

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

An Investigation of the Vanadium(II)–Vanadium(III) Couple with Polypyridine Ligands

BY LARRY E. BENNETT AND HENRY TAUBE

Received June 26, 1967

In harmony with earlier preliminary work, $V(\text{bipy})_3^{2+}$ has been shown to be a very much slower reducing agent than $\text{Cr}(\text{bipy})_3^{2+}$. The vanadium(III)–polypyridine species formed as the immediate product of the oxidation of the $V(\text{II})$ complex has been shown to be very labile. Ligand is lost rapidly and disproportionation or further oxidation ensues so that a VO^{2+} –polypyridine species is in fact the final product of the oxidation. Thus, although $V(\text{bipy})_3^{2+}$ does reduce $\text{Ru}(\text{NH}_3)_6^{3+}$, for example, E° for $V(\text{bipy})_3^{2+}, 3^+$ may in fact be much more negative than for $\text{Ru}(\text{NH}_3)_6^{2+}, 3^+$, the over-all reaction being driven by the instability of $V(\text{bipy})_3^{3+}$. Application of the “relative” Marcus theory to the rate data for a number of oxidants acting on vanadium(II)–polypyridine complexes suggests that E° for $V(\text{plpy})_m^{2+}, 3^+$ is somewhat more positive than -0.8 V. Our study is inconclusive on the matter of whether the self-exchange in $V(\text{bipy})_3^{2+}, 3^+$ is significantly less rapid than for $\text{Fe}(\text{bipy})_3^{2+}, 3^+$, for example.

The comparison of the rates at which outer-sphere reducing agents on the one hand and inner-sphere reducing agents on the other act on a common series of oxidizing agents is clearly of value in exploring the relation between rates and mechanisms of electron-transfer processes. Some comparisons of this kind have been made with $\text{Co}(\text{III})$ complexes as the common oxidizing agents.¹ Reactions of $\text{Cr}^{2+}(\text{aq})$ with these complexes have been extensively investigated, in part, at least because this particular reducing agent exhibits a marked preference for reacting by inner-sphere mechanisms. The ion $\text{Co}(\text{CN})_5^{3-}$ is interesting because with many oxidants both inner- and outer-sphere mechanisms operate, the latter being favored by increased concentration of cyanide ion.² The reagent $\text{Ru}(\text{NH}_3)_6^{2+}$, by virtue of its inertia to substitution, is restricted in reaction with $\text{Co}(\text{III})$ complexes to outer-sphere paths.³ Within the class of outer-sphere reducing agents, it represents an extreme in behavior because the ammonia ligands have no low-lying unoccupied orbitals, and thus effects arising from the delocalization of electrons over the ligands are at a minimum. Among the outer-sphere reducing agents, those in which the d electrons can be delocalized are of unusual interest. The ion $\text{Cr}(\text{bipy})_3^{2+}$ ⁴ has been offered¹ as exemplifying this class in its reactions with cobalt(III) complexes, but there is no conclusive proof that the reactions actually take place by outer-sphere mechanisms. The ion is known to be substitution labile, and thus although the activated complex for the reduction of a number of $\text{Co}(\text{III})$ complexes has been shown to contain three bipy groups, there is a possibility that one of the ligands in the activated complexes is monodentate to $\text{Cr}(\text{II})$.

In the context of these results it seemed worthwhile

to explore reactions of $V(\text{bipy})_3^{2+}$ as reductant. Since $V(\text{II})$ has a d^3 electronic configuration, substitution on the metal ion is expected to be much slower than for $\text{Cr}(\text{II})$, and therefore the geometry of $V(\text{bipy})_3^{2+}$ just prior to electron transfer is expected to be fixed with more certainty than it is for $\text{Cr}(\text{bipy})_3^{2+}$. Our interest in $V(\text{bipy})_3^{2+}$ was strengthened by the observation⁵ that $V(\text{bipy})_3^{2+}$ reacts with $\text{Co}(\text{III})$ complexes much less rapidly than does $\text{Cr}(\text{bipy})_3^{2+}$. This difference in behavior for ions of the same charge which are adjacent in the periodic table is notable, and the reasons for the difference are worthy of investigation. In terms of the “relative” Marcus theory,⁶ the difference can be associated either with an unusually slow rate for the self-exchange reaction in the couple $V(\text{bipy})_3^{2+}, 3^+$, or with a much less favorable driving force for the reduction of cobalt(III) complexes by $V(\text{bipy})_3^{2+}, 3^+$ as compared to $\text{Cr}(\text{bipy})_3^{2+}, 3^+$. Because of the unexpected complications in the chemistry of the $V(\text{II})$ – $V(\text{III})$ complexes which we encountered, we have been unable to provide a definite answer to the question of why $V(\text{bipy})_3^{2+}$ is such a slow reducing agent. The complications themselves are of interest; their description and the consideration of their implications for the operation of the redox couple is the main theme of this paper.

Experimental Section

Materials.—Hexaammineruthenium(III) chloride was recrystallized by adding cold hydrochloric acid to a cold, filtered aqueous solution of salt obtained from Johnson, Matthey and Co. We concluded, on the basis of measurements of the extinction coefficient at 328 $m\mu$, where $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ absorbs very strongly (extinction coefficient 1930 compared to ~ 75 for the hexaammine⁷), that the preparation contained less than 1% of the pentaammine complex.

Bis(2,2',2''-tripyridine)cobalt(III) perchlorate monohydrate and tris(2,2'-bipyridine)cobalt(III) perchlorate trihydrate were prepared and recrystallized following the procedure of Burstall

(1) A. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).

(2) J. Halpern and S. Nakamura, “Proceedings of the 8th Conference on Coordination Chemistry,” Vienna, Springer-Verlag, West Berlin, 1964, p. 271.

(3) J. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

(4) 2,2'-Bipyridine will be represented by bipy, 2,2',2''-tripyridine by trpy, 1,10-phenanthroline by phen, and the term polypyridine (plpy) will be used to describe the class of ligands. Ethylenediaminetetraacetic acid will be represented by H_4EDTA .

(5) A. M. Zwickel, unpublished work.

(6) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964); *J. Phys. Chem.*, **67**, 853 (1963).

(7) H. Hartmann and C. Buschbeck, *Z. Physik. Chem.*, **11**, 120 (1957).

and Nyholm⁸ but using perchlorate in place of chloride ion. *Anal.* Calcd for the trpy and bipy compounds: C, 42.8, 40.9; H, 2.94, 3.43; N, 10.0, 9.55. Found: C, 43.0, 40.9; H, 3.1, 3.55; N, 10.3, 9.50.

Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared by the method of Dwyer, *et al.*⁹ The molar extinction coefficients measured as 328 at 536 μ and 220 at 380 μ compare reasonably well with the average of those previously reported^{10,11} (300, 347 and 200, 246). *Anal.* Calcd: C, 28.70; N, 6.66; H, 3.79. Found: C, 28.65; N, 6.79; H, 3.96.

