a mixture of oxidant, buffer and Os(VIII). The plot of optical density against time was linear and the slope of each plot gave initial rate ( $k_0$ ) which has been expressed in terms of concentration. The reproducibility was more than  $\pm 3\%$ . The rate of loss of oxidant was followed up to 50% conversion of initial hexacyanoferrate(III). All the runs were taken in the presence of buffer and thereby pH of the solutions were maintained constant.

### Results and Discussion

**Stoichiometry**—The equivalents of ferricyanide ion consumed per mole of substrate have been found to be 2.8 and 3.2 respectively.

**Effect of varying [reactant]**—The order with respect to each reactant was determined from the measurement of initial rates of reaction by keeping the concentration, in turn, fixed in one case and varying the other. The values of  $k_0$  at various [oxidant] showed that the rate was independent of [oxidant] (Table 1). Again, when the concentration of the reducing substrate was changed, the initial [hexacyanoferrate(III)],  $[\text{OH}^-]$  and [catalyst] were kept constant. The values of initial rates along with the quotients,  $k_0/[\alpha\text{-keto carboxylate}]$  at various [substrate] are summarized in Table 2. The rates were directly proportional to the initial [substrate].

**Effect of varying  $[\text{OH}^-]$** —The effect of varying  $[\text{OH}^-]$  on the initial rates were studied at constant [reactants] as well as [catalyst]. The  $k_0$  values at different  $[\text{OH}^-]$  calculated from the corresponding pH values are given in Table 3. The  $k_0/[\text{OH}^-]$  values indicated the first-order dependence on  $[\text{OH}^-]$ .

**Effect of varying [catalyst]**—The [reactants] and the pH of the solutions were kept constant, while

TABLE 1 — EFFECT OF [OXIDANT] ON THE RATE OF REACTION

{(A)  $[\text{Glyoxylate}] = 2.50 \times 10^{-3}M$ ;  $\text{pH} = 9.8$ ;  $[\text{Os(VIII)}] = 5 \times 10^{-5}M$ ; temp. =  $33^\circ\text{C}$ . (B)  $[\text{Pyruvate}] = 2.40 \times 10^{-3}M$ ;  $\text{pH} = 10.2$ ;  $[\text{Os(VIII)}] = 5 \times 10^{-5}M$ ; temp. =  $31.5^\circ\text{C}$ }

		A				
$[\text{Fe(CN)}_6^{3-}] \times 10^4M$		0.499	0.999	1.50	2.00	2.50
$k_0 \times 10^8$ ( $M \text{ sec}^{-1}$ )		2.44	2.52	2.40	2.26	2.45
		B				
$[\text{Fe(CN)}_6^{3-}] \times 10^4M$		2.00	2.50	3.00	3.50	4.00
$k_0 \times 10^8$ ( $M \text{ sec}^{-1}$ )		8.44	8.57	8.57	8.10	8.17

TABLE 2 — ZERO ORDER RATE CONSTANTS AT VARYING [SUBSTRATE]

{(A)  $[\text{Fe}(\text{CN})_6^{3-}] = 1.50 \times 10^{-4} M$ ;  $[\text{Os}(\text{VIII})] = 5.0 \times 10^{-5} M$ ;  $p\text{H} = 9.8$ ; temp. =  $32.5^\circ\text{C}$ . (B)  $[\text{Fe}(\text{CN})_6^{3-}] = 2.0 \times 10^{-4} M$ ;  $[\text{Os}(\text{VIII})] = 5.0 \times 10^{-5} M$ ;  $p\text{H} = 10.2$ , temp. =  $30.5^\circ\text{C}$ }

	A				
[Glyoxylate] $\times 10^3 (M)$	2.50	3.75	5.00	6.25	7.50
$k_0 \times 10^8 (M \text{ sec}^{-1})$	2.09	3.30	4.45	5.53	6.38
$k_0/[\text{Substrate}] \times 10^6 (\text{sec}^{-1})$	8.36	8.80	8.90	8.85	8.50
	B				
[Pyruvate] $\times 10^3 (M)$	0.599	1.20	1.80	2.40	3.00
$k_0 \times 10^8 (M \text{ sec}^{-1})$	2.06	4.35	6.41	7.97	9.98
$k_0/[\text{Substrate}] \times 10^5 (\text{sec}^{-1})$	3.44	3.62	3.56	3.32	3.33

