period under a pressure of 0.02 mm and held there for 1 day. Some slight sublimation was noted.

Anal. Calcd for $C_{18}H_{13}Al$: Al, 10.52. Found: Al, 10.12.

A portion of the etherate was treated with iodine in hexane. Usual work-up yielded a semisolid organic residue. By infrared spectral comparison, the supernatant liquid was shown to be mainly iodobenzene and 2,2′-diiodobiphenyl, with some traces of 2-iodobiphenyl. The isolated solid was principally 2,2′-diiodobiphenyl (mp 109–109.5°, from ethanol). The detection of 2′-iodobiphenyl points to the possibility of some uncyclized 2-biphenylyldiphenylaluminum (8.06%). In other runs conducted at 200° for shorter periods, the aluminum analyses ranged from 8.0 to 8.8%. Alternatively, the presence of some 5-(2-biphenylyl)dibenzaluminole (8.11%) might explain the origin of the 2-iodobiphenyl and the low analyses in certain cases.

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Electron Transfer through Organic Structural Units. III. Chain Branching and Nitro and Thia Substitution in Bridging Groups for Oxidation–Reduction Reactions[1]

Edwin S. Gould

Contribution from the Department of Physical Organic Chemistry, Stanford Research Institute, Menlo Park, California. *Received November 19, 1965*

Abstract: The reactions of 30 carboxylatopentaamminecobalt(III) complexes (containing a variety of straight-chain, branched-chain, and aromatic ligands) with Cr^{2+} have been studied. A number of the acyclic ligands have alkylmercapto substituents, whereas most of the aromatic ligands are nitro derivatives. The specific rates for reduction of the acyclic derivatives have been found to be much more sensitive to steric crowding than are benzoato derivatives; α substitution is particularly effective in retarding reduction, the triethylacetato complex (VII, k = 0.0024 l. mole^{-1} sec^{-1}) being more resistant to reduction than any other carboxylato complex reported. The α-NH_3^+ substituent, as found in the complexes of the amino acids at low pH values, is also strongly rate retarding. The moderate increases in reduction rates observed when α,β unsaturation is introduced into acyclic ligands also appears to be steric, rather than electronic, in origin, and no special effects are noted on incorporating a second double bond in conjugation with the first (XVII). Conjugative enhancement of reduction, sometimes attributed to remote attack, is, as in earlier studies, confined to complexes derived from readily reducible ligands. Rate enhancement (from five- to fiftyfold) resulting from substitution of a sulfur atom α or β to the coordinated carboxyl appears to be general. Reductions of the nitro derivatives, which involve changes not only at coordinated cobalt, but also at the NO_2 groups, are complex and have not been separated into clean-cut kinetic steps. The very fast reduction of the nitro group of the *o*-nitrobenzoato complex is accompanied by some "leak through" of reducing capacity, resulting in a much more rapid reduction of Co(III) than would result from preliminary reduction of NO_2 to an amino group. With the *p*-nitro complex in 1.2 *M* $HClO_4$, release of Co(II) is delayed until 1.5–2.0 equiv of Cr^{2+} have been added (but, nevertheless, represents a very rapid reduction), whereas with the *m*-nitro isomer, 4 equiv of Cr^{2+} must be added before Co^{2+} appears. Leak through during the fast stages in these reactions is taken as a strong indication of reduction of coordinated Co(III) *via* remote attack at the nitro group or at a group derived from it by reduction. The nitro group (in the *ortho* sequence) and the nitroso group (in the *para* sequence) appear to be the principal "bridging" substituents. In addition, the reduction of the 3-nitro-4-methylbenzoato complex appears to involve a small degree of "*meta*-oriented remote attack" at the nitroso stage. The striking spectral changes occurring during the early stages of these reductions are considered. Evidence is cited (in the *p*-nitro reduction) for an intensely colored Cr(III)-bound nitro radical cation lying apart from the principal reduction sequence and also for a nitroso radical cation; both of these are observed in 1.2 *M* acid, but are destroyed in 0.024 *M* acid.

The specific rates at which pentaamminecobalt(III) complexes containing organic ligands are reduced with Cr^{2+} cover a range of over nine powers of ten when the structure of the organic group is suitably modified. Earlier research in this area[2,3] touched upon the following points, which probably involve less striking rate differences, but which, nevertheless, appear to warrant further investigation. (a) Although the reductions of benzoatopentaamminecobalt(III) complexes were found to be retarded only slightly by steric crowding,[3b] the sensitivity of noncyclic carboxylato complexes to steric effects was not examined. (b) Carbon–carbon unsaturation in the carboxylato ligand was shown to facilitate reduction of Co(III) in cases where the free ligand acid was readily reduced by Cr(II), but the picture with regard to nonreducible olefinic ligands was not clear.[2] (c) Substitution of an α-benzylmercapto group in the acetato complex resulted in a significant (greater than tenfold) acceleration of reduction, whereas α-alkoxy groups are generally slightly retarding.[2] However, only a single sulfur

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[1] This research was sponsored by the Stanford Research Institute Research and Development Fund. Support is gratefully acknowledged.

[2] E. S. Gould, *J. Am. Chem. Soc.*, 87, 4730 (1965).

[3] (a) R. T. M. Fraser, *ibid.*, 84, 3436 (1962); (b) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

Table I. Carboxylatopentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_2$

R	% Co		λ_{max}, mμ	ϵ_1	λ_{max}, mμ	ϵ_2
	Calcd	Found[d]				
Propionato (IV)	14.2	14.4	502	76.0	351	61.0
Trimethylacetato (VI)	13.3	13.3	502.5	72.3	346	63.9
Acrylato (X)	14.3	14.5	501	71.2	350	60.1
Maleato (XIX)	12.9	13.1	502.5	76.8	351	66.5
2,4,6-Trimethylbenzoato (II)	11.7	11.0	503	79.6		
Sorbato (XVII)	12.9	12.6	502.5	82.5		
Benzofuran-2-carboxylato (XII)	11.7	11.2	502	85.0		
trans-2-Phenylcyclopropanecarboxylato	11.7	11.2	501.5	73.8		
Mucato (XXII)	11.5	11.7				
Imidazole-4,5-dicarboxylato[a]	9.8	9.3	502	82	325[b]	100
Thiodiglycolato (XXIV)	12.0	12.5	502	77.6		
S-Phenylthioglycolato (XXVII)	11.5	11.9	500.5	70.6		
o-Nitrobenzoato	11.6	11.6	503	75.8		
m-Nitrobenzoato	11.6	11.9	502.5	75.6		
p-Nitrobenzoato[d]	11.6	11.4	502	78.8		
2-Nitro-3-methylbenzoato (XXXII)	11.3	10.9	501	82.1		
3-Nitro-4-methylbenzoato	11.3	11.4	501	73.4		
4-Nitro-3-methylbenzoato	11.3	11.7	500.5	82.9		
4-Nitro-3,5-dimethylbenzoato	11.0	10.8	501	78.5		
o-Nitrophenylacetato (XXXI)	11.3	11.9	501.5	65.8		
o-Nitrocinnamato	11.1	10.4	500	61.3		
p-Phenylazobenzoato	10.4	10.0	430	1160		
			536[c]	576	427[c]	850
4,4′-Azodibenzoato	9.7	9.9	475[b]	214		
4-Benzeneazosalicylato	10.1	10.1	465[c]	700	387[c]	580
Cinnoline-4-carboxylato[a]	9.6	9.6	502.5	69.0		
			498[c]	79.9		

[a] Triperchlorates. [b] Shoulder. [c] In 1.2 *N* $HClO_4$. [d] See ref 3b.

derivative of this type was examined, and the generality of the effect was not established. (d) The action of nitro substituents in these reductions was not defined, although it was observed that reaction of the *p*-nitrobenzoato complex was "immeasurably rapid"[4] and yielded, when a deficiency of Cr^{2+} was used, virtually no Co^{2+}.[3b] The present report describes further studies related to each of these questions.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate, chloropentaamminecobalt(III) perchlorate, sodium perchlorate solution (for kinetic experiments), and chromous solutions were prepared as described,[3b] and the concentration of the chromous solution was determined from the absorbance of the parent chromic solution.[2] Azobenzene-4,4′-dicarboxylic acid was prepared by oxidation of *p*-aminobenzoic acid with sodium perborate.[5] The remaining organic acids (Aldrich and Eastman products) were used as received. The europous solution was prepared by dissolving 0.25 mmole of Eu_2O_3 in 5 ml of 1.2 *N* $HClO_4$, then reducing the resulting solution with excess zinc amalgam (3 hr, 45°) in a vial sealed with a rubber serum cap.

Preparation of the Complexes. Most of the complexes were prepared in water from the aquo complex as described.[3b] In the preparations of many of the nitro complexes, precipitates formed early in the course of the reaction, but heating was nevertheless maintained for the usual 2 hr. At the end of this time, the precipitate, generally a mixture of the perchlorate and the carboxylate salts of the desired complex, was treated with 1 *M* $HClO_4$ at 75° for 5–10 min and the mixture was filtered. Cooling the filtrate yielded the very nearly pure perchlorate. In the preparations of the trimethyl- and triethylacetato complexes, a second liquid phase, rich in the added carboxylic acid, separated from the reaction mixture; the second phase was deeply colored, and a substantial fraction of the desired conversion appeared to take place in it. At the conclusion of the heating period, this phase was dissolved in hot 90% methanol, then added to the water–ether–$HClO_4$ mixture in the usual way.[3b] Certain of the sulfur-substituted complexes, *e.g.*, those derived from thiodiacetic acid, β,β′-thiodipropionic acid, and methionine, were unusually soluble in water and were therefore precipitated from their solutions in $HClO_4$ by addition of ethanol at 0°; complexes isolated in this manner generally gave unsatisfactory analyses but appeared to be suitable for rate measurements.

