Kinetics and Mechanism of the Osmium(VIII)-catalyzed Oxidation of Phosphite by Hexacyanoferrate(III) Ion in Aqueous Alkaline Media

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The oxidation of phosphite by alkaline $[Fe(CN)_6]^{3-}$ occurs with a measurable rate at 35 °C in the presence of Os^{VIII} according to equation (i) and rate law (ii), where k is the rate constant and K_3 is the equilibrium constant for

$$2[Fe(CN)_6]^{3-} + [HPO_3]^{2-} + 2[OH]^- \longrightarrow 2[Fe(CN)_6]^{4-} + [HPO_4]^{2-} + H_2O \qquad \text{(i)}$$

$$-d[Fe(CN)_6{}^{3-}]/dt = \frac{2kK_3[Os^{VIII}][OH^-][HPO_3{}^{2-}]}{1 + K_3[OH^-]} \qquad \text{(ii)}$$

the complex formation between Os^{VIII} and $[OH]^-$; k and K_3 are 1.0 ± 0.05 dm^6 mol^{-2} s^{-1} and 32 ± 3 dm^3 mol^{-1} respectively at 35 °C and $I = 1.0$ mol dm^{-3}. A spectrophotometric value of K_3 is 30 ± 6 dm^3 mol^{-1}. A mechanism consistent with the above facts has been suggested.

OSMIC ACID or osmium(VIII) in alkaline solution is known[1] as a catalyst for redox titrations. Solymosi and his co-workers[2] employed the catalyst for the quantitative oxidation of various substances including phosphite by hexacyanoferrate(III) in alkaline solutions. No kinetic study of the oxidation of phosphite by $[Fe(CN)_6]^{3-}$ seems to have been made so far. We recently reported[3] the uncatalyzed oxidation of hypophosphite by this ion in which the product, phosphite, was not oxidized further. The uncatalyzed oxidation of phosphite is very slow, but it is considerably catalyzed by Os^{VIII}. Quite a few catalyzed oxidations[4-13] of organic compounds have been studied, but only two oxidations of inorganic compounds,

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selenium(IV)[14] and tellurium(IV),[15] seem to have been made. The kinetic results in case of organic compounds are generally similar, but differ slightly in the oxidations of Se^{IV} *and* Te^{IV}. Since phosphite was one of the inorganic compounds studied previously, we thought a study of the kinetics of its oxidation might throw some light on the mechanism, and may enable us to suggest a common mechanism for all osmium(VIII)-catalyzed oxidations by $[Fe(CN)_6]^{3-}$ in alkaline solutions. We have carried out a 100-fold variation in the concentrations of phosphite, hydroxide ion, and Os^{VIII}, and a ten-fold variation in the concentration of $[Fe(CN)_6]^{3-}$.

TABLE 1

Initial rates and pseudo-second-order rate constants (k_2) in the osmium(VIII)-catalyzed reaction between phosphite and $[Fe(CN)_6]^{3-}$ ion at 35 °C, $[OH^-] = 0.05$ mol dm^{-3}, and $I = 1.0$ mol dm^{-3}

