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## Kinetics of the Reduction of Some Cobalt(III) Complexes by Chromium(II), Vanadium(II), and Europium(II)<sup>1</sup>

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Kinetic measurements are reported on the reduction of a variety of pentaamminecobalt(III) complexes by  $\text{Cr}^{2+}_{\text{aq}}$ ,  $\text{V}^{2+}_{\text{aq}}$ ,  $\text{Eu}^{2+}_{\text{aq}}$ , and  $\text{Cr}(\text{bipy})_3^{2+}$  ( $\text{bipy} = 2,2'$ -bipyridine). The resulting reactivity patterns are examined from the standpoint of providing a possible basis for distinguishing between inner- and outer-sphere electron-transfer mechanisms. The variation in rate, with  $\text{V}^{2+}$  as reductant, was found to be much smaller than with  $\text{Cr}^{2+}$  and to exhibit sufficient similarity to the variation in rate observed with  $\text{Cr}(\text{bipy})_3^{2+}$  (as well as with the rates of electrochemical reduction of the corresponding cobalt(III) complexes at a dropping mercury electrode) to suggest that both  $\text{V}^{2+}$  and  $\text{Cr}(\text{bipy})_3^{2+}$  react through outer-sphere mechanisms. These correlations also contribute to the confirmation of an important prediction of the Marcus theory of electron transfer. The reactivity of  $\text{Eu}^{2+}$  toward the halopentaamminecobalt(III) complexes was found, in contrast to the other reductants, to decrease in the order  $\text{Co}(\text{NH}_3)_5\text{F}^{2+} > \text{Co}(\text{NH}_3)_5\text{Cl}^{2+} > \text{Co}(\text{NH}_3)_5\text{Br}^{2+} > \text{Co}(\text{NH}_3)_5\text{I}^{2+}$ , a trend which is interpreted in terms of an inner-sphere mechanism. The rates of reaction of  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$  with  $\text{Co}(\text{NH}_3)_5\text{PO}_4$  all exhibited a marked pH dependence which is interpreted in terms of the protonation equilibria of the complex.

### Introduction

Previous investigations, notably by Taube and his co-workers, have revealed that the reduction of cobalt(III) complexes of the type  $\text{Co}(\text{NH}_3)_5\text{X}^{3-n}$  (where  $\text{X}^{-n}$  may be any one of a large number of ligands, e.g.,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{N}_3^-$ ,  $\text{SCN}^-$ ,  $\text{SO}_4^{2-}$ , etc.) may proceed either by outer- or inner-sphere mechanism,<sup>3-5</sup> with X acting as an inner-sphere bridge for electron transfer, in the latter case. With  $\text{Cr}^{2+}_{\text{aq}}$  or  $\text{Co}(\text{CN})_5^{3-}$  as reductant, evidence for an inner-sphere mechanism was deduced, in a number of cases, from the observation that electron transfer is accompanied by the transfer of X to the coordination shell of the newly formed (and substitution-inert)  $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{X}$  or  $\text{Co}^{\text{III}}(\text{CN})_5\text{X}$  ion, respectively.<sup>3,6</sup> With  $\text{Cr}(\text{bipy})_3^{2+}$  as reductant on the other hand, it has been concluded<sup>7</sup> that electron transfer proceeds through an outer-sphere mechanism to yield  $\text{Cr}(\text{bipy})_3^{3+}$ .

For many other reductants, for example the aquo ions  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$ , which yield substitution-labile products on oxidation, the mechanistic criteria which have been invoked in the above cases are inapplicable and it becomes necessary to invoke other, less direct, criteria to infer the mechanism of electron transfer. One such approach is through the study of the dependence of the rate for a given reductant and a series of oxidants  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ , in which the ligand X is varied, on the nature of the latter. It is reasonable to expect that the pattern of this dependence will differ as a consequence of whether X acts as an inner-sphere bridging ligand or whether the reactions proceed by an outer-sphere mechanism. In the latter case, it may further be anticipated on the basis of theoretical considerations formulated by Marcus<sup>8</sup> that, providing the electrostatic work terms are similar (or sufficiently small to be neglected), the reactivity pattern toward a series of such oxidants will be the same for different reductants. This criterion was invoked by Zwickel and Taube<sup>9</sup> to infer, on the basis of the rather limited data hitherto available, that the reduction of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  and  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  by  $\text{V}^{2+}$  (in contrast to  $\text{Cr}^{2+}$ ) proceeds through an outer-sphere mechanism.

