The Reduction by Metal Ions of Fumaratopentaamminecobalt(III) Complexes

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Abstract: The reduction of (methyl fumarato)pentaamminecobalt(III) has been reinvestigated. A variety of methods was used in searching for evidence of ester hydrolysis. All agreed in the conclusion, which is contrary to that published earlier, that there is no substantial amount of ester hydrolysis in the reactions, whether Cr^{2+}, V^{2+}, or Eu^{2+} is the reductant. The principal product of the reaction with Cr^{2+} is the carboxylate bound Cr(III) complex of the half-ester, but free ligand is also produced when the concentration of Cr^{2+} is kept low. The observations made on this product are consistent with the view that at least part of the reaction proceeds by remote attack and that the intermediate thus formed aquates or isomerizes to stable product on reaction with Cr^{2+}. Kinetic data for the half-ester complex and kinetic data as well as observations on product identification for the amidofumarato and methyl amidofumarato complexes are presented. These observations are interpreted in terms of reduction of the Co(III) complexes by dual mechanisms.

It has been reported that[1] the reactions of Cr^{2+}, V^{2+}, and Eu^{2+} with (methyl fumarato)pentaamminecobalt(III) lead to extensive hydrolysis of the ligand ester group. These observations as well as similar ones[2] with complexes having other half-ester dicarboxylic conjugated groups as ligands have been put forward as proof that in these particular systems reduction of the complex takes place by remote attack. We have had occasion to reexamine the reduction of $RoFuOCH_3^{2+}$ (Ro = pentaamminecobalt(III)) and,[3] contrary to the earlier observations, find that little ester hydrolysis accompanies the reaction whether Cr^{2+} or Eu^{2+} or V^{2+} reacts. Several methods of learning the identity of the products of the reaction have been applied including those used in the earlier work, and all agree on the conclusion as now stated.

In the present paper, we describe the results of the reinvestigation referred to. Because the function of these bridging groups in the act of electron transfer remains of interest, the studies were extended to include complexes containing other fumarate derivatives as ligands. It should be emphasized that, though our findings differ from the earlier ones, they do not negate the conclusion that reduction in these systems may take place by remote attack. In fact, the new evidence we offer indicates that the reaction $RoFuOCH_3^{2+} + Cr^{2+}$ takes place at least in part by remote attack. The observations are, however, inconclusive on how the bulk of the reaction occurs. It should perhaps also be noted here that remote attack has been proven as a mechanism for electron transfer in at least one system involving an extended bond system as the bridging function.[4]

Experimental Section

Preparation and Characterization of the Co(III) Complexes. 1. Fumaratopentaamminecobalt(III) Perchlorate. The compound $RoFuOH(ClO_4)_3$ was prepared by following procedures which are described elsewhere.[5] It was purified by using a silica gel cation-exchange column in the NH_4^+ form.[6] Elution with 0.4 *M* NaOAc readily removed Ro-fumarato as the +1 ion, a much more concentrated eluent being required to remove the aquo or hydroxy ion[7] from the column. Recrystallization of the isolated compound from dilute $HClO_4$ precipitated the complex with the organic ligand in its protonated form. Titration of the complex with standard alkali indicated an effective molecular weight within 4% of that of the anhydrous perchlorate. The infrared spectrum taken in a KBr matrix showed two strong absorptions in the carbonyl stretching region: one at 1710 cm^{-1}, the other at 1637 cm^{-1}. The lower energy absorption can be attributed to the carbonyl stretching mode of the bound carboxyl group, the higher to the same mode in the nonbonded carboxyl group.[8] Other bands diagnostic of the organic ligand are not clearly defined; strong absorptions due to ammonia and perchlorate modes pervade the region 1600–600 cm^{-1}. *Anal.* Calcd for $Ro(C_4H_3O_4)(ClO_4)_2$: C, 10.49; H, 3.96; N, 15.29. Found: C, 10.2; H, 3.7; N, 14.84.

2. (Methyl fumarato)pentaamminecobalt(III) Perchlorate. Methyl hydrogen fumarate was prepared by refluxing maleic anhydride with methanol for 4–5 hr.[9] The reaction was stopped when fumaric acid began to precipitate from solution. Recrystallization from 1:1 chloroform–ether effectively removed impurities. The white solid melted sharply at 144.5° and elemental analyses were excellent. The general procedure employed for preparing Ro-methyl fumarato perchlorate has been described.[10] Pentaamminecobalt(III) perchlorate was dissolved in DMF and the solution saturated with methyl sodium fumarate, a small amount of the protonated half-ester being added to buffer the solution. The solution was heated to 70° for 2–3 hr, and then cooled, and insoluble organic material was removed by filtration. The solution was concentrated by vacuum distillation and precipitation was prompted by adding acidic ($HClO_4$) ethanol. The complex was isolated and recrystallized from dilute $HClO_4$ in the usual manner. The high purity of the complex salt obtained rendered chromatographic separation unnecessary. Titration with standard base indicated that $RoFuOCH_3(ClO_4)_2$ contained less than 1% acid species. The average charge on the cation was determined by absorption on a cation resin in the acid form and titration of released acid with standard alkali. Based upon the molecular weight of the anhydrous salt, the average charge was found to be +1.97. The infrared spectrum of the solid in KBr showed carbonyl stretching bands at 1710 and 1637 cm^{-1}; other organic ligand frequencies appeared as shoulders on strong ammonia and perchlorate absorptions. *Anal.* Calcd for $Ro(C_5H_5O_4)(ClO_4)_2$: C, 12.72; H, 4.27; N, 14.84. Found: C, 12.66: H, 4.23; N, 15.10.

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(1) (a) R. T. M. Fraser, D. K. Sebera, and H. Taube, *J. Am. Chem. Soc.*, **81**, 2906 (1959); (b) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

(2) R. T. M. Fraser, *ibid.*, **83**, 564 (1961); *Proc. Chem. Soc.*, 317 (1960).

(3) Ro will often be used to denote $Co(NH_3)_5$; Fu to denote $O_2CCH{=}CHCO$ (fumarate).

(4) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **88**, 4295 (1966).

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

(6) R. B. Jordan, private communication.

(7) R. L. Burwell, Jr., R. G. Pearson, G. L. Haller, P. B. Tjok, and S. P. Chock, *Inorg. Chem.*, **4**, 1123 (1965).

(8) R. T. M. Fraser, *ibid.*, **3**, 1561 (1964).

(9) G. Dahlgren and F. A. Long, *J. Am. Chem. Soc.*, **82**, 1303 (1960).

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3. (Methyl terephthalato)pentaamminecobalt(III) Perchlorate. Methyl hydrogen terephthalate was obtained by half-saponification of the diester under conditions which caused precipitation of the half-ester as it formed.[11] The Ro complex was prepared from Ro–aquo perchlorate and ligand in DMF in a manner analogous to the Ro–methyl fumarato preparation from this solvent, but in this case the lithium salt of the half-ester was employed because the other alkali metal salts are insoluble in DMF. Titration of the Ro product recrystallized from dilute aqueous $HClO_4$ indicated only about 2% acid species was present. *Anal.* Calcd for $Ro(C_9H_7O_4)(ClO_4)_2$: C, 20.70; H, 4.25; N, 13.41. Found: C, 20.56; H, 4.27; N, 13.24.

