Remote Attack and Ester Hydrolysis on Electron Transfer[1]

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

The electron transfer reaction between Cr^{++} aq. and $(NH_3)_5CoL^{++}$ (where L is the phenyl or methyl half ester of fumaric or terephthalic acid) takes place through attack by the reductant at the carboxyl group remote from the cobalt center. Ester hydrolysis occurs, and the alcohol is found associated with the Cr(III) complex after reaction. Hydrolysis is also found when V^{++} aq. or Eu^{++} aq. are the reductants, but not when Fe^{++} ($C_2O_4^-$ present), nor is it found with the tris-dipyridyl complexes of V^{++} and Cr^{++}, showing that the formation of a bridge complex is a necessary concomitant. Using fumarate or terephthalate as conducting ligands, the nature of the terminal functional group has been varied: with $-CONH_2$, $-CONH\cdot CH_3$, $-CHO$, $-CO(C_6H_5)$ remote attack takes place but not with $-SO_2OH$ or $-CON(C_2H_5)_2$.

Introduction

Recent interest[3,4] has been shown in electron transfer reactions between chromous ion and pentamminocobalt(III) complexes $(NH_3)_5CoL^{++}$, when L is an organic ligand. The specific rate constants for a number of these systems have been determined,[4] and in the case of the methylfumarato complex the suggestion has been made that ester hydrolysis accompanies electron transfer. This point now has been investigated further and the hydrolysis of esters established as a rather general phenomenon during electron transfer. It has now also been established that chromous ions will attack the organic ligand at a point remote from the cobalt (III) center and electron transfer occurs by conduction through a conjugated system. Vanadous and europous ion also can react by remote attack. It has been found that the remote attack depends not only on the presence of a ligand permitting conjugation between the metal centers but also upon the nature of the functional group at the end of the organic system.

Experimental

Materials.—Pentamminoaquocobalt(III) perchlorate, the starting material for preparation of the cobalt(III) complexes, was prepared by the method of Basolo and Murmann.[5] The general method previously described[4] for preparing the complexes $[(NH_3)_5Co–L](ClO_4)_2$ was used for L = methyl fumarate, amidofumarate, methylamidofumarate, diethylamidofumarate, maleate, p-aldehydobenzoate, methyl terephthalate, phenyl terephthalate, $trans$-cyclopropanedicarboxylate, cis-cyclopropanedicarboxylate and p-sulfobenzoate.

Some variation of the conditions of time and temperature were necessary in preparing other complexes. Pentamminophenylfumaratocobalt(III) perchlorate was obtained only after heating at 70–80° for periods up to two days and then in low yield. Further heating caused significant hydrolysis of the half ester, with subsequent formation of the hydrogen fumarate complex. The pentammino(β)-benzoylacrylato complex was prepared by heating the reagents at temperatures 45–50° for long periods of time. Polymerization of the ligand occurred readily, yielding a brown tar which contained cobalt(III).

The hydrogen terephthalato complex was successfully obtained from the p-aldehydobenzoate by passing chlorine through an aqueous solution cooled in ice-water. The rate of oxidation was followed by titration. After pumping off the excess chlorine at room temperature, the solid complex was obtained by adding concentrated perchloric acid and recrystallizing the precipitate.

Elemental analyses of the nitrogen and chlorine content of the complexes were made. In general the method (Dumas) used for nitrogen gave low results; chlorine values agreed well, in every case within 1.3% of the calculated value.

A preliminary infrared examination of the complexes was made as they were prepared. When the absorption spectra were sharp and did not change after recrystallization of the solid, the compounds were submitted for analysis. The percentage of free organic acid in each complex was determined by titration with standard alkali.

All reagents used were analytical grade, unless otherwise specified. The chromous, europous and vanadous solutions were prepared by reduction in a nitrogen atmosphere over zinc.

Vessel for Oxidation-Reduction Reactions.—A 50 ml. flask with one male and one female joint was used. The oxidant solution was degassed with oxygen-free nitrogen, the flask fitted to the buret of the reductor and nitrogen flushed through the flask and buret. Air was excluded by fitting a side arm to the male joint and leading the exit gases through water. The required volume of reductant solution was measured in the buret and run directly into the reaction flask.

For experiments in which it was necessary to remove aliquots from the reaction mixture, the side arm was replaced by a capillary tube connected to the nitrogen supply. Samples then could be removed through the exit tube. The temperature during reaction was held constant by surrounding the flask with a Dewar containing water.

Distillation of Reaction Mixtures.—Solutions containing metal ions and organic compounds were transferred to a 40 ml. flask and treated with sodium bicarbonate to neutralize any acid present. An all glass distillation apparatus was used: the receiver was cooled in liquid nitrogen, the distilling flask was surrounded by an ice-bath and the exit tube of the receiver was connected to an oil pump through a trap cooled in liquid nitrogen.