With certain of the parent acids (*e.g.*, imidazole-4,5-dicarboxylic acid and those acids containing the azo linkage) treatment with aqueous NaOH yielded solutions having pH values above 8. For these, a more powerful (but less convenient) modification of the synthesis in dimethylformamide[2] was used. Ten millimoles of the carboxylic acid was heated with 5 ml of aqueous 1.75 *M* NaOH at 95° for 10–15 min, the solution was filtered hot, and the filtrate was evaporated to dryness under reduced pressure. The solid sodium salt was then pulverized and intimately mixed with 0.7 g of the DMF complex as its perchlorate.[2] The mixture of solids was treated with 1–2 ml of dimethylformamide and the preparation was kept at 80° for 45 min and then taken to dryness (rotary evaporation at 80°). The solid was pulverized in a mixture of 5 ml of water and 0.9 ml of concentrated $HClO_4$ and the preparation was heated to 70°, then filtered. To the filtrate was added an additional 2 ml of concentrated $HClO_4$, the mixture was cooled, and the solid complex was filtered off and recrystallized from hot water or (if the hydroperchlorate was desired) from 1 *M* $HClO_4$.

The above method failed with 4,4′-diphenic acid and 4,4′-stilbenedicarboxylic acid, both of which formed sodium salts appearing to be extremely insoluble in DMF. These two attempted preparations yielded red, crystalline solids having identical X-ray diffraction powder patterns, and both had a cobalt content corresponding closely to the DMF complex as its perchlorate. However, the absorption maximum was at 498 (rather than 505) mμ, and both materials were found to be reduced by Cr^{2+} at a specific rate close to 0.2 l. $mole^{-1}$ sec^{-1} (26.5°, μ = 1.4), *i.e.*, about 20 times as rapidly as the DMF complex which is readily prepared by heating the aquo complex with excess amide.[6]

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(4) D. K. Sebera, Ph.D. Thesis, University of Chicago, 1960.

(5) S. M. Mehta and M. V. Vakilwala, *J. Am. Chem. Soc.*, 74, 563 (1952).

(6) The composition of the product absorbing at 498 mμ, taken with the observed shift in the position of λ_{max} toward shorter wavelengths, suggests that the 498 product is a DMF complex having a Co–N bond, whereas the 505 product has a Co–O bond. This is in accord with recent indications (R. T. M. Fraser, *Inorg. Chem.*, 3, 1561 (1964)), that Co(III) involved in the sequence Co–N=C=O is reduced considerably more rapidly than that involved in the sequence Co—O=C=N.

Table II. Kinetic Data for Chromous Reduction of Pentaamminecobalt(III) Complexes

Organic ligand	Temp, °C	μ	$[H^+]$, M	k^a
Propionato	27.1	1.4	1.2	0.15
Acrylato	26.9	1.4	1.2	0.46
	27.0	1.3		0.42
Trimethylacetato	25.6	2.3	0.48	0.0096
Triethylacetato	25.8	2.3	0.48	0.0027
Benzofuran-2-carboxylato	22.0	1.3	1.2	0.37
trans-2-Phenylcyclopropanecarboxylato	22.4	1.3	1.2	0.23
			0.046	0.24
trans-3-Hexenedioic	22.0	1.3	1.2	0.20
			0.046	0.21
Sorbato	24.8	1.4	1.2	0.51
	27.1			0.61
	28.1			0.63
Maleato	23.0	1.2	0.012	170
			0.048	170
	23.7		0.12	200
			1.2	210
	23.8		0.24	200
	25.0	4.0	1.0	210
			4.0	230
Imidazole-4,5-dicarboxylato	25.0	1.2	1.2	34
			0.12	35
Mucato	22.0	1.3	1.2	>1.1 and 0.8[b]
			0.024	>1.1 and 0.8[b]
2,4,6-Trimethylbenzoato (II)	26.2	1.4	1.2	0.043
Thiodiglycolato (XXIV)	22.3	1.2	1.2	18
	22.1		0.4	38
	22.3		0.012	>300
β,β'-Thiodipropionato (XXV)	24.0	1.2	1.2	11
			0.24	9.8
Methylenebis (thioglycolato) (XXVI)	22.0	1.2	1.2	1.45
			0.023	1.37
S-Phenylthioglycolato (XXVII)	21.8	1.3	1.2	0.77
	23.0		0.046	0.83
Methioninato (VIII)	23.2	1.02	0.6	0.010
4,4′-Azodibenzoato[c]	25.8	1.2	1.2	7.7
4-Benzeneazosalicylato[c]	22.0	1.2	1.2	1.0×10^3
			0.012	0.7×10^3

[a] Specific rates in l. $mole^{-1}$ sec^{-1}. [b] Two components. [c] Rates are for reduction of the azo linkage, rather than Co(III).

Table I lists 25 complexes giving satisfactory analyses, together with molar extinction coefficients at their absorption maxima. In addition, complexes from the following five acids were prepared but were contaminated with from 7 to 20% of the parent acid: triethylacetic, β,β'-thiodipropionic, methylenebis(thioglycolic), *trans*-3-hexenedioic, and methionine. The degree of acid contamination in each of these impure complexes, except that of methionine, could be reduced by prolonged continuous ether extraction of their aqueous solution, but there was no apparent change in the rate constants for the reductions as purity increased. Several attempts were made to prepare the complex of triphenylacetic acid, but without success. S-*t*-Butylthioglycolic acid appeared to form a complex perchlorate, but when the resulting material was dissolved in water or in dilute $HClO_4$, decomposition occurred, yielding a white precipitate and a volatile material having a mercaptan-like odor.

Kinetic Experiments. Specific rates were determined by following the decrease in optical density at 502 mμ as previously described.[3b,2] Acidities were between 0.012 and 1.2 M and ionic strengths were kept at or near 1.3 by addition of $NaClO_4$ solution. Concentrations of the complexes were adjusted so that the change in absorbance during the progress of the reaction corresponded to greater than one-third of the total scale on the spectrophotometer. For complexes having specific rates of reduction less than 50 l. $mole^{-1}$ sec^{-1}, rates were run under pseudo-first-order conditions with the ratio Cr(II)/Co(III) between 10 and 250. For complexes having rate constants greater than about 50 l. $mole^{-1}$ sec^{-1}, the cobalt complex (about 3 mg) was in excess, and very small volumes (2–3 μl) of 1.0 M Cr^{2+} were added, using a graduated microsyringe; in such cases, absorbancy changes were read on the 0–0.2 slide wire. Temperatures were constant to within better than 0.2° during a given run. Reactions were allowed to proceed for at least 6 half-lives, and, except as noted below, good pseudo-first-order plots were obtained. When runs with different Cr(II) concentrations were made, first-order dependence on Cr(II) was observed. As in previous work, rate constants below 5 obtained from several points in a single run agreed to better than 6%, and those obtained from different runs at the same temperature checked to within about 10%. The larger specific rates, obtained with the more dilute solutions, are again less reliable; points within a single run check to within 10% and, between runs, to better than 20%. Rate curves on two different samples of the mucato derivative indicated the presence of two reducible components in each, one reduced at a specific rate somewhat greater than 1.1, the other at 0.8 l. $mole^{-1}$ sec^{-1}; both rates appeared to be independent of acidity in the range 0.024–1.2 M H^+.

None of the nitro-substituted complexes gave simple rate curves when reduced with Cr^{2+}. Generally, addition of a large excess of chromous brought about a very rapid rise of absorbance in the 460–510-mμ region, followed by a drop, which, in practically all cases, had more than one kinetic component. This drop was rapid for complexes in which the nitro group was situated *ortho* or *para* to the carboxyl, but slow for other nitro derivatives. In two instances (the *m*-nitro and the 2-nitro-3-methyl derivatives) the drop was, in turn, followed by a very slow rise in absorbancy about 15 min after addition of 0.2 M Cr^{2+}. When this upward drift did not occur, rate constants could sometimes be estimated for the decrease in absorbance, approximately first order in Cr^{2+}, during the final stages of reaction. These values fell into the range 0.005–0.03 l. $mole^{-1}$ sec^{-1}, *i.e.*, considerably below the rates of Co(III) reduction of the known pentaamminebenzoato derivatives; possibly, slow changes of the Cr(III) products are involved here. In some cases, the more rapid absorbance changes could be separated into two pseudo-first-order reactions (each, again, approximately first order in Cr^{2+}) by wide variation of initial concentrations of Co(III) and Cr(II). Thus, for reduction of the *o*-nitrobenzoato complex at 23.0° in 1.2 M acid, components having rate constants of approximately 18 and 400 l. $mole^{-1}$ sec^{-1} were observed; in 0.12 M acid, these values were 13 and 120. More specific identification of the kinetic components requires further investigation.

Similarly, for reduction of the *p*-nitro complex in 1.2 N acid, components with rate constants of approximately 1500 and 0.02 could be observed (at very low and very high Cr^{2+} concentrations, respectively), but most of the absorbance decrease could be attributed to neither of these reaction components.