The present investigation was undertaken with a view to further examining and extending this approach. A limitation on such studies is imposed by the fact that many of the reactions of interest are too fast for conventional kinetic measurements. In many cases it was found, however, that the rates could be conveniently measured with a stopped-flow apparatus and most of the results reported below were obtained in this way.

### Experimental

**Materials.**—Solutions of chromium(II) perchlorate were prepared from the corresponding chromium(III) salt, both electrolytically and by reduction with zinc amalgam, the two procedures giving consistent results. Chromium(III) perchlorate was prepared by reduction of an acidified solution of sodium dichromate with hydrogen peroxide.<sup>10</sup> Solutions of  $\text{Cr}(\text{bipy})_3\text{ClO}_4$  were prepared by addition of aqueous chromium(II) perchlorate to a solution containing an excess of bipy. Vanadium(II) perchlorate was prepared by reduction of a solution of vanadium(IV) perchlorate with zinc amalgam. Europium(II) perchlorate was prepared by dissolving europium(II) carbonate<sup>11</sup> in aqueous perchloric acid. Sodium perchlorate was prepared by neutralizing reagent grade perchloric acid with sodium carbonate. Other chemicals were of reagent grade.

The chromium(II) and europium(II) solutions were analyzed by adding an aliquot of the solution to a deoxygenated iron(III) solution and back-titrating the iron(II) produced with chromium(VI). Vanadium(II) was titrated with deoxygenated potassium permanganate in the presence of sulfuric acid.<sup>10</sup>  $\text{Cr}(\text{bipy})_3^{2+}$  was determined spectrophotometrically ( $\epsilon_{562.5 \text{ m}\mu} 4.34 \times 10^3 \text{ M}^{-1}$ ,  $\epsilon_{467 \text{ m}\mu} 3.95 \times 10^3 \text{ M}^{-1}$ ).

All the cobalt(III) complexes used as oxidants were prepared using previously reported procedures.  $\text{ROH}_2(\text{ClO}_4)_3$  (where  $\text{R} = \text{Co}(\text{NH}_3)_5$ ) was generated by treating a solution of  $\text{RCO}_3(\text{NO}_3)$  with perchloric acid.<sup>12</sup>  $\text{RCl}(\text{ClO}_4)_2$ ,<sup>13</sup>  $\text{RBr}(\text{ClO}_4)_2$ ,<sup>14</sup>  $\text{RF}(\text{ClO}_4)_2$ ,<sup>12</sup>  $\text{RNO}_2(\text{ClO}_4)_2$ ,<sup>13</sup>  $\text{RSO}_4(\text{ClO}_4)$ ,<sup>15</sup>  $\text{RNCS}(\text{ClO}_4)_2$ ,<sup>16</sup>  $\text{RS}_2\text{O}_3(\text{ClO}_4)$ ,<sup>17</sup>  $\text{ROAc}(\text{ClO}_4)_2$ ,<sup>13</sup> and  $\text{R}(\text{H-maleato})(\text{ClO}_4)_2$ ,<sup>18</sup> were prepared by standard procedures, described in the references cited. Separation from residual aquo complex was effected either by ion exchange or recrystallization, and the identity and purity of the products confirmed analytically and spectrophotometrically.  $\text{RI}(\text{ClO}_4)_2$  was prepared by the method of Haim and Taube<sup>19</sup> with care being taken to minimize product hydrolysis.  $\text{RN}_3(\text{ClO}_4)_2$  was prepared in the dark by the method of Linhard and Flygave.<sup>20</sup> Both the latter complexes were found to be light-sensitive and their reactions were studied in blackened vessels.  $\text{RPO}_4$  was

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TABLE I  
 SPECTRAL DATA (R = Co(NH<sub>3</sub>)<sub>5</sub>)

Complex	$\lambda_{\max}$ m $\mu$	$\epsilon_{\max}$
Co(en) <sub>3</sub> <sup>3+</sup>	465	87
RNH <sub>3</sub> <sup>3+</sup>	475	55
ROH <sub>2</sub> <sup>3+</sup>	490	47
RNCS <sup>2+</sup>	497	192
RNO <sub>3</sub> <sup>2+</sup>	500	57
ROAc <sup>2+</sup>	502	93
RF <sup>2+</sup>	510	44
RS <sub>2</sub> O <sub>3</sub> <sup>+</sup>	510	61
RSO <sub>4</sub> <sup>+</sup>	515	63
RN <sub>3</sub> <sup>2+</sup>	520	265
RPO <sub>4</sub>	525	90
RCl <sup>2+</sup>	533	49
RBr <sup>2+</sup>	550	53
RI <sup>2+</sup>	580	80

plunger of the receiving syringe, at the same time triggering the oscilloscope. The oscilloscope trace was recorded with a Polaroid camera.

