$$\left[\begin{array}{c} O \\ HO \end{array} \!\!\!> C\text{--}CH\!=\!\!=\!CH\text{--}C\!\!<\!\! \begin{array}{c} OCr \\ OCH_3 \end{array} \right]^{+++}$$

formed as product of the electron transfer process, and because of the known inertia of Cr(III) complexes to substitution, it would not be too surprising that a C–O rather than a Cr–O bond breaks on hydrolysis. However, this explanation is hardly reasonable for the analogous V^{+++} and Eu^{+++} complexes, because these cations form complexes which are extremely labile. Furthermore, because the V^{+++} and Eu^{+++} complexes are labile, half-ester complexes of the kind indicated can be formed directly from the cations and the ligands without resort to the indirect process involving electron transfer, but no ester hydrolysis in the corresponding blank experiments is observed. To accommodate the experimental results for Cr^{++}, V^{++} and Eu^{++} as reducing agents, we incline to the view that the activation for the hydrolyses takes place in an intermediate which contains the Co center as well as the reducing cations associated with the ligand.

When $Cr(dip)_3^{++}$ and $V(dip)_3^{++}$ are the reducing agents, electron transfer can take place readily by an outer-sphere activated complex.[9] Thus in the reactions of these reducing agents, direct bonds between metal ion and oxygens of the carboxyl groups probably are not involved. The fact that ester hydrolysis does not accompany electron transfer when the dipyridyl complexes are reducing

(9) A. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).

agents supports the view that the mechanism of reaction is different from that when Cr^{++}, V^{++} and Eu^{++} are used. This in turn suggests that when V^{++} and Eu^{++} react in the present systems, bridged activated complexes are formed. This probable conclusion is interesting for Eu^{++} and V^{++} because proof of the mechanisms by which they react have not been obtained by the direct method which can be applied to the reactions of Cr^{++}.

Even if our conclusion that the activation for hydrolysis takes place in an intermediate that contains the oxidizing and reducing metal ions directly bonded to the ligand is accepted, much remains to be discovered and explained about the electronic interactions between the metal ions and ligand group before the effect is understood. The explanation must accommodate the facts already explicitly mentioned, the fact that the effect is observed for a rare earth ion as well as transition metal ions and the fact that the rate of reaction by remote attack can be very sensitive to the nature of the functional group at the remote position. The last point is more fully documented by some of the systems described in another paper[8] and in the results reported here is illustrated by the fact that remote attack takes place when $-CONH_2$ and CONH (alkyl) are the remote functional groups but not to a significant extent when the group is $-CON(alkyl)_2$.

Activation Effects and Rates of Electron Transfer[1]

BY R. T. M. FRASER[2] AND H. TAUBE

The isomerization of maleic to fumaric acid which occurs as a result of electron transfer between $Cr_{aq.}^{++}$ or $V_{aq.}^{++}$ and $(NH_3)_5CoL^{++}$ (where L = hydrogen maleate or methyl maleate) has been studied and the ratio of fumaric to maleic acid is found to increase linearly with the hydrogen ion concentration of the solutions. The ester hydrolysis induced in the half ester ligands is shown to involve alkyl-oxygen fission almost quantitatively and aryl-oxygen fission up to 15% rather than the usual acyl-oxygen fission of ester hydrolysis. The specific rate constants for the electron transfer reactions of $Cr_{aq.}^{++}$ and a number of cobalt(III) complexes have been measured; those involving adjacent attack show no hydrogen ion dependence and have $k_2 \approx 0.16$ sec.$^{-1}$ at 25° ($\mu = 1$). When the ligand L is p-aldehydobenzoate or hydrogen terephthalate, the rate of reaction is too great to be measured. When p-sulfobenzoate and cyclopropane dicarboxylate are ligands, the rates are those characteristic of adjacent attack, and there is no increase in rate with the concentration of hydrogen ion.

Introduction

In an earlier paper[3] evidence was presented for electron transfer through the ligands in the reaction of Cr^{++} with certain complex ions of the type $(NH_3)_5Co(III)L$. A major part of this evidence was the observation that in some systems an ester group present in the ligand L but remote from the Co(III) center undergoes hydrolysis on electron transfer. In this paper, the emphasis is shifted from these observations as evidence for electron

(1) From a dissertation submitted by R. T. M. F. in partial fulfillment of the requirements for the Ph.D. degree, December, 1959.

(2) Bell Telephone Laboratories Predoctoral Research Fellow, 1959.

