precise energy values could be ascertained from them, although in truly tetrahedral complexes they provide fairly precise information.

Acknowledgments.—We are grateful for financial support to the National Science Foundation (Grant G-12312) and the United States Atomic Energy Commission (Contract AT(30-1)-1965). We thank Prof. C. J. Ballhausen for helpful correspondence and Dr. B. Figgis for stimulating discussions and the opportunity to read his manuscript in advance of publication, and Dr. P. Cossee for copies of his manuscripts in advance of publication.

Organic Anions as Bridging Groups in Oxidation–Reduction Reactions

BY D. K. SEBERA AND H. TAUBE

RECEIVED SEPTEMBER 23, 1960

A kinetic study has been made of the reactions of Cr^{++} with complex ions of the type $(NH_3)_5Co(III)L$ where L is acid succinate, methyl succinate (half-ester), acetate, acid fumarate, methyl fumarate (half-ester) and the three isomeric forms of phthalic acid. The data are interpreted on the basis that adjacent attack of Cr^{++} takes place in all cases except for acid fumarate, methyl fumarate and terephthalic acid. In these three cases, there is conjugation between the carboxylate group at the remote end and that bearing the Co(III) center, and it is postulated that Cr^{++} attacks the remote end. In these special cases, the rates of reaction are greater than in the others and, furthermore, a term in the rate law is observed which is first order in (H^+). The role of H^+ is interpreted as being that of adding to the carbonyl adjacent to the Co(III), thus improving conjugation between the Cr^{++} on the remote end and the Co(III) group.

In this paper we report the results of detailed kinetic studies of the reactions of Cr^{++} with some complex ions of the class $(NH_3)_5Co(III)$-L where L is an organic ion containing one or more carboxylic groups. Some early, rather rough kinetic studies[1] with systems of this type showed that large differences in rate are observed for different bridging groups and suggested that for certain of them, the reducing agent can attack at a site remote from the oxidizing center, the electron being conducted through the bridging group. This feature particularly encouraged us to undertake the present study, which includes some of the systems studied earlier, but others as well, chosen with a view to learning something about the subject of electron conduction through bridging groups. In the course of this work some novel kinetic effects have been uncovered, and strong evidence for electron conduction through several bonds in a molecule has been adduced; in fact, the experiments which provide proof of remote attack and which have already been published in part[2,3] grew out of the present work.

Experimental

Materials.—The salt $Co(NH_3)_5H_2O(ClO_4)_3$ was used as the source of the radical $Co(NH_3)_5$ which is common to all the oxidizing agents studied. The salt was prepared from $Co(NH_3)_5CO_3(NO_3)$[4] by treating a hot solution of the carbonato salt with concentrated perchloric acid. The crystals recovered on cooling were subjected to a second treatment with perchloric acid.

The general method for the preparation of most of the organic acid complexes referred to here consists in heating a solution containing $Co(NH_3)_5H_2O^{+++}$, the organic acid and (usually) the sodium salt for *ca.* 2 hr. at 70°. Acid and salt are in large excess, and the concentrations are as high as tolerated. Substitution is rapid enough and the equilibrium is sufficiently favorable in most of the systems so that substantial conversion of the aquo to the acido ion takes place. The perchlorate salt in each case is readily precipitated by adding perchloric acid. The difficulties that arise are in the

separation of the product desired from the aquopentamminecobalt (III) perchlorate and the organic acid which in many cases is only sparingly soluble. Cation exchange resins are especially useful in separating the acido ions from the aquopentammine cobaltic ion. Good samples of the compounds with L = acetate, acid succinate, acid maleate, acid fumarate, acid phthalate and acid isophthalate were obtained without much difficulty in the general way described. However, a good preparation of the acid terephthalate complex was not obtained. The principal component of the cobalt-containing preparation appeared to be the salt of the binuclear complex, and only *ca.* 20% of it was comprised by the substance taken to be the acid terephthalato complex. An attempt to prepare the simple complex from the binuclear one by controlled hydrolysis did not lead to improved yields. We also failed to obtain a good preparation of the muconato complex. The product resulting from the attempted preparation appeared to contain a number of components, which presumably are complexes of the various isomeric muconate forms. To get appreciable substitution in this system (as well as some others which have since been encountered), a much more prolonged period of heating is required than the approximate 2 hr. which suffice for the majority of complexes prepared for the present work.

All of the complexes containing dibasic acids precipitate from acid solution as the acid salts, a feature which is very useful in assessing the purity of the sample.

In every case, the purity of the sample was checked by titration with alkali. This is a direct method of establishing the equivalent weight of the compound when the ligand is an acido group. For most of the preparations described as "good" in the previous paragraph, the equivalent weight thus determined agreed with that calculated for the anhydrous perchlorate within 2%. The bisuccinato complex is an exception, and the agreement here was only within 4%. Another exception is the bifumarato perchlorate. The equivalent weight determined for this substance agrees accurately with the formula $Co(NH_3)_5C_4O_4H_3(ClO_4)_2 \cdot 1/_2HClO_4$, as does the analysis for N, Cl and H (obsd. 13.4, 17.4, 0.30%; calcd., 13.8, 17.4, 0.30%). Analyses for N and Cl were made on the other compounds as well. These agree satisfactorily with the formulas as described, except in the case of the bisuccinato salt. Here again the deviations from theoretical were somewhat outside the expected errors of analysis.