4. Fumaramato- (amidofumarato-) pentaamminecobalt(III) Perchlorate. Amidofumaric acid was prepared by shaking ethyl hydrogen fumarate in concentrated ammonia at room temperature for several minutes.[12] The resulting ammonium salt was conveniently transformed into the protonated form by dissolving the salt in a minimum amount of water and acidifying with HCl. The isolated white solid analyzed correctly for amidofumaric acid. Ro–amidofumarato perchlorate was prepared by heating the Ro–aquo complex in a DMSO solution containing an amidofumarate ion–amidofumaric acid buffer. Of the alkali salts, only the lithium salt has appreciable solubility in DMSO. (DMF could not be used because all alkali salts of amidofumaric acid are insoluble in this solvent.) The solution of Ro–amidofumarato was concentrated by vacuum distillation and precipitation was induced with 1-propanol. Initial recrystallizations of the complex were difficult. The complex was extremely soluble in aqueous solution, and it was necessary to add methanol and diethyl ether to induce precipitation. Subsequent recrystallizations, presumably reflecting increased purity of the complex, occurred with less difficulty and the precipitate became more crystalline. Base titration revealed that less than 2% acid species was present. *Anal.* Calcd for $Ro(C_4H_4O_3N)(ClO_4)_2$: C, 10.51; H, 4.19; N, 18.39; Cl, 15.51. Found: C, 10.23; H, 4.19; N, 17.94; Cl, 15.17.

The absorption spectra of these Ro–carboxylate complexes in the visible region are similar to those reported for other Ro–carboxylate complexes.[13] Maxima appear at 502 and 351 mμ; the molar extinction coefficients are also characteristic of carboxylate bonding (Table I). No change with acid concentration was observed in the Ro–fumarato spectrum over a range of pH 1–10.

Table I. Molar Extinction Coefficients of Ro–Carboxylato Complexes

Complex	ϵ_{351}	ϵ_{502}
Ro–fumarato	61.8	75.3
Ro–methyl fumarato	63.1	77.0
Ro–amidofumarato	62.7	76.2
Ro–methyl terephthalato	66.9	79.2

5. Fumaratopentaamminerhodium(III) Perchlorate. Aquopentaamminerhodium(III) perchlorate was prepared from the reaction in aqueous solution of A_5Rh–chloro chloride[14] with silver perchlorate. Agreement with published spectra in both the aquo and hydroxo forms was good.[15] Preparation of A_5Rh–fumarato was identical with that described for the Ro–fumarato complex except that the reaction was given 12 hr to reach completion. A single maximum at 320 mμ was observed in the electronic absorption spectrum of the complex, with ϵ_{320} 169. When a solution of the complex was made alkaline, no change in the spectrum was observed, indicating that no A_5Rh–aquo was present. *Anal.* Calcd for $A_5Rh(C_4H_3O_4)(ClO_4)_2$: C, 9.57; H, 3.61; N, 13.59; Cl, 14.13. Found: C, 8.36; H, 3.41; N, 13.46; Cl, 15.97, 16.00. The reason for the poor analysis probably lies in the incomplete conversion of A_5Rh–chloro chloride to A_5Rh–aquo perchlorate. An explosion occurred when the preparation of A_5Rh–aquo was attempted from the reaction of A_5Rh–chloro chloride with Ag_2O in alkaline solution.[16]

6. (Methyl acetate)pentaamminecobalt(III) Perchlorate. The complex was prepared by equilibrating solid Ro–sulfolane perchlorate with methyl acetate in a sealed tube at elevated temperatures (*ca.* 65°). The Ro–sulfolane complex was prepared by the reaction of Ro–azido perchlorate with $NOClO_4$ in tetramethylene sulfone (sulfolane).[17] Both Ro complexes undergo rapid substitution reactions in the presence of suitable nucleophiles, methyl acetate and sulfolane being readily replaced in the coordination shell, so that conventional preparative and analytical methods cannot be used. A detailed account of the preparation, analysis, and properties of these novel compounds will be reported separately.

7. (Methyl fumaramato)- (methyl amidofumarato-) pentaamminecobalt(III) Perchlorate. Esterification of amidofumaric acid was accomplished by dissolving the compound in methanol in the presence of catalytic amounts of concentrated sulfuric acid.[18] The isolated amide half-ester melted at 162–163°. The Ro–methyl amidofumarato complex was formed by the reaction of Ro–azido perchlorate with $NOClO_4$ in a solution of methyl amidofumarate in sulfolane. Extraction with ether removed the sulfolane but not excess amide. The complex was dissolved in water cooled to 0°, the insoluble organic material filtered off, and the complex recovered from the filtrate by adding methanol and ether. In this manner the complex was purified with a minimal amount of aquation having occurred. The initial absorption maximum in the visible region was at 509 mμ; the calculated molar extinction coefficient at the maximum assuming pure anhydrous salt was 66.5. The spectrum rapidly decayed to a final maximum at 492 mμ which gave a calculated extinction coefficient of 48. The close agreement of the calculated final ϵ value with that reported for Ro–aquo (ϵ_{491} 47.5) argues for the purity of the Ro–methyl amidofumarato preparation.

A violent explosion occurred during an attempted preparation of Ro–fumaramido perchlorate by the Ro–azido–$NOClO_4$ reaction in the presence of fumaramide in DMSO. The insolubility of the diamide in sulfolane precluded use of this solvent.

Other Reagents. Detailed descriptions of Ro–azido perchlorate[17] and $NOClO_4$[19] syntheses can be found in the literature. Anhydrous silver perchlorate was prepared by neutralization of silver carbonate with perchloric acid, the silver carbonate being prepared in turn by precipitation from a solution of silver nitrate with sodium carbonate. Heating the silver perchlorate in a muffle furnace at 200–250° for 12 hr removed the water of crystallization. Aqueous solutions of hexaaquochromium(III) perchlorate were formed from the reduction of primary standard potassium dichromate in acidic ($HClO_4$) solution either with hydrogen peroxide or with formic acid. The reductions were performed in concentrated solution, $KClO_4$ was removed by filtration at −10°, and the solutions were then diluted to the desired concentrations. Chromous ion was obtained from the chromic solutions both by reduction with zinc amalgam and by electrolytic reduction under an inert (N_2) atmosphere. Europous ion was prepared by dissolving europic oxide in dilute $HClO_4$ and reducing over zinc amalgam in a nitrogen atmosphere. Vanadous ion was prepared by reduction of ammonium metavanadate in dilute $HClO_4$ to vanadyl ion with sulfur dioxide, then reduction to vanadous over zinc amalgam, also under nitrogen. Stock lithium perchlorate solutions were prepared from two sources, the commercially available salt and that obtained from the neutralization of lithium carbonate with perchloric acid. The compounds from both sources were recrystallized from aqueous solution several times before use. Tests for Cl^-, ClO_3^-, and SO_4^{2-} gave negative results. Sodium perchlorate was similarly obtained from the reaction of sodium carbonate with perchloric acid. Molarities of the stock solutions were determined by absorption of aliquots on cation resins in the acid form and titration of the eluted protons with standard base and by gravimetric perchlorate analysis using tetraphenylarsonium chloride as precipitant. Results from the two methods agreed closely. A standard ceric solution in 1 *M* $HClO_4$ was prepared from $(NH_4)_2Ce(NO_3)_6$ and standardized by iodometric titration. Frequent restandardization was required because water slowly reduced ceric ion in this medium.

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[11] B. W. Hotten, U. S. Patent 2,808,428; *Chem. Abstr.*, **52**, 2918 (1958).

[12] E. A. Talley, T. J. Fitzpatrick, and W. L. Porter, *J. Am. Chem. Soc.*, **81**, 174 (1959).

[13] E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

[14] The symbol A_5Rh refers to the pentaamminerhodium(III) moiety.

[15] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

[16] S. M. Jorgensen, *J. Prakt. Chem.*, **135**, 451 (1883).