$10^4[Fe(CN)_6{}^{3-}]$ / mol dm^{-3}	$10^3[Na_2HPO_3]$ / mol dm^{-3}	$10^5[Os^{VIII}]$ / mol dm^{-3}	10^7 (initial rate) / mol dm^{-3} s^{-1}	k_2 / dm^3 mol^{-1} s^{-1}
1.0	50.0	1.0	6.92	1.38
2.0	50.0	1.0	7.03	1.41
3.0	50.0	1.0	7.59	1.52
4.0	50.0	1.0	8.18	1.63
5.0	50.0	1.0	6.85	1.37
6.0	50.0	1.0	7.14	1.43
7.0	50.0	1.0	7.44	1.49
8.0	50.0	1.0	7.44	1.49
9.0	50.0	1.0	7.14	1.43
10.0	50.0	1.0	6.85	1.37
11.0	50.0	1.0	7.44	1.49
12.0	50.0	1.0	7.14	1.43
			Mean	1.45 ± 0.06
8.0	1.0	1.0	0.28	2.80 *
8.0	2.0	1.0	0.41	2.05 *
8.0	4.0	1.0	0.70	1.75
8.0	6.0	1.0	0.89	1.45
8.0	8.0	1.0	1.37	1.70
8.0	10.0	1.0	1.67	1.67
8.0	20.0	1.0	2.50	1.25
8.0	30.0	1.0	3.71	1.24
8.0	40.0	1.0	5.00	1.25
8.0	50.0	1.0	6.00	1.25
8.0	60.0	1.0	8.18	1.36
8.0	70.0	1.0	9.09	1.30
8.0	80.0	1.0	9.70	1.20
8.0	90.0	1.0	11.2	1.24
8.0	100.0	1.0	13.9	1.39
8.0	200.0	1.0	27.8	1.39
8.0	300.0	1.0	38.8	1.29
8.0	400.0	1.0	55.8	1.39
8.0	500.0	1.0	65.1	1.32
			Mean	1.38 ± 0.07
8.0	50.0	0.10	1.17	2.34 *
8.0	50.0	0.20	1.52	1.52
8.0	50.0	0.40	3.02	1.51
8.0	50.0	0.60	4.29	1.43
8.0	50.0	0.80	4.85	1.21
8.0	50.0	1.0	5.76	1.15
8.0	50.0	2.0	12.5	1.25
8.0	50.0	3.0	17.9	1.30
8.0	50.0	4.0	27.9	1.39
8.0	50.0	5.0	37.2	1.48
8.0	50.0	6.0	43.4	1.45
8.0	50.0	7.0	47.8	1.37
8.0	50.0	8.0	54.5	1.36
8.0	50.0	9.0	63.6	1.41
8.0	50.0	10.0	71.2	1.42
			Mean	1.37 ± 0.07
			Mean of all the observations	1.40 ± 0.07

* Not included in the mean.

EXPERIMENTAL

Potassium hexacyanoferrate(III) and sodium hydrogenphosphite ($Na_2[HPO_3]\cdot 5H_2O$) were of B.D.H. AnalaR quality and their aqueous solutions were prepared by direct weighing. Phosphite solution was standardized iodimetrically[16] and could be stored for several months. The hexacyanoferrate(III) solutions were prepared daily. Sodium

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hydroxide and other chemicals used were of B.D.H. AnalaR quality. Osmic acid 'OsO_4' (Johnson, Matthey) was dissolved in 0.5 mol dm^{-3} Na[OH], analyzed iodimetrically, and stored in a cool dark place. Dilute solutions were prepared from this whenever required. Such solutions are quite stable [17] if the concentration of Na[OH] is greater than 0.3 mol dm^{-3}. All the solutions were prepared in doubly distilled water (second distillation from permanganate).

Kinetic Procedure.—Reactions were carried out in a thermostatted water-bath at 35 ± 0.1 °C unless mentioned otherwise. Hexacyanoferrate(III), phosphite, hydroxide, and other ingredients were kept in a reaction vessel to attain the temperature of the bath. Osmium(VIII) solution was kept separately. The reaction was started by adding the requisite amount of the osmium(VIII) solution. Aliquot portions (5 or 10 cm^3) were removed after suitable intervals of time and analyzed for $[Fe(CN)_6]^{3-}$ in a Spectronic 20 colorimeter at 415 nm after quenching the reaction in a known quantity of HCl. Hexacyanoferrate(II) is almost transparent [18] at this wavelength.

For the determination of the stoicheiometry under excess of phosphite, the phosphite was estimated by a suitable modification of the iodimetric method. The reaction mixture (5 cm^3 in 1.0 mol dm^{-3} Na[OH]) was mixed with $>$1.0 mol dm^{-3} HCl (5 cm^3), 0.01 mol dm^{-3} Zn[SO_4] solution (5 cm^3), and 5% Na[HCO_3] solution (10 cm^3). Iodine (10 cm^3, 0.01 mol dm^{-3}) was added and the mixture was left for 1 h for completion of the reaction. Hydrochloric acid (10 cm^3, 1.0 mol dm^{-3}) was then added and the excess of iodine was titrated against 0.01 mol dm^{-3} thiosulphate solution. Spectrophotometric measurements were made in a Beckman u.v. spectrophotometer using 1-cm cells. The results were independent of the order of mixing the reactants.

Initial rates were determined by the plane-mirror method.[19] Duplicate measurements were reproducible to ±5%. For most of the kinetic runs, the ionic strength (I 1.0 mol dm^{-3}) was adjusted with NaCl.

