508. *Potentiometric Studies of Some Dipyridyl Complexes.*

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The redox potentials of the tetracyanodipyridyl, tris-2 : 2′-dipyridyl, and tris-1 : 10-phenanthroline Fe(II)–Fe(III) octahedral complexes, as well as of the tris-2 : 2′-dipyridyl Ru(II)–Ru(III) complex, have been measured at different ionic strengths and temperatures. $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the cell reaction $ML_n^{m+1} + \frac{1}{2}H_2 = ML_n^m + H^+$ have been calculated, and the difference between the partial molal entropies of the reduced and the oxidized forms of the complex ions has been discussed.

We have shown elsewhere [1] that the partial molal entropy ($\bar{S}°_c$) of a complex ion in aqueous solution can be adequately represented by the empirical equation

$$\bar{S}°_c = A - BZ + Cn \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Z is the numerical value of the charge on the ion, n the number of ligand molecules bonded to the central atom, and A, B, and C are structural parameters. The parameter B denotes the change in $\bar{S}°_c$ per unit change in charge on the ion, and is most conveniently obtained from the temperature coefficient of the cell reaction:

$$ML_n^{m+1} + \tfrac{1}{2}H_2 = ML_n^m + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ML_n^{m+1} and ML_n^m denote two successive oxidation states of the complex ion. $\Delta S°$ for reaction (2) is given by:

$$\Delta S° = (\bar{S}°_m - \bar{S}°_{m+1}) + \bar{S}°_{H^+} - \tfrac{1}{2}S°_{H_2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the terms $\bar{S}°_m$ and $\bar{S}°_{m+1}$ are the partial molal entropies of the complex ion in its reduced and its oxidized state respectively. The difference between these values, which is numerically equal to B, can thus be obtained directly from the experimental value of $\Delta S°$.

Few complex-ion systems have been investigated over a range of temperature and ionic strength that enables a calculation of B to be made. In this paper we record results obtained for the tetracyanodipyridyl [$(CN)_4$ dipy], tris-2 : 2′-dipyridyl (dipy), and tris-1 : 10-phenanthroline (phen) iron(II)–iron(III) octahedral complexes, as well as for the tris-2 : 2′-dipyridyl ruthenium(II)–ruthenium(III) complex.

Since these systems entail determinations of oxidation–reduction potentials (E) at hydrogen-ion concentrations other than unity and at various ionic strengths, the following symbols will be used in this paper: E for the e.m.f. when oxidant and reductant are present in equimolal concentrations (redox potential) at $[H^+] = 1$ and $I \neq 0$; E' for the redox potential at $[H^+] \neq 1$; extrapolated values at zero ionic strength will be denoted by a superscript, *viz.*, $E°$ and $E°'$ respectively.

The Tetracyanodipyridyliron(II)–*Tetracyanodipyridyliron*(III) *System.*—Preliminary experiments had shown that the potassium salt of tetracyanodipyridyliron(II) exhibited a reversible colour change from straw-yellow in strongly acidic to orange-red in alkaline solution. A spectrophotometric investigation of this phenomenon was therefore undertaken before potentiometric measurements were made.

Fig. 1 (curves 1, 2, 4, and 5) shows absorption spectra for this compound in water and in 0·010, 0·89, and 3·10M-HCl respectively. Since the curves for the intermediate concentrations (2 and 4) are not isosbestic with respect to curve 1, for water, and curve 5, for the highest acid concentration, it follows that more than two species are present, and hence more than one ionization is involved. On the assumption that there are two ionizations:

$$[H_2Fe(CN)_4dipy]^0 = [HFe(CN)_4dipy]^{1-} + H^+ \quad (K_1) \quad . \quad . \quad . \quad (4)$$

$$[HFe(CN)_4dipy]^{1-} = [Fe(CN)_4dipy]^{2-} + H^+ \quad (K_2) \quad . \quad . \quad . \quad (5)$$

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[1] George, Hanania, and Irvine, *J. Chem. Phys.*, 1954, **22**, 1616.

analysis of the spectrophotometric data by a method of successive approximations was found to give self-consistent results with $K_1 \approx 0·5$, $K_2 \approx 0·02$, and with curve 3 in Fig. 1 representing the spectrum of the intermediate species $[HFe(CN)_4dipy]^{1-}$.