[17] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

[18] H. Schwartz, French Patent 1,348,769; *Chem. Abstr.*, **60**, 13192*c* (1964).

[19] M. M. Markowitz, J. E. Ricci, R. J. Goldman, and P. F. Winternitz, *J. Am. Chem. Soc.*, **79**, 3659 (1957).

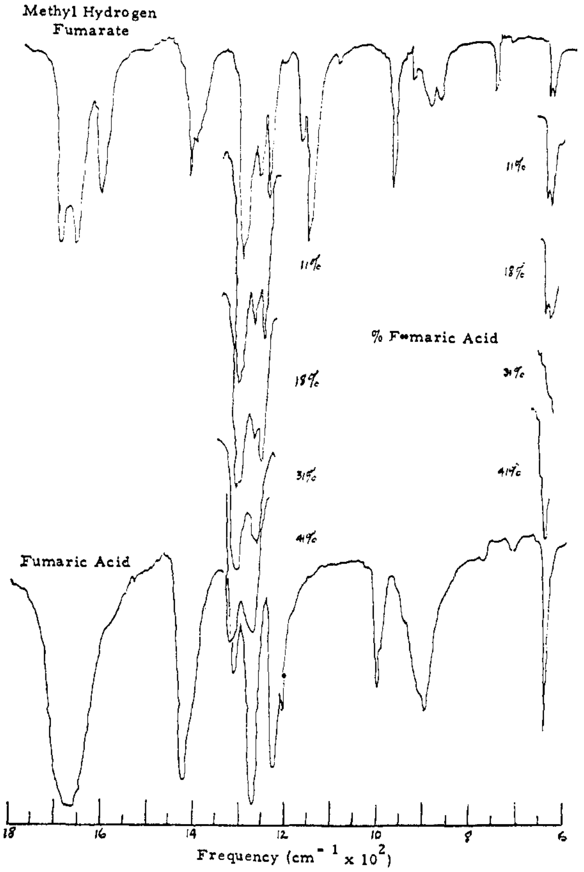

Figure 1. Infrared spectra of fumaric acid–methyl hydrogen fumarate mixtures.

All other reagents employed were commercially available compounds and were used without further purification.

Kinetic Studies. The apparatus used to deoxygenate and mix reagents for redox measurements has been described.[5,20] Generally, the course of reaction was followed spectrophotometrically at 351 or 502 mμ, corresponding to the absorption maxima for the Ro complexes. In the kinetic runs the oxidant was usually in slight excess. Data were treated using an equation derived elsewhere for a second-order reaction.[5] The extinction coefficients needed were obtained from the literature when possible, and otherwise were measured. The chromous ion reduction of Ro–methyl fumarato was studied as a function of temperature. Kinetic measurements were made at 10, 22, 32, and 42°; temperature was controlled to ±0.1°. A temperature gradient of 1–3° was noted between the thermostated cell compartment of the spectrophotometer and the external thermostating bath when reactions were conducted at temperatures far from ambient. In these instances, two temperature baths were used: one to thermostat the cell compartment; the other, set at the temperature of the cell compartment, to thermostat the unmixed reagents. Reduction of A_5Rh–fumarato by chromous ion was followed by watching the appearance of the chromium(III) product at 570 mμ. For this reaction chromous ion was in excess of oxidant.

Hydrogen ion concentration in the reaction solutions was adjusted with standard $HClO_4$, $LiClO_4$ being added when necessary to maintain ionic strength at 1.0 *M*. Stoichiometries of the reactions were determined by analysis of spent solutions for cobalt(II), using either the $Co(SCN)_4^{2-}$ [21] or $CoCl_4^{2-}$ [13] methods, and for total chromium content as CrO_4^{2-}.[22] These experimentally determined values and the value for the initially added chromous ion concentrations were compared over the range of temperature and [H^+] covered in the studies. Except where otherwise indicated, the stoichiometries were within 5% of the theoretical ratio of 1.00 Cr^{2+} per Co(III).

The kinetics of the Ro–methyl amidofumarato–chromous ion redox system were studied by an alternate procedure[23] by which reagents could be more rapidly deaerated, advantageous since Ro–methyl amidofumarato aquates rapidly, and by which an initial reading could be obtained that is much closer to the actual zero time of the reaction, advantageous because the reaction is quite rapid. The stoichiometry of the reaction was imperfect and about 30% more Cr^{2+} was oxidized than cobalt(II) produced. The situation did not improve upon reverting to the other procedure. The failure to recognize competing reactions must reflect uncertainty in the computed rate constant, and the recorded value should be taken as only approximate.

Measurements of the rates of aquation of the Ro complexes were made spectrophotometrically in a thermostated cell compartment at 502 mμ, the wavelength corresponding to maximum change in optical density for the reaction. Rate constants were then computed from the equation for first-order reactions by graphical means. Aquation rate constants of the chromic products formed in the oxidation of chromous ion by Ro–carboxylato complexes were similarly determined from the rate of change of optical density at 570 mμ. The Cr(III) species generated *in situ* were not separated from the other reaction products prior to the aquation studies.

Thermal Decomposition of Mercurous Fumarate. Precipitation of fumaric acid by mercurous nitrate from acidic solution as the dimercury salt is quantitative and specific in the presence of other dibasic organic acids, and is, moreover, rapid.[24] The half-ester ion, methyl hydrogen fumarate, is not precipitated by $Hg_2(NO_3)_2$. Decomposition of mercurous fumarate proceeds rapidly when the salt is heated with a yellow flame. Chromatographic separation of the gases evolved (on *sec*-butyl phthalate, firebrick matrix, using helium as the carrier gas) showed only carbon dioxide and carbon monoxide to be present. This result was corroborated by mass spectrometric analysis.

Titrations. Results of titrations of reaction product solutions have been used as evidence for ester hydrolysis,[1] and this kind of study was repeated in the present work. The titration curve obtained on adding standard base to the product solution resulting from the reaction of $RoFuOCH_3^{2+}$ and Cr^{2+} was compared directly to a curve obtained from titration of the solution resulting from the reaction of an equivalent amount of $RoFuOH^{2+}$ with Cr^{2+} ion, the concentrations of all reagents being identical in the two cases. In this way it was hoped that the errors due to uncertainties in the acidities of the reagents would be minimized. Any differences in the acidities of the reaction solutions could then be ascribed to differences arising from the reactions themselves. In the case of the cited example, the difference would lie entirely in the nature of the chromic product. For the $RoFuOCH_3^{2+}$ system, titration experiments were conducted under conditions of excess Ro complex, excess Cr^{2+}, and equivalent amounts of the two reagents. A single experiment was run using excess Eu^{2+} as reductant. The product solution from the reduction of Ro–amidofumarato with an equivalent amount of Cr^{2+} was also titrated All experiments were done at ambient temperature and at 0.06–0.10 *M* H^+.

Ligand Analysis. Recovery of the organic ligand from the reaction products was generally accomplished by ether extraction of the reaction solution. Chromic products call for labilization of the ligand, and this was accomplished by oxidizing Cr(III) with standard ceric perchlorate solution to dichromate.[25] Following this the pH content of the solution was raised to *ca.* 1 with solid sodium bicarbonate, the perchlorate was removed by precipitation with potassium chloride and filtration at the freezing point of the solution, and then the organic compound was extracted from the aqueous solution for *ca.* 12 hr using a continuous liquid–liquid extraction apparatus. During the extraction process the aqueous layer was kept at 0°. The organic material was isolated by vacuum distillation of the separated ether layer, dried under vacuum, weighed, and analyzed without purification. When dichromate was present in the aqueous layer, a considerable amount of chromic acid was extracted into the ether phase. This was removed before recovering the solid organic material by shaking the ether solution with solid lead nitrate. Ether extraction was not necessary when methyl hydrogen terephthalate was the ligand isolated. The organic material precipitated from solution upon oxidizing Ce(IV) with ceric perchlorate and was recovered directly by filtration.