To minimize photochemical decomposition, the ion Fe(EDTA)⁻ was generated just prior to use. A standardized solution of ferric ammonium sulfate, *ca.* $8 \times 10^{-3} M$, was added to a solution containing $1.0 \times 10^{-2} M$ trifluoroacetic acid and the desired excess of Na₂H₂EDTA.¹² The reactions were studied using oxidant solutions handled with minimal exposure to light.

Cratonatopentaamminecobalt(III) perchlorate was prepared and analyzed by a method similar to that of Butler and Taube.¹³ *Anal.* Calcd: Co, 13.76; C, 5.97; H, 4.51; N, 17.40. Found: Co, 13.5; C, 5.9; H, 4.65; N, 17.70.

Purified and analyzed samples of acetato- and chloropentaamminecobalt(III) perchlorate and twice-recrystallized sodium trifluoroacetate were supplied by D. Huchital, R. Butler, and R. Jordan, respectively.

The ligand 2,2',2''-tripyridine was recrystallized from reagent petroleum ether (bp 30–60°) after filtering off a brown residue.

Solutions of sodium perchlorate were prepared from reagent grade perchloric acid and primary standard sodium carbonate.

Solutions containing V(II) were prepared by reducing acidic (trifluoroacetic) solutions of recrystallized ammonium metavanadate at a mercury cathode. The solutions were analyzed by two methods—oxidizing V(II) with Fe(III), then determining excess Fe(III) by the I₂-S₂O₃²⁻ method, or oxidizing V(II) with excess Co(NH₃)₆Cl²⁺, then determining the latter spectrophotometrically, taking account of the V(III) absorption at 532 μ , with excellent agreement between the methods.

Vanadium(III) solutions were produced by controlled air oxidation of V(II), testing for the consumption of the lower oxidation state by spectrophotometric means, both directly on the solution¹⁴ and resorting to trpy to develop the color of the lower oxidation state.

Solutions containing hexaammineruthenium(II) were produced from Ru(NH₃)₆²⁺ using Cr²⁺(aq) (this generated by Zn amalgam) as described by Endicott and Taube.³

Stock solutions of V(bipy)₃²⁺ and V(tryp)₂²⁺ were generated using the V(II) stock solution and excess ligand. Enough ligand was added so that the solution, after complete complexation, would contain 10⁻³ *M* ligand in the case of trpy (10% ethanolic solution, pH 5.0) and 10⁻² *M* for the bipy (pH 4.5). The solutions after mixing were allowed to equilibrate for about 15 hr.

Conditions and Methods.—All reactions were studied at 25°. Except as otherwise noted, the ionic strength was maintained at 0.10 *M* with sodium trifluoroacetate. Doubly distilled water was used to make up the solutions. Air-sensitive reactants were prepared and handled under nitrogen which was purged of oxygen using a Cr(II) scrubbing solution. The limited solubility of tripyridine in water necessitated the use of 10% ethanolic solutions.

The course of the reactions was followed spectrophotometrically, observing the decrease with time in absorption in the low-energy charge-transfer band of the V(II) complex at a wavelength where it is the only appreciably absorbing species. When this condition is met, the equations

$$\ln \frac{A_t - A_\infty}{A_0 - A_\infty} = -kt[\text{oxid}]$$

$$\ln \frac{A_t}{A_t - A_\infty} - \ln \frac{A_0}{A_0 - A_\infty} = \frac{2A_\infty kt}{ab}$$

apply to the pseudo-first-order case (oxidant in excess) and to the second-order case (reactant concentrations comparable, V(II) in excess), respectively. *A*₀, *A*_{*t*}, and *A*_∞ are the absorbancies at time 0, *t*, and ∞. The V(II) extinction coefficient is *a*, and *b* is the path length.

When pH determinations could be made outside the reaction vessel, a Beckman Model G pH meter was used. For the measurements on the Co(trpy)₃²⁺-V(trpy)₂²⁺ system a standardized Beckman 39183 combination electrode was inserted into the reaction vessel through a 14/30 ground-glass joint using a rubber sleeve to provide an air-tight fit. The pH was measured on the expanded scale of a Beckman Expandomatic meter. On the basis of the studies reported by Bates¹⁵ we concluded that the pH can be measured in 10% ethanol with almost as much accuracy as in water. The absolute error in the pH measured was estimated to be less than 0.1 unit and the relative error to be considerably less than this.

For calculations of solution composition the value of 4.57 × 10⁻⁵ for the dissociation constant¹⁶ of Hbipy⁺ is used; for the conjugate acids derived from trpy we have used the constants 1.55 × 10⁻⁵ and 5.2 × 10⁻⁴ in the appropriate equation.¹⁷

In presenting the results of kinetic studies, the specific rates recorded are defined by the equation

$$\frac{-d[\text{V(II)}]}{dt} = k[\text{V(II)}][\text{oxid}]$$

By no means all of the kinetic data conform to the equation and in some cases, as will appear in the discussion of the results, *k* is a function of the concentration variables.

Results

Characterization of the Vanadium Complexes.—

The species V(bipy)₃²⁺ has been reported by several investigators.^{18–21} We have found Beer's law to apply to the absorption peak at 649 μ over a concentration range 2–15 × 10⁻⁵ *M* V(II) with ligand in excess. If enough time is allowed for the attainment of coordination equilibrium, the extinction coefficient at this wavelength varies less than 4% (within experimental error) on varying the concentration of free ligand²² from 1.6 × 10⁻⁴ *M* (2.4 × 10⁻⁵ *M* V(II), pH 5.0) to 106 × 10⁻⁴ *M* (1.5 × 10⁻⁴ *M* V(II), pH 5.5). (These concentrations are calculated on the assumption that each V(II) consumes three bipy.) A similar study was conducted with trpy as ligand at 767 μ with free trpy ranging from 4.8 × 10⁻⁵ *M* (8.0 × 10⁻⁵ *M* V(II), pH 4.4) to 170 × 10⁻⁵ *M* (8.0 × 10⁻⁵ *M* V(II), pH 5.5).

Some extinction coefficients for the V(II) complexes we have investigated are summarized herein: for V(bipy)₃²⁺, *a*_{max}⁶⁴⁹ = 6900 ± 200, *a*_{max}⁴⁰² = 4060 ± 120;

(15) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 204–227, 334.

(16) T. R. Harkins and H. Freiser, *J. Am. Chem. Soc.*, **77**, 1374 (1955).

(17) P. O'D. Offenhardt, P. George, and G. P. Haight, Jr., *J. Phys. Chem.*, **67**, 116 (1963).

(18) R. Murray, Ph.D. Thesis, University of London, 1962.

(19) S. Herzog and R. Taube, *Naturwissenschaften*, **43**, 35 (1956).

(20) S. Herzog, *Z. Anorg. Allgem. Chem.*, **294**, 155 (1958).

(21) J. M. Crabtree, D. W. Marsh, J. C. Tomkinson, R. J. P. Williams, and W. C. Fernelius, *Proc. Chem. Soc.*, 336 (1961).

(22) The concentration of free ligand refers throughout to that which is present uncomplexed by metal ion or by protons.

(8) F. H. Burstall and R. S. Nyholm, *J. Am. Chem. Soc.*, **72**, 3570 (1950).