Methyl half ester complexes of the fumarato, maleato and succinato complexes were prepared by reaction of the acid salts with diazomethane. The diazomethane in ether solution[5] is added slowly to a solution of the salt in 40% aqueous ethanol using approximately 20% excess. The approach of the end of the reaction can be noted by observing the rate at which successive portions of the diazomethane solution are

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

(2) R. T. M. Fraser, D. K. Sebera and H. Taube, *ibid.*, **81**, 2906 (1959).

(3) R. T. M. Fraser and H. Taube, *ibid.*, **81**, 5000 (1959).

(4) A. B. Lamb and K. J. Mysels, *ibid.*, **67**, 468 (1945).

(5) "Organic Syntheses," Coll. Vol. II,

decolorized. After reaction was complete, the aqueous solution was extracted 5 times with distilled ether, evaporated under vacuum at room temperature to a small volume, then after cooling to 0° concentrated $HClO_4$ was added. The crystals were collected, washed with water, ethanol and ether and after drying were redissolved in water and reprecipitated from perchloric acid. The preparations of half-ester were all free of the acid salt. The chlorine analysis on the fumarato compound (which was studied most intensively) agreed well with the calculated (14.97% vs. 15.02).

Cr^{++} was prepared in perchloric acid solution, using amalgamated Zn as reducing agent.

Method.—In preliminary experiments, the progress of the reaction was followed by quenching aliquots of the reaction mixture and titrating the residual reducing agent amperometrically. This method was given up in favor of the spectrophotometric one, which offers the advantage of greater convenience and improved precision, and avoids the complications which can arise in the quenching step.

The general procedure was to make up the reaction mixture in a vessel, then to transfer the mixture as quickly as possible to a spectrophotometer cell, using N_2 pressure to drive the solution. Vessel, solution and cell were thoroughly purged with oxygen-free N_2, and no noticeable loss of Cr^{++} occurred by air oxidation. The spectrophotometer cells had two openings, and each opening was fitted by a ground glass joint bearing a stopcock. The stopcocks were used to control the flow of fluid, and to isolate the contents after the cells were charged with solution.

The wave length 350 mμ was used to follow the course of the reaction. At this wave length, the Co(III) complexes have strong absorption (ϵ in the range 53 to 79) and Cr^{++} and the products have much weaker absorption. For reaction mixtures with Co(III) in excess, it was possible to determine the final optical density experimentally, and the equation

$$\frac{R_t}{Cr_t} = \frac{(O.D.)_t - \lambda[R_0(\epsilon_p - \epsilon_{Cr}) + Cr_0\epsilon_{Cr}]}{(O.D.)_t - (O.D.)_\infty} \quad I$$

was used to calculate the ratio of the concentration R_t of Co(III) at time t to that of Cr(II) at the same time. The other quantities in the equation are: O.D. = optical density, R_0 and Cr_0 the initial concentrations of Co(III) and Cr(II), respectively, ϵ_p and ϵ_{Cr} the extinction coefficients of the products (Co^{++} and Cr(III) in equivalent amounts) and of Cr^{++}, λ the cell length. For a second order reaction

$$k = \frac{2.303}{t(R_0 - Cr_0)} \log \frac{Cr_0 R_t}{Cr_t R_0}$$

so that

$$t = \frac{2.303}{k(R_0 - Cr_0)} \log \frac{Cr_0}{R_0} + \frac{2.303}{k(R_0 - Cr_0)} \log \frac{R_t}{Cr_t} \quad II$$

The specific rates were obtained from the slopes of plots of $\log R_t/Cr_t$ against time.

When Cr^{++} is equivalent to or in excess of Co(III), it is preferable not to wait for the optical density to reach a final value, because the second stage of reaction, involving dissociation of the Cr(III) complexes, sets in. Instead the equation

$$\frac{Cr_t}{R_t} = \frac{(O.D.)_0 - (O.D.)_t - Cr_0(\epsilon_R - \epsilon_p + \epsilon_{Cr})\lambda}{(O.D.)_0 - (O.D.)_t - R_0(\epsilon_R - \epsilon_p + \epsilon_{Cr})\lambda}$$

is used, which in effect makes use of the calculated value of $(O.D.)_\infty$ (ϵ_R is the extinction coefficient of the reactant Co(III) complex).