Determination of Methyl Alcohol.—The method was a modification of that proposed by Boos:[6] to 1 ml. of the test solution was added 0.4 ml. of a solution of 5 g. of potassium permanganate dissolved in 200 ml. of 15% phosphoric acid. After five minutes, enough sodium bisulfite was added to decolorize the solution, then 200 mg. of solid chromotropic acid was mixed in, and the solution was cooled in an ice-bath, 5 ml. of concentrated sulfuric acid added and the mixture shaken and left in the ice for two minutes. The optical density of the solution at 570 mμ was measured, a reagent blank subtracted and the alcohol content determined by comparison with standard curves previously prepared.

Potentiometric Measurements.—A Beckman model G pH meter equipped with glass and calomel electrodes was used in the titration of reaction mixtures with alkali. During these titrations nitrogen was blown through the solutions.

Measurements of infrared spectra were made on a Perkin–Elmer Model 21 equipped with sodium chloride optics.

Ether Extraction of Reaction Mixtures.—A simple continuous extractor was used: the tube between the reflux flask and the column, being lagged with three layers of cotton. Lubricant was not used on any joints, so the slight loss of ether entailed was not serious. Ether extracts were dried over sodium sulfate or potassium carbonate. When perchloric acid was present in the original solution, it was found possible to remove this from the ether by the addition of solid potassium chloride. Extracts were evaporated in a vacuum desiccator or on a hot plate.

(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) H. Taube, J. Am. Chem. Soc., 77, 4481 (1955).

(4) D. K. Sebera and H. Taube, 83, 1785 (1961).

(5) F. Basolo and R. K. Murmann, in "Inorganic Syntheses," Vol. IV, J. C. Bailar, editor, McGraw–Hill Book Company, Inc., New York, N. Y., 1953, p. 171.

(6) R. N. Boos, Anal. Chem., 20, 964 (1948).

Results

Investigation of the Cr(III) Product Solution.—
It has been shown[4] that the reaction between
chromous ion and the cobalt complex may be
represented satisfactorily by the equation

$$(NH_3)_5CoL^{++} + Cr^{++} + 5H^+ = Co^{++} + CrL^{++} + 5NH_4^+$$
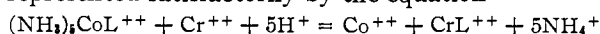
When the ligand L is the methyl half ester of
fumaric acid, titration of the mixture after reaction
shows an increase in acid content of the solution
equivalent to the amount of cobalt complex initially
present. This increase is best explained by hy-
drolysis of the methyl ester and, if this is so, then the
methyl alcohol must be present in the solution
either free, associated with the fumaric acid in some
way or associated with the chromium. An ex-
amination of the nature of the ligand L associated
with the chromium(III) after reaction was carried
out by extracting the solutions with ether. Pyro-
phosphate was added to the mixtures to form the
chromium(III)-pyrophosphate complex and release
L. The ether extracts were examined for methanol
as previously described. Infrared examination
and titration with alkali showed the presence of
any organic acid. Ether extractions were done
in two stages, extraction for 6 hr., then for a fur-
ther 18 with fresh ether. For this series of experi-
ments, Cr^{++} and the Co(III) half-ester complex
were each initially present at 1.2×10^{-2} M and
the concentration of $HClO_4$ was 0.10 M. When the
mixture after reaction was extracted with ether,
only 14% of the total fumarate was recovered
even after 29 hr. However, when the solution was
made 0.50 M in sodium pyrophosphate, ca. 67% of
the fumaric acid was recovered after 2 hr., and in
fact, 63% after only 6 hr. of ether extraction.

From a similar reaction mixture of the hydrogen
fumarate complex and chromous ion, after 0.5 M
$P_2O_7^{≡}$ had been added the percentage of organic
acid extracted was 64 and 5%, respectively, in the
6 and 18 hr. periods. Thus, whatever the cause of
the hold-back of 30% or so, it is not peculiar to the
half ester reaction.

To confirm that the extract was the free fumaric
acid and not the methyl ester, half of the solutions
made up from the extract after titration were
treated with an excess of concentrated hydro-
chloric acid and evaporated to dryness. This was
repeated twice. After removal of excess acid, no
increase in the titer figure of the organic material
was found. In every case the infrared absorption
spectrum obtained for the residues was identical
with that of fumaric acid. No trace of acids such
as malic, maleic or methoxysuccinic was found.

