

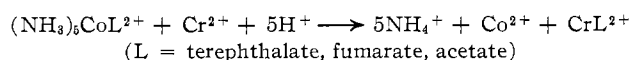
Electron Transfer by Remote Attack on Conjugated Ligands. The Reduction of Pentaamminephthalato- and Pentaamminehemimellitocobalt(III) Ions by Chromium(II) Perchlorate¹

By R. T. M. FRASER

Received August 26, 1963

Esterification of the noncoordinated carboxyl groups has shown that remote attack is possible in the chromium(II) reduction of *o*-carboxybenzoate complexes of pentaamminecobalt(III). While the rate of reduction by the adjacent path decreases along the series phthalato, methyl phthalato, dimethyl hemimellitato, the rate of remote attack increases. Increasing *ortho* substitution increases ΔH^\ddagger , but this is partly offset by an increase in ΔS^\ddagger . The rate constants observed at 25.6° are $k = 0.053 + 0.015[\text{H}^+] \text{ M}^{-1} \text{ sec}^{-1}$ for the methyl phthalato and $k = 0.040 + 0.025[\text{H}^+] \text{ M}^{-1} \text{ sec}^{-1}$ for the dimethyl hemimellitato.

Ligands such as 4-carboxybenzoate (terephthalate) have been shown² to be effective mediators for the oxidation-reduction reaction



because they supply a conjugated path from the point of attack of the chromium(II) to the cobalt(III) center. This remote attack is distinguished kinetically by a term in the rate law which is first order in $[\text{H}^+]$. While some conjugation is necessary for reduction to take place by this path, the amount required as measured by the mobile bond order can be small.³ Thus the pentaammineisophthalatocobalt(III) ion with bond order of zero reacts by adjacent attack only, with a rate constant² of 0.13 l. mole⁻¹ sec.⁻¹ at 25° (the rate constant for the reduction of monobasic ligands such as acetate is² 0.17 l. mole⁻¹ sec.⁻¹), but the rate of reduction of the 4'-carboxybiphenyl-4-carboxylato complex (with bond order 0.05) is extremely rapid.³ The rate of reaction of the 2-carboxybenzoate complex suggests that no remote attack occurs, even although the bond order is 0.16, but rather that all reduction is due to chromium(II) attack at the coordinated carboxyl; however, the kinetic studies² are complicated because of the ionizable hydrogen on the 2-carboxyl. Association of the cobalt complex with the reductant may occur without electron transfer,² and the oxidation-reduction process itself involves two paths, one arising from the reaction of the deprotonated complex which manifests itself as an acid-inverse term in the rate law. The configuration of the 2-carboxybenzoate ligand with respect to the carboxyl groups is the same as that of maleato, but pentaamminemaleatocobalt(III) perchlorate is reduced very rapidly with chromium(II), and the per cent of ester hydrolysis induced in the methylmaleato complex suggests that remote attack is possible.⁴ One reason for the difference in rate behavior may be attack by the reductant directly at the double

bond in the maleato,⁵ rather than through the free carboxyl group.

This paper describes experiments using esters as ligands to eliminate reaction by the deprotonated path.

Experimental

Materials.—Monomethyl phthalate was prepared from phthalic anhydride and methanol. The diester 2,6-dicarbomethoxybenzoic acid was prepared following the method of Graebe and Leonhardt.⁶ The pentaammine complexes were obtained by warming the esters with pentaammineaquocobalt(III) perchlorate at 70° for several hours, extracting the acid solution with ether, then precipitating the complexes from solution with concentrated perchloric acid pre-chilled in an ice bath. The crude preparations were purified by selective adsorption on Dowex 50 resin.³ Methods for preparing the sodium perchlorate used to adjust the ionic strength of the solutions and the preparation of the chromium(II) perchlorate have been described previously.³

Kinetic Measurements.—All rates were measured in a Beckman DK 1 spectrophotometer by following the rate of disappearance of the 500 m μ cobalt(III) absorption peak. The solutions were prepared so as to contain 0.15×10^{-4} , 0.3×10^{-4} , or 0.50×10^{-4} mole of the cobalt complex in 20 ml. of solution. Five or seven ml. of chromium(II) perchlorate (0.1 M) in 0.1 M perchloric acid was added as quickly as possible with thorough mixing. Prior addition of perchloric acid and sodium perchlorate made the final ionic strength 1.0 in all reactions. A 10-cm. double-walled optical cell was used for the rate studies, and water from a constant temperature bath was circulated between the walls to maintain the temperature of the solution constant to $\pm 0.05^\circ$. The reductant solution was held in the water bath for 10 min. before use.