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

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Blank studies indicated that none of the above procedures for isolating the oganic ligand had noticeable effects upon the relative amounts of half-ester and dibasic acid recovered. A slight selective extraction of methyl hydrogen fumarate by ether from aqueous solutions of half-ester–diacid mixtures was noticed, however. The infrared spectra of the organic compounds were taken as solids in KBr disks. Reproducibilities of spectra, both from half-ester–fumaric acid blanks and from organic material isolated from reaction solutions, were excellent. The ir spectrum of methyl hydrogen fumarate is very sensitive to the presence of small amounts of fumaric acid, fumaric acid content as low as 10% causing loss of resolution in the region 1350–1250 cm^{-1} and an increase in intensity of the low-energy peak of the doublet at 650 cm^{-1} relative to the other (Figure 1). Considering the selective extraction previously noted, as little as 15% fumaric acid in reaction product solutions can easily be detected by this method. The infrared spectra of methyl hydrogen terephthalate and amidofumaric acid are also sufficiently different from their respective dibasic acids that the acid and derivative can be readily distinguished.

When extraction of methyl hydrogen fumarate was made from an aqueous solution containing $HClO_4$, considerable degradation of the organic material occurred. The infrared spectrum was ill-defined, but the major peaks appeared to be those of fumaric acid.

Measurement of Ligand Labilization during the Redox Reaction. The ultraviolet absorption spectrum of methyl hydrogen fumarate showed a single maximum at 207 mμ, ϵ_{207} 1.54 × 10^4, comparing closely to that reported for fumaric acid, ϵ_{208} 1.52 × 10^4.[26] The Cr(III)–methyl fumarato ion, prepared by reaction of Ro–methyl fumarato with chromous ion and isolated by column chromatography, exhibited a peak at 210 mμ, ϵ_{210} 2.0 × 10^4; Ro–methyl fumarato, a peak at 224 mμ, ϵ_{224} 2.5 × 10^4. Blank experiments indicated that free organic material could be effectively removed from complex ions using a sulfonic acid type cation-exchange column. Aquation of the complexes while absorbed on the column was made negligible during the time required (*ca.* 30 min) for separating the free organic acid by cooling the column to 0°. A jacketed buret was used for this purpose, ice–water being circulated through the jacket by an external pump.

The procedure followed to determine the per cent noncomplexed organic acid in a reaction product solution was to dilute an aliquot of the solution 50–100-fold, pass an aliquot of the diluted solution containing about 6 × 10^{-3} mmole of chromium(III) species slowly through a 10-ml bed of resin cooled to 0°, and then wash the column with successive portions of water (usually five 25-ml portions) until only negligible absorption in the ultraviolet region was observed. From the known extinction coefficients of the organic species and the measured absorbances of the effluent solutions, the amount of ligand released could be easily determined. (The analysis does not distinguish between fumaric acid and the methyl half-ester, however.)

Instrumentation. Melting points were determined with a Buchi apparatus. Titration data were obtained using Beckman Model G and Expandomatic pH meters. Kinetic measurements were made on Cary Model 14 and 15 recording spectrophotometers. Electronic and vibrational spectra were determined with Cary 14 and 15 and Perkin-Elmer Model 421 spectrophotometers, respectively. Varian Associates Model A-60 and Atlas Model M-86 spectrometers were used to obtain proton nmr and mass spectra, respectively. Elemental analyses were made by E. Meier and J. Consul of the Stanford Microanalytical Laboratory.

Results

Kinetic Data for the Oxidation–Reduction Reactions. The kinetic plots for most of the runs were found to conform to the rate law

$$\frac{-\mathrm{d}[\mathrm{Co(III)}]}{\mathrm{d}t} = k_{\mathrm{obsd}}[\mathrm{Co(III)}][\mathrm{Cr}^{2+}] \qquad (1)$$

over at least 95% of the course of the reaction. When the complexes containing $FuOCH_3^-$ and $FuNH_2^-$ as ligands[27] are reduced, the rate law as a function of $[H^+]$ has the form

$$k_{\mathrm{obsd}} = k_0 + k_1[\mathrm{H}^+] \qquad (2)$$

A summary of the data obtained in the present work is given in Table II. The parameters k_0 and k_1 for the various complexes are summarized in Table III. The parameters were obtained from plots of k_{obsd} *vs.* $[H^+]$ using a least-squares treatment of the data.

Table II. Oxidation–Reduction Rate Data[a]

Ligand	[Oxidant]$_0$[b] × 10^3	[Reductant]$_0$[c] × 10^3	$[H^+]$	Temp, °C (±0.1°)	k_{obsd}, M^{-1} sec^{-1}
$FuOCH_3$	3.10	2.14	0.10	10.0	0.65
	2.98	1.92	0.10	10.0	0.66
	3.04	1.68	0.50	10.0	0.89
	3.00	1.94	0.75	10.0	0.95
	3.09	1.91	1.00	10.0	1.11
	3.26	2.40	0.10	22.0	1.27
	2.96	2.13	0.10	22.0	1.31
	3.16	2.21	0.25	22.0	1.31
	3.00	1.84	0.25	22.0	1.34
	2.91	2.14	0.50	22.0	1.41
	3.06	1.96	0.50	22.0	1.46
	3.09	2.51	0.75	22.0	1.65
	2.81	1.90	0.75	22.0	1.64
	2.87	2.32	1.00	22.0	1.68
	3.08	2.08	1.00	22.0	1.75
	3.12	2.12	1.00	22.0	1.87
	3.10	2.11	0.10	32.0	1.81
	2.95	2.18	0.10	32.0	1.92
	3.06	1.67	0.50	32.0	2.20
	2.94	2.03	0.50	32.0	2.34
	3.16	2.57	0.75	32.0	2.34
	2.92	1.95	0.75	32.0	2.44
	3.29	1.97	1.00	32.0	2.64
	3.10	2.34	1.00	32.0	2.40
	2.90	2.03	1.00	32.0	2.56
	2.94	2.16	0.10	42.0	3.34
	2.98	2.10	0.10	42.0	3.25
	3.05	2.16	0.25	42.0	3.40
	3.01	2.12	0.50	42.0	3.70
	2.88	2.23	0.75	42.0	3.84
	3.21	1.98	1.00	42.0	4.04
	2.95	1.93	1.00	42.0	3.96
$FuNH_2$	3.24	2.16	0.10	25.1	1.34
	3.11	2.16	0.30	25.1	2.05
	3.11	1.97	0.50	25.1	2.52
	3.12	2.08	0.75	25.1	3.01
	3.10	2.27	1.00	25.1	3.56
	3.39	2.12	1.00	25.1	3.69
FuOH	3.16	1.96	0.10	25.0	2.0
	1.50	1.03	1.00	25.0	5.6
NH_2FuOCH_3	3.4	1.4	1.00	10.0	4–5
FuOH	4.2	2.1	1.00	35.0	4.4 × 10^{-2}

[a] For all runs, μ = 1.0 *M* ($LiClO_4$); experimental uncertainty in the measured rate constants is *ca.* ±10%, except where discussed in the text. Concentrations are molar. [b] The oxidant was a complex of $(NH_3)_5Co^{3+}$ except in the last experiment of the table where it was a complex of $(NH_3)_5Rh^{3+}$. [c] The reductant was Cr^{2+}.

