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Conjugation and Mobile Bond Order in Electron Transfer Reactions¹

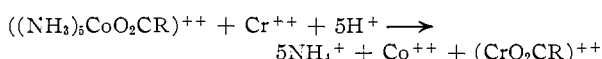
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The rates of electron transfer between Cr^{++} aq. or V^{++} aq. and pentamminecarboxylatocobalt(III) complexes (where the organic ligand is a dicarboxylic acid of benzene, biphenyl or naphthalene) have been measured, and the results compared with recent theoretical predictions relating the over-all rate of reaction with the mobile bond order of the bridging path. The rate law for complexes containing these condensed aromatic systems is usually of the form $(k_1 + k_2[\text{H}^+])[\text{CoL}^{++}][\text{Red}]$, and there is no term corresponding to transfer of the electron through the ligand by a non-protonated path. For transfer to take place through a biphenyl system, the rings must assume a coplanar configuration.

Introduction

It has been demonstrated² that electron transfer between Cr^{++} aq. and pentamminecobalt(III) complexes may take place through an organic acid as bridging group



With ligands such as acetate or butyrate, attack by the reductant is possible only at the carboxyl group attached to the cobalt; with fumarate or terephthalate, Cr^{++} aq. may react at either of the two carboxyl groups, giving adjacent and remote attack,³ and the specific rate constant for the reaction is then composed of two terms, one of which shows first order dependence on the hydrogen ion concentration of the solution.² This remote attack is possible only when a conjugated system extends from the Co(III) to the far carboxyl: with ligands such as methyl succinate the electron transfer proceeds only by adjacent attack.

The role of conjugation in the ligand has aroused some interest, and an attempt has been made⁴ to relate the over-all specific rate constant (for remote attack) to the mobile bond order⁵ between the terminal atoms of the bridge. This theory is based on the supposition that the over-all rate constant for the process may be related to the square of the electron exchange frequency, when the probability of electron transfer during the lifetime of the bimolecular intermediate is small. When the reacting metal centers are joined through a conjugated bridge (such as fumarate) the exchange frequency may be regarded, to a first approximation, as proportional to the mobile bond order $P\alpha\omega$, between the atoms to which the metals are attached: the rate constant should thus decrease as the length of the conjugated chain increases.

This paper reports rate constants measured for electron transfer between Cr^{++} aq. or V^{++} aq. and Co(III) through dicarboxylic acids of the benzene, biphenyl and naphthalene series. In the biphenyls, the ligands have been chosen so that a comparison may be made between those where conjugation can exist, due to coplanarity of the ring, and those where the rings are twisted.

(1) This research supported by a National Research Council of Canada Operating Grant.

(2) H. Taube, *Can. J. Chem.*, **37**, 129 (1959).

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

(4) J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960).

(5) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

Experimental

Materials.—4,4'-Dicarboxybiphenyl was prepared by refluxing 4-iodobenzoic acid (as the methyl ester) with copper powder in nitrobenzene. 2,2'-Diiodo-4,4'-dicarboxybiphenyl was obtained from 3-nitro-4-iodobenzoic acid⁶; Ti^{3+} was used to reduce the nitro intermediate. The 1,4- and 1,5-dicarboxynaphthalenes were prepared from the corresponding aminonaphthalenesulfonic acids.⁷

The pentamminecobalt(III) complexes were prepared by a method similar to that described elsewhere⁸: a slurry of pentammineaquocobalt(III) perchlorate was heated with a mixture of the sodium salt and the free acid of the organic ligand on a steam-bath. With organic acids of such high molecular weight, not only is substitution on the cobalt slow, but considerable decomposition of pentammineaquocobalt(III) ion occurs and the presence of halogen substituents in the ligand appears to increase the rate of this decomposition, in the order $-\text{F} < -\text{Cl} < -\text{Br} < -\text{I}$. The decomposition can be slowed down somewhat by immersing the reaction mixtures in a constant temperature bath maintained at 60°. To prepare the biphenyl complexes, the decomposition was allowed to proceed almost to completion. The resulting mixture was filtered, the filtrate made 0.1 M in perchloric acid, filtered again if necessary, and the remaining solution (A) containing unchanged pentammineaquocobalt(III) ion, the desired complex and any binuclear complexes poured onto a column of Dowex 50W-X12 resin. The mononuclear complex containing the organic ligand was eluted with 2 M perchloric acid. Yields were of the order of 2–10% based on (A). The complexes containing naphthalene dicarboxylic acids were prepared by warming the reaction mixture for five days in the constant temperature bath. Pentammine-terephthalatocobalt(III) perchlorate was prepared by chlorine oxidation of the *p*-aldehydobenzoato complex.⁹ Titration with standard alkali showed that 97% of the resulting mixture was the desired complex.