The drop in absorbance during reduction of the *p*-phenylazobenzoato complex likewise did not conform to a simple kinetic picture. The remaining azo complexes gave good pseudo-first-order plots, but, as was shown in the stoichiometry experiments, the absorbance changes were not linearly related to reduction of Co(III).

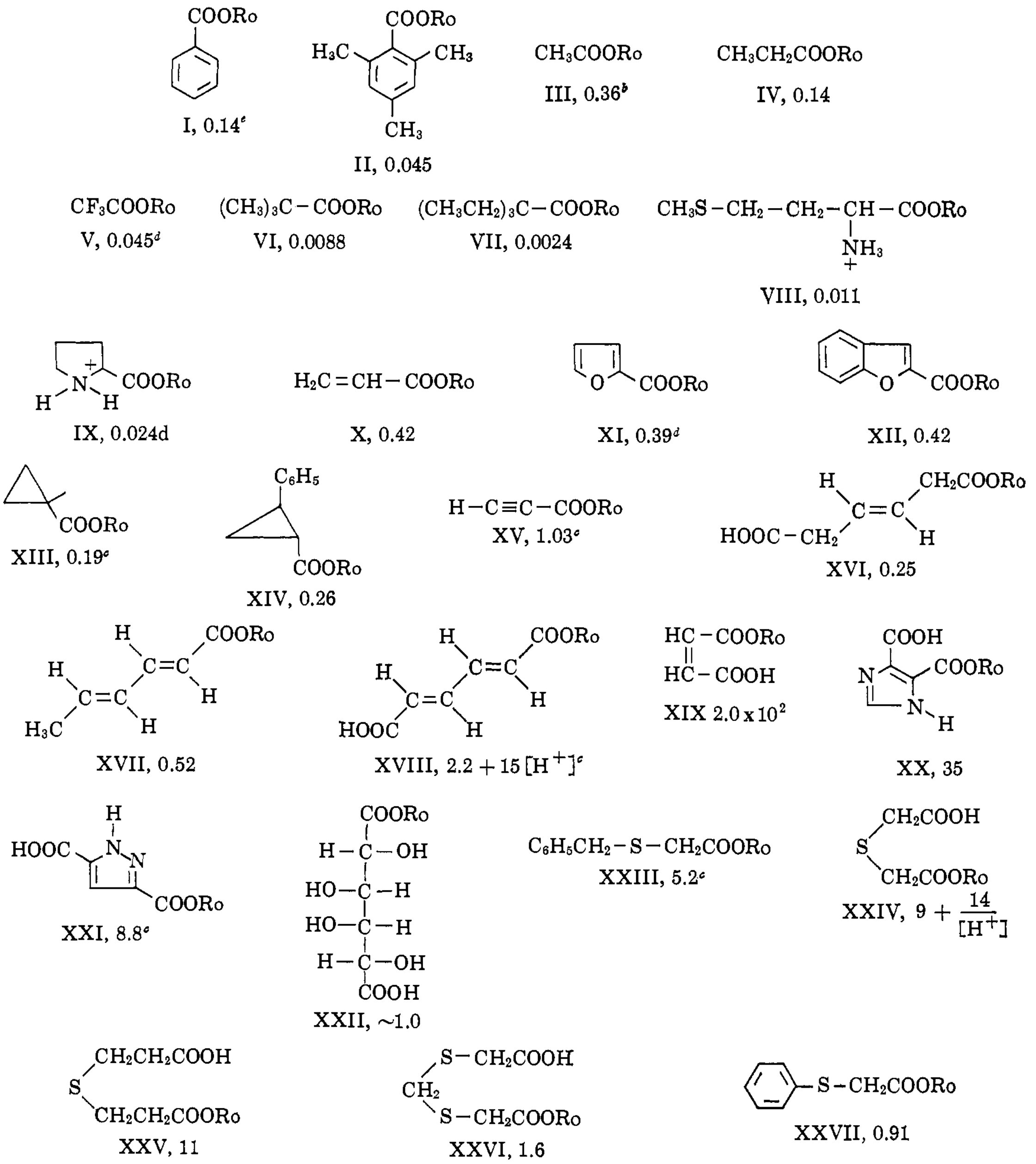
Stoichiometry Experiments. The reduction of Co(III) and the formation and destruction of colored intermediates in the reaction of Cr^{2+} with the nitro and azo complexes were followed using known concentrations of the complex in a 10-cm cell. The solution was purged with nitrogen, and known increments of Cr^{2+} solution were added through the cap using a 50-μl syringe. After each addition, the visible spectrum was scanned, and an aliquot of the resulting solution was removed, using a 1-ml syringe, and added to 9.0 ml of concentrated HCl. Concentrations of Co(II) in the resulting aliquots were then determined by measuring the absorbances of the HCl solutions at 692 mμ (ϵ for Co(II) in this medium was taken as 560), using the 0–0.2-range slide wire. (The time interval between Cr^{2+} addition and dilution of the aliquot with HCl was about 5 min.)

In addition, competition experiments, in which a deficiency of Cr(II) was treated with a number of carboxylato complexes, and oxidation–reduction experiments, in which the corresponding parent acids were treated with Cr(II), were carried out as described.[3b]

Results and Discussion

Specific Rates. Kinetic data are presented in Table II. Specific rates, summarized in Chart I, together with structural formulas, have been adjusted to a common temperature[2] (25.0°) and ionic strength[3b] (μ = 1.5); a few values obtained in previous work have

Chart I. Specific Rates for Chromous Reduction of Carboxylatopentaamminecobalt(III) Complexes[a]



[a] Specific rates given in l. mole⁻¹ sec⁻¹ at 25°; μ = 1.5. Ro = "roseo" = $(NH_3)_5Co$. Each of the complexes, except VIII and IX, has a net charge of 2+. [b] This value (E. Deutsch and H. Taube, unpublished experiments, Stanford University, 1965), arises from measurements within the range 0.04–1.0 M H^+, using a large excess of Cr(II). An older value of 0.18[11] is based on a smaller number of experiments carried out with a slight excess of Co(III). [c] See ref 2. [d] See ref 3b. [e] See ref 3a.

been inserted for comparison. (Of the rates in the present study, only that of the thiodiglycolato complex (XXI) is strongly acid dependent.) At one extreme lie the trimethylacetato (VI) and triethylacetato (VII) complexes, which are reduced far more slowly than any other carboxylatopentaamminecobalt(III) complex thus far characterized.[7a] At the other end of the reactivity scale is the maleato complex (XIX); this reacts more rapidly[7b] than nearly all other carboxylato complexes except for those pyridine and pyrazine derivatives which are thought to be reduced *via* an unusually stable radical cation intermediate.[2]

Alkyl Substitution and Steric Effects. Since the rates of reduction of carboxylato complexes of the type studied are remarkably insensitive to the incorporation of electron-attracting and electron-repelling groups into the organic ligand,[3b] it is most reasonable to ascribe the retarding effects of alkyl substitution in the present

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(7) (a) The specific rates for reduction of complexes VI and VII represent upper limits for the rate of electron transfer through the carboxyl group. These values are low enough so that a significant fraction of the observed reduction may occur *via* an outer-sphere activated complex: see, for example, A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). (b) R. T. M. Fraser, *ibid.*, **85**, 1748 (1963), Table II, records the specific rate for reduction of the maleato complex as (200 + 100[H^+]) l. mole⁻¹ sec⁻¹ (25°, μ = 1.0). However, according to Fraser's Table I, which seems to be the source of the rate expressions in his Table II, this rate law should describe the data at 14°, rather than at 25°. For 23°, using the data of Fraser's Table I, the specific rate should be 420 + 180[H^+]. Hence, the apparent agreement between the rate reported here and Fraser's acid-independent term is fortuitous. Moreover, the present experiments do not confirm his first-order acid term. The latter implies that reduction in 4.0 M H^+ should proceed twice as rapidly as in 1.0 M H^+, and thrice as rapidly as in 0.01 M H^+, in contrast to the values recorded herein.

series to steric causes. Although the direction of such effects corresponds to that observed in those carboxyl reactions which are strongly subject to steric hindrance in the conventional sense, there are differences in detail.

For example, esterification of free benzoic acid (ethanolic HCl, 15°) is retarded about threefold by a single *o*-methyl group and virtually prohibited (under similar conditions) by methyl substitution at both *ortho* positions.[8] In contrast, the reduction of the benzoato complex (I) is practically unaffected by one *o*-methyl substituent and retarded only threefold by two *o*-methyl groups (II). This difference almost certainly arises because esterifications and similar carboxyl reactions proceed through attack at the carbon atom of the carboxyl group, whereas in the reduction of these Co(III) complexes, attack (by Cr^{2+}) is at the oxygen. A molecular model of 2,6-dimethylbenzoic acid shows the oxygens to be much less effectively shielded by the *o*-methyls than is the carboxyl carbon.

In the aliphatic series, acetic and propionic acids are esterified at very nearly the same specific rates, but reduction of the propionato complex (IV) is only about one-third as rapid as that of the acetato, III. Retarding actions of three α-methyl groups on esterification and Co(III) reduction are more nearly equal (25-fold and 40-fold, respectively), but the striking (greater than 200-fold) drop in esterification rate when three α-methyl groups are replaced with α-ethyls appears to have no counterpart in the Co(III) reduction series. In accord with these differences, scale models indicate that as the aliphatic section of the acid is enlarged and modified, the greatest increase in shielding effectiveness toward the *oxygen* atoms results when alkyl groups are substituted for α hydrogens, whereas the shielding toward the carboxyl *carbon* improves most markedly when alkyl groups are substituted for β hydrogens (*e.g.*, in the conversion of α methyls to α ethyls).[9] The trends within the aliphatic series also suggest that the retarding action resulting from fluorine substitution at the α carbon is, contrary to an earlier suggestion,[3b] largely steric in origin, for the specific rate for reduction of the trifluoroacetato complex (V) lies between that of the acetato (III) and the trimethylacetato (VI), being rather closer to the latter. This order brings to mind that of Taft's steric substituent constants[10] (CH_3, 0.0; CF_3, -1.16; $C(CH_3)_3$, -1.54).

