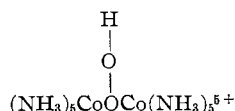


CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305The Reduction of Decaammine- $\mu$ -superoxo-dicobalt Ion by  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$ 

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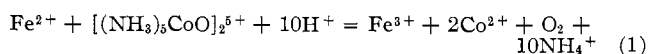
The reduction of  $(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5^{5+}$  by the agents  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$  in excess requires 5 mol of reductant per mol of oxidant. The primary act is a one-electron reduction of the superoxo ion, in which is formed an intermediate common to the three systems. The intermediate decomposes to  $\text{Co}^{2+}$  and  $\text{O}_2$ , rather than being reduced by the agents which generate it. The rate of decomposition is inverse in  $(\text{H}^+)$ , and we postulate that the intermediate in acidic solution has the form



The absorption spectrum of the intermediate was determined. It has an absorption maximum at  $\sim 500 \text{ m}\mu$  ( $\epsilon \sim 200 \text{ l./mol cm}$ ). The rates of reduction of the superoxo ion are first order in (complex) and first order in (reductant) and independent of the concentration of  $\text{H}^+$ . The reactions are limited in rate by the entropies, rather than the enthalpies of activation, the latter being very small.

## Introduction

Sykes<sup>1</sup> has reported on the kinetics of reduction of decaammine- $\mu$ -superoxo-dicobalt ion by  $\text{Fe}^{2+}$



We have been studying<sup>2</sup> the reduction of polynuclear  $\text{Co}(\text{III})$  complexes by  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$  and have turned to the reduction of  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$  to provide an extension of and comparison with Sykes's<sup>1</sup> results obtained with the weaker reducing agent  $\text{Fe}^{2+}$ .

## Experimental Section

**Materials.**—Except for the complex or present interest, the substances and solutions used have been described in the earlier publication.<sup>2</sup> Decaammine- $\mu$ -superoxo-dicobalt(III) perchlorate was prepared as described by Ebsworth and Weil.<sup>3</sup> The pale blue needles thus obtained were washed with alcohol, dried with ether, and immediately dissolved in 0.1 *M* perchloric acid (the perchlorate salt is quite unstable in the solid form and decomposes completely to a gray-green powder in a matter of hours). The resulting solution was stored in a black-taped flask at 4°, since fading of similar stock solutions stored at room temperature in clear glass had been previously noted. The solution stored as above was analyzed for cobalt by the method of Kitson<sup>4</sup> and the concentration of dimer was assumed to be half the concentration of total cobalt. Periodic spectrophotometric examination of the stock solution at 670  $\text{m}\mu$  ( $\epsilon 8381 \text{ l./mol cm}$ ) showed that loss of dimer under these conditions was slow (about 5% in 6 months).

**Stoichiometry.**—The extent of reaction was determined by the change in absorbance at 670  $\text{m}\mu$ . At this wavelength  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$  has maximum absorbance in the visible region and absorbance differences between the various reductants and their oxidized forms are almost at a minimum. The products of the reaction with  $\text{Cr}^{2+}$  were additionally analyzed by passing the diluted product solution through an ion-exchange column containing Dowex 50-X2 resin (200–400 mesh). The pink cobalt(II) band was washed off with 0.1 *M* perchloric acid and the hexa-aquochromium(III) band was removed and collected with a solution 0.5 *M* in both lithium perchlorate and perchloric acid.

The chromium was determined by oxidation to chromium(VI) by basic peroxide. The green chromium(III) dimer band was difficult to remove cleanly, so the total resin was treated by the peroxide oxidation and the solution was separated from the clean resin by settling and decantation. The solution containing chromium(VI) was diluted and analyzed spectrophotometrically.

**Stopped-Flow Kinetic Runs.**—The reactions under investigation are too rapid for batch techniques, and the rates were measured by means of the stopped-flow apparatus assembled and described by Stritar.<sup>5</sup> Runs were made at various temperatures, acidities, and concentrations of oxidant and reductant. Solution temperatures were found to agree with bath temperatures to within 0.3° at 6°, 0.1° at 15° and 33° and to within 0.01° at 25°. Corrected bath temperatures were used in calculations.

Early runs on the chromous reduction were done by observation at  $\lambda 670 \text{ m}\mu$ . Later, the reactions were followed at  $\lambda 292 \text{ m}\mu$  ( $\epsilon 2.59 \times 10^4 \text{ l./mol cm}$  for the decaammine-1-superoxo-dicobalt(III)ion), both because the stock solutions could be conserved and because the high rate constants for the europous and vanadous reductions called for more dilute solutions. All runs were performed at a total perchlorate concentration of 1.0 *M*.