RESULTS

Stoicheiometry.—In five determinations, the excess of $[Fe(CN)_6]^{3-}$ (two to five times the 1×10^{-3} mol dm^{-3} hypophosphite) was measured colorimetrically as described. One mol of phosphite required 1.96 ± 0.02 mol of $[Fe(CN)_6]^{3-}$. In six determinations, the excess of phosphite {1.2—2 times the 5×10^{-3} mol dm^{-3} $[Fe(CN)_6]^{3-}$} was estimated by the modified iodimetric method. One mol of phosphite required 1.98 ± 0.03 mol of $[Fe(CN)_6]^{3-}$. In all these reaction mixtures, $[OH^-]$ = 1.0 mol dm^{-3} and $[Os^{VIII}]$ = 1×10^{-5} mol dm^{-3}. The stoicheiometry therefore corresponds to equation (1).

$$2[Fe(CN)_6]^{3-} + [HPO_3]^{2-} + 2[OH]^- \longrightarrow 2[Fe(CN)_4]^{4-} + [HPO_4]^{2-} + H_2O \quad (1)$$

Hexacyanoferrate(III) *Dependence.*—The concentration of $[Fe(CN)_6]^{3-}$ was varied from 1×10^{-4} to 12×10^{-4} mol dm^{-3} at I = 3.0 mol dm^{-3} and at fixed concentrations of the other reactants. There was no change in the rate (Table 1).

Phosphite Dependence.—The phosphite was varied in the range 1×10^{-3}—5×10^{-1} mol dm^{-3} at I = 1.0 mol dm^{-3} (NaCl). A plot of the initial rate against the concentration of phosphite was linear and passed through the origin. The order in phosphite concentration is thus one. The results are shown in Table 1.

Osmium(VIII) *Dependence.*—The concentration of the catalyst was varied in the range 1×10^{-6}—1×10^{-4} mol dm^{-3} at fixed concentrations of the other reactants. The order in $[Os^{VIII}]$ was found to be one from a linear plot of the logarithm of the initial rate against the logarithm of the concentration of Os^{VIII} which passed through the origin. These results are also shown in Table 1.

Hydroxide Dependence.—The concentration of Na[OH] was varied in the range 5×10^{-3}—5×10^{-1} mol dm^{-3} at three different temperatures. The rate first increased and then tended to a limiting value with increasing hydroxide-ion concentration. The results are shown in Table 2 and Figure 1.

TABLE 2

Initial rates at different hydroxide-ion concentrations and temperatures in the osmium(VIII)-catalyzed reaction between phosphite and $[Fe(CN)_6]^{3-}$ at I = 1.0 (NaCl), $[Fe(CN)_6]^{3-}$ = 8.0×10^{-4}, and $[Na_2HPO_3]$ = 5.0×10^{-2} mol dm^{-3}

$[OH^-]$	10^7(initial rate)/mol dm^{-3} s^{-1}		
mol dm^{-3}	25	35	45 °C
0.005	0.59	1.25	2.71
0.010	1.02	2.22	5.08
0.025	2.00	4.34	8.00
0.05	2.73	6.20	10.9
0.075	3.30	6.82	12.1
0.10	3.57	7.44	12.9
0.20	4.44	8.06	14.0
0.30	4.83	8.68	14.6
0.40	5.00	9.09	15.2
0.50	5.13	9.30	16.0

Effect of Salts.—Sodium chloride, nitrate, and perchlorate were employed. The rate increased on increasing electrolyte concentration. Since the rate is independent of the concentration of $[Fe(CN)_6]^{3-}$, ion pairing [20] between Na$^+$ and $[Fe(CN)_6]^{3-}$ will have no effect on the rate. This, therefore, appears to be a salt effect. The results are given in Figure 2.