Reduction of the methioninato complex (VIII) is also slow. In this case, the α-amino group substituent (which is virtually completely converted to α-NH_3^+ under the conditions used) appears to be a particularly effective shielding group, not only because of its position, but also because of its positive charge, just as, in the benzoato series, *o*-NH_3^+ has been found to be a more effective shield against attack by positive Cr^{2+} than is the larger, but uncharged, *o*-iodo group.[2] In the prolinato complex (IX), the shielding efficiency of the positive NH_2^+ group appears to have been diminished slightly by tying it back into a ring system.

Unsaturated Ligands. Since increasing the degree of α substitution and, to a lesser extent, β substitution in an acyclic carboxylato ligand retards reduction of coordinated Co(III), α,β unsaturation would be expected to facilitate reduction, for each doubly bonded carbon has one less substituent than a singly bonded one. Thus, in the three-carbon series, the acrylato complex (X) is reduced more rapidly than the propionato (IV), and the acetylenic propiolato complex (XV) is reduced still more rapidly. This trend, again a steric one, appears to be quite independent of any electron-attracting or electron-transmitting properties of the double or triple bond and casts doubt on an earlier rationalization of the rapid reaction of the propiolato complex in terms of an intermediate radical cation.[2] The nearly identical rates for reduction of the acrylato (X), furoato (XI), benzofuran-2-carboxylato (XII), and sorbato (XVII) complexes indicate that once the stereochemical characteristics about the α and β carbons have been fixed, reduction by adjacent attack is remarkably insensitive to changes in the remainder of the ligand. Similarly, the rates of reduction of cyclopropane derivatives XIII and XIV, slightly greater than for the propionato complex, but less than for the acrylato, lie close to what would be predicted on steric considerations alone; there is no evidence that the ease of reduction of the complex is in any way affected by strain at C_α–C_β.

The trends among the complexes having unsaturated acyclic ligands appear to delineate the structural requirements for conjugative acceleration of reduction. Such rate enhancement has, in the past, been attributed to "remote attack" (*i.e.*, reduction of Co(III) in which the reducing agent initially attacks a site in the ligand other than the coordinated carboxyl), but the symmetry of the dicarboxylato ligands in the present study precludes identification of the site at which Cr^{2+} attacks. Monocarboxylato complexes exhibit no evidence for such acceleration, despite the presence of a double bond (X), a triple bond (XV), or a pair of double bonds (XVII) in conjugation with the carboxylato group, nor does the dicarboxylato complex such as the *trans*-3-hexenedioato (XVI), in which the double bond is out of conjugation with the carboxylato groups. Evidence for such enhancement is strong for the butadienedicarboxylato[2] (XVIII) and the fumarato[11] complexes, which have two carboxylato groups separated by a double bond, or by a pair of double bonds, in conjugation with both groups.[12] The reducing electron may also pass through the uncoordinated carboxylate

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[8] Steric hindrance in carboxylate reactions has been reviewed by M S. Newman in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 4.

[9] This distinction is in harmony with M. S. Newman's "rule of six": M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).

[10] R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952); see also the chapter by Taft in ref 8 (p 598). R. T. M. Fraser, *Nature*, **205**, 1207 (1965), has also considered steric and electronic effects in the rates of reduction of aliphatic carboxylatopentaamminecobalt(III) complexes, plotting the logarithms of the specific rates of reduction with Cr(II) against Taft's polar substituent constants and obtaining a plot which appears to scatter badly. On the other hand, an analogous plot (based on the present data) against Taft's *steric* substituent constants (E_s values) approximates a straight line, emphasizing the importance of steric effects in this series. Such a plot is found to have a slope (Taft's δ parameter) of 0.62.

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

[12] For reduction of the butadienedicarboxylato complex XVIII, the magnitude of the acid-independent term in the rate expression (about four times the value expected for the usual adjacent attack) is much less compelling evidence for conjugative acceleration (and by implication, remote attack) than is the existence of the first-order acid term. The apparent absence of such a term (see, however, ref 7) in reduction of the maleato complex is not very informative, for the magnitude of the observed acid-independent term is so great that a first-order acid term typical of complexes of this type (specific rate between 1.0 and 15) could be overlooked in the acid range studied.

group in the rapid reduction of the maleato complex (XIX), but earlier evidence that the Cr(III) product from this reduction is a chelate[13] blurs the distinction between adjacent and remote attack in this case since the reducing agent may be bound to both carboxyls in the activated complex.

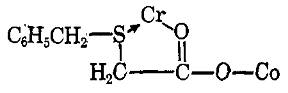
If conjugative acceleration be taken as evidence for remote attack, the requirement for the second carboxyl group may be considered in conjunction with earlier evidence,[2] here extended (Table III), that a ligand supporting such attack must be reducible with Cr(II). Thus, the second carboxyl group not only accelerates reduction of the Co(III) complex, but also facilitates reduction of the double bond in the free acid. Both effects probably arise because the carboxyl provides a coordination site for Cr(II) and, hence, a low energy path for interjection of the reducing electron into the conjugated system. In this connection, a possible distinction may be drawn between the reduction of the imidazoledicarboxylato complex (XX) and its isomer, the pyrazoledicarboxylato derivative (XXI). The imidazole complex is derived from a reducible acid, but yields what appears to be a nonchelated Cr(III) product (ϵ_{max} 31 (520 mμ) and 34 (405 mμ)), whereas the pyrazole complex is derived from a nonreducible acid, but very probably yields a chelated product (ϵ_{max} 50 (540 mμ) and 76 (400 mμ)).[2] Hence it is reasonable to ascribe the fast reduction of the imidazole derivative to remote attack (for the necessary structural elements are present), but to attribute the (slightly less) rapid reduction of the pyrazole derivative to chelation, presumably without electron transfer through the noncoordinated carboxyl.

Table III. Reduction of Carboxylic Acids with Cr(II)[a]

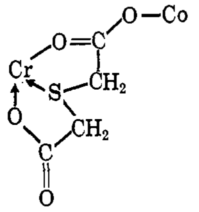
Acid	$[H^+]$, M	Reducing agent consumed, %	Color produced
Sorbic	0.6	0	
3-Hexenedioic	0.6	0	
Benzofuran-2-carboxylic	0.6	0	
Imidazole-4,5-dicarboxylic	0.9	9	
Mucic	1.2	11	
Cinnoline-4-carboxylic	0.6	11	Gray-green
p-Phenylazobenzoic	0.6	>84	Yellow
4,4′-Azodibenzoic	0.6	>90	Yellow
Maleic	1.2	>88	Lavender

[a] 15 min, 28°, concentration of organic acid 3.0 g/l., $[Cr^{2+}]$ 0.01 F.

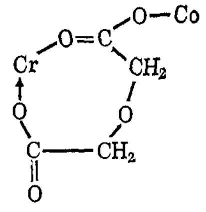
Thia Substitution. Complexes XXIII–XXVII feature a sulfur atom substituted α or β to the coordinated carboxyl. As a class, these react from five to fifty times as rapidly as the complexes of ordinary aliphatic ligands and are thus comparable to the complexes of α-hydroxy acids,[14] of which the mucato derivative (XXII) may be taken as an example. The acceleration due to sulfur substitution was first noted for the S-benzylthioglycolato complex (XXIII)[2] and was ascribed to chelation by sulfur in the transition state (XXVIII), although a chelated product did not appear to survive. Structures analogous to XXVIII may be drawn for complexes of each of the sulfur acids in the series, with the large inverse acid term observed in the reduction of XXIV suggesting predominant reduction through the "tridentate" transition state XXIX for this complex at high pH values. The rate-enhancing action of the sulfur atom persists, although to a lesser extent, when the basicity of the sulfur atom has been lowered by S-phenylation (XXVII); it disappears, however, when the sulfur is moved to the poorly chelating γ position and the positively charged NH_3^+ "shielding group" is interposed between the sulfur and the bound carboxylate (VIII).



XXVIII



XXIX



XXX

The generality of this effect is less surprising than the apparent absence of a similar one among alkoxy-substituted ligands. The difference between the oxygen and sulfur series is particularly striking in the case of the complex of thiodiglycolic acid (XXIV) and its oxygen analog. Reduction of the latter not only proceeds at a "normal" specific rate (0.17 l. mole^{-1} sec^{-1}), but, in addition, displays no indication of an inverse acid term in its rate law.[2] If the inverse acid term be taken as a sign of reduction, in part, through a chelated transition state, we may infer that contribution to the reaction through an eight-ring activated complex of type XXX is negligible unless the ring be anchored to the chromium ion at the middle, as well as at the ends, becoming, in effect, a pair of five-membered rings (XXIX).

Nitro Compounds. Plurality of Reduction Steps. Cr(II) reacts readily with the nitro-substituted carboxylato complexes in this series, reducing not only Co(III), but also the nitro group. The latter reductions proceed through a number of intermediate species, some of which may be intensely colored, and the over-all absorption changes cannot be easily separated into the component kinetic steps. Nevertheless, differences in behavior among the various nitro complexes are evident, even from relatively simple stoichiometry experiments.