**Attempts to Characterize the Intermediate.**—An attempt was made to detect an intermediate in the reduction with  $\text{V}^{2+}$  in 3–6 *M*  $\text{HClO}_4$ . A storage flask and attached spectrophotometric cell were immersed in an ice-salt bath at  $-15^\circ$ . After the solution was deaerated and cooled, an equimolar amount of vanadous solution was added to the storage flask and, after mixing, the solution was immediately transferred to the cell. The cooled cell was placed in a specially arranged compartment in the spectrophotometer and the spectrum was recorded. The special apparatus allowed the complete immersion of the cell in an ethylene glycol-water mixture at  $-15^\circ$  and eliminated the problem of fogging of the windows of the spectrophotometer itself as well as those of the cell.<sup>6</sup>

In a second method of spectrophotometric characterization of the intermediate the stopped-flow apparatus was used, the reaction conditions being low temperatures, high solution acidity, and high vanadous concentrations. With this combination of conditions the reduction of the superoxo complex takes place rapidly compared to the decomposition of the intermediate which is formed.

The syringes were driven forward at a low, but constant, motor speed and the intensity readings were recorded for both the

(1) A. G. Sykes, *Trans. Faraday Soc.*, **59**, 1325 (1963).(2) A. B. Hoffman and H. Taube, *Inorg. Chem.*, **7**, 904 (1968).(3) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).(4) R. E. Kitson, *Anal. Chem.*, **22**, 864 (1950).

(5) J. A. Stritar, Ph.D. Thesis, Department of Chemistry, Stanford University, Stanford, Calif., 1967.

(6) F. Nordmeyer, Ph.D. Thesis, Stanford University, Stanford, Calif., 1967.

moving solution and the stopped solution at the end of the redox reaction. For each different wavelength, the reaction was repeated. The spectra of vanadous and vanadium(III) ions under these conditions were determined on the Cary 15. The data obtained were used as described in the Results section to determine the absorption spectrum of the intermediate.

**Treatment of Data.**—Data from kinetic runs on the stopped-flow apparatus were treated in several different ways. The overall reaction involves two rate-determining steps, with different dependencies on pH, temperature, and reductant concentrations, and the steps can be separated or mixed, depending on reaction conditions. When the first reaction is rapid compared to the second, the absorbance data (taken as described by Stritar<sup>8</sup> from intensities recorded on film) for the second reaction were treated by the standard method for first-order reactions. When the second step is much faster than the first, the treatment is again straightforward, particularly for the reaction under pseudo-first-order conditions. The method of treatment of the data for second-order conditions is not given in detail but is described in detail elsewhere.<sup>7</sup>

When the rates were about equal, the intensity data were treated by means of an Algol 60 program described by Stritar.<sup>5</sup> The required data include initial and final intensities, intensities and times at various points in the reaction, initial concentrations of reactants, a series of equations describing the disappearance of reactants and intermediate, and the rate constant for the second reaction,  $k_{\text{obsd}}$ . Estimates are also needed for  $k_m$  (second-order rate constant for the reduction of the superoxo complex), extinction coefficient differences between the intermediate and products, and the possible error in the indicated starting time of the reaction. By an iterative process and least-squares analysis, the computer determined the values of the variables which gave the best fit for the data supplied, and it printed out the values of the variables and data numbers calculated from them.

**Conditions.**—All kinetic runs were done at a constant perchlorate ion concentration of 1.0 *M*. In runs at low acidities the anion concentration was maintained with lithium perchlorate.

## Results

**Spectrum of the Superoxo Complex.**—The spectrum of the decaammine- $\mu$ -superoxo-dicobalt(III) ion in acidic solution has peaks at  $\lambda$  292  $m\mu$  ( $\epsilon$   $2.59 \times 10^4$  l./mol cm),  $\lambda$  481  $m\mu$  ( $\epsilon$  260 l./mol cm), and  $\lambda$  670  $m\mu$  ( $\epsilon$  838 l./mol cm). The peaks 670 and 292  $m\mu$  were followed in the kinetic runs described.

**Stoichiometry.**—It was discovered early in the investigation of the vanadous ion reduction of  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$  that the total reaction involves at least two distinct steps. The stoichiometry checks were undertaken to determine how many electrons are transferred in each step. Complete reduction of the complex to  $\text{H}_2\text{O}$ ,  $\text{Co}^{2+}$ , and  $\text{NH}_4^+$ , requires 5 mol of reducing agent per mol of complex, and this stoichiometry was observed in the chromous ion reduction under all conditions tested. However, the reaction of europous ion in a 1:1 molar ratio with the superoxo complex resulted in the disappearance of approximately 50% of the complex, while similar treatment with vanadous ion resulted in about 93% disappearance. As will be discussed later, the initial reaction of each reducing agent produces an intermediate which displays identical kinetic behavior in all three systems. It was therefore assumed that the first step in each case was the same, producing a common intermediate. The differences in the stoichiometry can then be explained as arising

from different relative rates of the first and second reactions; as will be shown, the relative rates for the first reaction exhibit the trend (vanadous > europous > chromous). The highest consumption of the complex, as achieved with vanadous ion, indicates that the first step must involve the transfer of a single electron.