Table III. Rate Constants for Ro–Carboxylato Reductions

Reaction	Temp, °C (±0.1°)	k_0, M^{-1} sec^{-1}	k_1, M^{-2} sec^{-1}
$RoFuOCH_3$ *vs.* Cr^{2+}	10.0	0.61 ± 1.02	0.49 ± 0.03
	22.0	1.20 ± 0.03	0.56 ± 0.05
	32.0	1.84 ± 0.06	0.73 ± 0.09
	42.0	3.22 ± 0.04	0.80 ± 0.08
$RoFuNH_2$ *vs.* Cr^{2+}	25.1	1.24 ± 0.07	2.41 ± 0.10
RoFuOH *vs.* Cr^{2+}	25.1	1.32[a] (1.6)	3.48[a] (4.0)

[a] Reference 5. All other values from this work. Experimental error assigned to the rate constants represent one standard deviation calculated from the least-squares plots.

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[26] H. Ley and H. Wingchen, *Chem. Ber.*, **67**, 512 (1934).

[27] In the reduction of the acid fumarate complex, these terms appear as well as one inverse in $[H^+]$, the latter describing the reduction of the complex in the form $RoFuO^-$.

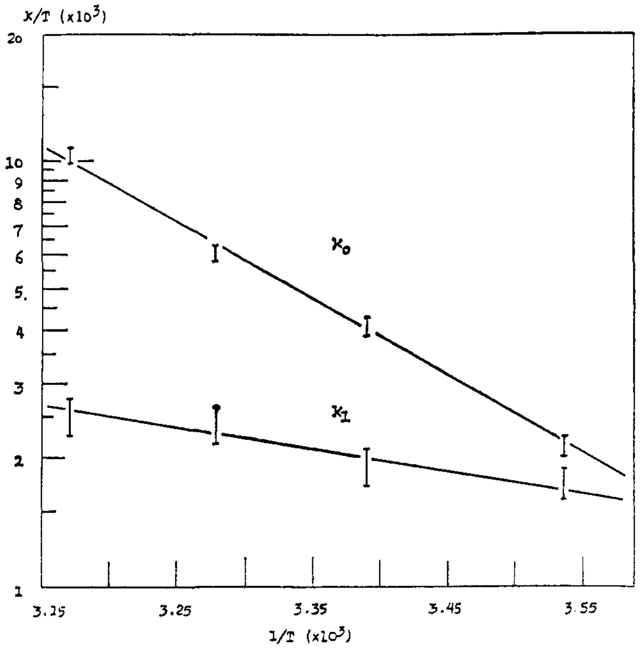

Figure 2. The rate constants for the reduction of acid-fumaratopentaamminecobalt(III) by Cr^{2+} as a function of temperature.

Though k_1 for the $RoFuOCH_3^{2+}$–Cr^{2+} reaction is not large, the rate term corresponding to it can probably not be dismissed as arising from a medium effect generated by the change in ionic composition as Li^+ is replaced by H^+. The rate constant obtained for a run at 22° with $[HClO_4] = 0.1\ M$ and using $NaClO_4$ in place of $LiClO_4$ to maintain the ionic strength was identical with that determined for a system containing $LiClO_4$.

Early results obtained with a sample of the complex treated for purposes of purification by eluting it from a silicic acid ion-exchange column were irreproducible. The later preparations, using DMF as a reaction medium, give reproducible results. The reproducibility was checked by using two sets of reagents, each set being derived from different starting materials. The $RoFuOCH_3^{2+}$ complex used for the final kinetic measurements was recrystallized eight times from dilute perchloric acid. It should be noted that the present results for the $RoFuOH^{2+}$–Cr^{2+} reaction are in good agreement with those published earlier.[5]

Activation parameters for the chromous ion reduction of Ro–methyl fumarato were calculated for both reaction paths from the Eyring equation. The plots of log k/T *vs.* $1/T$ are shown in Figure 2. The results are recorded in Table IV and, for comparison, activation parameters for the chromous reduction of Ro–fumarato are also presented.

Table IV. Activation Parameters for Chromous Reductions

	Organic ligand			
	Acid fumarate[a]		Methyl half-ester[b]	
Reaction path	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
Acid-independent (k_0)	6.7	−36	8.2 ± 0.4	−30 ± 1
Acid-dependent (k_1)	2.9	−45	2.2 ± 0.3	−52 ± 1

[a] Reference 5. [b] This work. Experimental error represents one standard deviation obtained from a least-squares analysis of the data, each graph point being weighted by an appropriate function of its variance: G. N. Williamson, *Biochem. J.*, **80**, 324 (1961).

Visible absorption spectra of the Cr(III) products from chromous reductions of Ro–carboxylato complexes are recorded in Table V; positions of maxima and their extinction coefficients are typical of those observed for Cr(III)–carboxylato complexes.[13]

Table V. Electronic Spectra of Cr(III) Complexes

Ligand	λ_{max}, mμ	ϵ_{max}	λ_{max}', mμ	ϵ_{max}'
Acid fumarate	567	29.8	412	28.4
Methyl fumarate	570	...	412	...
Amidofumarate	570	27.4	412	27.2
Water[a]	574	13.4	408	15.6

[a] J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

The reactions of Ro–methyl amidofumarato with chromous ion were run at 10° to minimize aquation of the Ro complex. Second-order plots were linear to only 60–80% reaction and the stoichiometry of the reaction was so poor (30% excess Cr^{2+} consumed) that accurate rate constants could not be computed. Likewise, acid dependence of k_{obsd} could not be determined. The reaction product spectrum suggested that the predominant chromic product is hexaaquochromic ion (ϵ_{574} 16, ϵ_{410} 19). Further, the fact that there is no change in the product spectrum over a time period beginning immediately after the redox reaction and extending to *ca.* 15 hr after reaction also implies that no Cr(III) product capable of aquating at a moderately rapid rate was formed, *i.e.*, that the reaction product is in fact Cr(III) aquo ion.

Reaction of A_5Rh–fumarato with excess chromous ion proceeded in at least two discrete steps. Oxidation of the first equivalent of Cr(II) was moderately rapid (see entries for last experiment in Table II), and strong uv absorptions tailing well into the visible region appeared in the reaction solution spectrum. Further oxidation of chromous ion was relatively slow and caused no increase in the uv absorptions; metal eventually precipitated from solution. Cation chromatography demonstrated that the product formed initially is a highly charged species, presumably containing both Rh(II) and Cr(III), and that subsequent oxidation of Cr(II) forms Cr(III) aquo. The rate of appearance of Cr(III) species did not fit well to a second-order plot, though nearly equimolar quantities of reagents were used. Linearity was observed to *ca.* 90% reaction when the data were fitted to a first-order plot, but this result is probably fortuitous.

During the phase of our work in which the rates of reaction of $RoFuOCH_3^{2+}$ with Cr^{2+} ion appeared to be irreproducible, it seemed important to check on the possibility of trace catalysis. Iron and copper were investigated because they are so ubiquitous and are involved in many catalytic redox processes. Ferrous ion when present at $5 \times 10^{-5}\ M$, the other conditions corresponding to those of the experiment of Table II, was shown to be without effect. Copper ion at $1 \times 10^{-4}\ M$ also did not affect the rate appreciably, although it did show behavior which is interesting in itself. It gives rise to powerful absorption in the uv region which extends into the visible region. We are inclined to ascribe it to the interaction of Cu^+, formed from Cu^{2+} and Cr^{2+}, with the π system of the ligand.[28] If this interpretation is correct, it seems remarkable that Cu^+ does not reduce Co(III) (copper is known[29] to be an effective catalyst in the reduction of a number of Co(III) complexes by $Ru(NH_3)_6{}^{2+}$).

