

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305,
AND THE UNIVERSITY OF CALIFORNIA AT DAVIS, DAVIS, CALIFORNIA 95616

Rates of Reduction of Carboxylatopentaamminecobalt(III) Complexes

BY MARTHA B. BARRETT, J. H. SWINEHART, AND H. TAUBE*

Received September 24, 1970

The rates of reduction by Cr(II) of selected carboxylatopentaamminecobalt(III) complexes have been reexamined and studied as a function of temperature. The rate of reduction of the acetato complex decreases as the acidity is raised to high levels. This and the sensitivity of the spectrum to $[H^+]$ suggest substantial association of H^+ with the complex. The second-order rate constants at 25° and $\mu = 1.0$ for formato, acetato, benzoato, chloroacetato, dichloroacetato, and pivalato (trimethylacetato) are 7.2, 0.35, 0.15, 0.12, 0.075, and 0.0070 $M^{-1} \text{ sec}^{-1}$, respectively. The rate constant for trifluoroacetato at 25° and $\mu = 0.2$ is 0.017 $M^{-1} \text{ sec}^{-1}$. The values of ΔH^\ddagger lie in the range 8.2–11.1 kcal/mol and those of ΔS^\ddagger in the range -27 to -36 eu. Inductive effects on the rate are small, but the comparison of the formato, acetato, and pivalato complexes shows that steric effects can be quite important. It was shown that with the acetato complex, at least 95% of the reaction proceeds by the inner-sphere mechanism. Even for the pivalato, which is strongly hindered, the inner-sphere path accounts for at least 70% of the reaction.

Introduction

Studies of the reduction of the carboxylatopentaamminecobalt(III) complexes have figured prominently in the development of the subject of oxidation-reduction reactions which involve electron transfer through organic bridging groups. Principally because they were considered to be the easiest to prepare, these complexes were the first¹ to be studied as interest grew in the role which organic molecules can play in mediating in electron transfer between metal ions. The results with the carboxylate complexes have served to indicate the importance of steric, inductive, and other more subtle factors which can affect the capacity of a bridging group to mediate in electron transfer.²

Though a large number of systems have been studied and though a variety of conclusions have been based on the results, the data are wanting in important respects. Many of the studies have been done at a single temperature, and even when the rates measured are fairly accurate, they are of limited usefulness in testing theories because the sensitivity of the rate pattern to temperature as a variable is not established. Beyond this, there are numerous instances³ recorded of disagreement in rates for a particular system under fixed conditions, and this irreproducibility in rates extends even to the reduction of acetatopentaamminecobalt(III), a reaction which has often been used as a standard for rate comparisons. Finally, the important question of the extent of transfer of the ligand from Co(III) to Cr(II) has not been examined carefully for any of the systems. In view of these limitations of the past studies and the significance of this class of systems,³ we have considered it worthwhile to undertake a careful reinvestigation of the rate of reduction of a number of the key complexes as a function of temperature, extending our interest in some cases to the identity of the Cr(III) products of the reactions. The series we have chosen features formate, acetate, chloroacetate, dichloroacetate, trifluoroacetate, benzoate, and trimethylacetate as ligands.

Experimental Section

All rate measurements were done under nitrogen as blanketing

* Address correspondence to this author at Stanford University.

(1) H. Taube, *J. Amer. Chem. Soc.*, **77**, 4481 (1955).

(2) H. Taube and E. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

(3) See, for example, the extension of the studies to Ru(III) as the oxidizing center: J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

gas. Dry "Hipure" (National Cylinder Gas Co.) nitrogen was passed through gas-scrubbing towers filled with 0.1 *F* chromium(II) perchlorate to remove oxidizing impurities.

Deionized distilled water was used in the preparation of all reactant solutions and in all syntheses and recrystallizations.

Lithium perchlorate was prepared by the addition of perchloric acid to either lithium carbonate or lithium hydroxide monohydrate.

Chromium(III) perchlorate solutions were prepared by hydrogen peroxide reduction of primary standard potassium dichromate in perchloric acid. Cr(II) solutions were generated by electrolysis or by freshly amalgamated zinc from chromium(III) perchlorate in mixtures of lithium perchlorate and perchloric acid.

Carboxylatopentaamminecobalt(III) complexes were prepared from aquopentaamminecobalt(III) and mixtures of the corresponding organic acid and its sodium salt. Solutions with a tenfold molar excess of total carboxylate over Co(III) were maintained with stirring at approximately 70° for 2–3 hr. After acidification with 1 *F* perchloric acid, the solution was cooled in an ice bath. Crystals were collected, washed with cold 1 *F* perchloric acid, cold water, cold ethanol, and ether, and then air dried. Some modifications were necessary for the synthesis of the benzoato and pivalato complexes.⁴

Dowex 50W-X2 resin was obtained as analytical grade from Bio-Rad Laboratories and further purified by the method of Deutsch.⁵

Isotope effect studies were carried out in deuterium oxide obtained from Bio-Rad Laboratories at greater than 99.8% enrichment. Deuterium perchlorate was prepared from anhydrous silver perchlorate and 31% deuterium chloride in deuterium oxide.

Analyses.—Co(III) in pentaammine complexes was determined by the alkaline hydrolysis method of Butler.⁶ Alkaline hydrolysis of the compound to give solid cobaltic oxide was followed by careful dissolution of the solid in concentrated hydrochloric acid. The resulting Co(II) was determined spectrophotometrically in a hydrochloric acid medium of controlled chloride concentration.

Total chromium concentration was determined spectrophotometrically as chromate ion⁷ after oxidation of the sample by hydrogen peroxide in base. Cr(II) concentration was measured spectrophotometrically using an extinction coefficient of 4.90 $M^{-1} \text{ cm}^{-1}$ at 715 nm. This value was determined from spectra of Cr(II) solutions, the concentrations of which had been determined by injecting an aliquot into a deoxygenated chloropentaamminecobalt(III) solution and measuring Co(II) produced. This extinction coefficient agrees well with that of Deutsch⁵ determined by injection of Cr(II) into acidic dichromate solutions and determination of the remaining excess dichromate.