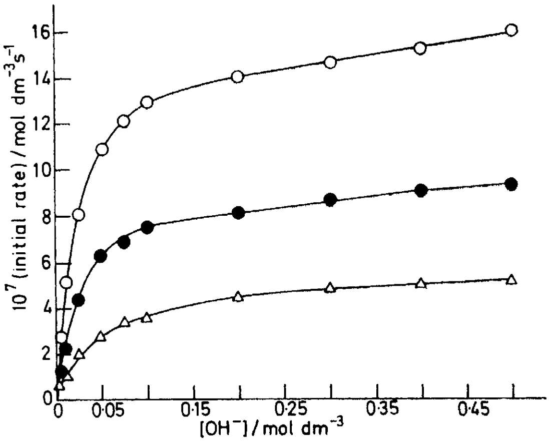

FIGURE 1 Hydroxide-ion dependence of the osmium(VIII)-catalyzed reaction between $[Fe(CN)_6]^{3-}$ and phosphite at $[Fe(CN)_6{}^{3-}]$ = 8.0×10^{-4}, $[HPO_3{}^{2-}]$ = 5.0×10^{-2}, $[Os^{VIII}]$ = 1×10^{-5}, and I = 1.0 mol dm^{-3} and 45 (○), 35 (●), and 25 °C (△)

Spectrophotometric Results.—A spectrum of 1×10^{-4} mol dm^{-3} Os^{VIII} in 0.5 mol dm^{-3} Na[OH] in the range 330—750

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nm showed no peak. Beers law is followed at 340 nm for osmium(VIII) solutions in the concentration range 2.5 × 10^{-5}—2.5 × 10^{-4} mol dm^{-3} at the three temperatures (25, 35, and 45 °C) and in 0.5 mol dm^{-3} Na[OH]. The absorbance ($D_{obs.}$) was then noted for mixtures of 1 × 10^{-4} mol dm^{-3} OsO_4 and different concentrations of hydroxide ion in the range 0.005—0.15 mol dm^{-3}. These results at $I = 1.0$ mol dm^{-3} (NaCl) and at 25, 35, and 45 °C are shown in Table 3. The maximum absorbance ($D_{comp.}$) for $[Os^{VIII}] = 1 \times 10^{-4}$, $[OH^-] = 0.5$, and $I = 1.0$ mol dm^{-3} was 0.26. A plot of $D_{obs.}$ against $[OH^-](D_{comp.} - D_{obs.})$ according to equation (2) [21] yielded a straight line from which K could be calculated; $D_{obs.}$, $D_{comp.}$, and D_x are the optical densities of the test solution, complex, and the uncomplexed Os^{VIII}, respectively. Values of K from a weighted non-linear least-squares treatment were 24 ± 4, 30 ± 6, and 42.5 ± 6 dm^3 mol^{-1} at 25, 35, and 45 °C respectively and at $I = 1.0$ mol dm^{-3}.

$$D_{obs.} = D_x + K[OH^-](D_{comp.} - D_{obs.}) \qquad (2)$$

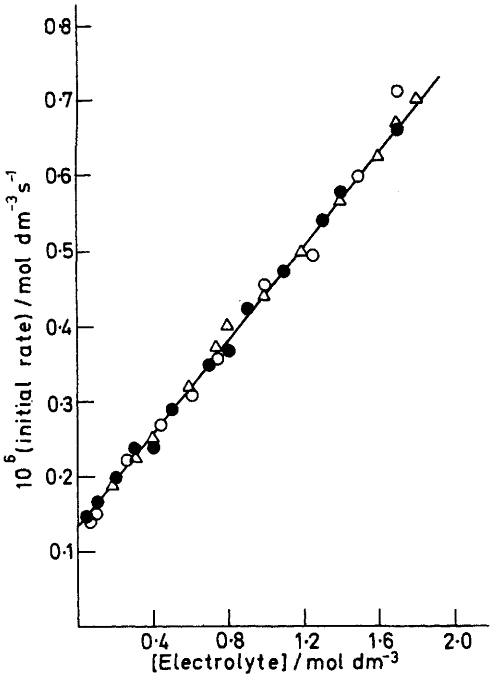

FIGURE 2 Effect of electrolytes on the osmium(VIII)-catalyzed reaction between $[Fe(CN)_6{}^{3-}]$ and $[HPO_3{}^{2-}]$ at $[Fe(CN)_6{}^{3-}] = 7.5 \times 10^{-4}$, $[HPO_3{}^{2-}] = 5 \times 10^{-2}$, $[Os^{VIII}] = 6.5 \times 10^{-6}$, and $[OH^-] = 0.05$ mol dm^{-3}, for (○) NaCl, (△) Na[NO_3], and (●) Na[ClO_4]

TABLE 3

Absorbance of Os^{VIII} at different hydroxide-ion concentrations, 340 nm, and $I = 1.0$ mol dm^{-3} (NaCl). $D_{comp.} = 0.26$

