molecule-fixed coordinate system with the z axis along the symmetry axis of the molecule. Components of the magnetic field $\vec{H}$ in the molecular coordinate system are[46]

$$\begin{aligned} H_x &= |H| \sin \Theta \cos \Phi \\ H_y &= |H| \sin \Theta \sin \Phi \\ H_z &= |H| \cos \Theta \end{aligned} \qquad (9)$$

Equations 9 are substituted in the general spin-Hamiltonian given in eq 1. Exact eigenvalues and eigenvectors for a given set of parameters arise from a diagonalization of the representation of the spin-Hamiltonian on the basis $\{|SM\rangle;\ S = {}^3/_2\}$, which is defined with respect to the molecule-fixed coordinate system. Eigenvalues, ordered according to increasing energy, are denoted

$$E^i(H, \Theta, \Phi); \qquad i = 1, 2, 3, 4 \qquad (10)$$

and the corresponding eigenvectors are denoted

$$|i\rangle = \sum_M c_M{}^i(H, \Theta, \Phi)|{}^3/_2M\rangle; \qquad i = 1, 2, 3, 4 \qquad (11)$$

for a given D, E, g_x, g_y, and g_z value.

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[46] This Euler angle convention is the same as that established by Kottis and Lefebvre.[36]

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The Chromium(II) Reduction of Maleatopentaamminecobalt(III)[1]

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An extensive study of the stoichiometry, kinetics, and mechanism of the Cr(II) reduction of maleatopentaamminecobalt(III) is reported. The inner-sphere reaction gives an initial 80:20 ratio of chelated to monodentate maleate complexes of Cr(III). Cr(II) catalyzes the equilibration of the two Cr(III) complexes on a time scale comparable to that of the initial Cr(II)–Co(III) reaction. A comparison of the rates of these two maleate-bridged redox processes suggests that electron transfer to the ligand is a reasonable description of the slow step. Stoichiometric studies show that no isomerization, hydration, or net reduction of the maleate bridging group attends any of the electron-transfer reactions. The methylmaleatopentaamminecobalt(III) complex is reduced by Cr(II) at nearly the same rate as is the maleato complex (150 *vs.* 200 M^{-1} sec^{-1}, 25.0°, μ = 1.00 M).

Introduction

Since the first report[2] in 1953 of a demonstrably inner-sphere electron-transfer reaction, systems featuring this kind of mechanism have received wide study. The class of inner-sphere reactions in which the bridging ligand is an organic molecule has itself developed into a major field. A recent review by Gould and Taube[3] indicates the scope of work in this area.

A system often touched on in earlir work is the Cr(II) reduction of maleatopentaamminecobalt(III) and the related ester complex methylmaleatopentaamminecobalt(III). Taube[4] first called attention to the rapid rate of reduction of the maleato complex compared to analogous reactions involving simple carboxylate bridging ligands. There followed reports on the stoichiometry of the chromium(II)–maleatopentaamminecobalt(III)[5,6] and the chromium(II)–methylmaleatopentaamminecobalt(III)[5–7] reactions by Fraser and Taube. These stoichiometric studies indicated substantial *cis–trans* isomerization of the ligand in conjunction with both electron-transfer reactions and quantitative ester hydrolysis in the latter case.

More recently Schwarz[8] has reported that he was unable to reproduce Fraser and Taube's observation[5,6] of *cis–trans* isomerization in the vanadium(II)–maleatopentaamminecobalt(III) reaction, and other reports[9,10] as well have cast doubt on various aspects of the earlier work. We have undertaken a detailed reinvestigation of the stoichiometry of the chromium(II)–maleatopentaamminecobalt(III) and chromium(II)–methylmaleatopentaamminecobalt(III) reactions. Besides dealing with issues raised previously, we report some novel effects which are not touched upon in the earlier work.

Fraser[11] has published rate data for the chromium(II)–maleatopentaamminecobalt(III) reaction, but Gould's[12] later study is in disagreement with the earlier rate law. Kinetic studies described here support Gould's results. Recent experiments by Hurst and Taube,[9] Nordmeyer and Taube,[13] and Diaz and Taube[14] as well as rate

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[1] Abstracted from the Ph.D. thesis of M. Olson, Stanford University, 1969.

[2] H. Taube, H. Myers, and R. Rich, *J. Amer. Chem. Soc.*, **75**, 4118 (1953).

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

[4] H. Taube, *J. Amer. Chem. So* , **77**, 4481 (1955).

[5] R. T. M. Fraser and H. Taube, *ibid.*, **81**, 5514 (1959).

[6] R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2242 (1961).

[7] R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

[8] W. M. Schwarz, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. I-36.

[9] J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1178 (1968).

[10] D. H. Huchital and H. Taube, *ibid.*, **87**, 5371 (1965).

[11] R. T. M. Fraser, *ibid.*, **85**, 1747 (1963).

[12] E. S. Gould, *ibid.*, **88**, 2983 (1966).

[13] F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

[14] H. Diaz and H. Taube, submitted for publication.

studies by Gould[12,15] amply support the continuing interest in inner-sphere reactions with unsaturated organic bridging groups.

Experimental Section

Reagents.—All common chemicals employed were of reagent grade. Tap distilled water was redistilled from alkaline permanganate. Water-pumped, compressed nitrogen was deoxygenated by passage through two consecutive gas-scrubbing bottles containing acidic 0.1 *M* Cr(II) solutions over amalgamated zinc.

Lithium perchlorate was prepared by the action of perchloric acid on lithium carbonate. The resulting solution was treated with Cr(II) for 24 hr, and then the lithium perchlorate was recrystallized five times to remove all chromium. A lithium perchlorate stock solution from this source was standardized by titrating the equivalents of acid displaced by a known volume from an acid-form cation-exchange resin. Lithium perchlorate was used throughout to maintain ionic strength.

Aqueous solutions of chromium(II) and chromium(III) perchlorate were prepared as described by Hurst and Taube[9] using the amalgamated zinc and hydrogen peroxide methods, respectively. Amalgamated zinc was prepared by activating mossy zinc in 1–2 *M* perchloric acid and treating it with a perchloric acid solution of Hg(II) prepared by dissolving an amount of red mercuric oxide corresponding to 2% of the weight of zinc present.

Pentaamminecobalt(III) Complexes.—Aquopentaamminecobalt(III) perchlorate was prepared by treating the nitrate salt of the carbonato complex[16] with perchloric acid. Two batches were used during the work; both had been recrystallized three times from perchloric acid solutions. *Anal.* Calcd for $[(NH_3)_5CoOH_2](ClO_4)_3$: Co, 12.8; H, 3.73; N, 15.2; Cl, 23.1. Found, I: Co, 12.8; H, 3.68; N, 15.2; Cl, 22.9. Found, II: Co, 12.6; H, 3.82; N, 15.1; Cl, 23.0.

Maleatopentaamminecobalt(III) perchlorate was prepared by the reaction of the aquo complex with maleic acid in aqueous solution. A 25-g (0.054-mol) batch of the aquo complex was dissolved in 400 ml of a solution prepared with 67 g (0.58 mol) of maleic acid and 11.5 g (0.29 mol) of sodium hydroxide. The mixture became homogeneous on heating to 70–80° at which temperature the solution was maintained for 3 hr on a steam bath. At the end of this period the hot solution was filtered into 150 ml of ice-cold 60% perchloric acid. A precipitate formed immediately, and the mixture was cooled to 10° before the solid was collected. The material was recrystallized twice by dissolving it in 250–300 ml of 40° water and filtering the solution while hot into 30 ml of 60% perchloric acid immersed in an ice–salt bath. The solid was sucked free of as much solvent as possible, rinsed with an ether–ethanol–ether sequence, and dried in a vacuum desiccator; yield 18 g (0.039 mol). Other methods of recrystallization gave material which was high in cobalt and low in titratable protons; presumably this product was contaminated with $[(NH_3)_5CoO_2CCHCHCO_2](ClO_4)$. *Anal.* Calcd for $[(NH_3)_5CoO_2CCHCHCO_2H](ClO_4)_2$: Co, 12.8; C, 10.5; H, 3.97; N, 15.3; Cl, 15.5. Found, I: Co, 12.7; C, 10.5; H, 4.21; N, 15.1; Cl, 15.1. Found, II: Co, 12.6; C, 10.6; H, 4.19; N, 15.1; Cl, 15.3. Ion-exchange analysis showed less than 4% aquo complex as impurity.

