and 0.5 ml. of ethyl iodide was allowed to react under a nitrogen atmosphere for 3 days at room temperature. Then 3.0 ml. of 1.0 *M* triphenylphosphine in ether was added. After reacting for 1.5 hr., the solution was centrifuged and the solvent evaporated at room temperature under reduced pressure. The residue was recrystallized twice by dissolving it in a minimum of methylene chloride, adding pentane, and cooling in Dry Ice and then twice more by dissolving it in warm ether, adding pentane, and cooling to 0°. There was obtained 0.20 g. of yellow-orange needles with the properties listed in Table I.

Rate of Reaction of 1-Acetoxy-π-allylcobalt Tricarbonyl with Triphenylphosphine. A solution of 30 ml. of 0.07 *M* $NaCo(CO)_4$[7] in ether, 0.5 ml. of acrolein, and 0.5 ml. of methyl iodide in a capped, nitrogen-filled bottle was heated in warm water (~50°) for 1 hr., and then the solvent was evaporated at 0° under reduced pressure. The residue was dissolved in 20 ml. of ether and centrifuged; the solution was put in a gasometric apparatus[8] at 25.0° which had been filled with ether-saturated carbon monoxide. The addition of 6.0 ml. of 1.0 *M* triphenylphosphine in ether caused gas evolution to begin. A series of 14 readings was taken, measuring the volume of gas evolved and the time. The average first-order rate constant for the reaction was 4.31×10^{-4} sec.$^{-1}$ and the average error was $\pm 0.10 \times 10^{-4}$ sec.$^{-1}$. The volume of gas evolved, 89.5 ml., corresponded to a concentration of 0.041 *M* of the cobalt compound. The infrared spectrum of the solution before adding the triphenylphosphine showed that only the expected complex was present, and the spectrum after the reaction with triphenylphosphine showed that the compound had reacted completely.

Acknowledgment. The n.m.r. spectrum was measured by Dr. M. M. Anderson of these laboratories.

Electron Transfer through Organic Structural Units. II. Conjugated and Reducible Ligands as Bridging Groups in Oxidation–Reduction Reactions[1]

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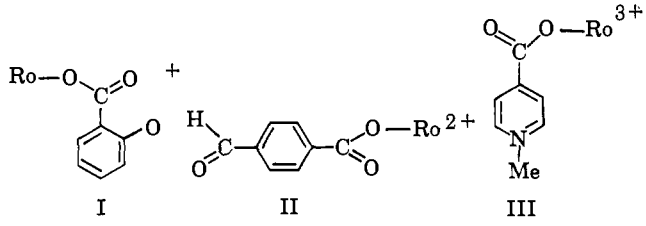
The specific rates of reduction of 33 pentaamminecobalt(III) complexes (containing a variety of acyclic, alicyclic, aromatic, and heterocyclic ligands) with Cr^{2+} have been measured and their dependence on $[H^+]$ noted. The values cover a range of over seven powers of ten. Noncarboxylated complexes, derived from imidazole, pyridine, and dimethylformamide, react much more slowly than those bound through carboxyl, emphasizing the effectiveness of the bound carboxyl group as an electron-transfer bridge. o-Aminocarboxylato complexes in acid solution are reduced at rates about half those for the usual ortho-substituted benzoato complexes, suggesting one-sided electrostatic shielding by the protonated nitrogen substituent; rate laws contain no inverse acid term, ruling out reduction through a chelated path involving amino nitrogen. In reduction of the o-iodoso compound IX and, possibly, the complex of pyridine-2,6-dicarboxylic acid N-oxide (X), preliminary rapid reduction of the I–O or N–O group is followed by reduction of Co(III) in the usual way. The terephthalato complex XII is reduced at the "normal" rate of 0.20 l. mole^{-1} sec.$^{-1}$, ruling out appreciable contribution by remote attack in this case. Additional examples of rate enhancement in the reductions of o-carbonylbenzoato derivatives are noted, the large (acid-independent) values for these rate constants supporting transient chelation in the transition state and electron transfer, at least in part, through the carbonyl group. The spectra of the Cr(III) products from reduction of a number of heterocyclic complexes (derived from pyrazole, pyridine, and pyrazine) indicate chelation, and the very high specific rates for these reductions support chelation in the activated complexes as well. With both the pyrazole (XXVI) and the pyrazine (XXIV and XXV) complexes, only one of the two ring nitrogens is protonated at the highest acidity used, the other nitrogen remaining free for chelation. Hence, there is no inverse acid dependence, as was observed for the pyridine-2-carboxylato and pyrrole-2-carboxylato complexes. The chelated paths for reduction of the pyrrole and pyrazole complexes are slower, by several powers of ten, than those for the pyridine and pyrazine complexes; this is attributed to the greater angular strain in forming fused 5,5 bicyclic systems and to nonplanarity of the bonds about tetrahedral nitrogen in the five-ring systems. The gluconato complex XXXIII is reduced at a rate comparable to other hydroxylated aliphatic derivatives, but the S-benzylthioglycolato complex XXXIV reacts surprisingly rapidly, suggesting rate enhancement by chelation with the alkylmercapto group in a situation where an alkoxy group is found to be inert. Further examples of remote attack, involving the p-formylbenzoato (II), trans,trans-muconato (XXXVI), and cinnoline-4-carboxylato (XXXVII) systems, are noted, and the proposal is made that this phenomenon is confined to ligands that are reducible. Reduction of pyrazine derivatives XXIV and XXV, and their parent acids, with Cr^{2+} yields intensely absorbing green species which are reduced rapidly with $(NH_3)_5CoCl^{2+}$; the possibility that these are radical cations of the type XXXVIII is considered.

(1) This research was sponsored by the Research Committee of the Division of Physical Sciences of Stanford Research Institute. The support of this committee is gratefully acknowledged.

The rates at which a large number of substituted carboxylatopentaamminecobalt(III) complexes are reduced with Cr^{2+} have been found to be relatively insensitive to the more ordinary inductive, conjugative, and steric effects which often influence organic reactivities.[2] At the same time, suitable structural modification of the carboxylato ligands in such complexes may greatly facilitate their reduction by bringing into play one of several less usual effects. For example, the very rapid reductions of the nonprotonated forms of the salicylato complex I and related *ortho*-hydroxylated benzoato complexes[2b] probably proceeds through a planar chelated transition state, whereas the rapid



I II III

Ro = "roseo" = $Co(NH_3)_5$

reduction of the *p*-formylbenzoato derivative II and related carbonyl substituted complexes[2b,3] appears to be initiated by "remote attack" of Cr(II) on the carbonyl group, which must be separated from the coordinated carboxyl by a system of conjugated double bonds. The (less strikingly) rapid reduction of the N-methylated pyridinecarboxylato complex III is thought to proceed through a conjugatively stabilized radical-cation intermediate,[2b] and similar intermediates may intercede in other such reductions of pyridinecarboxylate derivatives.

It has been noted that electron transfer from Cr^{2+} to coordinated cobalt(III) often takes place readily through ligands which, when free, are reducible,[2b] although such ligands need not suffer a net reduction in the electron-transfer process. Moreover, there is now evidence (*vide infra*) that remove attack is a somewhat less general phenomenon than previously supposed,[4] and, more particularly, that it may occur only with reducible ligands. However, the correlation between electron-transfer efficiencies of ligands and their reducibilities has not yet been precisely defined, nor has it been extended beyond the benzene and pyridine series.

In the present extension of the study of the reduction of pentaamminecobalt(III) complexes with Cr^{2+}, a number of additional organic ligands are considered, some of them conjugated, some reducible, and some having both characteristics.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,[2b,5] chloropentaamminecobalt(III) perchlorate, sodium perchlorate solutions (for kinetic experiments), and chromous solutions were prepared as described.[2b] The concentrations of the chromous solutions were taken as the same as those of the parent chromium(III) solutions, which, in turn, were determined from their absorbances at 408 mμ (ε 15.6) and 574 mμ (ε 13.4).[6] Organic acids, most of them available from the Aldrich Chemical Co., Milwaukee, Wis., were used as received, or, if badly discolored, after crystallization from ethanol or ethanol–toluene.