In an attempt to recover the alcohol which
should be produced if ester hydrolysis takes place,
the solutions of the methyl fumarate complex were
treated in a number of ways after reaction. These
were: (a) addition of sodium bicarbonate and dis-
tillation at low temperature and pressure; (b)
standing overnight before treatment (a); (c) re-
fluxing the residue from (a) with 2 M alkali for 2
hr., followed by distillation at atmospheric pres-
sure; (d) refluxing the residue from (b) in the same
way; (e) adding excess chromous ion and pyro-
phosphate after reaction; (f) adding pyrophosphate
after reaction; (g) refluxing the residue from (f)

with alkali; (h) adjusting the pH to 1.5 then ex-
tracting with ether. The percentages of the
methanol recovered in separate trails by the dif-
ferent methods were (a) 7, 2, 2, 6; (b) 16, 5; (c)
25, 20; (d) 44, 15; (e) 3; (f) 7; (g) 19, 7; (h) 10.
The treatment which led to the best recovery (70%)
was to make the solution 0.5 M in sodium pyrophos-
phate afer reaction, refluxing it for 16 hr. and then
distilling. For the experiments which have been
outlined, the oxidizing agent and reducing agent
were each at 1.0×10^{-2} M initially, and the con-
centration of perchloric acid varied from 0.5 to
1.0 M.

Blank experiments were performed; these
showed that the alcohol found in the distillates was
not due to hydrolysis caused by the sodium bicar-
bonate or by zinc ion (present in the chromous
solution) or by the chromic ion present after elec-
tron transfer. Further, when the reactant solu-
tion is made up using the acid fumarato complex
and having free methanol present then adding
chromous ion, it is found that none of the methanol
associates with chromium in the oxidation-reduc-
tion reaction. Thus it appears that methanol is not
captured in the oxidation–reduction process once it
is set free in solution.

The conclusion that the methanol is bound to the
chromic ion was confirmed by experiments using
a cation exchange resin. Reaction mixtures were
poured through Dowex 50-X and washed with
water. The chromium(III) complex was eluted
with 1 M $HClO_4$. By refluxing this eluate with
pyrophosphate for 16 hr., it was possible to re-
cover 90% of the methanol.

Direct ether extraction of the solutions after
electron transfer between Cr^{++} aq. and the phenyl
fumarate complex showed that approximately 64%
of the phenol was free in solution. The remainder
was obtained readily by pyrophosphate treatment.

**Reaction of Pentamminomethylfumaratocobalt
(III) Ion with Other Reductants. (a) Ferrous
Ion.—**In acid solution in the presence of oxalate,
there was no reaction between the complex and
ferrous ion. In neutral solution a fairly rapid re-
action took place, but methyl fumarate and not
fumaric acid was the product.

(b) Europous Ion.—In acid solution a rapid re-
action took place. After ether extraction an
organic acid was obtained in 93% yield (expressed
as total fumaric acid obtainable). Infrared ex-
amination confirmed that the acid was fumaric,
not the half ester methyl fumarate.

(c) Vanadous Ion.—After reaction of equivalent
amounts of the complex and reductant, ether ex-
traction of the reaction mixture yielded 95% meth-
anol and 97% fumaric acid. The initial hydrogen
ion concentration has little effect on these values.

(d) Chromous and Vanadous Tris-dipyridyls.—
With both dipyridyl complexes, a rapid reaction
took place. No free methanol was produced by
distillation, and alkali titration and infrared ex-
amination showed that the only product was
methyl hydrogen fumarate. An alcohol deter-
mination on the ether extracts (half esters will re-
spond to the test) showed in both cases 99% of the
total half ester was recovered.

Titration with Alkali of Reaction Mixtures of Other Pentamminocobalt(III) Complexes and Chromous Ion.—A number of cobalt(III) complexes containing organic ligands such as half esters or amides were treated with chromous ion. After reaction, the solutions were titrated with alkali. Table I lists the increase in equivalents of the hydrogen ion content beyond that calculated for reaction with no ester hydrolysis.

Only the phenylterephthalato showed any marked variation of extent of hydrolysis with initial acid content. This has been investigated further.[7]

As a check on the results obtained from titration experiments, ether extractions of some of the solutions were made and the percentage of organic acid obtained by titration of the residue. The results are shown in Table II. Infrared examination showed that the acids rather than the half-esters were obtained from the reaction of phenylfumarato or methyl terephthalato complexes.

The titration of the product solution obtained when the p-sulfobenzoate complex was used as oxidant failed to show evidence of the weakly acidic group –COOH which would be expected if Cr(III) were attached to the sulfonate. Since the ligand is associated with the Cr(III), the result implies that the point of attachment is the carboxyl end of the bi-functional ligand.