N,N-Dimethylformamidepentaamminecobalt(III) perchlorate was prepared by heating the aquo complex in slightly acidic DMF followed by precipitation with sodium perchlorate. Approximately 0.2 ml of 60% perchloric acid and 9.0 g (0.0195 mol) of aquopentaamminecobalt(III) perchlorate were added to 30 ml of DMF. The homogeneous solution was heated for 1 hr on a steam bath. Product precipitated when the solution was cooled in an ice bath and 30 ml of 8 *M* sodium perchlorate was added. The crude product was dissolved in 60 ml of water at 50° and the hot solution was filtered. When the filtrate was cooled in an ice bath, deep red crystals formed. They were collected, rinsed with absolute ethanol and anhydrous ether, and dried in a vacuum desiccator; yield 6 g (0.012 mol). The acidification of the preparative solution was found to suppress the formation of trace amounts of a yellow product, more strongly retained than the red DMF complex on a cation-exchange column. The yellow material is presumably hexaamminecobalt(III). There is considerable evidence that the red DMF complex prepared as described is coordinated through oxygen.[17] *Anal.* Calcd for $[(NH_3)_5CoOC(H)N(CH_3)_2](ClO_4)_3$: Co, 11.4; C, 6.99; H, 4.31; N, 16.3; Cl, 20.6. Found: Co, 11.4; C, 7.07; H, 4.48; N, 16.1; Cl, 20.4.

Methylmaleatopentaamminecobalt(III) perchlorate was prepared by the reaction of lithium methylmaleate with the dimethylformamidepentaamminecobalt(III) complex in DMF. Lithium methylmaleate was synthesized from lithium methoxide and maleic anhydride by a straightforward modification of Veibel and Pedersen's[18] preparation for the sodium and potassium salts. Two recrystallizations were carried out from a 1:2 mixture of methanol and 2-butanone. The solid melted with decomposition at 184–185°. The ratio of the methyl resonance to the symmetric quartet of the vinyl protons was 1.6 ± 0.1 from an nmr spectrum in D_2O. *Anal.* Calcd for $Li(O_2CCHCHCO_2CH_3)$: C, 44.1; H, 3.70. Found: C, 43.9; H, 3.62.

A homogeneous solution was prepared by dissolving 6.0 g (0.012 mol) of dimethylformamidepentaamminecobalt(III) perchlorate and 12.0 g (0.088 mol) of lithium methylmaleate in 36 ml of DMF and heating the reaction mixture to 75°. The solution was maintained at that temperature for 45 min under an atmosphere of dry nitrogen. The solution was cooled to room temperature in an ice bath and the solvent was removed on a rotary evaporator without heating. No precipitate appeared even after the solution had been reduced to a highly viscous oil. The residue was taken up in 50 ml of absolute ethanol and again evaporated to a viscous oil. After the residue had been dissolved a second time in 50 ml of ethanol, the alcohol solution was saturated with hydrated lithium perchlorate at 50°. Solid formed on cooling to $-5°$. After several hours of standing in the cold, the solid was collected. The addition of ether increased the ease with which the mixture could be filtered. This solid, heavily contaminated with lithium perchlorate, was dissolved in 25 ml of water at 45°, the solution was immediately filtered, and the filtrate was cooled in an ice-salt bath. The recrystallized solid was rinsed with ethanol and ether and dried in a vacuum desiccator; yield 1.5 g (0.0032 mol). Elution at pH 4.6 (acetate buffer) on a cation-exchange column separates the maleato and methylmaleato complexes. The above preparation contained no observable maleato complex (<2%). Use of the air-free conditions for the initial synthesis appeared to eliminate the formation of a red impurity with +2 charge. The spectrum of the impurity was identical with that for material isolated by Gould[12] from similar reaction mixtures. The use of lithium ion rather than sodium ion in the preparation was dictated by the observation that sodium perchlorate extensively coprecipitates with the methylmaleato complex. *Anal.* Calcd for $[(NH_3)_5CoO_2CHCHCO_2CH_3](ClO_4)_2$: Co, 12.5; C, 12.7; H, 4.27; N, 14.8; Cl, 15.0. Found: Co, 12.3; C, 12.3; H, 4.36; N, 14.6; Cl, 14.7.

Chromium(III) Complexes.—The chelated maleate complex, maleatotetraaquochromium(III) was prepared by ion-exchange separation of the products of the chromium(II)–maleatopentaamminecobalt(III) reaction. A 31-ml reaction mixture with initial concentrations (Co(III)) = 0.046 *M*, (Cr^{2+}) = 0.048 *M*, and (H^+) = 0.19 *M* was prepared. After allowing the reaction to sit under nitrogen for a few minutes at room temperature, air was bubbled through the solution. It was diluted to 150 ml with ice-cold water and charged onto a 24-mm diameter column containing 50 ml of AG50W-X2, 200–400 mesh, lithium-form cation-exchange resin. The column had been precooled to 5° and the entire separation was carried out in a cold room at 5°.

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[15] E. S. Gould, *J. Amer. Chem. Soc.*, **87**, 4730 (1965).

[16] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

[17] E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968).

[18] S. Veibel and C. Pedersen, *Acta Chem. Scand.*, **9**, 1674 (1955).

After a charging time of 50 min, elution followed with 0.50 *M* lithium perchlorate and 0.01 *M* perchloric acid. After passing 75 ml of eluent, the desired +1 band was collected in 35 ml. A typical solution was 2.6×10^{-2} *M* in the maleatotetraaquochromium(III) complex and completely free of Co(II) and Zn(II). The eluted solutions were stable on prolonged storage at 2° (90% of initial complex concentration maintained for over 100 days).

The monodentate maleatopentaaquochromium(III) complex could be prepared by a variant of the above procedure. An 85-ml reaction mixture with initial concentrations (Co(III)) = 0.026 *M*, (Cr^{2+}) = 0.029 *M*, and (H^+) = 0.77 *M* was used. In this case the solution required dilution to 750 ml to reduce the high ionic strength before charging onto the column. After passing 220 ml of eluent, including a minor +1 band, the +2 band was collected in about 90 ml. The resulting solution was 1.4×10^{-2} *M* in the desired +2 complex and contained some Zn(II) and Co(II).

The cation-exchange resin was purchased from Bio-Rad as the hydrogen form and treated as described by Deutsch.[19] After cleaning, the resin was filtered free of surplus water and stored in the dark. Immediately before use, a column was rinsed with water until the absorbance of the effluent at 220 nm in a 1-cm cell was less than 0.005. The same resin and method of preparation were used in all cation-exchange separations.

Analyses.—Analyses for C, H, N, and Cl were carried out by the Stanford University Department of Chemistry Microanalytical Laboratory.

Two spectrophotometric methods were used for chromium. One involved the oxidation of all chromium to chromate with basic peroxide. It is described by Deutsch.[19] Sporadic difficulties were encountered with this method in solutions containing coordinated maleate. Low results and turbid chromate solutions suggested that the organic acids interfered by causing the reduction of Cr(VI) to Cr(III). The method could be made reasonably successful by using enormous excesses of peroxide, but it was considered reliable only when some independent check was possible to identify analyses which were low in chromium.

Excellent results were obtained using the acidic permanganate oxidation of all chromium followed by colorimetric determination of Cr(VI) with 1,5-diphenylcarbohydrazide. The procedure is described by Saltzman.[20] The slight modification in the preparation of indicator solutions recommended by Urone[21] was employed. An extinction coefficient at 540 nm of 4.0×10^4 M^{-1} cm^{-1} per chromium was measured for the method using primary standard potassium dichromate as the source of standard solutions.

