595. *The Kinetics of the Oxidation of Some Bipyridyl and Phenanthroline Complex Ions by the Peroxydisulphate Ion in Aqueous Solution.*

By D. H. IRVINE.

The kinetics of the oxidation of the tris-2,2′- and tris-4,4′-dimethylbipyridylium(II), tris-αα′-bipyridylruthenium(II), tris-*o*-phenanthroline-iron(II), and tris-5-methylphenanthrolineiron(II) ions by the peroxydisulphate ion in aqueous solution have been studied at different temperatures under varying conditions of ionic strength. The rates of the reactions increase as the standard redox potential difference between the peroxydisulphate and complex ion couples increases, the velocity constants being well represented by the equation, $\log_{10} k_0 = \text{Constant} + x\,\Delta E^0$, x being $\sim 7{\cdot}0$. Similar equations are applicable to other redox systems.

MARCUS [1] concluded that the factors which are important in determining the speed of electron-transfer reactions are (1) the standard free-energy change of the redox step, (2) the Coulombic interaction of the ionic charges of the reactants, and (3) the solvation of the charged reactants. Solvation effects will account to some extent for the difference in rates between electron-transfer reactions involving simple aquated ions on the one hand and complex ions on the other, and in some cases must be the predominant factor, *e.g.*, in the fast exchange between $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ compared with that between Fe^{2+} and Fe^{3+}. Coulombic interaction is known to affect markedly the rate of an ionic reaction, and in some cases a simple relation exists between the product of the charges of the reactants and the A factor in the Arrhenius equation.[2] However, its relative importance in redox reactions is uncertain. A number of electron-transfer reactions have been shown to be fast despite the adverse nature of Coulombic interaction.

For (1), there are some isolated examples which suggest that this factor, or the overall free-energy change, is of some importance in determining the rate of a redox reaction. George and Irvine [3] suggest that it is the overall free-energy change which probably accounts for the difference between the rate of oxidation of the trisbipyridylruthenium(II) ion by ceric ion in aqueous perchloric acid on the one hand and that in aqueous sulphuric acid on the other. A similar suggestion has been made concerning the rates of oxidation of the trisbipyridylosmium(II) and tris-*o*-phenanthrolineiron(II) ions by thallic ion in aqueous perchloric acid.[4] Marcus [1] attributes the different rates of oxidation of some substituted quinols by ferric ion to the different free energies of the rate-determining step. Here, however, the assumption has to be made that the rate-determining step in all these reactions is the same, *viz.*, $Fe^{3+} + HQ^- \rightleftharpoons Fe^{2+} + HQ$, where HQ^- is the anion of the quinol. This may or may not be so, since the data are equally consistent with hydrogen-atom transfer and there is no way of deciding which mechanism operates in any given reaction.

In an attempt to establish unequivocally the importance of the standard free-energy change as a factor in determining the rate of a redox reaction, the kinetics of the oxidation of the complex ions, *viz.*, tris-4,4′-dimethylbipyridyliron(II), tris-αα′-bipyridyliron(II), tris-*o*-phenanthrolineiron(II), tris-5-methylphenanthrolineiron(II), and tris-αα′-bipyridylruthenium(II) by the peroxydisulphate ion were investigated. These ions each have roughly the same partial molal entropies in their reduced and oxidized forms,[5] so that solvation effects will affect their rates of oxidation to approximately the same extent. Further, being all bivalent ions, as is known from the effect of ionic strength on the redox potential of the M^{II}—M^{III} couples and confirmed in these experiments by the effect of

---

[1] Marcus, *J. Chem. Phys.*, 1957, **26**, 867.

[2] Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1941.

[3] George and Irvine, *J.*, 1954, 857.

[4] Irvine, *J.*, 1957, 1841.

[5] George, Hanania, and Irvine, unpublished work.

ionic strength on their rates of oxidation, coulombic interaction affects each system in the same way. Any difference, therefore, in the rates of oxidation of these ions by $S_2O_8^{2-}$ can probably be attributed to the different free-energy changes of the reactions. The latter are directly related to the standard redox potentials of the M^{2+}—M^{3+} couples, which vary from 0·941 v for the tris-4,4'-dimethylbipyridyliron$^{2+/3+}$ couple to 1·374 v for the tris-αα'-rutheniumbipyridyl$^{2+/3+}$ couple.

