# The Vanadium(II) Reduction of Tris(2,2′-bipyridine)cobalt(III) and the Dissociation of the Tris(2,2′-bipyridine)cobalt(II) Product

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The rate law for the vanadium(II) reduction of $Co(bipy)_3^{3+}$ (bipy = 2,2′-bipyridine), is independent of hydrogen-ion concentration and of the form, rate = $k[V^{2+}][Co(bipy)_3^{3+}]$. At 25 °C and $\mu = 2{\cdot}0$M ($LiClO_4$), $k = 1110$ l $mol^{-1}$ $s^{-1}$, $\Delta H^{\ddagger} = 3{\cdot}6 \pm 0{\cdot}1$ kcal $mol^{-1}$, and $\Delta S^{\ddagger} = -32{\cdot}6 \pm 0{\cdot}4$ e.u. The reaction is of the outer-sphere type. The subsequent dissociation (by aquation) of the product $Co(bipy)_3^{2+}$ has also been studied and the mechanism is discussed. At 25° the rate constant $k_1$ for cleavage of the first chelate ring is $36{\cdot}0$ $s^{-1}$, $\Delta H^{\ddagger}_1 = 12{\cdot}4 \pm 0{\cdot}4$ kcal $mol^{-1}$, and $\Delta S^{\ddagger}_1 = -10{\cdot}0 \pm 1{\cdot}6$ e.u., $\mu = 2{\cdot}0$M ($LiClO_4$). Activation parameters are compared with those for the corresponding dissociations of $Fe(bipy)_3^{2+}$ and $Ni(bipy)_3^{2+}$.

THE rates of vanadium(II) redox reactions are in some cases determined by the redox process (electron-transfer controlled),[1] and in others by the rate at which an inner-sphere activated complex is formed (substitution controlled).[2] Vanadium(II) reductions in which electron transfer is rate controlling can be classified as (*a*) slow inner-sphere reactions (standard free-energy change unfavourable or only slightly favourable),[3] (*b*) outer-sphere reactions in which there is no potential bridging ligand, *e.g.* with the oxidants $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$,[4] and (*c*) fast outer-sphere reactions which do not need to make use of a potential bridging ligand, *e.g.* $IrCl_6^{2-}$.[5]

In this paper the reaction of $V^{2+}$ with $Co(bipy)_3^{3+}$ is considered. Since the one-ended dissociation of 2,2′-bipyridine from cobalt(III) is slow, the reaction is clearly of type (*b*). It was decided to extend the above study to include the dissociation of the product $Co(bipy)_3^{2+}$. In so doing we wished to investigate further the mechanism proposed for the dissociation of $Fe(bipy)_3^{2+}$,[6] and (apparently) applying also to the dissociation of $Ni(bipy)_3^{2+}$.[7]

*Preliminary Experiments.*—The complex $Co(bipy)_3^{3+}$ is inert to substitution, and visible spectra of aqueous solutions, $[H^+] = 0{\cdot}05$—$2{\cdot}0$M, remain unchanged over 2 days. Reduction with vanadium(II) is rapid and was studied by the stopped-flow method. At 420 nm oscilloscope traces indicated three consecutive steps, Figure 1(a). By suitable choice of reactant concentrations the various stages could be separated Figure 1(b) and (c). The rate of increase of absorbance in the first stage is independent of $[H^+]$, and corresponds to the reduction of $Co(bipy)_3^{3+}$ ($\varepsilon = 57{\cdot}1$ l $mol^{-1}$ $cm^{-1}$) to $Co(bipy)_3^{2+}$ ($\varepsilon = 159$ l $mol^{-1}$ $cm^{-1}$). The second stage, a decrease in absorbance, is dependent on $[H^+]$, and corresponds to the dissociation of $Co(bipy)_3^{2+}$. Possible explanations of the third-stage are that it is due to the complexing of the bipyridine with the excess of $V^{2+}$ and/or the $V^{3+}$ product. When solutions of (i) $V^{2+}$ ($5{\cdot}7 \times 10^{-3}$M) and (ii) $V^{3+}$ ($1{\cdot}89 \times 10^{-3}$M) were prepared with bipyridine ($2 \times 10^{-3}$M) and $[H^+] = 0{\cdot}1$M, there was a marked increase in absorption over the visible range for (i) (peak *ca.* 597 nm), indicating considerable complexing, whereas for (ii) little or no change was observed. It is therefore concluded that the third-stage corresponds to the complexing of $V^{2+}$ with bipyridine. No reduction of $Co(bipy)_3^{3+}$ ($7{\cdot}7 \times 10^{-4}$M) by $V^{3+}$ ($2{\cdot}3 \times 10^{-2}$M) was observed at room temperature, $[H^+] = 0{\cdot}27$M, during 45 min. Full kinetic studies of the first and second stages are described below.