Aquation Rates. Rate constants for aquations of $RoFuOCH_3{}^{2+}$ and the Cr(III) products of the Ro–carboxylato–chromous ion reactions were determined spectrophotometrically; first-order plots were observed to be linear through at least 87% reaction. Measured rate constants are given in Table VI.

Table VI. Aquation Rate Data[a]

Aquating complex	Temp, °C (±0.1°)	$[H^+]$, *M*	$k_{obsd} \times 10^5$ sec^{-1}
Cr(III)–FuOH[b]	45.0	1.0	0.75_3
Cr(III)–$FuNH_2$[b]	45.0	1.0	0.79_8
Cr(III)–$FuOCH_3$[b]	45.0	1.0	0.75
Ro–$FuOCH_3$	45.0	1.0	0.54_0
Ro–NH_2FuOCH_3	10.7	1.0	4.9
	18.3	0.5	$13._8$
	18.3	1.0	$13._6$
	25.0	0.1	$38._5$
	25.0	1.0	$36._2$
	31.9	1.0	$78._0$
	31.9	1.0	$83._0$
Ro–methyl acetate	Ambient	...	$>2 \times 10^3$

[a] For all runs, $\mu = 1.0$ *M* ($LiClO_4$). Aquation rate constants for the carboxylato complexes are accurate to ±5%; for Ro–NH_2FuOCH_3, better than 10%. [b] Generated *in situ*.

The aquation rate of Ro–methyl amidofumarato ($RoNH_2FuOCH_3{}^{2+}$) is independent of H^+ over the range 0.1–1.0 *M* (Table VI). The degree of purity of the complex had no effect upon the measured rate constant. Linearity of the first-order rate plots was observed through *ca.* 90% reaction. The temperature dependence of the rate constant was measured and, from the Eyring equation, the activation parameters were calculated to be $\Delta H^{\ddagger} = 22.4 \pm 0.5$ kcal/mole, $\Delta S^{\ddagger} = 0.9 \pm 1.7$ eu (the error assigned to the constants represents one standard deviation as calculated from a least-squares analysis of the data). Very similar behavior has been observed for an amide-bound Cr(III) complex.[30] In the work referred to, the metal ion is shown to be attached to the oxygen rather than the nitrogen of the amido group.

The behavior, reported in detail elsewhere, of Ro–methyl acetate in a variety of nucleophilic solvents suggests that the complex solvolyzes rapidly. A solution of Ro–methyl acetate in water immediately gives the Ro–aquo spectrum; aquation is at least as rapid as the rate at which the complex dissolves. A lower limit on the rate constant of 2×10^{-2} sec^{-1} ($t_{1/2} = 30$ sec) for these conditions can thus be set. Nmr evidence indicated that the ester is displaced by water without being hydrolyzed.

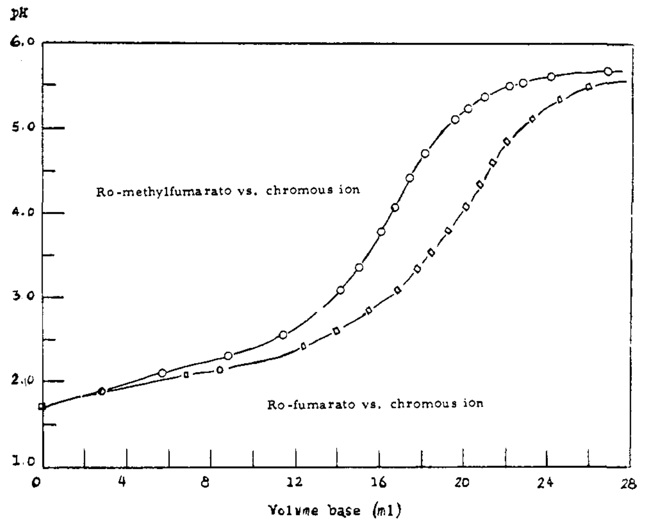

Figure 3. Titration curves of the product solutions from the reduction of Ro–methyl fumarato and Ro–fumarato by Cr^{2+}. The solutions were made up so that the curves would coincide if ester hydrolysis were complete.

Search for Ester Hydrolysis in the Reduction of $RoFuOCH_3{}^{2+}$. Use of $Hg_2{}^{2+}$. Addition of $Hg_2{}^{2+}$ to product solution of the reaction of Ro–fumarato with chromous ion results in moderately rapid formation of a white precipitate, the half-life for the reaction being several hours. The acceleration in rate can be regarded as analogous to the Hg^{2+}-assisted removal of halide from RoX^{2+}.[31] The gaseous decomposition products of the isolated precipitate are identical with those of mercurous fumarate and, on this basis, the salts are assumed to be the same. When $Hg_2(NO_3)_2$ was added to a product solution of the Ro–methyl fumarato–chromous ion reaction, no precipitate formed until several hours after addition. Only a very slight amount of precipitate was obtained after *ca.* 30 hr, and continued precipitate formation was observed for several days. The mass spectral analysis of the gases from the pyrolyzed solid was identical with that of mercurous fumarate. A plausible explanation of these observations is that little, if any, ester hydrolysis occurs during reduction of the Ro–methyl fumarato complex. Formation of a precipitate must await normal hydrolysis of the ester group, which is slow in acid solution.

Titration Data. The net reaction for systems of the type under study corresponds to the equation

$$(NH_3)_5CoL^{2+} + Cr^{2+} + 5H^+ = Co^{2+} + CrL^{2+} + 5NH_4{}^+ \quad (3)$$

(For reductants which are labile in their oxidized form, *e.g.*, europous ion, the reaction products are M^{3+} and HL, rather than ML^{2+}.) When methyl hydrogen fumarate is the ligand L, the occurrence of any ester hydrolysis results in an increase in the titrable acid content of the reaction product solution, and in the limit of 100% ester hydrolysis the acid content of the product solution should be that for reaction of an equivalent amount of Ro–fumarato complex.

Reductions with chromous ion were run using various preparations of the Ro–methyl fumarato complex (both from water and DMF solvents), and the curves constructed from titration of product solutions compared directly to those for reaction of an equivalent amount of the Ro–fumarato complex (Figure 3). Results are listed in Table VII. Quantitative determinations of the

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(28) Strong uv absorptions appear in deoxygenated solutions of Cu(I) (generated *in situ* from Cu(II) and Cu metal) containing Ro–$FuOCH_3{}^{2+}$ or methyl hydrogen fumarate, but not methyl hydrogen succinate. When O_2 is passed through the solutions the absorptions disappear, but they reappear when the solutions are again deoxygenated. Reduction of Ro–$FuOCH_3{}^{2+}$ by Cu(I) occurs very slowly.

(29) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

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

(31) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

Table VII. Titrations of Reaction Product Solutions

Reaction	Excess reagent	Increase in acid content/equiv of Ro complex reduced[a]
Ro–FuOCH$_3$ *vs.* Cr^{2+}	Cr^{2+}	0.14
		0.18
	None	0.20
	Ro–FuOCH$_3$	0.074
		−0.12
Ro–FuOCH$_3$ *vs.* Eu^{2+}	Eu^{2+}	−0.12
Ro–FuNH$_2$ *vs.* Cr^{2+}	None	0.39

[a] By comparison to the titration curve of the reduction of an equivalent amount of Ro–fumarato; experimental uncertainty in the results is *ca.* 0.15.

degree of ester hydrolysis varied from −12 to 20%, the average amount being 9% for the five determinations made. Results using europous ion as reductant indicate negligible ester hydrolysis. A high degree of accuracy cannot be expected for these measurements. Since 5 equiv of ammonia is released per equivalent of complex reacting, differences in purity between the Ro–fumarato and Ro–methyl fumarato complexes are magnified fivefold in the titration results for runs where the reductant is in excess. Similar considerations apply to differences in quantities of reductant added when the oxidant is in excess. Possible error introduced into the measurements from other sources is considerably less.

