CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

Dissociation of Tris(2,2′-bipyridine)vanadium(II) and Dissociation and Formation of Tris(1,10-phenanthroline)vanadium(II)

BY RALPH G. PEARSON AND O. A. GANSOW

Received February 26, 1968

The rate of dissociation of tris(2,2′-bipyridine)vanadium(II) and the rates of formation and dissociation of tris-(1,10-phenanthroline)vanadium(II) were determined. The dissociation of the bipyridine complex is strongly acid dependent whereas that of the phenanthroline complex is only slightly so in agreement with a mechanism of dissociation first proposed for similar iron(II) complexes. Both rates of dissociation and the rate of formation of the tris(1,10-phenanthroline)vanadium(II) ion were found to be slow, in agreement with a prediction for reactivity of d^3 electron systems.

Introduction

Complexes of the heterocyclic amines 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) have been important in the development of coordination chemistry.[1] The kinetics and mechanism of the formation and dissociation of the slowly reacting tris-bipyridine and tris-*o*-phenanthroline iron(II) and nickel(II) complexes were thoroughly examined some years ago.[2] Recently formation and dissociation rates for a number of other metal ions were also measured.[3] Relative rates of reaction of these octahedral complexes correlate well with an order of reactivity predicted from a crystal field model which assumes reaction to proceed by an SN1 dissociative mechanism.[4]

Kinetic studies of the dissociation of $Cr(bipy)_3^{2+}$ have also been done.[5] However, no detailed kinetic studies have as yet been reported for the similar vanadium(II) complexes. This work reports a study of the kinetics and mechanism of acid hydrolysis dissociation of the tris(2,2′-bipyridine)vanadium(II) and tris(1,10-phenanthroline)vanadium(II) complexes as well as the rate of formation of the above phenanthroline complex.

Both $V(bipy)_3^{2+}$ and $V(phen)_3^{2+}$ complexes are particularly suitable for kinetic studies since they have very intense absorption band(s) in the visible region. The vanadium(II)–bipy system has been examined thermodynamically and equilibrium constants have been obtained,[6] so the nature and concentration of species present in the aqueous solution equilibria are reasonably well defined. The reactions of the vanadium(II) complexes are slow; thus conventional spectrophotometric kinetic methods are easily employed.

Experimental Section

Materials.—All chemicals used were reagent grade. Solvents were deoxygenated by distillation under purified tank nitrogen. Methanol and ethanol were distilled from reagent grade magnesium metal. An analytically pure solution of $VOCl_2$ was prepared by boiling 0.05 mol of reagent grade V_2O_5 with 500 ml of concentrated hydrochloric acid. The reaction was continued until complete reduction occurred. The solution was then evaporated until cooling caused crystallization. It was then diluted to 1 l. with distilled water. Portions of this solution were then reduced to VCl_2 at a mercury pool cathode as needed.[7] A cathode current density of 0.01 A/cm^2 was used. Bipyridine was used as purchased from the G. F. Smith Co. and reagent grade 1,10-phenanthroline was obtained from the Fisher Co. All compounds were prepared in an all-glass system in an atmosphere of pure nitrogen. *Caution!* the perchlorate salts of the vanadium(II) complexes are known to detonate; thus a close reading of the references given is important.[8,9]

Preparation of Complexes. Bipyridine Complex.[8]—To prepare $[V(bipy)_3](ClO_4)_2$, ammonium perchlorate (0.9 g) was added to 30 ml of a previously prepared 0.1 *M* solution of VCl_2. To 50 ml of a 50% methanol–water mixture was added 1.5 g of bipyridine. These two solutions were then mixed and allowed to stand overnight at −10°. The product was filtered, washed three times with 2 ml of ice-cold water and two times with 15 ml of ether, and dried in a vacuum desiccator. The complex is deep green to black, depending on crystal size.