Preparation of the Complexes. Most of the complexes were prepared in water from aquopentaamminecobalt(III) perchlorate as described.[2b] In addition, certain complexes derived from very lipophilic parent acids could be prepared from the dimethylformamidopentaamminecobalt(III) complex in dimethylformamide as follows: 0.5 g. of the aquo perchlorate was converted to the DMF complex by heating in 3 ml. of DMF at 100° for 15 min. with intermittent shaking. The solid DMF complex could be precipitated by addition of 6 ml. of saturated aqueous $NaClO_4$, or, more conveniently, the DMF solution of the complex could be used directly. Ten mmoles of the parent carboxylic acid was dissolved in 3–5 ml. of hot DMF, and 0.40 ml. of 50% aqueous NaOH was added. The mixture was agitated vigorously and the solution of the DMF complex added. The preparation was kept at 80° for 45 min., concentrated to about 1.5 ml. *in vacuo* at 85° by rotary evaporation, and then added to a mixture of 5 ml. of water and 0.9 ml. of concentrated $HClO_4$, precipitating the parent acid. In some cases the parent acid could be extracted with ether, but more often it was removed by heating the preparation to 70°, then filtering. The solution was then diluted with an equal volume of saturated aqueous $NaClO_4$, kept at −10° for several hours, and the solid complex was filtered off and recrystallized from a minimum quantity of hot water. The yields in this method were poor (often less than 10%) with the most troublesome impurity being the unreacted DMF complex, which sometimes precipitated with, or instead of, the desired carboxylato complex. The DMF complex has an absorption maximum at 507 mμ (ε 80), rather than 502–503 mμ, and may be readily distinguished from the carboxylato complex (even in the presence of organic impurities) by its slow reaction with Cr^{2+}.

The noncarboxylated pyridine and imidazole complexes were also prepared from the DMF complex in DMF by treatment with a large excess of the free base (4 g. of base per gram of DMF complex) without addition of NaOH; conversion was virtually complete within less than 10 min. at 100°, as shown by the color change from cerise to yellow-brown. These complexes are extremely water-soluble, but moderate quantities of the difficultly soluble yellow hexaamminecobalt(III) perchlorate may be formed as well (in a manner not yet explained) and should not be mistaken for the heterocyclic complexes. The method as described is by no means general for complexes of heterocyclic bases; quinoline and 2,2′-bipyridyl yield the hexaammine perchlorate as the only isolable product, whereas attempted reactions with substituted thiazoles, triazoles, and benzimidazoles, tetrahydrofuran, and dioxane failed, and only the DMF complex was recovered.

For preparation of complexes having an NH_2 group *ortho* to the carboxylato, the parent acids (anthranilic

(2) (a) R. T. M. Fraser, *J. Am. Chem. Soc.*, **84**, 3436 (1962); (b) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

(3) (a) R. T. M. Fraser, *ibid.*, **83**, 4920 (1961); (b) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

(4) See, for example, D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(5) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1946).

(6) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

Table I. Analyses and Absorbancies of Pentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_2$

R	% Co Calcd.	% Co Found[2b]	λ_{max}, mμ	ϵ_1	λ_{max}, mμ	ϵ_2
Pyridine[a]	11.4	11.4	475	64.0	338	52
Imidazole (IV)[a]	11.7	11.5	475	60	330[b]	89
Dimethylformamide[a]	11.4	11.4	505	76.0	347	62.5
Acetoxyacetato	12.8	12.5	502	70.3	350	55.6
Cyclopropanecarboxylato	13.7	13.6	503	83.0	352	73.0
1,1-Cyclobutanedicarboxylato (XVII)	12.1	12.0	502.5	72.6	350	59.5
Oxydiacetato	12.4	12.6	502	71.6	348	60.0
3,5-Pyridinedicarboxylato	12.7	12.0	501.5	73.0		
o-Hydroxyphenylacetato	12.0	11.4				
N-Phenylanthranilato (VIII)	10.6	10.9				
Terephthalato (XII)	11.7	11.3	503	76.1		
Acetylenecarboxylato (XI)	14.3	14.2	501.5	84.9	348	75.6
o-Hydroxycinnamato (XVIII)	11.6	11.4	500.5	93.8	316	9×10^3
2,4′-Benzophenonedicarboxylato (XXII)	9.6	9.4	503	78.9		
2-Carboxy-4′-chlorobenzophenone (XXI)	9.8	9.5	501	75.5		
S-Benzylthioglycolato (XXXIV)	11.2	11.1	503	78.8		
Pyrazinecarboxylato (XXIV)	12.7	12.7	502.5	74.0		
4-Cinnolinecarboxylato (XXXVII)	11.5	11.4				
5-Uracilcarboxylato (XXXI)	12.0	11.4	502.5	79.5		
o-Aminobenzoato (VI)[a]	10.0	9.8	502.5	106.8		
p-Dimethylaminobenzoato (VII)[a]	9.7	9.1	500.5	96.0	295	7.4×10^4
2-Amino-3-carboxylatopyridine (V)[a]	9.9	9.7	501.5	103.8		

[a] Triperchlorates. [b] Broad shoulder.

acid in water, 2-aminonicotinic acid in DMF) were used without added NaOH; these complexes were most readily purified as hydroperchlorates, being precipitated from concentrated $HClO_4$ and recrystallized from 1 *F* $HClO_4$.

The terephthalato complex was prepared by oxidation of the *p*-formylbenzoato complex with sodium permanganate in dilute $HClO_4$ at 30°.[7] The permanganate solution was added until the violet color persisted, the excess permanganate reduced by addition of a few drops of ethanol, the MnO_2 filtered off, and the mixture worked up in the usual manner. If $KMnO_4$ was used in place of $NaMnO_4$, the product was contaminated with crystalline $KClO_4$.

All complexes studied kinetically were isolated as crystalline solids except the gluconato derivative, which resisted repeated attempts at crystallization; for this complex, measurements were carried out on solutions (which necessarily contained a large excess of gluconic acid) just after preparation. The N-phenylanthranilato complex could be dried and weighed but deteriorated rapidly in aqueous solution; hence, the specific rate for this complex is little better than an "order of magnitude" figure.

Table I lists 21 complexes giving satisfactory analyses. In addition, complexes from the following nine acids were prepared but were contaminated with 5 to 15% of the parent acid: *trans,trans*-butadienedicarboxylic (muconic), *p*-hydroxycinnamic, *o*-formylbenzoic, *o*-iodosobenzoic 6-hydroxynicotinic, 2,4-pyridinedicarboxylic, 2,6-pyridinedicarboxylic N-oxide, 2,3-pyrazinedicarboxylic, and 3,5-pyrazoledicarboxylic. Kinetic studies of the reductions of these impure complexes were carried out, but final purifications were not, generally because the quantity remaining was too small. Several attempts were made to prepare the complexes of the following acids, both in water and in DMF, but without success: acetylenedicarboxylic and oxaloacetic (these decarboxylated), N-acetylanthranilic, 4-acetamidobenzoic, 4,4′-diphenic, 2,6-dihydroxypyridine-4-carboxylic, 2-indoleacetic, 3-indoleacetic, 4-chloromercuribenzoic, 4,4′-azodibenzoic, 4,4′-stilbenedicarboxylic, quininic, benzeneazosalicylic, *o*-chlorophenyl-5-methylisoxazole-4-carboxylic, *p*-(6-hydroxy-3,4-xylylazo)benzoic, 2,2′-dithiodibenzoic, 3-dimethylaminobenzoic, imidazole-4,5-carboxylic, 3,5-dichloroanthranilic, 3-amino-2,4,6-tribromobenzoic, dithiodiglycolic, *o*- and *p*-formylcinnamic,[8a] and benzalacetophenone-4-carboxylic.[8b]

Spectra of the Complexes. These generally featured an absorption maximum at 502–503 mμ, considered to be typical of carboxylato complexes in this series, but variations were noted in some instances. A reversible change from pink to bright orange, with an accompanying broadening of the peak near 290 mμ and incursion of absorption into the violet, has been observed when a complex having an OH group *ortho* or *para* to COORo is treated with base; the pink and orange forms of these complexes are present in equivalent amounts at pH 9.8.[2b] Similar changes occur in the present series with the complexes of *o*- and *p*-hydroxycinnamic acid, and, surprisingly, with the complex of *o*-hydroxyphenylacetic acid. Complexes having an amino or substituted amino group *ortho* or *para* to COORo display the bright orange color in neutral solution but are converted to the pink form upon acidification. The *o*-amino and *p*-dimethylamino complexes are half-converted to their pink forms at pH 4. The N-phenylanthranilato complex VIII, in which the nitrogen atom is very weakly basic, exists predominantly in the orange form at pH 1 but is converted to the pink in concentrated acid. Similar, but less striking, changes occur on treating a solution of the uracil-5-carboxylato complex with base, whereas the cinnoline-4-carboxylato complex, in contrast, is converted reversibly from pink to orange on treatment with acid,

(7) The author is indebted to Mr. Darwin Thusius for suggesting this method.