The conclusion drawn from the titration experiments, even when considerable inaccuracy in the titration data is admitted, is that little ester hydrolysis occurs. Necessarily, the mineral acid content of the reaction solutions was low; therefore, these results are valid only for reactions proceeding by acid-independent paths. Differences in the shapes of titration curves in the pH region 2–5.5 indicate the presence of a weak acid in the Ro–fumarato–reductant product solutions which is absent (or nearly so) in the Ro–methyl fumarato–reductant product solutions. For the chromous reductions, this weak acid, undoubtedly Cr(III)–fumarato, is completely titrated above pH 4.5 as evidenced by the parallel slopes of the titration curves at lower acidities; a crude estimate of the acid dissociation constant, pK_a = 2.3, compares favorably to a pK_a = 3.2 determined for the Ro–fumarato complex.[5] Leveling of the curves above pH 5 has been attributed to titration of protons of water molecules coordinated to Cr(III).[32] With europous ion as reductant, titration of coordinated water does not begin until pH 6.5–7 is reached.

Previous titration data indicated an acid increase of 1 equiv, not only for the reductions of Ro–methyl fumarato but also for the Ro–amidofumarato–chromous ion system.[1b] Since for the latter system amide hydrolysis was thought to be unlikely, the results were interpreted in terms of coordination of the amide group in the chromic product, thus increasing the acidity of the nitrogen protons. A consideration of the results from the present study would seem to rule out the possibility of an amide-bonded chromic product (arguments are presented in the Discussion section). Comparison of the shape of the titration curve obtained with that of the reaction product from the Ro–fumarato–chromous ion reaction shows differences in the pH region 2–5.5, identical with those observed for investigations of the Ro–methyl fumarato–chromous ion system. The increase in acid content of the solution after reaction, equal to 39% of the total amount of the Ro complex reduced, is mainly ascribable to experimental error rather than to amide hydrolysis or coordination of Cr(III) to the NH$_2$ group.

Infrared Identification of Recovered Organic Ligands. (1) Ro–Methyl Fumarato. Reactions of chromous ion and the Ro–methyl fumarato complex were run over an acidity range of [H$^+$] = 0.1–4.4 *M;* single reactions using vanadous[33] and europous ions as reductants were also run at [H$^+$] = 1.0 *M*. All reactions were run at ambient temperature. Yields of organic material recovered were 80–90% of that theoretically possible. The ir spectra of isolated ligands were nearly identical with the reference spectrum of methyl hydrogen fumarate; in no instance were detectable amounts of fumaric acid present. An additional experiment was performed with chromous ion as reductant and using P$_2$O$_7$$^{4-}$ to labilize the organic ligand. Infrared analysis of the recovered ligand indicated that *ca.* 15% ester hydrolysis had occurred. Considering the extreme conditions required for ligand labilization (pH 8.5–9.0 for 20 hr), even this small amount of hydrolysis cannot be attributed to the reduction reaction. Cuprous ion was found not to catalyze ester hydrolysis during the redox reaction.

(2) Ro–Methyl Terephthalato. The extreme insolubility of the perchlorate salt in water required that reduction with chromous ion be carried out at low [H$^+$]. The infrared spectrum of recovered ligand compared quite closely to the reference methyl hydrogen terephthalate spectrum. Carbon–hydrogen analyses also indicated the material to be half-ester rather than terephthalic acid.

(3) Ro–Amidofumarato. The yield of organic ligand recovered by ether extraction was less than 20% of the theoretical value. Resolution of the infrared spectrum of the material was not exceptional, but it did correspond to a reference amidofumaric acid spectrum. Since amidofumaric acid is considerably more soluble in water than in ether, the poor yield of ligand recovered by ether extraction is consistent with the absence of amide hydrolysis. If amide hydrolysis had occurred, the fumaric acid which formed would have been extracted from the aqueous phase without difficulty.

Ligand Release during Chromous Ion Reduction of Ro–Methyl Fumarato. The quantity of ligand released during reaction when chromous ion was added to the reaction solution in 31 small aliquots was compared at several temperatures to that observed when the same amount of chromous ion was added in a single aliquot; for all runs [H$^+$] = 2.2 *M* so that reactions by the acid-dependent and acid-independent paths were approximately equal. A greater release occurred in the systems in which the chromous ion concentration during reaction was kept low; this difference in amount of ligand released increased with increasing reaction temperature (Table VIII).

The experiments were performed so as to minimize differences in the two systems in respect to the quantity of ligand released by spontaneous aquation of ligand-

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[32] D. K. Sebera, Ph.D. Thesis, University of Chicago, 1960.

[33] The reaction conditions for reduction by vanadous ion are not identical with those previously described.[1b] Our vanadous reagent contained considerable amounts of sulfate ion, which could possibly alter the reaction mechanism.

Table VIII. Ligand Release in the Chromous Reduction of Ro–Methyl Fumarato

Temp, °C (±0.10°)	Total reaction time, hr	% reduction	% ligand released: Single addition (1)	% ligand released: Multiple additions (2)	ΔL (2) − (1)
		Ro–FuOCH$_3$ *vs.* Cr^{2+}			
25.0	2.0	91	2.1	3.2	1.1
35.0	2.0	90	4.9	7.9	3.0
35.0	1.0	70	3.4	5.6	2.2
45.0	1.0	70	9.8	14.3	4.6
45.0	1.0	70	9.5	13.8	4.3
		Ro–FuOH *vs.* Cr^{2+}			
45.0	1.0	70	12.1	11.1	−1.0

containing reactant and product. These and other reactions which might alter the amount of free ligand in solution, *e.g.*, chromous ion catalyzed aquation of the Cr(III) product and chromous ion reduction of the free organic material, were shown to be unimportant or cancel in the two systems under the experimental conditions employed. This was done by substituting Ro–fumarato for Ro–methyl fumarato and duplicating the experimental procedures. Equal quantities of fumaric acid were released with single and multiple additions of chromous ion (Table VIII). Since the above reactions should exert comparable effects in the Ro–fumarato and Ro–methyl fumarato reductions, this observation implies that the differences noted in the amount of ligand released for the Ro–methyl fumarato systems are not due to the reactions mentioned above. The differences in the quantity of ligand released can thus be attributed to competitive reactions of an intermediate Cr(III) species without worry of their being artifacts. The intermediate suggested is an ester-bound Cr(III)–methyl fumarato complex. This intermediate disappears by the competitive processes (a) spontaneous aquation and (b) Cr^{2+}-catalyzed rearrangement. The activation energy for substitution (a) is expected to be higher than for electron transfer (b), and this is consistent with the fact that the yield of free ligand increases as the temperature is raised (see Table VIII).

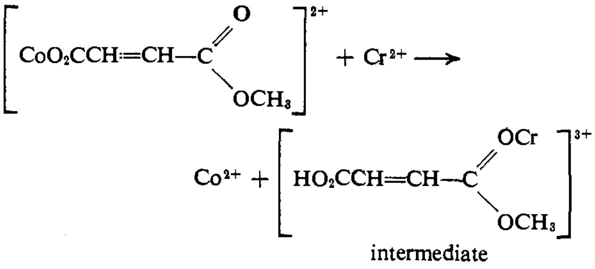
The data on ligand release make it possible to estimate an upper limit for the rate of outer-sphere reduction of RoFuOCH$_3{}^{2+}$ by Cr^{2+}. Attack by this mode would form free ligand, and the extent of this reaction is expected to be almost the same for RoFuOH^{2+} and RoFuOCH$_3{}^{2+}$. At 25° when [H$^+$] = 2.2 *M*, only *ca.* 2% of the ligand is noncoordinated after reduction. This leads to a value of $k_{\text{os}} \leq 5 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$. Since aquations of reactant, intermediate, and product are not allowed for in this calculation, k_{os} is probably much less than the upper limit which has been recorded for it.