Analysis of the Cr(III) product of experiments in which the  $\text{Cr}^{2+}$  concentration was five times that of the superoxo complex showed that about 60% of the Cr(III) appeared in condensed forms, and 40% as  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ .

**Kinetic Data for the Initial Reduction of the Superoxo Complex.**—The rate law for the reduction of  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$  by any of the three reductants ( $\text{M}^{2+}$ ) was found to be of the form

$$-d \ln ([(\text{NH}_3)_5\text{CoO}]_2^{5+})/dt = k_m(\text{M}^{2+}) \quad (2)$$

The values for  $k_m$  for the three reductants are shown in Table I.

$10^4(\text{M}^{2+}), M$	$(\text{H}^+), M$	Temp, °C	$10^{-3}k_m, M^{-1} \text{sec}^{-1}$
Cr <sup>2+</sup> Reductant			
71	0.97	34.5	2.28
142	0.97	32.7	2.44
71	0.10	33.2	2.32
71	0.97	25.2	2.39
142	0.97	25.2	2.30
71	0.10	25.2	2.19
71	0.97	14.8	2.12
71	0.10	13.1	2.12
142	0.97	14.1	2.06
V <sup>2+</sup> Reductant			
3.2	1.0	33.2	93.1
6.9	1.0	30.7	90.7
3.2	0.1	25.8	102
3.2	1.0	24.9	98.6
6.9	1.0	25.0	94.3
3.2	1.0	15.4	95.7
6.9	1.0	15.5	105
6.9	1.0	6.2	104
3.2	1.0	6.2	88.6
Eu <sup>2+</sup> Reductant			
2.50	1.0	25.0	20
2.73	0.1	12.5	18
6.80	1.0	12.5	25
5.02	1.0	25.0	36
6.80	1.0	25.0	34
7.50	1.0	25.0	26
13.6	1.0	25.0	30
2.50	0.1	25.0	29
2.73	0.1	25.0	27
6.80	1.0	32.1	24
13.6	1.0	32.2	26

<sup>a</sup> For Cr<sup>2+</sup> as a reductant, the complex concentration is  $(5.7-8.5) \times 10^{-4} M$ ; for V<sup>2+</sup> and Eu<sup>2+</sup>,  $1.6 \times 10^{-5} M$ .

It is clear from the data that the values of  $k_m$  are independent of the concentrations of the complex, of the reductant, and of hydrogen ion. The data for Cr<sup>2+</sup> and V<sup>2+</sup> were found to be satisfactorily reproducible; making the assumption that  $\Delta S^\ddagger$  is independent of temperature, they lead to the following values of the activation parameters: for Cr<sup>2+</sup>,  $\Delta H^\ddagger = 0.5 \pm 0.5 \text{ kcal/mol}$

(7) A. B. Hoffman, Ph.D. Thesis, Stanford University, Stanford, Calif., 1967.

