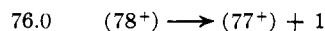


from ring-labeled species. Observed retentions of 6.5% from the α -isomer and about 100% from the *ortho* and *meta* are consistent with either or both of the above paths as the source of most of the $C_6H_5^+$ yield.

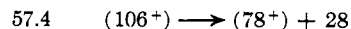
That the label is retained in even a small part of the $C_6H_5^+$ yield from benzaldehyde- α -*d* implies the existence of yet another contributing path. A metastable peak



in the spectrum of unlabeled benzaldehyde, not detected in the spectrum shown in Table I but clearly visible in the one measured on the high-mass instrument, identifies $C_6H_5^+$ as another $C_6H_5^+$ precursor. If the six hydrogen atoms in $C_6H_5D^+$ lose positional identity, 83%—neglecting possible isotope effects—of the $C_6H_5^+$ ions arising from this precursor should retain the label.

Comparison with Tropone

Comparison of the spectra of benzaldehyde and tropone supports the view that most fragment ions from the former arise by paths not involving ring expansion. The spectra differ markedly—a rather different state of affairs from that found with toluene, cycloheptatriene and the four other C_7H_8 isomers, the mass spectra of which have been reported.¹ Loss of a hydrogen atom to form $C_7H_7O^+$ contributes but little to the spectrum of tropone. The most abundant ion is $C_6H_6^+$, shown by the metastable peak



to arise by loss of CO from the parent ion. The many similarities in the spectra of tropone and benzene—especially the profiles at m/e 50 to 52 and 73 to 78—suggest that most of the smaller fragment ions formed from tropone stem from a $C_6H_6^+$ intermediate and, indeed, that common states of $C_6H_6^+$ are involved in decomposition of tropone and benzene.

The reaction apparently occurring in tropone—two C—CO bonds rupturing and a new bond forming across the gap from which CO is lost—seems to occur also in benzotropone and in many quinones and aromatic ketones in which the carbonyl group is incorporated in a ring,^{25,30,31} but little or no loss of CO occurs from the parent ions of aliphatic aldehydes.¹⁹ Loss of CO from benzaldehyde may arise from a ring-expanded, tropone-like intermediate. The driving force for other decomposition paths in benzaldehyde is evidently centered in the carbonyl group; ring expansion in $C_6H_6^+$ formation would parallel the behavior of other benzene derivatives and thus reflect the influence of the benzene ring.

(30) J. H. Beynon and A. E. Williams, *Appl. Spectry.*, **14**, 156 (1960).

(31) In cycloalkanes, in contrast, loss of CO is slight. High-resolution measurements show that the ions of parent mass less 28 units in the spectra of these compounds arise chiefly by loss of C_2H_4 [J. H. Beynon, R. A. Saunders and A. E. Williams, *Appl. Spectry.*, **14**, 95 (1960)], paralleling the loss of C_2H_4 from cycloalkanes [S. Meyerson, T. D. Nevitt and P. N. Rylander, in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed. Pergamon Press, New York, N. Y., 1963, p. 313].

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Kinetics and Mechanisms of the Hydrolysis of Some Chloroamminerhodium(III) Complexes^{1,2}

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RECEIVED FEBRUARY 20, 1963

The rates of hydrolysis of certain chloroamminerhodium(III) complexes were investigated as a function of steric effects, the extent of chelation and other variables. It was observed that various nucleophiles have no effect on the rate of chloride ion release from these systems. These results are similar to the behavior of analogous cobalt(III) systems. Striking differences were also found: (1) the rate of reaction of a rhodium(III) complex is insensitive to the charge on the complex, (2) alkali has little or no effect on the rate of hydrolysis and (3) reactions of rhodium(III) complexes occur with almost complete retention of configuration. These results are discussed in terms of probable mechanisms for reactions of rhodium(III) complexes.

Introduction

The literature contains numerous descriptions of the reactions of the ammine complexes of cobalt(III). The diacidotetraammines, $[CoA_4X_2]^+$, and the acidopentaammines, $[CoA_5X]^2+$, have been of particular interest.⁴ Extensive studies of the rates of hydrolysis of the complexes $[CoA_4X_2]^+$ and $[CoA_5X]^2+$ have been made as a function of a large number of variables.⁵

It is, therefore, somewhat surprising that so little information has appeared on the analogous complexes of the second and third row transition element members of the cobalt triad, rhodium and iridium. It would certainly be of interest to ascertain the effect of increasing size and effective nuclear charge of the central metal atom upon the reactions of the various complex

ions. The only quantitative kinetic studies of the reactions of acidoamminerhodium(III) and -iridium(III) complexes are those reported by Lamb⁶ for $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Br]^{2+}$ and by Lamb and Fairhall⁷ for $[Ir(NH_3)_5X]^{2+}$, X = Cl^- , Br^- , I^- and NO_3^- .

The dearth of information available on the reactions of diacidotetraamminerhodium(III) complexes may be logically ascribed to the fact that until very recently⁸ only a few isolated members of this group had been prepared. Any study of those compounds whose syntheses had been described would have precluded all but the sketchiest of comparisons to the members of the very prolific cobalt(III) family; indeed no examples of either geometric or optical isomerism were known. The successful synthesis of many of the necessary diacidotetraamminerhodium(III) complexes now makes possible quantitative comparisons between these systems and the analogous cobalt(III) compounds. This paper reports kinetic data on reactions of rhodium(III) systems and discusses these data in terms of the previously reported results on cobalt(III).

(1) This research was supported in part by the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)315, and in part by the U. S. Atomic Energy Commission under contract AT(11-1)-1087.

(2) Taken in part from the Ph.D. Thesis of S. A. Johnson, Northwestern University, 1961.

(3) National Institutes of Health Fellow, 1960–1961.

(4) In these general formulas, A_4 and A_5 indicate coordination to cobalt of four and five amine nitrogens, respectively; X represents a mononegative anion such as Cl^- , Br^- , I^- , CNS^- , N_3^- , NO_2^- or OH^- .

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, Chapter 3.

(6) A. B. Lamb, *J. Am. Chem. Soc.*, **61**, 699 (1939).

(7) A. B. Lamb and L. T. Fairhall, *ibid.*, **45**, 378 (1923).