The results recorded in this paper show that there is a direct relation between the rate and the standard free energy of a redox reaction.

Kinetics.—As in the oxidation of the trisdipyridylosmium(II) ion,[6] the oxidation of the tris-4,4'-dimethylbipyridyliron(II) ion by $S_2O_8^{2-}$ initially followed second-order kinetics, consistent with the equation

$$k = \frac{2{\cdot}303}{t(b - 2a)} \log_{10} \frac{a(b - 2x)}{b(a - x)}$$

where a is the initial concentration of $S_2O_8^{2-}$, b the initial concentration of the complex ion, and x the amount of $S_2O_8^{2-}$ used up in time t. Departure from second-order kinetics occurred after about 30—40% reaction, no doubt mainly for the same reason as that proposed for the trisdipyridylosmium(II) system. However, there is the further factor in this case that the oxidised form of the complex ion, as with other bipyridyl and phenanthroline complexes of iron, is not stable under the conditions of the experiment.

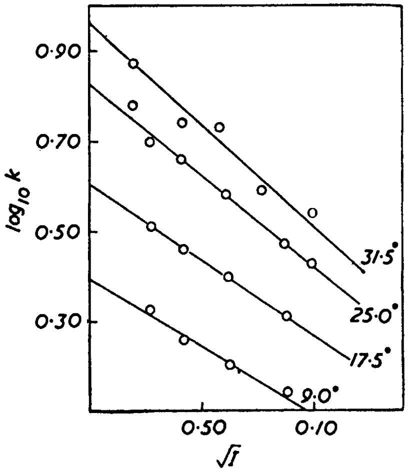


FIG. 1. $\log_{10} k$ *versus* $\sqrt{I}$ *plots for the reaction between tris-4,4'-dimethylbipyridyliron*(II) *ion and* $S_2O_8^{2-}$.

The rate of the reaction was measured at 9·0°, 17·5°, 25·0°, and 31·5° under varying conditions of ionic strength. The results are illustrated in Fig. 1 where $\log_{10} k$ is plotted against $\sqrt{I}$. The slopes of the lines are 3·30, 3·40, 3·75, and 4·20 at 9·0°, 17·5°, 25·0°, and 31·5° respectively. These are in fair agreement with the theoretical slope of 4·0 expected for a reaction between oppositely charged bivalent ions. Extrapolation of the $\sqrt{I}$ plot to zero ionic strength gives values of k_0, the true velocity constant, of 2·50, 4·00, 6·68, and 9·34 l. mole^{-1} sec.$^{-1}$ at 9·0°, 17·5°, 25·0°, and 31·5°, respectively. A plot of $\log_{10} k_0$ against $1/T$ yields:

$$k_0 = 3{\cdot}2 \times 10^8 \exp\,(-\,10{,}600/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Similar kinetic behaviour was observed in the oxidation of the tris-αα'-bipyridyliron(II), tris-*o*-phenanthrolineiron(II) and tris-5-methylphenanthrolineiron(II) ions. These reactions were followed under conditions where pseudo-first-order kinetics applied and departure from such kinetics was observed between 20 and 30% reaction. The oxidation of tris-αα'-bipyridylruthenium(II) ion was found, somewhat unexpectedly, to be catalysed by sunlight. However, in the absence of sunlight reproducible kinetics were obtained.

---

[6] Irvine, *J.*, 1958, 2166.

As in the case of the tris-4,4′-dimethylbipyridyliron(II) ion all the reactions were studied under varying conditions of ionic strength and at different temperatures. In all cases, except that of the tris-5-methylphenanthrolineiron(II) ion, the perchlorates of the complex ions were used. The perchlorate of tris-5-methylphenanthrolineiron(II) was, however, too insoluble, and a solution of the sulphate was used. Since the concentration of complex ion was of the order of 5×10^{-5}M no appreciable catalysis of the rate by sulphate ion [6] was expected.

The results are summarised in Table 1. In each case the A factor is low for a reaction between oppositely charged ions but is nevertheless much the same as that for the similar reaction between $Os(dipy)_3^{2+}$ and $S_2O_8^{2-}$. The slopes of $\sqrt{I}$ plots in the tris-αα′-bipyridylruthenium(II) system are much less than expected but there is no real reason to believe that the mechanism of the reaction differs from that for the others.

TABLE 1.