(9) F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 29 (1955).

(10) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(11) B. E' Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

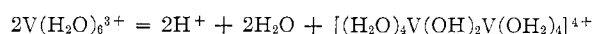
(12) Similar to the method described by A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, **8**, 206 (1956).

(13) R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, **87**, 5597 (1965).

(14) E. L. Martin and K. E. Bentley, *Anal. Chem.*, **34**, 354 (1962).

for $V(\text{phen})_3^{2+}$, $a_{\text{max}}^{645} = 7900 \pm 400$; for $V(\text{trpy})_2^{2+}$, $a_{\text{max}}^{767} = 9300 \pm 400$, $a_{\text{max}}^{402} = 7230 \pm 310$.

A solution of $5 \times 10^{-4} M$ $V(\text{III})$ and $5.7 \times 10^{-4} M$ trpy developed a red color over a period of *ca.* 1 hr (pH 3.5) with peaks at 685 and 474 $m\mu$ (absorbancies of 0.76 and 0.81, respectively) and a shoulder on the latter peak at 540 $m\mu$. Anderegg²³ has concluded, as have other workers referred to in his paper, that the dominant form of $\text{Fe}(\text{III})$ in phenanthroline and bipyridine solution is a dimeric species. An analogous species has been reported^{18,24,25} for $\text{Cr}(\text{III})$. The tendency of complexes of this kind to dimerize seems to parallel that of the aquo ions. In view of these facts and the fact that K for the reaction



has the value $10^{-8.9}$,²⁶ it is reasonable to suppose that $V(\text{III})$ in our solution also was dimerized. This conclusion is supported by the fact that the absorption band for the $V(\text{III})$ - trpy solution at 474 $m\mu$ in absorbancy, position, and shape is very similar to that of the aquo dimer.²⁷ It should also be noted that Morris²⁸ has observed a deep violet-purple color in $V(\text{III})$ -phen solutions which he attributed to the dimeric $(\text{phen})_2V(\text{OH})_2V(\text{phen})_2^{4+}$.

Substitution Reactions of the $V(\text{II})$ Complexes.—

The particular advantage of vanadium(II)-polypyridine complexes over the corresponding $\text{Cr}(\text{II})$ complexes is their greater inertia to substitution. Though it was not our primary purpose to study the rates of substitution in the vanadium complexes, we did consider it necessary to do a few experiments to learn approximately how labile they are.

A solution containing $V(\text{bipy})_3^{2+}$ when injected into a trifluoroacetate-trifluoroacetic acid buffer at pH 1.1 shows a first-order decrease in absorbancy at 649 $m\mu$ through 90% reaction, corresponding to a rate constant of $(2.7 \pm 0.4) \times 10^{-4} \text{ sec}^{-1}$. Using data from a similar experiment with $V(\text{trpy})_2^{2+}$ (now in 10% ethanolic solution and following the absorbance at 767 $m\mu$) plotted as for a first-order reaction, the slope continues to decrease approximating linearity as the reaction becomes too slow to follow conveniently. Consistent with these data and with the more exhaustive results for the $\text{Ni}(\text{II})$ - trpy and $\text{Co}(\text{II})$ - trpy systems,²⁹ we have assumed that the dissociation of the second tripyridine ($V(\text{trpy})_{\text{aq}}^{2+} \rightarrow V(\text{II})_{\text{aq}}^{2+} + \text{trpy}$) is rate determining. The dissociative half-life of $V(\text{trpy})_{\text{aq}}^{2+}$ is estimated from the approximately linear portion of the plot as roughly 36 hr. Extrapolation of the linear portion to $t = 0$ yields a reasonably close upper limit for the extinction coefficient of the product of the first stage as 80% of that for the original ion. Varying this value

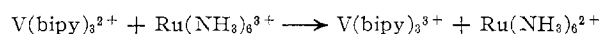
between 75 and 80%, the half-life for the dissociation of the first trpy gauged from the initial slope is 16 ± 4 hr. The rate of dissociation of $V(\text{phen})_3^{2+}$ is expected to be comparable to but slightly slower than for $V(\text{bipy})_3^{2+}$.²⁹

In a single experiment the formation of $V(\text{trpy})_2^{2+}$ from V_{aq}^{2+} was studied in the presence of a large excess of ligand (10% ethanol, pH 5.5, $[\text{trpy}] = 1.7 \times 10^{-3} M$). A plot of $\ln \{ [V(\text{II})]_0 - [V(\text{trpy})_2^{2+}] \}$ vs. t was linear with a slope of $-1.4 \times 10^{-3} \text{ sec}^{-1}$. This corresponds to a rate constant for the addition of the first ligand of $0.8 M^{-1} \text{ sec}^{-1}$ if, as seems likely from the cobalt and nickel results,²⁹ the addition of the first ligand ($V(\text{II})_{\text{aq}} + \text{trpy} \rightarrow V(\text{trpy})_{\text{aq}}^{2+}$) is rate determining. The formation of the bipy species was not amenable to straightforward analysis (one-half final absorbancy at 649 $m\mu$ for $8 \times 10^{-5} M$ $V(\text{II})$ solutions developed in 3 and 30 min with 1.2×10^{-2} and $1.0 \times 10^{-3} M$ bipy , respectively).

Stoichiometry.—Some general remarks on the stoichiometry are in order because it does not conform to the reasonable expectation that the change in oxidation state for vanadium is from +2 to +3. For the reactions $V(\text{bipy})_3^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$, $V(\text{trpy})_2^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$, $V(\text{bipy})_3^{2+} + \text{Co}(\text{bipy})_3^{3+}$, and $V(\text{bipy})_3^{2+} + \text{Fe}(\text{EDTA})^-$, even with an excess of the $V(\text{II})$ complex, 2 mol of oxidant was consumed for each mol of reductant under conditions approximating those of the kinetic studies. A complication was observed in some of the $\text{Ru}(\text{NH}_3)_6^{3+} + V(\text{bipy})_3^{2+}$ experiments owing to the slow development of a red color (not characteristic of the $V(\text{III})$ - bipy complex). We assume it is caused by a Ru - bipy species, since it is observed in solutions containing no vanadium. The final $V(\text{bipy})_3^{2+}$ concentration in these reactions was determined taking advantage of the fact that it but not the red complex is oxidized rapidly by O_2 . In some systems to be discussed below, evidence for the formation of a fugitive $V(\text{III})$ species was obtained.

$\text{Ru}(\text{NH}_3)_6^{3+}$ as Oxidant.—The complication in the bipy system arising from the slow development of the red color was avoided by having $\text{Ru}(\text{NH}_3)_6^{3+}$ in large excess and, this being provided for, the kinetic data obey simple kinetics over wide concentration ranges. The results of the kinetic studies with $\text{Ru}(\text{NH}_3)_6^{2+}$ are summarized in Table I.