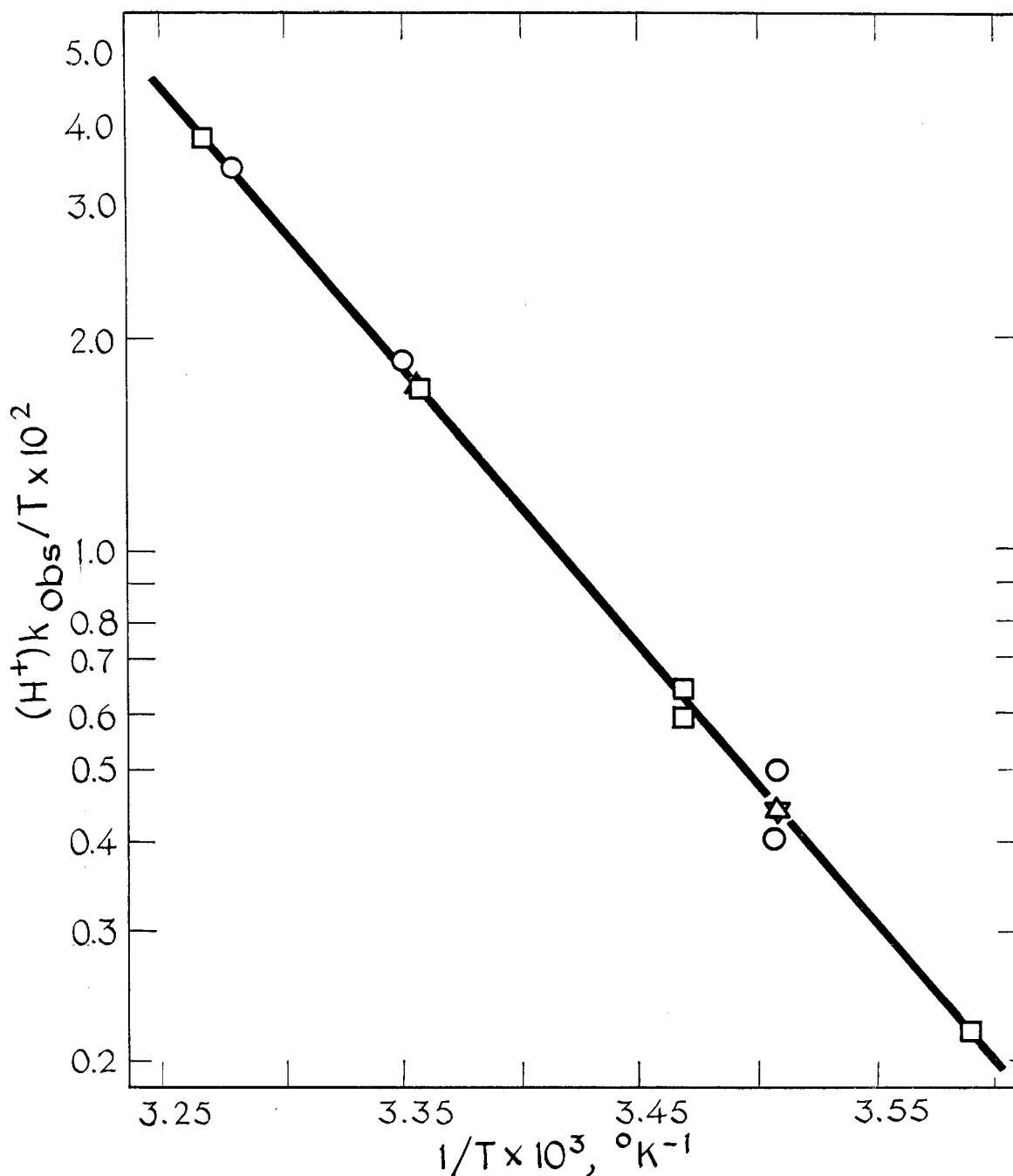


Figure 1.—The rate of decomposition of the intermediate as a function of temperature.

and  $\Delta S^\ddagger = -41 \pm 1$  eu; for  $\text{V}^{2+}$ ,  $\Delta H^\ddagger = -1.4 \pm 0.6$  kcal/mol and  $\Delta S^\ddagger = -45 \pm 1$  eu. The data for  $\text{Eu}^{2+}$  are less reproducible and scatter outside the limits of expected experimental error. Though the source of the difficulty was not traced, it yet seems safe to conclude that we have at least an approximate measure of the rate of reduction by  $\text{Eu}^{2+}$  and that, as for  $\text{Cr}^{2+}$  and  $\text{V}^{2+}$  as reductants, the activation energy of the reaction is very small.

**Kinetics of the Disappearance of the Intermediate.**—The results of the analysis of the kinetic data which pertain to the second phase of the reaction, that dealing with the disappearance of the intermediate (int), are recorded in Table II. The rate constant  $k_{\text{obsd}}$  is defined by the rate law

$$-d \ln (\text{int})/dt = k_{\text{obsd}} \quad (3)$$

The extreme right-hand column of Table II shows the values of  $k_1$  defined by the rate law

$$-d \ln (\text{int})/dt = k_1/(\text{H}^+) \quad (4)$$

The fact that eq 4 does describe the variation of rate with concentration of reductant and with the concentration of hydrogen ion is not readily apparent from Table II but is immediately apparent from an examination of Figure 1, in which  $k_1$  ( $\equiv k_{\text{obsd}}(\text{H}^+)$ ) is shown as a function of  $T$  in an Eyring plot. It is obvious that  $k_1$  is a function only of  $T$  among the variables tested in this work. Since  $k_1$  does not depend on the identity or concentration of the reducing agent which is used to produce it, we can conclude that the intermediate dis-