(8) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

TABLE I
 RATES OF HYDROLYSIS IN ACIDIC SOLUTION

Complex ^a	Medium	T, °C.	k _{obs} × 10 ⁴ , sec. ⁻¹	%Cl ₂ equil	"k ₁ " × 10 ⁴ , sec. ⁻¹
<i>trans</i> -[Rh(NH ₃) ₄ Cl ₂] ⁺	0.1 M HNO ₃	80	12.1	39	4.7
<i>trans</i> -[Rh(en) ₂ Cl ₂] ⁺	.1 M HNO ₃	80	10.4	26	2.7
<i>cis</i> -[Rh(en) ₂ Cl ₂] ⁺	.1 M HNO ₃	80	85	60	51
<i>cis</i> -[Rh(trien)Cl ₂] ⁺	.1 M HNO ₃	55	15	47	7.1
<i>trans</i> -[Rh(<i>m</i> -bn) ₂ Cl ₂] ⁺	.1 M HNO ₃	80	85	32	27
<i>trans</i> -[Rh(<i>dl</i> -bn) ₂ Cl ₂] ⁺	.1 M HNO ₃	80	12	30	3.6
<i>trans</i> -[Rh(tetrameen) ₂ Cl ₂] ⁺	H ₂ O	25	160	~50	~80
<i>cis</i> -[Rh(tetrameen) ₂ Cl ₂] ⁺	H ₂ O	25	110	~50	~55
<i>trans</i> -[Rh(bipy) ₂ Cl ₂] ⁺	0.1 M HNO ₃	80	...	0	...
[Rh(NH ₃) ₅ Cl] ²⁺	0.1 M HNO ₃	80	6.2	69	4.3
<i>trans</i> -[Rh(C ₂ O ₄) ₂ Cl ₂] ²⁻	H ₂ O	80	1.6	100	1.6
<i>cis</i> -[Rh(C ₂ O ₄) ₂ Cl ₂] ²⁻	H ₂ O	80	2.3	100	2.3

^a en = ethylenediamine; trien = triethylenetetramine; *m*-bn = *meso*-butylenediamine; *dl*-bn = *dl*-butylenediamine; tetrameen = (C,C')-tetramethylethylenediamine; bipy = 2,2'-bipyridine.

Experimental and Results

A. Preparation of Materials.—*trans*-[Rh(NH₃)₄Cl₂]NO₃, *cis*- and *trans*-[Rh(en)₂Cl₂]NO₃, *cis*-[Rh(trien)Cl₂]NO₃, *trans*-[Rh(*m*-bn)₂Cl₂]NO₃, *trans*-[Rh(*dl*-bn)₂Cl₂]NO₃, *cis*- and *trans*-[Rh(tetrameen)₂Cl₂]Cl and [Rh(NH₃)₅Cl](NO₃)₂ were prepared and analyzed as described previously.⁸

Dichlorobis-(2,2'-bipyridine)-rhodium(III) chloride was prepared by the method of Jaeger and van Dijk⁹ by the reaction of an aqueous solution of RhCl₃·3H₂O with 2,2'-bipyridine in ethanol. The product, a fluffy yellow crystalline substance, was washed with a little water, then with acetone to remove any unreacted bipyridine. The yield was approximately quantitative.

Anal. Calcd. for [Rh(bipy)₂Cl₂]Cl·2H₂O: C, 43.07; H, 3.62; N, 10.05; Rh, 18.45. Found: C, 42.45; H, 3.31; N, 10.24; Rh, 18.60.

Potassium *cis*-dichlorobis-(oxalato)-rhodate(III) was prepared by the method of Delepine.¹⁰ The crude product was recrystallized from water-ethanol. The fluffy golden yellow powder was obtained in 50% yield.

Anal. Calcd. for K₃[Rh(C₂O₄)₂Cl₂]·H₂O: C, 9.90; H, 0.44; Cl, 14.6. Found: C, 10.13; H, 0.36; Cl, 14.6.

B. Determination of the Rates of Chloride Ion Release from Chloro Complexes.—The rates of chloride ion release in these reactions were determined by three different methods: (1) **Titration of Chloride Ion.**—Whenever possible, a hydrolysis reaction was followed by direct titration of the chloride ion as it was released. In general, sufficient complex to make its concentration ~2.5 × 10⁻³ M was added to 50 ml. of H₂O (containing the other reactants if any) which had been thermostated at the desired temperature (±0.1°) in a constant temperature bath. At appropriate intervals a 5.00-ml. aliquot was removed from the reaction mixture and cooled to room temperature or slightly below. The sample was then made acidic by the addition of 1 ml. of 6 M HNO₃ and titrated with 0.01 M Hg(NO₃)₂ using sodium nitroprusside as the indicator.¹¹ Rate constants were determined graphically from the relationship

$$k = \frac{2.303}{t} \log \frac{(C_{\infty} - C_0)}{(C_{\infty} - C_t)} \quad (1)$$

where C_∞, C₀, and C_t represent the experimental concentration of chloride ion at infinite time, zero time and time *t*, respectively.

(2) **Conductometric Method.**—A reaction was followed conductometrically when a significant change in the conductivity was expected during the course of the reaction. In general, the finely powdered complex (1–2.5 × 10⁻³ M) and any other solid reactant were placed in one leg of a Y-shaped conductivity cell and 25 ml. of distilled water was pipetted into the other leg. The cell was then thermostated at the desired reaction temperature (±0.1°) in a constant temperature bath. When temperature equilibrium had been attained, the cell was inverted causing the water to run into the leg containing the complex which dissolved to begin the reaction. Measurements of the resistance of the solution were made at appropriate times using an industrial instruments conductivity bridge, model RC 16. Rate constants

$$k = \frac{2.303}{t} \log \left[\frac{R_0 - R_{\infty}}{R_0} \times \frac{R_t}{R_t - R_{\infty}} \right] \quad (2)$$

were evaluated graphically from equation 2 where R₀, R_∞ and

(9) F. M. Jaeger and J. A. van Dijk, *Z. anorg. allgem. Chem.*, **227**, 323 (1936).

(10) M. Delepine, *Anales soc. espan. fis. quim.*, **27**, 487 (1929).

(11) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1953, pp. 460, 547–549.

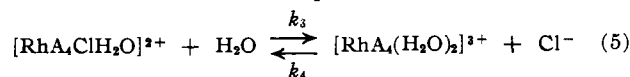
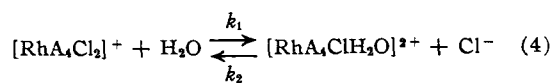
R_t are the measured resistances of the solution at zero time, infinite time and time *t*, respectively.