As is more fully described when the results using $\text{Co}(\text{trpy})_2^{3+}$ as oxidant are presented, the $V(\text{III})$ - trpy complex disproportionates very slowly compared to the rate at which the over-all reaction with $\text{Ru}(\text{NH}_3)_6^{3+}$ takes place. Thus it seems likely that in the present system $V(\text{III})$ disappears by being oxidized rather than by disproportionation to $V(\text{II})$ and $V(\text{IV})$. We therefore take the specific rates recorded for the oxidations with $\text{Ru}(\text{NH}_3)_6^{3+}$ as measuring the rates of the process



The sensitivity of the rates to the nature of the counterion are illustrated in Table II.

The variation of k with $[\text{ClO}_4^-]$ is remarkably linear

- (23) G. Anderegg, *Helv. Chim. Acta*, **45**, 1643 (1962).
 (24) A. Barnshaw and J. Lewis, *J. Am. Chem. Soc.*, **83**, 396 (1961); *Nature*, **181**, 1262 (1958).
 (25) R. G. Inskoop and M. Benson, *J. Inorg. Nucl. Chem.*, **20**, 290 (1961).
 (26) L. Pajdowski, *Roczniki Chem.*, **37**, 1351, 1363 (1963).
 (27) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).
 (28) B. Morris, reported by W. W. Brandt, F. P. Dwyer, and E. C. Gyarias, *Chem. Rev.*, **54**, 959 (1954).
 (29) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

TABLE I
 REACTION OF $\text{Ru}(\text{NH}_3)_6^{3+}$ WITH $\text{V}(\text{bipy})_3^{2+}$

$10^3[\text{V(II)}], M$	$10^3[\text{Ru(III)}], M$	$10^3[\text{bipy}], M$	$10^3[\text{Hbipy}^+], M$	pH	$k, M^{-1} \text{sec}^{-1}$
3.54	3.55	3.0	0.2	5.5	0.110
10.2	11.9	1.1	1.3	4.3	0.130
3.28	6.25	13.0	0.30	6.0	0.110
6.77	1.25	0.50	0.17	4.8	0.113
13.5	5.89	1.2	0.54	4.7	0.115
53.7	0.733	4.2	1.3	4.8	0.123
13.7	5.89	8.8	4.8	4.6	0.111
7.03	8.07	2.5	1.9	4.4	0.122
Av					0.117

 TABLE II
 EFFECT OF PERCHLORATE ON THE RATE OF THE
 $\text{V}(\text{bipy})_3^{2+}$ – $\text{Ru}(\text{NH}_3)_6^{3+}$ REACTION^a

$10^3[\text{Ru}(\text{NH}_3)_6^{3+}], M$	$[\text{ClO}_4^-], M$	$k, M^{-1} \text{sec}^{-1}$
4.55	0.010	0.349
1.32	0.025	0.589
1.32	0.049	0.963
1.29	0.076	1.42

^a $[\text{V(II)}] = 10^{-4} M$; $[\text{bipy}] = 0.002 M$; $[\text{Hbipy}^+] = 0.001 M$; $\mu = 0.11 \pm 0.01$, made up largely by NaClO_4 – NaCl .

over the concentration range covered. If the rate function $[\text{V(II)}][\text{Ru(III)}](k_1 + k_2[\text{ClO}_4^-])$ is adopted, k_2 is found to be $16.5 M^{-2} \text{sec}^{-1}$. Here k_1 refers to reaction in chloride rather than trifluoroacetate media.

When bipy is the ligand, even with V(II), the possibility exists that one end of the ligand is released from the metal ion in the activated complex. The likelihood of such a process taking place is much less for phen, and thus some experiments were done in which V(II) was complexed by the more rigid ligand. The results of these experiments are shown in Table III. Under the same conditions when $\text{V}(\text{bipy})_3^{2+}$ is the reducing agent, $k = 0.15 M^{-1} \text{sec}^{-1}$.

 TABLE III
 THE REACTION OF $\text{V}(\text{phen})_3^{2+}$ WITH $\text{Ru}(\text{NH}_3)_6^{3+}$ ^a

$10^3[\text{Ru(III)}], M$	$10^3[\text{phen}], M$	$10^3[\text{Hphen}^+], M$	pH	$k, M^{-1} \text{sec}^{-1}$
3.36	5.4	2.4	5.3	0.150
3.30	9.8	5.0	5.3	0.148
6.77	8.9	5.2	5.2	0.139
Av				0.146

^a $[\text{V(II)}] = 7 \times 10^{-5} M$; $\mu = 0.16$ – 0.17 , made up with NaO_2 – C_2F_3 .

Kinetic complications do appear in the oxidation of $\text{V}(\text{trpy})_2^{2+}$ with $\text{Ru}(\text{NH}_3)_6^{3+}$. A summary of the data for this system is presented in Table IV.

The data for the experiments at pH 5.5 corresponding to entries 1–5 of Table IV show no anomalies in the plots up to 90% of reaction, whether $[\text{Ru}(\text{NH}_3)_6^{3+}]$ was about equal to $[\text{V(II)}]$ or whether it was in large excess. At lower pH (*cf.* entries 6–8), the specific rates decrease as the reaction progresses and the values recorded in the table were taken from the initial rates. We conclude, on the basis that the data for experiment 7 were within experimental error superimposable on those for experiment 6, that the inhibition is little

 TABLE IV
 THE REACTION OF $\text{V}(\text{trpy})_2^{2+}$ WITH $\text{Ru}(\text{NH}_3)_6^{3+}$ ^a

Entry	$10^4[\text{Ru}(\text{NH}_3)_6^{3+}], M$	$10^4[\text{Ru}(\text{NH}_3)_6^{3+}], M$	$10^3[\text{trpy}], M$	$10^4[\text{Htrpy}^+], M$	pH	$k, M^{-1} \text{sec}^{-1}$
1	7.19	0	1.2	2.0	5.5	1.92
2	14.5	0	1.2	2.0	5.5	1.92
3	29.7	0	1.2	2.0	5.5	1.97
4	16.5	0	0.07	0.10	5.5	1.95
5	0.99	0	1.2	2.0	5.5	1.95
6	16.6	0	0.022	0.60	4.4	1.90
7	15.9	0	0.47	8.9	4.6	1.85
8	15.8	0	Low	Low	3.4	1.98
9	398	1.09	1.6	6.5	5.2	0.11
10	200	0.55	0.22	10.0	4.3	0.27
11	275	0	1.8	5.0	5.4	3.67
Av at $\mu = 0.10$						1.93

^a $[\text{V}(\text{trpy})_2^{2+}] = (5.0 \pm 0.5) \times 10^{-5} M$ except in no. 5 where it was $8.3 \times 10^{-5} M$; $\mu = 0.10$ except no. 9 (0.24), no. 10 (0.12), and no. 11 (0.16), maintained by $\text{NaO}_2\text{C}_2\text{F}_3$; solvent, 10:90 ratio of ethanol to water by volume.

affected by the concentration of free trpy. In experiments 9 and 10, $\text{Ru}(\text{NH}_3)_6^{2+}$ was added initially. The rate constants for these experiments show that $\text{Ru}(\text{NH}_3)_6^{2+}$ inhibits the reaction markedly (note that the higher value of μ in experiment 9 compared to 10 should lead to an even higher specific rate).