$\frac{[OH^-]}{mol\ dm^{-3}}$	Absorbance		
	25	35	45 °C
0.005 0	0.08	0.068	0.065
0.007 5	0.087 5	0.084	0.082
0.010	0.095	0.090	0.095
0.025	0.135	0.132 5	0.145
0.050	0.17	0.175	0.105
0.075	0.185	0.190	0.205
0.100	0.20	0.205	0.215
0.125	0.21	0.212 5	0.222 5
0.15	0.215	0.220	2.227 5

DISCUSSION

The order in $[Fe(CN)_6{}^{3-}]$ has been found to be zero, as reported earlier in the oxidations of acetone and ethyl methyl ketone,[4] ethanol and methanol,[5] lactic and glycolic acids,[6] acetaldehyde,[7] dioxan,[8] phenylglycolate [9,10] malate,[11,12] and tartrate.[12] It is obvious that $[Fe(CN)_6]^{3-}$ has no role in the formation of the activated complex and that some other species is the oxidant. The catalyst Os^{VIII} must be the oxidant. We have found that, if the catalyst and phosphite alone are mixed, the absorbance of the osmium(VIII) solution decreases. The Os^{VIII} is reduced to Os^{VI}. Similar behaviour was reported in the oxidations of ketones.[4]

The orders in phosphite and osmium(VIII) concentration are each one, and a limiting rate is obtained in the case of hydroxide ions. It appears that $[OH]^-$ is involved in an equilibrium step with either phosphite or the catalyst. Although a number of oxidations have been reported [4,7,8] in which $[OH]^-$ forms a reactive species with the substrate, no evidence has been given in support of this. The first [22,23] and second [24] dissociation constants of phosphorous acid are reported to be 0.107 and 7 × 10^{-7} mol dm^{-3} respectively at 25 °C, and the acid is only dibasic. Hence in our alkaline solutions the reaction of phosphite with $[OH]^-$ would be complete at $[HPO_3]^{2-}$ and no further reaction is possible. It is more logical to assume complex formation between the catalyst and $[OH]^-$.

Osmium tetraoxide is known [25] to yield a red solution of $[OsO_4(OH)_2]^{2-}$ in strong alkaline solutions and it is this complex which appears to be catalytic. In the alkaline solutions employed, OsO_4 seems to be completely converted into $[OsO_3(OH)_3]^-$. Further combination with $[OH]^-$ yields the reactive form $[OsO_4(OH)_2]^{2-}$. This is in line with the findings of Sauerbrum and Sandell [26] on the dissociation of osmic acid. The mechanism in equations (3)—(6) for the catalyzed reaction may be suggested, and leads to the rate law in (7) and (8). An

$$[OsO_3(OH)_3]^- + [OH]^- \underset{}{\overset{K_3}{\rightleftharpoons}} [OsO_4(OH)_2]^{2-} + H_2O \qquad (3)$$

$$[OsO_4(OH)_2]^{2-} + [HPO_3]^{2-} + H_2O \xrightarrow{k} [OsO_2(OH)_4]^{2-} + [HPO_4]^{2-} \qquad (4)$$

$$[OsO_2(OH)_4]^{2-} + 2[Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} [OsO_2(OH)_4] + 2[Fe(CN)_6]^{4-} \qquad (5)$$

$$[OsO_2(OH)_4] + [OH]^- \xrightarrow{\text{fast}} [OsO_3(OH)_3]^- + H_2O \qquad (6)$$

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alternative mechanism assuming complex formation with $\mathrm{P^{III}}$ can also be suggested [equations (9)—(11)].

$$-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t = \frac{2kK_3[\mathrm{Os^{VIII}}][\mathrm{OH^-}][\mathrm{HPO_3}^{2-}]}{1 + K_3[\mathrm{OH^-}]} \qquad (7)$$

$$= k_2[\mathrm{Os^{VIII}}][\mathrm{HPO_3}^{2-}] \quad \text{(at constant } [\mathrm{OH^-}]) \qquad (8)$$

$$\mathrm{Os^{VIII}} + \mathrm{P^{III}} \overset{K_9}{\rightleftharpoons} \text{complex (1)} \qquad (9)$$

$$\text{complex (1)} + [\mathrm{OH}]^- \overset{K_3}{\rightleftharpoons} \text{complex (2)} \qquad (10)$$

$$\text{complex (2)} \overset{k}{\rightleftharpoons} \text{products} \qquad (11)$$

If K_9 is very small, rate law (7) with an additional constant K_9 in the numerator would be obtained.