The first ionization occurs in such strongly acidic solution that no further study of it was made. However, the values for the second ionization constant, K_2, obtained directly from the detailed spectrophotometric measurements described in the next section, show satisfactory agreement with values obtained indirectly from the variation of redox potentials with pH, as described below. This further supports the assumption that only the two ionizations, represented by equations 4 and 5, are involved in the pH range which is covered in the present experiments.

(a) *Spectrophotometric determination of* pK_2. pK_2 was evaluated in terms of the concentrations of the two complex ions in equation (5), $[HFe(CN)_4dipy]^{1-}$ and $[Fe(CN)_4dipy]^{2-}$, the ratio of the concentrations being obtained from optical-density measurements. To avoid the complexities that would otherwise arise from the overlapping of the two ionizations, these measurements were made at 355 mμ where, as can be seen from Fig. 1, the species in the first ionization, equation (4), have equal absorption. With this condition holding, a change in optical density brought about by a change in H^+ concentration can be attributed wholly to a change in the relative concentrations of the two complex ions in equation (5).

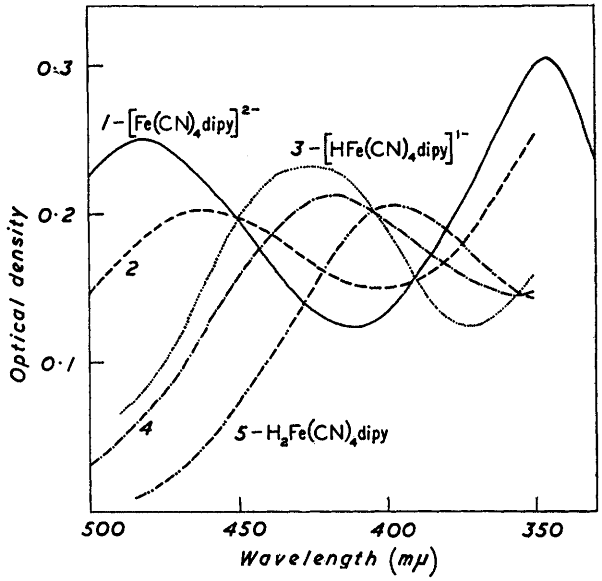


FIG. 1. *Absorption spectra for potassium-tetracyanodipyridyliron*(II). (1) *In water*; (2) *in* 0·010M-HCl; (3) *obtained by extrapolation*; (4) *in* 0·89M-HCl; (5) *in* 3·10M-HCl. *Solutions are* 10^{-4}M. *All the curves are interconvertible. Isobestic points occur at* 450 *and* 390 mμ *for the system* $[Fe(CN)_4(dipy)]^{2-}/[HFe(CN)_4dipy]^{1-}$ *and at* 405 *and* 355 mμ *for* $[HFe(CN)_4dipy]^{1-}/[H_2Fe(CN)_4dipy]^0$.

A series of solutions of the tetracyano-compound containing various concentrations of hydrogen chloride were made up, and the ionic strength was adjusted to a constant value by addition of " AnalaR " sodium chloride. The optical-density measurements at 355 mμ were made at constant temperature. The results of a typical experiment are recorded in Table 1.

TABLE 1. *Determination of* pK_2 *at* 20·0° *and* $I = 0·089$.

$[H^+]$ (10^{-2}M)	8·87	5·92	2·96	0·986	0·493
Optical density (*d*) at 355 mμ	0·175	0·188	0·204	0·243	0·263
pK_2	1·67	1·63	1·71	1·69	1·69

d_{355} for the pure acid and base species are 0·147 and 0·291 respectively.
Ionic strength was adjusted by " AnalaR " sodium chloride.