Results

General.—The net changes in all of the systems with the exceptions referred to later are represented by the type equation

$$(NH_3)_5CoL^{++} + Cr^{++} + 5H^+ = Co^{++} + CrL^{++} + 5NH_4^+$$
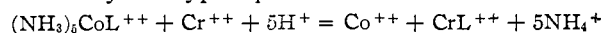
The feature that Co(III) and Cr^{++} react in equivalent amounts is proven by the measurements of optical densities of the reaction mixtures before and after reaction, as well as by the kinetic analyses, which themselves provide tests of stoichiometry when the initial concentrations of Co(III) and Cr^{++} are not much different. The cation exchange technique was used in earlier work to

prove that the transfer of the ligand to Cr does indeed take place. The conclusion was confirmed by the same method for the reaction when L = acetate, succinate, maleate and was extended to the fumarato and o-phthalato complexes. Even for systems in which such a direct test was not made, the optical density data seem to establish firmly that a complex of Cr(III) rather than the aquo ion is the reaction product. At $\lambda = 350$ mμ, the extinction coefficients of the Cr(III)–carboxylate complexes are approximately 1.5 that of $Cr(H_2O)_6^{+++}$ and, in each case, the final optical density was such as to indicate that Cr(III) was formed largely as complex. In several of the systems, too, the organic ion was present in sufficient concentration so that acid would precipitate if its ion were set free during the reaction. Only when Cr^{++} was present in excess was a precipitate of organic acid observed to form as a result of the oxidation-reduction reaction and then only after the solution was allowed to stand for a period of time long compared to that in which useful kinetic data could be obtained

Except when Cr^{++} is in excess, the limiting optical densities remain essentially constant for at least a day. With excess Cr^{++}, as noted in the preceding paragraph, the dissociation of the Cr(III) complexes takes place at an accelerated rate but in no case rapidly enough to cause serious difficulty in determining the specific rates.

This effect is sometimes revealed in the plots of $\log Cr_t/R_t$ vs. time, as slight deviations from linearity at the end of the reaction, when the optical density contributed by the residual Co(III) is not large compared to that contributed by the Cr(III) complex. The deviations do not appear when the oxidizing agent is in excess.

With L = acetate, acid succinate, methylsuccinate, acid fumarate, methyl fumarate, acid phthalate and isophthalate, the oxidation-reduction reactions were found to be first order in reducing agent and oxidizing agent. For all systems, this conclusion is based at least on the observation that for individual runs the plot of $\log R_t/Cr_t$ against time is a straight line and on the agreement in specific rates obtained from different experiments. For some reactions a systematic wide variation in initial concentrations was made, including runs with Cr^{++} in excess and runs with Co(III) in excess. With the exception that a slight complication can appear for the complexes of dicarboxylate ligands when (H^+) is low and the concentrations of the reagents are high, no deviations from simple kinetic behavior were observed. The deviation noted is most marked for the isophthalato complex as oxidant and is dealt with more fully in the later section devoted to the results with the oxidizing agent.

It should be noted that in acid solution all of the dibasic ligands bear a proton so that the net charge on the complex is $+2$. The values of the dissociation constants of all the acid complexes used (except that of terephthalate) were determined by titrations measuring the pH of the solutions using a glass electrode.[6] For all the acids

(6) Measurements made by D. K. Bearcroft, to be published.

pK at $25° > 2.4$. For the phthalato and fumarato complexes, special use is made of the values of pK, and these are recorded herewith as 2.6 and 3.2, respectively, at $25°$ and $\mu = 1.00$.

In the sections immediately following, the various systems are discussed separately and such special features are mentioned as seem important in appraising the kinetic data and evaluating their significance.

Succinic Acid and the Methyl Half-ester as Ligands.—The results of the kinetic measurements with the Co(III) complexes containing these ligands are summarized in Table I.

TABLE I

THE REACTION OF Cr^{++} WITH PENTAMMINECOBALT(III) COMPLEXES OF ACID SUCCINATE AND THE HALF-ESTER

$(\mu = 1.0)$

Ligand	(Co-(III))$_0$ × 10^3	(Cr-(II))$_0$ × 10^3	(H$^+$)	Temp., °C.	k, mole^{-1} sec.$^{-1}$
$^-O\diagdown C(CH_2)_2-C\diagdown^O_{OH}$	2.01	7.54	0.93	14.1	0.17
	1.56	3.79	0.055	14.1	.17
	1.68	2.94	1.00	25.1	.27
$^-O\diagdown C(CH_2)_2C\diagdown^O_{OCH_3}$	1.24	0.76	1.00	24.9	.16
	2.00	1.48	0.20	25.0	.17

Experiments using ion exchange resins indicate that the succinate complex of Cr(III) is formed largely in the unchelated form. This distinction can be made because in the unchelated form the complex will bear a charge of $+ 2$ in acid, in the chelated form, a charge of $+ 1$. The affinity of the succinate complex for the resin indicates that the charge is $+ 1$. Titration of the product reaction mixture when the half-ester complex is reactant indicates that the ester does not undergo much hydrolysis in the oxidation-reduction process.

Acetate as Ligand.—The experiments done with the acetate complexes as oxidizing agents do not seem to call for special comment. The few experiments with it are summarized in Table II.

TABLE II

THE REACTION OF Cr^{++} WITH $(NH_3)_5CoOAc^{++}$

$(\mu = 1.0)$

(Co(III))$_0$ × 10^3	(Cr(II))$_0$ × 10^3	(H$^+$)	Temp., °C.	k, mole^{-1} sec.$^{-1}$
2.55	1.75	1.00	37.7	0.23
2.35	1.82	0.074	37.4	0.23
2.72	1.72	0.050	25.0	0.18

The value of the specific rate at $25.0°$ agrees reasonably well with that reported earlier[1] and based on work done using a different method. The agreement for the succinate complex is not very good, however, and the present results are regarded as being more dependable than those obtained in the early, cursory survey of the field.