(3) **Spectrophotometric Method.**—It was often possible to find some wave length in the visible or ultraviolet region where the absorptions of the starting complex and the reaction product were sufficiently different that the reaction might be followed spectrophotometrically. Most of the reactions were followed at 80°. For these runs the solvent water containing any other reactants was first thermostated in the 80° (±0.1°), constant temperature bath and the complex (~2.5 × 10⁻³ M) was then added to it. At appropriate intervals a 3-ml. aliquot was removed from the reaction mixture and pipetted into an ice-cooled beaker. After the sample had been cooled to room temperature or slightly below it was placed in a 1-cm. quartz cell and its optical density was measured at the chosen wave length using a Beckman DU spectrophotometer. When the reaction could be followed at 55° or less, the cell compartment of the DU was thermostated at the desired temperature by circulating water around it from the constant temperature bath. A 3-ml. sample of the reaction mixture prepared as described above was placed in a 1-cm. quartz cell in the thermostated cell compartment and periodic measurements were made of its optical density. Rate constants were calculated graphically from the relationship

$$k = \frac{2.303}{t} \log \frac{A_{\infty} - A_0}{A_{\infty} - A_t} \quad (3)$$

where A_∞, A₀ and A_t are the measured optical densities at infinite time, zero time and time *t*, respectively.

Table I gives results of measurements of the rates of acid hydrolysis of the various complexes. Duplicate runs were made in every case and agreement was usually within 2–3%. First-order kinetics were found to be followed out to two or more half-lives. These solutions did not hydrolyze completely; less than half of the total coordinated chloride was generally found by titration at equilibrium. In such a case the observed rate constant calculated from eq. 1 is not a simple quantity but a composite of all four rate constants for the two reversible reactions



Furthermore, by analogy with other anation reactions, the reverse steps of 4 and 5 undoubtedly depend on the chloride ion concentration.

A somewhat similar situation was met by Lamb⁶ in his study of the acid hydrolysis of [Rh(NH₃)₅X]²⁺. In this example where only one halide ion can be released, Lamb showed that the observed constant is given by

$$k_{\text{obs}} = k_1 + k_2[\bar{X}^-] \quad (6)$$

where \bar{X}^- is an average value of the halide concentration during a run. Further, *k*₁ could be calculated from a knowledge of the equilibrium concentration of halide ion, C_∞.

$$k_1 = (C_{\infty}/C_0)k_{\text{obs}} \quad (7)$$

While such a procedure cannot be valid in cases where two replaceable chlorides are present, nevertheless " k_1 " was calculated from eq. 7 and the values obtained are given in Table I. They will be compared later with rate constants for base hydrolysis.

It may be noted that for complexes such as *cis*- and *trans*-[Co(en)₂Cl₂]⁺, the second chloride ion aquates at a rate only one-hundredth of that of the first. This is usually considered partly an effect of the increased positive charge in [Co(en)₂H₂OCl]²⁺ and partly as a result of dative π -bonding from chlorine to metal in the dichloro complex.¹²

Although we have no distinct data on complexes such as [RhA₄H₂OCl]²⁺, the data in Table I show little effect of charge on the rates of acid hydrolysis. For this reason we assume that k_1 and k_3 are, if not equal, at least very close, and k_2 and k_4 also comparable. This view is supported by the first-order behavior observed.

Whenever hydrolyses of [RhA₄Cl₂]⁺ were carried out in basic solution, 100% of the coordinated chloride was released at equilibrium and found by titration. Again the reaction is a two-stage process and we have no direct information on the behavior of [RhA₄OH-Cl]⁺ intermediates. However, it was found that at constant pH, good first-order kinetic plots were obtained over two or more half-lives. This can mean either that [RhA₄OHCl]⁺ reacts much faster than [RhA₄Cl₂]⁺, or that the two react at very nearly the same rate. As indicated above, it seems more likely that the latter is true. In any case, the values of the rate constants given in Table II are simply the observed first-order constants with no corrections.

The rates of base hydrolysis of [RhA₄Cl₂]⁺ were found to be independent of the concentration of hydroxide ion for all *trans* isomers for concentrations of base as high as 0.10 M. In the hydrolyses of *cis*-[RhA₄Cl₂]⁺ and [Rh(NH₃)₅Cl]²⁺, the order with respect to hydroxide ion was found to vary between zero and one. For comparison, [CoA₄Cl₂]⁺ hydrolyses are strictly first order in hydroxide ion above a pH of 8 or so.

At constant pH all of these systems may be described by the equation

$$k_{\text{obs}} = k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-] \quad (8)$$

where $k_{\text{H}_2\text{O}}$ is the rate constant for acid hydrolysis and k_{OH^-} is a second-order rate constant for reaction with hydroxide ion. The relative values of $k_{\text{H}_2\text{O}}$ and k_{OH^-} determine the apparent order with respect to hydroxide ion in different pH ranges. The data of Table II allow estimates of the constants in eq. 8 to be made as described in the following section.

The reactions of dilute solutions of *trans*-[Rh(en)₂Cl₂]⁺ with a variety of possible nucleophilic reagents were also studied. The reactions were found to go to completion. In every case simple first-order kinetics were observed. The rate constants are taken from the first-order slopes and are given in Table III. The rates are seen to be essentially independent of the nature and concentration of the reagent X. The observed product, however, is that in which X is in the coordination sphere. The products were assessed by spectra and by isolation and analysis.⁸ In the case of NH₃, the preparative run gave *trans*-[Rh(en)₂NH₃Cl]²⁺. However, this was for a short period of time (10 minutes at reflux). The kinetics run showed that after longer periods of time (several hours at 80°) both chlorides were released. In the case of thiourea, no product could be identified by preparation, but in the

TABLE II
RATES OF HYDROLYSIS IN BASIC SOLUTION

Complex	pH ^a	T, °C.	k × 10 ⁶ , sec. ⁻¹
<i>trans</i> -[Rh(NH ₃) ₄ Cl ₂] ⁺	8.9	80	8.5
	9.9	80	8.9
	12.7	80	8.6
<i>trans</i> -[Rh(en) ₂ Cl ₂] ⁺	8.9	70	1.5
	8.9	80	4.2
	8.9	90	11.6 ^b
	9.9	80	4.4
	12.7	80	5.1
	8.9	55	6.3
<i>cis</i> -[Rh(en) ₂ Cl ₂] ⁺	9.9	55	14
	11.9	35	7.3
	11.9	40	14
	11.9	45	27 ^c
	12.7	25	9.1 ^d
	8.9	55	16
<i>cis</i> -[Rh(trien)Cl ₂] ⁺	9.9	55	52
	11.9	25	19
	12.7	25	1.9 × 10 ^{2e}
	8.9	80	41
	9.9	80	38
	12.7	80	46
<i>trans</i> -[Rh(<i>m</i> -bn) ₂ Cl ₂] ⁺	8.9	80	41
	9.9	80	38
<i>trans</i> -[Rh(<i>dl</i> -bn) ₂ Cl ₂] ⁺	9.9	80	5.6
	12.7	80	6.1
<i>trans</i> -[Rh(tetrameen) ₂ Cl ₂] ⁺	12.7	25	1.0 × 10 ²
<i>cis</i> -[Rh(tetrameen) ₂ Cl ₂] ⁺	12.7	0	~7.5
<i>trans</i> -[Rh(bipy) ₂ Cl ₂] ⁺	12.7	80	Negligible
[Rh(NH ₃) ₅ Cl] ²⁺	8.9	80	9.1
	9.9	80	26
	12.7	80	Fast
<i>trans</i> -[Rh(C ₂ O ₄) ₂ Cl ₂] ³⁻	8.9	80	Dec.
<i>cis</i> -[Rh(C ₂ O ₄) ₂ Cl ₂] ³⁻	8.9	80	Dec.