At $I = 0·089$, measurements of pK_2 at 15·5°, 20·0°, and 27·2° yielded the values

1·65 ± 0·02, 1·68 ± 0·02, and 1·69 ± 0·02 respectively. Provided that ΔH is independent of ionic strength, as is generally assumed at low I, $\Delta H^\circ = -1{\cdot}3 \pm 1{\cdot}3$ kcal./mole.

The effect of ionic strength on $\mathrm{p}K_2$ is shown in Fig. 2 where $\mathrm{p}K_2$ is plotted against $\sqrt{I}/(1 + \sqrt{I})$ at 25°. The lowest value of I at which values could be obtained with any accuracy was 0·01. Below this, the acid concentration was too small to give a sufficiently large change in optical density, and as a consequence the errors in the calculation of $\mathrm{p}K_2$ were large. The plot of $\mathrm{p}K_2$ against $\sqrt{I}/(1 + \sqrt{I})$ is linear with a slope of −2·1. This value is in close agreement with the theoretical slope of −2·0 expected for a change in charge according to equation (5). Extrapolation to zero ionic strength gives $\mathrm{p}K^\circ_2 = 2{\cdot}17 \pm 0{\cdot}02$. ΔG° for the ionization is thus 2·97 ± 0·03 kcal./mole, and hence $\Delta S^\circ = -14{\cdot}3 \pm 5{\cdot}0$ e. u. On the basis that $\bar{S}^\circ_{\mathrm{H}^+} = 0$ (ref. 2), ΔS° is equivalent to the difference between the partial molal entropies of the tetracyanodipyridyliron(II) complex ion and its conjugate acid.

FIG. 2. *Effect of ionic strength on the ionization of* $[\mathrm{HFe(CN)_4dipy}]^{1-}$ *at* 25°. *Slope* = −2·1 (*theoretical value* −2·0). *Extrapolation gives* $\mathrm{p}K_2{}^\circ = 2{\cdot}17 \pm 0{\cdot}02$.

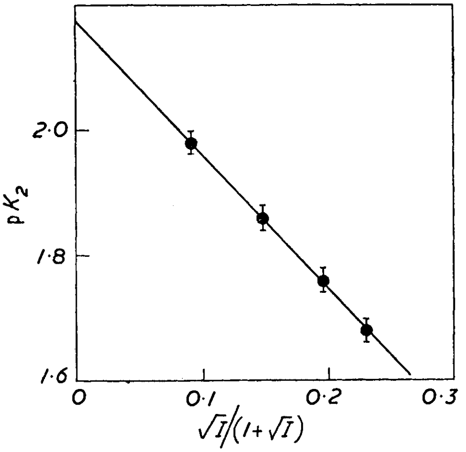
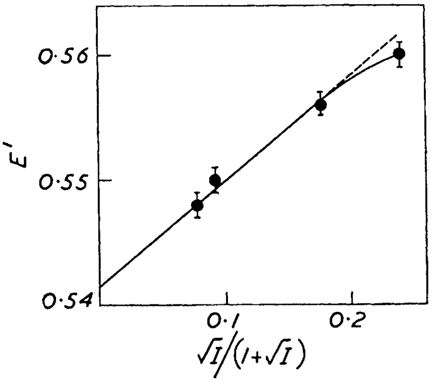


FIG. 3. *Variation of* E' *for the couple* $[\mathrm{Fe(CN)_4dipy}]^{1-}/[\mathrm{Fe(CN)_4dipy}]^{2-}$ *with ionic strength at* 25°. *Limiting slope* = 0·085 (*theoretical value* = 0·088). *Extrapolation gives* $E^{\circ\prime} = 0{\cdot}541_5$ v.