Hydrolysis Measurements.—The method previously described⁴ was used with slight modifications. The cobalt(III) solution was placed in a small flask directly in the water bath and stirred with a stream of nitrogen. The chromium(II) solution was injected through a serum cap fitted to the flask neck. The titrations were carried out on a Leeds and Northrup 4701 pH meter connected to a 10-mv. recorder.

Nomenclature.—The ligands formed from benzoic and *o*-phthalic acids, monomethyl phthalate, and dimethyl hemimellitato will be referred to the parent acid: *o*-phthalato becomes 2-carboxybenzoato (2-HO₂CC₆H₄COO⁻), monomethyl phthalato becomes 2-carbomethoxybenzoato (2-CH₃O₂C₆H₄COO⁻), and dimethyl hemimellitato becomes 2,6-dicarbomethoxybenzoato (2,6-(CH₃CO₂)₂C₆H₃COO⁻).

(1) This research was supported by a grant from the National Science Foundation.

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

(3) R. T. M. Fraser, *ibid.*, **83**, 4920 (1961).

(4) R. T. M. Fraser, *ibid.*, **83**, 564 (1961).

(5) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(6) C. Graebe and M. Leonhardt, *Ann.*, **290**, 217 (1896).

Results

Table I lists the results of the kinetic measurements and Table II the activation parameters for some substituted benzoato complexes.

TABLE I
THE REACTION OF Cr(II) WITH PENTAAMMINECOBALT(III)
COMPLEXES OF 2-CARBOMETHOXY- AND 2,6-DICARBOMETHOXY-
BENZOIC ACID

[Co(III)], $M \times 10^3$	[Cr(II)], $M \times 10^2$	[H ⁺], M	Temp., °C.	k , l. mole ⁻¹ sec. ⁻¹
2-Carbomethoxybenzoate				
1.20	2.0	0.2	25.6	0.056
1.20	2.0			0.056
1.85	2.59			0.055
0.55	2.59			0.056
				0.055 ± 0.0005
0.60	2.0	0.4	25.6	0.059
1.20	2.0			0.060
1.85	2.59			0.059
1.11	2.59			0.059
				0.0595 ± 0.0005
1.20	2.0	0.6	25.6	0.062
1.11	2.59			0.063
1.85	2.59			0.061
				0.062 ± 0.001
0.60	2.0	0.2	35.6	0.094
1.11	2.59			0.094
1.85	2.59			0.095
				0.0945 ± 0.0005
1.20	2.0	0.6	35.6	0.113
0.35	2.59			0.113
1.85	2.59			0.112
1.11	2.59			0.113
				0.1125 ± 0.0005
2,6-Dicarbomethoxybenzoate				
		0.2	25.6	0.045 ± 0.0005
		0.4	25.6	0.050 ± 0.0005
		0.6	25.6	0.055 ± 0.0005
		0.2	35.6	0.077 ± 0.0005
		0.4	35.6	0.087 ± 0.0005
		0.6	35.6	0.098 ± 0.0005

TABLE II
ACTIVATION PARAMETERS FOR THE ACID-INDEPENDENT PATH
(ADJACENT ATTACK)

Complex	ΔG^*_{obs} , kcal./ mole ⁻¹	ΔH^* , kcal./ mole ⁻¹	ΔS^* , e.u.	Ref.
2-Carbomethoxybenzoate	19.1 ± 0.2	8.05 ± 0.1	-37 ± 0.3	
2,6-Dicarbomethoxybenzoate	19.3 ± 0.2	9.1 ± 0.1	-34 ± 0.3	
Benzoate	18.7	4.9	-46	7
2-Carboxybenzoate	18.8	4.1	-49	2
2-Chlorobenzoate	18.9	6.0	-43	7
2-Iodobenzoate	19.0	2.8	-54	7

Discussion

Remote attack followed by electron transfer is a path for the reduction of pentaamminephthalatocobalt(III) complexes, although previous experiments² have not shown this.