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[1] For an example see B. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, 1967, **89**, 722.

[2] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1; N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 226; M. Green, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 509.

[3] Possible examples are the reaction of $Cr(H_2O)_5NCS^{2+}$ and $V^{2+}$, M. Orhanovic, H. N. Po, and N. Sutin, *J. Amer. Chem. Soc.*, 1968, **90**, 7224, and the reaction of *cis*- and *trans*-$Cr(NH_3)_4H_2OCl^{2+}$ with $V^{2+}$, R. B. Fisher, Ph.D. Thesis, Catholic University of America, Washington D.C., 1970.

[4] P. Dodel and H. Taube, *Z. phys. Chem.* (*Frankfurt*), 1965, **44**, 92; J. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.

[5] R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1036.

[6] (*a*) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807; (*b*) comments in F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn., p. 218.

[7] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1953, **75**, 5102.

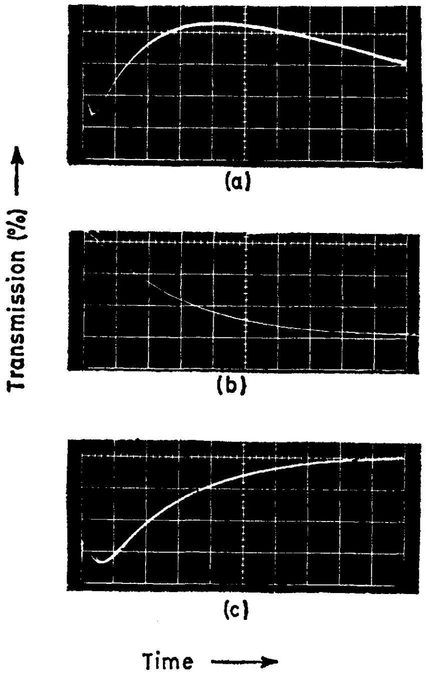

FIGURE 1 Oscilloscope traces for the reaction of $V^{2+}$ with $Co(bipy)_3^{3+}$. All three stages are illustrated in (a); (b) and (c) are traces for typical first and second stages with different time-bases and percentage transmissions. For (a), $[V^{2+}] = 3{\cdot}4 \times 10^{-2}$M, $[Co(bipy)_3^{3+}] = 7{\cdot}0 \times 10^{-4}$M, $[H^+] = 0{\cdot}5$M, temp. 25°, and time base 0·2 s/square

*The* $V^{2+}$ *Reduction of* $Co(bipy)_3^{3+}$ (*First Stage*).—The one-equivalent reaction (1), was studied under pseudo-

$$V^{2+} + Co(bipy)_3^{3+} \longrightarrow V^{3+} + Co(bipy)_3^{2+} \tag{1}$$

first-order conditions with the $V^{2+}$ reactant in large excess, and $[H^+]$ in the range 0·05—0·20M. Absorbance (OD) changes were monitored at 420 nm which is a minimum for the oxidant $Co(bipy)_3^{3+}$. As the rates of the first and second stages are comparable it was necessary to use a consecutive reaction treatment, (2),

$$\log(\mathrm{OD}_\infty - \mathrm{OD}_t + x\,e^{-k_d t}) = -\frac{k't}{2{\cdot}303} + \log y \tag{2}$$

the derivation of which is described in the appendix to reference 8. In this equation $k'$ and $k_d$ are first-order rate constants for the first and second stages, and $x$ and $y$ are constants. The constant $x$ is given by (3) where $A_0$

$$x = A_0\,k'\,\frac{(\varepsilon_B - \varepsilon_C)}{(k' - k_d)} \tag{3}$$

is the initial concentration of $Co(bipy)_3^{3+}$, and $\varepsilon_B$ and $\varepsilon_C$ are absorption coefficients for $Co(bipy)_3^{2+}$ and the products, respectively, at 420 nm. It is possible to evaluate $x$ and $k_d$ from equation (4) by plotting log

$$\log(\mathrm{OD}_t - \mathrm{OD}_\infty) = -\frac{k_d t}{2{\cdot}303} + \log x \tag{4}$$