Rates.—The rate of reaction of the cobalt(III) complex with Cr^{++} aq. or V^{++} aq. was measured by the rate of disappearance of the absorption maximum around 500 $\mu\mu$, using a Beckman DK1 or DK2 spectrophotometer. The method for mixing the reactants and filling the optical cells has been described elsewhere.¹⁰ An ionic strength of 1.0 was maintained in the reaction mixtures by prior addition of sodium perchlorate.

Results

Only two rate laws were required to describe all the systems examined in the range $[\text{H}^+] = 0.1$ to 0.8 M. These were

$$-d[\text{CoL}^{++}]/dt = k - [\text{CoL}^{++}][\text{Red}^{++}] \text{ or} \\ = (k_1 + k_2[\text{H}^+])[\text{CoL}^{++}][\text{Red}^{++}]$$

all reactions were first order in cobalt(III) and reductant concentration. The specific rate constants found are listed in Table I: in Table II these have been corrected to give the constants for the acid-

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(7) E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc. (London)*, 1739 (1936).

(8) H. Taube, *J. Am. Chem. Soc.*, **77**, 448 (1955).

(9) R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960).

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

TABLE I
 SPECIFIC RATE CONSTANTS (L. MOLE⁻¹ SEC.⁻¹)

Complex	$k_{Cr^{++}}$	$k_{V^{++}}$	Temp., °C.
Oxalato	>33 ^a	..	23.0
Acetato	0.18 ^b	0.43	25.0
Fumarato	1.32 + 3.48 (H ⁺) ^b	..	25.0
Benzoato	0.14	0.52	25.0
<i>o</i> -Phthalato	.07 ₅ ^b	1.01	25.0
<i>m</i> -Phthalato	.13 ^b	0.60	25.0
<i>p</i> -Phthalato	36 ^b	.43 + 0.44 (H ⁺)	21.0
<i>p</i> -Aldehydobenzoato	^c	.57 + .17 (H ⁺)	25.0
2'-Carboxybiphenyl-2-carboxylato	0.10 + 0.37 (H ⁺)	.12 + .15 (H ⁺)	21.0
4'-Carboxybiphenyl-4-carboxylato	^c	.14 + .15 (H ⁺)	21.0
4'-Carboxy-2,2'-diiodobiphenyl-4-carboxylato	0.12	.41	25.0
Naphthyl-1-carboxylato	.07	.14	21.0
Naphthyl-2-carboxylato	.11	.20	21.0
4-Carboxynaphthyl-1-carboxylato	.08 + 3.4 (H ⁺)	.15 + .11 (H ⁺)	21.0
5-Carboxynaphthyl-1-carboxylato	.08 + 2.8 (H ⁺)	.17	21.0
6-Carboxynaphthyl-2-carboxylato	.08 + 2.7 (H ⁺)	.20	21.0

^a Ref. 8. ^b Ref. 10. ^c Too fast to allow measurement.

 TABLE II
 SPECIFIC RATE CONSTANTS FOR REMOTE ATTACK

Complex	Cr^{++}		V^{++}	
	k_1'	k_2	k_1'	k_2^a
Fumarato	1.14	3.48
<i>p</i> -Phthalato	^b	..	0.0	0.44
<i>p</i> -Aldehydobenzoato	^b	..	.05	.17
2'-Carboxybiphenyl-2-carboxylato	..	0.37	..	.15
4'-Carboxybiphenyl-4-carboxylato	^b15
4-Carboxynaphthyl-1-carboxylato	0.0	3.4	.0	.11
5-Carboxynaphthyl-1-carboxylato	.0	2.8	.0	.0
6-Carboxynaphthyl-2-carboxylato	.0	2.7	.0	.0

^a From $k = k_{1(adj)} + k_{1(remote)} + k_2(H^+)$ where k_1' refers to remote attack, non-protonated path, k_2 to remote attack, protonated path (cf. ref. 3). The units of k_1' are l. mole⁻¹ sec.⁻¹, those of k_2 l.² mole⁻² sec.⁻¹. ^b Too fast to allow measurement.

independent and acid-dependent remote paths (by subtracting from the acid independent term the value of the specific rate constant for the reaction with the corresponding mono-carboxylic acid⁸).

