

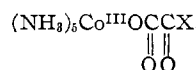
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The Reduction of α -Carbonylcarboxylic Acid Complexes of Pentaamminecobalt(III) by Chromous, Vanadous, and Hexaammineruthenium(II) Ions

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The rates of reduction by Cr^{2+} of the complexes of the class



(where X may be OH, O^- , NH_2 , H, CH_3 , or $\text{C}(\text{CH}_3)_3$) cover a wide range, decreasing when X is electron withdrawing. Chelated products are formed when X = OH, O^- , or NH_2 , but chelation does not appear to be a primary factor in producing an increase in rate. It is concluded that the availability of a low-lying orbital is the major factor producing the rate differences. When V^{2+} is the reducing agent, the rates of reaction differ only slightly from case to case. This fact, the fact that the rate is close to that expected for substitution on V^{2+} , and the direct proof with the oxalato complex that an inner-sphere activated complex is involved lead us to conclude that in these reactions substitution on V^{2+} is rate determining (or nearly so) for electron transfer. A comparison of the kinetic data for Cr^{2+} and V^{2+} suggests that a superexchange mechanism best explains the observations. With the outer-sphere reductant $\text{Ru}(\text{NH}_3)_6^{2+}$, the rates as with V^{2+} cover only a small range but the rate pattern is quite different from that for V^{2+} (or Cr^{2+}). In accord with other observations, the complex with the ligand having a higher negative charge—in this case $\text{C}_2\text{O}_4^{2-}$ vs. HC_2O_4^- —is reduced less rapidly, but the value of ΔH^\ddagger for the two complexes shows that the relationship noted cannot be general.

The influence of a chelating function in a ligand which is attached to the oxidizing group $(\text{NH}_3)_5\text{Co}^{3+}$ on the rate of reduction of the complex so constituted has been described for some systems.¹ Other studies² have directed attention to the fact that a low-lying unoccupied orbital for the ligand can have a marked effect on the capacity of the ligand to mediate in electron transfer. It seemed of interest to investigate a simple kind of ligand, namely, $\text{O}(\text{C}=\text{O})_2\text{X}$ which combines both functions and provides opportunity to vary the ligand properties by changing the identity of the group X. The work which we are describing was devoted to this kind of study, with $(\text{NH}_3)_5\text{Co}^{\text{III}}$ as the oxidizing center, using the reducing agents Cr^{2+} , V^{2+} , and $\text{Ru}(\text{NH}_3)_6^{2+}$.

The three reducing agents mentioned differ widely in properties and the particular choices were made for the following reasons. Past experience led us to expect, as indeed proved to be the case in this series as well, that Cr^{2+} would act by inner-sphere mechanisms. The reducing agent $\text{Ru}(\text{NH}_3)_6^{2+}$, on the other hand, by virtue of being slow to undergo substitution, is re-

stricted to reacting by outer-sphere mechanisms.³ The indications are that vanadous ion can react by either type of mechanism and it was hoped that comparison of the results obtained with the other two would lead to definite conclusions about the mechanism of reaction for V^{2+} in the present series.

The observations for some of the complexes are complicated by hydration of the carbonyl group, and this has added an interesting dimension to our studies. We have reported separately^{4a} on the results obtained^{4b} with the glyoxylatopentaamminecobalt(III) complex as oxidant and Cr^{2+} as reductant and here complete the report on the effects of hydration with the results on the other two systems which are affected by the hydration equilibrium, namely, those with X = CH_3 or $\text{C}(\text{CH}_3)_3$.

Experimental Section

Materials.—Triply distilled water was used in all experiments. Lithium perchlorate solutions were prepared by dissolving reagent grade lithium carbonate in standardized perchloric acid solutions, chromous perchlorate solutions by reducing standardized stock solutions of chromic perchlorate with amalgamated

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

(2) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

(3) J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).

(4)(a) H. J. Price and H. Taube, *ibid.*, **89**, 269 (1967); (b) H. J. Price, Ph.D. Dissertation, Stanford University, 1966.

zinc under an atmosphere of deoxygenated nitrogen, vanadous perchlorate solutions by zinc amalgam reduction of standard solutions of vanadyl perchlorate, and the vanadyl perchlorate solutions by adding barium perchlorate to vanadyl sulfate solutions and then removing the barium sulfate by decantation.

The vanadium content of the vanadyl solution was determined by oxidation to vanadium(V) using KMnO_4 followed by titration of vanadium(V) by standard Fe^{2+} solution, with diphenylamine-sulfonic acid as indicator. Vanadium(II) was analyzed by injecting a sample into a known excess of $\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}$ and measuring the amount of the latter complex remaining spectrophotometrically. Tests showed that vanadyl solutions were quantitatively reduced to vanadous by amalgamated zinc.

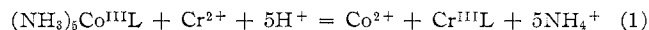
Hexaammineruthenium(II) solutions were prepared by reducing $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ solutions by amalgamated zinc under a nitrogen atmosphere. The $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, obtained from Johnson-Matthey and Co., was recrystallized from 1 *M* HCl before use.

Organic acids used in the preparation of the cobalt(III) complexes were obtained from Eastman Organic Chemicals, Matheson Coleman and Bell, and the Aldrich Chemical Co. Trimethylpyruvic acid was prepared according to the method of Glücksmann,⁵ which involved oxidizing pinacolone (obtained from Aldrich Chemical Co.) with KMnO_4 in basic solution.

Salts of the type $(\text{NH}_3)_6\text{CoL}(\text{ClO}_4)_2$, where L is the anion of an organic acid, were obtained following the method of Butler and Taube,¹ in which the aquoammine perchlorate is heated for several hours with a large excess of the sodium salt of the organic acid. The procedure was modified for the oxamate complex because sodium oxamate was found to be quite insoluble; in this case the lithium salt was used, which was prepared by adding lithium carbonate to a hot solution of oxamic acid. The aquo complex was then added to this solution and the preparation continued in the usual manner. The preparation of the glyoxylato complex has already been described.⁴

The cobalt complexes were analyzed for cobalt by the method of Kitson.⁶ The perchlorate content was determined following the method described by Gould and Taube,² with the modification suggested by Deutsch.⁷ This involved dissolving the complex in a solution of 2.5 *M* NH_4Cl + 0.1 *M* HCl, heating, adding a solution of tetraphenylarsonium chloride, and collecting and weighing the tetraphenylarsonium perchlorate formed. Before drying and weighing, the precipitate was washed with a saturated solution of tetraphenylarsonium perchlorate. The carbon, hydrogen, and nitrogen contents of the complexes were determined by the microanalytical laboratory of the Stanford University Chemistry Department. The analytical data for these complexes, except for the glyoxylato which was reported earlier,⁴ are shown in Table I.