The effects referred to can be understood qualitatively on the basis that the V(III) product formed in the initial electron-transfer act can (a) react with $\text{Ru}(\text{NH}_3)_6^{2+}$ or (b) proceed to products. The competition between (a) and (b) accounts for inhibition by $\text{Ru}(\text{NH}_3)_6^{2+}$. Process b must increase in rate at high pH if we are to account for the fact that the deviations from simple kinetics appear at lower pH. It seems likely therefore that (b) involves change in the coordination sphere of V(III) as well as oxidation. We were, however, unable to fit the data for experiments 6–10 by a simple mechanism embodying these ideas. In view of the evidence to be adduced later on the behavior of the V(III)–trpy system this is hardly surprising. There is no reason to reject the general conclusions we have reached as to the cause of the complications, but they do need further elaboration.

One experiment was performed in water rather than in 10% ethanol, under conditions corresponding to those for the experiments in Table I. The specific rate was measured as $0.5 M^{-1} \text{sec}^{-1}$, and the reactivity pattern for bipy *vs.* trpy in the V(II) system thus is in accord with that established for Fe^{30} and Co^{31} .

Co(bipy)₃³⁺ and Co(trpy)₂³⁺ as Oxidants.—With $\text{Co}(\text{bipy})_3^{3+}$ the reaction with $\text{V}(\text{bipy})_3^{2+}$ was observed to obey second-order kinetics above pH *ca.* 5.0. At higher acidity, the specific rates decrease as the reaction progresses, qualitatively as was observed for the $\text{V}(\text{trpy})_2^{2+}$ – $\text{Ru}(\text{NH}_3)_6^{3+}$ system. The effect could be eliminated by adding $\text{H}_2\text{EDTA}^{2-}$ which presumably reacts with the intermediate V(III) species, preventing reversal of the primary electron-transfer reaction.

(30) B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83**, 2061 (1961).

(31) B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959).

The data obtained for the present system in which the complication mentioned was eliminated by high pH are summarized in Table V.

TABLE V
REACTION BETWEEN $V(\text{bipy})_3^{2+}$ AND $\text{Co}(\text{bipy})_3^{3+}$
AT 25° AND $\mu = 0.10$

10^3 [V(II)], M	10^3 [Co(III)], M	10^3 [ClO ₄ ⁻], M	10^3 [bipy], M	10^4 [Hbipy ⁺], M	pH	k , M^{-1} sec^{-1}
8.23	2.04	6.12	7.8	5.7	5.5	6.26
5.18	1.08	6.24	7.3	3.6	5.6	6.69
7.60	2.08	6.24	1.5	40	4.9	6.54
7.33	2.08	6.24	13.5	8.0	5.6	6.06
11.5	4.09	12.4	7.1	0.7	5.4	8.03 ^a
2.98	0.53	12.5	7.7	1.7	6.0	8.83 ^a
2.89	0.53	12.4	7.2	0.7	5.4	8.64 ^a

^a Note effect of change in [ClO₄⁻].

The oxidant $\text{Co}(\text{trpy})_2^{3+}$ is unique among those investigated in that oxidation of V(II) to V(III) could be observed. A first-order dependence on the concentration of each of the reactants, independent of ligand concentration, was indicated by rate studies. The slight curvature evident in the kinetic plots, a complication which probably arises from the colored products or from rate-influencing subsequent reactions of the initial products, limits the accuracy of our value for the rate constant. The work with this oxidant was useful, however, in revealing something of the nature of the V(III) product.

We observed that when $\text{Co}(\text{trpy})_2^{3+}$ is mixed with an excess of $V(\text{trpy})_2^{2+}$ (1.1–2.4-fold), the absorbancy at 767 m μ (absorption peak for $V(\text{trpy})_2^{2+}$) decreases to a value which is slightly in excess of that expected for 1:1 stoichiometry. The spectrum of the solution after the initial rapid reaction shows the presence of a species other than $V(\text{trpy})_2^{2+}$ or $\text{Co}(\text{trpy})_2^{2+}$. When the absorption expected for the latter two species³² is subtracted from the total (assuming 1:1 stoichiometry) the residual spectrum closely resembles that which was described earlier for what we take to be the V(III) dimer coordinated by trpy.

The V(III) species is not stable but disproportionates at a slow rate so that eventually the total absorption can be accounted for stoichiometrically by $V(\text{trpy})_2^{2+}$, $\text{Co}(\text{trpy})_2^{2+}$, and V(IV)–trpy. An approximate value of $(2.6 \pm 0.6) \times 10^2 M^{-1} \text{sec}^{-1}$ was obtained for the specific rate of the initial rapid electron-transfer reaction. The disproportionation of the V(III) species requires time periods of the order of hours to be complete under the conditions used to measure the rate of the primary reaction ([V(II)] *ca.* $10^{-4} M$, [trpy] from 10^{-3} to $10^{-4} M$).

Measurements of the pH of the reacting solutions reveal something about the nature of the V(III) complex. If the reaction products were $\text{Co}(\text{trpy})_2^{2+}$ and $V(\text{trpy})_2^{2+}$, no change in pH would be expected. Instead it is found that there is a change in pH which parallels the absorbancy change until the initial stage

(32) Extinction coefficients of $\text{Co}(\text{trpy})_2^{2+}$ from A. R. Hogg and R. G. Wilkins, *J. Am. Chem. Soc.*, **84**, 341 (1962), and M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **15**, 74 (1943).

of the redox reaction is complete. Substantial changes (5.0 \rightarrow 4.8) were observed in times as short as 0.1 min. Data showing the change in pH for some reaction systems are summarized in Table VI.

TABLE VI
CHANGES IN pH IN THE REACTION OF
 $V(\text{trpy})_2^{2+}$ WITH $\text{Co}(\text{trpy})_2^{3+}$ AT 25° AND $\mu = 0.10$

$10^3[\text{Co(III)}]$, M	$10^6[\text{V(II)}]$, M	$10^4[\text{trpy}] +$ [Htrpy ⁺], M	pH ^a	pH _{eq} ^b
6.12	7.84	1.02	4.95	4.61
2.97	9.90	1.29	4.95	4.80
43.7	46.6	6.36	5.03	4.40

^a As measured by combining solutions in an identical manner but without the oxidant. ^b As measured after the initial change in absorbancy and pH is complete.

If it is assumed that no trpy is lost from V(III), then, to account for the observed changes in pH, it would be necessary to propose that each V(III) produces 0.63 ± 0.05 proton. In other cases it is known that the acidity of an aquo ion is little affected by partial replacement of water by polypyridines.^{33,34} If, as seems likely, V(III) does not deviate markedly from the pattern, at the pH values of the product solutions the release of at least one proton per V(III) would be expected (pK_1 and pK_2 for V(III)(aq) are²⁶ 2.85 and 3.85), and thus the assumption that no trpy is lost from V(III) does not account for the data. If, on the other hand, it is assumed that each V(III) loses one trpy, so that the trpy released now also affects the pH, the data then require that 1.27 ± 0.06 protons are released per V(III) in each of the experiments referred to in Table VI. This result is consistent with the dimeric formulation advanced in an earlier section for the V(III)–trpy species. One proton is produced by each of the OH⁻ groups forming the bridge; if it is assumed that the acid dissociation constant for the water molecule remaining in the coordination sphere of each V(III) is decreased by the OH⁻ groups in the first coordination sphere so as to lie in the range 10^{-4} – $10^{-5} M$ (or even lower than this with not all of the vanadium dimeric) the results on pH are accounted for. It is likely, although not conclusively established, that the pH changes in times as short as 0.1 min result from the loss of trpy from V(III).

