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Kinetics and Mechanism of the Oxidation of Tris(2,2′-bipyridyl)- and Tris(1,10-phenanthroline)-iron(II) Complexes with Peroxodisulphate in Acetate Buffers

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A detailed kinetics study of the oxidation of tris(2,2′-bipyridyl)iron(II), $[Fe(bipy)_3]^{2+}$, at 45 °C and tris(1,10-phenanthroline)iron(II) $[Fe(phen)_3]^{2+}$ at 50 °C with peroxodisulphate in acetate buffers of pH 3.2—5.9 has revealed that the reaction is inhibited by the organic ligand and the order with respect to $[S_2O_8{}^{2-}]$ is between one and zero. Reaction occurs by two mechanisms, both being dissociative and oxidative. One involves the complexation of $[FeL_3]^{2+}$ (L = bipy or phen) with $[S_2O_8{}^{2-}]$ yielding $[FeL_3 \cdot S_2O_8]$ [step (1)], dissociation of this complex yielding $[FeL \cdot S_2O_8]$ and a molecule of organic ligand [(2)], and internal redox reaction of the latter complex (3). The formation constants ($dm^3\ mol^{-1}$) for step (1) and rate constants for the dissociation (2) for bipy and phen were 33 ± 2 and $(1.4 \pm 0.1) \times 10^{-2}\ s^{-1}$, and 45 ± 4 and $(5.5 \pm 1.5) \times 10^{-4}\ s^{-1}$ respectively. The other mechanism involves the dissociation of tris to the bis complex with rate constants of $(1.12 + 0.12) \times 10^{-4}$ and $1.25 \times 10^{-5}\ s^{-1}$ for bipy and phen respectively, and the oxidation of the bis complex with $[S_2O_8]^{2-}$.

Our attention was drawn to the present reactions while working on the oxidation of iron(II) by peroxodisulphate.[1] Several workers[2–4] have studied the kinetics of this and related reactions,[5–7] but the mechanism is still not unequivocally established.[8] In general the reaction of complexes $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) (bipy = 2,2′-bipyridyl) with $[S_2O_8]^{2-}$ considered to be second order, but deviations from second-order character have been reported[3,5,7] after about 30—40% completion of reaction. Most workers[2,4,5,8] related this to ion-pair formation between the complex and peroxodisulphate. It has also been attributed to a change in stoicheiometry.[3] Since peroxodisulphate and peroxodiphosphate are isostructural and isoelectronic they are expected to behave similarly towards these complexes. In peroxodiphosphate oxidations the dissociative mechanism[9,10] (dissociation of the tris to the bis complex being rate determining) appears to be well established. Edwards and co-workers[9,10] have compared the mechanism of the oxidations of these iron(II) complexes by $[P_2O_8]^{4-}$ with that by $[S_2O_8]^{2-}$, and are of the opinion that in the case of peroxodisulphate it is not adequately described by a second-order equation, nor by a simple dissociative process.

The main feature of the dissociative mechanism is the retardation by the ligand (bipy) or (phen), but such behaviour has not been reported so far in peroxodisulphate oxidations. Another feature of this mechanism is that the rate is independent of the large concentration of the oxidant, which also has not been reported in the peroxodisulphate oxidations. Thus it appeared to us that a thorough kinetic study over a wide range of concentrations of the reactants would enable us to learn more about this reaction. We found that the ligand retards the rate and ion-pair or complex formation is indicated kinetically, but that there is no change in the stoicheiometry and no gas is evolved.

Experimental

Chemicals and Solutions.—2,2′-Bipyridyl (bipy) and 1,10-phenanthroline (phen) were from Riedel and used as such. Iron(II) sulphate was from E. Merck. Solutions of the ligands were prepared in 1.0 mol dm^{-3} H_2SO_4. The solutions of the complexes were prepared by mixing equivalent amounts of ligands and iron(II) sulphate. Peroxodisulphate was E. Merck G.R. quality. Perchloric acid was 60% Riedel AnalaR. Lithium perchlorate solution was prepared by neutralising perchloric acid with lithium carbonate to pH 6.8. All other chemicals were from BDH (AnalaR) or E. Merck (GR).

Doubly distilled water (second distillation from alkaline permanganate) was used in preparing all solutions and in kinetics experiments.

Analysis.—Bipyridyl and phenanthroline complexes were measured respectively at 520 nm ($\varepsilon = 9\,000 \pm 30$) and 510 nm ($\varepsilon = 11\,600 \pm 50\ dm^3\ mol^{-1}\ cm^{-1}$ on an EC colorimeter. Peroxodisulphate was determined iodometrically.[11]

U.v. and visible spectra of solutions were recorded on a Cecil Spectrophotometer with a 1-cm cell, immediately after mixing the reactants and also at different times till the reaction was over.