Cobalt was analyzed by Nordmeyer's[22] modification of Kitson's[23] colorimetric determination of Co(II) as the tetrathiocyanato complex. In solutions containing V(III) the Co(II) was separated from V(III) by cation exchange before analysis to avoid interference by V(III).

Free methanol in the reaction mixtures was collected by vacuum distillation and determined by Cr(VI) oxidation to carbon dioxide. Typically a 3-ml aliquot containing less than 1 mg of methanol was taken for analysis. The perchloric acid concentration was reduced to less than 0.1 *M* with base to minimize hydrolysis of any esters present. The aliquot was frozen in Dry Ice–acetone on one side of a Y-shaped tube, the tube was evacuated, and the solvent was transferred to the other side of the tube. Transfer was accomplished by cooling the collector with liquid nitrogen and maintaining the evaporating solution at near 20° with a water bath. It proved necessary to transfer essentially all the solvent to avoid loss of methanol.

For the oxidimetric analysis the methanol sample (<2 mg in <5 ml) was combined with 5.00 ml of standard 0.0191 *M* (0.115 *N*) potassium dichromate solution and 5 ml of a 1:2:2 (by volume) solution of concentrated phosphoric acid–concentrated sulfuric acid–water. The solutions were boiled for 1 hr in a 50-ml volumetric flask. The neck of the flask, acting as an air condensor, was adequate to prevent loss of methanol provided that the initial heating was not too rapid.

Excess dichromate was back-titrated with a 0.14 *M* Fe(II) solution using *p*-diphenylaminesulfonic acid as indicator. Known samples gave results that were accurate and reproducible within 5% even on samples containing only 0.6 mg of methanol.

Analytical Ion-Exchange Separations.—The methods of separating the organic acids and determining their amounts are described elsewhere,[24] and only the separation of the Cr(III) complexes requires comment here.

Mixtures of the monodentate and chelated 1:1 maleate complexes of Cr(III) were also analyzed by ion-exchange separation since the visible absorption spectra of the two complexes are very similar. Aliquots containing not more than 2 mmol of perchlorate ion in a 1–20-ml volume were charged onto a 10-mm diameter column containing 0.6 ml of lithium-form resin. The eluting solution contained lithium perchlorate (0.50 *M*) and perchloric acid (0.01 *M*). The first 4.0 ml was combined with the charging effluent to make up the +1, chelated fraction. Then +2, monodentate complex was removed in the following 15 ml. If desired, hexaaquochromium(III) could be removed with an additional 15 ml of 1.9 *M* perchloric acid leaving dimeric Cr(III)[25] on the column. The various fractions were subjected to total chromium analysis as described above.

Methods of Mixing Reactants.—In experiments on the stoichiometries of the various reactions and in those on the equilibrium constant between the monodentate and chelated maleate complexes of Cr(III), an all-glass mixing apparatus with a nitrogen atmosphere was employed. The Cr(II) was prepared in a storage vessel from which it could be drained into a 10-ml buret and measured into the reaction vessel.

The kinetics of the Cr(II)-catalyzed interconversion of the monodentate and chelated maleate complexes of Cr(III) were followed in a special apparatus which facilitated the periodic removal of an aliquot for quenching with air. Once the Cr(II) had been oxidized, the ratio of monodentate to chelated material could be determined by the ion-exchange method. Syringe methods failed because with them it was impossible to exclude oxygen with sufficient rigor to maintain Cr(II) concentrations at the 10^{-4} *M* level.

The apparatus designed to study the interconversion reaction involved two independent storage vessel–buret assemblies such as that described above. They both led into a reaction vessel made from a 250-ml round-bottom flask. The flask was equipped with a four-way stopcock of the design described by Zwickel.[26] At intervals during the reaction the stopcock was turned and *ca.* 5-ml aliquots of the reaction mixture were pumped out of the vessel under a positive nitrogen pressure. The aliquots were pumped directly onto a 15-ml medium-porosity sintered-glass funnel which had water-saturated air purging through it. Once the aliquot had been delivered, the stopcock was reversed and the outlet through which the solution had been pumped reverted to serving as the nitrogen outlet.

The Cr(II) was added from one of the burets at the start of the experiment. After the last aliquot had been taken, an excess of Fe(III) was added from the other buret to oxidize all remaining Cr(II). The residual solution in the reaction vessel was analyzed for Fe(II) by the *o*-phenanthroline method to ensure that the Cr(II) concentration had not changed during the experiment. Kinetic runs which were accompanied by a loss of more than 10% of the reducing power were rejected.

Rates of reaction of Cr(II) with the maleato- and methylmaleatopentaamminecobalt(III) complexes were measured on a stopped-flow apparatus. Its operation has been described elsewhere.[27] All rate constants, from both the stopped-flow and

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

(20) B. K. Saltzman, *Anal. Chem.*, **24**, 1016 (1952).

(21) P. F. Urone, *ibid.*, **27**, 1354 (1955).

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

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

(24) M. V. Olson and H. Taube, *J. Amer. Chem. Soc.*, **92**, 3236 (1970).

(25) Formed in quenching the reaction mixture with O_2.

(26) A. M. Zwickel, Ph.D. Thesis, The University of Chicago, 1959.

(27) J. A. Stritar, Ph.D. Thesis, Stanford University, 1967.

the ion-exchange experiments are the result of a standard least-squares fit of the appropriate kinetic plot.

Results

Stoichiometry.—Due to the reactivity of free maleic acid toward Cr(II),[12,28,29] the possibility exists of net reduction of the maleate ligand as a side reaction in the Cr(II)–Co(III) redox process. Gould,[12] however, has reported a 1.00:1.00 molar ratio of Co(II) produced to Cr(II) consumed (1.2 M H^+, 2 × 10^{-2} M Co(III), 1.4 × 10^{-2} M Cr(II)). The observations to be cited substantiate that finding and extend it to lower acidities.

In two experiments each at 25°, $\mu = 1.00$ M, with $(\text{Co(III)})_0 = 2.00 \times 10^{-2}$ M and $(\text{Cr(II)})_0 = 1.80 \times 10^{-2}$ M, with $(H^+) = 0.20$ M for the first and 0.86 M for the second, the ratios $(\text{Co(II)})_\infty/(\text{Cr(II)})_0$ were found to be 1.03 and 0.98, respectively.

A second aspect of the stoichiometry is the question of induced changes in the ligand which preserve its oxidation state.[5,6] In particular, the possibility that the formation of fumaric or malic acids might attend the redox reaction was investigated.

A reaction mixture was prepared under the same conditions as those for the second of the experiments referred to above. Immediately after the reaction the Cr(III) products were analyzed by ion exchange, and it was established that 53% of the products had a +1 charge and 47% had a +2 charge. The +1 and +2 fractions, between them, accounted for 0.186 mmol of Cr(III). Comparison with the 0.180 mmol of Cr(II) added shows that the reaction was quantitatively inner sphere giving complete ligand transfer from cobalt to chromium. The characterization of the +1 and +2 complexes will be discussed in more detail later. The relevant experiment here is the one in which the state of the organic ligand in these complexes was determined.

An aliquot of the reaction mixture was made 4.2 M in perchloric acid; after thermostating the aliquot for 11 hr at 60°, the Cr(III) present was again analyzed by ion exchange. Chromium found agreed with that calculated within 5%, and it was distributed as follows: 1% of charge +1 or +2, 99% of charge +3. Aquation, therefore, was essentially complete. The liberated organic products were analyzed by the anion-exchange method. The results are presented in Table I.