(3) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, 2239 (1961).

conduction through bridging groups to the activation of the bridging groups brought about by the electron transfer. New features of the activation of the bridging group for ester hydrolysis are brought out, kinetic data on certain of the systems are reported and evidence for an *additional* activation effect, *cis–trans* isomerism brought about by electron transfer, is outlined.

Experimental

The preparations of the cobalt(III) complexes and the reductants have been described previously.[3]

Determination of the Oxygen Isotopic Composition in Organic Compounds.—The organic material was purified and dried for several days and the oxygen isotope ratio de-

termined by the method of Anbar and Guttmann.[4] 40 mg. of the compound was mixed with 300 mg. of powdered mercuric chloride and cyanide (in the proportions 4:1). The resulting powder was poured into U-tubes 10 mm. in diameter, fitted with break-seals and 14/35 male joints. The tubes were evacuated, sealed and heated at 400° for 2 hr. After cooling, they were opened on a vacuum line, the contents transferred to similar U-tubes containing 1 g. of saturated zinc amalgam and cooled in liquid nitrogen. After ten minutes the tubes were evacuated and sealed, they were then heated at 200° for 2 hr. and opened on the vacuum line. Any water remaining in the sample was removed by cooling in a Dry Ice–methanol slush and the carbon dioxide condensed into tubes fitted with stopcocks. The isotopic ratio of O^{18}/O^{16} was determined on the mass spectrometer.

Spectrophotometric Measurement of Rates.—These measurements were made on a Cary Model 14 Spectrophotometer set at a point of maximum absorption of the cobaltic complex. The apparatus used in the measurements and the method of evaluating the specific rates have been discussed before.[5]

Results

A. Isomerism in the Reaction of Pentamminomaleato- and Pentamminomethylmaleato-cobalt (III) Ions with Reductants.

—In a preliminary study of the reaction mixtures obtained from the methylmaleato complex and chromous ion, two species, one of external valency one, the other of charge two, were found when the solutions were poured through cation exchange columns, after the method of King.[6] Fig. 1 shows the percentages of +1 and +2 forms found after reaction, as a function of the hydrogen ion concentration of the solutions. These two forms of the complex ion are taken to be the maleato (which can chelate) and the fumarato, respectively,[7] a conclusion which is supported by the results obtained by extracting the product solutions with ether but using V^{++} as the reducing agent.

Using vanadous ion as reductant, it is possible to extract the organic acid from solution without pyrophosphate treatment. It was found that not one but two organic acids were present, and it was possible to bring about a partial separation of these by ether extraction. The two acids were identified from their infrared spectra as maleic and fumaric acid. Table I lists the acid (as a percentage of the total organic acid in the cobalt(III) complex) extracted by the ether.

TABLE I

PERCENTAGE OF ORGANIC ACID EXTRACTED AFTER FRACTIONATION OF THE METHYLMALEATO COMPLEX WITH V^{++}

(H^+), M	Extraction time, hr.	% Extracted	Comment
0.5	0–3	85	Fumaric acid
	3–10	11	Mixture
	10–18	2	Maleic acid
0.1	0–3	56	Mixture
	3–10	30	Maleic acid
	10–18	11	Maleic acid
0.055	0–3	44	Mixture
	3–10	34	Maleic acid
	10–18	18	Maleic acid

The reaction of the methylmaleato complex with V^{++} was also carried out in D_2O to learn whether

(4) M. Anbar and S. Guttmann, Intern. J. Appl. Radiation and Isotopes, 5, 233 (1959).

(5) D. K. Sebera and H. Taube, J. Am. Chem. Soc., 83, 1785 (1961).

(6) E. L. King and E. B. Dismukes, ibid., 74, 1674 (1952).

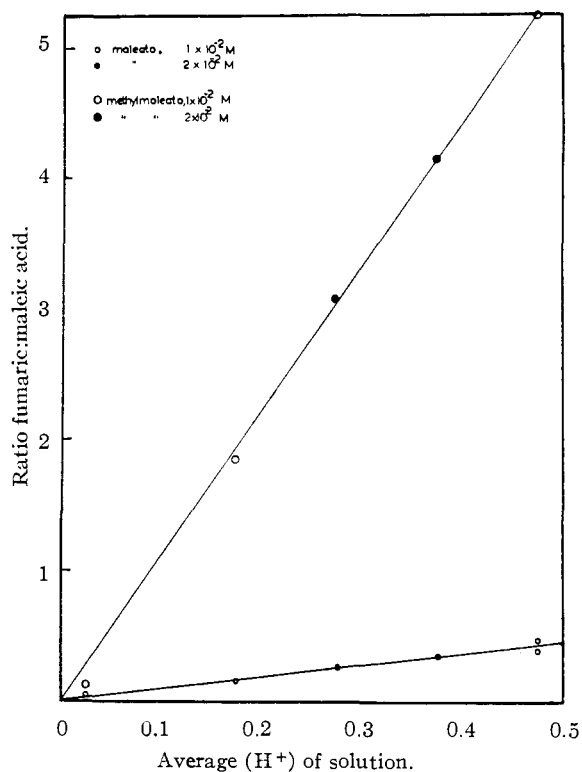(7) R. T. M. Fraser and H. Taube, ibid., 83, 2239 (1961).