$(\mathrm{OD}_t - \mathrm{OD}_\infty)$ against time, $t$, for the second stage. The absorbance $\mathrm{OD}_\infty$ corresponding to the end of the second stage of reaction, can only be obtained directly from oscilloscope traces for runs with $[H^+] > 0{\cdot}2$M. However with $[H^+] > 0{\cdot}2$M rate constants for the first and second stages are very similar, and while $k_d$ can be evaluated it is more difficult to obtain precise values of $k'$. At $[H^+] < 0{\cdot}2$M, $\mathrm{OD}_\infty$ had to be calculated due to interference from the third stage. Values of pseudo-first-order rate constants $k'$ (and hence second-order rate constants $k$) were obtained from plots of the left-hand-side of (2) against $t$, and were independent of hydrogen-ion concentration, Table 1. Some runs were also followed at 400 nm to see whether $VOV^{4+}$ (absorption maximum 425 nm),[9] which is formed when $V^{2+}$ reacts with oxygen, makes any contribution to the observed absorption changes. It can be seen from Table 1 that such runs are in good agreement with those followed at 420 nm. At 25° and $\mu = 2{\cdot}0$M ($LiClO_4$), $k = 1110$ l mol$^{-1}$ s$^{-1}$. Activation parameters $\Delta H^\ddagger = 3{\cdot}6 \pm 0{\cdot}1$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -32{\cdot}6 \pm 0{\cdot}4$ e.u. were obtained using a least-squares programme, where each data point was given equal weighting.

TABLE 1

Second-order rate constants for the reduction of $Co(bipy)_3^{3+}$ by vanadium(II), $\mu = 2{\cdot}0$M ($LiClO_4$), $\lambda = 420$ nm

| Temp. (°C) | $[H^+]$ (M) | $10^4[Co(bipy)_3^{3+}]$ (M) | $10^2[V^{II}]$ (M) | $k$ (l mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|
| 3·5 [a] | 0·05 | 6·25 | 2·26 | 625 (3) |
| | 0·10 | 7·00 | 1·21 | 660 (2) |
| | 0·10 | 7·78 | 2·21 | 657 [b] (3) |
| | 0·10 | 9·48 | 2·21 | 641 (4) |
| | 0·10 | 3·67 | 2·25 | 642 (3) |
| | 0·10 | 7·00 | 2·32 | 639 (2) |
| | 0·10 | 6·25 | 3·51 | 629 (3) |
| | 0·15 | 6·25 | 2·26 | 665 (2) |
| | 0·20 | 6·25 | 2·26 | 655 (4) |
| 10·0 | 0·05 | 6·99 | 2·29 | 768 (3) |
| | 0·10 | 6·99 | 2·29 | 773 (5) |
| 17·0 | 0·10 | 6·99 | 2·32 | 931 (3) |
| 25·1 | 0·05 | 7·00 | 3·41 | 1096 (4) |
| | 0·10 | 7·00 | 3·41 | 1122 (3) |

[a] Temperature 3·5 ± 0·2°. [b] $\lambda = 400$ nm.

*Dissociation of* $Co(bipy)_3^{2+}$ (*Second Stage*).—Rate constants, $k_d$, were evaluated from plots of log $(\mathrm{OD}_t - \mathrm{OD}_\infty)$ against $t$, equation (4). Except for initial curvature due to the first stage such plots were linear to >90% completion with $[H^+] > 0{\cdot}5$M, but were linear to only *ca.* 60% with $[H^+] = 0{\cdot}05$M, due to the incidence of the third stage. For complexes in which changes in spin multiplicity do not occur, dissociation of the tris (and bis) complexes is expected to be faster than that of the mono complex.[10] However absorbance $\mathrm{OD}_\infty$ readings at $[H^+] > 0{\cdot}5$M (when the third-stage makes no significant contribution) are as expected for the formation of $Co^{2+}$.* The absorbance changes which are observed are assigned to the dissociation (5). Species with partly

$$Co(bipy)_3^{2+} + 2H_2O \longrightarrow Co(bipy)_2(H_2O)_2^{2+} \tag{5}$$

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* Most of the final absorption at 420 nm is due to the $V^{2+}$ reactant which is present in large excess. A distinction between $Co^{2+}$ and $Co(bipy)_2^{2+}/Co(bipy)^{2+}$ is therefore difficult unless the cobalt(II) species have very different absorptions at this wavelength.

[8] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

[9] T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1964, **3**, 569.

[10] See for example ref. 6b, pp. 150—151.

dissociated, *i.e.* monodentate bipyridine are assumed to be short lived. Rate constants obtained by following the reaction at 400 or 385 nm are in good agreement with those at 420 nm, Table 2. The hydrogen-ion concentration was varied over the range 0·05—1·7M; Figure 2 shows the variation of $k_d$ with $[H^+]$ at four temperatures. The dependence on $[H^+]$ is consistent with the reaction scheme, which with slight modification (the inclusion of $k_{-3}$ and $k_4$) is as proposed previously for the dissociation of $Fe(bipy)_3^{2+}$.[6] Although $k_2$ is included contributions from this path are small and the evidence (deviations from linearity of plot of $1/k_d$ against $[H^+]^{-1}$) only slight. There are two possibilities: (i) that $k_3$ is rate determining, and $k_4$ is fast so that $k_{-3}$ does not contribute (as proposed previously, reference 6), and (ii) that $k_3$ and $k_{-3}$ are both fast so that $k_4$ is slow and rate determining.