The concentration of hydrogen ion in Cr(II) solutions was determined by potentiometric titration of a diluted sample with

(4) M. B. Barrett, Ph.D. Thesis, Stanford University, Stanford, Calif., 1968.

(5) E. Deutsch, Ph.D. Thesis, Stanford University, Stanford, Calif., 1967.

(6) R. D. Butler, Ph.D. Thesis, Stanford University, Stanford, Calif., 1967.

(7) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

0.1 *F* ethylenediamine under a nitrogen atmosphere. Glass and calomel electrodes served as indicator and reference electrodes, respectively. The saturated potassium chloride in the calomel electrode was replaced by 4 *M* lithium chloride to prevent precipitation of potassium perchlorate in the fiber junction.

Perchlorate in solutions and in carboxylatopentaamminecobalt(III) compounds was determined by the method of Gould and Taube.⁸

Microanalyses were performed by the microanalytical laboratories of Stanford University and the University of California at Berkeley.

Methods.—Reactions were monitored spectrophotometrically in Applied Physics Cary Methods 14 and 15 double-beam spectrophotometers or the Durrum-Gibson stopped-flow single-beam spectrophotometer. A Beckman DU single-beam spectrophotometer was used in the spectral study of the protonation of the acetatopentaamminecobalt(III) complex.

Reaction solutions were thermostated prior to mixing. Temperature control in all kinetic runs was within 0.1°.

Ionic strength was maintained by use of lithium perchlorate-perchloric acid mixtures.

Mixing was accomplished in an all-glass apparatus within 60 sec, by syringe techniques within 10 sec, and with the stopped-flow device within 5 msec.

Data Treatment

The absorbance of the reacting solution at a fixed wavelength was followed continuously as a function of time. The wavelength chosen corresponded to an absorbance peak for either the reacting Co(III) species or the Cr(III) product. Kinetics at the 500-nm cobalt peak, the 350-nm cobalt peak, or the 420-nm Cr(III) peak gave identical rate constants except in the case of the dichloroacetatopentaamminecobalt(III)-chromium(II) reaction. This reaction was followed at 500 nm to minimize interference by the subsequent reactions of Cr(II) with the dichloroacetate ligand after electron transfer.

The stoichiometry of the reactions of Cr(II) with the carboxylatopentaamminecobalt(III) complexes was ascertained from the amount of Co(II) produced under conditions of excess Co(III) on reaction with a known amount of Cr(II) or by the decrease in Cr(II) absorbance at 715 nm, in the reaction of Cr(II) in excess with a known amount of Co(III) complex.

Ion-exchange studies were carried out on Dowex 50W-X2 resin in lithium form at low temperatures. Column-induced hydrolysis of the Cr(III) species was minimized by using resin in the lithium form and eluent of low acid concentration and keeping the column at 5°. Product solutions, prepared by treating the corresponding carboxylatopentaamminecobalt(III) perchlorate with Cr(II) under nitrogen, with the excess Cr(II) then air-oxidized, were diluted to an ionic strength of less than 0.1 *F* and washed onto the column. The Cr(III) species of charge 2+ was eluted with 0.33 *M* lithium perchlorate with acid present at 0.05 *M*. The hexaaquochromium(III) was then eluted with 1.0 *M* lithium perchlorate, 0.15 *M* in acid. The fractions collected were analyzed for total chromium. Under optimum conditions recovery was greater than 98% and column-induced hydrolysis as determined by ion exchange of acetatopentaquochromium(III) was less than 3%. Appropriate fractions of the chromium bands could be obtained free of Co(II) for the determination of product spectra.

Co(II) was not completely separated from the carboxylatochromium(III) species, and thus cobaltic oxide was formed during the chromium analysis. This

precipitate was collected on fine-porosity sintered-glass filters and analyzed for Co(II). Recovery of Co(II) was approximately 95%.

In all cases the kinetic data conform to the rate law

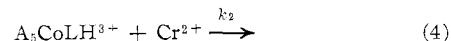
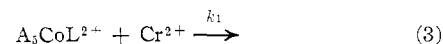
$$d[\text{Co(III)}]/dt = -k_{\text{obsd}}[\text{Co(III)}][\text{Cr(II)}] \quad (1)$$

In all cases, reactions were run under pseudo-first-order conditions, with Cr(II) in excess. For each system the initial concentration of Cr(II) was varied about 20-fold beginning with a fivefold excess. In no case was there a systematic trend in the second-order specific rates calculated from the data. Within each run, with Cr(II) in sufficient excess, pseudo-first-order behavior was observed for at least 90% completion of the reaction. The second-order specific rate k_{obsd} as defined in eq 1 was found to be independent of $[\text{H}^+]$ (range 0.1–0.7 *M*) except in the reduction of acetatopentaamminecobalt(III) complexes by Cr(II). The trifluoroacetato complex was not studied at hydrogen ion concentrations above 0.1 *M* because of its limited solubility.

Spectral evidence was found for the protonation of the acetatopentaamminecobalt(III) ion. When this protonation equilibrium is introduced as in



and when the reactions



are assumed as rate-determining steps, the rate law becomes

$$\frac{d[\text{Co(III)}]}{dt} = -\frac{k_1 + k_2 K_s [\text{H}^+]}{1 + K_s [\text{H}^+]} [\text{Cr}^{2+}] [\text{Co(III)}] \quad (5)$$

where $[\text{Co(III)}]$ refers to total Co(III) concentration.

A plot of experimental values of $\ln(k/T)$ vs. T^{-1} yielded a line of slope $\Delta H^\ddagger/R$ and intercept of $(\Delta S^\ddagger/R) + \ln(k_B/h) + \ln \kappa$ according to the Eyring formulation of absolute reaction rates where k_B is Boltzmann's constant, h is Planck's constant, and κ the transmission coefficient. Straight lines were obtained in all cases but that of the acetatopentaammine complex in 1 *F* hydrogen ion, with slight curvature noted in the case of the dichloroacetato complex. The entropy of activation was calculated from the intercept of the plots with the transmission coefficient κ assumed to be unity. The most probable error of ΔH^\ddagger was determined by application of the Student *t* values to the variance of the slope as determined by a least-squares regression of $\log(k/T)$ on T^{-1} . The most probable error was estimated to be ± 0.3 kcal/mol for all the reactions except that of dichloroacetatopentaamminecobalt(III), which was estimated to be ± 0.5 kcal/mol.