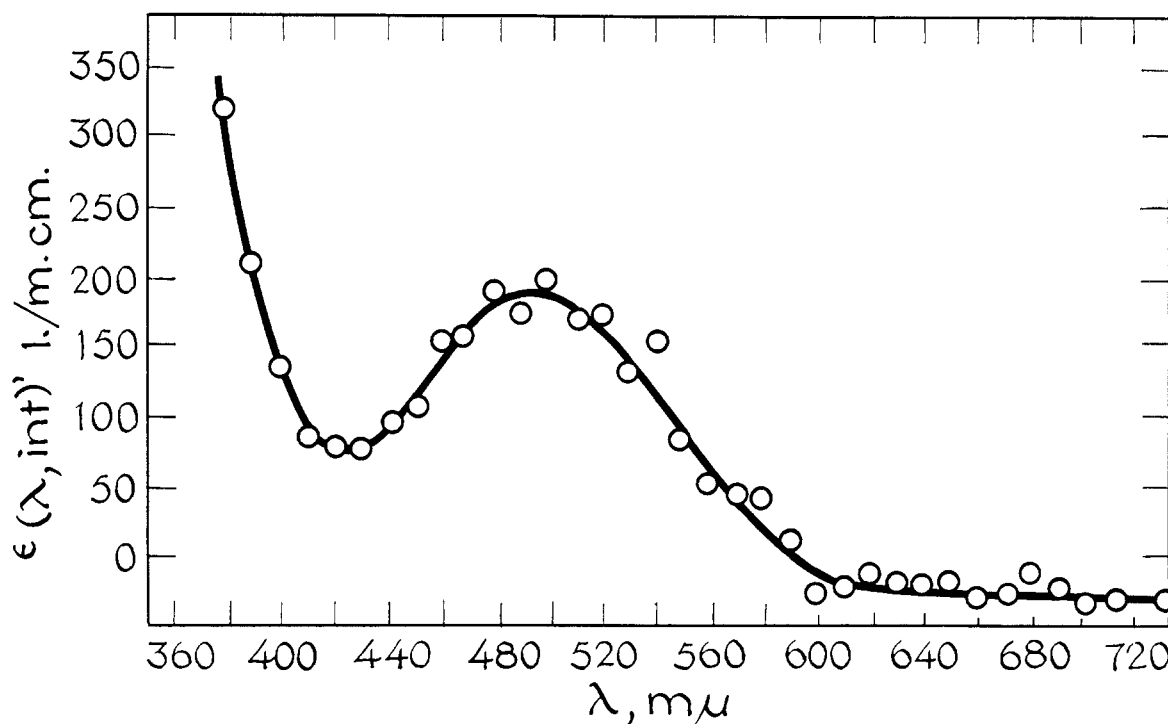


Figure 2.—Plots of  $\epsilon_{\lambda, \text{int}}$  and  $\log \epsilon_{\lambda, \text{int}}$  vs.  $\lambda$  for the intermediate in the superoxo-bridged dimer reduction by vanadous ion.

TABLE II  
KINETIC DATA FOR THE DISAPPEARANCE  
OF THE INTERMEDIATE<sup>a</sup>

M <sup>2+</sup>	(M <sup>2+</sup> ), M	(H <sup>+</sup> ), M	Temp., °C	$k_{\text{obsd.}}$ , sec <sup>-1</sup>	$k_{\text{obsd.}}(\text{H}^+)$ , M sec <sup>-1</sup>
V <sup>2+</sup>	$6.9 \times 10^{-4}$	1.00	30.8	$11.5 \pm 0.5$	11.5
Cr <sup>2+</sup>	$6.3 \times 10^{-2}$	0.83	32.4	$13.0 \pm 0.5$	10.8
Cr <sup>2+</sup>	$6.3 \times 10^{-2}$	0.83	25.0	$6.64 \pm 0.2$	5.50
Eu <sup>2+</sup>	$2.7 \times 10^{-2}$	1.00	25.0	$5.04 \pm 0.1$	5.04
V <sup>2+</sup>	$6.9 \times 10^{-4}$	1.00	25.0	$4.99 \pm 0.1$	4.99
V <sup>2+</sup>	$3.2 \times 10^{-4}$	1.00	15.3	$1.85 \pm 0.05$	1.85
V <sup>2+</sup>	$6.9 \times 10^{-4}$	1.00	15.5	$1.69 \pm 0.05$	1.69
Cr <sup>2+</sup>	$6.3 \times 10^{-2}$	0.83	12.5	$1.69 \pm 0.05$	1.40
Cr <sup>2+</sup>	$6.3 \times 10^{-2}$	0.50	12.6	$2.50 \pm 0.1$	1.25
Cr <sup>2+</sup>	$3.8 \times 10^{-2}$	0.89	12.6	$1.25 \pm 0.05$	1.11
Eu <sup>2+</sup>	$1.4 \times 10^{-3}$	1.00	12.5	$1.26 \pm 0.05$	1.26
Eu <sup>2+</sup>	$1.4 \times 10^{-3}$	0.50	12.5	$2.48 \pm 0.08$	1.24
V <sup>2+</sup>	$3.2 \times 10^{-4}$	1.00	6.2	$0.58 \pm 0.01$	0.58

<sup>a</sup> The reducing agent is present in large excess.

appears by decomposition rather than by being reduced by excess reducing agents.

**Characterization of the Intermediate.**—The attempts to record a spectrum of the intermediate on the Cary spectrophotometer were largely unsuccessful. To slow the second reaction sufficiently for observation by ordinary techniques requires the temperature to be low and the acidity to be high. Unfortunately, such conditions also favor the precipitation of various components in the solution. Good spectra were not obtained in these experiments, although a definite pink color which faded with time was observed visually in one case. Sykes<sup>1</sup> reported the appearance of a similar transient pink color in some of his studies done in 2 M hydrochloric acid.