Phenanthroline Complex.[1,9]—Attempts to isolate a pure sample of $[V(phen)_3](ClO_4)_2$ failed probably because of contamination by a vanadium(III) species. It was necessary to prepare it *in situ*. A saturated solution of *o*-phenanthroline was prepared; the solubility of this ligand in water at 25° is reported to be 0.016 *M* and this was verified by determination of ligand concentration as the iron(II) complex.[10] To 100 ml of the saturated solution was added 1 ml of 0.01 *M* VCl_2, making the concentration of complex $\sim 10^{-4}$ *M*. The solution is an intense blue with λ_{max} 645 mμ. If the phenanthroline to vanadium ratio is substantially lowered, the intensity of the absorption decreases and a shoulder appears on the blue side of the absorption band. In all solutions used for kinetic runs, no shoulder could be seen. At the wavelengths at which the runs were made, 660–700 mμ, the species giving rise to the "shoulder" has no absorption. A successful isolation of $[V(phen)_3](I_2)$ has been reported and its solution properties appear the same as the complex prepared *in situ*.[9]

Kinetic Runs.—Spectrophotometric methods were used to follow changes in absorption in the 400–800-mμ range. For the dissociation studies it proved convenient simply to follow loss of intensity of the strong visible absorptions, $\epsilon > 1000$, as the complex reacted. The final reaction products, protonated ligand and hydrated vanadous ions, have small molar absorbances,

---

[1] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

[2] (a) F. Basolo, J. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954), and references contained therein; (b) F. Basolo, J. Hayes, and H. M. Neumann, *ibid.*, **75**, 5102 (1953), and references contained therein.

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

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 3.

[5] B. Baker and B. Mehta, *Inorg. Chem.*, **4**, 848 (1965); J. P. Candlin, J. Halpern, and D. R. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[6] C. S. C. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, London, 1966, p 273

[7] W. P. Schaefer, *Inorg. Chem.*, **4**, 642 (1965).

[8] S. Herzog, *Z. Anorg. Allgem. Chem.*, **294**, 155 (1958).

[9] S. Herzog and U. Grimm, *Z. Chem.*, **4**, 32 (1964); S. Herzog, "Habilitation," Jena, E. Germany, 1957.

[10] G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. F. Smith Co., Columbus, Ohio, 1944.

$\epsilon \sim 50$, in the visible region, so at the 10^{-4} *M* concentration used, their absorption is negligible.

Beckman DU or Cary 14 spectrometers were used to record the absorbance changes. Standard 1-cm quartz cells fitted with serum caps penetrated by two syringe needles were deoxygenated by passing purified nitrogen into the cell through one of the needles, thus allowing a stream of nitrogen to flush the cell.

Either solid complex was dissolved in water or the complex prepared *in situ*. Calibrated, gas-tight syringes of the type commonly used for gas chromatography were used to add precise amounts of complex and acid solutions to the nitrogen-filled cells. The spectrometric cell compartments were thermostated to 25.0 ± 0.2°. Solutions used were preequilibrated to temperature in a thermostated water bath. Activation energies were obtained by following reactions over a 25° temperature range. All dissociation reactions were found to be first order in complex.

Formation of $V(phen)_3^{2+}$ was studied by recording the increase of the λ 760 mμ absorption of this ion. To the nitrogen-filled cells were added, during a series of kinetic runs, equal quantities of a 10^{-4} *M* VCl_2 solution and solutions of 1,10-phenanthroline varying in concentration from 0.016 to 0.0016 *M*. The kinetics of the reaction are, under these conditions, pseudo first order in the metal ion.

Results and Discussion

As observed in other dissociation studies of tris-bipyridine and tris-*o*-phenanthroline complexes, the rate of dissociation of the bipyridine complex, $V(bipy)_3^{2+}$, is strongly acid dependent while the effect of acid concentration on the dissociation of $V(phen)_3^{2+}$ is relatively small. The formation of the $V(phen)_3^{2+}$ ion is relatively slow, as is the dissociation of the vanadous complexes. Rate data are collected in Tables I and II.