Fig. 1.—Relative yields of fumaric and maleic acid as functions of hydrogen ion concentrations.

—HC= exchange with the solvent takes place. A solution containing 1.35×10^{-2} M methylmaleato complex and 0.7 M $HClO_4$ was prepared in 96% D_2O. An equivalent amount of vanadous ion was added. The solution was treated to recover the organic acid. The acid was dissolved in H_2O of normal isotopic composition and after recovery the infrared spectrum of the solid was taken.

Table II lists infrared absorption peaks for the acid which was recovered.

TABLE II

RELATION BETWEEN CALCULATED AND OBSERVED ABSORPTION FREQUENCIES

C–H fumaric, cm.$^{-1}$	C–D calcd., cm.$^{-1}$	Peaks found, cm.$^{-1}$
3040	2150	2200
2905	2060	2090
1310	926	940
1000	707	700

Upon repeating the experiment in a solution of low acid concentration to favor formation of maleic acid and using the extraction process for further separation, a sample of pure maleic acid was obtained. The infrared spectrum of this was identical with that of the normal acid—it showed no peaks due to C–D bands.

Maleate is not formed in appreciable amount when the fumarate complex reacts with Cr^{++}, V^{++} or Eu^{++}. Other work[5] has shown that no —HC= exchange occurs when acid fumarato pentamminecobalt(III) reacts with Cr^{++}.

B. The Position of Bond Breaking in the Ester Hydrolysis.

—Electron transfer reactions between

Cr_{aq}^{++} and the cobalt(III) complex were carried out in water enriched in O^{18}. Table III lists the O^{18} enrichment found in the product acid after extraction. The enrichment ratio (e.r.) in this table is the ratio of O^{18}/O^{16} compared to that of the starting material of normal isotopic composition.

TABLE III

ENRICHMENT OF ORGANIC ACID

Complex	Reductant	E.r. of product acid	% Enrichment[a]
Methylfumarato	Cr^{++}	1.048	
Methylfumarato	Cr^{++}	1.051	1.8 (av.)
Methylfumarato	V^{++}	1.072	2.6
Methylmaleato	V^{++}	1.066	2.4
Maleato	V^{++}	1.063	2.3

[a] Percentages obtained by considering one oxygen out of the four for each anion to be enriched.

The values of % enrichment are upper limits for the fraction of bonding-breaking at the acyl position since some exchange of the organic acid and the enriched solvent can be expected.

In the experiments using the phenylfumarato complex, both the phenol and the fumaric acid obtained after reaction were examined for O^{18} content. In the case of $Cr_{aq}.^{++}$ as reductant, only 60% of the total phenol could be obtained by extraction with ether without preliminary treatment of the chromium(III) residue with pyrophosphate. After pyrophosphate treatment, all the phenol was released. The values in Table IV give the fraction of bond breaking at the $-C\overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}}$ position and the C_6H_5+O position as calculated from the isotopic compositions of the fumaric acid, phenol and that of the solvent.

TABLE IV

POSITION OF BOND BREAKING IN THE REACTION OF THE PHENYLFUMARATE COMPLEX WITH REDUCING AGENTS

Compound	Reductant	0.1 M	0.5 M	0.25 M	0.05 M
Fumaric acid[a]	V^{++}	0.925	0.898	0.884	0.875
Phenol[b]	V^{++}	.071	.094	.105	.118
Phenol[b]	Eu^{++}	.022	.015[c]	.017	
Phenol[b]	Cr^{++}	.087	.055	.072	

(As calculated from the enrichment (a) of the fumaric product (b) of the phenol product, the reaction taking place with complex of normal isotopic composition in O^{18} enriched solvent.) [c] $H^+ = 0.41 M$.

The results with V^{++} as reducing agent provide a check on the isotopic balance which appears to be quite good.