Acid Fumarate and the Fumarate Methyl Half-ester as Ligands (Table III).

Experiments 3 and 4 provide a stringent test of the order of the reaction with respect to Cr^{++} and Co(III) concentrations. In experiment 3, (Cr^{++}) decreases by a large factor throughout the run, and in 4 (Co(III)) decreases by a large factor. The agreement in the specific rates is satisfactory. The group of experiments 6–14 were designed to study the influence of (H^+) on rate as well as the

TABLE III

ACID FUMARATE (–FH) AND THE METHYL HALF-ESTER (–FCH$_3$) AS LIGANDS $(\mu = 1.0)$

No.	Ligand	(Co-(III))$_0$ × 10^3	(Cr-(II))$_0$ × 10^3	(H$^+$)	Temp., °C.	Other	k, mole^{-1} sec.$^{-1}$
1	–FH	1.41	1.09	0.71	5.1	....	2.21
2	–FH	1.58	0.75	.24	5.5	....	1.06
3	–FH	1.47	0.77	.050	5.2	....	0.68
4	–FH	1.44	2.99	.050	4.6	....	.70
5	–FH	2.39	1.92	.010	4.8	....	.57
6	–FH	1.67	1.29	1.00	1.9	....	2.58
7	–FH	1.82	1.30	0.050	1.9	....	0.59
8	–FH	2.19	1.22	1.00	1.9	82 mole	2.86
9	–FH	1.88	1.22	0.050	1.9	% D$_2$O	0.53
10	–FH	1.22	0.72	1.00	14.3	....	3.52
11	–FH	1.21	0.97	0.30	14.3	....	1.57
12	–FH	1.69	1.11	0.050	14.3	....	0.90
13	–FH	1.23	0.57	1.00	25.1	....	4.87
14	–FH	1.03	0.74	0.053	25.1	....	1.48
15	–FCH$_3$	1.06	0.91	1.00	2.5	....	1.72
16	–FCH$_3$	1.51	1.19	0.047	2.5	....	0.48
17	–FCH$_3$	1.01	0.83	0.047	2.5	....	0.50

effect of changing from H_2O to D_2O. Experiment 5 was designed to expose the path corresponding to reaction of the fumarato rather than the acid fumarato complex. It is difficult to do experiments at an acidity low enough so that the bulk of the reactant complex is present in the dissociated form. The reaction consumes acid, but ordinary buffering agents cannot be used because the buffer anions become involved in the reaction. The initial concentration of H^+ is low enough in experiment 5 so that a considerable change in acidity takes place as NH_3 is released by reduction of the Co-(III) complex. The acidity was computed from point to point as the reaction progressed. Toward the end of the experiment, (H^+) had decreased to 0.003 M, and at this acidity the specific rate had increased by a factor of 1.7 over the initial value as recorded in Table III.

Some additional observations on the role of H^+ are important in understanding its effect on the rate of reaction. There is no evidence for appreciable association of H^+ with the acid fumarato complex—at any rate there is no noticeable change in the absorption spectrum of the complex ion when the acidity is changed from 0.3 to 2.5 M. An experiment was also done to learn whether hydrogen exchange takes place between the –C— H   H C– group of the fumarate complex and the solvent. For this experiment the reaction medium was D_2O containing 1 M HClO$_4$. The fumaric acid was separated from the reaction mixture and its infrared spectrum was taken. No bands characteristic of the –C— group were observed.

$|$
D

Experiments were done to learn whether ester hydrolysis accompanies electron transfer when the Co(III) complex of the methyl fumarate half-ester is the ligand. Titration of the reaction mixture with alkali shows that acid is produced equivalent to the Co(III) complex reduced. But when the reaction mixture is distilled at room tem-

perature, very little alcohol is recovered although blank experiments with methanol added to a solution containing Cr(III) show that the distillation procedure leads to complete recovery of the alcohol. The paradox implied by the two results has been resolved by subsequent work[2] (the alcohol is in fact bound to the Cr(III)), and it can be taken as proven that ester hydrolysis accompanies electron transfer through the ligand.

Acid Phthalate as Ligand (Table IV).

TABLE IV

THE REACTION OF Cr(II) WITH ACID
PHTHALATOPENTAMMINE COBALT(III)

$(\mu = 1.00 \pm 0.02)$

No.	$(Co(III))_0 \times 10^3$	$(Cr(II))_0 \times 10^3$	(H^+)	Temp., °C.	k, mole^{-1} sec.$^{-1}$
1	1.31	5.3	1.00	25.0	0.085
2	1.60	5.7	0.100	24.3	.173
3	1.40	4.0	.030	25.4	.392
4	1.52	7.6	.93	14.0	.057
5	1.67	3.8	.060	14.2	.093
6	8.3	5.7	.050	13.9	.060

Discussion of the cause of the abnormally low specific rate observed in experiment 6 is deferred until the next section. A similar effect appears in the data reported there and is more completely documented by them.

Isophthalate as Ligand (Table V).