Complex ion	Temp.	Slope ($\sqrt{I}$ plot)	$10k_0$ (l. mole^{-1} sec.$^{-1}$)	10^8A	E (kcal. mole^{-1})
Tris-αα′-dipyridyliron(II) ...	11·5°	3·80	2·29		
	19·6	3·70	3·72	5·7	12,400
	25·5	4·05	5·70		
	32·2	4·10	9·12		
Tris-*o*-phenanthrolineiron(II)	19·5	3·70	1·95		
	26·5	3·05	3·05	15·0	13,300
	33·0	3·50	5·25		
Tris-5-methylphenanthroline-iron(II)	17·0	3·6	1·12		
	33·0	3·0	1·30	1·6	12,600
Tris-αα′-bipyridylruthenium(II)	26·5	2·5 *	0·105		
	32·0	2·6 *	0·155	5·0	14,600
	40·0	2·5 *	0·282		

* $\log_{10} k$ plotted against $[\sqrt{I}/(1 + \sqrt{I})]$

Relation between the Rates and Standard Free-energy Changes.—The rates of oxidation of the trisbipyridylosmium(II) ion as well as of the tris-4,4′-dimethylbipyridyliron(II) ion, which are consistent with the oxidation of 2 mols. of the bivalent complex ion by 1 mole of $S_2O_8^{2-}$, suggest that the overall oxidation can be represented:

$$2M^{2+} + S_2O_8^{2-} \rightleftharpoons 2M^{3+} + 2SO_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where M^{2+} and M^{3+} represent respectively the bivalent complex ion and its oxidation product. The standard free-energy change corresponding to equation (2) is given by

$$\begin{aligned} \Delta G^0 &= -2F[E^0(S_2O_8^{2-}) - E^0(\text{complex})] \\ &= -2F\Delta E^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

where $E^0(S_2O_8)$ is the standard redox potential of the SO_4^{2-}–$S_2O_8^{2-}$ couple and is 2·01 v (see ref. 13) and E^0 (complex) that of the M^{2+}–M^{3+} couple. If the rates and standard free-energy changes of the above reactions are related, it follows from equation (3) that a similar relation exists between the rates and ΔE^0 values for these reactions. Table 2 shows the results for reactions at 25°, with those for trisbipyridylosmium(II) for comparison. E^0 values for the trisbipyridylosmium$^{2+/3+}$, tris-αα′-bipyridyliron$^{2+/3+}$, tris-*o*-phenanthroline-iron$^{2+/3+}$, and tris-αα′-bipyridylruthenium$^{2+/3+}$ couples are those from the work of Barnes, Dwyer, and Gyarfas,[7] and of George, Hanania, and Irvine.[5] The value for the tris-5-methylphenanthrolineiron$^{2+/3+}$ couple is estimated from the value of 1·06 v in 0·1M-sulphuric acid.[8] That for the tris-4,4′-dimethylbipyridyliron$^{2+/3+}$ couple was determined in this investigation. The results of the experiments are recorded below.

A plot of $\log_{10} k_0$ against ΔE^0 is shown in Fig. 2. Its linearity indicates a direct relation between the rates of these reactions and their standard free-energy changes. The evidence, however, does not distinguish whether it is the overall free-energy change or that of the rate-determining step which is significant, for in these systems where there is a common

[7] Barnes, Dwyer, and Gyarfas, *Trans. Faraday Soc.*, 1952, **48**, 269.

[8] Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313.

TABLE 2. *Effect of* ΔE^0 *on the rate of oxidation of some bipyridyl and phenanthroline complex ions by* $S_2O_8^{2-}$.

Complexion	ΔE^0	k_0 (l. mole^{-1} sec.$^{-1}$) (25°)	Complexion	ΔE^0	k_0 (l. mole^{-1} sec.$^{-1}$) (25°)
$Os(bipy)_3^{2+}$	1·13	49·0	$Fe(o\text{-}phen)_3^{2+}$	0·87	0·30
$Fe(4,4\text{-}Me_2\text{-}bipy)_3^{2+}$	1·07	6·68	$Fe(5\text{-}Me\text{-}phen)_3^{2+}$	~0·86	0·11
$Fe(bipy)_3^{2+}$	0·89	0·55	$Ru(bipy)_3^{2+}$	0·64	0·009