(8) (a) R. H. Wiley and P. H. Hobson, *J. Am. Chem. Soc.*, 71, 2430 (1949); (b) C. D. Gutsche, E. F. Jason, R. S. Coffey, and H. E. Johnson, *ibid.*, 80, 5756 (1958).

rather than base. The visible spectrum of the 6-hydroxynicotinato complex is not pH-dependent, suggesting that the complex exists as the amide form XIII. Pronounced shifts occur when a ligand having donor oxygen is replaced with one having donor nitrogen. The visible maximum for the pyridine complex lies at 475 mμ (ε 64), and that for the imidazole complex at 485 mμ (ε 60); both are yellow to the eye. The maximum for the DMF complex is at 506 mμ (ε 76), suggesting that the ligand is bound to Co(III) through oxygen rather than nitrogen.

Kinetic Experiments. Rates were evaluated by following the decrease of absorbance at 502 mμ as previously described.[2b] When an acid dependence was suspected, runs were carried out at two or more acidities between 0.008 and 1.2 *M*, but ionic strength was kept at or near 1.5 by addition of appropriate quantities of $NaClO_4$ solution. Some runs were carried out in a 10.0-cm. cylindrical cell, some in a 1.00-cm. square cell, and some (when only small quantities of complex were available) in a semimicrocell in which the sample compartment had a path length of 1.00 cm. but a width of only 0.30 cm.[9] For complexes having specific rates of reduction of less than 5 l. mole^{-1} sec.$^{-1}$, samples weighing 10–20 mg. (3–8 mg. with the semimicrocell) were used. Co(III) concentrations were 0.007–0.014 *M* in the 1-cm. cells and 0.0007–0.0014 *M* in the 10-cm. cell; with either path length, initial optical densities were 0.6–1.2 units. Rates were run under pseudo-first-order conditions with the ratio Cr(II)/Co(III) between 5 and 25 for the 1-cm. cells and between 10 and 250 for the 10-cm. cell. For complexes having rate constants between 5 and 70, samples weighing about 2 mg. were used in the 10-cm. cell, and a tenfold excess of 0.8 *M* Cr(II) solution was added using a graduated microsyringe (capacity 50 μl.); in such cases, the absorbancy changes fell in the range 0.04–0.15 optical density unit and were read using the 0–0.2 slide wire of the spectrophotometer. For complexes having rate constants greater than about 70, the complex (about 3 mg.) was held in excess, and very small volumes (2–3) of Cr^{2+} were added, again using the 0–0.2 slide wire to read absorbancy changes. Temperatures in the cell compartment, which was cooled with tap water, were reasonably constant (to better than 0.2°) during a single run, but fluctuated between 22 and 26° from day to day. Reactions were allowed to proceed for more than seven half-lives, and generally good pseudo-first-order plots were obtained. In those cases where successive runs with different Cr(II) concentrations were made, first-order dependence on Cr(II) was observed. For rate constants lying below 5, values obtained from several points in a single run agreed to better than 6%, whereas those obtained from different runs at the same temperature checked to within about 10%. The few values greater than 5 l. mole^{-1} sec.$^{-1}$ (obtained with the more dilute solutions) are less reliable; points within a run check to 10% and, between runs, to about 20%. For comparison, adjustment of rate constants to 25° (Chart I) was made by assuming an enthalpy of activation of 6 kcal. mole^{-1}, corresponding to a 4% increase per degree rise in temperature near 300°K. This procedure, admittedly approximate, is open to particular criticism when applied to both terms of a (H^+)-dependent reaction. However, this adjustment never exceeded 12% and was often much less than this; an error of as much as 40% in the assumed enthalpy of activation therefore introduces an error of less than 5% in the rate constant.

Stoichiometry Experiments. 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.[2b] Intense green colors formed immediately when pyrazinecarboxylic and pyrazinedicarboxylic acids were treated with Cr^{2+}, but unlike the blues and purples formed on reduction of acids in the pyridine series,[2b] these colors could be discharged by subsequent treatment with Co(III). Indeed, the pigment formed from pyrazine-2,3-dicarboxylic acid appeared to reduce $Co(NH_3)_5Cl^{2+}$ quantitatively, for the Co(II) found was equivalent to the Cr(II) originally added (see Table IV).

Spectra of the Products. Spectra of solutions resulting from a number of the reductions were taken, and the spectra of the chromium(III) products were obtained by subtraction of the absorbancies of Co^{2+} and Cr^{2+}. In cases where it was evident that the chromium(III) product reacted with excess Cr^{2+}, spectra were taken on solutions to which equivalent quantities of Cr^{2+} and the Co(III) complex had been added. These spectra, presented in Table II, confirmed formation of a carboxylatochromium(III) product (rather than the aquo complex) in each of the faster reductions except that of the *p*-formylbenzoato derivative and suggested chelation in the products from the gluconato, the pyridine-2,4-dicarboxylato, and the carboxylato derivatives of pyrazole and pyrazine. The spectra of the products from the uracil and cinnoline derivatives were unlike any other encountered thus far in this study; the one maximum reported for each is a very broad and flat shoulder to a much higher peak or peaks in the ultraviolet.

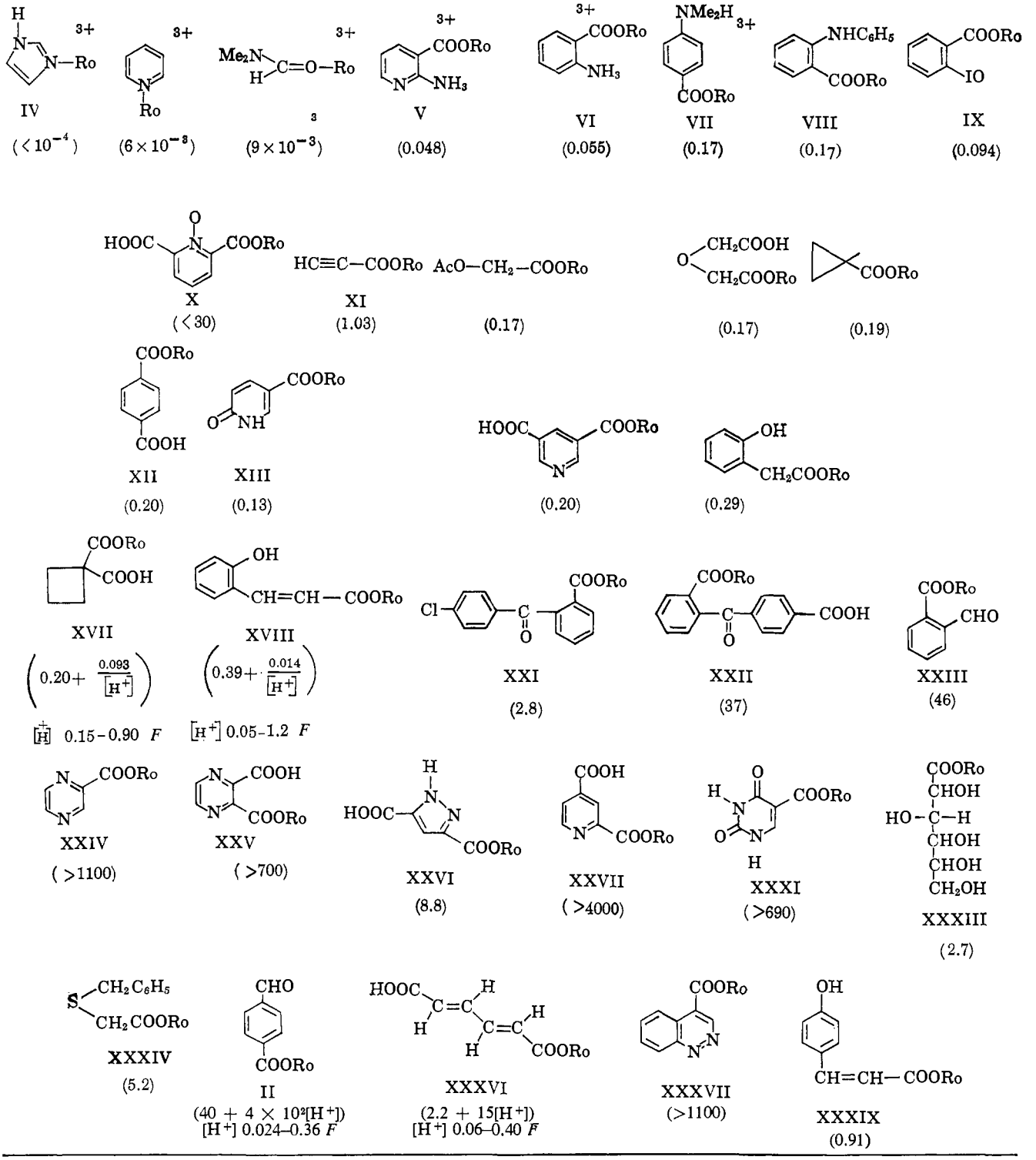
Table II. Absorbancies of Cr(III) Products Obtained from Chromous Reduction of Carboxylatopentaamminecobalt(III) Complexes