Stoichiometry Measurements.—The stoichiometry of the reactions of the cobalt complexes with Cr^{2+} in the simplest case is expressed by



There is, however, the possibility of deviation from this stoichiometry caused by reduction of the organic ligand by Cr^{2+} . Chromous ion is known to reduce free oxalic acid fairly rapidly,⁸ and it has been found also to reduce free glyoxylic and pyruvic acids.

The stoichiometry of the reaction of the oxalato complex with Cr^{2+} was studied using ion exchange to separate Cr(III) products and also by doing qualitative tests for the presence of reduced forms of the ligand. A solution of the oxalato complex at the desired ionic strength and acid concentration was placed in a small flask which was stoppered with a serum cap. A stream of deoxygenated nitrogen was passed through this solution to remove air. An excess of Cr^{2+} was then injected and the mixture allowed to stand for several hours to ensure that reaction had gone to completion. In one experiment the solution of oxalato complex

TABLE I
ANALYTICAL DATA FOR THE SALTS $[(\text{NH}_3)_6\text{CoO}_2\text{CCOX}](\text{ClO}_4)_2$

X	% Calcd		% Obsd		X	% Calcd		% Obsd			
	Calcd	Obsd	Calcd	Obsd		Calcd	Obsd	Calcd	Obsd		
OH	C	5.56	5.15	C(CH ₃) ₃	C	15.26	14.76	C	15.26	14.76	
	H	3.73	3.62		H	5.12	4.96		H	5.12	4.96
	N	16.21	16.70		N	14.83	14.55		N	14.83	14.55
	Co	13.6	13.4		Co	12.5	12.3		Co	12.5	12.3
	ClO ₄	46.1	45.8		ClO ₄	42.1	42.8		ClO ₄	42.1	42.8
CH ₃	C	8.38	8.6	NH ₂	C	5.57	5.39	C	5.57	5.39	
	H	4.22	4.2		H	3.98	3.94		H	3.98	3.94
	N	16.29	16.58		N	19.50	19.95		N	19.50	19.95
	Co	13.7	13.7		Co	13.7	13.3		Co	13.7	13.3
	ClO ₄	46.2	46.5		ClO ₄	46.1	46.8		ClO ₄	46.1	46.8

was dropped slowly into the Cr^{2+} solution in order to test whether the order of mixing had any effect on the results. The flask was then opened and an aliquot was removed, which was then diluted to the proper volume to reduce the ionic strength to <0.10 *M* and passed through a column of Dowex 50-X12 resin. The chromium(III) species were eluted with HClO_4 of various concentrations, following the procedure of King and Dismukes.⁹ The chromium content of the various fractions was determined spectrophotometrically after oxidation to chromate with H_2O_2 in basic solution.

To test for the presence of reduction products of oxalate, a sample of the undiluted reaction mixture was heated with KOH to free the ligands. This mixture was then filtered, and the filtrate was tested for the presence of glyoxylate and glycolate. The chromotropic acid test was used for glycolate and the 2,3,4-trihydroxybenzoic acid test for glyoxylate; both are described by Feigl.¹⁰

Experiments to determine the stoichiometry of the reaction of the glyoxylato complex with Cr^{2+} have been described elsewhere.⁴

Kinetic Measurements.—The kinetics of all reactions were followed spectrophotometrically by observing the decrease in absorbance corresponding to the disappearance of the Co(III) complexes. The reactions with Cr^{2+} and V^{2+} were carried out in $\text{LiClO}_4\text{-HClO}_4$ media at an ionic strength of 1.00 *M* and various acid concentrations up to 1.00 *M*. In all cases, the acid was in sufficient excess so that it was little depleted during reaction. The reactions with $\text{Ru}(\text{NH}_3)_6^{2+}$ were run in LiCl-HCl media at a lower ionic strength ($\mu = 0.50$) because of the limited stability of the ruthenium species in perchlorate media and the limited solubility. For the slower reactions (half-times of about 30 sec and longer) a Cary Model 14 recording spectrophotometer was used. For faster reactions (half-times as short as 15 msec) a stopped-flow apparatus was required.

The slower reactions were carried out in cylindrical spectrophotometric cells of either 5- or 10-cm path length, using ordinary syringe techniques. These methods have been adequately described by previous workers.¹ The details of the construction and operation of the stopped-flow apparatus will be described elsewhere.¹¹ The data obtained from the stopped-flow apparatus are in the form of a plot of optical transmittance against time. The transmittance is converted to absorbance, which is then treated according to one of the methods described below.

When oxidant and reductant were approximately equivalent, the specific rates were calculated by means of the equation

$$\log \left[A_t + \left(\frac{b}{a} - 1 \right) A_0 - \frac{b}{a} A_\infty \right] = \frac{b-a}{2.303} kt + \log \frac{b}{a} \quad (2)$$

where A_0 is the measured initial absorbance, A_∞ the final absorbance, and A_t the absorbance at any time t during the course

(5) C. Glücksmann, *Monatsh.*, **10**, 770 (1889).

(6) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

(7) E. A. Deutsch, private communication.

(8) R. M. Milburn and H. Taube, *J. Phys. Chem.*, **64**, 1776 (1960).

(9) E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

(10) F. Feigl, "Spot Tests in Organic Analysis," 5th ed, D. Van Nostrand Co., Princeton, N. J., 1954.

(11) J. Sritrar, Ph.D. Thesis, Stanford University, 1967.

of the reaction. The quantities a and b are the initial concentrations of reactants, b being in excess. The function on the left-hand side of eq 2 is plotted against t , and the rate constant k is obtained graphically from the slope of this plot.

Whenever possible, the experiments were done under pseudo-first-order conditions, with a large excess of reducing agent. Equation 2 then simplifies to

$$\log(A_t - A_\infty) = \log(A_0 - A_\infty) - \frac{b - a}{2.303} kt \quad (3)$$

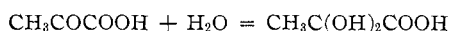
Again the rate constant was obtained graphically. In some cases the rate constants were calculated by the method of Guggenheim,¹² which is well suited for reactions such as those with $\text{Ru}(\text{NH}_3)_6^{2+}$, in which the product mixture undergoes a slow decomposition resulting in a faulty value of $A_\infty(\text{obsd})$. (The ion $\text{Ru}(\text{NH}_3)_6^{2+}$ at high concentration of acid undergoes decomposition reactions of unknown chemistry.^{12a})

Nmr Measurements.—The proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer. The instrument uses a probe frequency of 60 Mc and was operated at ambient temperature (approximately 37°) by personnel of the nmr spectroscopy laboratory of the Stanford University Chemistry Department.

Solutions of the material to be studied were prepared using D_2O as solvent. Either DHO or external TMS was used as the reference. Spectra were obtained for solutions of pure glyoxylic acid (obtained from K & K Laboratories) and for solutions of the chloride salts of the glyoxylato, pyruvato, and trimethylpyruvato complexes (the perchlorate salts of these complexes are too insoluble to give measurable signals).