The reactions were generally followed by observing the decrease in absorbance of the cobalt(III) complex at the wave length of maximum extinction in the vicinity of 500 m $\mu$  (see Table I). The reductant was generally in large excess so that the observed kinetics were of pseudo-first order. Exceptions to this were very fast reactions ( $t_{1/2} < 20$  msec.) where the initial concentrations of both reactants were kept as low as possible (and hence of the same order) to slow down the reaction; and the reactions involving Cr(bipy)<sub>3</sub><sup>2+</sup> as reductant which were followed by observing the disappearance of the latter (at 562 m $\mu$ ) with the oxidant in excess. The practical limits of the flow apparatus were  $5 \times 10^{-3}$  sec.  $< t_{1/2} < 30$  sec. Reactions with a half-life greater than 30 sec. were followed spectrophotometrically in a Cary Model 14 spectrophotometer, using a conventional thermostated absorption cell which was filled, following deoxygenation, by injecting the solutions from thermostated syringes through a mixing chamber similar to that of the stopped-flow apparatus.

In the reactions involving Cr<sup>2+</sup>, V<sup>2+</sup>, and Eu<sup>2+</sup>, the initial oxidant concentration was generally in the range  $10^{-4}$  to  $10^{-2}$  M

 TABLE II  
 SECOND-ORDER RATE CONSTANTS ( $k$ , M<sup>-1</sup> SEC.<sup>-1</sup>) FOR THE REDUCTION OF VARIOUS COBALT(III) COMPLEXES<sup>a</sup>

Oxidant	Reductant			
	Cr <sup>2+</sup>	V <sup>2+</sup>	Eu <sup>2+</sup>	Cr(bipy) <sub>3</sub> <sup>2+</sup> <sup>b</sup>
Co(en) <sub>3</sub> <sup>3+</sup>	$\sim 2 \times 10^{-6c}$	$\sim 2 \times 10^{-4}$	$\sim 5 \times 10^{-3}$	$1.8 \times 10^2$
RNH <sub>3</sub> <sup>3+</sup>	$8.9 \times 10^{-5e,d}$	$3.7 \times 10^{-3e,d}$	$2 \times 10^{-2b}$	$6.9 \times 10^{2e}$
ROH <sub>2</sub> <sup>3+</sup>	$0.5^f$	$\sim 0.5^d$	$0.15^g$	$5 \times 10^4$
RF <sup>2+</sup>	$> 2 \times 10^6$	2.6	$2.6 \times 10^4$	$1.8 \times 10^3$
RCl <sup>2+</sup>	$> 2 \times 10^6$	$\sim 5$	$3.9 \times 10^2$	$8 \times 10^6$
			$3.0 \times 10^2$ (17.2°)	
			$4.7 \times 10^2$ (31.2°)	
RBr <sup>2+</sup>	$> 2 \times 10^6$	25	$2.5 \times 10^2$	$5 \times 10^6$
		14 (14.6°)	$2.0 \times 10^2$ (17.8°)	
		40 (33.6°)	$3.0 \times 10^2$ (31.3°)	
RI <sup>2+</sup>	$> 2 \times 10^6$	$1.2 \times 10^2$	$1.2 \times 10^2$	...
		$0.9 \times 10^2$ (15.5°)		
RN <sub>3</sub> <sup>2+</sup>	$\sim 3 \times 10^5$	13	$1.9 \times 10^2$	$4.1 \times 10^4$
		6.6 (15.7°)	$1.5 \times 10^2$ (18.0°)	
		22 (32.8°)	$2.4 \times 10^2$ (31.7°)	
RNCS <sup>2+</sup>	19	0.3	$\sim 0.7$	$1.0 \times 10^4$
	12 (15.2°)			
	28 (35.1°)			
RSO <sub>4</sub> <sup>+</sup>	18	7.8 <sup>h</sup>	$1.4 \times 10^2$	$4.5 \times 10^4$
	13 (15.0°)		$1.0 \times 10^2$ (17.7°)	
	28 (35.0°)		$1.8 \times 10^2$ (31.8°)	
ROAc <sup>2+</sup>	0.18 <sup>i</sup>	0.43 <sup>j</sup>	0.18 <sup>j</sup>	$1.2 \times 10^3$
RNO <sub>3</sub> <sup>2+</sup>	$\sim 90$	...	$\sim 1 \times 10^2$	
RS <sub>2</sub> O <sub>3</sub> <sup>+</sup>	...	...	...	$8 \times 10^4$
R(maleate) <sup>+</sup>	...	...	...	$1.0 \times 10^3$