Results and Discussion

Stoichiometry.—It was shown that 1 mol (within 5%) of Cr(II) is consumed per mole of Co(III) in the Cr(II) reduction of the acetato-, benzoato-, pivalato-, formato-, and trifluoroacetatopentaamminecobalt(III) complexes. The stoichiometry of the reaction of Cr(II) with the chloroacetatopentaamminecobalt(III) complexes is complicated by the reactions of Cr(II) with the ligand.

Acetatopentaamminecobalt(III).—The second-order

specific rate for the reduction of acetatopentaamminecobalt(III) by Cr(II) decreases as $[H^+]$ increases, an effect not previously reported for reactions of this class. The specific rate at 25° at various acid concentrations appears in Table I.

TABLE I

THE ACID DEPENDENCE OF THE OBSERVED SECOND-ORDER RATE CONSTANT IN THE CHROMIUM(II)-ACETATOPENTAAMMINECOBALT(III) REACTION^a

$[H^+]$, M	$k_{\text{obsd.}}$, $M^{-1} \text{ sec}^{-1}$	$[H^+]$, M	$k_{\text{obsd.}}$, $M^{-1} \text{ sec}^{-1}$	$[H^+]$, M	$k_{\text{obsd.}}$, $M^{-1} \text{ sec}^{-1}$
0.10	0.347	0.50	0.316	0.88	0.294
0.25	0.332	0.62	0.304	1.00	0.280
0.37	0.329	0.75	0.298		

^a Probable error in k_{obsd} is 3%. $[Cr^{2+}] = 0.02 M$, $[Co(III)] = 2 \times 10^{-3} M$.

If $k_2 K_s [H^+] \ll k_1$, rate law (5) reduces to

$$k_{\text{obsd}} = k_1 / (1 + K_s [H^+]) \quad (6)$$

If this equation is valid, a plot of the reciprocal of k_{obsd} vs. $[H^+]$ will yield a straight line of slope $k_1^{-1} K_s$ and intercept k_1^{-1} . Such a plot of the data in Table I yields a straight line within experimental error. The plot appears in Figure 1. The value of k_1 obtained

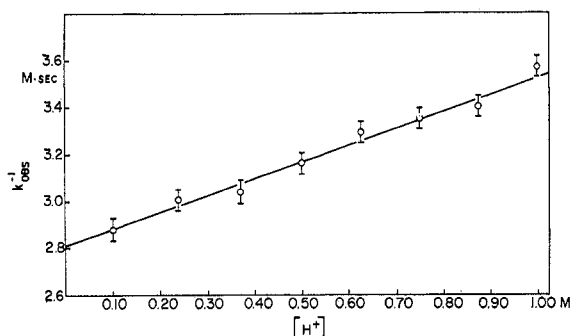


Figure 1.—The reciprocal of the observed second-order rate constant for the acetatopentaamminecobalt(III)-chromium(II) reaction as a function of hydrogen ion concentration at unit ionic strength.

from the intercept is $0.352 M^{-1} \text{ sec}^{-1}$, and the value of K_s calculated from the slope and from k_1 is $0.25 M^{-1}$.

In the absence of special effects such as are observed for fumarate as bridging ligand,⁹ the specific rate of the reaction of Cr(II) with a species of 3+ charge would not be expected to exceed the specific rate for the reaction with the 2+ charged species. Therefore, $k_2 K_s [H^+]$ would be expected to be less than 20% of k_1 up to 0.8 M hydrogen ion. The assumption that $k_2 K_s [H^+]$ is small appears to be consistent with the data, and the kinetic determinations are not sufficiently precise to lead to a determination of k_2 .

Independent evidence for the protonation of the acetatopentaamminecobalt(III) complex was obtained from the variation of the molar absorbance of the complex with hydrogen ion concentration in 4.0 M lithium perchlorate-perchloric acid mixtures. This medium was chosen to minimize activity effects and to make accessible a high acid concentration for more complete protonation of the complex. The absorbance of acetatopentaamminecobalt(III) solutions vs. blanks of the same lithium perchlorate-perchloric acid composition

was measured at both 352 and 502 nm, and the extinction coefficients are shown plotted in Figure 2.

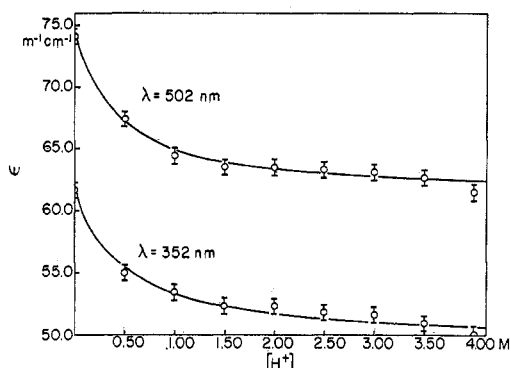


Figure 2.—The variation of molar absorbance of acetatopentaamminecobalt(III) ion with acid concentration in 4.0 M lithium perchlorate-perchloric acid mixture.

The molar absorbance observed will be the weighted average of the molar absorbances of the protonated and unprotonated species. $\epsilon_{\text{obsd}} = (\epsilon_1 [\text{unprotonated}] + \epsilon_2 [\text{protonated}]) / [\text{total cobalt(III)}]$ where the brackets indicate concentrations. If α is taken to represent the fraction of Co(III) complex present in the protonated form, $\epsilon_{\text{obsd}} = (1 - \alpha)\epsilon_1 + \alpha\epsilon_2$, and $K_s = \alpha / ((1 - \alpha) \cdot [H^+])$. The equilibrium constant K_s was estimated by iterative methods to be $2.2 M^{-1}$. The curves in Figure 2 are calculated from the estimated ϵ_1 and ϵ_2 at the given wavelength and the estimated K_s . The error in the calculated K_s caused by 1% imprecision in the determination of ϵ_{obsd} can be calculated from the plotted curve and is at least $\pm 0.5 M^{-1}$.