In the stopped-flow determination of the spectrum of the intermediate, high concentrations of both the

vanadous ion and the superoxo complex were used to speed up the first reaction and to provide a relatively large concentration of the intermediate. High acidity (1.87 M perchloric acid) and low temperature (10.8°) also helped lengthen the lifetime of the intermediate. Assuming a one-electron change in the first step, a four-electron change after decomposition of the intermediate, and validity of Beer's law for all species, the equations

$$A_{\lambda, \text{fs}} = \epsilon_{\lambda, \text{int}} b c_{\text{int}} + 4\epsilon_{\lambda, \text{V}^{2+}} b c_{\text{int}} + \epsilon_{\lambda, \text{V}^{3+}} b c_{\text{int}} + A_b \quad (5)$$

$$A_{\lambda, \infty} = [2\epsilon_{\lambda, \text{Co}^{2+}} + 5\epsilon_{\lambda, \text{V}^{3+}}] b c_{\text{int}} + A_b \quad (6)$$

are obtained where  $A_{\lambda, \text{fs}}$  is the absorbance of the flowing solution at wavelength  $\lambda$ ,  $A_{\lambda, \infty}$  is the final absorbance of the stopped solution at wavelength  $\lambda$ ,  $c_{\text{int}}$  is the concentration of intermediate at time of flow observation approximately equal to initial concentration of  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$ ,  $\epsilon_{\lambda, \text{m}}$  is the extinction coefficient of species M at wavelength  $\lambda$ ,  $b$  is the length of the light path through solution (0.224 cm), and  $A_b$  is the sum of the absorbances of species not involved in the reaction. Subtraction and rearrangement give

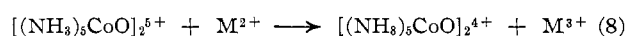
$$\epsilon_{\lambda, \text{int}} = \frac{\Delta A_{\lambda}}{b c_{\text{int}}} + 4[\epsilon_{\lambda, \text{V}^{3+}} - \epsilon_{\lambda, \text{V}^{2+}}] + 2\epsilon_{\lambda, \text{Co}^{2+}} \quad (7)$$

where  $\Delta A_{\lambda}$  is the difference between  $A_{\lambda, \text{fs}}$  and  $A_{\lambda, \infty}$ . Using the values for  $\Delta A_{\lambda}$ ,  $\epsilon_{\lambda, \text{V}^{2+}}$ , and  $\epsilon_{\lambda, \text{V}^{3+}}$  obtained as previously described and the values for  $\epsilon_{\lambda, \text{Co}^{2+}}$  tabulated by Nordmeyer,<sup>5</sup> the quantity  $\epsilon_{\lambda, \text{int}}$  was determined at 10- $\mu\text{m}$  intervals from 280 to 730  $\mu\text{m}$  and was plotted against wavelength as shown in Figure 2. The scatter in this plot is probably caused by inherent errors in the measurement of small absorbance changes over the high background of absorbance by the unreacted vanadous solution. The consistently negative value of  $\epsilon_{\lambda, \text{int}}$  in the region 580–730  $\mu\text{m}$  is believed to be the

result of a shift of the entire spectrum caused by mechanical problems with the stopping of the syringes. Such problems have been observed in other cases with the apparatus<sup>5</sup> and are evidently due to one syringe stopping slightly after the other and thus introducing a slight excess of the reagent contained therein into the light beam. The negative value of  $\epsilon_{\lambda, \text{int}}$  is not caused by the light emission from the solution. Runs with the light source off gave no discernible change in photomultiplier output during the reaction.

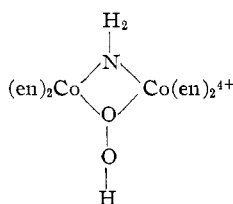
### Discussion

The course of the reaction with the reducing agents  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$  differs from that with  $\text{Fe}^{2+}$  only in the respect that the oxygen liberated in the decomposition of the intermediate generated by the one-electron reduction of  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$  is readily reducible by the reducing agents we have used, but not by  $\text{Fe}^{2+}$ . For the four reducing agents, the first step can be taken as

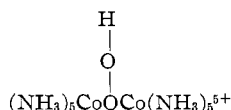


In no case, under the conditions studied, is there reason to suppose that the reducing agent attacks the +4 intermediate ion. Our work has gone beyond that of Sykes in that we have been able to show that the decomposition of the intermediate proceeds at a rate which is inverse in  $(\text{H}^+)$ . This result suggests that the intermediate is rapidly and almost completely protonated in acidic solution and that the decomposition of the intermediate to form  $\text{Co}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{O}_2$  takes place more rapidly for the nonprotic than it does for the protic form. This result is not difficult to understand in a qualitative way, for it is to be expected that  $(\text{H}^+)$  will stabilize the state  $\text{O}_2^{2-}$  relative to  $\text{O}_2$ .