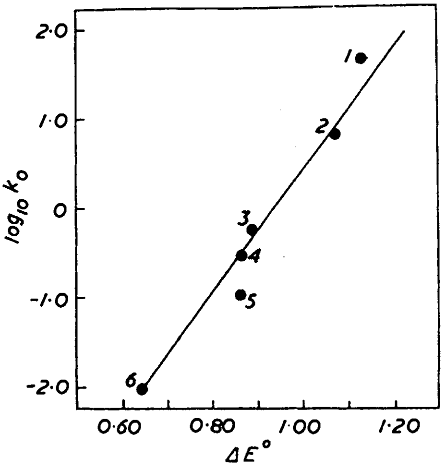
mechanism the two are directly related. The straight line in Fig. 2 can be represented by the equation,

$$\log_{10} k_0 = -6{\cdot}4 + x\Delta E^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $x \approx 7{\cdot}0$.

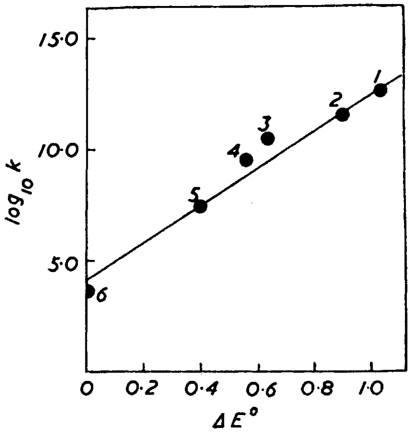
Consideration of other redox systems in the literature, where the reaction mechanisms are similar and both solvation and charge effects are comparable, shows that an equation similar to (4) also fits the data for these systems. Thus in Fig. 3 the values of $\log_{10} k$ for the reactions between Fe^{3+} and HQ^-,[9] Fe^{3+} and substituted HQ^-,[10] Fe^{3+} and HO_2^-,[11] and Co^{3+} and HO_2^- [12] are plotted against ΔE^0. ΔE^0 for the last two reactions are estimated from Latimer's values [13] to be approximately zero and 1·05 v respectively. ΔE^0 for the Fe^{3+}–HQ^- reactions are calculated from the values of ΔG^0 quoted by Marcus.[1] The straight-line plot in this equation is approximately represented by the equation

FIG. 2. *Relation between the rates of oxidation of some bipyridyl and phenanthroline complex ions by* $S_2O_8^{2-}$ *and* $\Delta E°$.



1, $Os(bipy)_3^{2+}$.
2, $Fe(4,4'\text{-}Me_2\text{-}bipy)_3^{2+}$.
3, $Fe(bipy)_3^{2+}$.
4, $Fe(o\text{-}phen)_3^{2+}$.
5, $Fe(5\text{-}Me\text{-}phen)_3^{2+}$.
6, $Ru(bipy)_3^{2+}$.

FIG. 3. *Relation between the rates of oxidation of some* HX^- *ions by* Fe^{3+}, Co^{3+}, *and* $\Delta E°$.



1, $Co^{3+} + HO_2^-$. 2—6, Fe^{3+} with ions from (2) duroquinol, (3) toluquinol, (4) quinol, and (5) 2,6-dichloroquinol, and with (6) HO_2^-.

$$\log_{10} k = 4{\cdot}0 + 9{\cdot}0\Delta E^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The idea that a relation exists between the rate of a redox reaction and its standard free-energy change is not new. Barron [14] showed that a plot of the logarithm of the time

---

[9] Baxendale, Hardy, and Sutcliffe, *Trans. Faraday Soc.*, 1957, **47**, 963.

[10] Baxendale and Hardy, *ibid.*, 1954, **50**, 808.

[11] Barb, Baxendale, George, and Hargrave, *ibid.*, 1951, **47**, 491.

[12] Baxendale, " Kinetics and Mechanism of Inorganic Reactions in Solutions," *Chem. Soc. Special Publ.* No. 1, London, 1954, p. 43.

[13] Latimer, " Oxidation Potentials," 2nd edn., Prentice-Hall, New York, 1952.