Results

Constitution of the Cobalt Complexes.—The nmr studies were undertaken to determine the extent of hydration (in solution) of the ligands for several of the cobalt complexes. It is known that in aqueous solution, pyruvic acid is partially hydrated, according to the reaction



This equilibrium is established slowly enough so that two different nmr signals are observed corresponding to the protons of the methyl group in the two different environments.¹³

In a previous paper⁴ we have described the use of the nmr method to show that the glyoxylato complex is essentially completely hydrated in solution. In the present case we are interested in the constitution of the pyruvato and trimethylpyruvato complexes, since both free acids are partially hydrated in solution. For both of these complexes two different signals were observed. The pyruvato complex shows peaks at -1.97 and -2.91 ppm (relative to external TMS), and the trimethylpyruvato complex shows peaks at -1.51 and -1.76 ppm. In each case the peak with the smaller chemical shift is that due to the hydrated form. From the integrals of the nmr bands, we determined that in aqueous solution 28% of the pyruvato complex is in the hydrated form, whereas only 7.7% of the trimethylpyruvato complex is hydrated.^{4b} The results

on the variation of the equilibrium constant for hydration with temperature will be reported elsewhere.

Stoichiometry of the Reactions.—The chromium(III) product of the reduction of the oxalato complex is the chelated oxalato ion, $\text{Cr}(\text{H}_2\text{O})_4\text{C}_2\text{O}_4^{+}$, which has a charge of $+1$. This ion was shown to be the product by an ion-exchange experiment and by comparing its spectrum with that of $\text{Cr}(\text{H}_2\text{O})_4\text{C}_2\text{O}_4^{+}$ prepared by Hamm's method.¹⁴ If reduction of the coordinated ligand by Cr^{2+} occurs, since $\text{C}_2\text{O}_4^{2-}$ is present in limited amount, some uncomplexed Cr(III) will be formed, presumably $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ or $(\text{H}_2\text{O})_3\text{Cr}_2(\text{OH})_2^{4+}$. The complex containing the reduced ligand would subsequently be reduced by Cr^{2+} , and because $\text{C}_2\text{O}_4^{2-}$ is reduced by Cr^{2+} to glycolate,¹⁵ the product of this reaction should be a chromium(III) species with charge $+2$. Thus, the amount of chromium(III) species of charges $+2$ and $+3$ formed should be a measure of the amount of ligand reduction.

The results of the stoichiometry experiments on the oxalato complex are shown in Table II. Experiment 1 was done with a solution of the cobalt complex added slowly to the Cr^{2+} , and experiment 2 with the Cr^{2+} added slowly to the Co(III). The results show that the course of the reaction is not affected by order of mixing. The numbers recorded in the table for the amounts of $+2$ and $+3$ species formed represent the maximum possible amount of ligand reduction. The actual amount of ligand reduction is probably less than the figures indicate for the following reasons: (1) some of the cobalt(II) product is eluted from the ion-exchange column with the Cr(III) fractions and the cobalt oxide formed later is not completely removed by filtration and may cause some interference in chromium determination; (2) a small amount of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is formed by the reaction of Cr^{2+} with oxygen, which occurs when the reaction mixture is opened to the atmosphere to destroy excess Cr^{2+} .

TABLE II
STOICHIOMETRY OF THE REACTION OF $(\text{NH}_3)_5\text{CoO}_2\text{CCOOH}^{2+}$
WITH Cr^{2+} AT 25°, $(\text{H}^+) = 0.2 M$, AND $\mu \sim 0.5$

	mmoles	
	Expt 1	Expt 2
Co ^{III} taken	20.8×10^{-2}	21.1×10^{-2}
Cr ²⁺ taken	98.5×10^{-2}	98.5×10^{-2}
Co ^{II} produced	20.9×10^{-2}	22.4×10^{-2}
Cr ^{III} products	1+	20.4×10^{-2}
	2+	1.8×10^{-2}
	3+	3.8×10^{-2}

The qualitative tests for the presence of glyoxylate or glycolate in the products of the reaction were negative for both experiments. Thus it is seen that the amount of ligand reduction, if it occurs at all, is certainly very small and probably accounts for less than 5% of the oxalato complex which reacts. It has already been shown that the same is true in the case of the glyoxalate complex. Deviations from stoichiometry

(12) Described by R. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed. John Wiley and Sons, Inc., New York, N. Y., 1961, p 49.

(12a) NOTE ADDED IN PROOF.—Work in progress (J. R. Kuempel) shows that release of NH_3 from $\text{Ru}(\text{NH}_3)_6^{2+}$ is first order in (H^+) .

(13) M. Becker, *Z. Elektrochem.*, **68**, 669 (1964).

(14) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958).

(15) R. M. Milburn and H. Taube, *J. Phys. Chem.*, **64**, 1776 (1960).

etry to this extent will not materially affect the results of the kinetic experiments.

The rate of reduction of pyruvic acid by Cr^{2+} is much slower than the rate of reduction of the pyruvate complex, and, in view of this and of the results with oxalate and glyoxylate as ligands, it was deemed unnecessary to investigate the stoichiometry for the pyruvate complex in detail. A rough measurement was made by observing the change in optical density at $501 \text{ m}\mu$ for a reaction mixture with Co(III) in slight excess. The change in optical density corresponded to what would be expected for quantitative reduction of the Co(III) center, and we can therefore conclude that less than 10% of the Cr^{2+} is consumed in reducing ligand.

It should be mentioned that the kinetic studies in most cases also provide evidence that the major reaction involves reduction of only Co(III) . When rate measurements are made with the reducing agent and Co(III) nearly equal in concentration, large deviations from the assumed stoichiometry would result in recognizable trends in the calculated specific rates, and such trends did not appear. This evidence, together with the direct experiments performed for the system which we considered to be the most likely to show ligand reduction, convinced us that excess consumption of reducing agent does not materially affect the specific rates recorded.

In every case, it is important to learn whether the ligand relinquished by Co(III) is taken up by the reducing agent and, furthermore, when it is transferred to learn whether the ligand is chelated to the oxidized form of the reducing agent. For Cr^{2+} as reductant, because chromium(III)-carboxylate complexes are substitution-inert, the first of these questions can readily be answered, and in some cases also the second. Table III shows data on the spectra of the chromium(III) products taken 5 min or more after reaction.

TABLE III
SPECTRAL PROPERTIES OF THE CARBOXYLATOCHROMIUM(III)
REACTION PRODUCTS

Ligand	$\lambda, \text{m}\mu$	ϵ_m	$\lambda, \text{m}\mu$	ϵ_m
Oxalate	418	40.1	556	34.8
Oxamate	412	53	~565	34
Pyruvate	410	21.0	555	19.9
Trimethylpyruvate	412	28.6	571	27.1

Ion-exchange experiments showed that over the whole range of (H^+) covered in our experiments, the chromium(III) product of the oxalate reaction is the chelated species CrC_2O_4^+ . The high values of the extinction coefficient recorded in Table III are in accord with this conclusion. The fact that, for the oxamatochromium(III) product, the values of extinction coefficient are high indicates that, when the oxamatochromium(III) complex is reduced, the Cr(III) product also contains the ligand mainly in the chelated form. By contrast, the values of extinction coefficient recorded for the pyruvatochromium(III) product are in the range of those expected for monodentate com-

plexes.¹⁶ The trimethylpyruvato complex may however be partly chelated.