C. **Rate Measurements.**—The form of the rate laws has been discussed.[5] Values obtained for the specific rates of a number of complexes are listed in Table V. k is defined by the relation

$$\frac{-d(Co(III))}{dt} = k(Cr^{++})(Co(III))$$

The ionic strength in each case was 1.01. Of the complexes studied, only the phenylfumarato and the phenylterephthalato showed a variation of rate with (H^+). The rate laws expressed in full for these complexes are

$$Rate = 1.38\ (Cr^{++})(CoL^{++}) + 0.61\ (Cr^{++})(CoL^{++})(H^+)$$
$$22°$$

$$= 0.80\ (Cr^{++})(CoL^{++}) + 0.75\ (Cr^{++})(CoL^{++})(H)^+$$
$$9°$$

for the phenylfumarato, and

$$Rate = 0.05\ (Cr^{++})(CoL^{++}) + 0.4\ (Cr^{++})(CoL^{++})(H^+)$$
$$24°$$

$$= 0.045\ (Cr^{++})(CoL^{++}) + 0.18\ (Cr^{++})(CoL^{++})(H^+)$$
$$9°$$

for the phenylterephthalato complex (concn. in mole l.$^{-1}$, time in sec.).

TABLE V

SUMMARY OF SPECIFIC RATE CONSTANTS FOR PENTAMMINO-COBALT(III) COMPLEXES AND CHROMOUS ION

$((NH_3)_5Co(III)L) = 1.0 \times 10^3\ M;\ \mu = 1.01$

Complex	$(Cr^{++})_s$, M	(H^+), M	Temp., °C.	k, M^{-1} sec.$^{-1}$
p-Sulfobenzoate	0.02	0.2	27	0.164
	.02	.4	27	.164
	.04	.2	27	.168
	.02	.2	8	.060
	.02	.4	8	.062
	.04	.2	8	.060
p-Aldehydobenzoato	.008	.2	20	>500
methyltereph-	.02	.2	25	.165
thalato	.02	.4	25	.167
	.02	.2	24	.155
	.02	.4	24	.170
	.02	.2	9	.096
	.02	.4	9	.100
	.04	.2	9	.097
Phenylterephthalato	.02	.2	27	.138
	.04	.2	27	.138
	.02	.2	24	.129
	.02	.4	24	.207
	.02	.6	24	.287
	.02	.2	9	.081
	.02	.4	9	.117
	.02	.1	9	.061
cis-Cyclopropane-dicarboxylato	.02	.2	30.5	.22
	.02	.4	30.5	.23
	.02	.2	8	.071
	.02	.4	8	.073
trans-Cyclopropane-dicarboxylato	.02	.2	25	.151
	.02	.4	25	.154
	.02	.1	8	.072
	.02	.2	8	.074
Phenylfumarato	.02	.1	22	1.45
	.02	.2	22	1.50
	.02	.4	22	1.60
	.02	.6	22	1.76
	.02	.2	9	0.95
	.02	.4	9	1.10
	.02	.6	9	1.23

The rates of reaction of chromous ion with the hydrogen terephthalato, the beta-benzoylacrylato and p-aldehydobenzoato complexes were too fast to be measured.

D. **Heats and Energies of Activation.**—Table VI lists ΔH^* and ΔS^* for the rate of electron transfer by the (H^+) independent path.

Discussion

Two kinds of activation of bridging groups concomitant with electron transfer have been discovered, the hydrolysis of esters and the isomerization of maleate to fumarate.

TABLE VI

EXPERIMENTAL HEATS AND ENTROPIES OF ACTIVATION FOR
THE (H^+) INDEPENDENT PATH

Complex	k_1 at 25°, M^{-1} sec.$^{-1}$	ΔH^*, kcal. mole^{-1}	ΔS^*, e.u.
p-Sulfobenzoato	0.16	8.3	−34
Methylterephthalato	.17	5.1	−45
Phenylterephthalato	.05	0.15	−62
Phenylfumarato	1.45	4.3	−43
cis-Cyclopropanedicarboxylato	0.16	8.1	−35
trans-Cyclopropanedicarboxylato	0.15	6.5	−41

Many features of the phenomenon of ester hydrolysis brought about by electron transfer and even the fact of ester hydrolysis itself are only incompletely understood. Thus the succession of formal changes which can be written[6] to account for electron conduction by a conjugated system does not involve the alkoxy group of the carboxyl at all and in itself does not provide an explanation of the hydrolysis. The present discussion of the phenomena will be less an effort to provide an explanation of the results than to summarize them, drawing attention to the features brought out in the present study which we consider to be particularly significant or interesting.