<sup>a</sup> Unless otherwise noted, conditions are: 25°,  $\mu_{\text{NaClO}_4-\text{HClO}_4} = 1.0$ . <sup>b</sup>  $\mu = 0.1$  <sup>c</sup>  $\mu = 0.4$ . <sup>d</sup> A. Zwickel and H. Taube, ref. 9. <sup>e</sup> A. Zwickel and H. Taube, ref. 7. <sup>f</sup>  $\mu = 1.2$ , extrapolated to 25° from data of A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 1288 (1961). <sup>g</sup> A. Zwickel, Ph.D. Dissertation, University of Chicago, 1959. <sup>h</sup> R. T. M. Fraser, *Inorg. Chem.*, **2**, 955 (1963). <sup>i</sup> D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961). <sup>j</sup> R. T. M. Fraser in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 287.

prepared by the method of Schmidt and Taube<sup>21</sup> and its purity confirmed both analytically and by pH titration. The spectra of all the complexes (Table I) were found to agree with previously reported data.

**Kinetic Measurements.**—Because of the sensitivity of the reductants to oxygen, all experiments were performed using deoxygenated solutions under an atmosphere of nitrogen which has been passed through an aqueous chromous solution.

Most of the reactions studied were too fast for conventional kinetic measurements and their rates were measured with a stopped-flow apparatus similar to that of Dulz and Sutin.<sup>22</sup> Thermostated syringes, driven with a variable speed motor, were used to force the oxidant and reductant solutions through an eight-jet lucite mixing chamber and quartz observation tube into a receiving syringe. Changes in the absorbance of the reacting solution were measured with a modified Beckman monochromator and photomultiplier whose output was coupled through a transistorized emitter follower circuit to a Tetrax Type 532 oscilloscope. Flow of the solutions was stopped by arresting the

(the lower limit being determined by the sensitivity of the apparatus). The initial reductant concentration was generally varied at least over a twofold range and first-order dependence on both reductant and oxidant concentrations confirmed.

The reactions involving RPO<sub>4</sub> exhibited a marked pH dependence which was examined in some detail. In most of the other reactions the solutions contained 0.5 M HClO<sub>4</sub> and 0.5 M NaClO<sub>4</sub> except for the reactions involving RNH<sub>3</sub><sup>3+</sup>, where solubility considerations dictated the use of a lower perchlorate concentration; the reaction medium in these cases was 0.1 M HClO<sub>4</sub>.

In the reactions involving Cr(bipy)<sub>3</sub><sup>2+</sup> as reductant the initial concentration of the latter was generally about  $2 \times 10^{-3}$  M, with the oxidant in substantial excess. The kinetics were of pseudo-first order in Cr(bipy)<sub>3</sub><sup>2+</sup> and also exhibited a first-order dependence on the initial oxidant concentration, which was generally varied over a twofold range. bipy was present in sufficient excess ( $\sim 2.5 \times 10^{-3}$  M) to ensure that the chromium(II) was predominantly in the form of Cr(bipy)<sub>3</sub><sup>2+</sup>. Varying the bipy concentration between  $5 \times 10^{-4}$  and  $2.5 \times 10^{-3}$  M had no effect on the rate of reaction with Co(en)<sub>3</sub><sup>3+</sup> in agreement with Zwickel and Taube's<sup>7</sup> earlier finding for the reaction of Cr(bipy)<sub>3</sub><sup>2+</sup> with RNH<sub>3</sub><sup>3+</sup>. The medium for the Cr(bipy)<sub>3</sub><sup>2+</sup> reactions was 0.1

(21) W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).