Though the final product in the case of the pyruvato complex is undoubtedly mainly the monodentate form, the possibility exists that the primary product is chelated but that rapid ring opening ensues, presumably by substitution at the carbon of the carbonyl function. Observations¹⁷ on the acetonatopentaamminecobalt(III) complex show that loss of acetone from the complex in water is rapid, but not so rapid that the rate in the water-acetone mixture cannot be measured by ordinary spectrophotometric techniques. Special experiments were done searching for absorption changes in the Cr(III) product of the pyruvato- Cr^{2+} reaction which might be attributed to ring opening, but no after effects of this kind were observed. If ring opening takes place, it is complete in less than 50 msec. Such rapid ring opening is unlikely, and we feel therefore that the primary Cr(III) product is not chelated when Cr^{2+} reacts with the pyruvato complex and that a similar situation probably obtains for the trimethylpyruvato and glyoxylato complexes.

Because V^{3+} is much less inert to substitution than is Cr^{3+} , the question of the identity of the products resulting immediately on electron transfer is not as easy to answer for V^{2+} as a reducing agent as it is for Cr^{2+} . The oxalato system seemed to us to offer the greatest promise of an unambiguous answer to the problem of mechanism for V^{2+} , and the $\text{V}^{2+}-(\text{NH}_3)_5\text{Co}-\text{C}_2\text{O}_4\text{H}^{2+}$ reaction was investigated to learn whether an inner- or outer-sphere mechanism operates. The affinity of V^{3+} for $\text{C}_2\text{O}_4^{2-}$ is high enough so that under our conditions the dominant form of the V(III) product is VC_2O_4^+ , but special experiments are needed to learn whether this is the primary V(III) product.

A direct experiment on the rate of formation of VC_2O_4^+ showed that at 1.0 M H^+ and 25° and with V^{2+} present at 0.35 M , the coefficient of the rate function $(\text{H}_2\text{C}_2\text{O}_4)(\text{V}^{3+})$ is $6.9 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$. Other experiments showed that the rate of formation of VC_2O_4^+ is not affected by V^{2+} . The reduction of the oxalato-pentaammine complex by V^{2+} was followed spectrophotometrically choosing $400 \text{ m}\mu$ as the wavelength. Of the substances in solution, VC_2O_4^+ by far absorbs light most strongly (ϵ for VC_2O_4^+ is 37 and the next most strongly absorbing species is V^{3+} with ϵ 8), thus simplifying the interpretation of the data. If VC_2O_4^+ is the initial product of the reaction, then the rate law is

$$-\frac{d(\text{Co(III)})}{dt} = \frac{d(\text{VC}_2\text{O}_4^+)}{dt} = k_r(\text{Co(III)})(\text{V}^{2+}) \quad (4)$$

When V^{2+} is in large excess, then

$$\ln \frac{(\text{Co(III)})_0}{(\text{Co(III)})_0 - (\text{VC}_2\text{O}_4^+)} = k't \quad (5)$$

where $k' = (\text{V}^{2+})k_r$. Thus if VC_2O_4^+ is the primary product, a plot of $\ln \{ (1 - (\text{VC}_2\text{O}_4^+)) / (\text{Co(III)})_0 \}$ against t should yield a straight line. Figure 1 displays the

(16) D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).

(17) F. Nordmeyer, private communication.

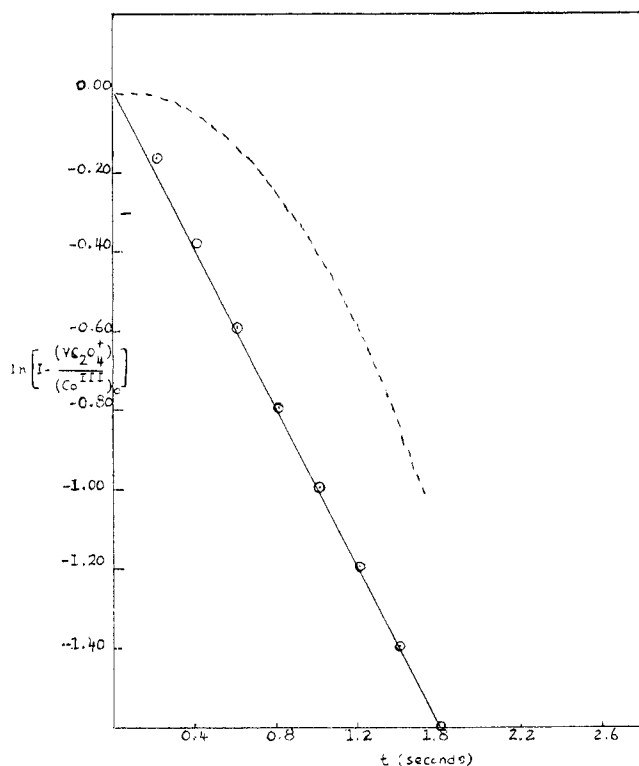


Figure 1.

results of an experiment done at $0.223 M V^{2+}$, $5.10 \times 10^{-3} M (Co(III))_0$, $1.0 M H^+$, $\mu = 1.5$, and 25° , and it is seen that the data conform quite well to a straight-line plot. The dotted curve shows the results that would be expected if V^{3+} and $H_2C_2O_4$ were the primary products and if $VC_2O_4^+$ then were formed in a following reaction. It is clear that the data do not agree with the expectations based on these assumptions. Whatever curvature is shown in the data is in an opposite sense, as would be expected if $VC_2O_4^+$ as a primary product dissociates slightly to V^{3+} and $H_2C_2O_4$. We conclude, therefore, that V^{2+} reacts with the oxalato-pentaamminecobalt(III) by an inner-sphere mechanism.