Kinetic Procedure.—The iron(II) complex along with a suitable acetate buffer in one flask and peroxodisulphate solution in another flask were equilibrated at the desired temperature ±0.1 °C in a thermostat. Reaction was initiated by adding a calculated volume of peroxodisulphate solution to the flask containing the iron(II) complex. Aliquots were withdrawn at suitable intervals of time and the concentration of the complex measured on a Spectronic 20 Bausch & Lomb colorimeter at a suitable wavelength as described.

In almost all experiments $[S_2O_8{}^{2-}]$ was in large excess over complex and pseudo-first-order plots yielded corresponding rate constants, k_0. When $[S_2O_8{}^{2-}] \approx$ [complex], initial rates were determined by the plane-mirror method.[12] Pseudo-first-order rate constants were then calculated by dividing by [complex]. The results were reproducible to ±3%.

Stoicheometry and Products.—Reaction mixtures with excess of iron(II) complex were kept for about 12 h for completion of the reaction and excess of Fe^{II} was determined colorimetrically at the appropriate wavelength as described. Excess of peroxodisulphate could not be employed since excess of Fe^{III}

Table 1. Pseudo-first-order rate constants in the reaction of $[Fe(bipy)_3]^{2+}$ with $[S_2O_8]^{2-}$ at $[Fe^{II}] = 5.0 \times 10^{-5}$ mol dm^3, $[Na_2SO_4] = 0.05$ mol dm^{-3}, pH 3.7, and 45 °C

$10^3[S_2O_8]^{2-}$ mol dm^{-3}	10^3k_0/s^{-1} at 10^3[bipy]/mol dm^{-3}									
	0.02	0.04	0.10	0.35	0.85	1.35	1.85	2.35	2.85	4.85
0.04										0.01
0.05					0.052		0.035		0.023	
0.06										0.0145
0.08										0.017
0.25				0.165	0.092	—	0.051	0.041		
0.50			0.56	0.21	0.12	0.092	0.076	0.059		
0.75			—	0.31	—	—	—			
1.0			0.81	0.41	0.33	0.25	—			
2.0			—	0.78	—	—				
2.5			1.35	1.0	0.71	0.59	0.55			0.47
5.0				1.6	1.3	—	1.1			0.85
10.0			2.5	2.4	2.3	2.2	2.1			1.6
20.0				3.8	3.6	—	3.3			3.1
30.0	5.9	6.0	5.8	5.8	5.7	5.6	—	—	5.5	—
50.0	7.7	7.7	—	7.3	—	—	—	—	—	—
75.0	8.7	8.8	—	—	8.8	—	8.8			
100.0	10.0	11.0	—	10.5	10.0	—	10.0			

interfered with its determination. The stoicheiometry $\Delta[Fe^{II}]/\Delta[S_2O_8^{2-}]$ from six experiments was found to be 1.9 ± 0.1 in both reactions. Thus it appears that 2 mol of Fe^{II} are oxidised by 1 mol of peroxodisulphate. No visible oxygen evolution was observed. Therefore we consider side reactions including decomposition of peroxodisulphate as negligible.

Cerium(IV) oxidation of iron(II) complexes yields a pale yellow solution[13] after 2 d of mixing the reactants which we found to absorb at 270 and 320 nm in the case of phen, and at 305 nm in the case of bipy. This must correspond[14] to dimers of Fe^{III}. The present reaction mixtures show characteristic bands at 515 and 520—525 nm for $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ complexes respectively, which gradually vanish upon oxidation with peroxodisulphate. Ultimately absorption peaks at 270 and 305 nm are observed for phen and bipy complexes respectively which correspond to the dimers of Fe^{III}. The reaction mixtures do not absorb[15] in the region 590—600 nm which is characteristic of $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$. Shakhashiri and Gordon[16] reported that detailed spectral studies on solutions of $[Fe(phen)_3{}^{3+}]$ are difficult to obtain since aquated Fe^{III} and its various hydrolytic forms exhibit absorption bands in the 300—400 nm region. Nevertheless a shoulder was observed at 350 nm for all resulting solutions.

Results

Oxidation of Bipyridyl Complex.—The order of one in $[Fe^{II}]$ was confirmed in two ways. The concentration of Fe^{II} was varied in such a way that the ratio of Fe^{II} to bipy was always 1:3 in the range (1—5) × 10^{-5} mol dm^{-3} with $[S_2O_8{}^{2-}] = 5.0 \times 10^{-3}$ mol dm^{-3} and $[Na_2SO_4] = 0.05$ mol dm^{-3} at 45 °C in acetate buffer of pH 3.7. The pseudo-first-order rate constant was found to be 1.55×10^{-3} s^{-1}. The concentration of Fe^{II} was also varied in the same range and under the same conditions but with constant [bipy] = 4.85×10^{-3} mol dm^{-3}. The pseudo-first-order rate constant was found to be 8.0×10^{-4} s^{-1}. Incidently this also shows that the reaction is inhibited by bipy.