Dissociation of Bipyridine Complexes.—Kinetic studies of the acid hydrolysis of tris(2,2′-bipyridine)-vanadium(II) perchlorate were performed using H_2SO_4 and $HClO_4$ solutions. Rates which agreed to within 2% were found by following the reaction at 412, 600, and 650 mμ. A compilation of reaction rates found at various acid concentrations is given in Table I. The acid dependence is shown in Figure 1. It should be noted that both upper and lower limiting rates are expected; however, the lower limiting rate was not obtainable because, at very low acid concentrations, the reaction is very slow and air oxidation of complex occurs faster than dissociation. Hence the experimental technique used does not allow reactions to run for longer than 8–12 hr. For all data reported, five or more runs were necessary to ensure reproducibility. Adventitious oxidation by air gave erratic results in a number of runs.

It will be noted in Figure 1 that rate constants for H_2SO_4 and $HClO_4$ of the same H^+ concentration gave different rate constants. The difference was only marked at high acid concentrations. It is considered that the $HClO_4$ data may be less reliable because of oxidation of vanadium(II), particularly at high concentration.

The dissociation of $V(bipy)_3^{2+}$ is observed to be first order in the complex, with no intermediates, isosbestic points, or residual absorbances being observed. It is likely that the dissociation is a stepwise process

$$H^+ + V(bipy)_3^{2+} \longrightarrow V(bipy)_2^{2+} + Hbipy^+$$

$$2H^+ + V(bipy)_2^{2+} \xrightarrow{\text{rapid}} V^{2+} + 2Hbipy^+, \text{ etc.}$$

with the rate-determining step being the loss of the first ligand. Reaction to the hydrated ion then follows rapidly. Since the spectrum of the tris complex is the same in strongly acid and neutral solutions, it is unlikely that any mechanism involving prior protonation of complex is involved.[11] The acid dependence of dissociation of bipyridine complexes is explained by the mechanism, depicted for the vanadium(II) complex in

TABLE I

RATE DATA FOR THE ACID HYDROLYSIS OF SOME VANADIUM(II) COMPLEXES

Medium	[Medium], *M*	Temp, °C	*k*, sec⁻¹
	$V(bipy)_3^{2+}$		
H_2SO_4	2.50	25.0	4.0×10^{-3}
	1.25	25.0	4.0×10^{-3}
	0.50	25.0	2.8×10^{-3}
	0.50	25.0	2.5×10^{-3}
	0.25	25.0	1.0×10^{-3}
	0.05	25.0	2.3×10^{-4}
$HClO_4$	1.25	25.0	1.9×10^{-4}
	0.50	25.0	1.4×10^{-4}
	0.25	25.0	7.8×10^{-5}
	0.13	25.0	4.3×10^{-5}
	0.10	25.0	3.2×10^{-5}
	0.10	25.0	2.2×10^{-5}
	0.01	25.0	6×10^{-6}
	0.10	35.0	8.6×10^{-4}
	0.05	35.0	3.8×10^{-4}
	0.01	35.0	5.8×10^{-5}
	0.10	45.0	2.3×10^{-3}
	0.01	45.0	3.1×10^{-4}
	0.005	45.0	1.1×10^{-4}
	$V(phen)_3^{2+}$		
HCl	0.30	45.0	1.8×10^{-4}
	0.60	45.0	1.8×10^{-4}
	1.00	45.0	1.8×10^{-4}
HTos[a]	0.30	45.0	6.5×10^{-5}
	0.50	45.0	7.4×10^{-5}
	0.75	45.0	8.0×10^{-5}
	1.00	45.0	8.8×10^{-5}
	0.50	34.3	3.2×10^{-4}
	0.50	51.0	1.2×10^{-3}
HTos +	0.50	25.0	6.8×10^{-5}
LiCl	0.50		
HTos +	0.50	25.0	7.0×10^{-5}
NaTos	0.50		

[a] HTos = *p*-toluenesulfonic acid.