^a pH values are those measured with a Beckman pH meter, model G, of the following media at 25°: 8.9, 0.1 M H₃BO₃-Na₂B₄O₇; 9.9, 0.1 M NaHCO₃-Na₂CO₃; 11.9, 0.1 M Na₂HPO₄-NaOH; 12.7, 0.1 M KOH. Corrections were not made for the change in pH of a buffer with increasing temperature. ^b E_a = 25.5 kcal. ^c E_a = 25 kcal. ^d Second-order rate constant $k = 2 \times 10^{-3} \text{ M}^{-1} \text{ sec.}^{-1}$ at 25°. ^e Second-order rate constant $k = 3 \times 10^{-2} \text{ M}^{-1} \text{ sec.}^{-1}$ at 25°.

kinetic run both chlorides appeared to be released and a product different from the hydroxy or aquo species was formed. In addition, qualitative studies of the rates of reaction of *trans*-[Rh(en)₂Cl₂]⁺ with Br⁻, CNS⁻, CN⁻, S₂O₃²⁻, SO₃²⁻ and N₃⁻ were made. In no case was the rate of reaction significantly greater than those given in Table III.

TABLE III
RATES OF THE REACTION *trans*-[Rh(en)₂Cl₂]⁺ + 2X → *trans*-[Rh(en)₂X₂]ⁿ⁺ + 2Cl⁻ FOR VARIOUS REAGENTS AT 80°

X	k × 10 ⁶ , sec. ⁻¹	X	k × 10 ⁶ , sec. ⁻¹
OH ⁻ (0.1 M)	5.1, ^b 4.0 ^a	I ⁻ (0.05 M)	5.1 ^c
NO ₂ ⁻ (0.1 M)	4.2 ^b	³⁶ Cl ⁻ (0.01 M)	4.0
NO ₂ ⁻ (0.05 M)	4.2 ^b	Thiourea (0.1 M)	4.9 ^d
I ⁻ (0.1 M)	5.2 ^c	NH ₃ (5.0 M)	4.0 ^a

^a Extrapolated from data at 78° obtained by U. Klabunde using chloride titration. ^b By chloride titration. ^c Spectrophotometric. ^d Conductometric.

These results can be explained most readily by assuming that the rate-determining step in every case is the hydrolysis of the dichloro complex. This is followed by the rapid replacement of coordinated water by the group X. This suggests that the value of k in Table III is the true rate of acid hydrolysis, $k_{\text{H}_2\text{O}}$, in eq. 8. The difference between this value of about $5 \times 10^{-5} \text{ sec.}^{-1}$ and the value of k_1 equal to $2.7 \times 10^{-5} \text{ sec.}^{-1}$ given in Table I can be attributed to the inapplicability of eq. 7. This equation assumes, for example, that

TABLE IV
A COMPARISON OF THE HYDROLYSIS BEHAVIOR OF *cis*- AND *trans*-[Rh(en)₂Cl₂]⁺ AND [Co(en)₂Cl₂]⁺

Complex	k_{H_2O} , sec. ⁻¹	k_{OH^-} , M^{-1} sec. ⁻¹	ρH where $k_{H_2O} =$ $k_{OH^-} [OH^-]$	k_{OH^-}/k_{H_2O}	T, °C.
<i>trans</i> -[Rh(en) ₂ Cl ₂] ⁺	$<5 \times 10^{-5}$	$<5 \times 10^{-4}$	>13	<10	80
<i>cis</i> -[Rh(en) ₂ Cl ₂] ⁺	$\sim 6 \times 10^{-5}$	~ 0.12	~ 10.7	$\sim 2 \times 10^3$	55
<i>trans</i> -[Co(en) ₂ Cl ₂] ⁺	3.2×10^{-3}	3×10^3	6	9×10^7	25
<i>cis</i> -[Co(en) ₂ Cl ₂] ⁺	2.5×10^{-4}	1×10^3	7.4	4×10^8	25

[Cl⁻] during a kinetic run is the same as that which exists at equilibrium. It will be noted that the value of k_{obs} in Table I, 12.1×10^{-1} sec.⁻¹, is greater than k_{H_2O} , as it must be since it is a sum of k_{H_2O} plus other terms.

Accordingly, the procedure used was to calculate the value of k_{H_2O} from data in alkaline media only, where the reactions go to completion. For those rhodium complexes where the rate varied with pH, k_{H_2O} was estimated from the value of k at the lowest values of the hydroxide ion concentration. An estimate of k_{OH^-} was made from the data at higher concentrations of base. Table IV shows comparable values of k_{H_2O} , k_{OH^-} and the pH where $k_{H_2O} = k_{OH^-} [OH^-]$ for *cis*- and *trans*-[Rh(en)₂Cl₂]⁺ and the corresponding complexes of cobalt(III).

C. Exchange of Radioactive Chloride ion by *trans*-Dichlorobis-(ethylenediamine)-rhodium(III) Nitrate.—The method used to determine the rate of exchange of radioactive chloride ion by *trans*-[Rh(en)₂Cl₂]⁺NO₃ was that of Gray.¹³ The exchange solution contained 2.00×10^{-3} M *trans*-[Rh(en)₂Cl₂]⁺NO₃ and 1.08×10^{-2} M HCl with a radioactivity of 2070 counts/100 λ min. The rate of the exchange was obtained graphically from the relationship

$$k = \frac{2.303}{t} \frac{2[Cl^-]}{2[cpv] + [Cl^-]} \log \frac{C_\infty - C_0}{C_\infty - C_t} \quad (9)$$

where [Cl⁻] and [cpv] are the concentrations of chloride ion and complex, respectively, and C_∞ , C_0 and C_t are the measured radioactivities at infinite time, zero time and time t . The value of k was 4.0×10^{-5} sec.⁻¹ at 80°.