Oxidation by EDTA Complexes.—Results obtained with $V(\text{bipy})_3^{2+}$ as reductant and $\text{Fe}(\text{EDTA})^-$ and $\text{Co}(\text{EDTA})^-$ as oxidants are summarized in Table VII.

In the reaction with $\text{Fe}(\text{EDTA})^-$ the stoichiometry was determined at 730 m μ to avoid interference from the highly colored $\text{Fe}(\text{II})$ –bipy product. A comparison of rate constants evaluated at this wavelength and at 649 m μ indicated negligible error arising from this iron product.

In the experiment with $\text{Co}(\text{EDTA})^-$, the stoichiometry, even with excess $\text{Co}(\text{EDTA})^-$, was intermediate between 1 and 2 mol of oxidant/mol of vanadium, a

(33) R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, **15**, 62 (1961).

(34) L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

TABLE VII

THE OXIDATION OF V(bipy)₃²⁺ BY Fe(EDTA)⁻ AND Co(EDTA)^{-a}

Oxidant	10 ⁴ [oxi- dant], M	10 ² [H ₂ - EDTA ²⁻], M	10 ³ [V(II)], M	10 ⁴ [bipy], M	pH	k, M ⁻¹ sec ⁻¹
Fe(EDTA) ⁻	7.54	0.137	4.9	4.8	5.6	21.5 ^b
Fe(EDTA) ⁻	36.3	1.46	8.5	7.6	5.3	24.0
Fe(EDTA) ⁻	7.57	1.44	4.5	4.2	5.4	23.8
Fe(EDTA) ⁻	3.96	1.51	50	45	5.3	23.2
Co(EDTA) ⁻	7.79	2.0	5.7	5.9	4.6	0.0520
Co(EDTA) ⁻	7.84	2.0	9.7	133	5.1	0.0537
Co(EDTA) ⁻	7.80	2.0	14	60	5.4	0.0533
Co(EDTA) ⁻	3.89	0.5	8.1	6	4.7	0.0547
Co(EDTA) ⁻	2.36	2.0	5.7	6	4.7	0.0580

^a $\mu = 0.10$ for the first four entries and 0.11 for the others; temperature, 25°. ^b This experiment demonstrates the independence of k of [H₂EDTA²⁻] (tenfold variation) but is slightly inaccurate due to some photodecomposition of Fe(EDTA)⁻.

situation which could arise from the partial formation of an unoxidizable V(III)-EDTA complex.³⁵ To avoid complications arising from this, rates were measured under pseudo-first-order conditions with the oxidant in large excess. At high [bipy], experiments 5 and 6 of Table VII, an acceleration in rate toward the end of the reactions was noted. We attribute this, as we do a similar effect with cobalt-ammine complexes, to catalysis by the Co(bipy)₃²⁺ couple. The results of a single experiment yielded a tentative value of 0.02 M⁻¹ sec⁻¹ for the specific rate of the Co(bipy)₃²⁺-Co(EDTA)⁻ reactions (assumed first order in each reactant).

Pentaamminecobalt(III) Complexes as Oxidants.—

All of the cobalt-ammine complexes investigated react very slowly with V(bipy)₃²⁺, and, for all, the pseudo-first-order rate plots showed curvature characteristic of catalysis by-products. Cobaltous ion added initially at a concentration level equivalent to that formed in the experiments, *ca.* 10⁻⁴ M, was found to produce a marked acceleration in rate.

Of the oxidants of this class, Co(NH₃)₅Cl²⁺ was the most thoroughly studied. The initial rates proved to be independent of [bipy] in the range 0.003–0.03 M and of initial pH in the range 4.5–7.0. The initial slopes in pseudo-first-order plots indicated first-order dependence on the concentration of each reactant over a range of a factor of 4, with a specific rate of (4.7 ± 0.5) × 10⁻³ M⁻¹ sec⁻¹ at 25° and $\mu = 0.25$.

A single experiment was done on the reduction of each of the ions Co(NH₃)₅(crotonate)²⁺ and Co(NH₃)₅(acetate)²⁺ by V(bipy)₃²⁺. These reactions as well are catalyzed by the products. From initial slopes, using data for experiments with oxidant in large excess, the values of k for the two oxidants were found to be 1.0 × 10⁻³ and 0.6 × 10⁻³ M⁻¹ sec⁻¹, respectively, at 25° and $\mu = 0.25$. The suggestion³⁶ that there is an unusual reactivity of the complex with the conjugated crotonate ligand was not confirmed. In view of this and the kinetic complications already mentioned,

(35) G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta*, **36**, 1089 (1953), report -0.80 V for the oxidation potential of V(EDTA)⁻.

(36) R. T. M. Fraser, Ph.D. Thesis, University of Chicago, 1959.

work with the present class of oxidants was discontinued.

Polarographic Studies.—Prior to the work with Co(trpy)₂³⁺, polarographic studies of solutions containing *ca.* 10⁻³ M V(trpy)₂²⁺ (pH 3.5–5.5, slight excess of trpy) revealed two anodic waves at -0.20 V (1 e⁻ wave) and -0.50 V (2 e⁻ wave)³⁷ which could be attributed to diffusion of the V(II) species to the electrode. When the free tripyridine concentration was made large to determine whether the dissociation of ligand from the oxidized product is reflected in the potential, a wave due to anodic oxidation of mercury in the presence of trpy completely dominated the -0.20-V wave preventing the application of this test. Experiments on the Co(trpy)₂³⁺-V(trpy)₂²⁺ system indicated that the time for water to enter the V(III) coordination sphere is comparable to or less than the polarographic drop time and showed moreover that trpy is lost from V(III) in times at least as short as 1–1.5 min. We conclude that coordinational changes of the V(III) affect the observed potential which cannot, therefore, apply to the V(trpy)₂²⁺ couple. Three-electrode triangular-wave oscillography, with the advantages of no mercury wave (Pt electrode) and a time constant of 1/60 sec, revealed only one well-defined wave (slightly irreversible), at $\sim +0.8$ V, which is probably due to a one-electron reduction of V(trpy)₂²⁺.³⁸

Discussion

All of the reactions which we have studied with V(II)-plpy species as reducing agents are irreversible. Despite the favorable over-all free energy changes associated with the reactions, they are slow compared to those of reducing agents such as Cr(bipy)₃²⁺^{1,39} and Fe(bipy)₃²⁺³⁰ acting on 1-e⁻ oxidants under the influence of favorable driving forces. The indications of the earlier studies on the relative rates at which Cr(bipy)₃²⁺ and V(bipy)₃²⁺ react with cobalt-ammine complexes are borne out by the present work. With the oxidant Co(NH₃)₅Cl²⁺, for example, the rate ratio (Cr(II)/V(II)) is *ca.* 10⁸.