Variation of $[S_2O_8{}^{2-}]$. The concentration of peroxodisulphate was varied under three different situations: (*a*) comparable concentrations of bipy and $[S_2O_8]^{2-}$, (*b*) [bipy] is small and $[S_2O_8{}^{2-}]$ is large, and (*c*) [bipy] is large and $[S_2O_8{}^{2-}]$ is small. These results are given in Table 1. In all cases a plot of $(k_0)^{-1}$ *versus* $[S_2O_8{}^{2-}]^{-1}$ yields a straight line with non-zero intercept conforming to a relationship (1). Since in

$$k_0 = A[S_2O_8{}^{2-}]/(1 + B[S_2O_8{}^{2-}]) \quad (1)$$

situations (*a*) and (*b*) the intercepts and slopes (Table 2) are different at different [bipy] and there is no simple relationship between the intercept and [bipy] and between the slope and [bipy], and also since the rate is inhibited by bipy, the rate equation is likely to be of the form (2). Again since at [bipy] =

$$k_0 = A[S_2O_8{}^{2-}]/(C[\text{bipy}] + D)(1 + B[S_2O_8{}^{2-}]) \quad (2)$$

4.85×10^{-3} mol dm^{-3} for the variation in $[S_2O_8{}^{2-}]$ in low and high ranges of concentrations the intercepts and slopes are not identical, the same rate equation (1) or (2) is not applicable for the two ranges, or in other words the constants *A*—*D* are not identical in the two situations.

Also since when $[S_2O_8{}^{2-}] \gg$ [bipy] the rate is almost independent of [bipy] and conforms to (1), the *D* term must be associated with $[S_2O_8{}^{2-}]$ and the general rate equation could be described by (3). The rate equation (3) predicts that the order

$$k_0 = A[S_2O_8{}^{2-}]^2/(C[\text{bipy}] + D[S_2O_8{}^{2-}])(1 + B[S_2O_8{}^{2-}]) \quad (3)$$

in $[S_2O_8{}^{2-}]$ is likely to be two in the lower range of concentration. However, the experimental results show that it is not even one. Thus the modified form (3) is not applicable in different situations, and the mechanism changes and yields a rate law showing an order in $[S_2O_8{}^{2-}]$ between one and zero.

Variation of bipy. The concentration of bipy was varied in the range 1.0×10^{-4}—4.85×10^{-3} mol dm^{-3} for different concentrations of peroxodisulphate in the range 5×10^{-5}—1×10^{-1} mol dm^{-3}. The results can be grouped in three categories: (*i*) when [bipy] $\approx [S_2O_8{}^{2-}]$, (*ii*) when $[S_2O_8{}^{2-}] \gg$ [bipy], and (*iii*) when [bipy] $\gg [S_2O_8{}^{2-}]$ (Table 1). In the first case a plot of $(k_0)^{-1}$ *vs.* [bipy] yields a straight line with non-zero intercept and the products of the intercept and $[S_2O_8{}^{2-}]$ and of the slope and $[S_2O_8{}^{2-}]$ are approximately constant. The rate equation therefore should be of the form (4). If [bipy]

$$k_0 = A[S_2O_8{}^{2-}]/(C[\text{bipy}] + D') \quad (4)$$

is varied at large $[S_2O_8{}^{2-}]$ there is almost no change in the rate

Table 2. Some constants of the reaction between $[Fe(bipy)_3]^{2+}$ and $[S_2O_8]^{2-}$ at 45 °C and pH 3.7; $[Na_2SO_4]$ = 0.05 mol dm^{-3}

10^3[bipy]/ mol dm^{-3}	$10^3[S_2O_8^{2-}]$/ mol dm^{-3}	Plot	Intercept (I)	Slope (S)	$K = I/S$	Plot of second derivative	$10^2k_1 = 1/I_2$/s^{-1}	$K = S_I/S_S$ mol^{-1} dm^3	k_2/k_3 mol dm^{-3}	10^4k_4 s^{-1}	k_5/k_6	Equation applicable
0.35	0.5—20	$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$	80	2.4	33	I *vs.* [bipy]						
0.85	2.5—100	$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$	100	3.25	31	$I_I = 68$						
1.85	2.5—100	$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$	125	4.2	30	$S_I = 3.3 \times 10^4$	1.5	30				(15)
4.85	2.5—100	$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$	175	4.8	36	S *vs.* [bipy]						
						$I_S = 2.2$						
						$S_S = 1.1 \times 10^3$						
0.02	30—100	$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$	77	2.3	33		1.3					(21)
4.85	0.04—0.08	$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$	1×10^4	4						1.0	0.082	(18)
0.35—2.35	0.25	$(k_0)^{-1}$ *vs.* [bipy]	3.2×10^3	9.0×10^6					2.8×10^3			
0.10—2.35	0.50	$(k_0)^{-1}$ *vs.* [bipy]	2.5×10^3	6.1×10^6					2.4×10^3			(15)
0.10—1.35	1.00	$(k_0)^{-1}$ *vs.* [bipy]	1.0×10^3	2.4×10^6					2.4×10^3			
0.10—1.85	2.50	$(k_0)^{-1}$ *vs.* [bipy]	0.4×10^3	0.95×10^6					2.4×10^3			
0.10—1.85	10	(k_0) *vs.* [bipy]	2.4×10^{-3}	zero		$(k_0)^{-1}$ *vs.* $[S_2O_8^{2-}]^{-1}$						
0.10—1.85	30	(k_0) *vs.* [bipy]	5.6×10^{-3}	zero		$I_I = 70$	1.4	35				(21)
0.10—1.85	100	(k_0) *vs.* [bipy]	1.1×10^{-2}	zero		$S_I = 2$						
0.85—4.85	0.05	$(k_0)^{-1}$ *vs.* [bipy]	8×10^3	1.2×10^7						1.25	0.075	(18)