A plot of (initial rate)$^{-1}$ against $[\mathrm{OH^-}]^{-1}$ should result in a straight line. This was found in the present investigation, yielding values of K_3 (from a weighted non-linear least-squares treatment) of 24 ± 4, 32 ± 3, and 44 ± 2 dm^3 mol^{-1}, and k values of 0.525 ± 0.03, 1.0 ± 0.05, and 1.6 ± 0.1 dm^6 mol^{-2} s^{-1} at 25, 35, and 45 °C respectively. These K values are in very good agreement with those obtained spectrophotometrically using equation (2). This is strong support for step (3). Values of $E^\ddagger$ and $\Delta S^\ddagger$ associated with k were 55 ± 17 kJ mol^{-1} and -79 ± 52 J K^{-1} mol^{-1} respectively; ΔH and ΔS associated with K_3 were 24 ± 1 kJ mol^{-1} and -146 ± 6 J K^{-1} mol^{-1}, and ΔH associated with the spectrophotometric value of K was found to be 23 ± 6 kJ mol^{-1}. At low phosphite and osmium(VIII) concentrations, the k_2 values were slightly higher; the reason for this is not obvious.

Complex formation with phosphite has been reported in oxidations by $\mathrm{Tl^{III}}$,[27] $\mathrm{Cr^{VI}}$,[28] $\mathrm{Mn^{III}}$,[29] and $\mathrm{Ce^{IV}}$.[30] Complex formation between the catalyst and the substrate has also been reported [6,12] in some studies but there is no supporting evidence, kinetic or otherwise. Unfortunately, here it is not possible to obtain such evidence. As soon as the catalyst (prepared in hydroxide solutions) is mixed with the substrate, an equilibrium involving the substrate and hydroxide ion is immediately established.

Phosphorus acid oxidations are characterized by equilibria involving active and inactive forms.[31,32] Such equilibria do not exist in alkaline solutions since the hydrogen-ion concentration is too small to convert the inactive into the active form. In other words the P–H bond in $[\mathrm{HPO_3}]^{2-}$ is not labilized and no lone pair of electrons on P is available for electrophilic attack by the oxidant. It is for this reason that $[\mathrm{HPO_3}]^{2-}$ and $[\mathrm{H_2PO_3}]^-$ (phosphite) are resistant [28,33] to oxidation but $\mathrm{H_3PO_3}$ is not. Strong oxidants like $\mathrm{Ag^{II}}$,[32,34] $\mathrm{Cu^{III}}$,[35] $\mathrm{Os^{VIII}}$, *etc.* are, however, able to form complexes with, and subsequently oxidize, the phosphite.

In all probability, steps (3) and (4) could form part of a general mechanism if $[\mathrm{HPO_3}]^{2-}$ is replaced by S, the substrate. Most of the workers [4,7] who have studied the catalyzed reactions employed a small range of hydroxide-ion concentration and failed to obtain a limiting rate. In the oxidation of glycolic and lactic acids, where the range of concentration of $[\mathrm{OH}]^-$ was 0.01—0.48 mol dm^{-3}, Singh and his co-workers [6] did find a limiting rate.

Considerable ion pairing has been reported in the oxidations of hypophosphite,[3] sulphite,[36] $\mathrm{As^{III}}$,[37] *etc.* by alkaline $[\mathrm{Fe(CN)_6}]^{3-}$. Since in the present case the rate is independent of the oxidant, any ion pairing between $\mathrm{K^+}$ or $\mathrm{Na^+}$ and $[\mathrm{Fe(CN)_6}]^{3-}$ will have no effect on the rate. A plot of the initial rate against the ionic strength or electrolyte concentration yielded an almost straight line showing no zero rate at zero electrolyte concentration. There might be a specific cationic effect in this case.

A complex of $[\mathrm{Fe(CN)_6}]^{3-}$ with the substrate formed by cyanide displacement has been proposed by a few workers [2b,5,38] but it has been shown [36a,39] subsequently that such a displacement probably does not occur.

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