TABLE I

INCREASE IN ACID CONTENT OF SOLUTION

Complex	Concn., M	$(H^+)_s$	(H^+) produced per equiv. of Co(III), ± 0.05
Methylmaleato	0.0148	0.098	1.02
Phenylfumarato	.014	.098	0.88
Amidofumarato	.0183	.098	1.10
Methylamidofumarato	.0166	.102	1.16
Diethylamidofumarato	.0145	.205	0
p-Sulfobenzoato	.0155	.155	0
p-Aldehydobenzoato	.0122	.566	0
Methylterephthalato	.0131	.102	0.96
Phenylterephthalato	.0135	.566	.92
Phenylterephthalato	.0091	.048	.23

TABLE II

ORGANIC ACID, HALF-ESTER AND ALCOHOL RECOVERED BY ETHER EXTRACTION

| Complex	Reductant	% Free acid	% Ester	% Alcohol
p-Aldehydobenzoato	Cr^{++}	96	..	..
	V^{++}	98	..	..
β-Benzoacrylato	Cr^{++}	97	..	..
	V^{++}	95	..	..
Phenylfumarato	Cr^{++}	80[a]	..	60
	V^{++}	98	..	96
Methylterephthalato	Cr^{++}	95[a]	..	6
	V^{++}	96	..	97

[a] Pyrophosphate added before ether extraction but without refluxing. As described earlier the alcohol bound to the Cr(III) is released only on prolonged refluxing.

Discussion

The experiments described show that the increase in acid content of the solutions which has oc-

curred on electron transfer is produced by ester hydrolysis. The proof of this conclusion is provided by the results of the extraction experiments which were done under conditions mild enough—as proven by blank experiments—so that half ester present after reaction would not have hydrolyzed. The result which is even more significant in respect to the mechanism of the reaction is that the alcohol formed on hydrolysis remains associated with the Cr(III). When methyl terephthalate is the ligand, this can only mean that Cr^{++} attacks the end of the ligand bearing the ester group and remote from the Co(III). Even when methyl fumarate is the ligand, it seems highly unlikely that the reducing agent attacks the carboxyl attached to the Co(III), for if this were the case it is unlikely that the methyl alcohol would find its way essentially quantitatively to the chromium. A blank experiment using acid fumarate as the ligand attached to Co(III) showed that free alcohol does not become associated with Cr^{++} in this system. This interpretation that remote attack occurs with the fumarate half-ester ligands also finds strong support in the results of kinetic studies done with complexes of these ligands.[4,8]

The experimental results obtained with other ligands of the present series also provide proof of remote attack. Thus if

$$\left[Cr\diagup\begin{matrix}O\\\\O\end{matrix}\diagdown C-CH=CH-C\diagup\begin{matrix}O\\\\NH_2\end{matrix} \right]^{++}$$
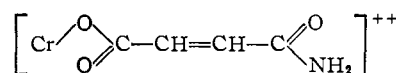
were the product of the reaction of Cr^{++} with the corresponding amido complex, the increase in acidity equivalent to the number of moles of Cr^{++} which react would not be expected. If, however, Cr^{++} is attached to the remote end of the Co(III) amido complex, an increase in acidity is expected whether the chromium associates with the oxygen or with the nitrogen. Furthermore, the observation that in the reaction with Cr^{++} of the Co(III) complexes of p-aldehydobenzoate or β-benzoylacrylate, the organic acid can be extracted directly and quantitatively from the reaction mixture, seems to prove that Cr^{++} attacks the carbonyl end of the ligand. If it attacked the carboxyl end (which is attached to Co(III)), the corresponding Cr(III) complex would be formed, as in all other cases of adjacent attack, and these complexes would not be expected to dissociate rapidly. It is not surprising however that the Cr(III) complex of a ketone or aldehyde carbonyl group dissociates rapidly enough to set the ligand free for extraction by ether.

In view of the considerations advanced, it seems likely that in the present series of compounds, at least in those cases in which chelation of the ligand *via* the two functional groups is excluded, ester hydrolysis accompanying electron transfer implies attack by the reducing agent at the ester group and electron transfer through the ligand molecule. In this context the experimental result that ester hydrolysis takes place also when V^{++} and Eu^{++} are the reducing agents is particularly significant. The chromium results alone could be given the simple interpretation that an intermediate such as is

(7) R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 2242 (1961).

(8) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2242 (1961).
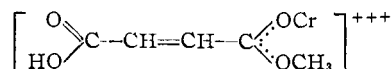
formed as product of the electron transfer process, and because of the known inertia of Cr(III) complexes to substitution, it would not be too surprising that a C–O rather than a Cr–O bond breaks on hydrolysis. However, this explanation is hardly reasonable for the analogous V^{+++} and Eu^{+++} complexes, 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

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(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-