self-quenching of metastable dye molecules, namely, D' + D → 2D, was comparable with induced decomposition of photoperoxide, step 13. In the case of chlorophyllin, however, concentration quenching of the metastable state is apparently unimportant (see above). Since about four molecules of oxidized PTD are involved in the formation of the observed product,[13] the highest observed over-all quantum yield, namely, 0.8, should be reduced by a factor of four. Hence $k_2/k_4 = 4$ or one out of every four molecules in the first excited singlet state is converted to the long-lived metastable species. From the observed oxygen dependence $k_5/k_{12} = 4.15 \times 10^{-3}$ mole l. If every encounter between D' and O_2 leads to a reaction, then $k_{12} = 6.6 \times 10^9$ sec. l. mole, so that the lifetime of the metastable species is $1/k_5 = 1.3 \times 10^{-5}$ sec., a value one-tenth that obtained with nitrobenzene quenching of the Krasnovsky reaction. Hence we

conclude that only one out of ten encounters between D' and O_2 leads to reaction. These calculated lifetimes demonstrate that oxygen reacts with the long-lived metastable species D' rather than with the first excited singlet species D*. Although oxygen quenched the fluorescence of chlorophyll,[33] this step does not appear to be of importance for chlorophyllin-sensitized photooxidation. The data for the chlorophyllin dependence shows that the induced decomposition, step 13, is 275 times more rapid than the oxidation of the substrate, step 15.

Binding of chlorophyllin *a* to PVP considerably enhances its photoreduction as shown in the photosensitized reduction of fast red S just as is the case for synthetic dyes.[15-17] For sensitized photooxidation the effect of binding is less pronounced because diffusion of oxygen to the excited molecule is retarded by the enveloping residues of the high polymer.[17]

Electron Transfer through Organic Structural Units.   Aromatic and Heterocyclic Carboxylates as Bridging Groups in Oxidation–Reduction Reactions

BY EDWIN S. GOULD[1] AND HENRY TAUBE

The specific rates of reduction of 49 carboxylatopentaamminecobalt(III) complexes (containing benzene, thiophene, furan, pyridine, and pyrrole rings) with Cr^{2+} have been measured and their dependence on (H$^-$) noted. The majority of these lie between 0.08 and 0.30 l. mole^{-1} sec.$^{-1}$, indicating the usual electron-transfer path through the coordinated carboxylato group with the formation of a carboxylatochromium(III) complex. A number of much higher values point to the operation of several special effects. The reduction of a complex having a carbonyl *para* to the carboxylato proceeds through remote attack on the carbonyl group, forming the parent carboxylic acid and $Cr^{II}H_2O l_6^{3+}$; the rates of such reductions exhibit a term first order in (H$^-$). If the carbonyl group lies *ortho* to the carboxylato, rates are again greater than normal, but the carboxylato group is bound to Cr(III) in the product, and the first-order acid term does not appear; acceleration here may be due to chelation and electron transfer through the carbonyl group, or, alternatively, may be attributed to conjugative stabilization of a radical-ion intermediate. Reduction of the complexes of dicarboxylic acids may proceed through the complex itself, (Ro-A-H)$^{2+}$, and through its conjugate base (Ro-A)$^-$. The conjugate bases are reduced with specific rates between 9 and 30. The basic path is observed only in those cases in which a strain-free model of a chelated transition state for reduction may be constructed, suggesting a chelated activated complex (although chelation does not appear to persist in the products). There is no evidence that a reducing electron may be transmitted through an –S– bridge in cases where such a bridge links conjugated carbon systems bearing carboxy groups. Rate laws for reduction of certain of the hydroxybenzoato complexes contain a term representing reduction of the conjugate base. This term appears only if the coordinated carboxyl is situated *ortho* to a hydroxy group. The specific rates for this path are very high (10^6–10^9) and suggest a transition state strongly stabilized by chelation; there is, however, no evidence for electron transfer through phenolic oxygen. Data on the pyridinecarboxylato complexes suggest that electron transfer through nitrogen occurs in reduction of the 4- and 2- (but not the 3-) carboxylato derivatives. The reductions of the 2-carboxy, the 2,6-dicarboxy, and the 2,5-dicarboxypyridine derivatives are fast, and deeply colored Cr(III) products, presumed to be chelates, are formed; but the reduction of the pyrrole-2-carboxylato derivative is much slower, and the predominant product appears to be nonchelated. In contrast to uncoordinated carbonyl-substituted benzoic acids, a number of the pyridinecarboxylato acids and their N-methyl derivatives are readily reduced by Cr^{2+} in the absence of Co(III). The general correlation between reducibility of the acid and reducibility of the Co(III) complex in this series suggests that, in some cases at least, reduction of the pyridinecarboxylato complexes may proceed through a radical-ion intermediate stabilized by conjugation. This description best applies to the surprisingly fast reduction of the protonated and N-methylated complexes of 4-pyridinecarboxylic acid.