 TABLE 3 — EFFECT OF  $p\text{H}$  ON THE RATE OF REACTION

{(A) [Glyoxylate] =  $2.5 \times 10^{-3} M$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 1.50 \times 10^{-4} M$ ;  $[\text{Os}(\text{VIII})] = 5 \times 10^{-5} M$ ; temp. =  $33.5^\circ\text{C}$ . (B) [Pyruvate] =  $2.40 \times 10^{-3} M$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 2.0 \times 10^{-4} M$ ;  $[\text{Os}(\text{VIII})] = 5 \times 10^{-5} M$ ; temp. =  $31.5^\circ\text{C}$ }

	A				
$p\text{H}$	9.8	10.0	10.2	10.7	—
$k_0 \times 10^8 (M \text{ sec}^{-1})$	2.94	4.56	7.23	25.9	—
$k_0/[\text{OH}^-] \times 10^4 (\text{sec}^{-1})$	4.66	4.56	4.57	5.17	—
	B				
$p\text{H}$	9.2	9.5	9.8	10.2	10.7
$k_0 \times 10^8 (M \text{ sec}^{-1})$	0.729	1.82	3.24	8.64	24.7
$k_0/[\text{OH}^-] \times 10^4 (\text{sec}^{-1})$	4.61	5.76	5.13	5.47	4.93

the [catalyst] was varied. The values of  $k_0/[\text{Os}(\text{VIII})]$  (Table 4) indicated that the rate of reaction was also directly proportional to the [catalyst].

*Influence of varying temperature and the activation parameters* — The temperature dependence of the reaction rates was studied at constant [substrate], [oxidant], [catalyst] and  $[\text{OH}^-]$ . The values of  $k_1$  have been calculated from the relation  $k_1 = k_0/[\text{substrate}]$  at various temperatures (Table 5). The plots  $\log k_1$  against  $1/T$  were linear. Thermodynamic parameters  $\Delta H$  and  $\Delta S$  have been evaluated and found to be  $26.2 \pm 2 \text{ kcal mole}^{-1}$  and  $3.4 \pm 6.0 \text{ cal deg}^{-1} \text{ mole}^{-1}$  for glyoxylic acid oxidation and  $21.8 \pm 1.5 \text{ kcal mole}^{-1}$  and  $-8.9 \pm 4.5 \text{ cal deg}^{-1} \text{ mole}^{-1}$  for pyruvic acid oxidation.

Krauss and Wilken<sup>9</sup> have shown that potassium salt of perosmic acid exists as  $K_2[\text{OsO}_4(\text{OH})_2]$ . It was, later on, shown by Sandel *et al.*<sup>10</sup> from spectrophotometric measurements in potassium hydroxide solution that osmium tetroxide yielded a value of  $\sim 10^{-10}$  for the first dissociation constant at  $25^\circ\text{C}$  whereas the second dissociation constant of the parent acid was much smaller ( $\sim 10^{-18}$ ) than that of first one. Although the exact composition of

 TABLE 4 — EFFECT OF VARYING  $[\text{Os}(\text{VIII})]$  ON THE REACTION RATE

{(A) [Glyoxylate] =  $2.50 \times 10^{-3} M$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 1.50 \times 10^{-4} M$ ;  $p\text{H} = 9.8$ ; temp. =  $33^\circ\text{C}$ . (B) [Pyruvate] =  $2.40 \times 10^{-3} M$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 2.0 \times 10^{-4} M$ ;  $p\text{H} = 10.2$ ; temp. =  $31.5^\circ\text{C}$ }

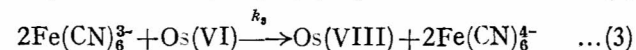
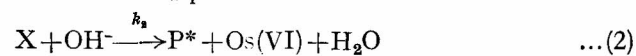
	A				
$[\text{Os}(\text{VIII})] \times 10^5 M$	5	10	15	20	25
$k_0 \times 10^8 (M \text{ sec}^{-1})$	2.68	5.35	8.13	11.0	13.8
$k_0/[\text{Os}(\text{VIII})] \times 10^4 (\text{sec}^{-1})$	5.36	5.35	5.42	5.50	5.52
	B				
$[\text{Os}(\text{VIII})] \times 10^5 M$	5	10	15	20	25
$k_0 \times 10^8 (M \text{ sec}^{-1})$	6.79	14.1	20.6	26.6	34.3
$k_0/[\text{Os}(\text{VIII})] \times 10^3 (\text{sec}^{-1})$	1.36	1.41	1.37	1.33	1.37