Ligand	λ_{max}, mμ	ϵ_1	λ_{max}, mμ	ϵ_2
o-Formylbenzoato	410	24.1	573	21.5
Acetylenecarboxylato	400	30.0	565	32.0
o-Hydroxycinnamato			570	35.4
Benzophenone-2,4′-dicarboxylato	410	35.5	570	29.0
S-Benzylthioglycolato	410	28.4	570	27.4
Butadienedicarboxylato	410	26.1	588	17.3
Gluconato	410	54	550	40
Pyrazole-2,5-dicarboxylato	400	76.0	540	49.8
Pyrazinecarboxylato	375	57	527	33.5
Pyrazine-2,3-dicarboxylato			530	50
Pyridine-2,4-dicarboxylato	410	42.0	527	46.5
Uracil-5-carboxylato			480[a]	54
Cinnoline-4-carboxylato			535[a]	44.3

[a] Broad shoulder.

(9) With practice, the open end of a 1.00-cm. square cell may be sealed with a flexible rubber serum cap (outside diameter of larger end, 11 mm.). The semimicrocell may be similarly sealed if the smaller end of the serum cap is cut off flush to the membrane. Semimicrocells were obtained from Pyrocell Manufacturing Co., Westwood, N. J.

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



[a] Rates in l. mole^{-1} sec.$^{-1}$ at 25° and μ = 1.5 are shown in parentheses. Ro = "roseo" = $(NH_3)_5Co$. Each of the complexes, except those indicated as 3+, has a net charge of 2+.

In several of the fast reactions, there was spectral evidence for at least one intermediate species. When the *p*-formylbenzoato complex is reduced with an equimolar quantity of Cr(II) in 1 *M* $HClO_4$, the absorbance at 502 mμ drops as expected, but the initial product appears to have a maximum at 520 mμ ($\epsilon \sim 21$) rather than 571 mμ. A second peak (near 405 mμ) with an absorbance nearly the same as that of the first is also present, but as additional increments of Cr(II) are added, the absorbance at 405 mμ increases markedly while the absorbance of the peak at longer wave length suffers little change (although its position gradually shifts to 550 mμ). After a 40% excess of Cr(II) has been added, the ratio of peak heights is approximately 3:2. If the reaction mixture obtained from mixing equimolar quantities of the reactants is extracted con-

tinuously with ether, the free parent acid has been found to be transferred quantitatively into the ether phase.[10] However, extraction of the parent acid from a reaction mixture obtained by reduction with excess Cr(II) appears to be much less complete.

Very similar behavior was noted in reduction of the pyridine-2,4-dicarboxylato complex: the high wave length peak shifted from 525 to 541 mμ upon addition of a 40% excess of Cr^{2+}, and the ratio of peak heights increased from 0.90 to 1.25. Here, however, the product appears to be the chelated carboxylatochromium(III) complex. When the pyrazinecarboxylato complex is treated in 1.2 *F* acid with an equimolar quantity of Cr^{2+}, a deep green pigment is formed very rapidly, due probably to a local excess of Cr(II); the green fades and yields a rust-colored precipitate which, in turn, dissolves with shaking, yielding the purple Cr(III) product reported. Similar intensely colored intermediates (but no precipitates) were observed in reduction of the pyrazinedicarboxylato, uracil-5-carboxylato, and cinnoline-4-carboxylato complexes.

The reactions of these intermediates appear to be considerably slower than the disappearance of the 502-mμ absorbance, but their intervention leads to difficulty in the rate studies by causing slight but noticeable drifts in the "infinity readings." Thus, for the *p*-formylbenzoato complex, apparent rate constants derived from experimental points late in the reaction were about 20% lower than those from points early in the reaction. The drifts are of less consequence for the cinnoline, uracil, pyrazine, and 2,4-pyridinedicarboxylato complexes, for which only lower limits are recorded.

Results and Discussion

The specific rates for reduction of pentaamminecobalt(III) complexes with Cr^{2+} (adjusted to 25° and $\mu = 1.5$) are summarized in Chart I. These values cover a range of over seven powers of ten. The low rates (less than 10^{-2}) for the first three complexes in the table, each noncarboxylated, stand apart from the others, with the very low upper limit for the imidazole complex (IV) particularly surprising in view of the apparent structural similarity between the —N—C=N— sequence in imidazole and the —O—C=O sequence in carboxylate.[11] The reduction of the pyridine complex[11b] yields $Cr(H_2O)_6^{3+}$, pointing to reduction *via* an "outer-sphere" activated complex, as in the reduction of the hexaamminecobalt(III) complex.[12] The outer-sphere mechanism may be assumed to operate also in the much slower reduction of the imidazole complex, but the mechanism of reduction of the DMF complex is, at present, in doubt.

o-Aminocarboxylates. Nonchelation through Nitrogen. The *o*-aminobenzoato (VI) and 2-aminonicotinato (V) complexes are listed as the protonated "pink" tripositive forms, which greatly predominate at the acidities studied. The reduction rates are about half of those which are observed for the usual substituted benzoato and pyridinecarboxylato complexes in the absence of both chelation and remote attack. It is suggested that the NH_3^+ group shields COORo on one side against attack by the positive chromous ion, and, further, that the retardation is mainly electrostatic in origin rather than steric. The iodo, phenoxy, and 2-cresoxy groups, which are bulkier but uncharged, have been found to be less effective retarders than NH_3^+ when situated *ortho* to COORo.[2b] Location is important, for the positive center in the *p*-dimethylamino complex VII and in the N-methylated pyridinecarboxylato complexes[2b] have little or no effect on rate of reduction, presumably because the positive center lies well out of the path of the attacking cation.

Interestingly, for the *o*-amino complexes, within the limits of experimental error, the rate was found to be independent of acidity in the range 0.2–1.2 *M* H^+. The situation here contrasts with that observed for five different *o*-hydroxybenzoato complexes, each of which is reduced with a rate law having a term inversely proportional to $[H^+]$.[2b] If such a term is taken as an indication of chelation in the transition state it must follow that chelation has, in effect, vanished in going from the *o*-hydroxy to the *o*-amino series. A rough upper limit for the rate constant associated with reduction of the nonprotonated form of *o*-aminobenzoato complex may be calculated by assuming that the inverse acid path might not be detected if it constituted less than 5% of the total reduction, and further assuming the pK_{BH^+} value for the complex to be about 3.5 (*i.e.*, 1 p*K* unit less than the pyridinecarboxylato complexes). The resulting value is about 10 l. $mole^{-1}$ $sec.^{-1}$, a far cry from the range of 10^5–10^9 calculated from data for the *o*-hydroxy derivatives. Moreover, the specific rate, admittedly approximate, for the N-phenylanthranilato complex VIII indicates that an upper limit of 10 is probably too high. Complex VIII, in which an amino nitrogen lies *ortho* to COORo, exists predominantly in the "orange" nonprotonated form at pH 0.7; yet its rate constant is seen to be only 0.17, virtually identical with that for the *o*-phenoxybenzoato complex.[2b]

This difference between the *o*-hydroxy series and the *o*-amino series is too striking to be ascribed merely to a difference in charge, especially since pyridine-2-carboxylato complexes, which have the same charge as the *o*-amino derivatives, are reduced rapidly.[13] It is rather more reasonable to infer that the *ortho* O^- substituent is enhancing the rate of reduction in large part by allowing electron transfer through phenolic oxygen, whereas electron transfer through amino nitrogen, as through imidazole nitrogen, may occur only with great difficulty.