(22) G. Dulz and N. Sutin, *ibid.*, **2**, 917 (1963).

$M$   $\text{NaClO}_4$  (pH adjusted to about 5 with  $\text{HClO}_4$ ), the use of a higher perchlorate concentration being complicated by solubility considerations.

The temperature of kinetic measurement was generally  $25.0 \pm 0.1^\circ$  and, in a few cases, was varied between  $15$  and  $35^\circ$  to determine  $\Delta H^*$  and  $\Delta S^*$ .

No attempt was made in these studies to identify the products of reaction or confirm directly the stoichiometry, which was assumed in each case to be,  $\text{Co}^{\text{III}} + \text{Red}^{\text{II}} \rightarrow \text{Co}^{\text{II}} + \text{Red}^{\text{III}}$ , on the basis of the many earlier observations on these and related reactions.

### Results

Values of the measured second-order rate constants  $k$ , defined by  $-d[\text{Co}^{\text{III}}]/dt = k[\text{Co}^{\text{III}}][\text{Red}^{\text{II}}]$  (where  $[\text{Co}^{\text{III}}]$  is the total concentration of the cobalt(III) complex and  $[\text{Red}^{\text{II}}]$  the concentration of the reductant ion) are summarized in Table II. The corresponding activation energies and entropies, where determined, are listed in Table III. These tables also include, for the sake of completeness and comparison, a few data previously reported in the literature. Where our measurements overlap earlier ones, good agreement was generally observed, and any significant discrepancies (e.g., in the case of some of the  $\text{Cr}(\text{bipy})_3^{2+}$  reactions) are attributable to differences in ionic strength or other medium effects. Attempts to measure the rate of reduction of  $\text{RNO}_3^{2+}$  by  $\text{V}^{2+}$  were unsuccessful due to complications apparently arising from rapid reaction of the reductant with  $\text{NO}_3^-$ . Measurements involving  $\text{RI}^{2+}$  are subject to somewhat greater uncertainty than most of the others and could not be extended above  $25^\circ$ , due to the instability of this complex toward hydrolysis.

TABLE III

ACTIVATION ENTHALPIES (KCAL./MOLE) AND ENTROPIES (CAL./MOLE DEG.)

Oxidant	$\text{Cr}^{2+}$		$\text{V}^{2+}$		$\text{Eu}^{2+}$	
	$\Delta H^*$	$\Delta S^*$	$\Delta H^*$	$\Delta S^*$	$\Delta H^*$	$\Delta S^*$
$\text{RNH}_3^{3+}$	14.7 <sup>a</sup>	-30 <sup>a</sup>	9.1 <sup>a</sup>	-40 <sup>a</sup>	...	...
$\text{ROH}_2^{3+}$	2.9 <sup>b</sup>	-52 <sup>b</sup>	...	...	...	...
$\text{RCI}^{2+}$	...	...	...	...	5.0	-30
$\text{RBr}^{2+}$	...	...	9.1	-22	4.7	-32
$\text{RI}^{2+}$	...	...	(4.6)	(-32)	...	...
$\text{RN}_3^{2+}$	...	...	11.7	-14	5.5	-30
$\text{RSO}_4^+$	6.2	-32	6.1 <sup>c</sup>	-34 <sup>c</sup>	6.7	-26
$\text{RNCS}^{2+}$	6.9	-29	...	...	...	...

<sup>a</sup> A. Zwickel and H. Taube, ref. 9. <sup>b</sup> A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **82**, 1288 (1959). <sup>c</sup> R. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).

Results for  $\text{RPO}_4$  are presented in Fig. 1 in the form of plots of  $\log k$  vs. pH. The insolubility of europium phosphate at high pH limited the measurements with  $\text{Eu}^{2+}$  to the region below pH 2.9. The kinetic data for these systems were interpreted by estimating the concentrations of  $\text{RPO}_4$ ,  $\text{RPO}_4\text{H}^-$ ,  $\text{RPO}_4\text{H}_2^{2-}$ , and  $\text{RPO}_4\text{H}_3^{3-}$  at each pH using the acid dissociation constants reported by Schmidt and Taube<sup>21</sup> [ $K_{\text{RPO}_4\text{H}_3^{3+}} =$