TABLE II

RATE DATA FOR THE FORMATION OF TRIS(1,10-PHENANTHROLINE)VANADIUM(II) AT 25°[a]

[phen], *M*	k_{obsd}, sec⁻¹	$k_f = k_{obsd}/[phen]$, M^{-1} sec⁻¹
5.2×10^{-3}	1.7×10^{-2}	3.27
3.8×10^{-3}	1.2×10^{-2}	3.16
2.5×10^{-3}	6.9×10^{-3}	2.78
7.0×10^{-4}	1.7×10^{-3}	2.50
7.0×10^{-3}	2.2×10^{-2}	3.18
	Av	3.0 ± 0.30

[a] Concentration of V^{2+} was less than 5×10^{-4} *M*. The concentration of phenanthroline has not been corrected for the small amount of HCl ($<1 \times 10^{-4}$ *M*) present in the VCl_2 solution.

---

[11] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **49**, 180 (1953); E. A. Healy and R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 3807 (1957).

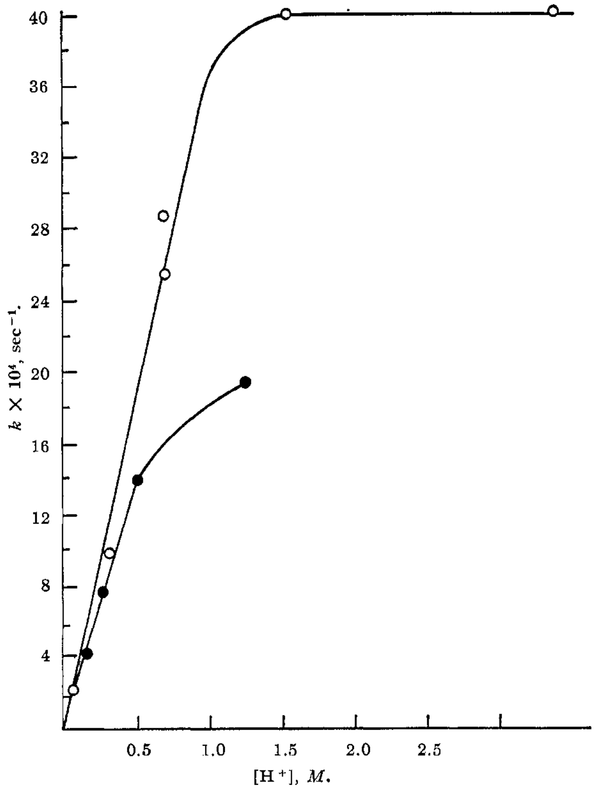

Figure 1.—Dependence of dissociation rate of tris(2,2′-bipyridine)vanadium(II) on hydrogen ion concentration: ○, in sulfuric acid; ●, in perchloric acid. The hydrogen ion concentration for H_2SO_4 was calculated from the data given by E. B. Robertson and H. B. Dunford, *J. Am. Chem. Soc.*, **86,** 5080 (1964).

Figure 2, first proposed to explain the acid hydrolysis of the $Fe(bipy)_3{}^{2+}$ ion.[2a] There are two dissociation pathways, one acid dependent. Assuming small steady-state concentrations of "half-bonded" intermediates, the value of the observed rate constant, k, is given by

$$k = \left(\frac{k_3 + k_4[H^+]}{k_2 + k_3 + k_4[H^+]}\right)k_1$$

At high acid concentrations, $k_\infty = k_1$; at low acid concentrations, $k_0 = k_1k_3/(k_2 + k_3)$. For the vanadium(II) complex, $k_\infty = 4.0 \times 10^{-3}$ sec^{-1}, $k_0 \leq 2 \times 10^{-5}$ sec^{-1}. The ratio $k_0/k_\infty = k_3/(k_2 + k_3) \leq 0.005$ is the probability that acid-independent dissociation will occur whenever the first V–N bond breaks. The value of this ratio is surprisingly small. Recently it has been shown[12] that Co, Ni, and Fe terpyridine complexes also have a very small value (about 10^{-4}) for the ratio of k_0/k_∞.