D. Hydrogen-Deuterium Exchange by *cis*- and *trans*-Dichlorobis-(ethylenediamine)-rhodium(III) Acetate.—The infrared method of Palmer¹⁴ was used to measure the rate of exchange of hydrogen for deuterium by *cis*- and *trans*-[Rh(en)₂Cl₂]⁺C₂H₃O₂. It was necessary to convert the complexes to the acetate salts because both the nitrates and chlorides were insufficiently soluble in the exchange medium, a deuterium acetate (0.1 M)-sodium acetate (0.1 M) buffer. The concentration of complex was 0.20 M. Pseudo-first-order rate constants were determined graphically from the expression

$$k = \frac{2.303}{t} \log \frac{(H_\infty - H_0)}{(H_\infty - H_t)} \quad (10)$$

where H_∞ , H_0 and H_t are peak heights at infinite time, zero time and time t , respectively. These pseudo-first-order rate constants were converted to second-order rate constants by dividing by the concentration of deuterioxide ion upon which the exchange exhibits a first-order dependence. An average value for the rate of each exchange was obtained from the values calculated for each of three peaks: the disappearing NH stretching overtone at 1530 mμ, the appearing OH stretching overtone at 1400 mμ, and the appearing OH stretching frequency at 1655 mμ; individual values

(13) H. B. Gray, Ph.D. Thesis, Northwestern University, 1960, p. 20; R. G. Pearson, H. B. Gray and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

(14) J. W. Palmer, Ph.D. Thesis, Northwestern University, 1959, pp. 17, 20; F. Basolo, J. W. Palmer and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

usually agreed within 10%. Average values found were $k = 4.5 \times 10^5$ M⁻¹ sec.⁻¹ for *cis*-[Rh(en)₂Cl₂]⁺ and 2.4×10^5 M⁻¹ sec.⁻¹ for *trans*-[Rh(en)₂Cl₂]⁺ at 58.6°.

E. Attempted Geometric Isomerization of *cis*- and *trans*-[Rh(en)₂Cl₂]⁺.—*cis*- and *trans*-[Rh(en)₂Cl₂]⁺NO₃ (1.2×10^{-3} M) were dissolved in 0.1 M KOH and a pH 8.9 borate buffer, respectively, the visible spectra of the two solutions immediately recorded, and the mixtures allowed to react until chloride titration indicated complete formation of [Rh(en)₂(OH)₂]⁺. The *cis* isomer required 24 hr. at room temperature, the *trans* isomer 24 hr. at 80°. The borate buffer was chosen for use with the latter because prolonged treatment with 0.1 M KOH at so high a temperature led to some degradation of the complex. Spectra of the two solutions were again recorded and sufficient concd. HCl to make each mixture slightly acidic (pH ~ 5) and enough solid KCl to make the total concentration of Cl⁻ 1 M in each solution were then added. The two reaction mixtures were allowed to stand for 1 week at 80° and their spectra again recorded. From Fig. 1, in which the various spectra are reproduced, it is evident that no measurable amount of either *cis* → *trans* or *trans* → *cis* isomerization has occurred.

F. Attempted Racemization of *l-cis*-[Rh(en)₂Cl₂]⁺.—The resolution of *rac-cis*-[Rh(en)₂Cl₂]⁺ and isolation of *l-cis*-[Rh(en)₂Cl₂]⁺Cl have been described previously.⁸ A 10-ml. sample of a 0.4% solution of *l-cis*-[Rh(en)₂Cl₂]⁺Cl in 0.1 M KOH was placed in a 10-cm. polarimeter tube in a modified Bellingham and Stanley polarimeter. The usual eyepiece was replaced by a light tight 1P28 photomultiplier tube connected to a photomultiplier microphotometer on which changes in light intensity were read as changes in current. Over a period of 24 hr. at 32°, the optical rotation of the sample dropped from -0.22° to -0.04° . Concentrated HCl and solid KCl were then added as described above to give a solution of pH ~ 5 and [Cl⁻] = 1 M. During the next 24 hr. the optical rotation rose to -0.20° , a value within experimental error of the initial rotation. Less quantitative studies of these reactions at 80° indicate a similar retention of optical activity by *l-cis*-[Rh(en)₂Cl₂]⁺ while undergoing hydrolysis and reformation.

Discussion

Similarities in the Behavior of Cobalt(III) and Rhodium(III) Complexes.—The results of this investigation show that rhodium(III) and cobalt(III) complexes have some similarities as well as some striking differences. Rates of acid hydrolysis of *trans*-[M(AA)₂Cl₂]⁺, where (AA) = en, *dl*-bn, *m*-bn and tetraammonium, increase in the order given for both cobalt and rhodium; the spread in rates is greater for cobalt than for rhodium, however. In the case of cobalt, the acceleration in rate by alkyl substitution was attributed to steric acceleration of an S_N1 dissociation mechanism.¹⁵ The smaller effect in rhodium is logically explained by the larger size of the rhodium ion and the reduction of steric strain in the ground

(15) R. G. Pearson, C. R. Boston and F. Basolo, *ibid.*, **75**, 3089 (1953).

state. It is also of interest to note that *trans*-[Rh(bipy)₂Cl₂]⁺ is extremely resistant to hydrolysis, whereas *trans*-[Co(bipy)₂Cl₂]⁺ hydrolyzes very rapidly.⁵ The reactivity in the latter case was attributed to steric strain in the bipyridine chelate ring.

This type of strain is less for the larger rhodium(III) and may account for the inertness of this system. Alternatively the rapid reaction for Co(III) may result from the π -bonding tendency of bipy which, as discussed later, is of less importance for Rh(III).

The retardation in rates of acid hydrolysis with increased chelation for rhodium(III) complexes (Table I) is similar to the chelation effect reported previously for the cobalt(III) complexes.⁵ Although the examples for rhodium(III) are not numerous, these do show that the effect again is smaller than that for cobalt(III).

As shown in Table III, the rate of reaction of *trans*-[Rh(en)₂Cl₂]⁺ with a variety of nucleophilic reagents was found to be independent of the nature or concentration of the incoming ligand. Such a result, with the exception of hydroxide ion, is the same as that known for reactions of cobalt(III) complexes in aqueous solution. These results indicate that the rate-determining step is the hydrolysis reaction which then is followed by a relatively rapid replacement of coordinated water by the new ligand. Either the initial hydrolysis proceeds by a purely dissociative process or else, if an SN₂ displacement mechanism is followed, other nucleophiles do not effectively compete with water.