The value of K_s at an ionic strength of 4.0 equal to $2.2 \pm 0.5 M^{-1}$ compared to $0.25 M^{-1}$ at an ionic strength of 1.0 is consistent with the expectation that the protonated species be stabilized as ionic strength increases.

A spectrophotometric determination of K_s in ionic strength 1.0 M mixtures was not attempted since the expected variation in ϵ_{obsd} in the range 0.1–1.0 M hydrogen ion consistent with the kinetically determined value of K_s would be less than 3%.

The temperature dependence of the specific rate for the reaction of Cr(II) with the acetatopentaamminecobalt(III) complex was determined at an ionic strength of 1.0 and hydrogen ion concentrations of 0.1 and 1.0 M. The data are summarized in Table II.

TABLE II
SPECIFIC RATES AND ACTIVATION PARAMETERS FOR THE ACETATOPENTAAMMINECOBALT(III)-CHROMIUM(II) REACTIONS^a

$[H^+]$, M	Temp, °C	k , $M^{-1} \text{ sec}^{-1}$	$[H^+]$, M	Temp, °C	k , $M^{-1} \text{ sec}^{-1}$
0.10	12.4	0.180 ^b	1.00	10.0	0.129
0.10	25.0	0.349 ^b	1.00	25.0	0.280
0.10	37.4	0.623 ^b	1.00	34.0	0.375

^a Conditions: $\mu = 1.00$, $[Cr^{2+}] = 0.020 M$, $[Co(III)] = 2.0 \times 10^{-3} M$. ^b At $\mu = 0.10$, $\Delta H^\ddagger = 8.2 \text{ kcal/mol}$ and $\Delta S^\ddagger = -32.6 \text{ cal/mol deg}$.

If it is assumed that the observed specific rate for 0.1 M hydrogen ion is a good estimate of k_1 , an assumption that is borne out by the measured value of K_s at 25.0° and ionic strength 1.0, then the activation parameters

(9) D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961).

determined at a hydrogen ion concentration of 0.1 *M* may be assigned to the unprotonated path.

The assumption that k_2K_s is small relative to k_1 and the limiting form for $k_{\text{obsd}}^{-1} = k_1^{-1} + k_1^{-1}K_s[\text{H}^+]$ lead to an estimate of the quantity $(1 + K_s)$ from the ratio of k_{obsd} at 0.1 *M* hydrogen ion to k_{obsd} at 1.0 *M* hydrogen ion. Values of k_{obsd} were interpolated from the Eyring plots to provide a means of estimating K_s as a function of temperature. The values calculated for K_s appear in Table III with the propagated error.

TABLE III

K_s AS CALCULATED FROM THE RATIO OF THE SECOND-ORDER SPECIFIC RATE OBSERVED IN 0.1 *M* HYDROGEN ION

Temp, °C	$k_{\text{obsd}}/k'_{\text{obsd}}$	K_s, M^{-1}
10.0	1.22 ± 0.06	0.22 ± 0.07
25.0	1.29	0.29 ± 0.08
34.0	1.48	0.48 ± 0.09

A plot of $\ln K_s$ vs. T^{-1} should yield a line with slope $\Delta H^\circ/R$ and intercept $\Delta S^\circ/R$. The estimated error in the calculated value of K_s is quite high; the data indicate ΔH° to be 6 ± 3 kcal/mol and ΔS° to be 20 ± 10 eu for the protonation of the acetatopentaamminecobalt(III) ion. These values of ΔH° and ΔS° seem to be rather reasonable for a reaction such as is represented by eq 2.

Similar protonation equilibria have previously been reported^{8,10} for carboxylatochromium(III) and -ruthenium(II) complexes.

The specific rate of the acetatopentaamminecobalt(III)-chromium(II) reaction was measured in deuterium oxide at an acid concentration of 0.5 *M* at an ionic strength of 1.0 at 25.0°. The observed rate constant was 0.112 $M^{-1} \text{sec}^{-1}$. The ratio of $k_{\text{obsd}}^{\text{H}_2\text{O}}$ to $k_{\text{obsd}}^{\text{D}_2\text{O}}$ equal to 2.8 seems high for a reaction in which it is not apparent that hydrogen bonds are broken. This ratio can be partially attributed to the complex being a stronger base in deuterium oxide, but since the rate is only slightly affected by the operation of the protonation equilibrium, only a small factor out of the total 2.8 can be assigned to this cause.

Rate data for the acetatopentaamminecobalt(III)-chromium(II) reaction were determined also at two other ionic strengths. For these experiments $[\text{H}^+] = 0.10$ *M*, $[\text{Cr}^{2+}]_0 = 0.020$ *M*, $[\text{Co(III)}] = 2.0 \times 10^{-3}$ *M*. With $\mu = 0.20$, k at 12.2, 25.0, and 36.5° was found to be 0.085, 0.177, and 0.328 $M^{-1} \text{sec}^{-1}$ leading to $\Delta H^\circ \ddagger$ calculated as 9.2 kcal/mol and $\Delta S^\circ \ddagger = -31$ eu. With μ at 2.00, k at 15.3, 25.0, and 37.5° was found to be 0.26, 0.48, and 1.04 $M^{-1} \text{sec}^{-1}$ with $\Delta H^\circ \ddagger$ calculated as 10.5 kcal/mol and $\Delta S^\circ \ddagger = -25$ eu. These data are offered for their descriptive interest¹¹ but are not extensive enough, particularly at low ionic strength, to justify detailed discussion.

Ion exchange of the product mixtures from the reaction of equivalent amounts of Cr(II) and acetatopentaamminecobalt(III) yielded less than 5% of the chromium product as hexaaquochromium(III) ion. This agrees well with the limit set by Deutsch⁵ from comparison of the product spectrum to that of acetatochromium(III) and hexaaquochromium(III). If the path responsible for appearance of hexaaquochromium(III) product were the outer-sphere attack of Cr(II) on

the carboxylatopentaamminecobalt(III), an upper limit for the specific rate of outer-sphere attack by Cr(II) would be 5% of the rate of inner-sphere attack or 0.015 $M^{-1} \text{sec}^{-1}$ at unit ionic strength and 25.0°.