TABLE V

THE REACTION OF Cr^{++} WITH ACID
ISOPHTHALATOPENTAMMINE COBALT (III)

$(\mu = 1.02 \pm 0.02)$

No.	$(Co(III))_0 \times 10^3$	$(Cr(II))_0 \times 10^3$	Temp., °C.	(H^+)	k, mole^{-1} sec.$^{-1}$
1	2.43	3.76	25.1	1.00	0.132
2	4.26	3.57	25.0	1.01	.113
3	6.68	5.67	25.0	1.00	.083
4	1.98	5.29	25.1	0.065	.13
5	1.84	6.73	14.3	0.97	.11
6	1.27	4.86	38.2	1.00	.16

Experiments 1, 2 and 3 of Table V show that the specific rates decrease as the initial concentration of the Co(III) complex increases. This effect is attributed to the formation in solution of complexes analogous to $Cr_2(OAc)_4$. The association becomes quite marked when the acidity is low and the concentration of the Co(III) complex is high, and the Cr(II) complex can be observed visually under these conditions. Since the effect is more marked at low acidity, the apparent decrease in specific rate with acidity which is noted in Table V can be attributed to this cause, although the possibility that there is a real variation of rate with acidity cannot be eliminated. The results for experiments 1, 5 and 6 at high acidity and low (Co(III)) probably are close to the true second order rate constants, and these provide the basis for the calculations of ΔH^* and ΔS^* which were made and have been entered in Table VI.

Acid Terephthalato as Ligand.—In Fig. 1 are shown the data for a typical experiment in which the material obtained in the attempted preparation of the terephthalato complex was used as oxidizing agent. It is clear from the data that there are at least two components in the reaction mixture. (The analysis to be presented shows that the data can be understood by assuming only two components.) If it is assumed that the component which reacts more rapidly (Form I) has an extinction coefficient per mole of Co(III) the same as the other form, it is estimated that approximately 20% of the Co(III) is present as form I. Thus when Cr^{++} is added in substantial excess of form I, the initial observations corresponding to the consumption of I are expected to conform to first order kinetics. Figure 2 shows the data of Fig. 1 when they are treated by subtracting from the total rate that for the reactions of the more inert component. The total initial consumption of Cr^{++} in experiments in which it is only in slight excess of form I showed that the assumption that form I has a normal extinction coefficient is at least approximately valid.

Acid titration of the material prepared and analysis leading to comparison of the cobalt and terephthalic content of the material indicate that the major constituent is the complex having two Co(III) centers for each terephthalate.

Summary of the Kinetic Data.—The variation of the rate with the concentration of Cr^{++} and Co(III) has been dealt with already, but the variation of the rate with acidity calls for further comment. Examination of the data shows that the rates of reaction of the acetato, the acid succinato and probably of the acid isophthalato complexes do not vary with acidity in the range of 0.1 to 1.0 M. A term in the rate law inverse in (H^+) can be expected for the latter two oxidizing agents, corresponding to the reactions of the proton-free ligand complexes, rather than the acido complexes, but these terms are not exposed at the lowest acidities studied. This term does appear in the range of acidity covered for the acid phthalato complex and for the acid fumarato complex but for the latter only at acidities below 0.01 M H^+.

A striking feature of the data for the acid fumarato and for the half-ester complex is that the rate at which they react with Cr^{++} *increases* linearly with acid at high enough concentration of acid. Thus for the acid fumarato complex, three terms are required to express the variation of rate with acidity, and the complete rate law takes the form

$$\frac{-d(RFH^{++})}{dt} = (Cr^{++})(RFH^{++}) \left[k_1 + \frac{k_2 K_D}{(H^+)} + k_3(H^+) \right]$$

$$\quad\quad\quad\quad\quad\quad I \quad\quad\quad II \quad\quad\quad III$$

$$A$$

Term III is by no means trivial, and in fact the data of Table III show that in 1 M acid this is the dominant term in the rate law. A similar term appears also when the methyl fumarate half-ester is ligand, and when acid terephthalate is ligand, but not when acid phthalate, acid isophthalate or acid succinate is the ligand.

Table VI summarizes the data on the specific rates for the various paths with the different oxidizing agents, the specific rates k_1, k_2 and k_3 being used in the same sense as in rate law A. Values of ΔH^* and ΔS^* have also been calculated when the data appear to justify analysis of the variation of rate with temperature. Even though the

TABLE VI

RATE AND ENERGETIC DATA[a]

	Acid			Path Anion			Protonated		
Complex	k_1, mole $^{-1}$ sec. $^{-1}$	ΔH_1^*, kcal.	ΔS_1^*, e.u.	k_2, mole $^{-1}$ sec. $^{-1}$	ΔH_2^*, kcal.	ΔS_2^*, e.u.	k_3, mole $^{-2}$ sec. $^{-1}$	ΔH_3^*, kcal.	ΔS_3^*, e.u.
Succinato	0.17 at 14.1°								
Maleato[b]	>50 at 1.9°								
	>30 at 25.1°								
Fumarato[d] (in H_2O)	0.48 at 1.9°	6.7	−36	1.1 at 5.4°			2.16 at 1.9°	2.9	−45
	0.75 at 14.3°						2.76 at 14.3°		
	1.32 at 25.1°						3.48 at 25.1°		
Fumarato[c,d] (in D_2O)	0.41 at 1.9°						2.45 at 1.9°		
Acetato	.18 at 25.1°	3.0	−52						
	.23 at 37.7°								
o-Phthalato[e]	.055 at 14.2°	4.4	−38	0.71 at 14.2°	12.8	−14			
	.075 at 25.1°			1.70 at 25.1°					
Isophthalato	.11 at 14.2°	2.1	−56						
	.13 at 25.1°								
	.16 at 38.2°								
Terephthalato	36 at 16.6°						9 at 16.6°		
Methylsuccinato	0.165 at 25.0°								
Methylmaleato	>10² at 2.3°								
	>10² at 14.1°								
Methylfumarato[d]	0.43 at 2.5°						1.28 at 2.5°		