Dissociation of Phenanthroline Complexes.—As discussed for $V(bipy)_3{}^{2+}$, the $V(phen)_3{}^{2+}$ ion dissociates in acid solution with complete loss of color in the visible region, with no intermediates or isosbestic points seen, so it is likely that dissociation of the first ligand determines the rate, with succeeding stepwise reactions being rapid. Similar to results obtained for other phenanthroline complexes, acid concentration has only a small effect on the hydrolysis rate.[4] Kinetic data are compiled in Table I.

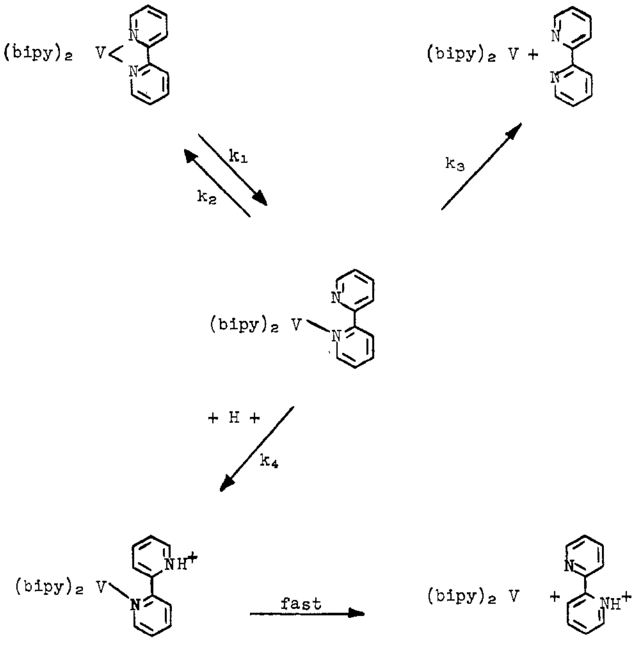

Figure 2.—Mechanism for the dissociation of tris(2,2′-bipyridine)-vanadium(II).

For hydrochloric acid, the rate is constant over a wide range of concentration of the acid, even though the ionic strength is also varying. For *p*-toluenesulfonic acid, the rate does change somewhat with concentration. However, if the ionic strength is held constant, the variation is less. The rate data as a function of concentration are shown in Figure 3. The activation energy for dissociation of $V(phen)_3{}^{2+}$ was found to be 21 ± 1 kcal, and $\Delta S^\ddagger$ was calculated as −8 eu. These values were determined in 0.50 *M* *p*-toluenesulfonic acid.

The dissociation of $V(phen)_3{}^{2+}$ is relatively acid independent because the rigid phenanthroline heterocycle cannot easily enter into any "half-bonded" structures. When a V–N bond is broken, either reclosure occurs or dissociation is effected by the breaking of the second V–N bond. Only the simple dissociation pathway is possible for this complex. Hence the observed rate constant is $k_1k_3/(k_2 + k_3)$.

Since no spectral change occurs at high acid concentration, a mechanism requiring prior protonation of complex is not likely. The rate is, however, dependent upon the nature of the ions present in the solution as shown in Figure 3. Effects such as those observed here have been found for dissociation of other phenanthroline complexes.[13,14] Jensen, Basolo, and Neumann have shown[14] that, in the presence of large anions, the rate of dissociation of the $Fe(phen)_3{}^{2+}$ ion is decreased substantially owing to association of the complex with the anions. Since the phenanthroline molecule is rigid, its tris complexes are not spherical but rather have three mutually perpendicular planes extending from the central ion leaving small pockets in which associated an-

---

[12] R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, **7,** 170 (1968).

[13] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50,** 24 (1954); J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **79,** 1286 (1957).

[14] A. Jensen, F. Basolo, and H. M. Neumann, *ibid.*, **80,** 2354 (1958).