Although the effects of ring substitution on the reductions of benzoatopentaamminecobalt(III) complexes have been investigated in some detail,[2] a number of potentially instructive substituents have not yet been

examined. Moreover, scant attention has been paid to heterocyclic carboxylato groups as "electron-transfer bridges" in such reactions. In the oxidation–reduction reactions comprising the present study, only one reducing agent, Cr^{2+}, has been used, but we have introduced considerable variation in the carboxylato group bound to tripositive cobalt. We have included, in addition to a number of new benzoato complexes, com-

(1) National Science Foundation Senior Postdoctoral Fellow, Stanford University, 1962-1963.

(2) (a) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, 2239, 2242 (1961); (b) R. T. M. Fraser, *ibid.*, **83**, 565 (1961); **84**, 3436 (1962); (c) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

plexes derived from furan-, thiophene-, pyrrole-, pyrrolidine-, and pyridinecarboxylic acids. The most interesting ligands in this series appear to be those having a carbonyl group or a pyridine ring, and those which may form a chelated chromium(III) product.

Experimental

Aquopentaamminecobalt(III) Perchlorate, $[Co(NH_3)_5H_2O]$-$(ClO_4)_3$.—This complex was prepared from carbonatopentaamminecobalt(III) nitrate, which was, in turn, prepared by air oxidation of a solution of $Co(NO_3)_2$, NH_3, and $(NH_4)_2CO_3$.[3] In our hands, preparation of the nitrate was capricious, for the product was often heavily contaminated with the carbonatotetraammine complex, coloring it maroon rather than the correct brick red. The best preparations were obtained when the air oxidation was very slow. The carbonato nitrate was converted to the aquo perchlorate by dissolving in hot water, then adding concentrated $HClO_4$ until effervescence ceased and further addition caused no further precipitation. An additional treatment with $HClO_4$ was needed to remove the last traces of nitrate from the brick red complex. The pure aquopentaammine complex, when heated with concentrated HCl, gives the purple precipitate, $[Co(NH_3)_5Cl]Cl_2$, and an almost colorless solution; a sample contaminated with the diaquotetraammine complex will yield a blue solution ($CoCl_4{}^{2-}$).

Additional Inorganic Materials.—Chloropentaamminecobalt(III) perchlorate was prepared from the corresponding chloride, $[Co(NH_3)_5Cl]Cl_2$, by dissolving the latter in hot $0.1\ M\ HClO_4$, adding one-third the volume of $60\%\ HClO_4$, then cooling. The desired perchlorate slowly crystallized and was filtered off, washed with ice water, and dried in air.

Chromous solutions were prepared by reducing a master solution of chromium(III) perchlorate, made up by adding the hexahydrate to $60\%\ HClO_4$, then diluting tenfold with boiled distilled water. The reduction was carried out under nitrogen with zinc amalgam, and the solution was stored over zinc amalgam in a serum-capped vessel. Samples were withdrawn with a volumetric syringe. The concentration of the solution was determined by adding a known volume to an excess of chloropentaamminecobalt(III) perchlorate solution under nitrogen, diluting tenfold with concentrated HCl, and reading the absorbance at $692\ m\mu$ ($\epsilon\ 560$) of the cobalt(II) formed.

Sodium perchlorate solutions for kinetic experiments were prepared by neutralizing reagent grade $60\%\ HClO_4$ with primary standard Na_2CO_3, boiling off the CO_2 formed, and then diluting to the required volume with boiled distilled water.

Organic Acids.—Commercially available acids were used as received, or, if badly discolored, after crystallization from methanol or water. Monomethyl terephthalate was obtained as a research sample from Hercules Powder Co.[4]

2,2′-Thiodibenzoic acid was prepared from the sodium salts of thiosalicylic acid and o-chlorobenzoic acid.[5]

o-Phenoxybenzoic acid resulted from metalation and carbonation of diphenyl ether by the procedure described by Gilman and Oita for preparation of 2,2′-oxydibenzoic acid,[6] m.p. 112° (lit.[6] 114°).

2-Methyl-2′-carboxydiphenyl ether was prepared from o-chlorobenzoic acid, o-cresol, and sodium methoxide.[7] The reaction mixture was kept at 210–215° under nitrogen for 20 min., cooled, and then dissolved in 5% NaOH. The acid and excess cresol were precipitated with HCl, redissolved in NaHCO₃, and the cresol extracted with ether (five times the volume of aqueous solution). The acid was reprecipitated with HCl, then recrystallized from EtOH. A 2.3-g. portion of the acid was then dissolved in 20 ml. of 2% NaOH, heated to 95°, and carefully oxidized with 1.6 g. of $KMnO_4$. The mixture was allowed to stand overnight, the permanganate color discharged by addition

of ethanol, the MnO_2 filtered off, and the resulting 2,2′-oxydibenzoic acid precipitated with HCl, after which it was recrystallized from glacial HOAc.