Clearly the organic product of the redox reaction is almost pure maleic acid. An upper limit to the amount of fumaric acid produced during the reaction is even lower than 0.6% since a small amount of fumaratopentaamminecobalt(III) was present in the batch II preparation of the maleato complex used in the experiment. The presence of a small impurity of the fumarato complex was expected since the Matheson maleic acid used in the preparation analyzed for 1.4% fumaric acid. Evidence presented elsewhere[24] on the efficient hydration of maleate bound to Cr(III) suggests that the small amount of malate observed is also not associated with the redox reaction. Since the conversion of maleic acid to either fumaric or malic acid is thermodynamically favorable,[30-32] the results are decisive in eliminating >2% induced changes in the bridging group.

TABLE I

ORGANIC PRODUCTS ON AQUATION OF A CHROMIUM(II)–MALEATOPENTAAMMINECOBALT(III) REACTION MIXTURE[a]

Carboxylic acid	Amt found × 10^5, mol	% of total acid found
Maleic	3.34	98.0
Fumaric	0.022	0.6
Malic	0.045	1.3
Total	3.41	
Calcd ligand present[b]	3.56	

[a] Electron transfer in 0.86 M $HClO_4$; aquation in 4.2 M $HClO_4$. [b] The calculation assumes that the 10% of the ligand coordinated to the remaining Co(III) was quantitatively released during the aquation procedure.

As indicated above, the electron-transfer reaction is quantitatively inner sphere, giving a mixture of Cr(III) complexes with charges +1 and +2. The complexes are assumed to be, respectively, the chelated maleatotetraaquochromium(III) ion and the monodentate maleatopentaaquochromium(III) complex. The principal features of the visible spectra of the two complexes are given in Table II.

TABLE II

SPECTRAL FEATURES OF THE MONODENTATE AND CHELATED CHROMIUM(III) MALEATE COMPLEXES[a]

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
Chelated	415	23.2	582	25.2
Monodentate	412	23.1	574	24.4

[a] Spectra taken at room temperature, 0.50 M lithium perchlorate, and 0.01 M perchloric acid.

Experiments on the relative proportions of the two products showed that under normal reaction conditions, with Co(III) in 10% excess, the ratio of +1 to +2 product decreases with increasing acidity. In reactions with a very large excess of Co(III) over Cr(II), however, the ratio was essentially invariant with acid concentration. These effects are illustrated in Table III. The fact that the reaction goes cleanly by an inner-sphere mechanism is also further documented by the data.

TABLE III

CHROMIUM(III) PRODUCT DISTRIBUTIONS IN THE CHROMIUM(II)–MALEATOPENTAAMMINECOBALT(III) REACTION[a]

Run	$(H^+)_t$, M	10^2-$(\text{Cr(II)})_0$, M	$10^2(+2)$, M	$10^2(+1)$, M	$10^2[(+1) + (+2)]$, M	% ion of charge +2	% ion of charge +1
a	0.20	1.80	0.51	1.32	1.83	28 ± 1	72 ± 2
b	0.86	1.80	1.02	0.88	1.90	54 ± 1	46 ± 1
c	0.86	1.80	0.86	0.99	1.85	46 ± 1	54 ± 1
d	0.10	0.100	0.0875	0.0167	0.104	84 ± 1	16 ± 1
e	0.50	0.100	0.0882	0.0215	0.110	80.5 ± 1	19.5 ± 1

[a] $\mu = 1.00$ M; 25.0°; $(\text{Co(III)})_0 = 2 \times 10^{-2}$ M. [b] The uncertainties are based on the degree of agreement between duplicate analyses.

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(28) C. E. Castro, R. D. Stephens, and S. Mojé, *J. Amer. Chem. Soc.*, **88**, 4964 (1966).

(29) A. Malliaris and D. Katakis, *ibid.*, **87**, 3077 (1965).

(30) G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," Chemical Catalog Co., 1932, Chapter 8.

(31) L. T. Rozelle, *Dissertation Abstr.*, **21**, 475 (1960).

(32) L. T. Rozelle and R. A. Alberty, *J. Phys. Chem.*, **61**, 1637 (1957).

A mechanism that is consistent with the results in Table III is one in which the initial reaction between Cr(II) and Co(III) gives the 80:20 ratio of chelated to monodentate products observed when Co(III) is initially present in 20-fold excess over Cr(II) (runs d and e). The acid-dependent behavior obtained under second-order conditions is interpreted as a consequence of a subsequent Cr(II)-catalyzed interconversion of the initial Cr(III) products. The irreproducibility between runs b and c is explicable in terms of the fact that the mixing times in the experiments were not fast compared to the competing kinetic processes.

Kinetics.—The stopped-flow rate measurements on the chromium(II)–maleatopentaamminecobalt(III) reaction are summarized in Table IV. The degree of agreement between duplicate runs, as well as the reproducibility of rate constants calculated from different traces of the same run, indicate a precision of about ±5% for the values of *k*.

TABLE IV

KINETICS OF THE REACTION BETWEEN CHROMIUM(II) AND MALEATOPENTAAMMINECOBALT(III)[a]

Run[b]	Temp, °C	10^3-(Co(III))$_0$, *M*	10^2-(Cr(II))$_0$, *M*	$(H^+)_0$, *M*	*k*,[c] M^{-1} sec^{-1}
1	25.0	1.5	2.0	0.08	210
2	25.0	1.5	2.0	0.08	195
3	25.0	1.5	2.0	0.30	192
4	25.0	1.5	10.0	0.30	210
5	25.0	1.5	2.0	0.50	190
6	25.0	0.60	1.0	0.50	223
7	25.0	1.5	2.0	0.70	196
8	25.0	1.5	2.0	0.91	198
9	25.0	1.5	2.0	0.010	195
10	25.0	0.70	2.0	0.0040	216
11	13.0	1.5	2.0	0.50	169
12	15.0	0.60	1.0	0.50	184
13	17.0	1.5	2.0	0.50	184
14	20.0	0.60	1.0	0.50	206
15	21.0	1.5	2.0	0.50	186
16	29.0	1.5	2.0	0.50	240
17	30.0	0.60	1.0	0.50	252

[a] μ = 1.00 *M*. [b] All experiments except those noted just following were conducted using samples of the maleato complex from batch I. Experiments 6, 12, 14, and 17 employed batch II complex and independent sources of all reagents. [c] Calculated for $d(Co(III))/dt = -k(Co(III))(Cr(II))$. Disappearance of Co(III) followed at 503 nm.

Within the limits imposed by an inherent imprecision of 5%, the data establish the rate law as follows for 25°, (H^+) = 0.01–0.91 *M*: $d(Co(III))/dt = -(200 \pm 10\ M^{-1}\ sec^{-1})(Co(III))(Cr(II))$.

Good linearity of individual pseudo-first-order plots to 90% completion confirms the first-order dependence on Co(III). Acceptable agreement between the pairs of runs 3 and 4 as well as 5 and 6 supports a first-order dependence on Cr(II). The results represent an extension of Gould's earlier measurements[12] and are entirely consistent with them. Gould arrived at the same rate law and also reported an average rate constant of $2.0 \times 10^2\ M^{-1}\ sec^{-1}$ (μ = 1.2 *M*, corrected to 25°).

Run 10 is of special interest because it represents the lowest acidity studied. There is a large uncertainty in the calculated value of $(H^+)_\infty$ since the (+1)/(+2) product ratio is not known for experiments at very low acid. On the assumption that the reaction gave exclusively +1 product, the calculated value of $(H^+)_\infty$ is 1.2×10^{-3} *M*. If only +2 product was formed, the calculated $(H^+)_\infty$ drops to 5×10^{-4} *M*. Since the dissociation constant for the maleatopentaamminecobalt(III) ion at 25° and μ = 1.00 *M* is 1.82×10^{-3} *M*,[33] a substantial and changing fraction of deprotonated complex was present during the reaction. The complete lack of curvature in kinetic plots from run 10 suggests that the deprotonated complex reacts at a rate comparable to that of the protonated species.

The kinetic data from Table IV at (H^+) = 0.50 *M* are presented as an Eyring plot in Figure 1. They lead to the following values of the activation parameters: $\Delta H^\ddagger$ = 2.9 ± 1 kcal/mol, $\Delta S^\ddagger$ = −38 ± 3 eu.