Preferential Reduction of the Ligand. Stoichiometry studies involving twelve complexes are reported in Table III. Two of these, the *o*-iodoso derivative IX

(10) Such extraction has been reported by Fraser[3b] and by D. LaFollette (M.S. Thesis, Stanford University, 1964) and has been confirmed in these laboratories.

(11) (a) These low rates may be compared with the rates of chromous reduction of the carbamato (9.1 + 107[H^+] l. $mole^{-1}$ $sec.^{-1}$) and N-coordinated urethan (160 l. $mole^{-1}$ $sec.^{-1}$) pentaamminecobalt(III) derivatives reported by R. T. M. Fraser (*Inorg. Chem.*, 3, 1561 (1964)), who finds that substitution of nitrogen for oxygen in a coordinated carboxylato may greatly enhance its effectiveness as a bridge for electron transfer. Thus, the effects of such a substitution may be subtle, and more nitrogen-coordinated complexes should be examined before the relationships become clear. (b) This reduction of the pyridine complex has been studied in greater detail by F. Nordmeyer and A. M. Sargeson (unpublished experiments, Stanford University, 1964), who record the slightly lower rate constant 0.004 l. $mole^{-1}$ $sec.^{-1}$ at 25° and $\mu = 1$.

(12) See, for example, A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, 83, 793 (1961).

(13) E. S. Gould and H. Taube, *ibid.*, 85, 3706 (1963).

and the pyridine N-oxide complex X, both of them with easily reducible ligands, stand out as examples in which the ligand takes up reducing electrons from Cr^{2+} and is itself reduced, transmitting none, or nearly none, to coordinated Co(III). Their behavior thus resembles that reported for the *p*-nitrobenzoato complex.[2b] Significantly, the rate constant for reduction of the *o*-iodoso complex is the same as that reported for the *o*-iodo derivative[2a,b] strongly indicating that, in the presence of excess Cr(II), the reduction of the iodoso complex to the iodo is merely a fast step preceding the rate-determining reduction of Co(III) in the *o*-iodo derivative. A similar picture may apply in the reduction of complex X, derived from the N-oxide of 2,6-pyridinedicarboxylic acid; both this complex and that derived from 2,6-pyridinedicarboxylic acid itself[2b] give an intense royal blue color, observed for no other members of the series, when reduced with Cr^{2+}. However, both reductions are so rapid that only upper limits have been determined in each case.[14]

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

Ligand	Yield of Co(II), %
Aquo	1.0
o-Hydroxycinnamato	1.0
p-Hydroxycinnamato	1.0
Pyrazinecarboxylato	1.0
Cinnoline-4-carboxylato	1.0
Benzophenone-2,4′-carboxylato	1.0
o-Formylbenzoato	1.0
Pyrazine-2,3-dicarboxylato	0.90
Acetylenecarboxylato	0.87
S-Benzylthioglycolato	0.94
Pyridine-2,6-dicarboxylato N-oxide	<0.14
o-Iodosobenzoato	0.11

[a] $[H^+] = 1.2F$; $[Co(III)]/[Cr(II)] = 1.8 \pm 0.2$.

Some ligand reduction appeared to occur with the propiolato (acetylenecarboxylato) complex XI; and the parent acid itself was found to be readily reducible (Table IV). Since reduction of cobalt(III) occurs in preference to irreversible reduction of the ligand (the selectivity being 87/13), ligand reduction cannot be a necessary antecedant to Co(III) reduction, although the two reactions may proceed through a common intermediate. On the other hand it is also possible that the two reductions are independent, as seems to be the case with the levulinato complex[2b]; finally, ligand reduction could occur after the organic group has been transferred to chromium. No rigorous basis for a choice as yet exists in this case.

Nonreducible Ligands. Adjacent Attack in Reduction of the Terephthalato Complex. Twelve of the complexes listed in Chart I are reduced with specific rates between 0.08 and 0.50 l. mole^{-1} sec.$^{-1}$, the range considered to be characteristic of the usual mode of reduction *via* adjacent attack at 25°. The most noteworthy of these is the terephthalato derivative XII, which, as the purified perchlorate, is reduced at very nearly the same rate as

(14) The upper limit for reduction of the pyridine-2,6-dicarboxylato complex (150 l. mole^{-1} sec.$^{-1}$, ref. 2b) differs from that given for the N-oxide complex simply because different Cr(II) concentrations were used in the two reductions. Both complexes are over 95% reduced in less than 5 sec.

Table IV. Reduction of Carboxylic Acids with Chromium(II)[a]

Acid	$[H^+]$, F	Reducing agent consumed, %	Color produced
Anthranilic	1.2	0	
o-Hydroxycinnamic	0.6	6	
p-Hydroxycinnamic	0.6	0	
Benzophenone-2,4′-dicarboxylic	0.6	0	
S-Benzylthioglycolic	1.2	0	
Uracil-5-carboxylic	1.2	0	Pale green
Pyrazine-2,3-dicarboxylic	1.2	0	Dark green
Pyrazole-2,5-dicarboxylic	0.6	0	
o-Formylbenzoic	0.6	4	
p-Formylbenzoic	0.6	6	
Butadiene-1,4-dicarboxylic	0.6	26	
Pyrazinecarboxylic	1.2	60	Dark green
Acetylenedicarboxylic	1.2	73	Yellow-brown
Pyridine-2,6-dicarboxylic N-oxide	1.2	>80	Deep blue
o-Iodosobenzoic	0.6	82	
Pyridine-2,4-dicarboxylic	1.2	>94	Purple

[a] 15 min.; 25°; concentration of organic acid, 3.0 g./l.; $[Cr(II)] = 0.01$ *M*.

are a number of *para*-substituted benzoato complexes, among them the *p*-methoxy, the *p*-carbomethoxy, and the *p*-dimethylamino derivatives. The acid-independent and presumably "normal" specific rate of 0.20 observed here for the terephthalato complex differs by over two orders of magnitude from the literature value[4] (36 + 9[H$^+$] l. mole^{-1} sec.$^{-1}$ at 16.6°), a value obtained, however, from measurements on a minor and incompletely identified component in a reaction mixture. The newer value,[15] even if an unusually large experimental error is assumed, effectively rules out appreciable contribution by remote attack in the reduction of this complex, just as the virtually identical rate constant (0.20) for reduction of the methylterephthalato complex[2b] rules out remote attack in that case also.[16] It is perhaps significant that the remaining well-authenticated examples of remote attack appear to be confined to (a) systems such as fumarato[17] and 4-carboxylatopyridine,[2b] which are themselves reduced by Cr^{2+}; and (b) systems having a reducible functional group, most notably carbonyl, in conjugation with the bound carboxylate.[18]

(15) The specific rate reported here for the terephthalato complex is in reasonable agreement with the value of 0.23, subsequently obtained by F. Nordmeyer and H. Taube from a sample independently prepared by treatment of the DMF complex with terephthalic acid.

(16) In the past, ester hydrolysis during reduction of the *p*-COOMe complex[3b] and the methyl fumarato complex[4] has been cited as evidence in support of remote attack. Unpublished experiments by Gould and Taube (Stanford University, 1963) indicate that the *p*-COOMe complex is reduced by vanadium(II) without ester hydrolysis. The relationship between hydrolysis and remote attack is, at present, not clear. More recently, J. Hurst and H. Taube (Stanford University, 1964) find that the ester linkage is also preserved during the chromous reduction of the methyl fumarato complex, although the rate law for this reduction exhibits a large first-order acid term, generally taken as a strong indication of remote attack.

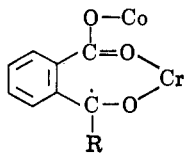
(17) Studies of reductions of fumarato systems with Cr(II) are being currently carried but by D. Katakis, Nuclear Research Center, Greek Atomic Energy Commission, Athens.