(b) *E.M.F. measurements.* The value of $\mathrm{p}K_2$ being known, and also that $\mathrm{p}K_1 < 0$, it was possible to obtain redox potentials corresponding to the two couples $[\mathrm{Fe(CN)_4dipy}]^{1-}/[\mathrm{Fe(CN)_4dipy}]^{2-}$ and $[\mathrm{Fe(CN)_4dipy}]^{-1}/[\mathrm{HFe(CN)_4dipy}]^{1-}$ by working at appropriate hydrogen chloride concentrations. The former was obtained directly from measurements at a constant HCl concentration of $2{\cdot}48 \times 10^{-4}$M, ionic strength being controlled by addition of " AnalaR " sodium chloride. Fig. 3 shows a plot of E' against $\sqrt{I}/(1 + \sqrt{I})$ at 25°. The slope, +0·085, is in good agreement with the theoretical Debye–Hückel slope, 0·088, for a couple in which the charge change is from −1 on the oxidised form to −2 on the reduced form. Extrapolation to zero ionic strength gives $E^{\circ\prime} = 0{\cdot}541_5$ v, and hence ΔG° for the reaction:

$$[\mathrm{Fe(CN)_4dipy}]^{1-} + \tfrac{1}{2}\mathrm{H_2} = [\mathrm{Fe(CN)_4dipy}]^{2-} + \mathrm{H^+} \quad . \quad . \quad . \quad . \quad (6)$$

is −12·5 kcal./mole. Measurements of E' at 1·6° ± 0·2°, 12·4° ± 0·2°, 20·8° ± 0·1°, 25·0° ± 0·1° and constant ionic strength ($I = 0{\cdot}10$) gave $0{\cdot}611_0$, $0{\cdot}586_5$, $0{\cdot}568_5$, $0{\cdot}560_0$ v respectively, from which $\mathrm{d}E'/\mathrm{d}t$ is $-(2{\cdot}18 \pm 0{\cdot}07) \times 10^{-3}$ v/degree. ΔH° for reaction (6) is thus $-27{\cdot}4 \pm 0{\cdot}5$ kcal./mole, and $\Delta S^\circ = -50 \pm 1{\cdot}6$ e. u. Consequently, the difference between the partial molal entropies of the two complex ions, $\bar{S}^\circ_{(-2)} - \bar{S}^\circ_{(-1)}$, is $-34{\cdot}6 \pm 1{\cdot}6$ e.u. A negative entropy difference is expected for this type of charge change, and the

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[2] Latimer, " Oxidation Potentials," Prentice-Hall, Inc., New York, 1952.

comparatively large value can be attributed to the fact that the peripheral nitrogen atoms carry some charge as a result of double-bond formation, thereby exerting a strong influence on surrounding water molecules.[3]

For the cell reaction in more acidic solutions, which takes the form:

$$[\mathrm{Fe(CN)_4dipy}]^{-1} + \tfrac{1}{2}\mathrm{H_2} = [\mathrm{HFe(CN)_4dipy}]^{1-} \quad . \; . \; . \; . \quad (7)$$

measurements of E' at different temperatures were carried out at a hydrogen chloride concentration of 0·197M, where about 90% of the tetracyanodipyridyliron(II) ion is in its conjugate acid form. The results gave $\mathrm{d}E'/\mathrm{d}t = -(1{\cdot}80 \pm 0{\cdot}10) \times 10^{-3}$ v/degree. Measurements of E' were also made at three weaker acid concentrations at 25° and $I = 0{\cdot}10$. These values should fit the relation:

$$E' = (E')_6 + 0{\cdot}059 \log (K_2 + [\mathrm{H}^+])/K_2 \quad . \; . \; . \; . \; . \quad (8)$$

where E' is the measured redox potential and $(E')_6$ is the redox potential of the couple in equation (6), $[\mathrm{Fe(CN)_4dipy}]^{1-}/[\mathrm{Fe(CN)_4dipy}]^{2-}$ at 25° and $I = 0{\cdot}10$. By using the appropriate value of pK_2 (1·66 obtained from Fig. 2), equation (8) was tested by calculating $(E')_6$ from the measured E' values at the various hydrogen chloride concentrations. Table 2 shows the constancy of $(E')_6$ values thus calculated, and their agreement with the value of E' measured directly in the H$^+$-independent range. This substantiates the view that no other ionization on either the oxidised or reduced forms occurs in this system within the pH range investigated.