[a] Some of the values differ from provisional values reported (*Can. J. Research*, **27**, 129 (1959)). [b] Lower limit for k (not k_1) is reported. [c] Using a linear extrapolation to 100% D_2O. [d] Using data of experiments 6–17, Table III. [e] Obtained by plotting specific rates recorded in Table IV as function of H^+.

data for the phthalato complex at the two temperatures studied conform to a rate law containing terms I and II as defined in rate law A, the value of ΔH^* which is implied by the data may be in considerable error. The complication arising from
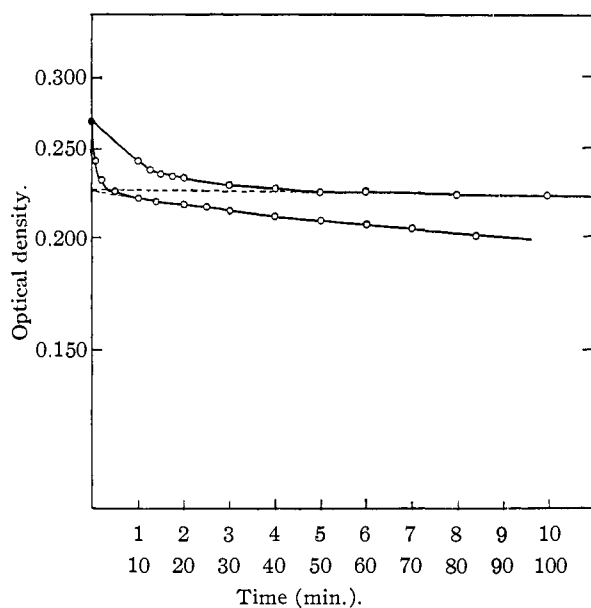

Fig. 1.—Optical density of reaction mixture of p-phthalato complex and Cr as a function of time. $R^+ = 0.196$ g./liter, $(Cr^{++})_0 = 0.40 \times 10^{-3}$ M, $(H^+) = 1.00$ M, temp. = 16.1°, $\mu = 1.01$.

the formation of the Cr^{++}-carboxylate complex affects term II particularly. Both in the case of phthalato and the isophthalato complexes, it is assumed that it has only a minor effect on the data relating to path I.

Discussion

Important among the present results is the demonstration for at least several of the systems examined, that the rate of reaction is first order in
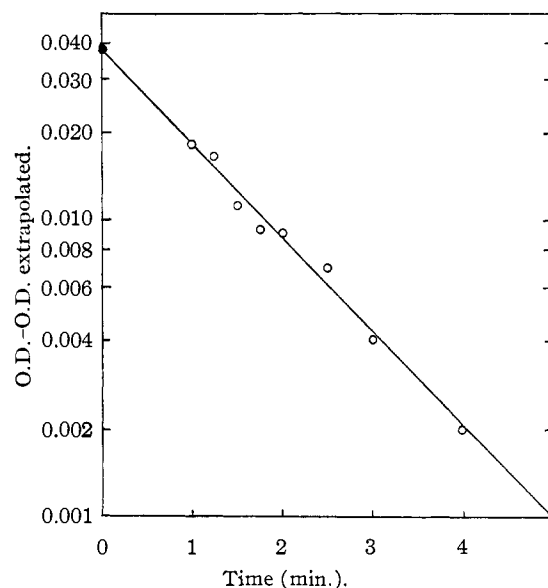

Fig. 2.—Difference in optical density between that observed and that extrapolated from the slowly reacting portion of Fig. 1.

the oxidizing agent and in the reducing agent. The general conclusion based on the early preliminary results[1] that there are large differences in the rate at which carboxylate complexes react with Cr^{++} is borne out also by the present work, and the suggestion that conjugated systems of bonds can serve to conduct the electron is better il-

lustrated by certain of the systems which have been described in the present paper. In the light of the proof[2] that electron transfer can take place by remote attack of Cr^{++}, some features of the rate data readily can be understood.