(18) The new data on the terephthalato complex, taken as a strong indication of reduction *via* adjacent attack, necessitate revision of a number of conclusions drawn in the preceding paper in this series.[2b] For example, it no longer may be stated that the slow reduction of a sulfur-bridged complex such as XIV indicates that the sulfur atom does not easily transmit a reducing electron from one conjugated system to another, since it is extremely likely that the 4,4′-dicarboxylatobiphenyl derivative (with the sulfur deleted) would, despite conjugation, likewise be reduced slowly. Moreover, the rapidly reduced complex of 2,5-

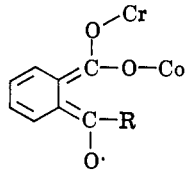
Among the remaining complexes reduced with rate constants less than 0.5, the cyclobutanedicarboxylato derivative XVII displays an inverse acid term. Here, a path involving the deprotonated form, and proceeding through a chelated activated complex, is reasonable, for a strain-free model (discounting the internal strain associated with the cyclobutane ring) may be assembled. If pK_A for this complex is assumed to be approximately 3.4, the specific rate for reduction of the deprotonated form is calculated to be about 200, comparable to the corresponding term in the reduction of the dimethylmalonato complex.[19]

The smaller inverse acid term in the rate law for reduction of the *o*-hydroxycinnamato complex XVIII is much more surprising. If the p*K* value for this complex is taken as about 9, in common with other phenolic pentaamminecobalt(III) complexes,[2b] this term (unless it is an artifact) corresponds to a specific rate, for the deprotonated form, of about 10^7. Nevertheless, it apparently cannot be rationalized convincingly on the basis of any combination of the effects that have thus far been defined.[20]

Chelation in the Transition State. Carbonyl Derivatives. The increased rate of reduction when a carbonyl group is incorporated *ortho* to COORo in the benzoato complex[2b] has been taken as evidence for a chelated activated complex XIX, in which electron transport takes place, at least in part, through the carbonyl oxygen. However, the resulting carboxylatochromium(III) product is not chelated, and the enhanced rate may, alternatively, be attributed to stabilization of a radical-cation intermediate XX (and the transition state leading to it) by the carbonyl group. This ambiguity of interpretation applies also to the



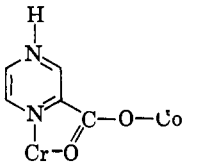
XIX



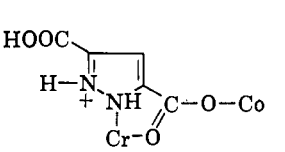
XX

reduction of the chlorine-substituted *o*-benzoyl complex XXI, the 2,4′-benzophenonedicarboxylato complex XXII, and the *o*-formylbenzoato complex XXIII in the present series. For each of these, the specific rate is well above the range observed for reduction of the usual benzoato complexes, and none exhibits a first-order hydrogen ion term in the rate law.[21] Note that the specific rates for reduction of complexes XXII and XXIII are comparable to the acid-independent term in the rate law for reduction of the *p*-formylbenzoato derivative II and some 30 times as great as the specific rates for reductions of the N-methylated pyridine-4-carboxylato complex III and its N-protonated analog (1.3 and 1.4 l. mole^{-1} sec.$^{-1}$ at μ = 3.0).[2b] This is of interest because reduction of the *p*-formyl derivative almost certainly proceeds *via* electron transfer through the carbonyl group, whereas with the pyridine-4-carboxylato derivatives, the rate enhancement must be rationalized on a different basis and has been attributed to stabilization of the radical-cation intermediate. The rate data for the *ortho*-carbonyl complexes thus favor, to a degree, the picture of reduction *via* transient chelation and electron transfer through carbonyl (*i.e.*, XIX, rather than XX). A third possibility, remote attack without chelation, followed by rapid formation of the carboxylatochromium(III) product, is much less likely. Such a path, in analogy to all other reductions thought to proceed through remote attack at a carbonyl or carboxyl group, should feature a rate law having a term first order in H^+, contrary to observation.

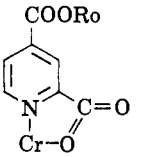
Chelation in the Reduction of Heterocyclic Derivatives. The high absorbancies of the solutions resulting from reduction of complexes XXIV–XXVII indicate chelation in the Cr(III) products. These reductions are unusually rapid; except for the pyrazole complex XXVI, only lower limits to *k* have been determined. Thus, it is likely that chelation occurs in the transition states and persists in the products. The same type of planar chelated activated complex proposed in the reduction of the pyridine-2-carboxylato complex[2b] should apply also to reduction of the pyrazinecarboxylato derivative XXVIII, with electron transfer through the Cr–N bond again a strong possibility.



XXVIII



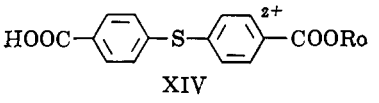
XXIX



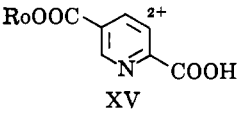
XXX

In contrast to the pyrazine complex, the rate of reduction of the pyridine-2-carboxylato complex in strong acid is easily measurable, not necessarily because its specific rate is much less, but rather because the complex (pK_A = 4.5) exists, under the conditions used in the reductions, principally as the N-protonated

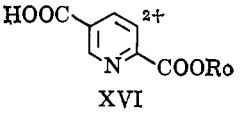
pyridinedicarboxylic acid, assumed to have structure XV and to react *via* remote attack, more probably has structure XVI and is reduced rapidly because of chelation in the transition state.



XIV



XV



XVI

(19) R. Butler, Ph.D. Thesis, Stanford University, 1964.

(20) The specific rate of 10^7 is similar to those observed with a number of *ortho*-hydroxylated benzoato complexes for which a planar chelated transition state in the deprotonated path has been suggested. An activated complex of this type cannot be seriously considered here. If the complex, like the parent acid, is in the *trans* form, it cannot form a chelate at all. If isomerization to *cis* has somehow occurred during preparation or isolation (and this is unlikely), a chelated transition state, necessarily featuring an eight-membered ring would, as shown by molecular models, be highly strained and seriously puckered. Under such circumstances, rate enhancement might be expected but should be much less pronounced.

(21) The absence of a hydrogen ion term in the rate law for the reduction of the complex of benzophenone-2,4′-dicarboxylic acid suggests that the $Co(NH_3)_5$ group is bound to the 2-carboxyl (XXII), rather than to the 4′-carboxyl. If the 4′-carboxyl were coordinated, reduction *via* remote attack, in the manner observed for the *p*-formyl and *p*-benzoyl derivatives, proceeding at an acid-dependent rate, would be expected. The formation of a carboxylatochromium(III) product, rather than $Cr(H_2O)_6^{3+}$ (Table II), in the reduction of this complex with excess Cr(II) does not appear to carry any simple structural implication in view of the evidence that the product initially formed by reduction of the *p*-formylbenzoato complex (see Experimental Section) is converted to another species in the presence of excess Cr(II).

form, in which the nitrogen can participate in neither chelation nor electron transfer.

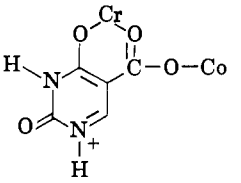
The doubly N-protonated forms of complexes XXIV, XXV, and XXVI would be expected to be even stronger acids than the singly N-protonated forms of the pyridinedicarboxylato complexes which, under conditions akin to those used in the reductions, have been found to be immeasurably strong.[2b] This means that at the highest acidities used in the present study (1.2 *F*), a major fraction of each of these complexes exists in a form having the COORo group lying "α" to a nonprotonated nitrogen atom, *i.e.*, in a favorable position for reduction *via* chelation.[22]

Reduction of the pyrazoledicarboxylato complex XXVI may be compared with that of the pyrrole-2-carboxylato complex. The nonprotonated form of the latter is reduced with a specific rate of 2.6,[2b] but in acid solution, the protonated form greatly predominates, and the basic (presumably chelated) path, although kinetically detectable, constitutes only a minor fraction of the over-all reduction. On the other hand, monoprotonation of the pyrazole complex should not interfere with reduction *via* chelation (XXIX), and the predominant product in reduction of the pyrazole derivative should be chelated, in contrast to that obtained from the pyrrole complex. The observed absorbancies confirm this.