Table 3. Hydrogen-ion dependence in the reaction of $[Fe(bipy)_3]^{2+}$ with $[S_2O_8]^{2-}$ at $[Fe^{II}] = 5.0 \times 10^{-5}$, $[Na_2SO_4] = 0.05$, $[bipy] = 2.5 \times 10^{-4}$, $[S_2O_8{}^{2-}] = 5.0 \times 10^{-2}$ mol dm^{-3}, and 45 °C

pH	3.2	3.9	4.3	4.5	4.7	4.8	5.2	5.5
$10^4[H^+]$/mol dm^{-3}	6.31	1.26	0.501	0.316	0.199	0.158	0.0631	0.0316
10^3k_0/s^{-1}	6.8	5.7	4.8	4.2	3.8	3.4	3.5	3.4

and hence the rate equation should not include [bipy]. However, the rate is not independent of $[S_2O_8{}^{2-}]$ even at this large concentration. The rate constants obey a relationship like (1). In the third case a plot of $(k_0)^{-1}$ *versus* [bipy] gives a straight line with non-zero intercept, but the intercept and slope do not obey a relationship like that of the first case and hence the form of the rate equation is either (1) or (5).

$$k_0 = A'[S_2O_8{}^{2-}]/(C'[bipy] + D'[S_2O_8{}^{2-}]) \quad (5)$$

Variation of hydrogen ion. The rate is independent of $[H^+]$ in its lower range of concentration, but increases with increasing $[H^+]$ beyond 2×10^{-5} mol dm^{-3}. The results are given in Table 3. Though the rate is reported[17] to attain limiting values at high $[H^+]$, we did not investigate such concentrations. The protonation constant[18] of bipyridyl is 2.16×10^4 mol^{-1} dm^3 at 25 °C and 3.09×10^4 at 20 °C and hence the $[H^+]$ dependence may be related to the protonated species.

Oxidation of Phenanthroline Complex.—The concentration of Fe^{II} was varied in the range $(2—9) \times 10^{-5}$ mol dm^{-3} at fixed $[S_2O_8{}^{2-}] = 4 \times 10^{-3}$ mol dm^{-3} and fixed $[phen] = 1 \times 10^{-3}$ mol dm^{-3} and the pseudo-first-order rate constant was found to be 2.4×10^{-4} s^{-1} at 50 °C and pH 5.9.

Effect of peroxodisulphate concentration. The concentration of $S_2O_8{}^{2-}$ was varied from 5×10^{-5} to 1.0×10^{-1} mol dm^{-3} at fixed different concentrations of phen in the range 2×10^{-5}—5×10^{-3} mol dm^{-3} as shown in Table 4. In all cases a plot of $(k_0)^{-1}$ *versus* $[S_2O_8{}^{2-}]^{-1}$ is linear with non-zero intercept. On the basis of the values of the intercepts and slopes (Table 5) the results seem to fall in two groups: (*a*) variation of $[S_2O_8{}^{2-}]$ in the high range at fixed low [phen] and (*b*) variation of $[S_2O_8{}^{2-}]$ in the low concentration range at fixed high [phen]. The results in the first category show that the rate is almost independent of [phen] and hence seem to follow the reduced form of one of the rate equations (6) and (7). Since according to

$$k_0 = P[S_2O_8{}^{2-}]/(Q[phen] + R)(1 + P[S_2O_8{}^{2-}]) \quad (6)$$

$$k_0 = P[S_2O_8{}^{2-}]/(Q[phen] + R[S_2O_8{}^{2-}])(1 + P[S_2O_8{}^{2-}]) \quad (7)$$

situation (*b*) the order in $[S_2O_8{}^{2-}]$ is not one, the rate seems to follow equation (8).

$$k_0 = P[S_2O_8{}^{2-}]/(Q[phen] + R[S_2O_8{}^{2-}]) \quad (8)$$

Variation of phenanthroline. Phenanthroline was varied from 1×10^{-5} to 1×10^{-2} mol dm^{-3} at fixed three distinct ranges of concentration of peroxodisulphate, *i.e.* when $[S_2O_8{}^{2-}]$ is large, small, and when $[S_2O_8{}^{2-}]$ and [phen] are comparable. The results are given in Table 4. For large $[S_2O_8{}^{2-}]$ the rate is almost independent of [phen] but the rate constants at different $[S_2O_8{}^{2-}]$ obey a rate equation of the type (9) since a plot of

$$k_0 = P[S_2O_8{}^{2-}]/(1 + P[S_2O_8{}^{2-}]) \quad (9)$$

$(k_0)^{-1}$ *versus* $[S_2O_8{}^{2-}]$ is linear with non-zero intercept. For all other situations a plot of $(k_0)^{-1}$ *versus* [phen] is linear with non-zero intercept and hence the rate equation (10) or (11) should hold.