The rates of reduction lie in a range particularly favorable to precise measurement, for the half-lives of the pseudo-first-order reactions are about 7 min. The changes in rate observed as the acidity of the

TABLE III
PER CENT HYDROLYSIS OF 2,6-DICARBOMETHOXYBENZOATE AT
35.60^a

Av. [H ⁺], M	% found	% calcd.
0.076	2	5.6
0.282	22	18
0.363	36	22

^a The observed rate laws are, for the 2-carbomethoxybenzoate
 $R = \{0.053 + 0.015[H^+]\} [Cr(II)][Co(III)] M \text{ sec.}^{-1}$ at 25.6°
 $R = \{0.085 + 0.045[H^+]\} [Cr(II)][Co(III)] M \text{ sec.}^{-1}$ at 35.6°
 and for the 2,6-dicarbomethoxybenzoate complex
 $R = \{0.040 + 0.025[H^+]\} [Cr(II)][Co(III)] M \text{ sec.}^{-1}$ at 25.6°
 $R = \{0.067 + 0.052[H^+]\} [Cr(II)][Co(III)] M \text{ sec.}^{-1}$ at 35.6°

solutions is increased, although small, are significant and cannot be attributed to changing medium. Complexes for which the acid-independent reaction has been demonstrated conclusively do not show this behavior⁷: the rate constants for the benzoato are 0.117 at 0.2 M H^+ and 0.118 at 0.6 M H^+ at 20°, and for the reaction of the 2-chlorobenzoato complex $k = 0.076$ (0.2 M) and 0.074 (0.6 M) at 22°. Esterification of the noncoordinated carboxyls achieves three purposes: reduction by the deprotonated path or association with the reductant is eliminated, and any remote attack will be accompanied by induced ester hydrolysis.⁸ The results in Table III show that ester hydrolysis does in fact occur, and the percentages found agree reasonably well with those calculated from the rate law by methods outlined previously.⁴

Any oxidation-reduction process between metal ions involving bridging can be broken into at least three elementary steps: (i) the attack by the reductant on the ligand to form a binuclear complex, (ii) the actual electron transfer, and (iii) the dissociation of the binuclear complex to products. If (ii) alone is rate controlling, the over-all rate of reduction should be related to the mobile bond order of the path used in the electron transfer.⁹ In fact, when the ligand contains carboxyl groups, either as the sites for reductant attack or coordinated to the oxidant, (ii) is not the slowest step, and experiment shows the rate bears no relation to the bond order.³ Steric factors become important and the introduction of bulky groups into the 2-position slows down the rate.⁷ The introduction of a carboxyl group into the parent pentaamminebenzoatocobalt(III) complex at the 2-position decreases the rate at 25° by a factor of two, from 0.14 to 0.074 $M^{-1} \text{ sec.}^{-1}$. Introduction of a second carboxy group in the 6-position might be expected to decrease the rate again by a factor of two, and this is just what is observed for the 2,6-dicarbomethoxybenzoate, where the rate of reduction by the acid-independent path is 0.040 $M^{-1} \text{ sec.}^{-1}$. The agreement may be fortuitous, since on the basis of the above argument the reduction of the 2-carboxy and the 2-carbomethoxy benzoate complexes should be the same. It is possible, however, that the

(7) R. T. M. Fraser, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 287.

(8) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, 2239, 2242 (1961).

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

rate constant as measured for the 2-carboxybenzoate is not the rate constant applying to adjacent attack alone. Introduction of the second ester group, while decreasing the rate of adjacent attack, increases the possibilities of remote attack: the reductant has twice the opportunities for forming the binuclear complex. If the two ligands investigated have the same affinity for the extra proton, this advantage decreases with increasing temperature, as shown by the second term in the rate laws.

The reason given in the past for the absence of remote attack when the ligand is phthalic acid was that the two carboxyl groups cannot lie in the same plane. If protonation of the coordinated carboxyl occurs,

coplanarity becomes possible. A very small amount of conjugation between the two metal centers should provide a sufficient path for the reduction to occur, but even so it is unlikely that the remote attack can ever be detected experimentally. The term for remote attack will probably be small in comparison with those for the adjacent attack and the deprotonated path, and no side reactions can be induced to yield additional evidence. Nor does a plot of ΔH^* against ΔS^* resolve the problem as it did in the case of the fumarate complexes⁷: the values fall on the line of the other *ortho*-substituted complexes, which have an isokinetic temperature of 70°.¹⁰