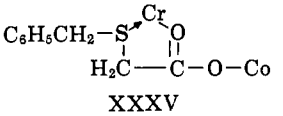
Despite chelation, the rate constant for reduction of the pyrazoledicarboxylato complex is less, by several powers of ten, than those for a number of the six-ring heterocyclic complexes. At least three structural features may be thought to contribute to this difference in rates: (a) there is, as may be shown by assembling molecular models, considerably more angular strain in a system having a five-membered chelate ring fused to a five-heterocyclic ring than in a five to six fused system; (b) the positive chromous ion must approach the N–N linkage of the pyrazole ring, a region which, in acid solution, bears an extra positive charge; and (c) because of the tetrahedral configuration of the bonds about the chelate nitrogen, the Cr–N bond must lie out of the plane of the ring. As with the basic path for reduction of the pyrrolecarboxylato complex, the rate of reduction of the pyrazole derivative is comparable to values for a number of complexes derived from chelating aliphatic ligands.[19]

The complex derived from pyridine-2,4-dicarboxylic acid is indicated in Chart I with cobalt bound to the 2-carboxyl (XXVII), in analogy to structure XVI proposed for the 2,5-dicarboxylato complex.[18] If this assignment be correct, the observed very fast reduction of the 2,4 compound may be classed mechanistically with those of the 2-carboxylato and the 2,5-dicarboxylato derivatives in the pyridine series[2b] and pyrazine derivatives XXIV and XXV.[23]

In the product resulting from reduction of the uracil-5-carboxylato complex XXXI, the characteristic Cr(III) absorption peaks are very nearly obscured by absorption "tailing off" from the maxima in the ultraviolet; hence, the spectrum indicates neither the presence nor the absence of chelation. However, the very high specific rate may be taken as evidence for intervention of a chelated activated complex featuring a nearly planar six-membered ring (XXXII).



XXXII



XXXV

Oxygen and Sulfur Chelation in Aliphatic Ligands. The effects of hydroxy and alkoxy groups on the reduction of aliphatic carboxylatopentaamminecobalt(III) complexes have been examined by Butler and Taube,[19] who find that incorporation of an α-hydroxy group (as in glycolate, lactate, or benzilate) enhances reduction rates by one to two powers of ten. This is almost certainly a chelation effect, and in one case the initial formation of a chelated product, which subsequently opens to a (more stable) open-chain species, has been demonstrated. With an α-alkoxy or -phenoxy group, however, this accelerating action virtually disappears, and rates return almost to "normal" (*i.e.*, 0.1–0.5 l. mole^{-1} sec.$^{-1}$ at 25°), presumably because effective chelation requires the strong O–H dipole. Accordingly, in the present series, the specific rate for reduction of the highly hydroxylated gluconato complex XXXIII (virtually identical with that for the glycolato complex) occasions no surprise, nor do the "normal values" (both 0.17) for the acetoxyacetato and the oxydiacetato complexes, which have α oxygen atoms which are only weakly coordinating. Moreover, the high absorbance of the gluconato product(s) (Table II) is consistent with chelate formation.[24]

On the other hand, the reduction of the S-benzylthioglycolato complex XXXIV is remarkably rapid. The observed (acid-independent) specific rate (5.2) is perhaps the most astonishing value in the present series, for in this complex, both remote attack and conjugative stabilization of a radical-cation intermediate are ruled out, and the ligand is not reduced by Cr^{2+} under the conditions used (Table IV). The least unsatisfactory rationalization of this rate enhancement is

(22) It is suggested that the preferred position for protonation in pyrazine derivatives XXIV and XV and in the pyrazole derivative XXVI is the nitrogen atom at the greater distance from the positive cobalt center, thus leaving the nearer nitrogen free for coordination to chromium. However, the rationalization of the high rates of reduction for these complexes at high acidities does not require this. All that is necessary is that a substantial fraction of the monoprotonated form of these complexes be protonated in this way and that this fraction be independent of acidity in the range studied. Under such circumstances, the mobile equilibrium between tautomers ensures rapidity of reaction.

(23) In the less likely, but more interesting, circumstance that coordination has occurred at the 4-carboxyl, the observed reduction may be likened to that of the nonprotonated form of the pyridine-4-carboxylato complex, for which remote attack through the ring nitrogen has been suggested[18]; but there would be two significant differences. The 2,4-dicarboxylato complex, like the 2,5 and the 2,6 complexes, but unlike the 4-carboxylato, would be expected to be an immeasurably weak base in dilute aqueous solution (Table V, ref. 2b); hence, at the acidities used, practically none should be in the protonated (less active) form, and reduction rate should not be a function of pH. Secondly, the N–Cr species, which in the reduction of the 4-carboxylato complex could not be detected, appears to be the final product from the 2,4-dicarboxylato derivative, having been trapped by chelation, which, by this interpretation, originated in the activated complex (*i.e.*, XXX). Such a reduction would then provide us with a (first) chemical proof of the occurrence of remote attack through the pyridine ring.

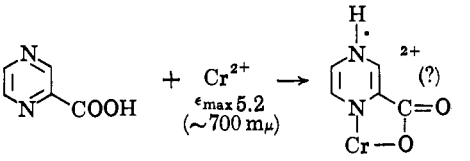
(24) Of the five hydroxy groups in the gluconato complex, only the α-, β-, and γ-hydroxyls are likely to become involved in a chelated transition state (which would then have, a five-, six-, or seven-ring, respectively). The present evidence does not permit a choice between the various alternatives; very probably, all three chelates are present in the product.

in terms of chelation in the activated complex (*e.g.*, XXXV); yet, there is no indication that the Cr(III) product is chelated, and, more important, chelation involving an alkylmercapto group would not be expected in a situation where chelation involving alkoxide is negligible.[25] Although a few instances are known in which alkylmercapto complexes of first-row transition metals are more stable than the corresponding alkoxide complexes,[26] additional sulfur-containing complexes in the $(NH_3)_5Co^{III}$ series should be examined before this effect is considered to be general.

Remote Attack. In reduction of the complexes in Chart I, evidence for remote attack is strongest for the *p*-formylbenzoato (II), the butadienedicarboxylato (XXXVI), and the cinnoline-4-carboxylato (XXXVII) derivatives. A different functional group is presumed to be involved in each case, the aldehyde group in II, the uncoordinated carboxylate in XXXVI, and the 1-nitrogen atom in XXXVII. The rate laws for the formylbenzoato[27] and butadiene[28] derivatives include a very substantial term first order in H^+, whereas the cinnoline complex is reduced immeasurably rapidly at the lowest acidity studied. With none of these is chelation possible.

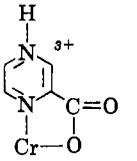
This triad emphasizes once again the interdependence between the reducibility of a ligand and its ability to support remote attack. Cinnoline derivatives are reduced with ease,[29] and both the *p*-formyl and the butadiene parent acids have been found to be partially reduced by dilute Cr^{2+} in acid solution (Table IV). The relationship between remote attack in the complex and reduction of the unbound ligand is obviously not a simple quantitative one, for such ligands as *p*-formylbenzoato, which support remote attack most effectively, are reduced relatively slowly (although detectably) in their uncomplexed forms. Neither is such a relationship a reciprocal one, for, as has been shown, there are reducible ligands which, when complexed, do not support remote attack. Nevertheless, the (unidirectional) qualitative correlation appears to be sufficiently general so that any indication of remote attack in the reduction of a pentaamminecobalt(III) complex derived from a nonreducible carboxylato ligand should be examined with care.[30]

Radical-Cation Intermediates in Adjacent Attack. The rapid formation of intensely absorbing green pigments when unbound pyrazinecarboxylic and dicarboxylic acids are reduced with Cr^{2+}, the immediate bleaching of such pigments with $Cl(NH_3)_5Co^{2+}$, and the more gradual bleaching with oxygen suggest that the pyrazine ring system has been reduced to a radical, perhaps bound to Cr(III) as a radical cation



XXXVIII

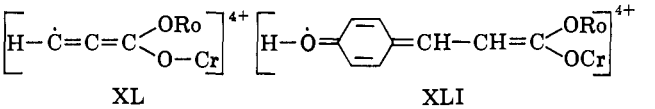
$\epsilon_{max} > 900$ (648 mμ)



ϵ_{max} 34 (527 mμ)

(*e.g.*, XXXVIII), and adds credence to the notion that, in favorable cases, chromous reduction of carboxylatocobalt(III) complexes may likewise proceed through a radical-cation intermediate. Stabilization of such an intermediate should, in principle, expedite reduction, but with the pyrazine derivatives in this study, this effect would be expected to be overshadowed by the very large rate enhancements due to chelation and (perhaps) to the occurrence of remote attack. When chelation and remote attack are ruled out, as in the reduction of the N-methylpyridine derivative III, the more modest acceleration, thought to be due to stabilization of the transition state leading to the radical-ion intermediate, may be noted.