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(13) H. Taube, *J. Am. Chem. Soc.*, 77, 4481 (1955). We find the extinction coefficients for the Cr(III) product in this case (ϵ_{max} 24 (520 mμ) and 25 (415 mμ)) to be surprisingly low for a chelate of this type. Spectral changes similar to those observed in the reductions of the *p*-formylbenzoato and pyridine-2,4-dicarboxylato complexes[2] were observed in the reduction of the maleato complex. When slightly more than 1.0 equiv of Cr(II) per mole of Co(III) was added, the absorption maximum shifted from 520 to 570 mμ with, however, very little change in extinction coefficient. At the same time, the absorbance at the 415-mμ maximum increased by about 30%.

(14) R. Butler and H. Taube, *ibid.*, 87, 5597 (1965).

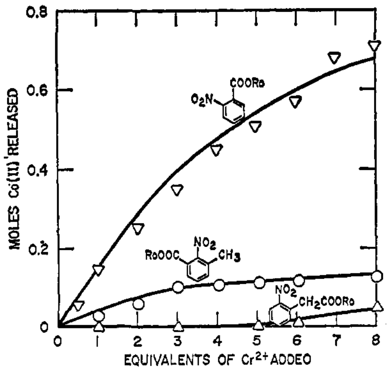

Figure 1. Release of Co^{2+} from nitro-substituted carboxylatopentaamminecobalt(III) complexes on treatment with Cr^{2+}: *o*-nitro derivatives, [H$^+$] = 1.2 *M*, [Co(III)]$_{initial}$ = 2.0 × 10^{-3} *M*; 5-min waiting period after each addition of Cr^{3+}.

Table IV summarizes the yields of Co(II) resulting from the reaction of 1 equiv of Cr^{2+} with an excess of various carboxylato complexes. Reactions with the nitro complexes in these experiments are complete a few seconds after mixing, but it is seen that over 90% of the reducing capacity of the added Cr^{2+} is consumed in reduction of the ligand rather than in reduction of Co(III). Extreme cases are the *m*- and *p*-nitrobenzoato complexes, which in 1.2 *M* acid formed no detectable Co(II) under these conditions, and indeed formed none even when treated with more than an equimolar quantity of Cr^{2+}.

Table IV. Yields of Co(II) from Reduction of Carboxylatopentaamminecobalt(III) Complexes[a]

Ligand	Yield of Co(II), %
Aquo	100
Maleato	100
Sorbato	100
3-Hexenedioato	100
Mucato	94
o-Nitrobenzoato	15
m-Nitrobenzoato	0
p-Nitrobenzoato	0 10[b]
o-Nitrocinnamato	10
4-Nitro-3-methylbenzoato	10
o-Nitrophenylacetato	6
2-Nitro-3-methylbenzoato	4
4,4′-Azodibenzoato	3
4-Nitro-3,5-dimethylbenzoato	3[b]
p-Phenylazobenzoato	0
4-Benzeneazosalicylato	0

[a] [H$^+$] = 1.2 *M*; [Co(III)] = 0.02 *M*; [Cr(II)] = 0.014 *M*; Cr(II added to Co(III). [b] [H$^+$] = 0.012 *M*.

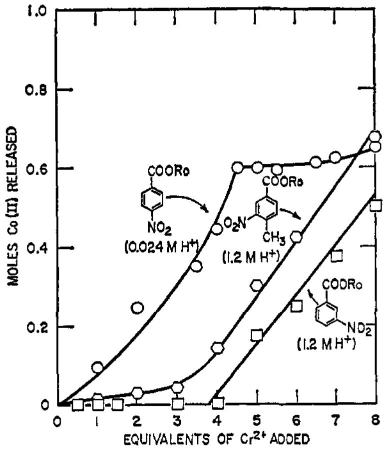

Figure 2. Release of Co^{2+} from *m*- and *p*-nitrobenzoato derivatives on treatment with Cr^{2+}: [Co(III)]$_{initial}$ = 2.0 × 10^{-3} *M*; 5-min waiting period after each addition of Cr^{2+}.

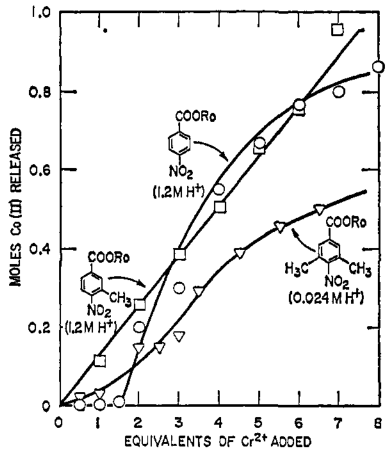

Figure 3. Release of Co^{2+} from *p*-nitrobenzoato derivatives on treatment with Cr^{2+}: [Co(III)]$_{initial}$ = 2.0 × 10^{-3} *M*; 5-min waiting period after each addition of Cr^{2+}.

The release of Co(II) (moles of Co^{2+} per mole of Co(III) complex taken) as measured amounts of Cr^{2+} are added to solutions of the various mononitro complexes is indicated in Figures 1–3. During the early stages of the reductions (less than 4–5 equiv of Cr^{2+} added), reactions appeared to be complete within a few seconds after mixing. With larger quantities of Cr^{2+} (especially in the case of *m*-nitro complex), reactions were slower, and it was found that extension of the time interval between addition of Cr^{2+} and measurement of Co(II) resulted in slightly higher values of the latter without, however, changing the essential nature of the curves.[15] The most striking differences among the various plots are their intercepts. No Co(II) is obtained from the *m*-nitro complex until more than 4 equiv of Cr^{2+} is added, whereas with the *o*-nitro isomer, Co(II) appears immediately after addition of Cr^{2+} but its quantity is small (*e.g.*, addition of 2.0 equiv of Cr^{2+} releases only 0.3 equiv of Co(II)). Release of Co(II) from the *p*-nitro derivative in 1.2 *M* acid requires 1.5–2 equiv of Cr^{2+}. However, in 0.024 *M* acid, release of Co(II) is immediate but levels off after 4.5 equiv of Cr^{2+} is added.

With the *m*-nitro complex, the "break" at 4 equiv of Cr^{2+} indicates that the ligand accepts four electrons before any reduction of Co(III) occurs. Thereafter, Cr^{2+} may attack the four-electron reduction product

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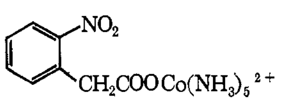
(15) The reductions of Co(III) in the *m*- and *p*-aminobenzoato complexes, which would be formed if complete reductions of the ligands preceded reduction of Co(III), have a half-life of about 1 hr at the concentrations used in these stoichiometry experiments. For the o-amino derivative, the corresponding half-life would be 2.5 hr.

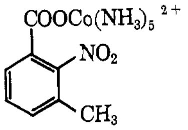
(presumably the 3,3′-azodibenzoato complex or its equivalent) either at nitrogen, further reducing the ligand, or at carboxyl, reducing Co(III). The two types of reduction should compete after a total of 4–6 equiv of Cr^{2+} has been added and possibly, if reduction of the ligand at that point is slow, in the 6–8 Cr^{2+} equiv region as well. Reduction of Co(III) is obviously slow since increasing the added Cr^{2+} from 6.0 to 7.0 equiv results in release of only 0.14 equiv of Co(II) in the time allowed for reaction.

Rate Enhancement of Reduction by the *o*-Nitro Group. When Cr(II) is added to the *o*-nitro derivative, the major fraction of the reductant becomes involved in reduction of the ligand, but there is a significant "leak through" of reducing power (about 15% during the early stages of reaction) to Co(III). Reduction of both ligand and Co(III) under these conditions is several orders of magnitude faster than the usual reduction of carboxylate-bound cobalt(III) *via* adjacent attack.[16] There is rate enhancement here, not only by the *o*-nitro group, but also by one or more of its reduction products, for the rapid release of Co(II) continues as the total number of Cr^{2+} equivalents is increased from 0 to beyond 5. During this reduction, strong absorption at 430 mμ ($\epsilon > 800$), almost certainly due, at least in part, to one or more azo derivatives, becomes noticeable (at about 2 equiv of Cr^{2+}), rises to a maximum (at 4.5 equiv), and drops off (at 6.0–6.5 equiv). The apparent convexity of the *o*-nitrobenzoato reduction curve suggests that there is more leak through of reducing capacity in the early stages of reaction, when the predominant species is the nitro complex, than in the latter stages when most of the nitro groups have been reduced (to nitroso and thence to azo complexes), but differences are slight.

It seems very likely indeed that the marked rate-enhancing action of the *o*-NO_2 group (in contrast to the observed rate-retarding action of the structurally similar *o*-COOH group[11]) is associated with the ability of NO_2 to accept a reducing electron, forming a metastable radical ion (which, in the case of the present Co(III) complexes, would be a radical cation). Such nitro radical ions have been studied in some detail, both in aqueous[17] and nonaqueous[18] solutions. Following its formation, such a species might then be reduced further, might disproportionate, or might undergo an internal shift of the reducing electron from the nitro group to Co(III), releasing Co(II). The evidence that an *o*-nitroso group and an *o*-azo linkage likewise facilitate reduction of bound Co(III) indicates that these groups may accept a reducing electron also; polarographic studies[19] point to formation of a radical ion in the reduction of aromatic azo compounds, but the question has apparently not been investigated for the nitroso group.