Results of Rate Measurements.—The kinetic data on the various reactions, with the exception of those dealing with the reduction of the glyoxylate complex with Cr^{2+} which has been described elsewhere,⁴ are presented in Tables IV–VIII. The coefficient k is defined by the rate

$$-\frac{d(Co(III))}{dt} = -\frac{d(\text{reductant})}{dt} = k(Co(III))(\text{reductant}) \quad (6)$$

Since three of the oxidants, namely, the glyoxylate, the pyruvato, and the trimethylpyruvato complexes, exist appreciably in the hydrate form (the glyoxylate, in fact, is mainly in the hydrate form) the hydrate-carbonyl equilibrium must be taken into account in analyzing the kinetic data. With Cr^{2+} as reductant and the pyruvato or trimethylpyruvato complexes as oxidants, the reaction with the carbonyl form is so rapid that under our conditions this part of the reaction could be observed with essentially no interference from the hydrated form. In these two cases, the value of

TABLE IV
THE REDUCTION OF OXALATOPENTAAMMINECOBALT(III)

Reductant	(Reductant) $\times 10^3, M$	(Co(III)) $\times 10^4, M$	(H ⁺), M	Temp, $^\circ C$	$k, M^{-1} \text{sec}^{-1} \times 10^{-1}$	
Cr^{2+} ^a	7.8	5.2	1.00	25	50	
	3.9	5.5	1.00	25	47	
	7.8	5.6	0.50	25	93	
	7.8	5.3	0.20	25	216	
	7.8	5.6	0.10	25	412	
	7.8	5.2	1.00	16	39.2	
	3.9	5.5	1.00	16	34.3	
	7.8	5.6	0.50	16	69	
	7.8	5.3	0.20	16	156	
	7.8	5.2	1.00	8	25.0	
	7.8	5.6	0.50	8	48.2	
	7.8	5.3	0.20	8	113	
	V^{2+} ^a	0.44	9.4	1.00	37	3.45
		0.47	8.8	1.00	33.5	2.34 ^c
0.37		8.5	1.00	32	2.06	
0.95		16.9	1.00	25	1.17	
0.46		9.9	1.00	25	1.31 ^c	
0.46		9.7	0.50	25	1.19 ^c	
0.46		9.3	0.10	25	1.37 ^c	
0.46		9.6	0.042	25	1.82	
0.47		9.7	0.014	25	2.83	
0.47		9.9	0.013	25	2.39	
0.41		8.9	1.00	15.5	0.59	
$Ru(II)$ ^b	5.23	8.4	1.00	15.0	0.65	
	0.39	8.9	1.00	14.5	0.37	
	10.3	10.3	0.100	30	0.053	
	10.3	10.0	0.0050	30	0.088	
	10.0	10.0	0.50	25	0.069	
	10.2	9.7	0.10	25	0.047	
	10.3	9.7	0.015	25	0.082	
	10.3	9.6	0.0073	25	0.027	
	10.3	9.5	0.0073	25	0.030	
	10.4	10.3	0.100	14.6	0.0162	

^a $\mu = 1.00$ in $HClO_4-LiClO_4$ medium. ^b $\mu = 0.50$ in $HCl-LiCl$ medium. ^c In duplicate; average deviation from mean, 2%.

TABLE V
THE REDUCTION OF OXAMATOPENTAAMMINECOBALT(III)

Reductant	(Reductant) $\times 10^3, M$	(Co(III)) $\times 10^4, M$	(H ⁺), M	Temp, $^\circ C$	$k, M^{-1} \text{sec}^{-1}$	
Cr^{2+} ^a	7.6	4.6	1.00	35	305	
	8.0	4.6	1.00	25	186	
	3.8	5.1	1.00	25	193	
	7.6	4.6	0.100	25	187	
	7.6	4.4	1.00	16	115	
	7.6	4.3	1.00	15	117	
	7.6	4.4	1.00	8	86	
	V^{2+} ^a	2.1	1.37	1.00	35.1	40.4
		3.2	2.58	1.00	25	20.6
2.6		1.81	1.00	25	20.9 ^c	
2.6		1.81	0.110	25	20.2	
2.6		1.98	1.00	15.0	9.9	
$Ru(II)$ ^b	10.4	10.1	0.010	35.2	0.44	
	10.4	10.3	0.010	30.1	0.30	
	10.6	10.1	0.010	25.3	0.224	
	10.8	10.3	0.010	14.6	0.107	

^a $\mu = 1.00$ in $HClO_4-LiClO_4$ medium. ^b $\mu = 0.50$ in $HCl-KCl$ medium. ^c In duplicate. Individual values 20.8, 21.0.

$Co(III)$ used in the rate equation is that of the carbonyl form. When V^{2+} and $Ru(NH_3)_6^{2+}$ are the reducing agents, in every case the oxidation-reduction reaction is slow enough so that equilibrium is maintained be-

TABLE VI
 THE REDUCTION OF PYRUVATOPENTAAMMINECOBALT(III)

Reductant	(Reductant) × 10 ³ , M	(Co(III)) × 10 ³ , M	(H ⁺), M	Temp, °C	k, M ⁻¹ sec ⁻¹
Cr ²⁺ ^a	19.5	4.9	1.00	25	9.9 × 10 ³
	5.5	4.0	1.00	25	11.2 × 10 ³
	19.5	4.9	0.50	25	10.2 × 10 ³
	5.5	3.7	1.00	16	7.7 × 10 ³
	5.5	3.6	1.00	8	5.9 × 10 ³
V ²⁺ ^a	26.0	1.7	1.00	33	17.6 ^c
	26.0	1.7	1.00	31.8	15.3
	47.4	4.8	0.10	25	10.4 ^c
	46.1	3.3	1.00	25	10.0 ^c
	23.6	1.6	1.00	25	10.2 ^c
	52.3	3.3	1.00	15.1	4.9 ^d
Ru(II) ^b	98.0	8.4	0.050	35	0.53
	100.0	9.5	0.038	35	0.53
	101.0	8.9	0.058	25	0.21
	101.0	9.5	0.014	25	0.20
	99.5	8.2	0.013	15.3	0.081
	102.0	9.9	0.50	15.1	0.086

^a $\mu = 1.00$ in HClO₄-LiClO₄ medium. ^b $\mu = 0.50$ in HCl-LiCl medium. ^c In duplicate. Average deviation from means, <1.0%. ^d In triplicate. Average deviation from means, 2.0%.

 TABLE VII
 THE REDUCTION OF GLYOXYLATOPENTAAMMINECOBALT(III)

Reductant	(Reductant) × 10 ³ , M	(Co(III)) × 10 ³ , M	(H ⁺), M	Temp, °C	k, M ⁻¹ sec ⁻¹
V ²⁺ ^a	3.2	2.4	1.00	35	15.7 ^c
	3.2	2.6	1.00	25	8.4 ^c
	3.2	1.8	1.00	25	8.1
	2.6	1.8	1.00	25	7.5
	3.2	2.3	0.10	25	8.6 ^c
	6.5	4.3	1.00	15	4.1 ^c
Ru(II) ^b	9.6	9.0	0.01	35.3	0.21
	10.5	9.0	0.01	24.8	0.089
	10.4	9.0	0.01	15.2	0.046

^a $\mu = 1.00$ in HClO₄-LiClO₄ medium. ^b $\mu = 0.50$ in HCl-LiCl medium. ^c In triplicate. Average deviation from means, 2%.

