

The Reduction of the Tris-(2,2'-bipyridyl) and the Tris-(1,10-phenanthroline) Complexes of Iron(III) by Hydroxide Ion

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interest that the subsequent uptake of O_2 by the Fe^{II} products⁶ was clearly recorded by the electrode.

Kinetic Data.—The reaction with an excess of base was first order in complex throughout (Figure 1) and for a

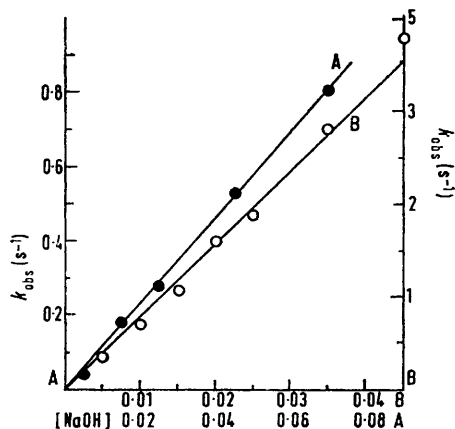


FIGURE 2 Variation of pseudo-first-order rate constants (k_{obs}) with NaOH molarity. A = $Fe(bipy)_3^{3+}$; 23.50 °C; B = $Fe(phen)_3^{3+}$; 5.5 °C

series of NaOH concentrations (see Figure 2) the rate law is, $-d[Fe(biL)_3^{3+}]/dt = k[Fe(biL)_3^{3+}][OH^-]$. There is, within the experimental error, no evidence for an $[OH^-]$ -independent term. Addition of free ligand did not affect the rates. The results of preliminary measurements without accurate temperature control (recorded as 21.7 °C) together with those for a series of more accurately controlled temperatures are given in the Table. The experimental

TABLE

	Temp. (°C)	k (dm ³ mol ⁻¹ s ⁻¹)	Number of runs
a	5.5 ± 0.1	2.07 ± 0.10	6
	15.3 ± 0.1	5.9 ± 0.4	5
	23.5 ± 0.03	11.60 ± 0.1	5
	24.88 ± 0.03	13.60 ± 0.1	3
	34.7 ± 0.2	31.5 ± 2.0	5
	(21.7)	9.75 ± 0.01	22
b	5.5 ± 0.1	78 ± 5	7
	10.3 ± 0.05	120 ± 20	4
	14.9 ± 0.1	193 ± 15	5
	(21.7)	285 ± 20	14

^a $[Fe(bipy)_3^{3+}]$ (0.19–1.07) × 10⁻⁴M; $[NaOH]$ 0.0025–0.50M; $[NaCl]$ (1 – $[NaOH]$)M. ^b $[Fe(phen)_3^{3+}]$ (0.90–1.84) × 10⁻⁴M; $[NaOH]$ 0.0025–0.125M; $[NaCl]$ (1 – $[NaOH]$)M.

accuracy is much better for the bipy system than for the faster reacting phen complex. For the bipy system Figure 3 gives $k = 10^{12.54} e^{-(65.1 \pm 0.8)kJ/RT}$, while for the phen system the data conform to $k = 10^{14.4} e^{-(65 \pm 2)kJ/RT}$.

Figure 4 illustrates that the salt effect is that expected for a reaction between two ions of charge +3 and –1 (the line drawn has a slope of –3.00). We have used the Davies⁷ expression $f(I) = [I^{1/2}/(1 + I^{1/2})] - 0.2I$ which for 3:1 salts of large cations usually holds up to an ionic

strength (I) of ca. 0.10 and in accordance with this we find that below $I = 0.20$, $\log_{10} k = \text{constant} - 3.0f(I)$ (the constant here has the value 1.95).

DISCUSSION

Equation (1) adequately describes the rate-determining step for both complexes. For the bipy system

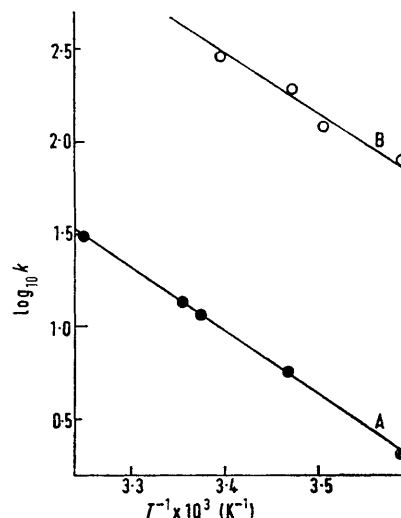


FIGURE 3 Arrhenius plot for $Fe(bipy)_3^{3+} = A$ and for $Fe(phen)_3^{3+} = B$

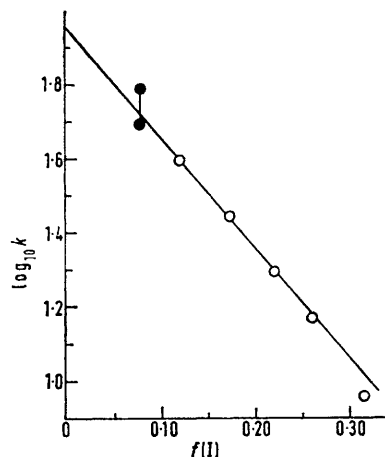


FIGURE 4 $Fe(bipy)_3^{3+}$, Davies plot, see text. ○ NaOH = 0.0095M; I with NaCl; 15.35 °C, ● NaOH = 0.0075M, no NaCl, measured at 25 °C, extrapolated to 15.35 °C

equation (2) gives the stoichiometry and since H_2O_2 has been detected in concentrated solutions of the reactants² we consider the reaction scheme given below to be reasonable. Steps (b) and (d) are speculative but receive some support from the analysis of analogous reactions by Taube⁸ and Uri,⁹ while reaction (c) has