TABLE 2

First-order rate constants for the dissociation of $Co(bipy)_3^{2+}$, $\mu = 2{\cdot}0M$ ($LiClO_4$), $\lambda = 420$ nm

| Temp. (°C) | $[H^+]$ (M) | $10^4[Co(bipy)_3^{3+}]$ (M) | $10^2[V^{II}]$ (M) | $k_d$ ($s^{-1}$) |
|---|---|---|---|---|
| 3·5 [a] | 0·05 | 6·25 | 2·26 | 0·436 (2) |
| | 0·10 | 3·67 | 2·25 | 0·795 (3) |
| | 0·10 | 7·78 | 2·21 | 0·755 [b] (5) |
| | 0·10 | 9·48 | 2·25 | 0·734 (4) |
| | 0·10 | 6·25 | 3·51 | 0·753 (1) |
| | 0·10 | 6·25 | 2·26 | 1·10 (2) |
| | 0·20 | 6·25 | 2·26 | 1·34 (2) |
| | 0·50 | 8·15 | 7·90 | 2·54 [c] (3) |
| | 0·70 | 8·15 | 7·90 | 3·07 [c] (3) |
| | 1·00 | 8·15 | 8·55 | 3·73 [c] (2) |
| | 1·40 | 8·15 | 8·55 | 4·22 [c] (3) |
| | 1·70 | 8·15 | 8·55 | 4·56 [c] (3) |
| 10·0 | 0·05 | 6·99 | 2·29 | 0·80 (2) |
| | 0·10 | 6·99 | 2·29 | 1·43 (2) |
| | 0·50 | 10·2 | 8·10 | 4·22 [c] (2) |
| | 1·00 | 10·2 | 8·10 | 6·08 [c] (3) |
| | 1·50 | 10·2 | 8·10 | 7·36 [c] (3) |
| 17·0 | 0·05 | 6·99 | 2·35 | 1·42 (1) |
| | 0·10 | 6·99 | 2·35 | 2·65 (1) |
| | 0·50 | 10·2 | 8·10 | 6·77 (2) |
| | 1·00 | 10·22 | 8·10 | 10·16 [c] (3) |
| | 1·50 | 10·22 | 8·10 | 12·47 [c] (3) |
| 25·1 | 0·05 | 7·00 | 3·41 | 2·67 (3) |
| | 0·10 | 7·00 | 3·41 | 5·13 (1) |
| | 0·50 | 10·22 | 8·10 | 13·3 [c] (3) |
| | 1·00 | 10·22 | 8·10 | 18·7 [c] (3) |
| | 1·50 | 10·22 | 8·10 | 23·9 [c] (3) |

[a] Temperature = 3·5 ± 0·2°. [b] $\lambda = 400$ nm. [c] $\lambda = 385$ nm.

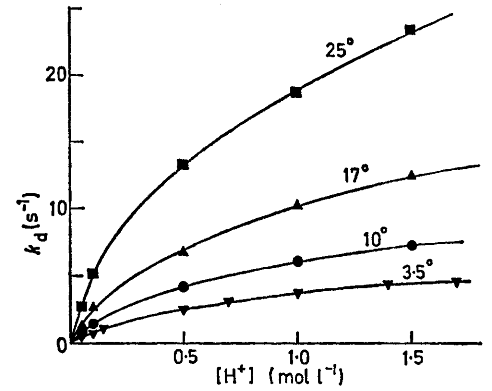
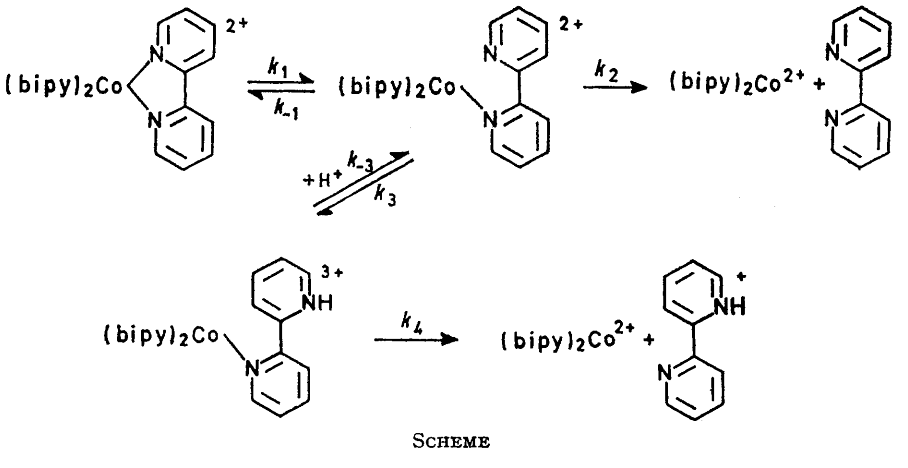