The proximity of NO_2 to COORo in the *o*-nitro complex raises the question as to whether the reducing electron is transmitted from one group to the other through the space outside the benzene ring or, alternatively (since the two groups are in conjugation), whether there is transfer of the electron through the ring itself (*i.e.*, reduction by remote attack). Comparison of the "Co(II)-release profile" of the *o*-nitrophenylacetato complex (XXXI) with that obtained from the *o*-nitrobenzoato complex (Figure 1) is pertinent here. Color changes during the early stages of reduction of XXXI, as with the *o*-nitrobenzoato complex, are complete within a few seconds after mixing, but virtually no Co(II) is released from XXXI until over 5 equiv of Cr^{2+} is added. Molecular models show that the nitro and carboxyl groups in XXXI may come into close proximity, but, obviously, there cannot be any conjugative relationships between them. It thus seems reasonable to ascribe the substantial leak through of reducing capacity from nitrogen to Co(III) observed in the early stages of the *o*-nitrobenzoato complex to transmission through the ring. This conclusion is reinforced by the behavior of the *p*-nitro derivatives.


XXXI


XXXII

It is interesting that very little Co(II) is released during the early stages of reduction of the 2-nitro-3-methyl complex (XXXII) (Figure 1). The nitro group in this complex, and the nitroso and azo groups formed from it by reduction, are held out of the plane of the ring by the two *ortho* substituents; moreover, nonbonding interaction between nitro and carboxyl is minimal when *both* groups are out of the plane of the ring. Although the lack of coplanarity does not interfere with acceptance of a reducing electron by NO_2 (even aliphatic nitro compounds have been found to be reduced to radical ions with ease[17b]), it appears in this case to reduce sharply the extent of electron transfer through the ring.

Reduction of the *p*-Nitrobenzoato Complex. Remote Attack. The reduction of the *p*-nitro complex in 0.024 *M* $HClO_4$ (Figure 2) results initially in the steady release of Co(II), corresponding to approximately one-eighth the added Cr^{2+}. After about 4.5 equiv of reductant has been added, the liberation of Co(II) suddenly ceases, and no more is formed until over 6.5 equiv of Cr^{2+} is put in, after which the release of Co(II) slowly resumes. During the initial (very fast) release, strong absorption at 465 mμ ($\epsilon_{app} > 600$) is observed; this reaches a maximum at 4.5 equiv but drops off sharply in the 6.0–6.5-equiv range.

The point at which the release of Co(II) levels off (4.5 equiv of Cr^{2+}) corresponds to the formation of about 0.6 mole of Co(II); thus, 3.9 equiv of Cr^{2+} was used to reduce the ligand. This indicates that, up to that point, the major part of the added Cr^{2+} is involved in a four-electron reduction of the nitro complex, forming a Cr(III)-bound azo compound, after which the added reductant is consumed almost exclusively in reaction with the azo linkages. Finally, as azo reduction draws near to completion, reduction

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[16] Although rates for the early stages of reduction were not measured, approximate values for the final two (slowest) steps were found to be 18 and 400 l. mole^{-1} sec^{-1} at 23° (see the Experimental Section).

[17] (a) P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963); (b) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, 83, 3909 (1961).

[18] D. H. Geske and A. H. Maki, *ibid.*, 82, 2761 (1960).

[19] M. E. Runner and G. Balog, *J. Electrochem. Soc.*, 102, 2266 (1955).

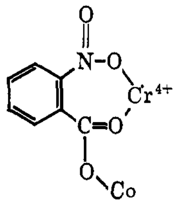
of the remaining Co(III) resumes. The regular slope of the Co(II) release curve before the 4.5-equiv "plateau," coupled with the steady increase of absorption at 465 mμ as Cr^{2+} is added, argues against the accumulation of a stable intermediate having an oxidation level between nitro and azo and suggests that nearly all Co(II) released in the 0–4.5-equiv region was derived from one-electron reduction of a single Co(III) species. This immediate precursor cannot be the azo derivative, for this is reduced in the 4.5–6.5-equiv region with virtually no release of Co(II); it might, however, be the nitro complex itself or the nitroso complex, and experiments in more acidic media suggest that it is the latter.

More particularly, when the *p*-nitro complex is treated with Cr^{2+} in 1.2 *N* $HClO_4$ (Figure 3), *1.5–2 equiv of* Cr^{2+} *must be added before Co(II) is formed in measurable quantity.* Within the remainder of the fast-reaction region for this complex (2–4.5 equiv of Cr^{2+}), Co(II) is steadily released, but as more than 4.5 equiv of reductants is added, rates of reduction (both of ligand and of Co(III)) drop off drastically. The delay in Co(III) reduction until almost 2 equiv of reductant has been added indicates that the nitro complex is reduced, accepting two electrons and forming the nitroso complex, more rapidly than the Co(III) bound to it is reduced and liberated. The major portion of electron "leak through" to Co(III) in this sequence appears to be at the nitroso stage, and some in the 4.5–6.5 (azo) region is observed also. Beyond 6.5 equiv, reactions are necessarily slow.

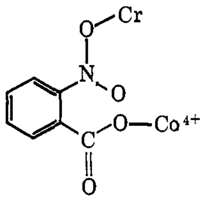
If this picture be correct, the 1.5–2 equiv delay in release of Co(II) from the *p*-nitro complex in 1.2 *N* acid implies not only that the nitro–nitroso conversion is faster than reduction of Co(III) in the nitro complex, but also that it is substantially faster than reduction of Co(III) in the nitroso complex as well, for if this were not the case, a measurable fraction of the nitroso complex would be reduced to Co(II) soon after its formation, *i.e.*, in the 0–1.5-equiv region. The disappearance of this delay when the reaction medium is changed from 1.2 to 0.024 *M* acid indicates that reduction of Co(III) in the nitroso complex (and perhaps in the nitro complex as well) competes more favorably with the nitro–nitroso conversion at low acidities. Since it is very unlikely that lowering the acidity will raise the rate of Co(III) reduction in either of these complexes, it may be inferred that the reduction of the nitroso group is substantially more rapid at the higher acidity, an inference in keeping with (but not demanded by) the proton requirement for the conversion.[20] On the other hand, the disappearance of the "plateau" at 4.5 equiv when the acidity is raised from 0.024 to 1.2 *M* indicates that reduction of Co(III) bound to the azo complex(es) competes more favorably with reduction of the –N=N– group in strongly acidic solution. Here, it is likely that electron transfer to Co(III) through the azo group is strongly acid dependent, whereas reduction of the azo group itself is not; indeed, reduction of the azo group in the complex of benzeneazosalicylic acid (the final complex in Table II) has been found to be only 30% faster in 1.2 *M* than in 0.012 *M* $HClO_4$.

The Co(II) release curve for the 4-nitro-3,5-dimethylbenzoato complex in 0.012 *M* $HClO_4$ is shown in Figure 3; in this complex, methyl groups in both positions *ortho* to NO_2 hold the latter out of the plane of the benzene ring. Although there is less leak through of reducing capacity than is observed for the *p*-nitro complex, the difference is slight, being far less striking than that observed in the *o*-nitro series. The contrast here suggests that for reduction of bound Co(III) *via* electron transfer through a reducible nitrogen-containing group, coplanarity of the carboxyl with the ring is a far more important requirement than is coplanarity of the nitrogen substituent. Moreover, it tends to favor the notion that in the *p*-nitro series, a major part of electron transfer to Co(III) during the rapid stages of reaction involves a nitroso group, rather than a sterically more demanding nitro group.

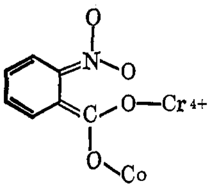
The rationale presented here for acceleration of Co(III) reduction by the *p*-nitro substituent is thus different from that for the *o*-nitro group. Rate enhancement by *o*-nitro suggests structures XXXIII and XXXIV in analogy to similar ones considered in connection with rate enhancement by carbonyl-containing substituents.[2b,21] A third structure, XXXV, denoting merely rate enhancement of adjacent attack by stabilization of a radical cation intermediate by the nitro group, appears less likely than XXXIII or XXXIV (which feature Cr^{2+} attacking the nitro group) in light of past experience[3b] that rate enhancement in this fashion is generally modest (a single power of ten) as compared to rate enhancement by remote attack or by chelation (which may amount to several powers of ten). Structures analogous to XXXIII and XXXIV may be drawn for the *o*-nitroso and the 2,2′-azo complex in accord with the fast (although partial) release of Co(II) in the 2–4- and the 4–6-equiv regions in reduction of the *o*-nitro derivative. In the *p*-nitro series, available evidence suggests the key intermediate to be the Cr(II)–nitroso adduct (XXXVI) which, after its formation, may be reduced further to an azo derivative or, alternatively, may undergo transfer of the unpaired electron to Co(III).



XXXIII



XXXIV



XXXV

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[20] An alternate possibility, suggested by one of the referees, is that a major portion of electron "leak through" in 0.024 *M* acid may occur at the one-electron reduction stage, *i.e.*, through a nitro radical ion. In 1.2 *M* acid the disproportionation of such a radical ion, which requires protons, may be accelerated, with its steady-state concentration no longer high enough to allow a substantial contribution to the processes yielding Co(II).