$$k_0 = P'[S_2O_8{}^{2-}]/(Q[phen] + D') \quad (10)$$

$$k_0 = P'[S_2O_8{}^{2-}]/(Q'[phen] + D'[S_2O_8{}^{2-}]) \quad (11)$$

Effect of hydrogen ion. The pH was varied from 5.9 to 3.25 at fixed concentrations of the reactants. The results are given in Table 6. The rate decreases to a limiting value with increasing $[H^+]$.

Discussion

Several workers[2–4,6–8] have studied the oxidation of these complexes with peroxodisulphate, but none reported the inhibition by bipy or phen. Similarly ion pairing between $[S_2O_8]^{2-}$ and iron(II) complexes has been reported only by Raman and Brubaker[2] and suggested by Burgess and Prince[4] and by Blandamer *et al.*[8] The reason for this appears to be that the formation constant of the ion pair or complexation is not large and hence such a phenomenon would be kinetically indicated only at large $[S_2O_8]^{2-}$ which the previous workers did not employ. Secondly, since from different plots (Tables 2 and 5) the

Table 4. Pseudo-first-order rate constants in the reaction of $[Fe(phen)_3]^{2+}$ with $[S_2O_8]^{2-}$ at $[Fe^{II}] = 5.0 \times 10^{-5}$ mol dm^3, $[Na_2SO_4] = 0.1$ mol dm^{-3}, pH 5.9 and 50 °C

$10^3[S_2O_8]^{2-}$	10^3k_0/s^{-1} at 10^3[phen]/mol dm^{-3}										
mol dm^{-3}	0.02	0.05	0.075	0.85	1.35	1.85	2.35	3.35	3.85	4.85	10.0
0.05										0.0051	
0.10										0.0072	
0.20										0.009	
0.50		0.07	0.065								
2.0	0.27										
3.0			0.40	0.30	0.24	—	0.145	0.105	—	0.075	
4.0	0.48	—	0.40	—	—	—	—	—	—	—	
5.0	0.60	0.55	0.49	0.40	—	0.25	0.175	0.14	—	0.10	
8.0	—	—	—	0.67	0.48	—	0.275	0.22	—	0.16	
10.0	0.96	0.91	0.83								
20.0	1.8	1.7	1.65								
50.0	—	4.9	4.8	4.9	—	—	4.9	—	4.8	4.7	4.6
75.0	—	—	—	5.5	—	—	5.5	—	5.4	5.3	—
100.0	—	6.5	6.5	—	—	6.3	6.2	—	6.1	6.0	6.0

Table 5. Some constants of the reaction between $[Fe(phen)_3]^{2+}$ and $[S_2O_8]^{2-}$ at 50 °C and pH 5.9; $[Na_2SO_4]$ = 0.1 mol dm^{-3}

10^3[phen]/ mol dm^{-3}	$10^3[S_2O_8{}^{2-}]$/ mol dm^{-3}	Plot	Intercept (I)	Slope (S)	Plot of second derivative	$K = I/S$ mol^{-1} dm^3	$10^3k_4I/I_I$ mol^{-1} dm^3	$k_2/k_3 = S/I$ s^{-1}	$10^5k_4 = 1/I$ mol^{-1} dm^3	$10^2k_5/k_6$	Equation applicable
0.02	2.0—20	$(k_0)^{-1}$ *vs.* $[S_2O_8{}^{2-}]^{-1}$	300	6.8		44					
0.05	0.5—100	$(k_0)^{-1}$ *vs.* $[S_2O_8{}^{2-}]^{-1}$	300	6.4		47	3.3				(21)
0.075	0.5—100	$(k_0)^{-1}$ *vs.* $[S_2O_8{}^{2-}]^{-1}$	300	6.6		45					
4.85	0.05—0.2	$(k_0)^{-1}$ *vs.* $[S_2O_8{}^{2-}]^{-1}$	8×10^4	5.8					1.25	1.45	(18)
0.85—4.85	3.0	$(k_0)^{-1}$ *vs.* [phen]	1.2×10^3	2.40×10^6	I *vs.* $[S_2O_8{}^{2-}]^{-1}$			2.0×10^3			
0.35—4.85	5.0	$(k_0)^{-1}$ *vs.* [phen]	0.85×10^3	1.85×10^6	$I_I = 180$			2.1×10^3			
0.85—4.85	8.0	$(k_0)^{-1}$ *vs.* [phen]	0.60×10^3	1.15×10^6	$S_I = 3.3$	55	5.5	1.9×10^3			(15)
					S *vs.* $[S_2O_8{}^{2-}]^{-1}$						
					$I_S = 3 \times 10^5$						
					$S_S = 6.9 \times 10^3$	43					
0.85—3.5	50	(k_0) *vs.* [phen]	4.7×10^{-3}	zero	$(k_0)^{-1}$ *vs.* $[S_2O_8{}^{2-}]^{-1}$						
0.85—3.5	75	(k_0) *vs.* [phen]	5.4×10^{-3}	zero	$I_I = 130$						
1.85—10	100	(k_0) *vs.* [phen]	6.0×10^{-3}	zero	$S_I = 3.75$	35	7.7				(21)