FIGURE 2 The variation of the rate constant $k_d$ with $[H^+]$ for the dissociation of $Co(bipy)_3^{2+}$



SCHEME

For (i) assuming stationary-state kinetics for the half-bonded unprotonated species, equation (6) is obtained.

$$k_d = \frac{k_1(k_2 + k_3[H^+])}{(k_{-1} + k_2 + k_3[H^+])} \qquad (6)$$

For (ii) assuming stationary-state kinetics for both half-bonded species (7) is obtained,

$$k_d = \frac{k_1(k_2 + K_3k_4[H^+])}{(k_{-1} + k_2 + K_3k_4[H^+])} \qquad (7)$$

where $K_3 = k_3/k_{-3}$. The hydrogen-ion dependences in (6) and (7) are seen to be of the same form. The second condition and equation (7) is to be preferred (see Discussion section); however values of $k_1$ which are evaluated are the same for both equations. On rearranging (7) gives (8) where $a = k_2/K_3k_4$. At $[H^+] > 0{\cdot}2M$, $a$ can be neglected and a plot of $1/k_{obs}$ against $1/[H^+]$ is linear.

$$\frac{1}{k_d} = \frac{k_{-1}}{k_1K_3k_4}\frac{1}{(a + [H^+])} + \frac{1}{k_1} \qquad (8)$$

Points at lower $[H^+]$ can be fitted to the same straight line if a value of $a$ of *ca.* 0·007 mol l$^{-1}$ is assumed at all temperatures, Figure 3. However this value is of low precision. Values of $k_1$ and $k_{-1}/K_3k_4$ have been obtained from the intercepts and gradients of the plot of $1/k_d$ against $[H^+]^{-1}$ ($[H^+] > 0{\cdot}2$M), and are listed in Table 3.

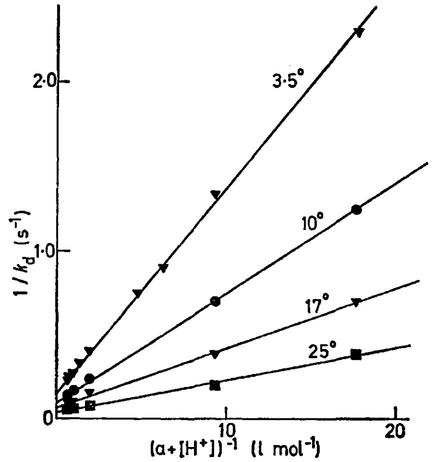


FIGURE 3 The dependence of $k_d$ on hydrogen-ion concentration for the dissociation of Co(bipy)$_3{}^{2+}$, equation (6)

Activation parameters obtained from the $k_1$ values are given in Table 4. Alternatively with $a = 0{\cdot}007$ mol l$^{-1}$, and including all the data in Table 2, $\Delta H^{\ddagger}{}_1 = 11{\cdot}5 \pm 0{\cdot}8$ kcal mol$^{-1}$ and $\Delta S^{\ddagger}{}_1 = -13{\cdot}4 \pm 2{\cdot}7$ e.u. A least-squares treatment was used in all computations, and each data point given equal weighting. From the ratio of limiting low [H$^+$] to high [H$^+$] values of $k_d$ we estimate $k_2/(k_2 + k_{-1})$ to be $<0{\cdot}0045$ at 25°.*

TABLE 3

The evaluation of rate constants, as defined in reaction scheme, for the dissociation of Co(bipy)$_3{}^{2+}$, $\mu = 2{\cdot}0$M (LiClO$_4$)

| Temp. (°C) | $k_1$ [a] (s$^{-1}$) | $k_{-1}/k_1K_3k_4$ [b] (mol l$^{-1}$ s) | $k_{-1}/K_3k_4$ (mol l$^{-1}$) |
|---|---|---|---|
| 3·5 | 6·8 ± 0·09 | 0·124 ± 0·002 | 0·84 |
| 10·0 | 11·4 ± 0·5 | 0·0749 ± 0·003 | 0·85 |
| 17·0 | 21·5 ± 0·5 | 0·0508 ± 0·008 | 1·09 |
| 25·1 | 36·0 ± 5·2 | 0·0239 ± 0·003 | 0·86 |

[a] Intercepts as computed from graph of $1/k_d$ against $[H^+]^{-1}$, $[H^+] > 0{\cdot}2$ M. [b] Gradients as computed from graph of $1/k_d$ against $[H^+]^{-1}$, $[H^+] > 0{\cdot}2$ M.