Differences in the Behavior of Cobalt(III) and Rhodium(III) Complexes.—One unexpected difference between rhodium(III) and cobalt(III) is the effect of the charge on the complex on its rate of reaction. Data in Table I show that the rates of acid hydrolysis of [Rh(NH₃)₅Cl]²⁺, *trans*-[Rh(NH₃)₄Cl₂]⁺ and [Rh(C₂O₄)₂Cl₂]⁻³ are all very nearly the same. This contrasts with the fact that *trans*-[Co(NH₃)₄Cl₂]⁺ reacts approximately 10³ times faster than does [Co(NH₃)₅Cl]²⁺. One reason given for this thousandfold difference in rate is that these reactions of cobalt(III) are primarily dissociative in type. Thus, the larger cationic charge makes more difficult the breaking away of chloride ion. On this basis it would appear that reactions of rhodium(III) involve opposing effects of charge separation and charge neutralization which results in the rates of reaction being insensitive to the charge on the complex. This argument then leads to a bimolecular displacement mechanism for the reactions of these rhodium(III) complexes. A similar behavior with respect to ionic charge is observed for reactions of platinum(II) complexes which are known to proceed by an SN₂ mechanism.¹⁶

An alternative explanation for the greater reactivity of [Co(NH₃)₄Cl₂]⁺ compared to [Co(NH₃)₅Cl]²⁺ is that π -bonding of the remaining chloro ligand tends to stabilize the transition state for the reaction of the tetraammine system. There is considerable evidence that coordinated atoms containing unshared pairs of electrons such as Cl, O and N do indeed greatly increase the lability of other ligands bonded to the same metal atom and that π -bonding does occur.^{12,17} Since anions commonly bound to cobalt(III) usually bind through atoms with unshared pairs of electrons, it is possible that the apparent effect of reducing the positive charge of a complex is due largely to π -bonding from the anions.¹⁸ On this basis one would conclude

(16) Reference 5, p. 194; F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, **1**, 551 (1962).

(17) G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, **45**, 1425 (1962).

(18) In the case of [Co(CN)_xX]^{3-x} in which the CN⁻ is a π -electron accepting group, the lability of X is relatively small: A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962).

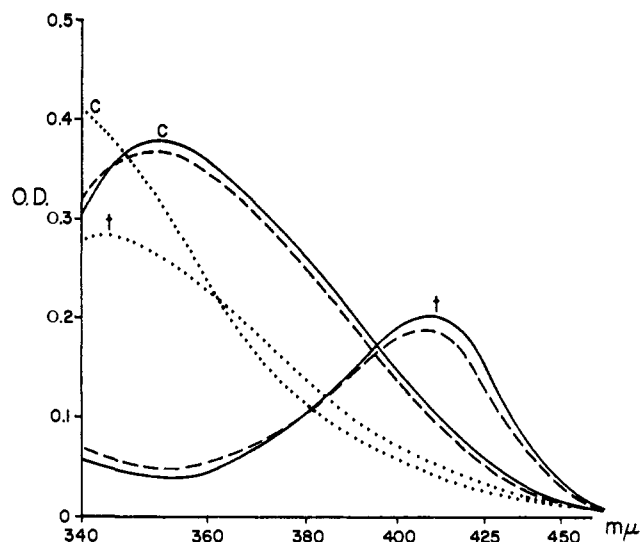
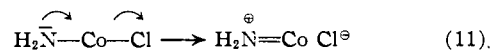


Fig. 1.—Spectral changes during base hydrolysis and reformation of *cis*- and *trans*-[Rh(en)₂Cl₂]⁺: $\frac{[\text{Rh}(\text{en})_2\text{Cl}_2]^+}{\text{KOH}} \rightarrow \frac{[\text{Rh}(\text{en})_2(\text{OH})_2]^+}{\text{KCl}} + \frac{[\text{Rh}(\text{en})_2\text{Cl}_2]^+}{\text{HCl}}$; c = *cis*, t = *trans*.

that either π -bonding does not occur in rhodium(III) complexes or that its effect on rates of reaction is small.

This conclusion is strongly supported by the remarkable observation that the rates of hydrolysis of *trans*-[RhA₄Cl₂]⁺ are the same at pH 1 and 13. In contrast to this the cobalt(III) amines hydrolyze some million times faster in base than in acid. The rapid base hydrolysis of cobalt(III) amines is attributed to an acid-base pre-equilibrium to give an amido species or conjugate base which then undergoes dissociation. Such a process is designated as an SN₁CB mechanism. The reactivity of the conjugate base is believed to be due to π -bonding of the amido group stabilizing the transition state.



There is no reason to feel that this reaction path is not also available to the rhodium(III) system. These amines are such weak acids that their acid strengths are not known. However, the acid strengths of the two analogous metal systems are not expected to be grossly different; for [M(NH₃)₅H₂O]³⁺ the *pK_a* values are Rh(III) = 5.9 and Co(III) = 5.7.¹⁹ Furthermore the rate of hydrogen exchange for *trans*-[Rh(en)₂Cl₂]⁺ is sufficiently fast to permit reaction by such a process. Again it must be concluded that either the extent of π -bonding or its effect on the rate of reaction is not very large for rhodium(III). It may be noted from Table IV that even in the case of *cis*-[Rh(en)₂Cl₂]⁺ where there is a noticeable base hydrolysis, the ratio of *k*_{OH⁻}/*k*_{H₂O} is very much less for rhodium than it is for cobalt. The same is true for [Rh(NH₃)₅Cl]²⁺.

It is not completely clear why [Rh(NH₃)₅Cl]²⁺ and *cis*-[Rh(en)₂Cl₂]⁺ behave differently from *trans*-[Rh(AA)Cl₂]⁺ with respect to base hydrolysis. The results could be explained by an SN₁CB mechanism providing these complexes are stronger acids than are the *trans*-[RhA₄Cl₂]⁺. This would result in a greater concentration of the conjugate base which then begins to contribute to the over-all rate of hydrolysis. There is no information on the acid strengths of these rhodium(III) complexes. However, the *pK_a* values for

(19) J. N. Brønsted and K. Volquartz, *Z. physik. Chem.*, **134**, 97 (1928)

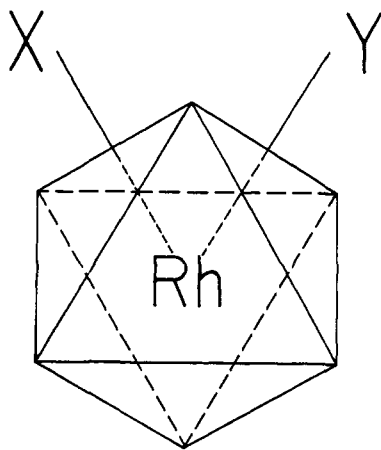
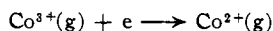


Fig. 2.—Seven-coordinated transition state for rhodium(III) complexes; X and Y are leaving and entering groups.

the analogous platinum(IV) compounds are $[\text{Pt}(\text{NH}_3)_6\text{Cl}]^{+3} = 8.40$, $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{+2}$ *cis* = 9.70, *trans* = 11.3 and $[\text{Pt}(\text{pn})_2\text{Cl}_2]^{+1}$ *cis* = 8.22, *trans* = 10.8 (pn = propylenediamine).²⁰ These relative strengths are in the direction needed to account for the base hydrolysis kinetic data and may be sufficient to account for them. On the other hand, the deuterium exchange studies do not indicate any great difference between *cis*- and *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]^{+1}$.