The acetato, butyrato[1] and acid succinato complexes all react with Cr^{++} at about the same rate. In each case, attack by Cr^{++} is limited to a carboxyl adjacent to Co(III), and the immediate environment for the Cr^{++} is about the same for all, hence the similar rates. It is interesting that the polar group at the remote end of the succinate ligand does not help much to increase the rate of reaction. Thus presumably chelation of the Cr^{++}

by the remote $-C\diagdown\!\!\!\!\overset{\textstyle O}{}_{OH}$ does not take place in the

activated complex. The experiments on ester hydrolysis prove that when the methyl half-ester of fumaric acid is the ligand, Cr^{++} attacks the oxidizing complex at the remote or ester-bearing end. The mechanism involving remote attack by the reducing agent which is made possible by the bond-system in the fumarate half-ester ligand does not require as close an approach of Cr^{++} to the Co(III) center, and the higher rate can be ascribed to the circumstance that the repulsion of the two positive centers in the activated complex is lessened. Since the kinetic results for acid fumarate as ligand are almost identical with those for the half-ester, we ascribe similar mechanisms to the reactions of the two complexes with Cr^{++}.

The results for the complexes of the three phthalic acids fit in with the idea that remote attack by the reducing agent can take place when the sensitive ligand has suitable properties. Thus conjugation is not possible between the carboxyl groups of the isophthalate complex, so that Cr^{++} presumably attacks the complex at the carboxyl adjacent to the Co(III), and a slow rate of reaction is observed. The two carboxyls in the acid phthalato complex are likely not coplanar, and effective conjugation again is not possible. But it is possible for the terephthalato complex and here a rapid rate of reaction is observed.

The observation that the rates at which the acid fumarato or methyl fumarato complexes react with Cr^{++} increase linearly with the concentration of hydrogen ion is a striking and, we believe, novel effect. The experiment on the exchange of the group -C—C- with D_2O shows that the additional proton is not attached to C in such a way as to become equivalent to those already there. The suggestion[7] that the proton is used to redistribute electrons in the carboxyl adjacent to Co(III), thus improving conjugation between Cr^{++} at the remote end and Co(III) still seems to us to be reasonable. It is consistent with the observation that the rate by the H^+ promoted path is at least somewhat greater in D_2O with D^+ as catalyst, than in H_2O with H^+ as catalyst.[8] The

basicity of the oxygen in question although quite low for the half-ester complex may become much greater in the activated complex as electrons are redistributed to provide for the net change taking place. It is significant that the H^+ effect is observed precisely in those cases in which remote attack can reasonably be invoked but not in those in which adjacent attack only can take place.

It is remarkable that the rates of reaction are so nearly the same for the acid fumarato complex, the deuterio form and for the methyl half-ester. This seems to imply that breaking the O–H (or O–D or O–CH₃) bond is not part of the rate determining step for the electron transfer process, although these processes do take place eventually. One reasonable possibility that accommodates the observation is that the result of the rate determining step is the attachment of Cr (as Cr^{+++}) to the remote end and the loss of Co (as Co^{++}) from the other, the further changes then taking place in the resulting Cr^{+++} complex of abnormal structure. Another is that the rate-determining act is the formation of a bi-nuclear *intermediate* which contains both Cr and Co, the further changes then taking place in this intermediate. The present observations do not lead to a distinction between these possibilities, important as this distinction is, but observations to be published (Fraser and Taube) favor the second.
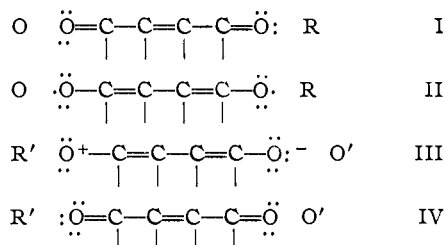
The paths for the reactions of complexes of the proton-free forms of the dibasic acids have only been explored incompletely. It can reasonably be expected that in those cases in which the free carboxyl group is close to the carboxyl bearing the Co^{+++}, the sensitivity to removal of the proton will be greatest. In support of this supposition, the "proton-free" path for the phthalato complexes comes out quite clearly in the present results, but that for the isophthalato and succinato is not exposed. The suggestion of course applies to the proton-free complexes at equivalent concentrations, so that for the observations as made in acidic solution, the dissociation constants of the acid complexes is also an important factor in determining the contribution by the proton-free path at any particular acidity. The rates at which the fumarato and the acid fumarato complexes react are not much different. It is possible that a single proton may actually benefit the electron transfer process in the same way that a second proton does, so that although there is a net decrease in rate when the first proton is added (because of the neutralization of the negative charge), this decrease is not as great as would be the case if the proton were not also useful. It is in fact possible that in the proton-free path, Cr^{++} does not attack the remote end of the fumarate but rather the carboxyl adjacent to the Co(III).

The Co(III)–Cr^{++} system as it has been applied seems to provide a means of learning which ligands can readily conduct electrons from the reducing

(7) H. Taube, *Can. J. Research*, **27**, 129 (1959).

(8) Professor F. A. Long has raised the point that even for very strong acids, K_d is expected to be greater in H₂O as compared to D₂O by a factor greater than that implied by the ratio of k_1 in H₂O as com-

pared to D₂O. It may be that the acids on which this supposition is based are not good models for the present case. A better model is probably provided by $(NH_3)_5CoH_2O^{+++}$; for this acid K_d in H₂O is compared to D₂O is 1.5 (ref. 6); for $Fe(H_2O)_6^{+++}$ the corresponding ratio is 1.0 (J. Hudis and R. W. Dodson, *J. Am. Chem. Soc.*, **78**, 911 (1956).

agent to the acceptor center. But in every case, the mechanism by remote attack competes against adjacent attack, so that ligands which have a small though definite capacity for electron conduction are not recognized and, in any case, the relative rates at which reaction by remote attack takes place, even when corrected for the different degrees of electrostatic repulsion in the activated complex, do not provide a measure of the relative conductances of the ligands in the usual sense (as for example when the conductances of metals are compared). The electron transport is presumably very rapid, and the different groups differ in the facility with which they adopt a configuration appropriate to the conduction process.