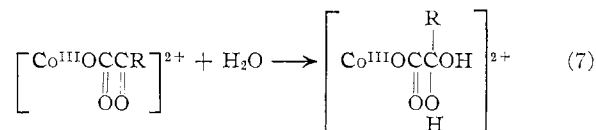
 TABLE VIII
 THE REDUCTION OF
 TRIMETHYLPYRUVATOPENTAAMMINECOBALT(III)

Reductant	(Reductant) × 10 ³ , M	(Co(III)) × 10 ³ , M	(H ⁺), M	Temp, °C	k, M ⁻¹ sec ⁻¹
Cr ²⁺ ^a	3.8	5.7	0.30	34	10.8 × 10 ³
	3.8	5.7	0.30	25	9.0 × 10 ³
	3.8	5.5	0.10	25	9.7 × 10 ³
	3.8	5.6	0.05	25	9.3 × 10 ³
	3.8	5.7	0.30	15	7.4 × 10 ³
V ²⁺ ^a	6.5	3.2	1.00	40	5.5
	6.5	3.2	1.00	35	4.3
	6.5	2.7	1.00	25	2.13
	6.5	3.6	1.00	25	2.04
	6.5	3.6	1.00	14.3	0.96 ^c
Ru(II) ^b	10.4	9.9	0.10	35	0.83
	10.5	10.4	0.10	25	0.39
	10.4	9.9	0.10	15.3	0.18

^a $\mu = 1.00$ in LiClO₄-HClO₄ medium. ^b $\mu = 0.50$ in LiCl-HCl medium. ^c In duplicate. Individual values 0.98, 0.94.

tween the carbonyl and hydrated forms of the complexes. Since this is the case and the activated complexes differ only in water content, it is impossible on the basis of the present kinetic evidence to distinguish between the reaction of the hydrate and the carbonyl forms. Thus, for want of evidence leading to a dis-

inction between the two formulations for the activated complex, the total Co(III) concentration was used in calculating the specific rates. It should be noted that since ΔH for the equilibrium



is not zero,^{4b} the values not only of ΔS^\ddagger but also of ΔH^\ddagger shown in Tables X and XI are affected (but only slightly) by the hydration equilibrium.

Inspection of the data in Tables IV-VIII shows that in numerous instances reactions were run in duplicate or in triplicate. The average deviation from the mean in these cases is 3% and in only a few instances is it as great as 5%. The trends in the values of k with the concentration variables which we shall point to are much in excess of this and therefore can be taken to result from real chemical effects.

In every case, the reactions have been shown to be first order in Co(III), this reagent usually being in deficit compared to the reductant. In most of the systems, the reactions were shown to be first order in the reducing agent as well, either by changing its initial concentration while it remains in excess or by introducing it at a concentration low enough so that it is appreciably depleted during the reaction. The variation of rate with reductant concentration was least thoroughly tested with Ru(NH₃)₆²⁺, but in one system, namely, in reaction with the pyruvato complex, the variation of rate with reductant concentration was investigated and the rate was shown to vary strictly with the first power of the Ru(II) concentration. It is reasonable to assume that this simple behavior obtains in the other systems, since they are all closely related.

In no case did we observe effects attributable to inhibition by the products, and the only other significant concentration variable then is (H⁺). Its effect can be dealt with very simply: the rates of reaction are affected by (H⁺) over the concentration range we have covered only in the reduction of the oxalate complex and here for each reductant the rate can be expressed by an equation of the form

$$-\frac{d(\text{Co(III)})}{dt} = (\text{Co(III)})(\text{reductant}) \left[k' + \frac{k''}{(\text{H}^+)} \right] \quad (8)$$

The coefficients k' and k'' can readily be extracted from the data on the variation of k with (H⁺), and since the dissociation constant for [(NH₃)₅CoC₂O₄H]²⁺ acting as an acid is known, the value of k appropriate to the rate function ((NH₃)₅CoC₂O₄⁺)(reductant) can be calculated.

It should be noted that the rate law we have observed for the reduction of the oxalate complex differs from that reported by Fraser,¹⁸ his rate law containing a term first power but none inverse in (H⁺). Fraser's measurements were made by ordinary syringe techniques. If one calculates an approximate half-time for the re-

action from his recorded concentrations and rate constant, it is clear that he was able to observe at most only the last 10% of the reaction. Some of our observations indicate that secondary processes might begin to interfere in the final stages of the reaction. In any case, through use of the stopped-flow apparatus we were able to observe the reaction over 90% of its course, and we therefore believe that our results are more reliable.

Tables IX to XI summarize the rate constants for the various reactions and the values of ΔH^\ddagger and ΔS^\ddagger where they have been determined.

TABLE IX
KINETIC PARAMETERS FOR THE REDUCTION OF THE
CARBOXYLATOPENTAAMMINECOBALT(III) COMPLEXES
BY CHROMOUS ION ($\mu = 1.00$)

Ligand	$k^{a,c}$	$\Delta H^\ddagger^{b,c}$	$\Delta S^\ddagger^{b,c}$
Binoxalate	1.0×10^2
Oxalate	4.6×10^4	2.3	-20
Oxamate	1.90×10^2	8.8	-19
Glyoxylate	$>7 \times 10^3$
Pyruvate	1.1×10^4	5.8	-21
Trimethylpyruvate	9.3×10^3	2.9	-31

^a The second-order rate constant at 25° expressed in units of $M^{-1} \text{ sec}^{-1}$. ^b Activation enthalpy is expressed in kilocalories per mole and activation entropy in calories per mole per degree. ^c Rate constants are accurate to $\pm 5\%$.

TABLE X
KINETIC PARAMETERS FOR THE REACTION OF THE
CARBOXYLATOPENTAAMMINECOBALT(III) COMPLEXES
WITH VANADOUS ION ($\mu = 1.00$)

Ligand	$k^{a,c}$	$\Delta H^\ddagger^{b,c}$	$\Delta S^\ddagger^{b,c}$
Binoxalate	12.5	12.2 ± 1.2	-13 ± 1
Oxalate	45 ± 5
Glyoxylate	8.24	11.0	-17
Pyruvate	10.2	11.6	-15
Trimethylpyruvate	2.11	11.9	-17
Oxamate	20.7	11.6	-14

^a Second-order rate constant at 25° in units of $M^{-1} \text{ sec}^{-1}$. ^b Activation energy and entropy are in units of kilocalories per mole and calories per mole per degree, respectively. ^c Unless otherwise noted, the accuracy of the specific rate is $\pm 5\%$.

TABLE XI
KINETIC PARAMETERS FOR THE REACTION OF THE
CARBOXYLATOPENTAAMMINECOBALT(III) COMPLEXES
WITH HEXAAMMINERUTHENIUM(II) ION ($\mu = 0.50$)

Ligand	$k^{a,c}$	$\Delta H^\ddagger^{b,c}$	$\Delta S^\ddagger^{b,c}$
Binoxalate	0.50	16.1	-6.1
Oxalate	0.10	6.4 ± 2.0	-41 ± 7
Glyoxylate	0.089	13.1	-19.5
Pyruvate	0.20	15.9	-8.2
Trimethylpyruvate	0.39	13.1	-16.5
Oxamate	0.22	11.0	-24.7

^a Second-order rate constant at 25° in units of $M^{-1} \text{ sec}^{-1}$. ^b Activation energy and entropy are in units of kilocalories per mole and calories per mole per degree, respectively. ^c Unless otherwise noted, the accuracy of the specific rate is $\pm 5\%$.