TABLE 2. *Variation of the measured redox potential, E', with* [H$^+$] *at* 25°.

I*	0·10	0·10	0·10	0·20
[H$^+$] (10^{-3}M)	0·248	2·48	24·8	197
E' (meas.) (v)	0·560	0·562	0·577	0·619
$(E')_6$ (calc.) (v)	0·560	0·560	0·559	0·563 †

* Ionic strength was adjusted by " AnalaR " sodium chloride.
† Value calculated by using pK_2 = 1·60 at I = 0·20.

Substituting the values $[\mathrm{H}^+] = 1$ and $(E')_6 = 0{\cdot}560$ in equation (8) gives the mean value of the redox potential, $E = 0{\cdot}658 \pm 0{\cdot}001$ v, for the couple $[\mathrm{Fe(CN)_4dipy}]^{1-}/[\mathrm{HFe(CN)_4dipy}]^{1-}$ of cell reaction (7). Hence $\Delta G° = -15{\cdot}2$ kcal./mole. From the value of $\mathrm{d}E'/\mathrm{d}t$ obtained at 0·198M-hydrogen chloride, $\Delta H° = -27{\cdot}5 \pm 0{\cdot}6$ kcal./mole and $\Delta S° = -41{\cdot}3 \pm 2{\cdot}2$ u. e. The difference between the partial molal entropies of the reduced and the oxidized form of the complex ion (equation 7) is, therefore, $-25{\cdot}7 \pm 2{\cdot}2$ e. u. This difference is surprisingly large considering that the charges on the complex ions are the same. Similar anomalous behaviour has been observed in the ferro–ferricyanide system, and an explanation in terms of some special structural features in the conjugate-acid species has been suggested.[4]

It is clear that the ionization represented by reaction (5) is the difference between reactions (6) and (7). From the thermodynamic quantities for reactions (6) and (7), we obtain for the ionization in reaction (5): $\Delta H° = -0{\cdot}5 \pm 1{\cdot}1$ kcal./mole, and $\Delta S° = -8{\cdot}9 \pm 3{\cdot}8$ e. u. These values are in reasonable agreement with those obtained directly by spectrophotometric measurements described in section (a) above, *viz.*, $\Delta H° = -1{\cdot}3 \pm 1{\cdot}3$ kcal./mole, $\Delta S° = -14{\cdot}3 \pm 5{\cdot}0$ e. u.

*The Tris-*o*-phenanthrolineiron*(II)*–Tris-*o*-phenanthrolineiron*(III) *Couple.*—Hume and Kolthoff [5] had shown that this couple has a potential of 1·06 v in 1·0M-sulphuric acid at 25°. At very high acid concentration they also observed that the redox potential decreased as the acid concentration increased, and attributed this to an ionization on the oxidized form. Dwyer and McKenzie [6] measured the potential of this system at various acid strengths

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[3] Cobble and Adamson, *J. Amer. Chem. Soc.*, 1950, **72**, 2276.
[4] George, Hanania, and Irvine, *Rec. Trav. chim.*, 1955, **74**, 759.
[5] Hume and Kolthoff, *J. Amer. Chem. Soc.*, 1943, **65**, 1895.
[6] Dwyer and McKenzie, *J. Proc. Roy. Soc., New South Wales*, 1947, **81**, 93.

and obtained a value of 1·120 v at zero acid strength and 25°. The exact ionic strength was not recorded, but if it is assumed that the concentrations of the reduced and the oxidized form were each of the order of 10^{-3}M the value at zero ionic strength would be 1·14 v.

We have measured the redox potential of this system at different ionic strengths and temperatures. Except where specified, the experiments were carried out in $4·5 \times 10^{-3}$M-nitric acid, with the ionic strength adjusted by " AnalaR " sodium nitrate. At this acid concentration no oxidation of the iron(II) complex by nitrate was observed during the time of measurement. Further, according to Hume and Kolthoff,[5] no complication due to ionization of the oxidized form was to be expected.