The stereochemical evidence also strongly supports the idea that π -bonding is much less important for rhodium(III) complexes than for cobalt(III) in hydrolysis reactions. For rhodium the evidence presented here is that both acid and base hydrolysis occurs with complete retention of both geometric and optical configuration. For cobalt, base hydrolysis is generally accompanied by large amounts of isomerization and racemization. This has been explained by postulating rearrangement of the intermediate amido complex into a trigonal bipyramidal structure in which π -bonding is more efficient.¹² Acid hydrolysis also leads to geometric rearrangement in cases of π -electron donating ligands *trans* to the leaving group. In such cases a trigonal bipyramidal structure is also favored because of the better π -bonding. If these interpretations are valid, it must mean that π -bonding in rhodium(III) complexes is not important enough to lead to rearrangement to a trigonal intermediate.

It is interesting to speculate on why some systems such as those of cobalt(III) seem to show great sensitivity to π -bonding and others such as rhodium(III) and chromium(III) are much less sensitive. Since π -bonding from an amido group involves donation of electrons to the metal and hence, in a formal sense, reduction of the metal ion to a lower valence state, ease of reduction may be a dominant factor.²¹ Thus it is easier to reduce cobalt(III) to cobalt(II) than to reduce the trivalent states of rhodium and chromium to their divalent states. A consideration of the third ionization potentials of the gaseous ions gives the figures Cr = 30.95 e.v., Co = 33.49 e.v. and Rh = 31.05 e.v. That is, the process



occurs with greater evolution of energy than for the other metals. More examples are needed, however, to test this theory of susceptibility to π -bonding.

(20) A. A. Grinberg, L. V. Vrublevskaya, Kh. I. Gil'dengershel and A. I. Stetsenko, *Russian J. Inorg. Chem.* (translation), 462 (1959); R. C. Johnson, F. Basolo and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 59 (1962).

(21) We are indebted to Dr. M. Green for calling our attention to this point of view.

Probable Mechanism for the Hydrolysis of Chloroamminerhodium(III) Complexes.—Though some of the above discussion seems to lead to opposed conclusions, it is possible to postulate a detailed reaction mechanism for rhodium(III) which is consistent with the experimental results and also correlates with the behavior of corresponding complexes of cobalt(III). The general mechanism for rhodium(III) involves a transition state in which the five inert ligands remain in nearly their original positions, forming a square pyramid. Two other ligands, the leaving and entering groups, occupy nearly equivalent positions above the base of the square pyramid, and at much longer distances from the metal ion than the five inert ligands. Figure 2 illustrates a possible structure for the transition state. In the hydrolysis reactions the entering group is always water. Such a transition state is very similar to, but not identical with, that postulated²² for the exchange reactions of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and the acid hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$.

In the latter cases the mechanism was said to be intermediate between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ because of the independence of the rate on the nature of the incoming ligand.²³ The properties of rhodium(III) and the experimental data suggest that an $\text{S}_{\text{N}}2$ label is more appropriate for this case. That is, the much slower reactions of rhodium(III) compared to cobalt(III), and the independence of the rate constant on the ionic charge of the complex both point to a greater participation of the entering water molecule in the transition state for rhodium(III). Nevertheless the effect of bulky groups and the independence of the rate on added nucleophiles suggest that, like cobalt(III), the bulk of the energy of activation is needed to stretch the Rh-Cl bond to a critical distance.

The transition state of Fig. 2 will, of course, account for the stereochemical results of retention of configuration and geometry. It is an example of *cis* attack.⁵ The juxtaposition of the leaving and entering groups helps to explain why anions are not good nucleophilic reagents for complexes in which the leaving group is also anionic. It is remarkable that NH_3 does not accelerate the release of chloride ion from *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]^{+1}$. This reagent was chosen because it would be very similar in size and charge effects to H_2O . At five molar concentration surely some of the second coordination sphere of the complex ion would consist of NH_3 rather than H_2O molecules. Yet no increased rate due to the greater basicity or greater polarizability of ammonia is observed.

A comparison of rhodium(III) and cobalt(III) on the basis of crystal field theory is instructive. Both ions are d^6 and are spin-paired so that crystal field stabilization is large, only the stable t_{2g} d orbitals being filled. The loss of CFSE corresponding to the formation of the transition state of Fig. 2 has recently been calculated by Hush.²⁴ The value is approximate only and depends on the distances and angles assumed, but is of the order of $3.5Dq$ for a d^6 system, where Dq refers to the chloride ion as a ligand in the spectrochemical series. Dq is about 3 kcal. for cobalt(III).

Since Dq for rhodium(III) is 50% greater than for cobalt(III),²⁵ it is predicted that the activation energy for rhodium complexes will be about 5 kcal. greater than for cobalt complexes, if the mechanism remains

(22) Reference 5, pp. 98–101 and p. 165; R. G. Pearson, *J. Chem. Educ.*, **38**, 164 (1961).

(23) In the anation reaction of many aquo complexes, Eigen has shown that the reaction rate is independent of the nature of the incoming anion once an ion-pair between the aquo complex and the anion has been formed (M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962)).

(24) N. S. Hush, *Australian J. Chem.*, **15**, 378 (1962).

(25) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500, 518 (1956).

the same. The observed values of E_a for rhodium(III) are in fact about 2 kcal. greater than for corresponding cobalt(III) complexes. Since many other energy terms contribute to the activation energy, this suggests that, apart from crystal field effects, rhodium(III) would react faster than cobalt(III).²⁶ This could either imply that the rhodium-chlorine bond energy is weaker, or that the larger size of rhodium(III) allows more nucleophilic assistance from the entering water molecule. The latter inference is in better agreement with the observation that the reactions of rhodium(III) have more SN2 character than those of cobalt(III).