DISCUSSION

Standard oxidation-reduction potentials for the couples V$^{2+}$/V$^{3+}$ (−0·255 V),[11] V$^{3+}$/VO$^2$ (0·36 V),[11] and Co(bipy)$_3{}^{2+}$/Co(bipy)$_3{}^{3+}$ (0·37 V) [12] are consistent with our observation that V$^{2+}$ but not V$^{3+}$ will reduce Co(bipy)$_3{}^{3+}$. In pulse-radiolysis studies on Co(bipy)$_3{}^{3+}$, Waltz and Pearson [13] have observed the formation of the excited $t_{2g}{}^6e_g{}^1$ cobalt (II) form, which rapidly reverts to the more stable $t_{2g}{}^5e_g{}^2$ state. The final product of the reduction by V$^{2+}$ is the high-spin form of Co(bipy)$_3{}^{2+}$, which has an electronic configuration $t_{2g}{}^5e_g{}^2$, and no evidence was obtained for intermediate formation of the low-spin $t_{2g}{}^6e_g{}^1$ complex. The outer-sphere reactions of Co(bipy)$_3{}^{3+}$ and Co(bipy)$_2$(O$_2$CCH$_3$)$_2{}^+$ (ref. 14) are the first V$^{2+}$ reductions to be studied with oxidants having ligands with extensive $\pi$-delocalization. Not unexpectedly both reactions are considerably faster than the V$^{2+}$ reductions of Co(NH$_3$)$_6{}^{3+}$ and Co(en)$_3{}^{3+}$.

The rate constant for the V$^{2+}$ reduction of Co(bipy)$_3{}^{3+}$ (1·1 × 10$^3$ l mol$^{-1}$ s$^{-1}$ at 25°) is to be compared with the value 7·6 × 10$^3$ l mol$^{-1}$ s$^{-1}$ which can be calculated using the Marcus equations (8) and (9).[15] These equations

$$k_{12} = (k_{11}\,k_{22}\,K_{12}f)^{\frac{1}{2}} \tag{8}$$

$$\log f = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/Z^2)} \tag{9}$$

enable $k_{12}$ for the redox reaction involving net chemical change to be calculated from rate constants $k_{11}$ and $k_{22}$ for the related isotopic exchange reactions, and the equilibrium constant $K_{12}$ for the redox process (which was obtained from the standard oxidation-reduction potentials). Rate constants used in this calculation were 1 × 10$^{-2}$ l mol$^{-1}$ s$^{-1}$ for the V$^{2+}$–V$^{3+}$ reaction,[16] and 7 l mol$^{-1}$ s$^{-1}$ for the Co(bipy)$_3{}^{2+}$–Co(bipy)$_3{}^{3+}$ reaction.[17] A value of $Z = 10^{11}$ l mol$^{-1}$ s$^{-1}$, the collision frequency for two uncharged species, was used. The agreement between experimental and calculated values is considered satisfactory.

The data obtained for the dissociation of Co(bipy)$_3{}^{2+}$ fit the reaction scheme proposed by Basolo *et al.* for the dissociation of Fe(bipy)$_3{}^{2+}$.[6] This same scheme has been assumed to apply to the dissociation of Ni(bipy)$_3{}^{2+}$,[7] and may be applicable also to the dissociation of other complexes which are catalysed by hydrogen-ions, *e.g.* Ni(en)$_3{}^{2+}$.[18] In the present study ($\mu = 2{\cdot}0$M) we were unable to measure directly the limiting (high H$^+$) rate constant which is equal to $k_1$. However it was possible to obtain $k_1$ graphically (Figure 3), and in Table 4 rate constants and activation parameters are compared with those for other similar reactions.[6,19] The trend in enthalpies of activation, $\Delta H^{\ddagger}$, for these reactions can be explained in terms of crystal-field theory.[10,20] Thus

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* Three experiments on the dissociation of Co(bipy)$_3{}^{2+}$ are reported by R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, 1968, **7**, 170. Sulphuric acid was used to vary the hydrogen-ion concentration in this work (personal communication from Professor R. G. Wilkins).

[11] W. Latimer, 'Oxidation States of the Elements and their Potentials in Aqueous Solution,' Prentice Hall Inc., New York, 1952, 2nd edn., The I.U.P.A.C. sign convention is used.

[12] E. Paglia and C. Sironi, *Gazzetta*, 1957, **81**, 1125.

[13] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.

[14] R. G. Linck and co-workers have studied the reaction of V$^{2+}$ and Co(bipy)$_2$(O$_2$CCH$_3$)$_2{}^+$ and find $k = 6000$ l mol$^{-1}$ s$^{-1}$ (25°), $\Delta H^{\ddagger} = 3{\cdot}4 \pm 0{\cdot}4$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -32{\cdot}4 \pm 1{\cdot}2$ e.u. We are grateful to Professor Linck for communicating these results to us prior to publication.