Benzoatopentaamminecobalt(III).—No evidence was found for a hydrogen ion dependence of k_{obsd} for the benzoatopentaamminecobalt(III)-chromium(II) reaction in the range 0.1–0.7 *M* hydrogen ion. The extinction coefficient of the cobalt complex in 4.0 *M* perchlorate media of varying acid concentration was constant within experimental error. Rate constants were determined as a function of temperature at three ionic strengths, with the hydrogen ion concentration 0.1 *M*. Values of the specific rate determinations and activation parameters appear in Table IV.

TABLE IV

SUMMARY OF KINETIC DATA ON THE REDUCTION OF BENZOATOPENTAAMMINECOBALT(III) BY CHROMIUM(II)

μ	Temp, °C	$k, M^{-1} \text{sec}^{-1}$	$\Delta H^\circ \ddagger, \text{kcal/mol}$	$\Delta S^\circ \ddagger, \text{eu}$
0.20	12.3	0.366	9.6	-31
0.20	25.0	0.075		
0.20	35.0	0.139		
1.00	15.1	0.091	9.0	-32
1.00	25.0	0.153		
1.00	35.0	0.267		
2.00	12.5	0.088	9.3	-31
2.00	25.0	0.188		
2.00	35.0	0.313		

The variation of activation parameters with ionic strength is much smaller than that observed for the acetatopentaamminecobalt(III)-chromium(II) reaction in going from an ionic strength of 1.0 to 2.0.

Formatopentaamminecobalt(III).—The kinetics of the formatopentaamminecobalt(III) reaction with Cr(II) were studied on the Gibson-Durrum stopped-flow spectrophotometer at unit ionic strength. For a series of experiments at $[\text{H}^+] = 0.50$ *M*, $[\text{Co(III)}]_0 = 2.0 \times 10^{-3}$ *M*, and $\mu = 1.0$, at 6.3, 15.0, and 25.3°, k ($M^{-1} \text{sec}^{-1}$) was observed as 2.56, 4.0, and 7.2. The values of $\Delta H^\circ \ddagger$ and $\Delta S^\circ \ddagger$ are calculated as 8.3 kcal/mol and -27 eu, respectively.

Pivalatopentaamminecobalt(III).—The reaction was studied at an ionic strength of 2.0. No hydrogen ion dependence of the observed second-order rate constant was noted in the range 0.1–1.1 *M* perchloric acid and no variation of extinction coefficient of the Co(III) complex with acid concentration in 4.0 *M* lithium perchlorate-perchloric acid mixtures was observed. The temperature range of the study was extended to 50.6° in order to detect any curvature in the Eyring plot which might indicate a change in mechanism from inner-sphere to outer-sphere attack. No significant curvature was noted. The kinetic data for this system are summarized as follows: with $[\text{H}^+] = 0.10$ *M* and $[\text{Co(III)}] = 3.0 \times 10^{-3}$ *M*, at 12.1, 25.1, 36.5, and 50.6°, $10^3k = 2.9, 7.0, 14.7,$ and $33.2 M^{-1} \text{sec}^{-1}$, leading to $\Delta H^\circ \ddagger = 11.1$ kcal/mol and $\Delta S^\circ \ddagger = -31$ cal/mol deg.

Ion exchange at 5° of product solutions resulting from approximately 1:1 mixtures of Cr(II) and pivalatopentaamminecobalt(II) complex yielded from 16 to 30% hexaaquochromium(III). Some of the hexaaquochromium(III) product may have been formed by hydrolysis of the pivalatopentaquochromium(III) after

(10) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(11) P. V. Manning, R. C. Jarnagin, and M. Silver, *J. Phys. Chem.*, **68**, 265 (1964).

electron transfer, and thus only an upper limit for the rate of outer-sphere attack by Cr(II) of carboxylatopentaamminecobalt(III) complexes at 25° can be estimated. Taken as 30% of the rate of the inner-sphere attack of pivalatopentaamminecobalt(III), the upper limit becomes $2 \times 10^{-3} M^{-1} \text{ sec}^{-1}$ at an ionic strength of 2.0.

Trifluoroacetatopentaamminecobalt(III).—Because of the limited solubility of the complex, the kinetic determinations were made at 0.2 ionic strength, and this limited the range of hydrogen ion concentrations which could be covered. The specific rates (10^2k , $M^{-1} \text{ sec}^{-1}$) at $\mu = 0.20$, $[H^+] = 0.10$, and $[Co(III)] = 1.0 \times 10^{-3} M$ and at 12.4, 15.5, 25.1, and 41.0° were observed to be 0.78, 0.97, 1.68, and 3.80. From these data, ΔH^\ddagger is calculated as 9.3 kcal/mol and ΔS^\ddagger as -35 eu.

Chloroacetatopentaamminecobalt(III).—The reaction of Cr(II) with monochloroacetate is slow enough (*vide infra*) so as not to interfere with the kinetic measurements on the Co(III)-Cr(II) reaction. One mole of Cr(II) was consumed per mole of Co(III) after completion of electron transfer and before there was a significant contribution from the slow subsequent reaction of Cr(II) with the ligand. Whether the Cr(II) reacts with ligand bound to Cr(III) or only with free ligand was not determined.

No acid dependence was observed for the second-order rate constant in the region 0.1–0.7 M hydrogen ion. Good first-order kinetics were obtained in excess Cr(II) from absorbance *vs.* time data at 500 nm. The rate constants (k , $M^{-1} \text{ sec}^{-1}$) at $\mu = 1.00$, $[H^+] = 0.10 M$, and $[Co(III)] = 2.0 \times 10^{-3} M$ and at 13.0, 25.0, and 37.2° are 0.057, 0.120, and 0.214, respectively. From these data ΔH^\ddagger is calculated as 8.9 kcal/mol and ΔS^\ddagger as -33 cal/mol deg.