TABLE 5 — EFFECT OF VARYING TEMPERATURE ON RATE CONSTANT

{(A) [Glyoxylate] =  $2.5 \times 10^{-3} M$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 1.5 \times 10^{-4} M$ ;  $p\text{H} = 9.8$ ;  $[\text{Os}(\text{VIII})] = 5.0 \times 10^{-5} M$ ; (B) [Pyruvate] =  $2.40 \times 10^{-3} M$ ;  $[\text{Os}(\text{VIII})] = 5.0 \times 10^{-5} M$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 1.50 \times 10^{-4} M$ ;  $p\text{H} = 10.2$ }

Temp. ( $^\circ\text{C}$ )	$k_1 \times 10^5 (\text{sec}^{-1})$	
	(A) Glyoxalate	(B) Pyruvate
34	0.786	—
35	—	2.66
40.5	1.89	5.34
45.5	—	8.48
46	3.98	—

perosmic acid was not known, the perosmate anion which acted as a catalyst was probably  $\text{OsO}_5\text{H}^-$  and not  $\text{OsO}_5\text{H}_2^{2-}$ . It was, therefore, suggested that complex was formed by the interaction of substrate (S) with  $\text{HO}_5\text{O}^-$  which was designated by Os(VIII). The complex (X) finally reacted with  $\text{OH}^-$  to give reaction products and Os(VI). The latter was finally oxidized by two molecules of hexacyanoferrate(III) to give Os(VIII) (Scheme 1).



Scheme 1

The rate of formation of complex is given by relation (4)

$$\frac{d[\text{X}]}{dt} = k_1'[\text{S}][\text{Os}(\text{VIII})] - k_{-1}[\text{X}] - k_2[\text{X}][\text{OH}^-] \quad \dots(4)$$

Applying steady state approximation, the [complex] is given by Eq. (5)

$$[\text{X}] = \frac{k_1'[\text{S}][\text{Os}(\text{VIII})]}{k_{-1} + k_2[\text{OH}^-]} \quad \dots(5)$$

The rate of disappearance of hexacyanoferrate(III) is given by Eq. (6)

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k_1'k_2[\text{S}][\text{Os}(\text{VIII})][\text{OH}^-]}{k_{-1} + k_2[\text{OH}^-]} \quad \dots(6)$$

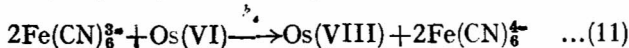
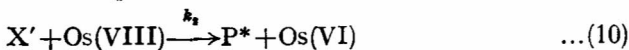
Assuming  $k_{-1} \gg k_2$ , i.e. step (2) to be the rate-determining, the product  $k_2[\text{OH}^-]$  will still be a smaller quantity, hence

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k_1'k_2[\text{S}][\text{Os}(\text{VIII})][\text{OH}^-]}{k_{-1}} \quad \dots(7)$$

$$= k[\text{S}][\text{Os}(\text{VIII})][\text{OH}^-] \quad \dots(8)$$

where  $k = 2k_1'k_2/k_{-1}$ .

Alternatively, it could be proposed (Scheme 2) that the substrate reacts with the  $\text{OH}^-$  to give an intermediate compound (X') followed by its reaction with Os(VIII) in a slow step to give oxidation product (P\*) and Os(VI). The latter is finally oxidized by two moles of hexacyanoferrate(III) regenerating Os(VIII) by fast step.



Scheme 2

Thus a probable rate law which might be proposed for the oxidations of glyoxylate and pyruvate ions is given by Eq. (8) and this indicates first order dependence of reaction rate on [substrate], [catalyst] and  $[\text{OH}^-]$ . The value of  $k$  (average of five deter-

minations) comes out to be 2750 at  $32.5^\circ$  and  $4360\text{M}^{-2}\text{sec}^{-1}$  at  $30.5^\circ\text{C}$  in the oxidation of glyoxylic and pyruvic acids respectively. The reported values at a particular set of conditions indicate that  $k_{\text{pyruvate}} > k_{\text{glyoxylate}}$ . The activation parameters calculated in Table 5 also support the above contention which indicates that more energy will be required to oxidize glyoxylate than pyruvate ion. The observed stoichiometry of 2.8 and 3.2 for glyoxalate and pyruvate ion oxidation respectively can be explained considering that steps<sup>8</sup> (12) and (13) take place to the extent of 60 and 40% respectively whereas steps<sup>8</sup> (14) and (15) take place to the extent of 80 and 20% respectively. The details regarding the formation of reaction products have been described in preceding paper.

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