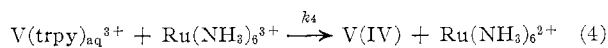
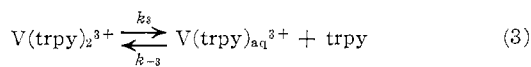
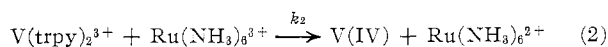
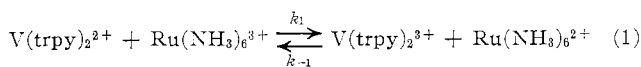
Our work shows that the V(II)-plpy species differ in an important respect from the 1-e⁻ reductants complexed by polypyridine which have thus far been studied. Whereas in the other cases the net changes in question involve 1-e⁻ processes in which the coordination sphere about the metal remains intact for reasonable periods subsequent to electron transfer, in the present case the net changes involve two electrons per vanadium and the coordination sphere is in every instance disrupted following transfer of the first electron. Our pH studies of the V(trpy)₂²⁺-Co(trpy)₂³⁺ reaction show

(37) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1958, p 363. The Latimer convention will be used in describing the potentials (referenced to the normal hydrogen electrode) of half-reactions: W. M. Latimer, "Oxidation Potentials of the Elements," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(38) For a more detailed account of the polarographic work, see L. E. Bennett, Ph.D. Thesis, Stanford University, 1966.

(39) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

that ligand is released rapidly following the formation of the initial V(III) product in the redox process. Further, V(IV), with one exceptionally strong vanadium–oxygen bond in aqueous solution, does not interact with as many as six N atoms presented by polypyridine ligands.⁴⁰ Thus the assertion as to the irreversibility of the net reactions which we have studied does not necessarily apply to what can reasonably be taken to be the first stage in the process, namely, the oxidation of V(plpy)_n²⁺ to V(plpy)_n³⁺. In fact, with Ru(NH₃)₆³⁺ acting on V(trpy)₂²⁺, the results suggest reversibility in the first stage, the net irreversible change being consummated by the further consumption of V(trpy)₂³⁺, as in the mechanism shown below



The effect of pH on the kinetics of the net reaction cannot be accounted for by reaction 1 or 2. We take this as indicative that reaction 3 followed by 4 can contribute substantially to the consumption of V(trpy)₂³⁺ with any of k_3 , k_{-3} , or k_4 being pH dependent. Thus rapid substitution changes in the initial V(III) species can intervene to carry the over-all reaction forward even when oxidation of the initial product does not take place rapidly compared to the rate at which it is formed.

The contribution to the over-all free energy change of such processes subsequent to the initial one-electron transfer leaves open the possibility that E° for the V(plpy)_n^{2+,3+} couple is more negative than for any of the complementary couples we have studied, the oxidizing members of which are capable of reaction with the V(II)–plpy species. In the context of the Marcus theory,⁶ the slowness of the reactions may then simply be a result of the fact that the first step involving oxidation of V(II)–plpy species has an unfavorable driving force. Once this barrier has been surmounted, reaction is completed by the further oxidation of the V(III) complex or by dissociation of the complex followed by further oxidation. We will show that a reasonably consistent interpretation of our observations can be made on this basis.

The inhibition of the V(trpy)₂²⁺–Ru(NH₃)₆³⁺ reaction by Ru(NH₃)₆²⁺ is consistent with the view expressed. Using $t_{1/2} \leq 0.5$ min for the half-life of reaction 3, k_3 becomes $\geq 2.3 \times 10^{-2} \text{ sec}^{-1}$. Now for the reverse of reaction 1 with [Ru(NH₃)₆²⁺] $\sim 2 \times 10^{-5} M$ to compete against reaction 3—and the pH-dependent inhibition by Ru(NH₃)₆²⁺ indicates this to be the case—requires $k_{-1} > \sim 10^3 M^{-1} \text{ sec}^{-1}$. Combining this lower limit with the observed value of k_1 of $\sim 1.9 M^{-1} \text{ sec}^{-1}$ and with the value of E° for the Ru(NH₃)₆^{2+,3+} couple⁴¹ yields for the V(trpy)₂^{2+,3+} couple a value of < -0.25

(40) R. Trujillo and F. Brito, *An. Real Soc. Espan. Fis. Quim.*, **B53**, 533 (1957); reported in ref 34.

V. (In the present context it is appropriate to observe that the reason for the difference in behavior of V(bipy)₃²⁺ as against V(trpy)₂²⁺ in reaction with Ru(NH₃)₆³⁺, the latter but not the former showing inhibition by Ru(NH₃)₆²⁺, is probably the fact that ligand dissociation from V(bipy)₃³⁺ is more rapid than from V(trpy)₂³⁺.)

An approach to estimating how negative E° for the V(bipy)₃^{2+,3+} couple can be made by assuming the validity of the relative Marcus theory.⁶ The equilibrium quotient K_{12} for several of our reactions can be calculated using the equation $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$, where k_{12} and k_{22} are the known rate constants for the cross reaction and the self-exchange for the oxidizing couple, respectively, while k_{11} represents a value for the unknown V(bipy)₃^{2+,3+} self-exchange rate constant assumed on the basis described below. The factor f is given by the equation

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

where Z is the collision frequency of the uncharged molecules in solution and is taken as $10^{11} M^{-1} \text{ sec}^{-1}$.

We feel that the best available rough estimate of how large k_{11} might be in this t_{2g}^3 – t_{2g}^2 system can be obtained from the t_{2g}^6 – t_{2g}^5 systems, M(bipy)₃^{2+,3+} or M(phen)₃^{2+,3+}, where M is Fe, Ru, or Os. Previous work^{30,31} as well as our own demonstrates that the bipy and phen ligands bestow comparable reactivity on the metal centers so that either can be used for our purpose. Since it appears unlikely that the Fe, Ru, and Os self-exchange rates will differ substantially from one another, we have chosen the highest established lower limit of $10^7 M^{-1} \text{ sec}^{-1}$ in this group⁴² as our assumed value of k_{11} . The Co(plpy)_m^{2+,3+} couple was rejected from consideration for our purpose since the changes in spin state and in population of the σ -antibonding orbitals on electron transfer almost certainly cause the self-exchange rate for this couple to be anomalously low. The results of the calculations using this assumed value for k_{11} are summarized in Table VIII for the couples for which the relevant data are known.

Allowance must be made for the fact that the various parameters which have been used have not all been measured under the same conditions. It is likely, however, that the rate constants are not affected by more than a factor of 10 because of differences in ionic strength, and the values of E_{11}° (calcd) are therefore not in error on this account by more than *ca.* 0.06 V. The application of the Marcus theory, if k_{11} is taken to be $10^7 M^{-1} \text{ sec}^{-1}$, therefore leads to a value of E° for V(bipy)₃^{2+,3+} of -0.8 V. If k_{11} is taken to be larger (note that the limit for a diffusion-controlled reaction would be $\sim 10^{10} M^{-1} \text{ sec}^{-1}$), then E_{11}° would be calculated as being even more negative.

