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Adjacent and Remote Attack in Electron Transfer through Conjugated Ligands

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A study has been made of the reaction of chromous ion with the series of complexes $[(NH_3)_5Co-X](ClO_4)_2$, where X is the monoester of a dibasic organic acid joined to the cobalt through the free carboxyl group. Using the extent of ester hydrolysis which accompanies electron transfer as a measure of extent of reaction by remote attack, evidence is presented for attack by chromous ion simultaneously at both carboxyl groups. The results on ester hydrolysis, together with information from rate law studies, show that while the rate of adjacent attack remains relatively constant, the rate of attack through the remote carboxyl is greatly influenced by the nature of the ester group. In some cases this results in the disappearance of reaction by the reductant at the remote carboxyl with electron transfer through the non-protonated ligand.

Introduction

Recent discoveries by Taube and his co-workers have shown that the reaction of pentamminocobaltic complexes with Cr^{++} aq. may occur through suitable organic bridging groups associated with the cobalt.[1] In cases where the ligands are simple aliphatic acids, adjacent attack occurs and the specific rate constants found for the electron transfer process are almost independent of the nature of the ligand beyond the carboxyl group. There is no acceleration of the rate by mineral acid and no ester hydrolysis.[2] Rate comparisons for a series of complexes containing ligands such as acetate and succinate on the one hand and fumarate and terephthalate on the other suggest that attack by the Cr^{++} at a remote position followed by movement of the electron through the bond system becomes possible when conjugation exists.[3] The specific rate constants increase from 0.17 mole^{-1} sec.$^{-1}$ (acetate, succinate) to 1.1 (fumarate) and from 0.98 mole^{-1} sec.$^{-1}$ (o-. m-phthalate) to about 40 (p-phthalate).[1] For the fumarate and p-phthalate attack by the chromous ion takes place at the carboxyl group remote from the cobalt center, with electron transfer through the ligand. The rate of reaction increases with increase in mineral acid content of the solutions, and this observation is offered as further evidence for remote attack,[3] as protonation of the carboxyl adjacent to the cobalt increases the conjugation between the two metal centers and the bridging group is thus a better conductor for the electron transfer process. Further evidence has been found for remote attack by the reductant[4]: when the ligand is methyl fumarate, titration of the reaction mixture immediately after the oxidation–reduction process has occurred shows that acid has been produced, equal in amount to the complex consumed, and both fumaric acid and methyl alcohol are found associated with the chromium. Similar results are obtained with phenyl fumarate[5,6] and methyl terephthalate[6] as ligands.

The form of the rate law for the reaction of chromous ion and cobalt(III) complexes containing conjugated ligands is

$$v = k_1 (Cr^{++})(CoL^{++}) + k_2 (H^+)(Cr^{++})(CoL^{++})$$

(for L = fumarate, $k_1 = 1.1$, $k_2 = 3.6$ at $25°^2$) k_1 and k_2 are usually large, and ester hydrolysis occurs only in cases where remote attack is possible. The table shows the increase in acidity found for a number of cobalt(III) complexes after reaction. The phenylterephthalato complex is a particularly

TABLE I

INCREASE IN ACID CONTENT OF SOLUTIONS[6]

Complex	Concn., M	(H^+), M	H^+, addl. (eq.)
Methylmaleato	0.0148	0.098	1.02 ± 0.05
Phenylfumarato	.014	.098	$0.88 \pm .05$
Methylterephthalato	.0131	.102	$.96 \pm .05$
Phenylterephthalato	.0135	.566	$.92 \pm .05$
Phenylterephthalato	.0091	.048	$.23 \pm .05$
Methylsuccinato[2]	.002	.20	0

interesting case; the form of the rate law for the reaction with chromous ion is

$$V = 0.05 (Cr^{++})(CoL^{++}) + 040(H^+)(Cr^{++})$$

(CoL^{++}) at $24°$ ($\mu = 1$, specific rate constants expressed as $l.^2$ mole^{-1} sec.$^{-1}$ etc.). The rate constant for the acid-independent path (k_1) is small here and almost identical with that for the reaction of the acid phthalato complex,[1] where attack by the chromium is possible only at the adjacent carboxyl group. This comparison and the evidence that at intermediate acidities ester hydrolysis is not complete on electron transfer suggest that the reducing agent acts by both remote (acid-dependent term) and adjacent (acid-independent term) attack. The present study was undertaken to determine, by using ester hydrolysis as evidence of remote attack and combining this evidence with rate law data, whether simultaneous adjacent and remote attack by chromium takes place at ligands other than phenyl terephthalate, particularly at fumarates.