One of the striking features of the process of ester hydrolysis accompanying electron transfer is that—at least when alkyl half esters are the ligands —fission takes place adjacent to the alkyl group rather than adjacent to the carbonyl group as would be the case for ordinary hydrolysis of the ester. The tracer experiments which support this conclusion seem to us to be convincing, and the conclusion finds additional support in experiments which have been done using esters of crotyl alcohol and of optically active alcohols.[8] The observation that bond fission takes place at the alkyl–oxygen bond shows that the activation for hydrolysis is not of the kind that is brought about by acids. Therefore, the metal ion at the remote end cannot be regarded simply as a positive center acting by its influence on the carbonyl oxygen of the ester. The observation eliminates as a requirement of the mechanism for the alkyl esters that the alcohol-chromium complex be formed while the chromium is substitution labile, that is before it has become Cr(III), because the complex can be formed by the transfer of a carbonium ion to an oxygen which is firmly bonded to chromium. The experiments with the phenylfumarato group as ligand, however, do seem to require that the Cr-alkoxy bond be established while the chromium is substitution labile. The extent of capture of phenol, ca. 40%, as shown by the results in extracting the product solutions, much exceeds the extent of $C_6H_5 + O$ bond fission, which is only about 10%. The extent of capture may in fact greatly exceed 40%, since the rate of spontaneous loss of phenol from the coordination sphere of a chromic complex is not known.

An apparent paradox in the observations is that the carbonyl group of an aldehyde or ketone group in the remote position conjugated through an aromatic ring with the carboxyl bearing the Co(III) brings about rapid electron transfer but without demanding the dramatic rearrangements that take place when an ester group occupies the remote position. On the other hand the terephthalate half-esters, though they do contain a carboxyl group, bring about electron transfer much less rapidly. The apparent paradox is resolvable if, as seems certain,[5] the rates do not measure the conductance of the bridging groups but measure the ease with which the atomic readjustments necessary to have effective conjugation take place. Among these would be the readjustment of the plane of the remote carbonyl or carboxyl to the plane of the benzene ring in terephthalate, changes in bond length, as well as the changes common to the systems in the first coördination spheres and the solvent layers about the ions. The activation for ester hydrolysis is then an effect that accompanies the electron transfer process when a suitable functional group is present. Thus, it may require binding the metal ion to both oxygens of the remote carboxyl group, and the intermediate responsible may derive stability from the interaction of the metal ion centers through the conjugated system.[3] From this point of view, activation for hydrolysis is not a necessary consequence of electron transfer through the ligand, but the conditions necessary for remote attack by the reducing agent are minimum conditions for activation for hydrolysis.

The above is at best a phenomenological analysis of part of the problem, and it leaves unanswered a number of the questions which are raised by the observations. Why for a series of fumarate half-ester complexes is the rate almost independent of the nature of the ester group, and in fact independent of whether the remote carboxyl bears H, D, CH_3[5] or C_6H_5, but in the terephthalate series, the rate is quite sensitive to these changes? And why in the fumarate series, when amide rather than carboxyl constitutes the remote functional group, is the rate sensitive to the degree of substitution on the amide nitrogen?[9] Why, for the fumarate esters, including phenyl fumarate as ligand, does ester hydrolysis take place by both paths ((NH_3)$_5$CoL^{++})(Cr^{++}) and ((NH_3)$_5$CoL^{++}) (Cr^{++})(H^+)) but with phenyl terephthalate only by the path corresponding to the second term above? This conclusion is indicated by the fact that the ester hydrolysis increases as the second term of the rate law accounts for an increasing fraction of the total reaction and it is supported by additional data.[10] Why does the methyl terephthalato complex react at the slow rate characteristic of adjacent attack, but still undergo essentially complete hydrolysis? The methyl terephthalato complex seems so much out of line with the behavior of other esters of the series that we

(8) R. T. M. Fraser, Proc. Chem. Soc., 317 (1960). When but-2-enyl is the alcohol radical, but-3-en-1-ol is the principal product (80 ± 5% yield) and the balance is rearranged to but-3-en-1-ol; when (+)-S-butyl is the alcohol radical, some, but not complete, racemization is observed on hydrolysis.