[15] R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853; *Ann. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Chem. Phys.*, 1965, **43**, 679.

[16] K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921.

[17] Estimated from available data, see p. 1951 of ref. 13.

[18] A. K. Shamsuddin-Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1960, 2901.

[19] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1965, **4**, 929.

[20] P. Ellis and R. G. Wilkins, *J. Chem. Soc.*, 1959, 299.

TABLE 4

Summary of kinetic data for dissociation of the (first) chelate ring of some metal complexes [a]

| Complex | $k_1(25°)$ ($s^{-1}$) | $\Delta H^‡$ (kcal $mol^{-1}$) | $\Delta S^‡$ (e.u.) | Ref. |
|---|---|---|---|---|
| $Fe(bipy)_3^{2+}(t_{2g}^6)$ | $7.8 \times 10^{-4}$ | 27·4 [b] | +15·5 [b] | 6 |
| $Co(bipy)_3^{2+}(t_{2g}^5e_g^2)$ | 36·0 | 12·4 | −10·0 | This work |
| $Ni(bipy)_3^{2+}(t_{2g}^6e_g^2)$ | $3.2 \times 10^{-3}$ | 21·6 | +3·1 | 19 |
|  | $18.0 \times 10^{-3}$ | 21·2 | +4·5 | 6, 7 |
| $Ni(bipy)(H_2O)_4^{2+}(t_{2g}^6e_g^2)$ | $5 \times 10^{-5}$ | 23·1 | +0·3 | 19 |
| $Cu(bipy)(H_2O)_4^{2+}(t_{2g}^6e_g^3)$ [d] | 0·2 [c] | 13·5 | −13·2 | 19 |
| $Zn(bipy)(H_2O)_4^{2+}(t_{2g}^6e_g^4)$ [d] | 15·9 [c] | 11·5 | −10·9 | 19 |
| $Hg(bipy)(H_2O)_n^{2+}(t_{2g}^6e_g^4)$ [d] | 25·1 [c] | 10·1 | −15·1 | 19 |

[a] A rate constant 0·38 $s^{-1}$ at 25°, $\Delta H^‡ = 22.6 \pm 0.5$ kcal $mol^{-1}$ has been observed for the dissociation of $Cr(bipy)_3^{2+}$ in 0·5M NaCl (B. R. Baker and B. D. Mehta, *Inorg. Chem.*, 1965, **4**, 853). The full dependence on [$H^+$] does not appear to have been investigated however, and we are uncertain as to which path or paths this value refers to. [b] Values $\Delta H^‡ = 26.1 \pm 0.08$ kcal $mol^{-1}$ and $\Delta S^‡ = 14.8 \pm 0.28$ e.u. have been obtained in aqueous $H_2SO_4$ solutions by Dr. M. V. Twigg, Erindale College, Univ. of Toronto. [c] The rate of dissociation was determined by the addition of a second metal ion ($Hg^{2+}$ or $Cu^{2+}$) which was initially uncomplexed. Rate constants observed are assumed equal to $k_1$ see ref. 19. [d] Data not available for tris complexes.

crystal-field stabilization energies decrease for the complexes in the series $Fe^{II}$(low spin) > $Ni^{II}$ > $Co^{II}$. On the other hand entropies of activation, $\Delta S^‡$, for these reactions are more difficult to rationalize. Previously the more positive value observed for $Fe(bipy)_3^{2+}$ has been explained by the greater ligand freedom in the expanded-state intermediate between low-spin $Fe(bipy)_3^{2+}$ and high-spin $Fe(bipy)_2(H_2O)_2^{2+}$.[20] We suggest that the more positive $\Delta S^‡$ value $Fe^{II} > Ni^{II} > Co^{II}$ may also be due to the greater degree of $S_N1$ character [21] in the reactions of $Fe(bipy)_3^{2+}$, and to a lesser extent $Ni(bipy)_3^{2+}$. Such an explanation will only hold if the complex $Fe(bipy)_3^{2+}$ with a half-bonded bipy ligand remains low spin, and at present this point remains unconfirmed. Greater $S_N2$ character is, on the other hand, observed with $Co(bipy)_3^{2+}$ and other reactants with similar $t_{2g}$ and $e_g$ electronic populations, since qualitatively an incoming ligand is more readily able to bond and assume equivalence with existing ligands. On this basis the dissociations of the complexes of $Zn^{II}$ and $Hg^{II}$ (Table 4) are also likely to have some $S_N2$ character. The value of $\Delta S^‡$ obtained for the $Cu^{II}$ complex suggests greater $S_N2$ character than might have been expected by analogy with $Ni^{II}$. Comparisons with $Zn^{II}$, $Hg^{II}$, and $Cu^{II}$ are, of course, only valid if the complexes remain octahedral.