Experimental

Materials.—Monomethyl fumarate, monoethyl terephthalate and mono-(cyclo)-hexyl terephthalate were prepared from the diesters by treatment with one equivalent of alcoholic sodium hydroxide.[7] Monophenyl fumarate was prepared by refluxing sodium phenoxide and maleic anhydride in toluene.[8] The half esters of phenol, p-chlorophenol, p-cresol, p-nitrophenol and p-aminophenol with terephthalic acid were prepared by slowly adding terephthaloyl chloride to a stirred alkaline solution of one equivalent of the phenol in water. The solution was left for several hours, filtered, then warmed with very dilute sodium carbonate solution

(1) H. Taube, Can. J. Chem., 37, 129 (1959).
(2) D. K. Sebera and H. Taube, to be published.
(3) H. Taube, "International Conference on Coördination Chemistry 1959," Chem. Soc. (London) Spec. Pub. No. 13, p. 57.
(4) R. T. M. Fraser, D. K. Sebera and H. Taube, THIS JOURNAL, 81, 2906 (1959).
(5) R. T. M. Fraser and H. Taube, ibid., 81, 5000 (1959).
(6) R. T. M. Fraser and H. Taube, to be published.

(7) J. J. Sudborough, J. Chem. Soc. (London). 87, 1843 (1905).
(8) C. A. Bischoff and A. von Hedenstrom, Ber., 35, 4087 (1902).

until effervescence ceased. Upon acidification of the mixture the half ester was precipitated and could be collected and dried. The chemicals used in the preparations were the purest commercially available.

Pentamminoaquocobaltic perchlorate was prepared by the method of Basolo and Murmann.[9] From this material all the pentammino cobaltic complexes which contained organic ligands were prepared. The method used was to heat together an excess of the half-neutralized organic acid and the aquo-cobaltic salt on a water-bath at 70° for a period ranging from 2 hr. to two days. The hot solution was acidified and filtered, this removed the unreacted portion of the organic acid. The filtrate was cooled in an ice-bath and the cobalt complex precipitated by further addition of concentrated perchloric acid. The complex was filtered off and dried, then recrystallized from water. To check the purity of the complexes the chlorine content was determined, and since all the ligands used were half esters any organic acid present as an impurity or complexed with the cobalt was detected easily by titration with alkali. No trouble was experienced in preparing the pure samples of the ester complexes.

A 0.10 molar chromous solution was prepared in a Jones reductor from chromic perchlorate (itself obtained from potassium dichromate) by the method of Lingane and Pecsok.[10]

Reaction.—A quantity of the complex equivalent to approximately 1×10^{-4} g. mole was dissolved in a small volume of perchloric acid and the solution transferred to a 50 ml. flask equipped with a side arm passing under water and fitted to that buret of the reductor. The flask and solution were flushed with oxygen-free nitrogen to thoroughly degas the system, then an equivalent of the chromous solution added. During the reaction a stream of nitrogen was passed through the flask. After the reaction was complete (a period of fifteen minutes to two hours), the solution was transferred to a beaker and titrated with 0.1 M standard alkali. The course of the titration was followed on a pH meter sensitive to 0.02 pH unit. During the series of experiments, three pH meters were used: a Beckman Model G, a Zeromatic and a Doran pH meter. All gave similar results. As the maximum increase in acidity corresponded to less than one milliliter of alkali, titrations were made with a buret which could be read to 0.01 ml. and near the expected end-point pH readings were made after each 0.05 ml. of alkali added. The solution was stirred by means of a stream of nitrogen. A plot of pH against ml. of alkali added was made, then by taking the values of tangents at intervals of 0.05 ml. along this plot the first and second differential curves were constructed. The amount of alkali required to neutralize both the mineral and the organic acids present after electron transfer was determined from the second differential curve.

Results

The percentage hydrolysis for a number of complexes was determined as a function of the hydrogen ion concentration by allowing the reactions to go to completion, then determining the acid content of the solution in excess of that calculated when ester hydrolysis is excluded from consideration. The results are shown in Table II.

The percentage hydrolyses recorded are all accurate to ±2%. The number of compounds of this type which can be used in making the measurements is limited: for instance, it was found impossible to prepare pentammino-p-aminophenylterephthalatocobaltic perchlorate free from strong acid: when the complex was precipitated from weakly alkaline solution, some decomposition occurred. The p-chlorophenylterephthalate complex was also unsatisfactory because some replacement of ammonia in the compound by chloride took place.