intercepts and slopes are different in different ranges of concentrations of the ligands and peroxodisulphate, the reaction seems to occur by two mechanisms. Thirdly since the reaction is inhibited by ligand, it is certainly dissociative, but mixed with the oxidative process. Based on the above results the two mechanisms in equations (12)—(14) and (16) and (17) can be

Mechanism 1

$$[\mathrm{FeL_3}]^{2+} + [\mathrm{S_2O_8}]^{2-} \overset{K}{\rightleftharpoons} [\mathrm{FeL_3{\cdot}S_2O_8}] \qquad (12)$$

$$[\mathrm{FeL_3{\cdot}S_2O_8}] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{FeL_2{\cdot}S_2O_8}] + \mathrm{L} \qquad (13)$$

$$[\mathrm{FeL_2{\cdot}S_2O_8}] \xrightarrow{k_3} \text{products} \qquad (14)$$

suggested, ignoring the $[\mathrm{H^+}]$ dependence. The rate law for mechanism 1 is as in equation (15) with the assumption that

$$\frac{-\mathrm{d}[\mathrm{Fe^{II}}]}{\mathrm{d}t} = \frac{Kk_1k_3[\mathrm{Fe^{II}}][\mathrm{S_2O_8}^{2-}]}{(1 + K[\mathrm{S_2O_8}^{2-}])(k_2[\mathrm{L}] + k_3)} \qquad (15)$$

since k_2 is large the concentration of $[\mathrm{FeL_2{\cdot}S_2O_8}]$ would never be significant. In general mechanism 1 is predominant for large

Mechanism 2

$$[\mathrm{FeL_3}]^{2+} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} [\mathrm{FeL_2}]^{2+} + \mathrm{L} \qquad (16)$$

$$[\mathrm{FeL_2}]^{2+} + [\mathrm{S_2O_8}]^{2-} \xrightarrow{k_6} \text{products} \qquad (17)$$

$$\frac{-\mathrm{d}[\mathrm{Fe^{II}}]}{\mathrm{d}t} = \frac{k_4k_6[\mathrm{Fe^{II}}][\mathrm{S_2O_8}^{2-}]}{(k_5[\mathrm{L}] + k_6[\mathrm{S_2O_8}^{2-}])} \qquad (18)$$

$[\mathrm{S_2O_8}^{2-}]$ and mechanism 2 for lower values of $[\mathrm{S_2O_8}^{2-}]$. In addition, since the rate is almost independent of the concentration of ligand for large $[\mathrm{S_2O_8}^{2-}]$, the reaction seems to occur also by a third mechanism which is essentially mechanism 1 in which step (14) is replaced by (19), and the rate law is (20). For

$$[\mathrm{FeL_2{\cdot}S_2O_8}] + [\mathrm{S_2O_8}]^{2-} \xrightarrow{k_7} \text{products} \qquad (19)$$

large $[\mathrm{S_2O_8}^{2-}]$ equation (20) seems to reduce to (21). This is

$$\frac{-\mathrm{d}[\mathrm{Fe^{II}}]}{\mathrm{d}t} = \frac{Kk_1k_7[\mathrm{Fe^{II}}][\mathrm{S_2O_8}^{2-}]^2}{(k_2[\mathrm{L}] + k_7[\mathrm{S_2O_8}^{2-}])(1 + K[\mathrm{S_2O_8}^{2-}])} \qquad (20)$$

likely if $k_2 \approx k_7$ and K is small. The same rate law (21) can be obtained from (15) when [L] is small. Thus whether [L] is large or small, rate law (21) holds for large $[\mathrm{S_2O_8}^{2-}]$. The various rate laws under different situations were verified by making suitable plots (data in Tables 2 and 5). Thus it would appear that the mechanism is essentially dissociation of the iron(II) complex, but this is preceded by ion pair/complex formation and followed by redox reaction. It is not exclusively the one, as in the oxidation by peroxodiphosphate,[9,10] since the rate is not independent of $[\mathrm{S_2O_8}]^{2-}$ when it is independent of [L].

$$\frac{-\mathrm{d}[\mathrm{Fe^{II}}]}{\mathrm{d}t} = \frac{Kk_1[\mathrm{Fe^{II}}][\mathrm{S_2O_8}^{2-}]}{(1 + K[\mathrm{S_2O_8}^{2-}])} \qquad (21)$$