To help differentiate between an inner- or outer-sphere mechanism for the vanadous reactions, the rate of the reaction of the binoxalato complex with V^{2+} was measured in D_2O solvent. The reacting species are then $V(D_2O)_6^{2+}$ and $(NH_3)_5CoO_2CCO_2D^{2+}$. The protons of the coordinated ammonia molecules do not

exchange with solvent in the time necessary to complete the experiment. The rate constant for the reaction in D_2O is $10.6 M^{-1} \text{ sec}^{-1}$ at 25°. The solvent isotope effect is thus expressed by the ratio $k_{H_2O}/k_{D_2O} = 1.18$. Similar experiments have been done¹⁹ for V^{2+} reactions which are known to be outer sphere.²⁰ For the V^{2+} reduction of $Co(NH_3)_6^{3+}$, $k_{H_2O}/k_{D_2O} = 1.7$, and, for the reduction of $Co(NH_3)_5H_2O^{3+}$, $k_{H_2O}/k_{D_2O} = 2.6$. Thus, if the present reactions proceed by an outer-sphere mechanism, a solvent isotope effect of approximately 2 would be expected. The very small isotope effect actually observed then indicates that the reaction of the oxalato complex is not of the outer-sphere type.

Discussion

Conclusions about the nature of the activated complexes for the reactions have been stated in the preceding section. Before searching for broader implications of the observations, it is in order to develop the earlier conclusions somewhat further.

In considering the data for Cr^{2+} , we begin with noting that the reactions of Cr^{2+} with the class of oxidizing agents under consideration are of the inner-sphere type. The rates are observed to cover a wide range, and, since the ligands contain a chelating function, it is important to decide whether the rate variation is simply a reflection of the varying capacity of the ligands to form complexes by chelation. Such an explanation does not account for the rate differences. The oxamate complex leads to a stable chelate in the $Cr(III)$ product while pyruvate does not, yet the rate of reaction for the former is much lower than it is for the latter. It should be noted that in the present series all rates are higher than for the α -hydroxy ligands,¹⁰ yet with the exception of the oxamate and oxalate ions, the α -hydroxy ligands are probably better complexing agents than the ligands of the present series. Finally, it is appropriate to recall the evidence presented earlier indicating that the pyruvate ligand does not pass through a chelated stage in being transferred to chromium by electron transfer.

The binoxalate, oxalate, and oxamate groups are in all likelihood chelated in the activated complexes. The alternative possibility that monodentate $Cr(III)$ complexes are formed which then chelate rapidly is rendered unlikely by observations¹⁵ which have been made on the monodentate acid malonatochromium(III) ion. Ring closure is very slow ($k(25^\circ) = 4.0 \times 10^{-6} + 2.2 \times 10^{-7}(H^+)$), and although differences between malonate and oxalate can be expected because of ring size, these differences are not expected to be large, both chelated configurations being quite stable.

All in all, it seems quite safe to conclude that although some of the ligands are chelated to $Cr(III)$ in the activated complex, this factor is by no means responsible for all of the large rate differences observed.

The evidence based on examination of the products

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(20) P. Dodel and H. Taube, *Z. Physik. Chem. (Frankfurt)*, **44**, 92 (1965).

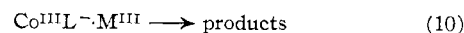
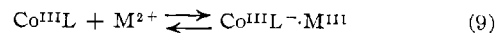
favoring an inner-sphere mechanism for the reduction of the oxalate complex by V^{2+} seems to be convincing. The comparison of the rates of reaction for the different ligands gives a basis for extending this conclusion to the other complexes, and moreover suggests that for most members of this series, substitution in the first coordination sphere of V^{2+} is rate determining. Supporting this interpretation is the fact that rates of reduction of the various Co(III) complexes are so nearly alike. The main differences that exist find a ready explanation on the basis of the proposal made. Prominent among these differences is the fact that the oxalato complex reacts the most rapidly; this can be ascribed to the negative charge on the ligand, the negative charge being expected to increase the rate of substitution. Because of its steric requirements, the $C(CH_3)_3$ group can reasonably be expected to decrease the rate of substitution, and the rate of reduction of the complex containing the bulkiest ligand, namely, trimethylpyruvate ion, is, in fact, the slowest. Perhaps the strongest support for the conclusion that substitution of V^{2+} is rate determining is the fact that a specific rate of $10\text{--}20 M^{-1} \text{sec}^{-1}$ is quite reasonable for this process. It should be noted that V^{2+} reduces $CrSCN^{2+}$ at almost the same rate as it reacts to form a complex with SCN^- , the rate constants being 7 and $9 M^{-1} \text{sec}^{-1}$ at 25° and $\mu = 1.0$.²¹ The redox reaction in this case has been shown to involve an inner-sphere activated complex.

It should also be noted that the reaction of V^{2+} with VO^{2+} to form $[VOV]^{4+}$, which must involve a bridged activated complex, is governed²² by kinetic parameters very similar to those we report for the $V^{2+}\text{--}VO^{2+}$ reaction; ΔH^\ddagger and ΔS^\ddagger are reported as 12.3 kcal/mole and -16.5 eu, respectively. A reaction which has kinetic parameters²³ similar to ours ($k = 13 M^{-1} \text{sec}^{-1}$ at 25° and $\mu = 1.0$, $\Delta H^\ddagger = 11.7$ kcal/mole and $\Delta S^\ddagger = -14$ kcal/mole deg) is the reduction of $(NH_3)_5\text{--}CoN_3^{2+}$ by V^{2+} . Espenson²⁴ has shown that the reduction of *cis*-(en)₂Co(N₃)₂⁺ by V^{2+} takes place by an inner-sphere mechanism. In view of this result and the similarity of the kinetic parameters for the $(NH_3)_5\text{--}CoN_3^{2+}\text{--}V^{2+}$ reaction to ours, it seems likely that substitution on V^{2+} is rate determining in the reduction of the azidopentaammine as well.

The factor which in the reactions of Cr^{2+} may be mainly responsible for the large differences in rate is the accessibility to the reducing electron of a low-lying orbital on the ligand. Such an orbital would be needed whether electron transfer takes place by intermediate formation of a radical ion or by a superexchange mechanism.²⁵ The arguments which follow, based on a comparison of the results for the two inner-sphere reduc-

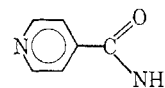
tants studied, suggest that a radical-ion mechanism does not account for all of the data.