(9) The experiments which provide the basis for this comparison are not reported in detail because the specific rates were not measured with precision. They sufficed, however, to show that at 25° with (H^+) at 0.10 M, and μ = 0.1, the specific rate for the reaction of Cr^{++} with the amidofumarato complex is ca. 0.4 M^{-1} sec. $^{-1}$, and with the diethyl-amidofumarato complex it is 0.10 M^{-1} sec. $^{-1}$.

(10) R. T. M. Fraser, J. Am. Chem. Soc., 83, 564 (1961).

are inclined to raise a question about the identity of the compound in spite of the fact that it conforms well to the expected analysis (calcd.: Co, 13.9%, N, 15.9%; found: Co, 13.9%; N, 14.9%) and in spite of the fact that it is known to be a half-ester complex (the solid material has no titratable acid but acid is produced on electron transfer).

The kinetic data reported for the complexes, with the exception of those for the methylterephthalato complexes, appear to be internally consistent. In those cases in which remote attack reasonably can be expected, rapid rates are observed and perhaps more significantly, there is a term in the rate law proportional to the concentration of hydrogen ion. The specific rate for the p-sulfobenzoate complex is low and the rate is independent of acid. Both observations imply that in this case adjacent attack occurs, and this is consistent with the fact that the carboxylate rather than the sulfonate complex of Cr(III) is formed.[3] The difference in behavior of the terephthalato and p-sulfobenzoato complexes demonstrates that conjugation of the carboxyl group with the aromatic ring is much more readily achieved than for a sulfonate group. The specific rates observed for the dicarboxylic acids derived from the cyclopropane ring show that in these systems also conjugation between the carboxyl groups through the cyclopropane structure is not achieved readily.

We have little to add at the present time to the suggestion made earlier[7] about the mechanism of cis–trans isomerism brought about by electron transfer. The suggestion is that in effect a radical is formed with H added to the double bond but made up by an electron from the reducing agent and a proton from the solvent. This interpretation in turn suggests that a radical of finite life is formed when maleate is the bridging ligand. A similar radical does not appear to be formed when fumarate is the bridging group. This conclusion is based less on the fact that maleate does not form from fumarate than it is on the fact that fumarate does not undergo exchange with the solvent of the ethylene hydrogen even in strongly acidic solution when it acts as the bridging group.[5] It seems likely that the mechanism of electron transport for the two bridging groups is different, the maleate only conforming to a "chemical" mechanism involving the formation of a radical intermediate.

The data of Fig. 1 show that fumarate formation and maleate formation proceed by parallel paths, with the former reaction involving one more proton in the activated complexes than does the latter. For the half ester complexes these paths are to be described by the rate functions $(Cr^{++})(NH_3)_5CoH_2C_4O_4CH_3^{++})$ and $(Cr^{++})((NH_3)_5CoH_2C_4O_4CH_3^{++})(H^+)$, with the former path leading to the formation of the maleato complex of Cr(III) and the latter to the fumarato complex. Since the acid maleato complex gives a similar dependence of the relative rates of formation of the maleato and fumarato product complexes we infer that the corresponding rate terms are $(Cr^{++})((NH_3)_5CoH_2C_4O_4H^{++})$ and $(Cr^{++})(NH_3)_5CoH_2C_4O_4H^{++})(H^+)$. The higher yield of the maleato Cr(III) complex which is obtained when the acid maleato Co(III) complex reacts compared to that obtained when the methylmaleato Co(III) complex reacts suggests that in the activated complex for the formation of the maleato Cr(III) complex, chelation of the bridging group with chromium takes place. For effective chelation, the negative charge on the end of the maleato remote from Co(III) must be freed, and this is easier to accomplish when H^+ rather than CH_3^+ occupies the remote carboxyl.

If it is indeed true that the maleato complexes react by transfer of the electron to the ligand in the first step, the ester hydrolysis accompanying electron transfer requires special consideration. It is difficult to see why electron conduction to the ligand *requires* such a dramatic redistribution of electrons in the alkoxy bond as to produce loss of the alkyl group, particularly when we bear in mind that ketonic or aldehydic carbonyls readily rearrange to a conducting state (*cf.* paragraph following Table V). A possible explanation is that for the part of the reaction leading to fumarate formation, ester hydrolysis takes place after fumarate is formed by the process, whatever its character, that ordinarily leads to fumarate ester hydrolysis on electron transfer; while for the maleate product, ester hydrolysis may occur for a different reason, which is that the alkoxyl group yields to the demand of the maleate for closing the chelate.

These suggestions as well as the questions raised call for further experiments, some of which are obvious, and others which will become obvious only after the phenomena are better understood.