The studies by Thewalt and Marsh,<sup>8</sup> in which they show that the ion<sup>9</sup>  $(\text{en})_4\text{Co}_2\text{NH}_2\text{OOH}^{4+}$  has the structure



suggest that in the protonated intermediate we have encountered the form



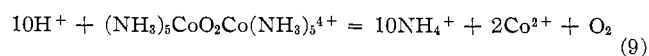
This formulation of the complex is compatible with the spectrum observed for the intermediate which shows the long-wavelength maximum in the absorption to be close to that of  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ . In the parent ion each oxygen bears a cobalt atom,<sup>10</sup> and thus a very facile rearrangement of the bridging group in the reduced form

is indicated, a rearrangement which is likely facilitated by  $(\text{H}^+)$ .

It should be noted that solid red salts containing the ion  $[(\text{NH}_3)_5\text{CoO}]_2^{4+}$ <sup>9</sup> have been isolated and are known to decompose in solution to produce oxygen. No other determinations of the spectrum of the protonated intermediate in solution have been described, but the reflectance spectrum of a solid bisulfate salt of the protonated peroxo-bridged dimer has been recorded.<sup>11</sup> It has a peak around 500  $m\mu$ , with a smaller peak around 670  $m\mu$ . The long-wavelength peak can be ascribed to the presence of the superoxo complex as an impurity.

The low reactivity of the intermediate to the reducing agents  $\text{Cr}^{2+}$  and  $\text{V}^{2+}$  is remarkable, in view of the rapidity with which these ions reduce  $\text{H}_2\text{O}_2$ .<sup>12</sup> The low reactivity has important implications for the mechanism of reduction of  $\text{O}_2$  by metal ions. Many such reactions<sup>13</sup> proceed at a rate which is first order in  $(\text{O}_2)$  and second order in the concentration of the reducing agent. It is reasonable to suppose that a binuclear peroxide complex is a product of the rate-determining step. Our results suggest that in such a complex, the peroxide is protected from further attack by the reducing agent.

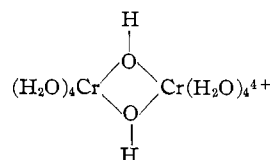
If to the reaction leading to decomposition of the intermediate



is added the reduction of  $\text{O}_2$  by the reducing agents



the total stoichiometry when the reducing agent is in excess is accounted for. Among the reducing agents, it is only for  $\text{Cr}^{2+}$  that we are in position to learn something about reaction 10 as it occurs in the system. The reaction of  $\text{O}_2$  with  $\text{Cr}^{2+}$  is known<sup>14</sup> to produce mainly the "chromic dimer"



as product, and thus the results on the identity of the  $\text{Cr}(\text{III})$  product of the reaction may have some significance. If the reaction of  $\text{Cr}^{2+}$  with  $\text{O}_2$  followed its normal course, ca. 80% of the  $\text{Cr}(\text{III})$  product would be expected as "dimer." The fraction of dimer (or other condensed species) found is considerably less than this. Whether the defect from the expected yield is due to the special concentration conditions obtaining for the  $\text{Cr}^{2+}-\text{O}_2$  reaction in our case or whether to  $\text{Cr}^{2+}$  reacting with  $\text{O}_2$  in some metastable form remains to be settled.

The most remarkable feature of the kinetics of the reduction of the superoxo complex by the reducing agents we have used is the fact that the values of  $\Delta H^\ddagger$  are close to zero (for  $\text{V}^{2+}$  as reductant,  $\Delta H^\ddagger$  in fact

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(9) The facts that Werner's red salt contains  $\text{Co}(\text{III})$  and is an acid salt were established by L. R. Thompson and W. K. Wilmarth, *J. Phys. Chem.*, **56**, 5 (1952).

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seems to be negative, though still small) and the rates are limited by the entropy of activation. The facile reduction of  $[(\text{NH}_3)_5\text{CoO}]_2^{5+}$  compared to  $[(\text{NH}_3)_4\text{CoOH}]_2^{4+}$  is not surprising. When the superoxo ion is oxidant, the electron is absorbed into an orbital centered largely on the oxygen,<sup>3</sup> and the bond rearrangement accompanying electron transfer is small—thus note that the molecular framework remains intact on electron transfer. However, when the dihydroxo-bridged species is the oxidant, the electron absorbed enters an orbital centered largely on Co, which is antibonding with respect to Co and one or more ligands. Rather drastic rearrangement of the molecular structure preceding electron transfer is called for, and the rate of reduction is correspondingly less.