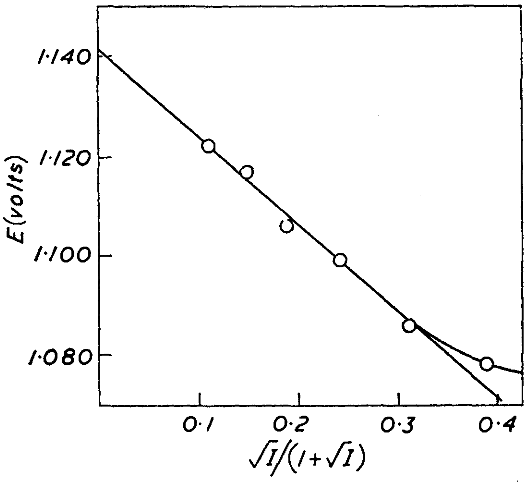

FIG. 4. *Variation of E′ for the couple* $[Fe(phen)_3]^{2+/3+}$ *with ionic strength at* 25·5°. *Slope* = −0·017 (*theoretical value* = −0·0148). *Extrapolation gives* $E^{\circ\prime}$ = 1·141 v.

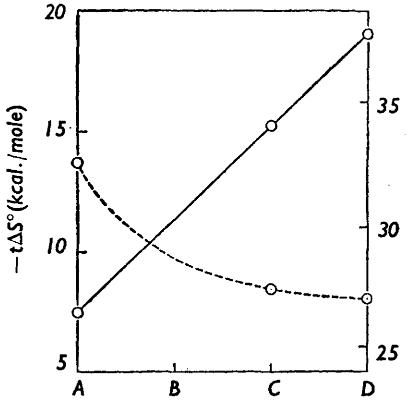

FIG. 5. *Relation between tΔS° and ΔH° with the ligand for the trisdipyridyl-, hexacyano-, and mixed dipyridylcyano-complexes of iron*(II) *and iron*(III).

A, $Fe(dipy)_3^{2+/3+}$. *B*, $Fe(dipy)_2(CN)_2^{0/1+}$. *C*, $Fe(dipy)(CN)_4^{2-/1-}$. *D*, $Fe(CN)_6^{4-/3-}$.

The results of measurements at 25·5° and different ionic strengths are shown in Fig. 4 where E' is plotted against $\sqrt{I}/(1 + \sqrt{I})$. The slope (—0·017) is in fair agreement with the theoretical slope (—0·0148) for a couple in which there is a charge of +2 on the reduced and +3 on the oxidized form. The extrapolated value $E^{\circ\prime} = 1·141$ v. Measurements at 1·9°, 10·5°, 20·4°, 25·5°, 31·2°, all at $I = 0·10$, gave values of 1·118, 1·101, 1·111, 1·099, and 1·092 v respectively. dE'/dt is thus $-9·0 \times 10^{-4}$ v/degree, from which $E^{\circ\prime}$ (25° and zero ionic strength) is calculated to be 1·147 ± 0·005 v. For the reaction:

$$[Fe(phen)_3]^{3+} + \tfrac{1}{2}H_2 = [Fe(phen)_3]^{2+} + H^+ \quad . \; . \; . \; . \quad (9)$$

ΔG° is, therefore, —26·5 ± 0·1 kcal./mole, ΔH° is —32·7 ± 0·5 kcal./mole and ΔS° is —20·8 ± 2·0 e. u., giving $\bar{S}^\circ_{(2+)} - \bar{S}^\circ_{(3+)} = -5·2 \pm 2·0$ e. u.