TABLE IV

RATE CONSTANTS ( $M^{-1} \text{SEC}^{-1}$ ) FOR REDUCTION OF PHOSFATOPENTAAMMINECOBALT(III) COMPLEXES

Complex	Reductant		
	$\text{Cr}^{2+}$	$\text{V}^{2+}$	$\text{Eu}^{2+}$
$\text{RPO}_4$	$4.8 \times 10^9$	$1.4 \times 10^7$	...
$\text{RPO}_4\text{H}^-$	$8.3 \times 10^3$	$1.6 \times 10^2$	$5 \times 10^2$
$\text{RPO}_4\text{H}_2^{2-}$	0.3	2.3	6
$\text{RPO}_4\text{H}_3^{3-}$	0.3	4.5	$\sim 3$

$4.7$  ( $\mu = 3.0$ );  $K_{\text{RPO}_4\text{H}_2^{2+}} = 2.2 \times 10^{-4}$  ( $\mu = 1.0$ );  $K_{\text{RPO}_4\text{H}^-} = 3.2 \times 10^{-9}$  ( $\mu = 1.0$ ), all at  $25^\circ$ ] and fitting the observed pH dependence of the rate. The rate constants which gave a satisfactory fit (illustrated by the solid curves in Fig. 1) are listed in Table IV.

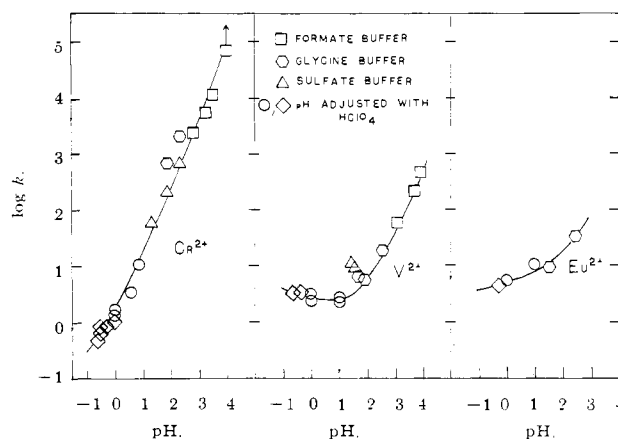


Fig. 1.—pH dependence of the apparent rate constant for the reduction of phosphatopentaamminecobalt(III) at  $25^\circ$ . Ionic strength adjusted with  $\text{NaClO}_4$  to 1.0, except for experiments at  $\text{pH} < 0$  ( $\diamond$ ) in which the ionic strength was 5.0. Points represent experimental values. Curves are calculated using the rate constants in Table IV.

It is believed that the rate constants obtained in this way for  $\text{RPO}_4\text{H}^+$  and  $\text{RPO}_4\text{H}_2^{2+}$  are fairly reliable while the estimates for  $\text{RPO}_4$  and  $\text{RPO}_4\text{H}_3^{3+}$  are necessarily limited by the impossibility of extending the pH range of the kinetic measurements into the region of predominance of those species.

Preliminary measurements on the reduction of  $\text{RPO}_4$  by  $\text{Cr}(\text{bipy})_3^{2+}$  indicated that this reaction does not proceed directly but rather through a dissociation product of  $\text{Cr}(\text{bipy})_3^{2+}$ , the dissociation step being rate determining. The kinetics of this reaction were found to be first order in  $\text{Cr}(\text{bipy})_3^{2+}$  and zero order in  $\text{RPO}_4$ , the first-order rate constant ( $0.37 \text{ sec}^{-1}$  at  $25^\circ$ ,  $\mu = 0.1$ ) being the same as that for the dissociation of  $\text{Cr}(\text{bipy})_3^{2+}$  in strongly acidic solutions. This system is still under investigation.

### Discussion

As a starting point for the interpretation of the above results, it is assumed (although not explicitly demonstrated in every case) that, except with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Co}(\text{en})_3^{3+}$  as oxidants (which presumably always react by outer-sphere mechanisms) reduction by  $\text{Cr}^{2+}$  proceeds by an inner-sphere mechanism involving electron transfer through the bridging ligand X, while the reductions by  $\text{Cr}(\text{bipy})_3^{2+}$  under our conditions are of the outer-sphere type.