The results have been treated graphically by making two types of linear plots, $(k_0)^{-1}$ *versus* $[\mathrm{S_2O_8}^{2-}]^{-1}$ and *versus* [bipy] or [phen], yielding in almost all cases different slopes and different intercepts. Further plots were made of intercept/slope *versus* [bipy]/[phen] in the first case and *versus* $[\mathrm{S_2O_8}^{2-}]^{-1}$ in the second case. These plots too are linear with slopes and intercepts which enable us to calculate the different constants. The formation constant (K) is 33 ± 2 and 45 ± 4 $\mathrm{dm^3\ mol^{-1}}$ for bipy at 45 °C and phen at 50 °C respectively. The dissociation rate constants of $[\mathrm{FeL_3{\cdot}S_2O_8}]$ are $(1.4 \pm 0.1) \times 10^{-2}$ and $(5.5 \pm 1.5) \times 10^{-4}\ \mathrm{s^{-1}}$ for bipy at 45 °C and phen at 50 °C respectively, those for the dissociation of $[\mathrm{FeL_3}]^{2+}$ are $(1.12 \pm 0.12) \times 10^{-4}$ and 1.25×10^{-5} respectively. Step k_2 is about 2 000—3 000 times larger than k_3 in both cases. In contrast k_5 is smaller than k_6. The value of k_5 for phen is reported[19] to be $2 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and thus the value of k_6 for phen would be approximately $1.3 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and for bipy it would be $2.5 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. These are just rough guides to the values of k_6 since k_2 values at 45 and 50 °C are not known. The values for such a step in oxidations[10,16] by $[\mathrm{P_2O_8}]^{4-}$ and $[\mathrm{ClO_2}]^-$ have been estimated to be $3 \times 10^5\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. It is because of this difference in the values of k_6 that mechanism 2 is quite obvious in the cases of $[\mathrm{P_2O_8}]^{4-}$ and $[\mathrm{ClO_2}]^-$, but not so in the case of $[\mathrm{S_2O_8}]^{2-}$.

The values of k_4 should be identical with those determined for dissociation of the tris complex by Basolo *et al.*,[17] but a strict comparison cannot be made since the conditions are different. However, our value for bipy is about ten times larger than that for phen, as also found by them.[17] The value of k_1 cannot be compared with the second-order rate constant found by Burgess and Prince[4] and Irvine[3] for the oxidation with peroxodisulphate, but the values for bipy are about two to three times larger than that for phen, as is also obvious from the k_1 values in Tables 2 and 5. It is difficult to compare the results with those of Raman and Brubaker[2] since they have given a second-order rate constant ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$) for the dissociation (≈0.92 for bipy and 0.55 for phen, both at 40 °C). The values of the ion-pair formation constant reported by them[2] are about ten times larger than those found by us. One reason why comparisons cannot be made is that acid dissociation of the complexes is slowed by the presence of electrolytes.[20]

Ion pairing between $[\mathrm{S_2O_8}]^{2-}$ and $[\mathrm{FeL_3}]^{2+}$ has been suggested by some workers,[2,4,8] but the process appears to be more complicated. Since during the dissociative process a molecule of ligand is released from the complex and $[\mathrm{S_2O_8}]^{2-}$ is supposed to remain intact with the complex till it undergoes redox reaction, peroxodisulphate must be closely attached to the iron atom or in other words it penetrates the co-ordination sphere of the iron. Some change in the u.v. spectrum of the complex after mixing it with $[\mathrm{S_2O_8}]^{2-}$ also indicates the process to be a complex formation. We did not consider the association[21,22] of $[\mathrm{S_2O_8}]^{2-}$ with potassium ions since such a process seems to be unlikely in the presence of $[\mathrm{FeL_3}]^{2+}$.

Burgess and Prince[7] have rationalised the oxidations of $[\mathrm{FeL_3}]^{2+}$ and related complexes[16] in two categories. In the first there is direct oxidation to $[\mathrm{FeL_3}]^{3+}$ as in case of cobalt(III),[23] cerium(IV),[24] manganese(III),[25] *etc.* The mechanism is simply oxidative. In the other category the rate-determining dissociation of the complex $[\mathrm{FeL_3}]^{2+}$ is followed by rapid oxidation of intermediates as in reactions with peroxodiphosphate,[10] chlorite,[16] and hydrogen peroxide.[26] The mechanism is known as dissociative. However, hydrogen peroxide oxidation is peculiar. Though it occurs through a dissociative mechanism, the product $[\mathrm{FeL_3}]^{3+}$ is that corresponding to an oxidative mechanism. There is a complicated reaction[27] between $[\mathrm{FeL_3}]^{3+}$ and $\mathrm{H_2O_2}$ yielding $[\mathrm{FeL_3}]^{2+}$ and this might perhaps account for this unusual behaviour. The oxidation of phen and several substituted and related complexes[6–8] of $\mathrm{Fe^{II}}$ by $[\mathrm{S_2O_8}]^{2-}$ has been regarded as a composite one, with a rate law (22). The first term refers to dissociation of the complex and second to the direct bimolecular reaction. If we consider the two mechanisms suggested by us together, and reduce mechanism 2