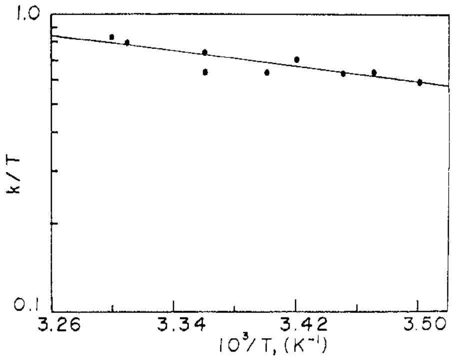

Figure 1.—Eyring plot for the chromium(II)-maleatopentaamminecobalt(III) reaction.

Chromium(II)-Catalyzed Redistribution of the Chromium(III) Products.—The chromium(II)-catalyzed interconversion of the two Cr(III) maleate complexes was postulated to explain the acid dependence of the Cr(III) product distribution when the Cr(II)–Co(III) reaction was carried out under second-order conditions. Direct observation of the catalyzed interconversion proved possible. Addition of Cr(II) to the chelated maleate complex rapidly produces equilibrium mixtures of the monodentate and chelated ions. Two experiments were carried out at 25.0 and 40.0°, μ = 1.00 *M*. At least 5 min (25° experiments) and as much as 20 min (40° experiments) was allowed for the equilibration to occur at a Cr(II) concentration of 2×10^{-3} *M*. Later experiments on the kinetics show that even the 5 min at 25° is adequate to ensure that equilibrium is established.

TABLE V

EQUILIBRIUM DISTRIBUTION BETWEEN MONODENTATE AND CHELATED MALEATE COMPLEXES OF Cr(III)

(H^+), *M*	K_1^{25}, M^{-1}	K_1^{40}, M^{-1}
0.1	15.2	12.5
0.2	18.8	12.2
0.4	14.7	12.5
0.7	13.9	13.9
Av	15.6 ± 2.2	12.8 ± 0.8

Table V shows the results. K_1 is the formal equilib-

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(33) D. B. Mandelin, unpublished results.

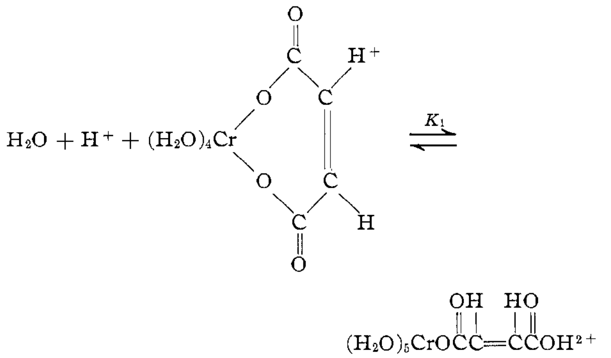
TABLE VI

KINETICS OF THE Cr(II)-CATALYZED EQUILIBRATION OF THE MONODENTATE AND CHELATED Cr(III) MALEATE COMPLEXES[a]

Run	Temp, °C	(H^+), M	$10^4(Cr^{2+})_\infty$, M Calcd	$10^4(Cr^{2+})_\infty$, M Found	$10^3(Cr(III)_{tot}$, M Calcd	$10^3(Cr(III)_{tot}$, M Found[b]	n[c]	k_{obsd}, M^{-1} sec^{-1}	k_f, M^{-1} sec^{-1}	k_r, M^{-1} sec^{-1}
1	25.0	0.10	1.99	2.04	2.87	2.69	4	17.7	10.8	6.9
2	25.0	0.15	2.04	2.09	2.88	2.76	5	15.9	11.1	4.8
3	25.0	0.20	2.02	1.82	2.86	2.87	7	19.5	14.8	4.7
4	25.0	0.35	1.99	2.10	2.36	2.42	4	28.2	23.8	4.4
5	25.0	0.50	1.94	1.88	2.36	2.34	5	38.2	33.9	4.3
6	25.0	0.50	1.02	0.96	2.88	2.79	5	45.7	40.5	5.2
7	25.0	0.70	2.00	1.79	2.36	2.38	5	51.4	47.1	4.3
8	40.0	0.70	2.00	1.93	2.53	2.48	4	77.4	69.6	7.8
9[d]	5.0	0.70	2.00	2.06	2.36	2.37	5	20.2	18.9	1.28
10[d]	5.0	0.96	2.02	2.04	2.53	2.47	5	25.2	24.0	1.19

[a] $\mu = 1.00\ M$. [b] The analyzed value of $(Cr(III))_{tot}$ represents the average of the $n - 1$ values for $(CrM^+)_t + (CrMH^{2+})_t$. It was used to obtain the zero-time point. The value of $(Cr(III))_{tot}$ calculated from the preparation of the reaction mixture is reported for comparison. [c] n is the number of data points, including the zero-time point, used in the kinetic plot for k_{obsd}. [d] K_1 for the 5° runs was taken as 21 by extrapolation from the measurements at 25 and 40°. k_{obsd} is not sensitive to this estimate at high acid, but the partitioning of k_{obsd} between k_f and k_r is sensitive to the chosen value.

rium constant, expressed in terms of concentrations at unit ionic strength, for the reaction



$$H_2O + H^+ + (H_2O)_4Cr(\text{maleate}) \overset{K_1}{\rightleftharpoons} (H_2O)_5CrOC(=O)CH{=}CHC(=O)OH^{2+} \quad (1)$$

$$K_1 = \frac{(CrMH^{2+})}{(CrM^+)(H^+)}$$

The kinetic system involved in the Cr(II)-catalyzed interconversion of the two chromium(III) maleate complexes can be represented by the net ionic equation and rate law

$$Cr^{2+} + CrM^+ + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CrMH^{2+} + Cr^{2+}$$

$$d(CrM^+)/dt = -k_f(Cr^{2+})(CrM^+) + k_r(Cr^{2+})(CrMH^{2+})$$

Since the Cr(II) concentration is invariant with time, integration of the rate law gives the familiar form for a reversible first-order system

$$(CrM^+)_t - (CrM^+)_{eq} = [(CrM^+)_0 - (CrM^+)_{eq}] \times \exp[-(Cr^{2+})k_{obsd}t]$$

$$k_{obsd} = k_f + k_r$$

The values of k_f, k_r, and $(CrM^+)_{eq}$ can be calculated from k_{obsd}, K_1 ($K_1 = (CrMH^{2+})_{eq}/(CrM^+)_{eq}(H^+)$), and the known total concentration of Cr(III) ($(Cr(III))_{tot} = (CrM^+)_t + (CrMH^{2+})_t$).

$$k_f = \frac{k_{obsd}}{1 + 1/(K_1(H^+))}; \quad k_r = \frac{k_{obsd}}{1 + K_1(H^+)}$$

$$(CrMH^{2+})_{eq} = \frac{(Cr(III))_{tot}}{1 + 1/(K_1(H^+))}; \quad (CrM^+)_{eq} = \frac{(Cr(III))_{tot}}{1 + K_1(H^+)}$$

Table VI gives the results of the kinetic experiments. The k_f values from the 25.0°, $2 \times 10^{-4}\ M$ Cr(II) runs are plotted *vs.* (H^+) in Figure 2. The least-squares fit of the data indicates that k_f and k_r have the following dependence on (H^+)

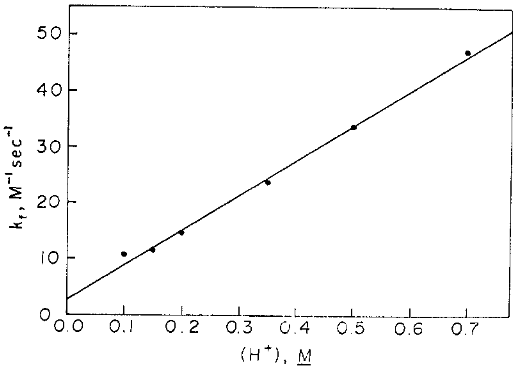


Figure 2.—Acid dependence of k_f for the Cr(II)-catalyzed interconversion of the monodentate and chelated maleate complexes of Cr(III).

$$k_f = [63(H^+) + 2.7]\ M^{-1}\ sec^{-1}$$

$$k_r = [4.0 + 0.17(H^+)^{-1}]\ M^{-1}\ sec^{-1}$$

Consideration of the agreement between the values of k_f at different acidities calculated from the least-squares equation and the experimental values indicates an uncertainty in the coefficient of the first-order acid path for k_f, and of the individual k_f measurements, of *ca.* ±10%. The zeroth-order acid path for k_f cannot be defended as necessarily real on statistical grounds. The k_r equation, of course, is related to that for k_f by the equilibrium constant K_1 ($k_f/k_r = K_1(H^+)$).