A striking feature of the results in Table II is the much greater variation in rate, with variation in the oxidant, exhibited by  $\text{Cr}^{2+}$  than by the other reductants. It seems reasonable to attribute this, in part at least, to the inner-sphere bridging role of X in these reactions, correspondingly large variations in rate having been observed in the  $\text{Cr}^{2+}-\text{Cr}^{\text{III}}\text{X}$ ,<sup>23</sup>  $\text{Cr}^{2+}-\text{Cr}^{\text{III}}(\text{NH}_3)_5\text{X}$ ,<sup>24</sup> and  $\text{Co}(\text{CN})_5^{3-}-\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}^6$  reactions, which also proceed through inner-sphere bridging mechanisms. Another contributing factor here may be the fact that the oxidation of  $\text{Cr}^{2+}_{\text{aq}}$  involves the transfer of an electron from an antibonding  $e_g$  orbital with a consequent reorganization of the coordination shell (i.e., adjustment of the metal-ligand bond lengths) and resulting Franck-Condon barrier which is probably more severe than for the other reactants. The marked dependence of the rate on the bridging ligand X may thus reflect the important role which displacement of the latter makes toward reducing this barrier.<sup>25</sup>

(23) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(24) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

(25) L. Orgel, "Report X Conseil Chimie Solvay," Brussels, 1956, p. 289.

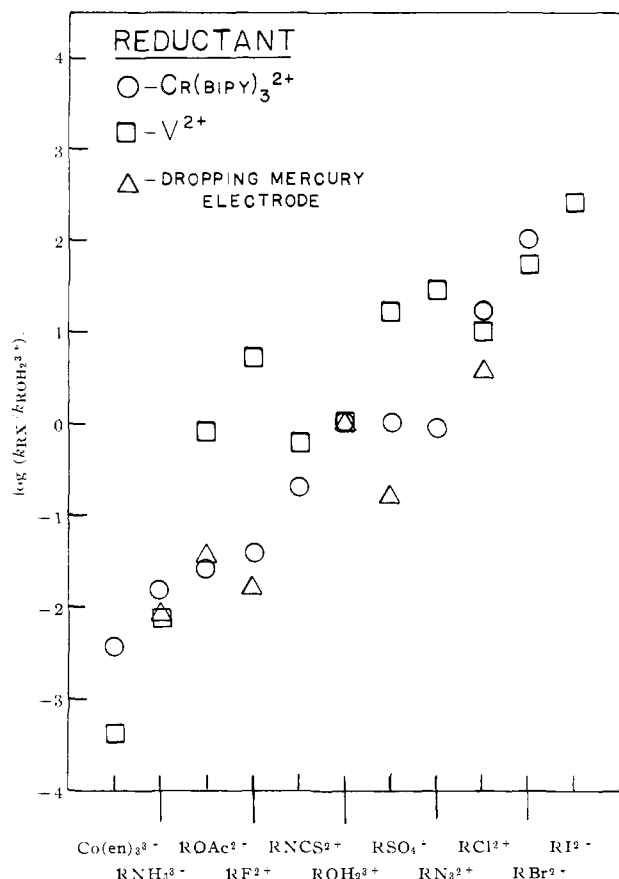


Fig. 2.—Relative rate constants at 25° (referred in each case to the rate for  $\text{ROH}_2^{3+}$ ) for the reduction of various cobalt(III) complexes arranged in approximate order of increasing reactivity. Ionic strengths:  $\text{Cr}(\text{bipy})_3^{2+} - 0.1$ ;  $\text{V}^{2+} - 1.0$ ; dropping mercury electrode (based on data of Vlček<sup>27</sup>)  $- 0.4$ .

The rates for  $\text{V}^{2+}$  exhibit a somewhat smaller variation with X. It is tempting to infer from this that oxidation of  $\text{V}^{2+}$  proceeds by an outer-sphere mechanism, a conclusion reinforced by the strikingly parallel trends exhibited (Fig. 2) by the rates for  $\text{V}^{2+}$  and  $\text{Cr}(\text{bipy})_3^{2+}$ , both of which further show a correlation with the corresponding rates of electrochemical reduction of pentaamminecobalt(III) complexes at a dropping mercury electrode determined by Vlček.<sup>26</sup> More limited correlations along these lines have previously been noted, and similarly interpreted, by Zwickel and Taube<sup>9</sup> and by Marcus<sup>8</sup> and are in accord with the predictions of the Marcus theory.<sup>8</sup>

The general order of increasing reactivity of the cobalt(III) complexes, depicted in Fig. 2, is seen to be approximately the same as the order of decreasing excitation energy,  ${}^1\Gamma_1(t_{2g})^6 \rightarrow {}^1\Gamma_4(t_{2g}^5e_g)$ , of the complex, reflected in the wave lengths in Table I, due to decreasing ligand field strength of the hetero-ligand, X. Vlček<sup>26, 27</sup> has previously called attention to a quantitative correlation along these lines in the case of the electrochemical reduction process and has discussed its possible significance, suggesting that both the exci-

tation and electron-transfer processes may involve a  $t_{2g} \rightarrow e_g$  electronic promotion.