Discussion

Evidence acquired during the present investigations demonstrates conclusively that very little hydrolysis accompanies reduction of the cobalt(III) center in the Ro–methyl fumarato and Ro–methyl terephthalato complexes. These observations are contrary to reports of earlier studies on these complexes, although the present experimental procedures include those followed in the earlier work. No particular source of experimental error can be identified in studying the description of the procedures of the earlier work. While it is true that perchlorate ion was not removed from aqueous solutions of the organic ligand before ether extraction in the previous studies, and present investigations indicate that failure to do so causes considerable amounts of ester hydrolysis, nevertheless the methyl half-ester, rather than the acid, was isolated in the previous work when Ro–methyl fumarato was reduced with reagents which probably react by an outer-sphere mechanism, *i.e.*, chromous and vanadous tris-bipyridyl ions. This implies that experimental conditions during ether extraction were not so harsh as to cause extensive ester hydrolysis.

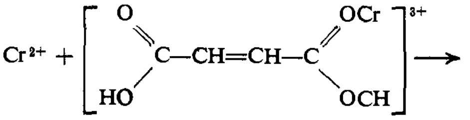
The results cited in the previous paragraph show that the ligands remain intact on electron transfer. The study of the product absorption spectra for the systems with the half-ester and the amide fumarate as ligands shows moreover that these ligands are bound to Cr(III) at the carboxylate ends. This conclusion gets the strongest support from the study of the rates of aquation, which prove to be typical of those of carboxylate rather than amide[30] or ester bound complexes.

The fact that the ligands are bound at the carboxyl ends to Cr(III), though consistent with the conclusion that attack takes place at the adjacent carboxyl group, by no means demands it. It is possible that the primary product is formed by remote attack, as illustrated below for the half-ester complex



(4)

and that the intermediate then rapidly is isomerized to the final product by Cr^{2+} as shown in eq 5.



$[\text{CrFuOCH}_3]^{2+} + \text{H}^+ + \text{Cr}^{2+}$ (5)

This kind of mechanism, though it may at first sight seem contrived, has much to recommend it. It is not completely *ad hoc*, for it has in fact been observed in other systems.[30,34] Moreover, it provides a natural explanation of the fact that the half-ester is released to the solution when the steady-state concentration of Cr^{2+} is kept low in the reduction of the half-ester Co(III) complexes (when Cr^{2+} is low, the intermediate has a greater opportunity to lose the ester ligand by aquation before the Cr^{2+} can cause isomerization to the stable, carbonyl-bound form).

$$[(\text{H}_2\text{O})_5\text{CrCH}_3\text{OFuH}]^{3+} + \text{H}_2\text{O} \longrightarrow \text{Cr(H}_2\text{O)}_6{}^{3+} + \text{HFuOCH}_3 \quad (6)$$

Finally, the observations made with the complex having

$$\underset{\text{H}_2\text{N}}{\text{O=C}}\text{—CH=CH—}\underset{\text{OCH}_3}{\text{C=O}}$$

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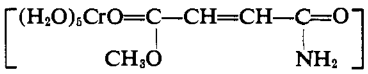
[34] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, 87, 4210 (1965).

as ligand suggests that, in this case, Cr^{2+} attacks at the ester end. Attack at the amide end can be eliminated from consideration because the Cr(III) product is the hexaaquo ion rather than a ligand complex. An outer-sphere-activated complex is unlikely because the rate of reaction is so high. Attack at the ester end would explain the high rate and the nature of the products. In view of the known behavior of the ester complex of $Co(NH_3)_5{}^{3+}$, a complex of the type



$$\left[(H_2O)_5CrO{=}\underset{CH_3O}{\underset{|}{C}}{-}CH{=}CH{-}\underset{NH_2}{\underset{|}{C}}{=}O\right]$$

is also expected to aquate rapidly.

The arguments made in the previous paragraph only serve to show that it is possible that reduction of the various Ro–fumarato complexes by Cr^{2+} take place by remote attack. As positive evidence that this is the case, we have the fact that reduction of the methyl amidofumarate complex yields $Cr(H_2O)_6{}^{3+}$ (to the extent that the arguments presented earlier are accepted, the results imply that the reaction in this particular system proceeds mainly by remote attack) and the fact that there is partial release of ligand, dependent on $[Cr^{2+}]$, when the half-ester complex is reduced by Cr^{2+} (this argues for at least some remote attack in the latter case). Direct evidence based on identification of intermediate or final products for remote attack in the other cases (*i.e.*, amidofumarate or acid fumarate as ligands) is entirely lacking.

Though only partial conclusions about the mechanism of reaction have been reached, it is of interest to examine the rate data in their light. The fact that the reduction of $RoFuOH^{2+}$ shows a k_1 term has been used[5] as evidence for remote attack, the supporting argument being that the effect of the proton is to associate with the adjacent carbonyl, thus redistributing the double bond and improving conjugation between the metal ion centers. This explanation remains plausible, but it is by no means obligatory. If adjacent attack is assumed, the high value of k_0 compared to the corresponding term for succinate can be ascribed to the presence in the fumarate but not succinate of a low-lying, unoccupied orbital, and the k_1 term can be rationalized by assuming protonation at the remote end, the addition of the positive charge lowering the energy of the unoccupied orbital.

The question at issue probably is not resolvable in "either–or" terms and both mechanisms may contribute to reaction, the relative contributions depending on the particular ligand and on whether the k_0 or k_1 path is in question. It is quite likely that the k_0 path corresponds largely to adjacent attack. This view is supported by the observation that the value for k_0 is almost the same for $FuOCH_3^-$, $FuNH_2^-$, and $FuOH^-$ as ligands; moreover, taking account of the reduced steric requirement[10] for the unsaturated fumarate as compared to the saturated succinate system, a value of k_0 as large as 1.2 for adjacent attack, compared to $\sim$0.20 for succinate,[5] is not unexpected, even without making allowance for an influence on the rate of the conjugated bond system in fumarate. The values of k_1 do depend on the nature of the substituents on the remote end of the fumarate ligand, and this suggests at least a partial contribution by remote attack, in harmony with the conclusion reached on the basis of the ligand release data.

Assuming remote attack by the acid-catalyzed path for ligands having conjugated bond systems between two carboxylate functions, it has been suggested[5] that in providing a new reaction path the proton acts associating with the carbonyl oxygen adjacent to the Co(III) center. The high rate of reduction when $O{=}C(H_2N)$-$CH{=}CHC(OCH_3){=}O$ is ligand shows that the suggestion as to the role of the proton has merit. The oxygen attached to Co(III) is expected to have more double-bond character as part of an amide rather than of a carboxyl group. The increase in the rate of attack when methyl amidofumarate rather then methyl fumarate is ligand can than be understood on the basis of the increase in double-bond character in the O–C bond on the Co, leading to improved conjugation.

Acknowledgment. Financial support for this research by the National Institutes of Health, Grant 13638-01, is gratefully acknowledged. Acknowledgment is also made to the National Science Foundation, Grant G-22661, for the spectrophotometer.