The calculations made with the above assumptions and purpose would indicate that E° for V(II)–V(III)

(41) T. Meyer, Ph.D. Dissertation, Stanford University, 1966. Recent measurements suggest -0.10 V as E° for the couple Ru(NH₃)₆^{2+,3+}, a value somewhat higher than that obtained by Endicott and Taube.³ Because the later work was more exhaustive than the earlier, we feel that the newer value is the more nearly correct.

(42) D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **43**, 3765 (1965).

TABLE VIII
CALCULATION OF E° FOR $V(\text{bipy})_3^{2+,3+}$
USING THE MARCUS THEORY^a

Oxidant	k_{12} , $M^{-1} \text{sec}^{-1}$	k_{22}	E_{22}°	E_{11}°
$\text{Ru}(\text{NH}_3)_6^{3+}$	0.12	$\sim 1 \times 10^3$ ^b	-0.10 ^b	-0.81
$\text{Co}(\text{bipy})_3^{3+}$	6.4	~ 20 ^c	0.37 ^e	-0.75
$\text{Fe}(\text{EDTA})^-$	23	$> 10^4$ ($> 10^3$ at 0°) ^d	-0.12 ^f	< -0.62
$\text{Co}(\text{EDTA})^-$	0.054	4×10^{-7} ^d	-0.60 ^g	-0.78

^a Subscripts 1 and 2 refer to the reducing and oxidizing couples, respectively. ^b See ref 41. ^c P. Ellis, R. G. Wilkins, and R. P. J. Williams, *J. Chem. Soc.*, 4456 (1957). ^d See ref 12. ^e E. Paglia and C. Seroni, *Gazz. Chim. Ital.*, **87**, 1125 (1957). ^f G. Schwarzenbach and H. Heller, *Helv. Chim. Acta*, **34**, 576 (1951). ^g D. A. Buckingham and A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p 245.

might be shifted to a more negative value by as much as 1 V when H_2O as ligand is replaced by bipy. It is likely that although there undoubtedly is a marked shift to more negative values, the shift is not quite as large as this. The replacement of H_2O on $\text{Ru}^{2+,3+}$ by bipy or phen shifts the potential by *ca.* 1 V^{43,44} and the shift is expected to be greater for Ru than for V because six rather than three t_{2g} electrons are involved in back-bonding. A value of E° for $V(\text{trpy})_2^{2+,3+}$ as low as -0.8 V would moreover require k_{-1} to exceed diffusion control (10^{12} greater than $k_{-1} \cong 2$). Thus, to the extent that the Marcus theory is valid, E° for $V(\text{bipy})_3^{2+,3+}$ is indicated as being somewhat less negative than -0.8 V and k_{11} as being somewhat less than $10^7 M^{-1} \text{sec}^{-1}$. A lower self-exchange rate in the $t_{2g}^3-t_{2g}^2$ as compared to the $t_{2g}^6-t_{2g}^5$ system could conceivably arise from decreased electron delocalization over the π^*

(43) See footnote g of Table VIII.

(44) E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4**, 1692 (1965).

ligand orbitals in the former due to decreased electron-electron repulsions.

It should be noted also that if E° is as negative as -0.8 V, dissociation of bipy from $V(\text{bipy})_3^{3+}$ must take place with a specific rate of $\sim 10^8 \text{sec}^{-1}$ if inhibition by $\text{Ru}(\text{NH}_3)_6^{2+}$ is not to be observed in the $V(\text{bipy})_3^{2+} \rightarrow \text{Ru}(\text{NH}_3)_6^{3+}$ reaction. Though the requirement on this rate is less stringent than this if, as seems indicated, the actual value of E_{11}° is less negative than -0.8 V, it yet remains clear that $V(\text{bipy})_3^{3+}$ is very substitution labile, much more so than is $V(\text{bipy})_3^{2+}$, the factor likely being much in excess of 10^6 . With H_2O as ligands, V(III) is only slightly more labile than is V(II).⁴⁵ The change in relative lability as H_2O is replaced by bipy is probably a result of the greater advantage which the ion in the lower oxidation state can take of the capability of the conjugated ligand to interact with the t_{2g} electrons of the metal ion. The possibility is also open that when an electron is removed from $V(\text{bipy})_3^{2+}$, a water molecule can move into the first coordination sphere of V(III) (electronic configuration t_{2g}^2). Proton dissociation from such a water molecule would take place readily, and this would facilitate release of other ligands.

Acknowledgments.—Financial support for this work by the National Science Foundation, Contract NSF GP 5322 and NSF GP 2406, is gratefully acknowledged, as is fellowship support for L. E. B. We also wish to thank Professor W. Reinmuth of Columbia University for making the oscillopolarography apparatus available to us.

(45) R. G. Wilkins and M. Eigen, "Mechanisms of Inorganic Reactions," *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF ENGINEERING SCIENCE,
OSAKA UNIVERSITY, TOYONAKA, OSAKA, JAPAN

Novel Metal Complexes Involving a Multiply Bridged Nitrogen Atom

By SEI OTSUKA, AKIRA NAKAMURA, AND TOSHIKATSU YOSHIDA

Received June 12, 1967

A reaction of $(t\text{-C}_4\text{H}_9\text{N})_2\text{S}$ with $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$ or $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ produced a black, paramagnetic (1.68 BM, $g = 2.035$), trinuclear complex, $t\text{-C}_4\text{H}_9\text{N}(\pi\text{-C}_5\text{H}_5\text{Ni})_2$ (I). The chemical and physical properties of I suggested a trigonal-pyramidal structure with an apical nitrogen atom on a triangle of nickel atoms. The preliminary results of a three-dimensional, single-crystal X-ray analysis confirmed this structure and revealed a considerable distortion from C_{3v} symmetry. The three Ni-Ni distances are 2.34, 2.27, and 2.21 Å. A similar reaction of $(t\text{-C}_4\text{H}_9\text{N})_2\text{S}$ with $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$ gave a dark green, binuclear diamagnetic complex, $(\pi\text{-C}_5\text{H}_5\text{Co})_2(t\text{-C}_4\text{H}_9\text{N})_2\text{CO}$ (II). Based on the physical measurements, the structure of II was deduced to be a di-*t*-butylurea complex where each nitrogen atom bridges the two cobalt atoms. The crystal structure has also been determined from single-crystal X-ray analysis which revealed a short Co-Co distance (2.367 Å). A reaction scheme involving a metal-nitrene intermediate was proposed for the formation of II.

Introduction

Recently, there have been found a number of polynuclear organometallic complexes which involve metal-metal bonds. They are subjects of growing interest regarding their chemical structure as well as the physi-

cal properties such as temperature-dependent magnetic behavior.¹ Studies on the reaction of N-*t*-butylsulfurdiimide, $(t\text{-C}_4\text{H}_9\text{N})_2\text{S}$, with bis(π -cyclopenta-

(1) J. Lewis, "Plenary Lecture at VIIIth International Conference on Coordination Chemistry, Vienna, Austria, 1964," Butterworth and Co. Ltd., London.