The Trisdipyridyliron(II)-*Trisdipyridyliron*(III) *Couple*.—Hume and Kolthoff[5] had found that this couple had the same value as the corresponding phenanthroline couple in 1M-sulphuric acid. Dwyer and McKenzie[6] quote a value of 1·096 v at zero acid strength. Measurements in $4·5 \times 10^{-3}$M-nitric acid with $I = 0·056$ were carried out at 10·5°, 20·9°, and 31·1° and gave values of 1·104, 1·096, 1·085, and 1·074 v, respectively. dE'/dt is thus $-1·0 \times 10^{-3}$ v/degree. Assuming the variation of E' with ionic strength to be the same as that for the phenanthroline couple allows $E^{\circ\prime}$ at 25° to be estimated as 1·120 ± 0·005 v, a slightly lower value than for the phenanthroline couple. For reaction (9), ΔG° is, therefore, —25·6 ± 0·1 kcal./mole, ΔH° is —32·7 ± 0·5 kcal./mole, and ΔS° —23·8 ± 2·0 e. u. $\bar{S}^\circ_{(2+)} - \bar{S}^\circ_{(3+)}$ is thus —8·2 ± 2·0 e. u.

These thermodynamic results enable one to calculate the corresponding data for the reaction:

$$\mathrm{Fe^{3+}} + 3\mathrm{dipy} = [\mathrm{Fe(dipy)_3}]^{3+} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (10)$$

which cannot be obtained directly, since on adding 2,2′-dipyridyl to ferric ion one does not obtain the blue trisdipyridyliron(III) ion, but a brown solution containing binuclear

$$\mathrm{Fe^{3+}_{aq.}} + \tfrac{1}{2}\mathrm{H_2} = \mathrm{Fe^{2+}_{aq.}} + \mathrm{H^+} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (11)$$

$$[\mathrm{Fe(dipy)_3}]^{3+} + \tfrac{1}{2}\mathrm{H_2} = [\mathrm{Fe(dipy)_3}]^{2+} + \mathrm{H^+} \quad . \;\; . \;\; . \;\; . \quad (12)$$

$$\mathrm{Fe^{2+}_{aq.}} + 3\mathrm{dipy} = [\mathrm{Fe(dipy)_3}]^{2+} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (13)$$

species.[7] Considering reaction (10), as well as (11)—(13), it can be seen that the thermodynamic quantities, ΔG°, etc., for reaction (10) are given by:

$$(\Delta G^\circ)_{10} = (\Delta G^\circ)_{11} + (\Delta G^\circ)_{13} - (\Delta G^\circ)_{12} \quad . \;\; . \;\; . \;\; . \;\; . \quad (14)$$

and similar equations hold for ΔH° and ΔS°. The data for reaction (11) were estimated from the E value and the partial molal entropies of the ions quoted by Latimer.[2] Those for reaction (13) were taken from Baxendale and George's results.[8] From these values we find for reaction (10), $\Delta G^\circ = -15{\cdot}4$ kcal./mole, $\Delta H^\circ = -1{\cdot}2$ kcal./mole, and $\Delta S^\circ = +47{\cdot}5$ e. u. Thus unlike the formation of trisdipyridyliron(II) ion, which is highly exothermic ($\Delta H^\circ = -24{\cdot}3$ kcal./mole), the formation of the trisdipyridyliron(III) ion is due almost entirely to the large favourable entropy change.

An interesting correlation is observed between $t\Delta S^\circ$ (t = temperature) and ΔH° with the ligand when one compares the couples $[\mathrm{Fe(dipy)_3}]^{2+/3+}$, $[\mathrm{Fe(dipy)(CN)_4}]^{2-/1-}$, and $[\mathrm{Fe(CN)_6}]^{4-/3-}$. This is shown in Fig. 5, where $-t\Delta S^0$ increases markedly and almost linearly as one replaces dipyridyl by cyanide, whereas $-\Delta H^0$ decreases, the decrease being non-linear and less marked than the increase in $t\Delta S^\circ$. Interpolation from these curves suggests that a reasonable value of E for the couple $[\mathrm{Fe(dipy)_2(CN)_2}]^{0/1-}$, which cannot be obtained experimentally because of the low solubility of $[\mathrm{Fe(dipy)_2(CN)_2}]^0$ species, is about 0·8 v. This type of correlation seems to offer a useful method of obtaining thermodynamic results for couples containing mixed ligands when no direct measurements can be made.