[14] Barron, *J. Biol. Chem.*, 1932, **97**, 287.

required to attain 50% autoxidation of a number of similar leuco-dyes against E^0 for the dye couple is linear. Bolland and Ten Have,[15] in studying the inhibitory effects of phenolic compounds on the thermal oxidation of ethyl linoleate, found similarly that the logarithm of the relative efficiency of inhibition, which is directly related to the chain-termination between RO_2 and the phenol, varies directly with E^0 for the phenol couple. These and the above examples seem to indicate that the relation is general for redox reactions. The relation is particularly useful since it enables one to predict the rate of a given redox reaction once the rates of similar reactions are known. On the other hand, it may be used to confirm the mechanism of a given reaction once the rate of the reaction has been established.

Measurement of E^0 *for the Tris-*4,4′*-dimethylbipyridyliron*(II)*-tris-*4,4′*-dimethylbipyridyliron*(III) *Couple.*—The redox potential of this couple was measured at different ionic strengths and temperatures. At 25° E varied with ionic strength according to the equation, $E = 0{\cdot}941 - 0{\cdot}20\ [\sqrt{I}/(1 + \sqrt{I})]$. The slope of this line is in fair agreement with the theoretical slope of $-0{\cdot}15$ for a couple in which there is a charge of $+2$ on the reduced and $+3$ on the oxidized form. At constant I (0·105) the values of E at 15·0°, 25·0°, and 33·5° were 0·927, 0·920, and 0·913 v respectively. $\mathrm{d}E/\mathrm{d}T$ is thus $-0{\cdot}00075$ v per degree. For the reaction

$$\mathrm{Fe(4,4'\text{-}Me\text{-}bipy)_3}^{3+} + \tfrac{1}{2}\mathrm{H_2} \rightleftharpoons \mathrm{Fe(4,4'\text{-}Me\text{-}bipy)_3}^{2+} + \mathrm{H^+}$$

$\Delta G^0 = -21{\cdot}6$ kcal./mole, $\Delta H = -26{\cdot}8$ kcal./mole, and $\Delta S^0 = -17{\cdot}5$ e.u.; $\bar{S}^0_{\text{red.}} - \bar{S}^0_{\text{ox.}}$ is therefore $-1{\cdot}9$ e.u. ($\bar{S}^0$ for H^+ being assumed to be zero), which is of the same order of magnitude as $\bar{S}^0_{\text{red.}} - \bar{S}^0_{\text{ox.}}$ for other bipyridyl and phenanthroline complexes.[5]

EXPERIMENTAL

Materials.—Solutions of tris-4,4′-dimethylbipyridyliron(II), tris-αα′-bipyridyliron(II), and tris-*o*-phenanthrolineiron(II) were prepared from weighed amounts of the perchlorate salts. The latter were obtained by addition of a solution of sodium perchlorate to the sulphate solutions. Tris-αα′-bipyridylruthenium(II) perchlorate was precipitated from a solution of tris-αα′-bipyridylruthenium(II) chloride hexahydrate. The chloride was obtained from the G. Fredrick Smith Chemical Company. The perchlorate of tris-5-methylphenanthroline-iron(II) was too insoluble for use and a solution of the sulphate was used instead. This was prepared by adding exactly three equivalents of 5-methylphenanthroline to one of " AnalaR " ferrous ammonium sulphate and making up to the appropriate volume.

The preparation of sodium perchlorate solution has already been described, as well as the conductivity water used in these experiments.[4,6] " AnalaR " potassium peroxydisulphate was used without purification.

Rate Measurements.—The reactions were followed spectrophotometrically at the wavelength maxima of the complex ions. In all cases the oxidized forms had negligible absorption. Duplicate runs agreed to within 5%.

E.M.F. Measurements.—The apparatus used has already been described.[16] The method was that of adding the appropriate amount of standard ceric sulphate solution to the complex ion to give an approximately equimolar mixture of the reduced and the oxidized form, and then determining simultaneously the E.M.F. potentiometrically and the concentrations of reduced and oxidized forms spectrophotometrically. The concentration of complex ion was $\sim 10^{-3}$M for E.M.F. and 10^{-4}M for spectrophotometric measurements. A Unicam Quartz spectrophotometer was used. Ionic strength was varied by the addition of " AnalaR " sodium nitrate.

I thank Mr. S. A. Olaitan for his help with the E.M.F. measurements.

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE,
IBADAN, NIGERIA.

[*Received, March* 9*th*, 1959.]

---

[15] Bolland and Ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 252.

[16] George, Hanania, and Irvine, *J.*, 1957, **3048**.