[21] If it is assumed that XXXIII or XXXIV (or XXXV) may react in two ways, resulting ultimately in reduction either of Co(III) or NO_2, then these structures must be regarded as intermediate species; alternatively, they may be taken as transition states with Co(III) reduction occurring through XXXIII and nitro reduction through XXXIV. The structure analogous to XXXIV, denoting reduction by remote attack without chelation, was eliminated in the case of *o*-carbonyl (but not *p*-carbonyl) derivatives by isolation of the carboxylatochromium(III) product, but the plurality of products resulting from the multistep reactions in the nitro series rules out straightforward judgment here.

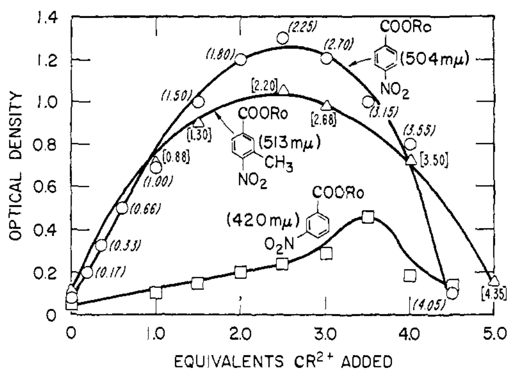
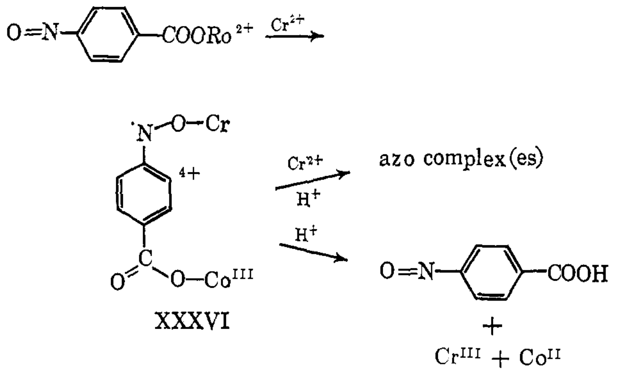
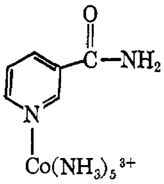


Figure 4. Appearance and disappearance of strongly absorbing species from nitrobenzoatopentaamminecobalt(III) complexes on treatment with Cr^{2+}: [H$^+$] = 1.2 *M*, [Co(III)]$_{\text{initial}}$ = 2.0 × 10^{-3} *M;* path length = 1.00 cm. Values in parentheses represent equivalents of Cr^{2+} used in reducing the ligand; 1-min waiting period after each addition of Cr^{2+}.

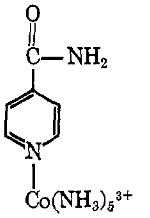
The analogy drawn here between nitro and carbonylbenzoato derivatives leads to an additional point. There is some evidence that reduction *via* remote attack may occur through a *m*-carbonyl substituent, although much more slowly than through an *o*- or *p*-carbonyl group.[22] Similarly, the Co(II) release curve of the 3-nitro-4-methylbenzoato complex (Figure 3) indicates a barely measurable release of Co(II) in the 0–3-equiv region, followed by liberation of over 0.1 mole of Co^{2+} in the 3–4-equiv region. As with the *o*- and *p*-nitro series, all reactions in the 0–4-equiv region are fast (with rate constants, in this case, greater than 250 l. mole^{-1} sec^{-1}). Thus, there is significant leak through here also, the major part once again appearing to involve the nitroso complex.



XXXVI

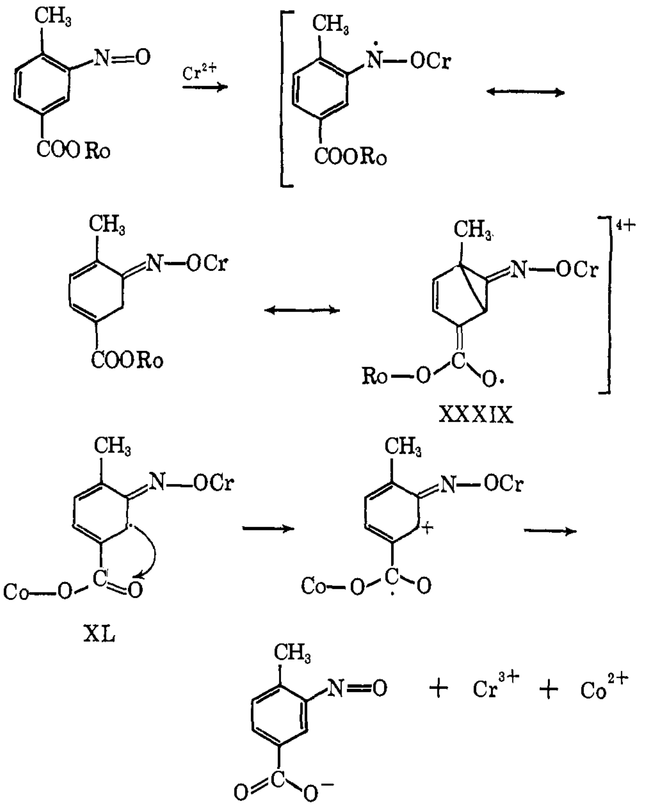


XXXVII



XXXVIII

The conjugative relay of electronic effects to a reaction center from a *meta* position may be represented pictorially by "*meta*-bonded" structures such as XXXIX. Structures of this sort appear to be most appropriate for certain heterolyses of aromatic molecules in electronically excited states;[23a] although they have been used in the past to account for *meta*-activation in nonexcited systems,[23b] they have not been widely accepted in this connection. In this case, a more satisfactory alternative might involve electron transfer, through space, from the *ortho* carbon to the uncoordinated oxygen of the carboxyl (XL), after which the reaction may proceed in the usual manner.



XXXIX

XL

Evidence for Chromium-Bound Radical Cation Intermediates. During the Cr^{2+} reductions of a number of the nitrobenzoato complexes, intensely colored materials form. The position and magnitude of their absorption maxima, as well as their appearance and disappearance points within the reduction sequence, distinguish them from the corresponding azo compounds, the most intensely colored of the "even-electron" intermediates. The most stable of these ($\epsilon_{\max}$ >1000[24] (504 mμ)) is formed from reduction of

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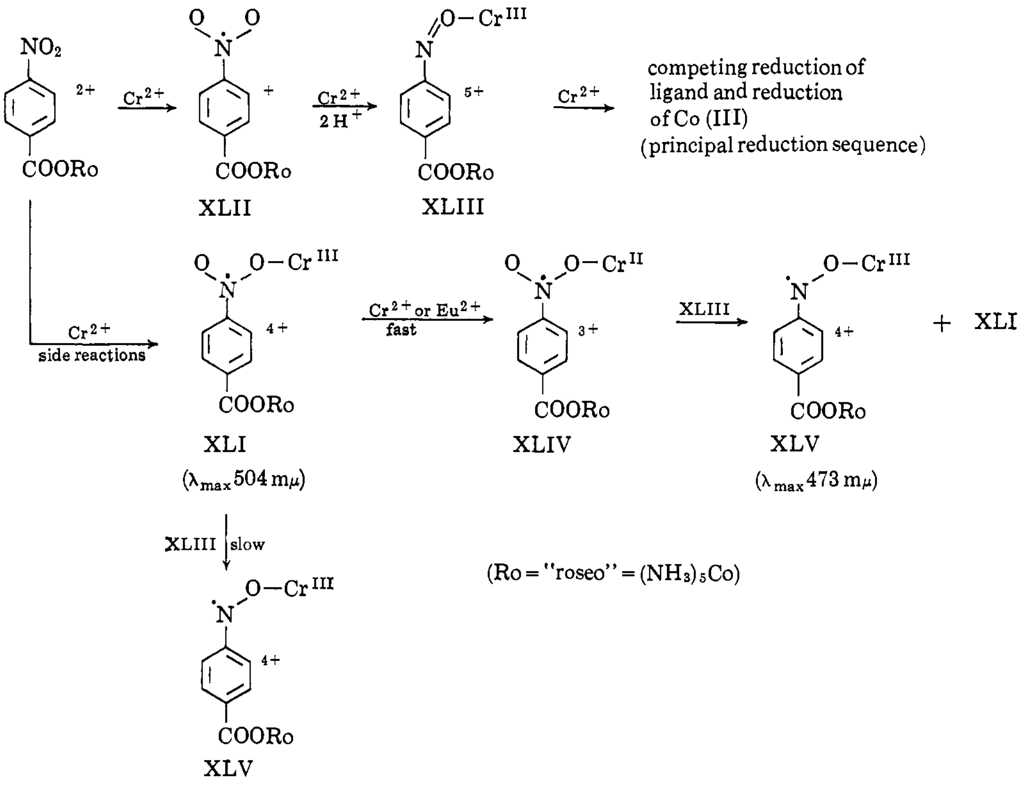
[22] The reduction of the 2-hydroxy-5-formylbenzoato complex (ref 3b) exhibits an acid-independent term of 0.55 (two to three times "normal") in its rate law. Moreover, the reduction of the 3-formylbenzoato complex has been found to occur with liberation of the free parent acid (D. LaFollette, M.S. Thesis, Stanford University, 1964). Further evidence for remote attack in "improperly conjugated" systems stems from the work of H. Taube and F. Nordmeyer (Stanford University, 1965), who have observed that reduction of the pyridine complex XXXVII, as well as that of XXXVIII, occurs through Cr^{2+} attack at the amide group.