The 10% error limits on the k_f values from runs 5 and 6 overlap. The agreement is consistent with the postulated first-order dependence on Cr(II). Runs 7, 8, and 9 allow an approximate calculation of the activation parameters for the first-order acid path of k_f. Figure 3 shows the Eyring plot for the three points: $\Delta H^{\ddagger} = 6 \pm 2$ kcal/mol; $\Delta S^{\ddagger} = -31 \pm 7$ eu. Since the experiments were carried out at 0.70 M H^+, over 95% of the forward reaction was being carried by the first-order acid path at 25°. In the Discussion the value of $\Delta H^{\ddagger}$ for the acid-independent path of k_r will be useful. It is calculated to be 9 ± 2 kcal/mol.

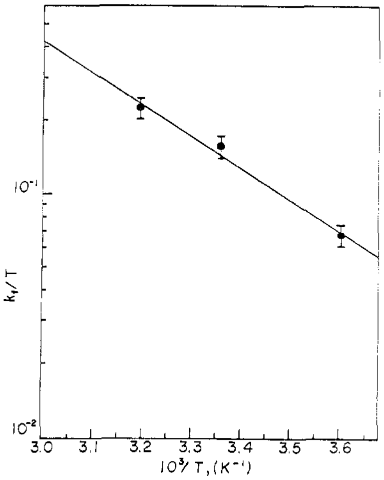


Figure 3.—Eyring plot of k_f for the Cr(II)-catalyzed interconversion of the monodentate and chelated maleate complexes of Cr(III).

The Chromium(II)–Methylmaleatopentaamminecobalt(III) Reaction.—Two reaction mixtures were prepared containing Cr(II) and methylmaleatopentaamminecobalt(III). Various aspects of the stoichiometry were measured in both cases. Table VII summarizes the results.

Table VII

Aspects of the Stoichiometry of the Chromium(II)–Methylmaleatopentaamminecobalt(III) Reaction[a]

$(H^+)_0$, M	$10^2(Co(II))_\infty$, M	$10^2(+1\ Cr(III))_\infty$, M	$10^2(+2\ Cr(III))_\infty$, M	10^2(free $CH_3OH)_\infty$, M
0.20	1.82	0.05	1.75	0.057
0.86	1.72	0.05	1.71	0.11

[a] $\mu = 1.00$ M, 25.0°; $(Co(III))_0 = 2 \times 10^{-2}$ M; $(Cr(II))_0 = 1.80 \times 10^{-2}$ M.

The following aspects of the stoichiometry are established quantitatively (95%) by the data in Table VII: (1) the reaction is inner sphere; (2) the Cr(III) product has a +2 charge; (3) 1 mol of Co(II) is produced per mole of Cr(II) consumed; (4) methanol is not liberated during the reaction.

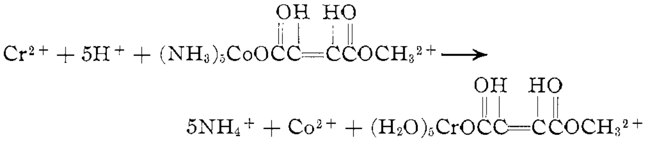
The Cr(III) products were isolated from the second reaction mixture by an ion-exchange separation carried out at 5°. Ninety per cent of the perchloric acid in a 6-ml aliquot of reaction mixture was neutralized with potassium bicarbonate. The solution was filtered free of potassium perchlorate and charged onto a 12-mm cation column containing 2 ml of resin. Elution with 10 ml of 0.51 M lithium perchlorate–0.01 M perchloric acid brought the +2 band to the bottom of the column. The band was collected (>80%) in the following 10-ml fraction. The solution was 7.9×10^{-3} M in chromium and 3.6×10^{-3} M in Co(II).

The visible absorption spectrum of the methylmaleatopentaaquochromium(III) complex was almost identical with that for the monodentate maleatopentaaquochromium(III) species. Correcting the spectrum of the above solution for the Co(II) present using Nordmeyer's[22] spectrum for cobaltous ion, the maxima were located at 412 and 573 nm with extinction coefficients of 23.8 and 25.0 M^{-1} cm^{-1}, respectively.

An experiment was carried out treating the isolated +2 Cr(III) complex with Cr(II) at low acid and analyzing for any +1 Cr(III) complex formed. The conditions were as follows: $(Cr(III)) = 4.7 \times 10^{-3}$ M, $(Cr^{2+}) = 1.00 \times 10^{-3}$ M, $(H^+) = 0.05$ M, $\mu = 1.00$ M, 25.0°. After 5 min the Cr(II) was quenched with air. Analysis showed 4.2×10^{-3} M +2 ion, $0.1_4 \times 10^{-3}$ M +1 ion. Under these conditions 56% of the monodentate maleatopentaaquochromium(III) complex would have been converted to +1, chelated complex. The experiment adds support to the conclusion, already indicated by the data in Table VII, that the Cr(III) product is methylmaleatopentaaquochromium(III).

An aliquot of the second reaction mixture in Table VII was made 4.2 M in perchloric acid and aquated for 6 hr at 60°. Aquation was 97.4% complete. The calculated quantity of released ligand was 3.50×10^{-5} mol, assuming that the remaining Co(III) aquated completely. Of the 3.26×10^{-5} mol found, the analysis was as follows: 95.7% maleic acid, 2.1% methylmaleic acid, <0.6% malic acid, and 2.1% fumaric acid.

The overall stoichiometric results on the chromium(II)–methylmaleatopentaamminecobalt(III) reaction can be summarized by the net ionic equation



$$\mathrm{Cr^{2+} + 5H^+ + (NH_3)_5CoO\overset{\overset{O}{\|}}{C}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}\overset{\overset{O}{\|}}{C}OCH_3{}^{2+}} \longrightarrow$$
$$\mathrm{5NH_4{}^+ + Co^{2+} + (H_2O)_5CrO\overset{\overset{O}{\|}}{C}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}\overset{\overset{O}{\|}}{C}OCH_3{}^{2+}}$$

Two stopped-flow kinetic experiments were carried out. The following conditions were common to both experiments: $(Co(III))_0 = 6.0 \times 10^{-4}$ M, $(Cr(II))_0 = 1.00 \times 10^{-2}$ M, $\mu = 1.00$ M, 25.0°. At 0.100 M acid, $k = 1.6 \pm 0.2 \times 10^2$ M^{-1} sec^{-1}. The 0.965 M acid experiment yielded a value for k of $1.38 \pm 0.02 \times 10^2$ M^{-1} sec^{-1}. The oxidant solution was about 2 hr old when used in the 0.1 M acid case and 1.25 hr old in the 0.96 M acid experiment. Although traces were recorded over nearly a 1-hr interval on both occasions, there was no trend with time in the values. The lack of a steady increase in rate suggests that ester hydrolysis of the cobalt complex to give maleatopentaamminecobalt(III) was not occurring to a significant extent.