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

(10) J. J. Lingane and R. L. Pecsok, Anal. Chem., 20, 425 (1948).

Phenylterephthalato			Ethylterephthalato		
Av. (H$^+$), M	Hydr., % (±2)	Temp., °C.	Av. (H$^+$), M	Hydr., % (±2)	Temp., °C.
0.532[a]	92	22	0.666	97	25
.384	80		.426	98	
.245	67		.241	97	
.150	51		.195	96	
.025	23		.102	93	
p-Cresylterephthalato			Cyclohexylterephthalato		
0.588	85	23	0.630	97	22
.222	55		.420	95	
.101	35		.420	93	
.042	13		.079	90	
Phenylfumarato			Methylfumarato		
0.492	93	22	0.531	96	22
.376	92		.335	93	
.223	89.5		.159	92	
.148	89		.025	90	
.063[a]	88.5				

[a] Fraser and Taube, ref. 6.

Discussion

If the rate of reaction of Cr^{++} aq. with the cobaltic complex can be expressed in the form

$$v = k_1(\text{Cr}^{++}) + k_2(\text{H}^+)(\text{Cr}^{++})(\text{CoL}^{++})$$

where the first term denotes adjacent attack with no hydrolysis, the second remote with accompanying hydrolysis, then the ratio (% hydrolyzed/% not hydrolyzed) at any hydrogen ion concentration is given by $k_2(\text{H}^+)/k_1$. The per cent. hydrolysis is given by

$$100k_2(\text{H}^+)/[k_1 + k_2(\text{H}^+)]$$

However, if k_1 itself is complex and consists of two terms $k_{1(adj)} + k_1'_{(remote)}$ where $k_{1(adj)}$ is the specific rate constant for adjacent attack without hydrolysis; $k'_{(remote)}$ is the rate constant for attack at the remote carboxyl with electron transfer by the non-protonated path producing ester hydrolysis, then the per cent. hydrolysis is given by

$$100[k_1'_{(remote)} + k_2(\text{H}^+)]/[k_1 + k_2(\text{H}^+)]$$

From these two expressions the per cent. hydrolysis as a function of acidity can be plotted if the values of k_1 (or $k_{1(adj)}$ and $k_1'_{(remote)}$) and k_2 are known or can be deduced from rate law measurements. At the temperature at which the potentiometric titrations were made, the reaction velocities for the electron transfer are

$v = 0.049$ (Cr^{++})(CoL^{++}) + 0.37 (H$^+$)(Cr^{++})(CoL^{++}) for phenylterephthalato[6]

$v = 1.13$ (Cr^{++})(CoL^{++}) + 4 (H$^+$)(Cr^{++})(CoL^{++}) for methylfumarato[2]

$v = 1.38$ (Cr^{++})(CoL^{++}) + 0.6 (H$^+$)(Cr^{++})(CoL^{++}) for phenylfumarato[6]

$v = 0.04$ (Cr^{++})(CoL^{++}) + 0.19 (H$^+$)(Cr^{++})(CoL^{++}) for p-cresylterephthalato[11]

p-cresylterephthalato.[11] The rate laws for the other complexes have not yet been determined. Assuming that the specific rate constants for adjacent attack are 0.05 l.^{2} mole^{-2} sec.$^{-1}$ in the terephthalate series[2] and 0.17 l.^{2} mole^{-2} sec.$^{-1}$ (as for
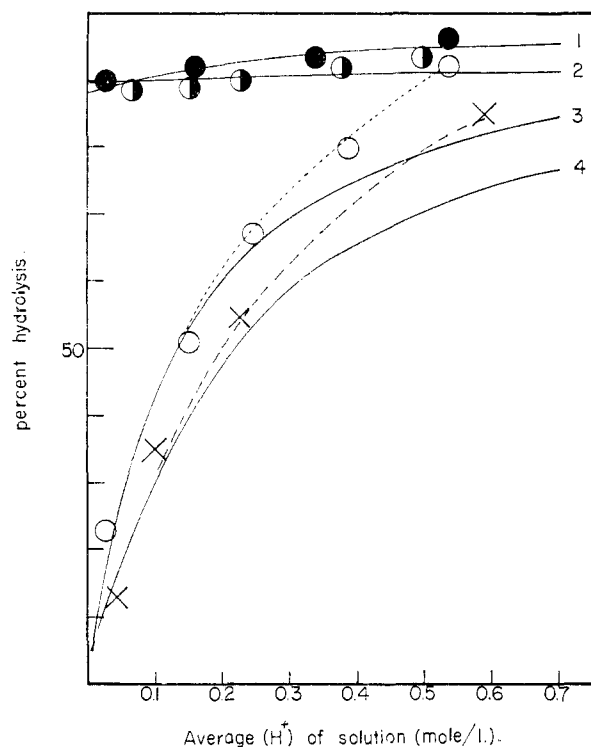
(11) R. T. M. Fraser, unpublished results.