Crystal field theory can also be used in another comparison of rhodium and cobalt. Rearrangement of a

(26) For example, Cd(II) is more labile than Zn(II) (M. Eigen, private communication) and Sr(II) is more labile than Co(II), ref. 23.

square pyramid to a trigonal bipyramid involves a considerable loss in CFSE for a spin-paired d^1 -system, about $7.5Dq$ units by the usual approximate calculation. This indicates that only a comparable lowering of the energy, due to reduced ligand-ligand repulsion and to π -bonding, would allow rearrangement to occur. The larger size of rhodium, the greater value of Dq and the reduced importance of π -bonding all make rearrangement to a trigonal bipyramid unlikely for rhodium compared to the case of cobalt. This agrees with the stereochemical results of retention of configuration. It also predicts far less probability for complexes of rhodium(III) to react by a dissociation mechanism since stabilization of a five-coordinated intermediate by rearrangement to a trigonal bipyramid is of great importance in SN1 reactions of octahedral complexes.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

Factors Controlling the Rate of Electron Transfer. II. Chelating Ability of Ligands such as Oxalate, Succinate, Maleate and Phthalate¹

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RECEIVED NOVEMBER 5, 1962

Rate constants of the order 15–30 l. mole⁻¹ sec.⁻¹ for the acid-independent path are observed on reduction of tetraamminecobalt(III) complexes containing ligands such as acetate, succinate and phthalate by chromium(II) or vanadium(II). The tetraamminemaleate is an exception, with $k = 125$ l. mole⁻¹ sec.⁻¹, and a mechanism is proposed to account for this. In general, chelation in the transition state is not an effective path for electron transfer.

Much use has been made recently of Co(III) pentaamine complexes to study electron transfer through carboxylic acids as bridging groups.^{2,3} In particular, a study of the chromous ion reduction of the pentaaminemalonatocobalt(III) complex has been reported⁴ and the possibility of chelation of the Cr(II) by the malonate ligand discussed. The effect on the rate of reduction was concluded to be negligible. This paper reports the examination of some tetraamminecobalt(III)-chromous (or vanadous) ion oxidation-reductions, made in the light of the results of the corresponding pentaamminecobalt(III) reductions. It is found that chelation of the reductant by the ligand can take place if certain restricting steric conditions exist, but the effect is not common, nor is it as an efficient path for electron transfer as is a system of conjugated double bonds singly coordinated to the reductant.

Experimental

Materials.—The tetraamine $(\text{NH}_3)_4\text{Co}(\text{CO})_3(\text{ClO}_4)_5$ was used as the starting material in preparing the dicarboxylatocobalt(III) ions. Methods available in the literature were used for the preparation of *trans*-diacetato-,⁶ *cis*-succinato-,⁷ *cis*-phthalato-⁸ and *cis*-maleatetetraamminecobalt(III) perchlorates.⁷ In each case, the residue obtained from the reaction of the organic acid and the tetraamminecarbonatocobalt(III) perchlorate was dissolved in the least volume of hot water, the solution poured into an ether-alcohol mixture and the gummy precipitate collected on a spatula. This residue was triturated with more of the alcohol-ether solvent until a fine powder was obtained.

cis-Diacetatotetraamminecobalt(III) perchlorate was obtained by heating freshly prepared diaquotetraamminecobalt(III) perchlorate with potassium acetate.⁶

Tetraammineoxalatocobalt(III) perchlorate was obtained by the method of Palmer.⁹ Pentaamine complexes were obtained

by heating pentaammineaquocobalt(III) perchlorate with a mixture of the organic acid and sodium salt.²

Analyses.—The nitrogen, perchlorate and free acid ($-\text{CO}_2\text{H}$) content of each complex were determined as stated previously.¹ In all cases the values obtained were within 2% of those calculated on the basis of formula weights. The titrations with standard base showed that complexes of dibasic acids did in fact contain one chelated ligand, not two ligands each coordinated by one carboxyl group, and so were the *cis* isomers. *cis*- and *trans*-diacetatotetraamminecobalt(III) perchlorates were also compared with recorded optical spectra.¹⁰

Solutions of sodium perchlorate were prepared by neutralizing A.R. sodium hydroxide pellets dissolved in triply distilled water with A.R. perchloric acid. The preparation of the chromium(II) and vanadium(II) perchlorate solutions has been described previously.³

Method.—Immediately before the kinetic measurements approximately 50 mg. of the cobalt complex was dissolved in 5 cc. of water. The solution was shaken with Dowex 1 ion-exchange resin in the perchlorate form (to remove any traces of other anions), filtered, then perchloric acid was added to give a solution 0.2 molar in $[\text{H}^+]$. This was shaken with Dowex 50 to remove any cationic species with external charges greater than one, filtered, and diluted to the required volume with the perchloric acid-sodium perchlorate solution. The initial Co(III) concentration was established spectrophotometrically at either 525 $m\mu$ (500 $m\mu$ for the pentaamine cobalt(III) complexes) or 355 $m\mu$. Nitrogen was passed through the solutions to remove any trapped oxygen.¹ All reaction mixtures used in the kinetic studies contained Co(III) in excess. The rate of reduction was followed in a Perkin-Elmer 350 or Beckman DKI spectrophotometer by observing the rate of disappearance of either the 525 $m\mu$ or the 365 $m\mu$ absorption maximum of the Co(III) complex. Acid-catalyzed aquation of the complexes does not occur to any significant extent during the reduction, at least under the conditions of $\mu = 1.0$ and $0.2 < [\text{H}^+] < 1.0 M$.¹¹

The method of Sebera and Taube² was used to determine the rate constants. Because the cobalt(III) complex was present in excess in all measurements, the reactions were followed spectrophotometrically to completion: in this way, the final optical density could be determined experimentally. In most cases, sets of duplicate runs (same cobalt(III) and chromium(II) or vanadium(II) concentrations) were made at both absorption maxima: these gave rate constants within $\pm 3\%$ of each other.

(1) Part I: *J. Am. Chem. Soc.*, **84**, 3436 (1962).

(2) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(3) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239, 2242 (1961).

(4) G. Svartos and H. Taube, *ibid.*, **83**, 4172 (1961).

(5) "Inorganic Syntheses," Vol. VI, E. G. Rochow, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 173.

(6) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949).

(7) J. C. Duff, *J. Chem. Soc.*, **119**, 385 (1921).

(8) J. C. Duff, *ibid.*, **119**, 1982 (1921).

(9) W. C. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p. 547.

(10) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

(11) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).