Two complexes in the present group, both reduced at rates comparable to that of complex III and its N-protonated analog, may fall into this category. Both the acetylenecarboxylato (XI) and *p*-hydroxycinnamato (XXXIX) are α,β-unsaturated, and, for each, a conjugatively stabilized radical-cation intermediate (XL and XLI) may be envisaged. Nevertheless, it is



XL XLI

recognized that the evidence for such intermediates is decidedly weaker than for those derived from members of the pyridine- and pyrazinecarboxylato series. Uncharitably viewed, the suggested radicals XL and XLI represent pictorial support of what appears to be the least unsatisfactory rationalization of reduction rates somewhat greater than "normal." But there remains an uneasy feeling that, despite the large number of aromatic derivatives that have been studied, boundaries between "normal" and "abnormal" behavior among aliphatic and olefinic carboxylato complexes have not been satisfactorily established.

(25) A suggestion of the same trend appears to comparing the rates of reduction of the *o*-thiomethylbenzoato (0.38) and *o*-methoxybenzoato (0.28) complexes.[2b] Here, however, the difference is so small that structural rationalization is risky.

(26) See, for example, K. Baker and G. W. A. Fowles, *Proc. Chem. Soc.*, 362 (1964), for examples of such a trend among Ti(IV) complexes. D. B. Copley, F. Fairbrother, and A. Thompson, *J. Chem. Soc.*, 315 (1964), report a similar trend in complexes of Nb(V).

(27) An approximate value, $30 + 5 \times 10[H^+]$, has been reported for the specific rate of reduction of the *p*-formylbenzoato complex at 0°, but the value reported here appears to be the first for reaction at or near room temperature. Note that the coefficient for the hydrogen ion term at 0° is 50, rather than 540, as erroneously recorded.

(28) For a more detailed study of the reduction of the butadienedicarboxylato (muconato) complex, see D. K. Sebera and F. Nordmeyer, *Inorg. Chem.*, in press.

(29) See, for example, P. W. Neber, G. Knoller, K. Herbst, and A. Trissler, *Ann.*, **471**, 113 (1929).

(30) In the biphenyl series, for example, Fraser[3a] reports the biphenyl-4,4′-dicarboxylato complex to be reduced "immeasurably rapidly" and the 2,2′-dicarboxylato reduced with a rate law having a substantial first-order hydrogen ion term; both of these observations are taken as indications of remote attack. Measurements in these laboratories do not confirm the first-order acid term for the 2,2′ complex; in fact, the reduction of this complex may be retarded by increasing acidity (ref. 2b, Table IV). A number of attempts to prepare the 4,4′ complex were made, using both Fraser's procedure and the more severe DMF method here described, but in no case was there an indication that significant quantities of this complex were formed before decomposition of all Co(III) species in solution.

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A Study of the Reaction of Hydroxide Ion with $B_{20}H_{18}^{-2}$

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The reaction of aqueous hydroxide ion with $B_{20}H_{18}^{-2}$ produces $B_{20}H_{17}OH^{-4}$ (isomer i) which subsequently rearranges to a second $B_{20}H_{17}OH^{-4}$ (isomer ii). Both $B_{20}H_{17}OH^{-4}$ ions may be protonated to produce a $B_{20}H_{18}OH^{-3}$ ion. Structures were assigned on the basis of ^{11}B n.m.r. spectra. Oxidation of $B_{20}H_{18}OH^{-3}$ with a variety of oxidants produced $B_{20}H_{17}OH^{-2}$. The kinetics of the reaction of OH^- with $B_{20}H_{18}^{-2}$ was of the form rate $= k_1[B_{20}H_{18}^{-2}] + k_2[OH^-]\cdot[B_{20}H_{18}^{-2}]$. A mechanism is proposed for the hydroxide ion reaction.

Introduction

The preparation,[2,3] structure,[2,4] and reactions[2,3,5,6] of the $B_{20}H_{18}^{-2}$ ion have been the subject of considerable research. Among the reactions of $B_{20}H_{18}^{-2}$ is its facile reaction with hydroxide ion in aqueous media to produce the $B_{20}H_{17}OH^{-4}$ ion[5] which was first formulated[2] as $B_{10}H_9OH^{-2}$. Three recent, brief accounts[2,3,5] of that reaction have appeared, and it is the purpose of this paper to extend these discussions further.

Isomeric $B_{20}H_{17}OH^{-4}$ Ions. The reaction of the triethylammonium salt of $B_{20}H_{18}^{-2}$ with aqueous hydroxide ion consumed 4 equiv. of base and liberated 2 equiv. of triethylamine. The $B_{20}H_{17}OH^{-4}$ ion

$$4OH^- + B_{20}H_{18}^{-2} + 2(C_2H_5)_3\overset{+}{N}H \longrightarrow 3H_2O + 2(C_2H_5)_3N + B_{20}H_{17}OH^{-4}$$

(isomer i) formed in this reaction was quantitatively rearranged to an isomeric ion (isomer ii) when heated in aqueous solution or when treated with acid followed by the addition of excess base. A large-scale preparative method was devised for isomer ii which involved the slow reaction of $B_{20}H_{18}^{-2}$ with aqueous triethylamine solutions and subsequent rearrangement. Both isomers of $B_{20}H_{17}OH^{-4}$ consumed 1 equiv. of acid when subjected to potentiometric titration. The resulting $B_{20}H_{18}OH^{-3}$ ion was isolated as its cesium, tetramethylammonium, or triethylammonium salt. Neutralization of the cesium or tetramethylammonium salts with excess base produced isomer ii. Similar treatment of the triethylammonium salt gave isomer i. However, if the triethylammonium salt was heated for 30 min. in ethanol at the boiling point and then neutralized, isomer ii resulted. These results suggest that two isomeric $B_{20}H_{18}OH^{-3}$ ions are in equilibrium and represent intermediates in the rearrangement sequence. One of these $B_{20}H_{18}OH^{-3}$ isomers appears to separate selectively from aqueous solutions as the triethylammonium salt, and the other isomer separates as the cesium or tetramethylammonium salt. The latter isomer is apparently produced when the triethylammonium salt of the former isomer is heated in ethanol solution. The ^{11}B n.m.r. spectra of the cesium (or tetramethylammonium) salt and the isolated triethylammonium salt were virtually identical at 19.3 Mc./sec., and all salts displayed a B–H–B bridge absorption at 1800 cm.$^{-1}$ in the infrared. These results are in agreement with those of Chamberland and Muetterties.[3]

The direct conversion of $B_{20}H_{17}OH^{-4}$ isomer i to the isomer ii under equilibrium conditions proves that isomer ii is the thermodynamically more stable member of the isomer pair. The direct formation of isomer i from $B_{20}H_{18}^{-2}$ is therefore a result of kinetic control of the reaction products. The isomerization reaction observed in this system appears to be analogous to the isomerization reactions observed in the parent $B_{20}H_{18}^{-4}$ system.[6]

During the course of the chemical characterization of the $B_{20}H_{17}OH^{-4}$ and $B_{20}H_{18}OH^{-3}$ ions, $B_{20}H_{18}^{-2}$ was converted to $B_{20}H_{17}OCH_3^{-4}$ by reaction with methoxide ion in anhydrous methanol. These results and the facile oxidation of $B_{20}H_{17}OH^{-4}$ to $B_{20}H_{17}OH^{-2}$ are in agreement with the results of Chamberland and Muetterties.[3]

The ^{11}B N.m.r. Spectra of $B_{20}H_{17}OH^{-4}$ Isomers. The charge, empirical formula, and chemical behavior of the $B_{20}H_{17}OH^{-4}$ isomers identify them as hydroxy-substituted derivatives of the $B_{20}H_{18}^{-4}$ ions.[6] It has been shown[3,6] that the ^{11}B n.m.r. spectra of the $B_{20}H_{18}^{-4}$ ions can be readily interpreted if it is assumed that the resonances for the apical boron atoms of the B_{10} polyhedra occur at low field between -12 and $+6$ p.p.m. and that resonances for the equatorial boron atoms occur at high field near 28 p.p.m. It has also been shown that for equatorially substituted $B_{10}H_9OH^{-2}$ there is a shift to the low-field region for the equatorial atom attached to the hydroxyl group.[7] The ^{11}B

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(4) R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.*, 86, 3568 (1964).
(5) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, 85, 3704 (1963).
(6) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *ibid.*, 87, 1893 (1965).