Fig. 1.—Percentage ester hydrolysis as a function of acid content of the solutions, calculated from rate law data (solid lines): 1, $[(NH_3)_5CoO_2CCH=CHCO_2CH_3]^{++}$; 2, $[(NH_3)_5-CoO_2CCH=CHCO_2C_6H_5]^{++}$; 3, $[(NH_3)_5CoO_2CC_6H_4CO_2-C_6H_5]^{++}$; 4, $[(NH_3)_5CoO_2CC_6H_4CO_2C_7H_3]^{++}$. Values obtained from titrations are shown for comparison.

the acetato, etc.[1]) in the fumarate series, the values for $k_{1(adj)}$, $k_1'_{(remote)}$ and k_2 (obtained as previously discussed) are listed in Table III.

TABLE III

SPECIFIC RATE CONSTANTS

Complex	$k_{1(adj.)}$, $l.^2$ mole^{-2} sec.$^{-1}$	$k'_{1(remote)}$, $l.^2$ mole^{-2} sec.$^{-1}$	k_2, $l.^3$ mole^{-2} sec.$^{-1}$
Cresylterephthalato	0.04	0	0.19
Phenylterephthalato	.049	0	0.37
Methylfumarato	.17	0.96	4
Phenylfumarato	.17	1.21	0.6

These values were substituted in the expressions derived for percentage hydrolysis: the calculated hydrolyses are compared in Fig. 1 with the experimental values obtained. The agreement is good at low acid concentrations but falls off in the phenyl- and cresyl-terephthalato cases as the acid content is increased. The agreement shows that a relationship can be established between the kinetic data and the observations on the per cent. of ester hydrolysis. Therefore, for the ethyl and cyclohexyl terephthalate complexes, the experimental values

obtained for the hydrolysis on electron transfer have been used to calculate the ratios $k_1'_{(remote)}$ $k_{1(adj.)}$ and $k_2/k_{1(adj.)}$ for these complexes in their reaction with Cr^{++}. Since a plot of the ratio % hydrolyzed/% non-hydrolyzed against (H^+) will yield a straight line of slope $k_2/k_{1(adj.)}$ and intercept $k_{1(remote)}/k_{1(adj.)}$, these values were obtained by a simple least-squares treatment of the data. Table IV shows the two ratios together with the values calculated from rate measurements for the other four complexes. It should be noted that a least squares treatment of the experimental values obtained at the three lowest acidities for the phenyl- and cresylterephthalato complexes reproduces the curve obtained from the measurements within 5%.

TABLE IV

RATIOS OF $k_1'_{(remote)}/k_{1(adj.)}$ AND $k_2/k_{1(adj.)}$

Complex	$k'_{1(remote)}/k_{1(adj.)}$ Calcd.	Exp.	$k_2/k_{1(adj.)}$ Calcd.	Exp.
Ethylterephthalato	..	18.6	..	35
Cyclohexylterephthalato	..	3.3	..	38
p-Cresylterephthalato	0	0	4.8	5.0
Phenylterephthalato	0	0	7.6	7.7
Methylfumarato	5.7	6.7	23	20
Phenylfumarato	7.1	7.4	3.5	4.6

It is at once clear that remote attack with electron transfer by the non-protonated path is completely eliminated in the terephthalate series by esterification with a phenol, while in the fumarate series, reaction by this path is little affected and certainly not decreased. In both, attack at the remote position with electron transfer by the protonated path is decreased considerably—by a factor of $5^3/_4$ in the terephthalate and almost $6^3/_4$ in the fumarate series. The results obtained using the cyclohexyl ester show that this effect cannot be ascribed to the size of the phenyl group but must be related in some way to the aromatic properties of the phenol. At high acid concentrations, the experimental values for the phenyl esters of the terephthalato complexes rise above values from rate law studies: as protonation increases at the carboxyl group adjacent to the cobalt center, this position is deactivated for attack by the chromium. At none of the acid concentrations studied, however, could reaction by this path be completely prevented.

The titration studies show that attack does take place at both positions in conjugated ligands—no case has been found where adjacent attack by the chromium disappears in favor of remote attack.