The Trisdipyridylruthenium(II)-*Trisdipyridylruthenium*(III) *Couple.*—Dwyer [9] quotes a value of 1·31 v for this couple at zero ionic strength. At $I = 0{\cdot}82$, the present measurements yielded values of 1·282, 1·276, and 1·269 v at 1·7°, 11·4°, and 21·2°. These values give $\mathrm{d}t'/\mathrm{d}t = -6{\cdot}7 \times 10^{-4}$ v/degree. At $I = 0{\cdot}060$ and 21·1° the measurement gave $E' = 1{\cdot}336$ v, and using the same extrapolation as in the case of the iron–dipyridyl and -phenanthroline systems we estimate $E^{\circ\prime}$ to be $1{\cdot}374 \pm 0{\cdot}005$ v. Hence for the reaction:

$$[\mathrm{Ru(dipy)_3}]^{3+} + \tfrac{1}{2}\mathrm{H_2} = [\mathrm{Ru(dipy)_3}]^{2+} + \mathrm{H^+} \quad . \;\; . \;\; . \;\; . \quad (15)$$

$\Delta G^\circ = -31{\cdot}6 \pm 0{\cdot}1$ kcal./mole, $\Delta H^\circ = -36{\cdot}3 \pm 0{\cdot}5$ kcal./mole, and $\Delta S^\circ = -15{\cdot}8 \pm 2{\cdot}0$ e. u. $\bar{S}^\circ_{(2+)} - \bar{S}^\circ_{(3+)}$ is therefore $-0{\cdot}2 \pm 2{\cdot}0$ e.u.

The difference in partial molal entropies for this, as well as for the iron complexes, is very much smaller than might have been expected in view of the value of +43 e. u. for the ferrous–ferric aquo-ion system. Similar behaviour is observed in the trisdipyridylosmium(II)–trisdipyridylosmium(III) system, where, using the data of Barnes, Dwyer, and Gyarfas,[10] we have calculated $\bar{S}^\circ_{(2+)} - \bar{S}^\circ_{(3+)} = 0{\cdot}8$ e.u. The small entropy difference for all these complexes suggests that the large organic molecule effectively shields the central metal atom, so that changes in its charge hardly affect surrounding water molecules in the second co-ordination shell.

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[7] Simon and Haufe, *Z. anorg. Chem.*, 1936—1937, **230**, 100; Blau, *Monatsh.*, 1898, **19**, 650.

[8] Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 55.

[9] Dwyer, *J. Proc. Roy. Soc., New South Wales*, 1949, **83**, 138.

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

EXPERIMENTAL

The potassium salt of tetracyanodipyridyliron(II) was prepared as described by Barbieri.[11] Spectrophotometric titration with standard ceric ammonium nitrate showed it to be 99% pure.

Solutions of trisdipyridyl- and tris-*o*-phenanthroline-iron(II) were prepared by adding slightly more than three molar equivalents of 2,2′-dipyridyl and *o*-phenanthroline respectively to exactly one equivalent of " AnalaR " ferrous ammonium sulphate, and making up the appropriate volume.

Trisdipyridylruthenium(II) chloride was used in the experiments involving the ruthenium complex cation. It was prepared and purified by Burstall's method.[12]

All other reagents were of " AnalaR " quality.

E.M.F. Measurements.—The apparatus used has already been described.[13] The method adopted was to add the appropriate amount of standard ceric ammonium nitrate solution to the reduced forms of the complex ions so as to give an approximately equimolar mixture of the reduced and oxidized forms, and then determine simultaneously the E.M.F. potentiometrically and the concentrations of reduced and oxidized forms by spectrophotometric measurements. Concentrations of complex ions of about 10^{-3}M were used for potentiometric measurements and of about 5×10^{-5}M for spectrophotometric measurements. The latter measurements were made with a Unicam quartz spectrophotometer.

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[11] Barbieri, *Atti R. Accad. Lincei*, 1934, **20**, 273.

[12] Burstall, *J.*, 1936, 173.

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