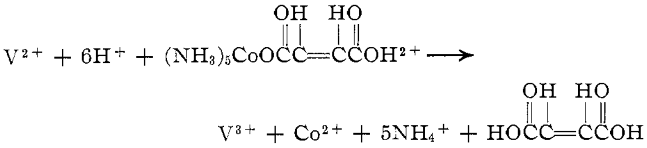
The two results establish that there is not a substantial acid dependence. For $\mu = 1.00$ M, 25.0°, the rate law can be summarized as: $-d(Co(III))/dt = [(1.5 \pm 0.1) \times 10^2\ M^{-1}\ sec^{-1}](Co(III))(Cr(II))$.

The Vanadium(II)–Maleatopentaamminecobalt(III) Reaction.—One experiment was carried out to establish basic aspects of the stoichiometry of the V(II) reduction of maleatopentaamminecobalt(III).[5,6,8] The conditions of the reaction were as follows: $(V(II))_0 = 1.80 \times 10^{-2}$ M, $(Co(III))_0 = 2.00 \times 10^{-2}$ M, $(H^+)_0 = 0.83$ M, $\mu = 1.00$ M, 25.0°. The reaction mixture was allowed to sit for 15 min after mixing before it was opened to the air.

Analysis for Co(II) produced showed a 1.72×10^{-2} M concentration present at the end of the reaction. An aliquot of the reaction mixture calculated to contain

3.60×10^{-5} mol of free ligand was prepared for anion-exchange analysis in the usual way. Because of the substitution lability of V(III), no treatment was necessary to liberate any of the organic product which may have been transferred to V(III) during the redox reaction. On analysis, 3.42×10^{-5} mol was accounted for, distributed as follows: 99.4% maleic acid, 0.5% fumaric acid, 0.3% malic acid.

The results reported here establish that the stoichiometry is straightforward

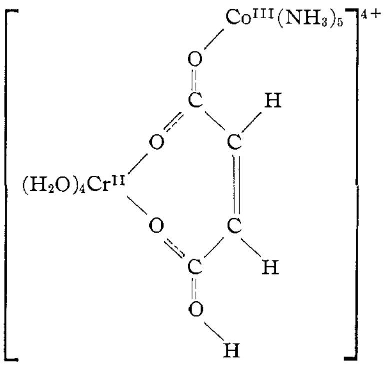


$$\mathrm{V^{2+} + 6H^+ + (NH_3)_5CoO\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}\overset{O}{\overset{\|}{C}}OH^{2+} \longrightarrow V^{3+} + Co^{2+} + 5NH_4^+ + HO\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}\overset{O}{\overset{\|}{C}}OH}$$

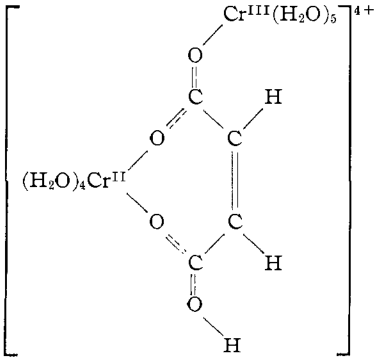
Discussion

The major sources of disagreement between the present results and literature reports are cited in the Introduction. Other authors[3,9,10] have commented on the impossibility of reconciling similar discrepancies which have occurred in related systems. No effort at such a reconciliation, therefore, will be incorporated into the discussion of the observations reported here.

Reactions with Maleate Bridges.—The observations on the 80% of the chromium(II)–maleatopentaamminecobalt(III) reaction which gives chelated maleatotetraaquochromium(III) are consistent with the formulation for the activated complex shown in A. The correct placement of the labile proton on the ligand is not indicated by the kinetic data. However, since the dominant form of maleatopentaamminecobalt(III) under the reaction conditions contains the singly protonated ligand, the independence of acidity exhibited by the rate constant requires that the composition of the activated complex be the same as that shown in A. Structure A is appealing because no carboxylate oxygen bears more than one acidic group (proton or metal ion). Presumably the lack of a first-order acid term, such as the one observed when fumarate is the bridging ligand,[9,34] is associated with the fact that Cr(II) chelates maleate in the activated complex. An acidic group can be present on each oxygen, therefore, without the presence of an extra proton.



A



B

On similar grounds, a reasonable formulation for the activated complex for the Cr(II)-catalyzed conversion of the Cr(III) monodentate complex to the chelate is the structure shown in B. This activated complex corresponds to that for the dominant, and perhaps exclusive, observable path for the Cr(II)-catalyzed ring-closing reaction. It is noteworthy that the activated complexes in A and B are identical except for the nature of the oxidizing centers. In A, a pentaamminecobalt(III) moiety is the oxidizing center whereas in B pentaaquochromium(III) serves that function.

Since the proposed activated complexes differ only in the identity of the oxidizing center, the ratio of the rates for the two reactions is a measure of the degree to which the oxidizing center participates energetically in activation. Since the chelate path for the Cr(II)–Co(III) reaction represents 80% of the total rate, the rate for that path is 160 M^{-1} sec^{-1}. The acid-independent term for the corresponding Cr(II)–Cr(III) reaction has a rate of 4.0 M^{-1} sec^{-1}. The Co(III)/Cr(III) ratio, therefore, is 40.

Possible comparisons of this type have received attention by Nordmeyer and Taube,[13] Gould and Taube,[3] and Diaz and Taube.[14] The two analogous ratios that fall in a group with the maleate results are the isonicotinamide case[13] and the acid-independent path in the *cis*-fumaratoaquotetraamminecobalt(III) system. The appropriate ratios, respectively, are 10 and 80. The latter number is based on the assumption that the activated complexes for the acid-independent paths in the chromium(II)–*cis*-fumaratoaquotetraamminecobalt(III) and the chromium(II)–fumaratopentaaquochromium(III) reactions are analogous doubly bridged species. The supporting argument is less straightforward than that for either the isonicotinamide or maleate cases. For "simpler" ligands (chloride, thiocyanate, hydroxide, and fluoride) the ratios range from 3×10^4 to 3×10^7.[13] It would appear that the three systems involving unsaturated organic bridging groups more nearly represent the chemical mechanism[3] in which electron transfer to the ligand is rate determining.

One point that requires attention is the rationale for Co(III)/Cr(III) ratios such as 10 and 40 for paths attributed to the chemical mechanism. In the limiting case of no activation of the oxidizing center in the transition state, a value near unity is perhaps expected. Nordmeyer and Taube[13] rationalized the value of 10 for the isonicotinamide case in terms of the possibility that

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

the transfer of an electron to the ligand might be somewhat reversible, especially in the Cr(II)–Cr(III) system. The maleate case could partake of that effect as well. However, another factor which may be important is the fact that coordination of a ligand to a pentaaquochromium(III) unit will provide a somewhat different electronic structure than coordination to the pentaamminecobalt(III) moiety. Hexaaquochromium(III), for instance, is about 15 times more acidic than aquopentaamminecobalt(III)[19,35] even after correction for the statistical factor of 6. Especially when both reductant and oxidant are coordinated to the same carboxyl group, as in the maleate comparison, even a limiting chemical mechanism could give a ratio which differed substantially from unity in either direction.

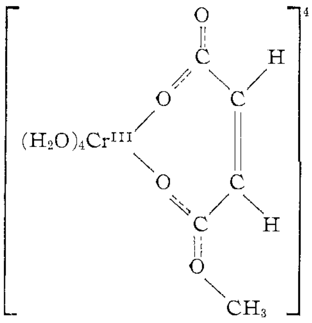
The difference in activation energies for the Cr(II)–Cr(III) and Cr(II)–Co(III) reactions (9 kcal/mol *vs.* 2.9 kcal/mol, respectively) may reflect the effect of the oxidizing center in this way. The activation parameters for the Cr(II)–Co(III) case are not susceptible to simple interpretation since parallel paths are involved. Despite these difficulties, the point remains that the redox reaction does not exploit the additional driving force of the Co(III) reduction with maleate or isonicotinamide as the bridging group to nearly the extent that it does with ligands such as fluoride and hydroxide.

No similar comparison is possible with the 20% of the chromium(II)–maleatopentaamminecobalt(III) reaction which gives monodentate maleatopentaaquochromium(III) product. The analogous Cr(II)–Cr(III) electron-transfer reaction would be an exchange process involving no net chemical change, and the measurements in question have not been made. It needs to be recognized that the relevant activated complexes could involve attack by Cr(II) at either carboxylate group.