An $S_N2$ assignment might at first seem inconsistent with the $S_N1$ mechanism (or dissociative interchange mechanism) which is generally assumed to apply to the formation of complexes of 2+ metal ions. Thus many complexing reactions, in particular those of $Ni^{2+}$ and $Co^{2+}$, fit the Eigen mechanism (ref. 6*b*, page 154), reactions (10)—(11), where the incoming ligand L forms an

$$M(H_2O)_6^{2+} + L \rightleftharpoons M(H_2O)_6^{2+}, L \qquad (10)$$

$$M(H_2O)_6^{2+}, L \longrightarrow M(H_2O)_5L + H_2O \qquad (11)$$

ion-pair in the first stage, and the second stage involves $S_N1$ dissociation of a water ligand. With chelating ligands such a mechanism might be considered to apply to the attachment of the first end of the ligand. Little information is available as to the mechanism by which ring closure occurs. Indeed the best way of obtaining such information is to study the dissociation reaction as in the present instance and assume microscopic reversibility. Thus it is possible that monodentate complex formation is $S_N1$ with most metal ions while for the second stage (chelate-ring formation), an $S_N2$ process will often prevail. This is reasonable in view of the close proximity of the free end of the chelating ligand. Previously $S_N2$ steps have been proposed in the chelation of EDTA to both cobalt(III) [22] and chromium(III).[23] Indeed it is difficult in the chromium(III) case to conceive a rate constant as high as 330 $s^{-1}$ except in terms of such an $S_N2$ mechanism. The possibility that the reactions of $Fe(bipy)_3^{2+}$ with the stronger nucleophiles $CN^-$ (ref. 24) and $OH^-$ (ref. 25) may be $S_N2$ rather than $S_N1$ is also noted.

The ratio of rate constants $k_2/(k_{-1} + k_2)$ is a measure of the number of times complete dissociation occurs once the first metal–N bond has dissociated. For $Co(bipy)_3^{2+}$ and $Fe(bipy)_3^{2+}$ the values of this ratio are <0·0045 and 0·16 respectively. Clearly with the partly dissociated form of $Co(bipy)_3^{2+}$ there is a much greater tendency for the chelate ring to reform than with $Fe(bipy)_3^{2+}$. The quantity $k_{-1}/K_3k_4 = 0.86$ for $Co(bipy)_3^{2+}$ at 25° is also of interest. For the alternative condition giving equation (6) $k_{-1}/k_3 = 0.86$ which suggests that $k_3$ involving protonation is relatively slow and certainly not approaching the diffusion-controlled limit as is often the case with protonated reactions. It is possible that the slowness of this reaction is due to the steric requirement that the uncoordinated ligand must first rotate away from the metal before protonation can occur. However on balance the value of 0·86 would seem to us strong evidence supporting equation (7). The behaviour observed here is to be compared with that for the dissociation of $Fe(phen)_3^{2+}$, where such a rotation cannot occur,[6] and the reaction is independent of [$H^+$].

## EXPERIMENTAL

The perchlorate salt of tris(2,2′-bipyridine)cobalt(III), $[Co(bipy)_3](ClO_4)_3,3H_2O$ was prepared as described in ref. 26. In order to determine the spectrum of tris(2,2′-bipyridine)-cobalt(II) a *ca.* 50% excess of 2,2′-bipyridine was added to a solution of $CoCl_2,6H_2O$ containing a few drops of methanol (*ca.* 0·25M). Visible spectra of the cobalt(III) ($\varepsilon = 68.9$ l $mol^{-1}$ $cm^{-1}$ at 450 nm) and cobalt(II) complexes were in

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[21] For a recent example see D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, 1968, **90**, 608.

[22] I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 1958, 260.

[23] R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc.* (*A*), 1971, 1494.

[24] J. Burgess, *J.C.S. Dalton*, 1972, 203.

[25] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

[26] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.

good agreement with those reported.[13] From Figure 1 in ref. 13 the minimum at 420 nm for $Co(bipy)_3^{3+}$ is clearly a suitable wavelength for following the reduction to $Co(bipy)_3^{2+}$. All other reagents were prepared as described previously in work from these laboratories. At 420 nm $V^{2+}$ has $\varepsilon = ca.\ 0{\cdot}3\ l\ mol^{-1}\ cm^{-1}$, and $Co^{2+}$ has $\varepsilon = ca.\ 0{\cdot}6\ l\ mol^{-1}\ cm^{-1}$.

Dr. K. M. Davies prepared the sample of the perchlorate salt of tris(2,2′-bipyridine)cobalt(III). We thank a referee for helpful comments relating to equations (6) and (7), and Professor R. G. Wilkins and Dr. J. Burgess for correspondence. R. D. acknowledges the award of an S.R.C. post-doctoral fellowship and M. G. an S.R.C. studentship.

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