The mechanism of conduction by the conjugated systems is itself a matter of some general interest. It can be represented formally by the succession of changes

$$O \quad \ddot{O}{=}C{-}C{=}C{-}C{=}\ddot{O}{:} \quad R \qquad I$$

$$O \quad \cdot\ddot{O}{-}C{=}C{-}C{=}C{-}\ddot{O}\cdot \quad R \qquad II$$

$$R' \quad \ddot{O}^{+}{-}C{=}C{-}C{=}C{-}\ddot{O}{:}^{-} \quad O' \qquad III$$

$$R' \quad {:}\ddot{O}{=}C{-}C{=}C{-}C{=}\ddot{O} \quad O' \qquad IV$$

State III is arrived at when the conjugated system gains an electron from the reducing agent and loses one to the oxidizing agents. If state II is written

with opposed spins, all the states represented are resonance forms of the ground state. The representation presumably corresponds to the "double exchange" mechanism discussed by Halpern and Orgel.[9] These authors have outlined the features of the different mechanisms which can be considered, including in addition to that already mentioned, the super-exchange mechanism and the ordinary chemical mechanism involving net loss of an electron to the oxidizing center as the first step, or net gain of an electron from reducing agent as the first step. The second two may be distinguishable from the first two because of the chemical consequences of forming radical ions from the bridging ligand. But it is not clear how the first two can be distinguished from each other unless the conductance of the groups is actually measured and related to the properties of the bridging group, the properties of interest including the energy required to generate the excited states. If as we surmise a binuclear intermediate is in fact formed, none of the descriptions offered may be particularly apt, since then the important consideration is not how the electron gets from the donor to the acceptor center but, rather, the energy levels of the intermediate and how they are populated.

(9) J. Halpern and L. E. Orgel, *Disc. Farada Soc.*, in press (1960).

# Kinetics of Nickel(II) Ligand Exchange Reactions: Cyanide Ion and (Ethylenedinitrilo)-tetraacetate Ion

By D. W. Margerum, T. J. Bydalek and John J. Bishop

Nickel(II) forms mixed complexes with cyanide and (ethylenedinitrilo)-tetraacetate ions. The transition between the octahedral, paramagnetic EDTA complex and the planar, diamagnetic cyanide complex is kinetically controlled by the presence of three cyanide ions around nickel. This study indicates that it is not necessary to postulate a direct bimolecular exchange between $Ni(CN)_4^{-2}$ and nickel complexes such as previously reported.

Introduction

In this work the formation and dissociation kinetics of the tetracyanonickelate ion are studied in the presence of the EDTA anion (Y^{-4}). The reaction

$$NiY^{-2} + 4CN^- \rightleftharpoons Ni(CN)_4^{-2} + Y^{-4} \qquad (1)$$
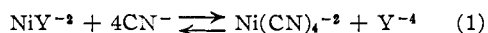
involves both the displacement of a multidentate ligand by monodentate ligands and the transition from an octahedral, paramagnetic complex to a planar, diamagnetic complex. This work indicates that this transition is kinetically controlled by the presence of cyanide ions about nickel.

As a result of radiocyanide exchange experiments the $Ni(CN)_4^{-2}$ complex has been considered labile.[1,2] However, there is a slow exchange of radionickel between $Ni(CN)_4^{-2}$ and the nickel

complexes of ethylenediamine, oxalate, tartrate[3] and several amino acids.[4] The sluggishness of these systems must be attributed in part to the cyanide complex since the other complexes are labile. Thus, rapid exchange is observed with $Nien_3^{+2}$ and Ni^{+2} and with $Nien_3^{+2}$ and $en^{5,6}$. In addition, the nickel(II) complexes of oxalate and tartrate are considered labile.[7] Although the exchange of radiocyanide with $Ni(CN)_4^{-2}$ has been too rapid to measure the exchange of radionickel with this complex is not appreciable within one minute at pH 4 to 8. The precipitation of $Ni(CN)_2$ prevents a more detailed study.[8] Since the formation rate of $Ni(CN)_4^{-2}$ from Ni^{+2} and CN^- is very rapid, some dissociation step of CN^- from a

(1) A. W. Adamson, J. P. Welker and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).

(2) A. G. MacDiarmid and N. F. Hall, *ibid.*, **76**, 4222 (1954).

(3) F. A. Long, *ibid.*, **73**, 537 (1951).

(4) R. C. Calkins and N. F. Hall, *ibid.*, **80**, 5028 (1958).

(5) J. E. Johnson and N. F. Hall, *ibid.*, **70**, 2344 (1948).

(6) D. S. Popplewell and R. G. Wilkins, *J. Chem. Soc.*, 4098 (1955).

(7) H. Taube, *Chem. Revs.*, **50**, 69 (1952).