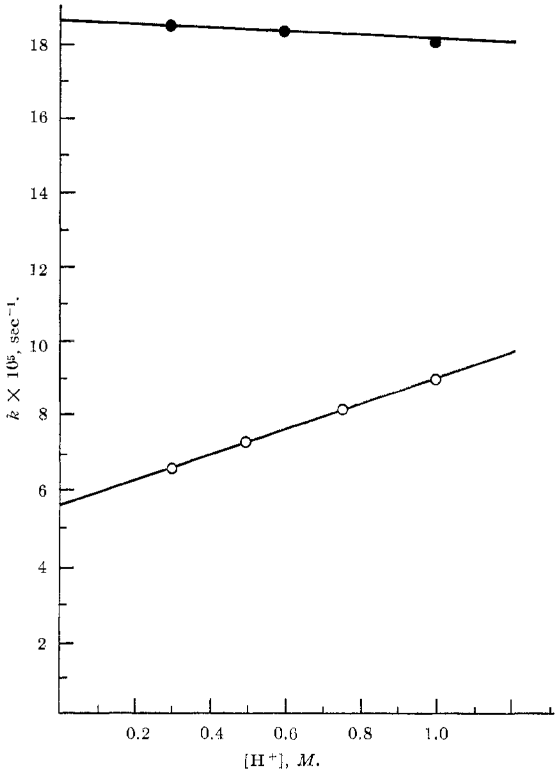

Figure 3.—Dependence of dissociation rate of tris(1,10-phenanthroline)vanadium (II) on concentration of HCl (●) and *p*-toluenesulfonic acid (○).

ionic species could reside. This association probably accounts for the observed decrease in rate when tosylate is present.

Formation of $V(phen)_3^{2+}$.—For this study, pseudo-first-order conditions in metal ion were realized by using large concentrations of phenanthroline, which also ensured thermodynamically complete formation of the tris complex. A plot of the pseudo-first-order rate constant *vs.* phenanthroline concentration is linear and passes through the origin; the rate data are collected in Table II. The reaction is thus second-order over-all, being first order in both metal ion and ligand. While a detailed study was not made, it appeared that the rate of growth of the final absorption was the same at all wavelengths. In other words, no intermediates were detected. There are two possible interpretations for these results: one is that the formation of the mono complex is rate determining, the bis and tris complexes being formed rapidly; the other is that all three complexes form at nearly equal rates and that their absorption spectra are similar in the 600–800-mμ region, the extinction being proportional to the number of coordinated groups. In either case the second-order rate constant, $k_f = k_{obsd}/[\text{phen}]$, is the true rate constant for the formation of the mono species.

No decision can be made about the magnitude of the rate constants for the second and third stages of formation from these studies. The absorption spectra of the intermediate complexes $V(phen)^{2+}$ and $V(phen)_2^{2+}$ are not known, though they are expected to be different from $V(phen)_3^{2+}$. Formation constants for the phen system are not known for vanadium(II), though the complexes are expected to all be somewhat more stable than the corresponding bipy complexes. The latter values are 4.9, 4.7, and 3.8 for the logarithms of the three successive formation constants.[6] In other cases studied it has been found that the three successive formation rate constants are very similar, but not equal.[15]

The rate constant 3.0 M^{-1} sec^{-1} for the reaction

$$V^{2+} + \text{phen} \longrightarrow \text{Vphen}^{2+}$$

may be compared with other recent data for similar formation reactions of V^{2+}. Table III collects the available rate data for V^{2+} complexes, together with the corresponding data for Ni^{2+} complexes. It can be seen that the reactions of vanadium(II) are unusually slow, even slower than for nickel(II) systems. The exception is the dissociation of the phenanthroline complexes, which is abnormally slow for nickel.

Table III

Rate Constants for V^{2+} Compared to Those for Ni^{2+} in Water at 25°

Reaction	V^{2+}	Ni^{2+}	Ref
M^{2+} + SCN^- form	9.0 M^{-1} sec^{-1}	6 × 10^3 M^{-1} sec^{-1}	*b, c*
M^{2+} + bipy form	0.3 M^{-1} sec^{-1}	1.6 × 10^3 M^{-1} sec^{-1}	*d–f*
M^{2+} + phen form	3.0 M^{-1} sec^{-1}	3.2 × 10^3 M^{-1} sec^{-1}	*f, g*
M^{2+} + terpy form	0.8 M^{-1} sec^{-1}	1.4 × 10^3 M^{-1} sec^{-1}	*e, h*
$M(bipy)_3^{2+}$ dissn[a]	<2 × 10^{-5} sec^{-1}	2.4 × 10^{-3} sec^{-1}	*f, g*
$M(phen)_3^{2+}$ dissn	1 × 10^{-4} sec^{-1}	6 × 10^{-6} sec^{-1}	*f, i*