A cursory examination of the reaction of Cr(II) with free monochloroacetic acid was made. The reaction at 0.35 M H^+ with Cr(II) in excess followed at 400 nm obeyed first-order kinetics. If the reaction rate is assumed to be first-order in $[Cr^{2+}]$, k is calculated as $1.7 \times 10^{-4} M^{-1} \text{ sec}^{-1}$, or much slower than the reduction of the Co(III) complex. Ion exchange of the final product solutions, after the completion of a step still slower than the reduction of the acid, yielded hexaaquochromium(III) and chlorochromium(III) in approximately equal proportions. Two moles of Cr(II) is consumed for each mole of organic acid.

Dichloroacetatopentaamminecobalt(III).—The reaction of Cr(II) with free dichloroacetate or dichloroacetate bound to Cr(III) appears to occur at rates of the same order as the rate of electron transfer to Co(III) (*vide infra*). The kinetics of the Cr(II)-Co(III) reaction were studied at 500 nm, since a consideration of the spectra of acetatochromium(III),⁵ hexaaquochromium(III),⁵ and chloropentaaquochromium(III)¹² indicates that the absorbance change due to the reaction of Cr(II) with carbon-bound substituted Cr(III) to give 1 mol of chloropentaaquochromium(III) and 1 mol of hexaaquochromium(III) will be minimized with respect to the absorbance change due to the Cr(II)-Co(III) electron transfer. The acetatochromium(III) spectrum is assumed to be a reasonable estimate of that of

the carbon-bound chromium species in the 500-nm region.¹³

Absorbance *vs.* time data obtained at 500 nm and treated by the Guggenheim method gave plots linear over at least 80% of the reaction. Absorbance *vs.* time data at 350 and 420 nm did not fit a simple rate expression for a one-step reaction, and apparently the successive reactions of Cr(II) with the ligand contribute at these wavelengths.

Since the major contribution to the absorbance at 500 nm is that of the Co(III) complex, the specific rates determined at 500 nm were assumed to represent the Cr(II)-Co(III) electron transfer.

Three moles of Cr(II) was consumed per mole of Co(III) complex at times such that reduction of Co(III) and of the dichloroacetate to monochloroacetate is complete.

No acid dependence of the specific rate was noted for the dichloroacetatopentaamminecobalt(III)-chromium(II) reaction. The kinetic data are summarized as follows: at $\mu = 1.00$, $[H^+] = 0.10 M$, and $[Co(III)] = 2.0 \times 10^{-3} M$ and at 13.0, 25.0, and 37.2° $k = 0.038, 0.075, \text{ and } 0.127 M^{-1} \text{ sec}^{-1}$, respectively; ΔH^\ddagger and ΔS^\ddagger are calculated as 8.1 ± 0.5 kcal/mol and -36 cal/mol deg, respectively. Deviations from linearity in the Eyring plot for the dichloroacetatopentaamminecobalt(III)-chromium(III) data were noted. These may arise from the lower precision of the specific rate determinations by the Guggenheim method or from contributions from the interfering chromium(II)-dichloroacetate reactions. If the plot is assumed to be linear, the estimate of probable error in ΔH^\ddagger is approximately ± 0.5 kcal/mol.

The reaction of Cr(II) with free dichloroacetate as followed spectrophotometrically fixing on Cr(III) absorption was found to obey the rate law

$$\frac{d[Cr(III)]}{dt} = k_1[Cr^{2+}][DA^-] + k_2[Cr^{2+}][DAH]$$

The values of k_1 and k_2 at 25° are $0.07 \pm 0.03 M^{-1} \text{ sec}^{-1}$ and $0.15 \pm 0.06 M^{-1} \text{ sec}^{-1}$. The immediate reaction consumes 2 mol of Cr(II) for each mole of organic acid and yields a product which has an abnormally high absorbance at *ca.* 415 nm, which is a feature characteristic of Cr^{III}-C species having carbon bound to Cr(III).^{14,15} Our substance is likely $(H_2O)_5CrC(H)(Cl)CO_2H^{2+}$.¹⁴ It reacts to form monochloroacetic acid, and this reaction has the interesting feature that it is catalyzed by Cr^{2+} .

Reductions with V²⁺.—A number of kinetic data on reductions with V(II) can be understood on the basis that substitution on $V(H_2O)_6^{2+}$ is rate determining.^{16,17} It seemed of interest to extend the measurements with V(II) to at least a few members of the class of oxidizing agents under investigation. The experiments were done with reducing agent in excess, and in each case good pseudo-first-order behavior was observed. The pseudo-first-order specific rates so obtained were shown to vary directly with $[V^{2+}]$. The kinetic data are summarized in Table V.

(13) Subsequent work (W. Schmidt, J. H. Swinehart and H. Taube, *J. Amer. Chem. Soc.*, **93**, 1117 (1971)) showed that ϵ for $CrC(H)(CH_2)OC_2H_5^{2+}$ at the long-wavelength maximum (560 nm) is 23, very close to the value for the acetate complex at its maximum, 24 at 570 nm.

(14) F. A. L. Anet and E. LeBlanc, *J. Amer. Chem. Soc.*, **79**, 2649 (1957).

(15) J. K. Kochi and P. E. Mocadlo, *ibid.*, **88**, 4094 (1966).

(16) B. R. Baker, M. Orhanovic, and N. Sutin, *ibid.*, **89**, 722 (1967).

(17) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(12) J. E. Finholt, K. G. Caulton, and W. J. Libbey, *Inorg. Chem.*, **3**, 1801 (1964).

TABLE V
THE REDUCTION OF SOME
CARBOXYLATOPENTAAMMINECOBALT(III)
COMPLEXES BY VANADIUM(II)^a

Temp, °C	<i>k</i> , M ⁻¹ sec ⁻¹		
	Formato	Benzoato	Acetato
6.4	0.70
12.8	0.457
15.1	1.56	0.296	...
25.0	3.63	0.63	1.15
35.0	...	1.28	2.19
ΔH^\ddagger , kcal/mol	13.9	12.4	11.6
ΔS^\ddagger , eu	-13	-18	-19

^a Conditions: $\mu = 1.00$, $[H^+] = 0.50 M$, $[V^{2+}]_0 = 0.10 M$, $[Co(III)]_0 = 4.0 \times 10^{-3} M$.