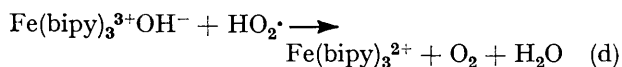
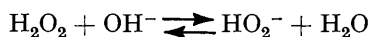
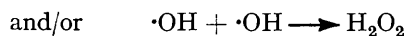
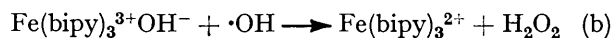
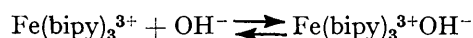
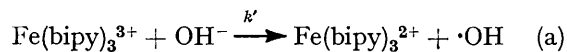
⁶ G. Nord and T. Pizzino, *Chem. Comm.*, 1970, 1633.

⁷ C. W. Davies, *J. Chem. Soc.*, 1938, 276.

⁸ H. Taube, *Chem. Rev.*, 1963, **63**, 269.

⁹ N. Uri, *Chem. Rev.*, 1952, **50**, 375.

been measured and is known to be fast.¹⁰ The k values in the Table and Figures are for the overall reaction and are therefore equal to $2k'$ where k' is the rate constant for reaction (a).



From transition-state theory,¹¹ ΔS^\ddagger for reaction of $\text{Fe}(\text{bipy})_3^{3+}$ is $-17 \text{ JK}^{-1} \text{ mol}^{-1}$ and for $\text{Fe}(\text{phen})_3^{3+}$ is *ca.* $+21 \text{ JK}^{-1} \text{ mol}^{-1}$. Although the absolute values have of course no significance, it may be meaningful that this is also of the order found for the partial molar entropy *difference* of the two couples.¹² The activation parameters for reactions (a) and (c) are similar in that ΔS^\ddagger is small and negative in both cases, $\Delta S^\ddagger = -21 \text{ JK}^{-1} \text{ mol}^{-1}$ for (c) while ΔH^\ddagger is only about one half of that calculated for ΔH° from the thermodynamic data given in references 9 and 12, $\Delta H^\ddagger = 63 \text{ kJ mol}^{-1}$, $\Delta H^\circ = 113 \text{ kJ mol}^{-1}$ for (a): $\Delta H^\ddagger = 27 \text{ kJ mol}^{-1}$, $\Delta H^\circ =$

59 kJ mol^{-1} for (c). We are tempted to speculate that the transfer of an electron to a ligand of the complex may occur in the rate-determining step. Certainly, the work described here provides another illustration of the fact that bipyridyl-type ligands are generally found to cause rapid electron transfer.¹³

Although we are unable to find other examples of reactions in which the products are highly reactive and which are directly comparable with (a) and (c), we note that Brubaker *et al.*¹⁴ have studied the *reduction* of the peroxydisulphate ion by substituted bipy and phen complexes of iron(II). Here, not only are the activation energies much less than that required for symmetrical breaking of the peroxide bond, but also there is a linear correlation between the free energies of activation and the standard free energies of the redox steps which are attributed to reaction of the $[\text{Fe}(\text{biL})_3^{2+}\text{S}_2\text{O}_8^{2-}]$ complex. We have no experimental evidence for the ion-pair $\text{Fe}(\text{biL})_3^{3+}\text{OH}^-$ for which the formation constant would be expected to be only about unity in our medium and which we have included in our reaction scheme. We have found, however, that the rate of reduction of $\text{Os}(\text{bipy})_3^{3+}$ by OH^- is considerably slower than that of the Fe^{III} complex, as would be expected if the order of reactivity is controlled by the standard free-energy changes (*cf.* 5·13); we are investigating this further.

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¹⁰ J. H. Baxendale, 'Kinetics and Mechanism of Inorganic Reactions in Solution,' *Chem. Soc. Special Publ.* No. 1, 1954, p. 43.

¹¹ K. J. Laidler, S. Glasstone, and H. Eyring, 'The Theory of Rate Processes,' McGraw-Hill, New York, 1941.

¹² D. A. Buckingham and A. M. Sargeson in 'Chelating Agents and Metal Chelates,' eds. Dwyer and Mellor, Academic Press, New York, 1964, p. 253.

¹³ F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' J. Wiley, New York, 1967, ch. 6 and references therein.

¹⁴ S. Raman and C. H. Brubaker, jun., *J. Inorg. Nuclear Chem.*, 1969, **31**, 1091.