[23] (a) See, for example, H. E. Zimmerman and S. Somasekhaar, *J. Am. Chem. Soc.*, 85, 923 (1963); (b) F. M. Beringer and S. Sands, *ibid.*, 75, 3319 (1953); C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor, and T. Alfrey, Jr., *ibid.*, 74, 4848 (1952).

[24] Since the concentrations of these pigments have not been deter-

Chart II



the p-nitro complex in 1.2 M $HClO_4$. A similar, but apparently much less intensely colored, species (ϵ_{max} >130 (504 mμ)), is formed from Cr^{2+} reduction of p-nitrobenzoic acid, but no pigment of this sort is detectable if the reduction, either of the complex or of the parent acid, is carried out with Eu^{2+}, another one-electron reducing agent of comparable potential.

The brick-red color of the pigment appears when less than $^1/_6$ equiv of Cr^{2+} is added to 1 mole of the p-nitro complex.[25] As each additional increment (up to a total of 4.5 equiv of Cr^{2+}) is added, the absorbance first drops off rapidly, then increases more slowly, reaches a maximum value, and, once again, drops off. This final fading is very slow when the initial concentration of p-nitro complex is 10^{-4} M, but is easily measurable at 10^{-3} M. When more than 4.5 equiv of Cr^{2+} is added, absorbance at 504 mμ disappears irreversibly.

The absorbancies at 504 mμ (before the slow final fading) at various stages of the reduction are shown in Figure 4; the Cr(II) values in parentheses, representing reductant consumed by the ligand, are obtained by subtracting Co(II) released (measured in the stoichiometry experiment) from Cr(II) added. The resulting curve, showing a broad maximum in the 2.0–3.5-equiv region, strongly indicates that this pigment is a minor by-product, rather than a major intermediate in the principal reaction sequence, for the concentration of such an intermediate should change greatly during the addition of 1.5 equiv of fast-acting reductant. The virtually immediate appearance of the 504-mμ species, and its steady build-up in the 0–2-equiv region while the nitro compound is still present, indicates that this pigment is a *one-electron reduction product from the nitro complex*, analogous to nitro radical anions described by other workers.[17,18] Since it is not formed when the reduction is carried out with Eu^{2+}, it may be assumed to be bound to chromium, as well as to Co(III).

When the 504-mμ pigment is subjected to several bleachings and regenerations in the 2.4–4.0-equiv region, a new peak at 473 mμ develops. This 473-mμ absorption largely disappears, along with the 504-mμ absorption, in the 4.5–5-equiv region; like the 504-mμ pigment, the 473-mμ pigment is not formed when the reduction is carried out with Eu^{2+} instead of Cr^{2+}. Moreover, the 473-mμ species is formed slowly, at the apparent expense of the 504-mμ complex, when solutions in which the latter has been generated are held at room temperature (with oxygen excluded). The 504-mμ pigment may be bleached rapidly and irreversibly by addition of excess sodium acetate to the brick-red solution and is not observed at all when reduction of the nitro compound is carried out in 0.024 M $HClO_4$, rather than 1.2 M.[26] In reduction of 0.024

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mined, only lower limits for their extinction coefficients can be given. If, as is believed, they constitute only a small fraction of the nitro complex originally added, actual values will be many times these limits.

(25) The initial formation of the 504-mμ pigment (in the presence of excess p-nitro complex) exhibits pseudo-first-order kinetics, corresponding, assuming a reaction first order in complex, to a second-order rate constant of 200 l. $mole^{-1}$ sec^{-1} at 25°.

(26) A possible rationale for some of the observed change involving the 504-mμ pigment is indicated in Chart II. The tetrapositive radical cation XLI is proposed for the 504-mμ pigment, but since this species almost certainly lies outside of the principal reduction sequence, it is suggested that the principal sequence involves attack at NO_2 without formation of a new bond, forming radical cation XLII, which is reduced quickly to the nitroso derivative, XLIII. The relatively small changes in concentration of the pigment in the 2.0–3.5-equiv region indicate that its steady-state concentration is fixed by the original concentration of the nitro complex. The quick fading on treatment with Cr(II) or Eu(II) shows that the pigment is being reduced further, possibly to a chromium(II) radical cation, represented as XLIV, but the regeneration of the 504-mμ absorption points to reoxidation by a species present in excess in the 2–3.5-equiv region but absent beyond the 4.5-equiv region, *i.e.*, the nitroso complex XLIII.

M acid, the principal deeply colored species exhibits a maximum at 466 mμ ($\epsilon > 600$), which, unlike the 473-mμ species formed in 1.2 *M* acid, persists well beyond the 5.0-equiv region and is therefore assigned to one or more azo intermediates.

During Cr^{2+} reduction of the 4-nitro-3-methylbenzoato complex in 1.2 *F* HClO$_4$, a species strongly absorbing at 513 mμ is formed. The development and disappearances of this pigment as successive portions of reductant are added (Figure 4) parallel the behavior of the 504-mμ complex derived from the *p*-nitrobenzoato derivative; hence it may be likewise ascribed to a Cr(III)-bound, one-electron reduction product. With the *m*-nitrobenzoato complex, on the other hand, transient absorption (λ_{max} 420 mμ) develops more gradually, reaches a maximum at about 3.5 equiv, then virtually disappears at 4.0–4.5 equiv (Figure 4), suggesting that the principal absorbing species is the three-electron reduction product, that is, a nitroso radical cation analogous to XLV.[27] In this case, the possibility that this radical ion is an intermediate in the principal reduction sequence cannot be excluded.

In summary, the present study of nitro complexes, despite the tentative nature of some of the conclusions drawn, reemphasizes the lesson that acceptance of a reducing electron by a group in conjugation with COOCo(III) in the ligand is not at all tantamount to reduction of the coordinated Co(III). Although structural features favoring one process often favor the other, the detailed requirements for the two are generally different.

Acknowledgments. The author is grateful to Mr. F. Nordmeyer, Mr. E. Deutsch, and Mr. D. LaFollette for making known the results of their experiments prior to publication. He is also indebted to Professor Henry Taube for a number of valuable discussions.

The 473-mμ absorption is most prominent in the 2.5–4.5 (nitroso) region and appears to be formed in a one-electron oxidation which also regenerates XLI; it is therefore assigned to the three-electron reduction product, here represented as radical cation XLV. The intense absorption of this species indicates coordination to Cr(III), both here and in its presumed precurser, XLIII.

The conversion of the 504- to the 473-mμ species in the absence of added Cr(II) is fastest in the 2–3-equiv region, that is, when the concentration of the nitroso complex is presumably greatest. This points to conversion of the nitroso complex to its radical cation XLV, but here the electron donor appears to be XLI, rather than its Cr(II) counterpart XLIV, which accomplishes the same reduction more rapidly.

Since the rate of formation of XLI should not be pH dependent, its nonappearance at higher pH values indicates that it is being consumed rapidly, not by reduction (which should proceed no more rapidly at the higher pH), but rather by heterolysis to the more faintly colored and more reactive radical cation XLII.

(27) The alternate three-electron reduction product, an azoxy derivative, is ruled out here by the position of the maximum. Aromatic azoxy compounds generally exhibit peaks near 320 mμ, but not, in the absence of other chromophoric groups, near 420 mμ: see, for example, M. J. Kamlet, "Organic Electronic Spectral Data," Interscience Publishers, Inc., New York, N. Y., 1960, p 442.

The Relaxation of Protons in Liquid Ammonia by Nickel(II) and the Kinetics of Ammonia Exchange

T. J. Swift and H. H. Lo

Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio. *Received February 16, 1966*

Abstract: Anhydrous solutions of Ni(NH$_3$)$_6$(ClO$_4$)$_2$ in liquid ammonia were prepared, and the proton nmr spectra were recorded as a function of temperature. The line shapes were shown to be the result of spin–spin relaxation of protons with no detectable contribution from spin–lattice relaxation of ^{14}N. Moreover, the temperature dependence of the proton T$_2$ revealed that the relaxation process is chemical exchange controlled below about 0° and that the relaxation mechanism is the "chemical shift" mechanism. With these facts established, quantitative kinetic studies were performed with solutions of Ni(NH$_3$)$_6$(ClO$_4$)$_2$ in ammonia to which a small amount of HClO$_4$ had been added to produce the collapse of the ^{14}N triplet. The first-order rate constant for the ammonia exchange was found to be $1.9 \pm 0.1 \times 10^5$ sec^{-1} at 25°; ΔH^* is 10.1 ± 0.5 kcal/mole and ΔS^* is -0.5 ± 1 eu. The coupling constant, A/h, is $3 \pm 1 \times 10^6$ cps.

In a recent investigation Swift and Sayre[1] have shown that certain rapid reactions directly involving water molecules in aqueous solution may be used to obtain information concerning the hydration of cations. The authors employed manganous ion as their "probe" reagent and list the following requirements for a probe in order that the probe may be suitable for the study of ion hydration. (1) It must react directly with water molecules. (2) The rate constant for the direct reaction between the probe and primary hydration sphere waters must differ considerably from the rate for all other types of water molecules. (3) The lifetime of the probe must be obtainable from a precisely measurable experimental quantity.

In the interpretation of their results concerning the hydration numbers of several doubly changed ions, the authors have introduced the possibly sizable role of the solvent structure in the determination of the solvation numbers of ions in solution.

As a consequence of these results, a series of investi-

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(1) T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, **44**, 3567 (1966).