Discussion

Comparison with Previous Data.—The purpose of the present work in part was to resolve discrepancies in published values of the kinetic parameters for the systems which were studied and to correct earlier, often less careful measurements. In Table VI our results with

TABLE VI
KINETIC DATA ON THE REACTIONS OF Cr(II) WITH
CARBOXYLATOPENTAAMMINECOBALT(III). SUMMARY
AND COMPARISON WITH LITERATURE VALUES

Ligand	μ	<i>k</i> (25°), M ⁻¹ sec ⁻¹		ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	Ref
		<i>k</i>	ΔH^\ddagger			
Formate	1.00	7.0	18
	...	0.13	19
	1.00	7.2	8.3	-27	...	This work
Acetate	1.00	0.18	3.0	-52	...	9
	0.21	0.17 ^a (0.19) ^b	1
	0.09	0.085 (~0.1) ^b	11
	0.30	0.176 (0.20) ^b	11.45	-26.6	...	20
	1.00	0.347	8.2	-33	...	This work
Benzoate	1.00	0.14	4.9	-46	...	21
	1.00	0.153	9.0	-32	...	This work
	1.00	0.10	7.9	-37	...	21
Chloroacetate	1.00	0.12	8.9	-33	...	This work
	1.00	0.074	2.5	-55	...	21
Dichloroacetate	1.00	0.075	8.1	-36	...	This work
	1.3	0.0096	22
Pivalate	1.00	0.0070	11.1	-31	...	This work
	3.0	0.052	8
Trifluoroacetate	0.20	0.0170	9.3	-35	...	This work

^a At 23°. ^b Extrapolated or interpolated from present data for ionic strength shown.

Cr(II) as reducing agent are summarized and compared with values taken from the literature,^{1,8,9,11,18-22} and the comparisons are commented on in the following text.

Two independent measurements for the formato complex agreeing, we feel that the discrepant result for this complex can be set aside.

The vagaries in the specific rates for the acetato complex referred to by Fraser²³ (a range 0.14–0.32 M⁻¹ sec⁻¹ is mentioned) can perhaps be attributed to variations in $[H^+]$, the present work showing that the reactivity of this complex to Cr²⁺ is somewhat sensitive to this parameter. The effect of hydrogen ion concentration does, however, not explain the disagreement with the earlier results of Sebera and Taube.⁹ This disagreement may have its origin in the fact that their extinction coefficient for the acetato complex is in

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

(19) R. T. M. Fraser, *Proc. Int. Conf. Coord. Chem.*, **8th**, 1964, 268 (1964).

(20) J. W. Cobble, private communication, based on work by J. R. Vriesinga, Department of Chemistry, Purdue University.

(21) R. T. M. Fraser in "Advances in Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 287.

(22) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966).

(23) R. T. M. Fraser, *Advan. Chem. Ser.*, **No. 49**, 121 (1964).

error. The earlier work was done with [Co(III)] and [Cr(II)] nearly equivalent. In this situation, the extinction coefficients of reactants and products enter the calculation of the specific rate. The present values of specific rate are consistent with an early rough value, with the value measured by Manning, *et al.*, and with the values of Vriesinga and Cobble²⁰ which cover a wider temperature range. Vriesinga's measurements extend from 0 to 120° and show that ΔH^\ddagger is constant over the whole range.

The remaining values require little comment. Agreement with reported specific rates is satisfactory when account of differences in ionic strength is taken. There are differences in the activation parameters, in some cases. On this point we feel that the present results obtained taking care for purity of materials and designed for precision are preferable to the older values.

The present results remove some of the seemingly erratic fluctuations in ΔH^\ddagger (with compensatory changes in ΔS^\ddagger) which is to be seen in the earlier reports. In particular, the relation between ΔH^\ddagger and ΔS^\ddagger noted by Fraser²¹ appears, to some extent at least, to be a reflection of error in determining ΔH^\ddagger . For the series of reactions, the values of ΔF^\ddagger are nearly alike, and thus accidental error in ΔH^\ddagger will be reflected in a compensatory error in ΔS^\ddagger , leading to an apparent linear relation between ΔH^\ddagger and ΔS^\ddagger . With the exception of ΔS^\ddagger observed in the reduction of the formato complex, the values of ΔS^\ddagger are remarkably alike for the series. This means that the particular order of rates observed at 25° will persist over a considerable temperature range, thus providing a stable basis for considering the influence of steric and other factors on the rates of reaction.

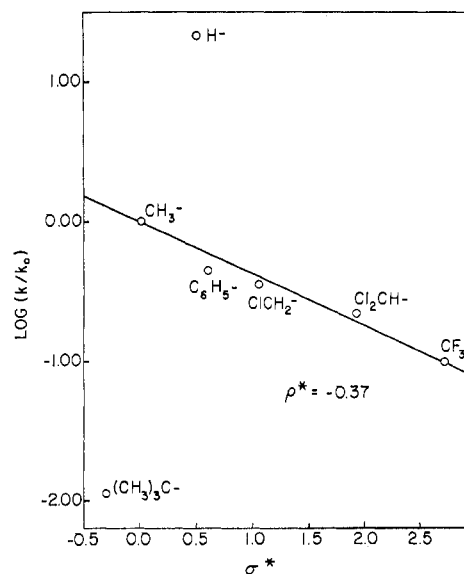


Figure 3.—The logarithm of the ratio of *k*/*k*₀ as a function of the Taft inductive parameter σ^* , where *k* refers to the reaction of $(NH_3)_5CoCOCR^{2+}$ with chromium(II) and *k*₀ refers to the reaction of the acetatopentaamminecobalt(III) complex with chromium(II).

Inductive and Steric Effects.—In Figure 3 the values of $\log(k/k_0)$ (where the acetato complex is used as the standard) for the various complexes are shown plotted against the Taft σ^* parameter.²⁴ It is seen that a line

(24) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1963.

can be drawn through the points, exclusive of those for the formate and pivalato complexes. "Experiments" were performed with space-filling molecular models, using for the configuration of carboxylato on Co(III) that determined²⁵ for the acetato complex in a solid and using a square-pyramidal arrangement for $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. Whether the carbonyl or bridging oxygen is used as the site for attack by $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, steric repulsions for the pivalato complex are by far the most severe, and those for the formate, the least. In the series with acetate and its derivatives as ligands, when at last one α hydrogen is left, an arrangement can be found in which the steric repulsions are not materially different from one case to the next. Even for the benzoato and trifluoroacetato complexes, the steric requirements appear to be little different from those of the acetato.