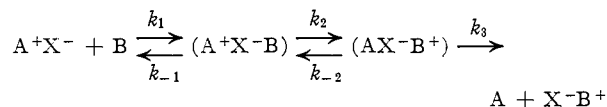
Discussion

The Effect of Mobile Bond Order.—Perhaps the most striking feature of Table II is the number of cases where k_1' equals zero; in these condensed systems remote attack and subsequent electron transfer by a non-protonated path appears to be the exception. This is in marked contrast to the reactions involving chromous ion and fumarate as ligand¹⁰ and has been found previously only in the *p*-phthalate series when the remote carboxyl is esterified with a phenol.^{3,11} It may be noted here that the rate law found for the reaction of the phenylterephthalato complex with V⁺⁺ aq. at 25° ($-d[CoL^{++}]/dt = (0.50 + 0.17[H^+])[CoL^{++}][V^{++}]$) is very similar to that of the V⁺⁺-*p*-aldehydobenzoato reaction listed in Table I. This emphasizes a difference between the reaction of V⁺⁺ aq. and Cr⁺⁺ aq. With chromous ion, the reactions

(11) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, in press (1961).

with complexes containing ligands such as terephthalate, *p*-aldehydobenzoate and 4-carboxybiphenyl-4-carboxylate are very fast, while those with the complexes containing phenylterephthalate or 2'-carboxybiphenyl-2-carboxylate can be measured easily. With vanadous ion, the terephthalato, phenylterephthalato and *p*-aldehydobenzoato complexes react at about the same rate, as do the two biphenylcarboxylates.

The over-all process for the electron transfer may be expressed as⁴



thus k_{bi} (the rate constant for the over-all process) = $k_1/[1 + (1 + k_{-2}/k_3)k_{-1}/k_2]$. With the assumptions $k_2 = k_{-2}$, $k_{-1} = k_3$, $k_{-1} \gg k_2$ (corresponding to a small probability of electron transfer during the lifetime of the intermediate A^+X^-B), $k_{bi} \approx k_1k_2/k_{-1}$ and the transition probability then determines the rate. The simple theory points out a relationship between this probability and the square of the exchange frequency in systems where coupling of the metal centers by the bridging ligand is weak, and further simplifications indicate a direct relationship between the exchange frequency and the mobile bond order of the ligand. As a minimum, then, the theory should show that for a series of dicarboxylic acids rate constants for the oxidation-reduction process should decrease as the mobile bond order of the path for electron transfer decreases. For the ligands examined in this work, the trend of decreasing bond order is oxalate \gg fumarate \gg *o*-phthalate $>$ *p*-phthalate \sim 4-carboxynaphthalene-1-carboxylate $>$ 6-carboxynaphthalene-2-carboxylate $>$ 4'-carboxybiphenyl-4-carboxylate \sim 2'-carboxybiphenyl-2-carboxylate \sim 5-carboxynaphthalene-1-carboxylate. This trend is not affected whether the basic group (benzene, naphthalene), the basic group plus one carboxyl or the basic group plus one carboxyl and one ionic carboxylate group is taken as the measure of bond order (the magnitudes of the differences will of course depend very much on the particular system of bond orders

TABLE III

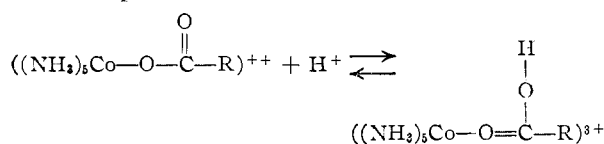
MOBILE BOND ORDERS (p_{rs}) IN CONJUGATED SYSTEMS	Carbon r	Carbon s	Bond order
Butadiene	1	4	0.42 ^b
Hexatriene	1	6	.30 ^b
Benzene	1	2	.67
	1	3	0
	1	4	0.33
1,2-Divinylbenzene	α^a	ω^a	.16
1,4-Divinylbenzene	α	ω	.15
Naphthalene	1	4	.36 ^b
	1	5	.08 ^b
	2	5	0 ^c
	2	6	0.16 ^c
1,4-Divinyl-naphthalene	α	ω	.17
2,6-Divinyl-naphthalene	α	ω	.08
1,5-Divinyl-naphthalene	α	ω	.04
Biphenyl	4	4'	.10 ^b
	2	2'	.11 ^d
4,4'-Divinylbiphenyl	α	ω	.05

^a α , ω refer to the terminal carbons of each vinyl group.

^b Ref. 4. *B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson and Cie., Paris, 1952. Derived from functions listed on p. 197.