[a] Limiting rate constant at zero acid concentration. [b] B. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89,** 722 (1967); see also J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7,** 250 (1968). [c] A. G. Davis and W. M. Smith, *Proc. Chem. Soc.*, 380 (1961). [d] Quoted by R. G. Wilkens and M. Eigen, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, Chapter 3. [e] L. E. Bennett and H. Taube, *Inorg. Chem.*, **7,** 254 (1968). [f] See ref 3. [g] This work. [h] R. H. Holyer, C. P. Hubbard, S. F. A. Kettle, and R. G. Williams, *Inorg. Chem.*, **5,** 622 (1966). [i] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75,** 5102 (1953).

Crystal field theory indeed predicts that complexes of vanadium(II), a d^3 system, will react slowly. The order of reactivity predicted[4] for the divalent ions of the first transition series is Cu, Zn, Mn > $Fe(t_{2g}^4e_g^2)$ > Co > $Cr(t_{2g}^4)$ > V, Ni > $Fe(t_{2g}^6)$. This is in very good agreement with what is observed.[16] The reactivities of Ni and V are predicted equal on the simple crystal field basis. Table IV shows a collection of activation energies and predicted crystal field activation energies for the series V to Zn. The loss in crystal field stabilization energy calculated for going from an octahedral (possibly distorted) structure to a square-pyramidal structure is called the crystal field activation energy, CFAE.[17] The greater its magnitude, the slower the reaction should be. The value of the crystal field parameter, Dq, is about 4.5 kcal/mol for phenananthroline and bipyridine ligands.

---

(15) D. W. Margerum, R. I. Bystroff, and C. V. Banks, *J. Am. Chem. Soc.*, **78,** 4211 (1956); R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 4514 (1957).

(16) See footnotes *d* and *f* of Table III.

(17) N. S. Hush, *Australian J. Chem.*, **15,** 378 (1962); see also T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory," Harper and Row, New York, N. Y., 1965, Chapter 5.

TABLE IV
KINETIC DATA AND CFAE'S FOR THE DISSOCIATION OF SOME COMPLEXES OF THE FIRST TRANSITION SERIES

System	Complex	$\Delta S^{\ddagger}$, eu	E_a, kcal	CFAE, Dq
d^3	$V(phen)_3^{2+}$ [a]	−8	21.3	2
	$V(bipy)_3^{2+}$ [a]	Slow	...	2
d^4	$Cr(bipy)_3^{2+}$	+13	22.6	1.4
d^5	$Mn(phen)_3^{2+}$	Fast	...	0
d^6	$Fe(phen)_3^{2+}$	+28	32.1	4
	$Fe(bipy)_3^{2+}$	+17	28.4	4
d^7	$Co(phen)_3^{2+}$	+5	19.4	0
d^8	$Ni(phen)_3^{2+}$	+1	26.2	2
	$Ni(bipy)_3^{2+}$	+2	22.2	2
d^9	$Cu(phen)_3^{2+}$	Fast	...	0
d^{10}	$Zn(phen)_3^{2+}$	Fast	...	0

[a] This work. For other sources see ref 4, p 150.

The substitution reactions of d^3 systems are also predicted to be slow by valence bond theory.[18] In this approach d^8 systems are predicted to be labile, since they would be ionic or outer-orbital complexes.[18] The slower reactions of V(II) than of Ni(II) somewhat substantiate this conclusion. However, nickel complexes are certainly much less labile than those of Mn(II), high-spin Fe(II), Co(II), Cu(II), and Zn(II), all of which are outer-orbital, or ionic, complexes. The activation energy for dissociation of $Ni(phen)_3^{2+}$ is greater than that for $V(phen)_3^{2+}$ (Table IV). In the case of formation of the monothiocyanate complexes, the activation energy is greater[19] for V^{2+} than for Ni^{2+}.