If the points for the formate and pivalato complexes are excluded as reflecting the influence of steric effects quite different from the others, a value of -0.37 is shown by the others for ρ^* . If the benzoato, chloroacetato, and trifluoroacetato complexes still show some effect of steric repulsions, the actual value of ρ^* will be even smaller in magnitude. In any case, the data show the rates are relatively insensitive to inductive effects.

Point of Attack by Reducing Agent.—The upper limit on the rate of outer-sphere attack on the acetato complex has already been given as $0.015 M^{-1} \text{sec}^{-1}$ and on the pivalato as $2 \times 10^{-3} M^{-1} \text{sec}^{-1}$. Except for the benzoato complex, where the possibility of electron transfer to the π system exists, it seems unlikely that a substantial fraction of the Cr(III) is formed as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ in any of the systems. To obtain actual values of the specific rates of outer-sphere attack in this and in the other cases would be a matter of some interest. It would, however, require a considerable refinement of ion-exchange techniques and a study in each case of the catalysis by Cr^{2+} of the aquation reaction. It thus would constitute a major study in its own right.

For the inner-sphere path, the question of whether Cr(II) attacks the bridging or carbonyl oxygen needs also to be answered. The experiments with space-filling molecular models indicate that as far as steric effects are concerned, when formate is the bridging group, both oxygens are about equally accessible. In the absence of steric effects a rate of attack at the bridging oxygen well in excess of $0.6 M^{-1} \text{sec}^{-1}$ would be expected in the present series.^{25a} The basis for this conclusion is that $0.6 M^{-1} \text{sec}^{-1}$ represents the rate of attack²⁶ by Cr^{2+} on OH_2 in the coordination sphere of $\text{Co}(\text{NH}_3)_5^{3+}$, and the inductive effect of two protons is substantially greater than that of, say, $\text{C}(=\text{O})\text{H}^+$ (note that the acidity of H_3O^+ is much greater than that of $\text{HOC}(=\text{O})\text{H}$). Thus the value of $7 M^{-1} \text{sec}^{-1}$ measured for the rate of attack by Cr(II) on the formate complex seems quite reasonable for attack on the bridging (or cobalt) oxygen in comparison with 0.6 for the aquo complex which involves direct attack on the cobalt oxygen.^{26b}

(25) E. B. Fleischer and R. Frost, *J. Amer. Chem. Soc.*, **87**, 3998 (1965).

(25a) NOTE ADDED IN PROOF.—D. L. Toppen and R. G. Linck (*Inorg. Chem.*, in press) have shown the "aquo" path reported^{25a} for the reaction of Cr(II) with aquopentaamminecobalt(III) is an artifact produced by NaClO_4 rather than LiClO_4 having been used to replace HClO_4 in maintaining the ionic strength, and their work thus invalidates the argument presented in this paragraph.

(26) (a) A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **81**, 1288 (1959); (b) W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).

Arguments² have been presented in support of the conclusion that resonance transfer, rather than stepwise transfer, is involved in the reduction of the acetato complex by Cr(II). Resonance transfer through a single bridging atom from Cr(II) to Co(III) has abundant precedent, but resonance transfer for this electronic structure type through a number of bonds does not. This cannot be used as evidence for attack at the bridging oxygen but does point to the conclusion that if attack is at the carbonyl oxygen, an interesting dimension is added to the subject.

Rather convincing arguments³ for attack by Cr(II) at the carbonyl oxygen of a carboxylate complex of pentaammineruthenium(III) have been advanced. The parallelism of rates between the Ru(II) and Co(II) cases has been cited³ as evidence for similar mechanisms. The argument does, however, seem to be incomplete; a parallelism would not be surprising also if Cr(II) attacked Co(III) at the bridging and Ru(III) at the carbonyl oxygen.

Studies by Huchital²⁷ provide precedent for the model involving attack at the bridging oxygen. He reported that Cr(II) catalyzes the conversion of *cis*-diaquodioxalatochromium(III) to *trans*-diaquodioxalatochromium(III) without the formation of the mono-oxalato species as an intermediate. To account for the simultaneous transfer of two oxalates, Cr(II) must be bound to both oxalates in the activated complex, and the only oxygens which allow this mode of attack are those that are directly attached to Cr(III).

Vanadium(II) as Reducing Agent.—Previous results on the reduction of the acetato and benzoato complexes gave for k ($\mu = 1.00$, 24°) the values 0.43 and 0.52 , respectively, to be compared to 1.15 and 0.63 as determined by us. The agreement in specific rates is rather satisfactory but not in the activation parameters. ΔH^\ddagger is reported in the earlier work as 5.8 and 6.7 kcal/mol, respectively, to be compared with 11.6 and 12.4 kcal/mol as reported by us.

Though the activation parameters recorded here conform reasonably well with those for electron-transfer reactions in which substitution on $\text{V}(\text{H}_2\text{O})_6^{2+}$ is rate determining, it would be premature to draw the conclusions that we are dealing with inner-sphere reactions. For the benzoato complex, in particular, the rate is much less than for a case such as the binoxalato-pentaamminecobalt(III) complex where it is shown that an inner-sphere mechanism operates. Unless some factor operates to make substitution of the benzoato as the ligand on Co(III) into $\text{V}(\text{H}_2\text{O})_6^{2+}$ much slower than that of oxalate in similar circumstances, we are forced to conclude that a preequilibrium concentration of $\text{Co}^{\text{III}}\text{OCOV}^{\text{II}}$ can be maintained, and, this being the case, there is no reason to expect ΔH^\ddagger and ΔS^\ddagger , even by an inner-sphere mechanism, to be the same as it is in cases where substitution is known to be rate determining.

Acknowledgment.—Financial support for this research by the Atomic Energy Commission, Grant No. AT-04-3-326-PAT, and by the National Science Foundation for purchase of the spectrophotometer, under Grant No. G22611, is gratefully acknowledged.

(27) D. Huchital, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M7.