Table 6. Hydrogen-ion dependence in the reaction of $[Fe(phen)_3]^{2+}$ with $[S_2O_8]^{2-}$ at $[Fe^{II}] = 5.0 \times 10^{-5}$, $[Na_2SO_4] = 0.1$, $[phen] = 2.5 \times 10^{-4}$, $[S_2O_8{}^{2-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, and 50 °C

pH	5.9	5.57	5.0	4.8	4.63	4.41	4.27	4.02	3.73	3.45	3.25
$10^4[H^+]$/ mol dm^{-3}	0.0126	0.0269	0.01	0.158	0.234	0.389	0.537	0.955	1.86	3.55	5.62
10^4k_0/s^{-1}	5.2	4.8	4.7	4.5	4.3	4.0	3.8	3.6	3.6	3.5	3.5

for large concentrations of peroxodisulphate and mechanism 1 for small concentrations of reactants (but $[S_2O_8{}^{2-}]$ is large enough for mechanism 2), we obtain rate law (22). Thus the

$$-d[Fe^{II}]/dt = (k_1 + k_2[S_2O_8{}^{2-}])[Fe^{II}] \qquad (22)$$

results of previous workers seem to be in accordance with the general mechanisms 1 and 2. We did not consider the two rate laws (15) and (18) together since it would have led to a complicated situation incapable of verification in a simple way. It is difficult to draw a line for the concentration of peroxodisulphate which is small for mechanism 1 and large for mechanism 2, and to know which of the rate laws (15) or (18) would be applicable for a particular situation, but there is no difficulty in identifying the rate law for situations when $[S_2O_8{}^{2-}]$ is large or extremely small.

Hydrogen-Ion Dependence.—We ignored the hydrogen-ion dependence while deriving the rate law for three reasons: (*i*) the effect of $[H^+]$ on the rate is not significant. A 200- to 500-fold variation in $[H^+]$ causes a 1.5- to 2-fold change in the rate; (*ii*) the rate does not change upon an about ten-fold variation in $[H^+]$; and (*iii*) a consideration of the $[H^+]$ dependence in combination with other variables would yield a complex rate law for which verification may perhaps be difficult.

In general the dissociation of $[Fe(phen)_3]^{2+}$ is reported[19,27,28] to be independent of acidity, and that of $[Fe(bipy)_3]^{2+}$ is independent at low acidity[29] but the rate increases to a limiting value[30] with increasing $[H^+]$ at high acidity. Our results are more or less similar in the case of bipy, but in the case of phen the rate decreases with increasing acidity to a limiting value. Earlier workers did not find the change with acidity, perhaps because they did not investigate the reaction at low acidity. In contrast with this, we did not make investigations at high acidity. One way to explain the hydrogen-ion dependence is that bipy/phen may be protonated and the two species may have different reactivity. The dissociation constants K_a (mol dm^{-3}) for $Hbipy^+$ and $Hphen^+$ are reported[31,32] to be 2.88×10^{-4} and 9.33×10^{-6} respectively at 25 °C. In case of phen the region of no change starts at $[H^+] \approx 1 \times 10^{-4}$ mol dm^{-3} beyond which $[H^+] \gg K_a$ and one can understand the involvement of $Hphen^+$ in the rate law. In case of bipy the region of no change ends at $[H^+] \approx 2 \times 10^{-5}$ mol dm^{-3} after which the situation $K_a \gg [H^+]$ no longer holds and one can explain the involvement of bipy species in the rate law. Another way to explain the acid dependence, at least in case of the bipy complex, is its protonation[27,30,33] as in equation (23)

$$[Fe(bipy)_3]^{2+} + H^+ \rightleftharpoons [HFe(bipy)_3]^{3+} \qquad (23)$$

and subsequent dissociation as in (24). The presence of protonated species has been disputed by several workers[18,34] and in our case it is doubtful whether they would exist in any large or even meaningful concentration, since the hydrogen-ion concentration is about 10^{-6}—10^{-4} and the protonation constant[30] is about 10^4 mol^{-1} dm^3 at 45 °C. The hydrogen-ion dependence in the case of bipy has been explained[17,35] on the basis of greater flexibility of the bipy ligand allowing one co-ordinating nitrogen to dissociate while leaving the other intact, resulting in a half-bonded structure. Considering the equation given by Basolo *et al.*,[17] from the value of $k_0 = 1.2 \times 10^{-4}$ s^{-1} at 25 °C one can calculate a value at 45 °C of 3.2×10^{-3} s^{-1} which is quite comparable to our constant value of 3.4×10^{-3} s^{-1} at low acidities.

$$[HFe(bipy)_3]^{3+} \rightleftharpoons [Fe(bipy)_2]^{2+} + Hbipy^+ \qquad (24)$$

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