The variation of the rate constants for  $\text{Eu}^{2+}$  does not appear to parallel closely that for any of the other reductants. This system does however present a feature of very great interest, namely the order of reactivity of  $\text{Eu}^{2+}$  toward the halopentaamminecobalt(III) complexes, which follows the sequence  $\text{RF}^{2+} > \text{RCl}^{2+} > \text{RBr}^{2+} > \text{RI}^{2+}$ . This is the reverse of that found for  $\text{V}^{2+}$ ,  $\text{Cr}(\text{bipy})_3^{2+}$ , and  $\text{Co}(\text{CN})_5^{3-}$  as reductants and of most other electron-transfer systems thus far studied including the  $\text{Cr}^{2+}$ - $\text{CrX}^{2+}$  and  $\text{Cr}^{2+}$ - $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$  reactions.<sup>23, 24</sup> The sequence for  $\text{Eu}^{2+}$  is difficult to reconcile with an outer-sphere mechanism and the only explanation for it which we are able to suggest is that it reflects a contribution to the driving force for reaction derived from increasing thermodynamic stability of the europium(III) halide product complex in going along the series  $\text{EuI}^{2+}$ ,  $\text{EuBr}^{2+}$ ,  $\text{EuCl}^{2+}$ , and  $\text{EuF}^{2+}$ . The implication of this is that these reactions proceed, in part at least, by an inner-sphere mechanism.

The reactivities of  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$  toward the phosphato complexes all appear to follow the same order  $\text{RPO}_4 > \text{RPO}_4\text{H}^+ > \text{RPO}_4\text{H}_2^{2+} \sim \text{RPO}_4\text{H}_3^{3+}$  and indeed the rate constants for each complex do not vary much from one reductant to another. This is considered as suggestive of, but hardly compelling evidence for, the operation of a common mechanism. Unfortunately corresponding rate constants for  $\text{Cr}(\text{bipy})_3^{2+}$  are not available for comparison, since the reaction with this reductant appears to proceed through an indirect mechanism (see previous discussion) involving a rate-determining dissociation of  $\text{Cr}(\text{bipy})_3^{2+}$ .

It has been suggested<sup>4</sup> that measurements of  $\Delta S^\ddagger$ , which should be sensitive to the structure of the activated complex, might provide another basis for distinguishing between inner- and outer-sphere electron-transfer mechanisms. Neither earlier results nor those obtained in this study (Table III) appear to offer much encouragement in this direction. Most of the activation entropies are seen to lie in the range  $-(25 \pm 10)$  e.u. The variation is probably not greatly outside the range of experimental uncertainty and no systematic trend is discernible. Measurements are presently under way in this laboratory of the volume of activation of some of these reactions, another kinetic parameter of potential interest from this standpoint.

A final comment would appear to be in order, emphasizing the lack of justification, within the context of the general approach adopted here, for assuming that the reactions of a given reductant, even with a series of closely related oxidants, all proceed through the same mechanism. Thus, it has recently been shown<sup>6</sup> that the reduction of pentaamminecobalt(III) complexes by  $\text{Co}(\text{CN})_5^{3-}$  may proceed either by outer- or inner-sphere mechanisms. A similar conclusion is indicated for  $\text{V}^{2+}$ , convincing evidence having previously been advanced that the reduction of methylfumaratopentaamminecobalt(III) and related complexes by this reductant proceeds through an inner-sphere bridging mechanism involving remote attack by  $\text{V}^{2+}$  on the conjugated ligand.<sup>28</sup>

(26) A. A. Vlček in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, p. 590.

(27) A. A. Vlček, *Discussions Faraday Soc.*, **26**, 164 (1958).

(28) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, 2239, 2242 (1961).