Acknowledgment.—This work was supported by the National Science Foundation under Grants 3400 and 6341 X to Northwestern University. The authors are indebted to Dr. W. P. Schaefer of the California Institute of Technology for a helpful exchange of information.

[18] H. Taube, *Chem. Rev.*, **50**, 69 (1952).

[19] J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).

CONTRIBUTION FROM THE INORGANIC MATERIALS RESEARCH DIVISION, LAWRENCE RADIATION LABORATORY,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

Nuclear Magnetic Resonance Studies of the Coordination of Vanadyl Complexes in Solution and the Rate of Elimination of Coordinated Water Molecules

BY K. WÜTHRICH AND ROBERT E. CONNICK

Received March 15, 1968

The temperature dependence of the O^{17} nmr line width in O^{17}-enriched aqueous solutions of the vanadyl complexes with the chelating ligands ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), 2-picolyliminodiacetate (PIDA), iminodiacetate (IDA), 5-sulfosalicylic acid (SSA), and Tiron (TIR) has been measured. The dependence on temperature of the complex formation equilibria was obtained from esr studies, so that the concentrations of the various paramagnetic species present in solutions of VO^{2+} ions and one of the ligands were known over the whole temperature range studied. The data obtained for $VO(EDTA)^{2-}$ show that a possible exchange of the doubly bonded "vanadyl oxygen" would be too slow to be observed by the O^{17} nmr technique. The exchange of the water molecule in the axial position opposite the vanadyl oxygen in $VO(SSA)_2^{4-}$ and $VO(TIR)_2^{6-}$ contributes at most a very small line broadening which is consistent with a very short lifetime with respect to chemical exchange of the axial water. Large relaxation effects arise from the presence of the 1:1 complexes with IDA, SSA, and TIR which have equatorial positions available for coordination of water molecules. The influence of the ligands in adjoining positions on $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and the first-order rate constant k of the water exchange from the equatorial coordination sites and on the scalar coupling constant A/h of O^{17} in the equatorial positions has been studied. The data obtained from solutions of the complexes with the tetradentate ligands NTA and PIDA can be interpreted in terms of a pyramidal structure of these compounds. The vanadyl oxygen and the four equatorial positions would then be at the corners of a tetragonal pyramid, with V^{4+} somewhat above the plane of the base. In a similar pyramidal structure of the hydrated vanadyl ion one would expect only four waters to be tightly bound, which would be consistent with the experimental data. A comparison of the O^{17} relaxation data with chemical shift measurements and proton relaxation experiments reported by others indicates that, in addition to the effects arising from the chemical exchange from the equatorial positions, the nuclear resonance in the bulk water of VO^{2+} solutions is influenced by the exchange of loosely coordinated waters. This may correspond to weak coordination of water molecules in the axial position opposite the vanadyl oxygen and on the four faces of the pyramid formed by VO^{2+} and the four more tightly bound equatorial waters.

I. Introduction

In dilute aqueous solutions of vanadyl ions a single nuclear magnetic resonance of O^{17} or H^1 can be observed which corresponds to that of the bulk water modified by the exchange of O^{17} and protons in and out of the coordination spheres of V^{4+}. Measurement of the line width of that resonance in metal ion solutions is a convenient method for studying the rate of exchange of O^{17} and H^1 between the bulk water and the coordination spheres of the metal ions, as well as the interaction between the unpaired electrons of the metal ion and the nuclei of the coordinated water molecules.[1] Half the line width at half-height, $\delta\omega$, expressed in radians per second, is equal to the reciprocal of the apparent transverse relaxation time T_2 and is given by

$$\delta\omega = \frac{1}{T_2} = \frac{1}{T_{2H_2O}} + \frac{1}{T_{2p}} = \delta\omega_{H_2O} + \delta\omega_p \qquad (1)$$

[1] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); **41**, 2553 (1964).