^c Ref. c from values on p. 638.

taken): the divinyl system is probably most satisfactory. Table III lists the bond orders for the systems under study (for example, the bond order of oxalate is related to that of butadiene): although the values may be changed slightly by taking into account the carboxyl oxygens rather than additional carbon atoms, the difference should be slight. The variation in rates for the complexes other than oxalate should be small even if based on the squares of the bond orders: and this is not found experimentally when Cr^{++} is the reductant where large variations occur (k for the terephthalato complex has been estimated¹⁰ at 36 sec.⁻¹ at 16.6°). Further, the rate laws for some complexes display a term corresponding to electron transfer by remote attack, non-protonated path, while the laws for other very similar complexes do not. It would be desirable to express the term $k_2[\text{H}^+][\text{CoL}^{++}][\text{Red}]$ as $k_2/K[\text{CoLH}^{3+}][\text{Red}]$ where K is the constant for the equilibrium



and to compare k_2/K values rather than k_2 values, but even this would not explain why the reaction rate of the 1,4-substituted naphthalene complex with V^{++} increases with $[\text{H}^+]$, whereas that for the 1,5- or 2,6-substituted does not. Using $(k_1' + k_2)$ as the basis of comparison, the experimental order of decreasing rate constants for chromous ion is oxalato $\sim p$ -phthalato \gg 4'-carboxybiphenyl-4-carboxylato $>$ fumarato $>$ 4-carboxynaphthalene-1-carboxylato $>$ 5-carboxynaphthalene-1-carboxy-

lato \sim 6-carboxynaphthalene-2-carboxylato \gg 2'-carboxybiphenyl-2-carboxylato. For the vanadous ion, the cobalt(III) complexes in order of decreasing rate constant are fumarato $>$ p -phthalato $>$ 4'-carboxybiphenyl-4-carboxylato \sim 2'-carboxybiphenyl-2-carboxylato $>$ 4-carboxynaphthalene-1-carboxylato.

The suggestion⁴ has been made that electron transfer between t_{2g} orbitals should be favored through π -orbitals, transfer between e_g orbitals and through σ -orbitals. In these reactions involving Co(III) complexes, increasing conjugation (by increasing $[\text{H}^+]$) appears to favor the electron transfer process when $\text{Cr}^{++}\text{aq.}$, transferring an electron from a t_{2g} orbital, is the reductant, rather than when $\text{V}^{++}\text{aq.}$ is the reductant.

At present, it appears that the simple theory, while successful in explaining in retrospect the effect of protonation of the ligand, is not capable of predicting relative rates of electron transfer even in a closely related series as the complexes containing the naphthalene dicarboxylic acids. While this is disappointing, in view of the assumptions made it is not too surprising, since the differences in mobile bond orders are small.

The Effect of Conjugation.—Although in benzene $P_{12} = 0.67$ and $P_{14} = 0.33$ ($P_{\alpha\omega}$ 1,4-divinylbenzene = 0.15, $P_{\alpha\omega}$ 1,2-divinylbenzene = 0.16), remote attack by $\text{Cr}^{++}\text{aq.}$ occurs only with p -phthalato complex, not with the o -substituted. The explanation advanced¹ for this surprising result is that the two carboxyls in the o -phthalate cannot be planar because of their size, thus conjugation through the bridge is not possible. With maleate—a ligand of almost the same configuration—attack by the Cr^{++} is to the ligand not through it,^{1,12} and conjugation between the carboxyls is unnecessary.

With the biphenyl ligands, conjugation again depends on steric factors—the relative orientation of the rings. In the 4,4' disubstituted biphenyl, the rings may lie in the same plane, conjugation is possible between the two carboxyls, and the rate of reaction is either very fast (with $\text{Cr}^{++}\text{aq.}$) or shows a term dependent on $[\text{H}^+]$ (with $\text{V}^{++}\text{aq.}$), indicating remote attack. When iodine atoms are present in the 2,2' positions, the rings are no longer coplanar, conjugation no longer exists and this results in the disappearance of the acid-dependent term from the specific rate constant—only adjacent attack takes place in the electron transfer. Further, the rate constants for the reaction of the 2,2'-diiodo-4,4'-dicarboxybiphenyl complex with either Cr^{++} , or V^{++} are almost identical with those for the benzoato complex with the corresponding reductant.

Acknowledgments.—The author wishes to thank Professor H. Taube, University of Chicago, for his interest in the research.

(12) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **81**, 5514 (1959).