Our kinetic results differ from those of Sykes<sup>1</sup> in that we have observed only a single path for the reductions, whereas he reports three parallel paths for the reduction by  $\text{Fe}^{2+}$ . These paths differ in the way they depend on  $(\text{H}^+)$ . The rate law reported by him has the form

$$-d \ln \{[(\text{NH}_3)_5\text{CoO}]_2^{5+}\} / dt = (\text{Fe}^{2+})[(k_A/(\text{H}^+)) + k_B + k_C(\text{H}^+)]$$

His value of  $k_B = 4.73 \times 10^{-2} M^{-1} \text{sec}^{-1}$  at  $25^\circ$  ( $E_B = 9.6 \text{ kcal/mol}$ ) is directly comparable to the specific rates we have recorded. The importance of the term first

order in  $(\text{H}^+)$  when  $\text{Fe}^{2+}$  is the reducing agent is not unexpected. We have concluded that the dominant form of the intermediate in acidic solution contains one proton more than the reactants, and the kinetic assistance by the proton in forming the intermediate is not unexpected when a weak reducing agent is used. The term inverse in  $(\text{H}^+)$  may reflect the fact that  $\text{OH}^-$  stabilizes  $\text{Fe(III)}$  over  $\text{Fe(II)}$ , and some kinetic assistance from the stabilization can be expected.

All of the reactions are probably of the outer-sphere type. Direct attack on oxygen may be prevented by the steric requirements of the  $\text{NH}_3$  ligands on the cobalt centers. The operation of an outer-sphere mechanism can explain why  $\text{Cr}^{2+}$  reacts less rapidly than does  $\text{V}^{2+}$ . The changes in dimension required when  $\text{Cr}^{2+}$  is oxidized more than compensate for the greater driving force for the  $\text{Cr}^{2+}$  compared to the  $\text{V}^{2+}$  reaction.

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## The Acid-Catalyzed Aquation of Hexaammineruthenium(II) and Pentaamminepyridineruthenium(II) Complex Ions

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The aquation rates of  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$  have been measured in acidic aqueous solutions. It is found that the rate of loss of coordinated ammonia or pyridine from these increases with increasing hydrogen ion concentration, the differential rate law for the loss of the first  $\text{NH}_3$  from  $\text{Ru}(\text{NH}_3)_6^{2+}$  being:  $-d[\text{Ru}(\text{NH}_3)_6^{2+}]/dt = k_1[\text{H}^+][\text{Ru}(\text{NH}_3)_6^{2+}]$ , where  $k_1 = (1.24 \pm 0.03) \times 10^{-3} M^{-1} \text{sec}^{-1}$  at  $25^\circ$ . The pentaamminepyridine complex ion aquates at a somewhat slower rate. Electron-withdrawing substituents on the pyridine ring stabilize the complex, resulting in even slower aquation rates. The stoichiometries and rate laws are described. To explain the results, a mechanism is proposed in which an interaction of a proton with ruthenium  $\pi$  d electrons labilizes the metal–nitrogen bonds.

### Introduction

Recent experiments in this laboratory have been concerned with the preparation and characterization of ruthenium complex ions of the type  $\text{Ru}(\text{NH}_3)_5\text{pyX}^{2+}$ , where X is a variable group attached to the pyridine ring.<sup>1</sup> In the course of this research it was noticed that these complexes undergo slow aquation reactions in acidic solutions at rates which increase with increasing hydrogen ion concentration. This interesting observation led us to investigate these reactions more carefully and to extend the experiments to include the simpler ion  $\text{Ru}(\text{NH}_3)_6^{2+}$ .

### Experimental Section

**Materials.**—Water, which had been passed through an ion-exchange column and then distilled, was redistilled in an all-glass apparatus from basic potassium permanganate before being used to prepare the solutions.  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ , obtained from Johnson Matthey and Co., London, was purified by double recrystallization from 1 M HCl and from water.  $\text{Ru}(\text{NH}_3)_5\text{Cl}_2$  was prepared from  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  as described in the literature.<sup>2</sup> The syntheses of  $\text{Ru}(\text{NH}_3)_5\text{py}(\text{ClO}_4)_2$  and  $\text{Ru}(\text{NH}_3)_5\text{pyX}(\text{ClO}_4)_2$ , where X = *m*- $\text{CH}_3$ , *m*-Cl, *p*- $\text{CH}_3$ , and *m*- $\text{CO}_2\text{CH}_3$ , are also reported elsewhere.<sup>1</sup>

All kinetic experiments involving  $\text{Ru}(\text{NH}_3)_6^{2+}$  were run in 1.0 M ionic strength mixtures of *p*-toluenesulfonic acid ( $\text{C}_7\text{H}_7\text{SO}_3\text{H}$ ) and lithium *p*-toluenesulfonate ( $\text{C}_7\text{H}_7\text{SO}_3\text{Li}$ ). These mixtures

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