For the radical-ion mechanism²⁶ we write



Two extreme cases can be considered: (a) step 9 is rate determining or (b) reaction 9 is formulated as an equilibrium and step 10 is rate determining. If case a obtains, the reactions for V^{2+} are expected to be much slower than for Cr^{2+} (Cr^{2+} reduces the ligands much more rapidly than does V^{2+}). However, in fact, with oxamate as ligand, the rate of reaction for V^{2+} is only a few times slower than that of Cr^{2+} , despite the fact that for V^{2+} , substitution rather than electron transfer is rate determining. If alternative b is considered, we have in one case the radical ion in equilibrium with $V^{2+}\text{--}V^{3+}$, in the other with $Cr^{2+}\text{--}Cr^{3+}$. The concentration of radical ion would be reflected in the difference in equilibrium reducing power of the two reductants and is therefore expected to be *ca.* 10^3 higher when Cr^{2+} reacts. The rate of Co(III) reduction should be proportional to the radical-ion concentration and is in every case therefore expected to be *ca.* 10^3 times greater for Cr^{2+} as reductant than for V^{2+} . This is clearly not the case (it should be remembered that the rates recorded for V^{2+} are lower limits for the rates of electron transfer because, in most of the cases, substitution in the coordination sphere of V^{2+} is rate determining), and we thus conclude that a radical-ion mechanism cannot account for all of the observations. We suggest that in some of the cases a superexchange mechanism operates; that is, there is resonance transfer involving preparation at the acceptor site and at the donor site prior to electron transfer. By this mechanism the state $Co^{III}L\text{--}M^{3+}$ is not directly involved but enters as affecting the energy barrier which the electron must penetrate in completing reaction.

In the reactions with



as ligand the conclusion was reached²⁷ that the mechanism approaches the radical ion limit. The differing conclusions in the isonicotinamide case and that under present consideration would be no cause for concern, even if we could be quite certain that both conclusions are correct. Both mechanisms seem to be reasonable ones, and whether one extreme or another obtains will depend, among other factors, on how readily the ligand can be converted by the reducing agent to a radical ion.

The variations in rate observed for the outer-sphere reductions of the complexes are quite small, certainly much smaller than in the case of Cr^{2+} . The pattern has little in common either with that observed for Cr^{2+}

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(24) J. H. Espenson, *ibid.*, **89**, 1276 (1967).

(25) P. George and J. S. Griffith, "The Enzymes," Vol. 1, Academic Press Inc., New York, N. Y., 1959, Chapter 8.

(26) We need not consider $Co^{III}L\text{--}M^{III}$ as the products of reaction 9 because no kinetic effects of the products M^{III} have been observed.

(27) F. R. Nordmeyer, Ph.D. Thesis, Stanford University, 1966.

or V^{2+} . A striking feature of the data is that despite the fact that the rates of reaction differ little from case to case, the values of ΔH^\ddagger and ΔS^\ddagger do change considerably. In the inner-sphere reactions, quite rigid constraints are placed on the geometries of the activated complexes, and therefore on the distribution of electric charge within them, and as a result the values of ΔS^\ddagger do not vary capriciously. However, it may be that in the outer-sphere activated complex where such severe constraints do not exist a slight change in the distribution of charge in the Co(III) complex, for example, can call for a considerable change in the way oxidant and reductant are arranged in the activated complex, thus affecting ΔS^\ddagger .

An explanation of the variation of rate for the outer-sphere reactions with properties of the ligand will be difficult to develop because a satisfactory theory must account not only for the rates at a particular temperature but also for the way the rate pattern changes with temperature. We are in no position to offer such an

explanation and extensive discussion of the observations is therefore out of order. We do, however, wish to point to the comparison of the kinetic parameters for $C_2O_4H^-$ and $C_2O_4^{2-}$ as ligand. In accord with observations made for the reduction of an aquo *vs.* hydroxo ion by an outer-sphere mechanism,³ the rate for the protonated ligand is found to be greater than for the unprotonated one. Comparison of the values of ΔH^\ddagger for the two has shown, despite the inaccuracy of that recorded for the oxalate complex, that at a low temperature the rate for the oxalato complex will exceed that for the binoxalate. Thus the rate comparison for a complex containing a protonated ligand *vs.* that for a proton-free ligand must be used with caution in diagnosing mechanisms until the subject is better understood.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation of the Tris-Type Complexes of Cobalt(III) with Two Different Kinds of α -Amino Acids¹

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The complexes of carbonatobis(aminoacidato)cobaltate(III) have been prepared by the reaction of the tricarbonatocobaltate anion with an aminoacidate anion; the compounds obtained are $K[Co(gly)_2CO_3] \cdot H_2O$, $K[Co(L-ala)_2CO_3] \cdot 3H_2O$, and $K[Co(L-val)_2CO_3] \cdot 3.5H_2O$. The reaction of the carbonatobis(glycinato) complex with L-valine led to formation of a mixed amino acid complex, $[Co(gly)_2(L-val)]$, and three among the four possible isomers of the complex, *i.e.*, $\beta(+)_D$, $\beta(-)_D$, and $\alpha(+)_D$, have been isolated by means of the solubility difference. Using the other carbonate complexes, the following isomers were also obtained as water-insoluble forms: $\beta(+)_D$ - $[Co(L-val)_2(gly)]$, $\beta(+)_D$ - $[Co(L-val)_2(L-ala)]$, $\beta(-)_D$ - $[Co(L-val)_2(D-ala)]$, and $\beta(+)_D$ - $[Co(L-ala)_2(D-ala)]$. All of these isomers are characterized by the ORD and CD spectra, and the vicinal effect of optically active valine is also considered.

In our previous paper dealing with the preparation of tris(aminoacidato) complexes,² we concluded that the method using cobalt(III) hydroxide, which was originated by Ley and Winkler,³ is convenient for preparing the α (*trans* or peripheral) isomer, while the method using the hexaamminecobalt(III) cation, which was devised by Neville and Gorin,⁴ is advantageous for preparing the β (*cis* or facial) isomer. The third method using the tricarbonatocobaltate(III) anion was found to give both forms in about equal amounts. Dunlop and Gillard⁵ have recently used these three methods for the preparation and isolation of tris(L-alaninato)cobalt-

(III); the hydroxide method gives predominantly the α isomers, the hexaammine method gives only the water-insoluble $\beta(+)_D$ isomer, and the tricarbonato method gives all of the four isomers with a little predominance of the α isomers. Denning and Piper⁶ have obtained both (+) and (-) isomers of *trans*- α -tris(L-leucinato)cobalt(III) by using a slightly modified tricarbonato method and corresponding *cis*- β -isomers from the hexaammine method ((+) and (-) signs refer to the sign of the net rotational strength of the low-energy absorption band). They have also succeeded in separating three isomers of the possible four of tris(L-prolinato)cobalt(III), *i.e.*, *cis*- $\beta(+)$, *cis*- $\beta(-)$, and *trans*- $\alpha(-)$, from a reaction mixture of tricarbonatocobaltate(III) and L-proline. The method using hexaamminecobalt(III) failed to give any product. Before this,

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