(10) J. E. Leffer, *J. Org. Chem.*, **20**, 122 (1955).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF SOUTHAMPTON, SOUTHAMPTON, ENGLAND

The Reactions of Group VI Metal Carbonyls with Pyrrolidine, Piperazine, and Morpholine

BY G. W. A. FOWLES AND D. K. JENKINS

Received August 19, 1963

Pyrrolidine and morpholine react with group VI metal carbonyls to give simple substituted products $L_nM(CO)_{6-n}$, where $n = 1$ and 2. Piperazine reacts with excess of $Mo(CO)_6$ and $W(CO)_6$ to give $(C_4H_{10}N_2)[M(CO)_5]_2$. The trisubstituted carbonyls $L_3M(CO)_3$ have been prepared for $L =$ piperazine and morpholine by displacement of either toluene or mesitylene from the π -complexes. The infrared spectra of the complexes have been measured and assignments made.

Morpholine complexes have been prepared previously from the carbonyls of iron, cobalt, and nickel,¹⁻³ but the preparation involved the disproportionation of the carbonyls with the formation of complexes that were ionic in nature, *e.g.*, $[Fe(C_4H_8NO)_6]Fe_4(CO)_{13}$. In this paper we report on products obtained by the reaction of pyrrolidine, piperazine, and morpholine with the group VI metal carbonyls. These compounds are diamagnetic and appear to be simple substitution complexes analogous to the various amine complexes prepared photochemically by Strohmeier and co-workers.⁴⁻⁶ Thus, in reactions involving excess of carbonyl, morpholine displaced one mole of carbon monoxide to give the adducts $M(CO)_5(C_4H_8NO)$; the chromium and molybdenum compounds were monomeric in benzene solution. When morpholine was used in excess, two moles of carbon monoxide were displaced from both molybdenum and tungsten hexacarbonyls, giving the disubstituted products which were insoluble in non-polar solvents but sparingly soluble in nitromethane; the corresponding chromium compound could not be isolated, but when the reaction was carried out in toluene solution the π -complex $(CH_3C_6H_5)Cr(CO)_3$ was isolated as well as $(C_4H_8NO)Cr(CO)_5$.

Both the mono- and disubstituted complexes were

obtained from the reactions of the molybdenum and tungsten hexacarbonyls with pyrrolidine. The mono-substituted complexes were monomeric in benzene solution. In the corresponding reactions involving piperazine with the carbonyl in excess, the only products that could be isolated were the compounds $(C_4H_{10}N_2)[M(CO)_5]_2$.

Trisubstituted complexes could not be prepared from the carbonyls themselves, but the molybdenum compounds $Mo(CO)_3L_3$ were readily prepared by displacing mesitylene or toluene from the π complexes π -(arene)- $Mo(CO)_3$ ⁷ by either morpholine or piperazine.

The infrared spectra of the morpholine complexes suggest that bonding is through nitrogen rather than oxygen. Thus in all the complexes the C—O—C stretches (found at 1079 and 875 cm^{-1} in morpholine itself) remain unchanged, while the N—H stretching frequency changes from 3320 cm^{-1} in morpholine to 3260 cm^{-1} in $(C_4H_8NO)_2Mo(CO)_4$; there is a similar lowering of the N—H stretching frequency of between 50 and 100 cm^{-1} in the other complexes, possibly resulting from electron withdrawal from nitrogen *via* the σ -bond upon coordination.

The carbonyl stretching frequencies of the $LM(CO)_5$ complexes can be assigned on the basis of work by Orgel⁸ and Cotton and Kraihanzel.⁹ Each spectrum

(1) W. Hieber and N. Kahlen, *Ber.*, **91**, 2223 (1958).

(2) W. Hieber, W. Kroder, and E. Zahn, *Z. Naturforsch.*, **15b**, 325 (1960).

(3) W. Hieber and R. Wiesboeck, *Ber.*, **91**, 1146 (1958).

(4) W. Strohmeier and D. von Hobe, *ibid.*, **94**, 761 (1961).

(5) W. Strohmeier, K. Gerlach, and D. von Hobe, *ibid.*, **94**, 164 (1961).

(6) W. Strohmeier and K. Gerlach, *ibid.*, **93**, 2087 (1960).

(7) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(8) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(9) F. A. Cotton and C. S. Kraihanzel, *ibid.*, **2**, 533 (1963).