Although a small first-order acid path could be easily overlooked for the 20% of the reaction which gives monodentate Cr(III), the kinetic data require that the dominant behavior of the monodentate path be acid independent. The contrast with the fumarate system which exhibits important first-order acid behavior[9,34] is striking. A reasonable explanation is provided by the special geometry of maleate. Several lines of evidence[36] suggest that there is hydrogen bonding between the carboxylate groups in bimaleate ions. Pekkarinen[37] has shown that the rate of the ester hydrolysis of methyl hydrogen maleate is independent of hydrogen ion concentrations up to 0.02 *M*. Methyl hydrogen fumarate, like methyl acetate, under these conditions undergoes hydrolysis which is dominantly first order in acid. Apparently the single acidic proton in methyl hydrogen maleate can both satisfy the basicity of the carboxylate group and polarize the carbonyl group of the ester function at the other end of the molecule.

Quite likely a similar effect is operational in the monodentate path of the chromium(II)–maleatopentaamminecobalt(III) reaction. It is noteworthy that if the proton is "assigned" both to the carbonyl group adjacent to Co(III) and to one oxygen from the remote carboxyl group, the ony free oxygen is on the remote group. If it is, in fact, assumed undesirable to place more than one acidic group on an oxygen in the activated complex for electron transfer, remote attack by Cr(II) is predicted.

The Chromium(II)–Methylmaleatopentaamminecobalt(III) Reaction.—The similarity of the rates found for the Cr(II) reductions of the maleato- and methylmaleatopentaamminecobalt(III) complexes suggests the possibility that the activated complexes are similar. Since chelation offers the dominant mode of attack by Cr(II) in the maleato case, it is reasonable that substantial chelation could accompany the methylmaleato reaction as well. Chelation would presumably lead initially to the Cr(III) complex shown in C.



C

The spontaneous chemistry of the coordinated ester in a chelating ligand is expected to involve rapid ester hydrolysis.[10,38] However, the observed absence of ester hydrolysis can be understood if C, on being formed by electron transfer, undergoes rapid Cr(II)-catalyzed ring opening. Attack by Cr(II) at the free carbonyl oxygen could lead to an activated complex identical with that for the Cr(II)-catalyzed ring opening of the maleatotetraaquochromium(III) complex except for the presence of a methyl group instead of a proton on the other carboxyl function. Assuming that a methyl group has a similar inductive effect to that of a proton, the rates should be comparable. The comparison requires an estimate of the pK_a of a coordinated carboxyl group. Deutsch and Taube[19] have estimated the affinity of a carboxyl group coordinated to Cr(III) for a proton as 0.2. Application of this value to the rate term for k_f (60(H$^+$) M^{-1} sec^{-1}) gives an estimate of 300 M^{-1} sec^{-1} as the second-order rate constant for Cr(II)-catalyzed ring opening of C. Since the Cr(II)–Co(III) rate is only 150 M^{-1} sec^{-1} in the methylmaleato system, Cr(II)-catalyzed ring opening could, in fact, reasonably prevent C from lasting long enough to undergo ester hydrolysis even under conditions for the initial redox reaction involving a moderate excess of Co(III).

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(35) R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 897 (1968).

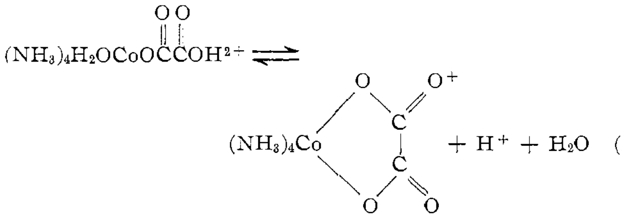
(36) R. E. Dodd, R. E. Miller, and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 2790 (1961).

(37) L. Perkkarinen, *Ann. Acad. Fenn., Ser. A2*, No. 85 (1957).

(38) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6032 (1968).

The Monodentate and Chelated Maleate Complexes of Cr(III).—A conspicuous feature of the behavior of the monodentate and chelated maleate complexes of Cr(III) is the relative thermodynamic stability of the monodentate species. Based on studies of the stabilities[39] of maleate complexes of labile cations, maleate has generally been regarded as a strongly chelating ligand. Most of the stability constants were measured, however, either without variation of pH or over such narrow ranges of pH that no test of the number of protons involved in the equilibrium was possible. Nonetheless, arguments based on the magnitude of the stability constants, in comparison with values for related ligands such as fumarate, do suggest a chelate effect.[40] All the measurements on labile systems, however, were made at much higher pH's than those reported for Cr(III). At pH's above 3, the acid range of most previous measurements, the dominant behavior of maleate may well be chelating.

A basis of comparison with the Cr(III) results is supplied by Andrade and Taube's[41] estimate of the driving force for ring closing in the *cis*-binoxalatotetraamminecobalt(III) ion. Their estimate is based on the collection of equilibrium data from several sources. It also involves the assumption that the affinity of *cis*-diaquotetraamminecobalt(III) for binoxalate to form the monodentate *cis*-binoxalatoaquotetraamminecobalt(III) complex is the same as the affinity of aquopentaamminecobalt(III) for binoxalate. The argument is reasonable, although not rigorous, and leads to an estimate of 10 as the equilibrium constant for ring closing (eq 2).


(2)

$$K = ((NH_3)_4CoC_2O_4^+)(H^+)/((NH_3)_4H_2OCoC_2O_4H^{2+}) \approx 10 \ (\mu = 0, 25°).$$

To the extent that this estimate is valid, it offers perspective on the value of 0.06 measured for the maleate–chromium(III) system. Oxalate forms five-membered chelate rings with little strain. For maleate chelates, in contrast, the ring has seven members and the added rigidity imposed by the olefinic linkage.

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[39] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964, p 406.

[40] J. M. Peacock and J. C. James, *J. Chem. Soc.*, 2233 (1951).

[41] C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

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Mechanism of Tetracyanonickelate Formation from Mono(aminocarboxylate)nickel(II) Complexes

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The rate of formation of $Ni(CN)_4^{2-}$ is first order in nickel aminocarboxylate concentration and varies from first to third order in cyanide ion concentration, depending upon the level of the cyanide ion concentration and the nature of the aminocarboxylate ligand. Sexadentate, pentadentate, tetradentate, and tridentate ligands are compared and their rates of reaction (at the same cyanide ion concentration) vary by ratios as large as 10^8. Nevertheless, the reactions proceed by a similar mechanism. In each case three cyanide ions and a segment of the aminocarboxylate ligand are coordinated to nickel(II) in the rate-determining step. The observed variation in cyanide ion reaction order is caused by the relatively rapid formation of mixed cyanide–aminocarboxylate complexes. All the reverse reactions are first order in $Ni(CN)_4^{2-}$ concentration, first order in the aminocarboxylate ligand concentration, and inverse first order in cyanide ion concentration.

Introduction

Cyanide ion reacts with mono(aminocarboxylato)nickel(II) complexes, NiL^{2-n}, to give tetracyanonickelate ion and to displace the aminocarboxylate ligand (eq 1). The speed of the reaction is highly dependent upon the cyanide ion concentration and is inversely dependent on the stability constant of NiL^{2-n}. In the present work the kinetics of the forward and reverse reactions for eq 1 are examined for six aminocarboxylates ($EDDA^{2-}$, NTA^{3-}, $EGTA^{4-}$, $HPDTA^{4-}$, $HEEDTA^{3-}$, and 1,2-$PDTA^{4-}$) and are compared with the behavior of four others (IDA^{2-}, $MIDA^{2-}$, $EDTA^{4-}$, and $CyDTA^{4-}$). Table I gives the struc-

$$NiL^{2-n} + 4CN^- \rightleftarrows Ni(CN)_4^{2-} + L^{n-} \qquad (1)$$

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