4-Methyl-4′-carboxydiphenyl ether was prepared, with some difficulty, from p-cresol and p-chlorobenzoic acid, using an analogous procedure. However, after removal of solvent at 130°, the reaction mixture was pulverized, then kept under nitrogen at 310–320° for 15 min. The acid obtained by a work-up similar to that described for the 2,2′-product was oxidized with $KMnO_4$, yielding roughly equal amounts of the desired 4,4′-oxydibenzoic acid and p-chlorobenzoic acid. The two acids were separated by dissolving in boiling methanol and then cooling, whereupon the dibasic acid crystallized.

o-Methylmercaptobenzoic acid was prepared by methylating the sodium salt of thiosalicylic acid with dimethyl sulfate.

4,4′-Dithiodibenzoic acid was prepared from p-aminobenzoic acid by diazotization and coupling with Na_2S_2, using the procedure described for the 2,2′-isomer,[8] then reduced to p-mercaptobenzoic acid using sodium hyrosulfite[9] (hood!). After refluxing for 1 hr. the reaction mixture was cooled and acidified. The precipitated acid was filtered off, pressed dry, and separated from elemental sulfur by dissolving in hot ethanol and filtering. Nitrogen was bubbled through the ethanolic solution for 30 min. to remove H_2S, the solution dried with anhydrous K_2SO_4, and the ethanol removed *in vacuo*.

4,4′-Thiodibenzoic acid was prepared from the salts of p-chlorobenzoic acid and p-mercaptobenzoic acid, using a procedure analogous to that for the 2,2′-isomer.[5] The reaction mixture was kept at 300–320° for 10 min., cooled, and extracted with 10% NaOH. Acidification precipitated a crude green acid, which was crystallized from methanol, giving a white acid, m.p. 295°, in 15% yield. *Anal.* Calcd. for $C_{14}H_{10}O_4S$: C, 61.2; H, 3.7; S, 11.7. Found: C, 61.3; H, 3.8; S, 11.9.

Furan-3,4-dicarboxylic acid was prepared by saponification of its diethyl ester.[10]

Thiophene-3,4-dicarboxylic acid diethyl ester was prepared from P_2S_5 and diethyl 1-formyl-2-diethoxymethylsuccinate[10] by refluxing for 4 hr. in toluene (hood!),[11] then saponifying to its parent acid.

N-Methyl-2-carboxypyridinium perchlorate and the corresponding 3- and 4-carboxy isomers were prepared in solution by methylation of the appropriate pyridinecarboxylic acid with methyl iodide.[12] The unreacted methyl iodide was removed *in vacuo*, the iodide precipitated with a slight excess of $AgClO_4$, and the excess silver ion precipitated by slow addition of saturated NaCl. The preparation was filtered, concentrated to about 2 M by rotary evaporation, then acidified to pH 3–4. The resulting solution was used for preparation of the cobalt complex. An analogous procedure with pyridine-2,5-dicarboxylic acid led to N-methyl-2,5-dicarboxypyridinium perchlorate solution, but pyridine-2,6-dicarboxylic acid resisted methylation.

Preparation of the Complexes.—The general procedure, applicable to well over half of the complexes studied, involved treating 20 mmoles of the parent acid with 10 ml. of 1.75 N NaOH, heating at 80° for 10 min., and then filtering. To the filtrate, which should have a pH value less than 6.5, was added a solution of 1.0 g. of aquopentaamminecobalt(III) perchlorate in 2 ml. of hot water. The mixture was kept at 75–80° for 2 hr. (a bath of refluxing ethanol was convenient here), then cooled, and added to a large separatory funnel containing 5 ml. of water, 1.9 ml. of 9 F $HClO_4$, and 150 ml. of ether. The unchanged parent acid precipitated, but dissolved in the ether layer on shaking. After a 15-min. wait, the layers were separated, and the aqueous layer was re-extracted with another 150 ml. of ether. Ether was then removed from the aqueous layer by drawing air through for 10 min., 10 ml. of 9 F $HClO_4$ was added, and the preparation was allowed to stand at −10° for 2 hr. The precipitated complex was filtered off, dissolved in a minimum quantity of hot water (80°), and the solution cooled to 0°. The recrystallized complex was then filtered off and dried *in vacuo* at 35° for 10 hr. Washing with ethanol or methanol[2c] was not advisable in most cases since many of the complexes dissolved readily in the alcohols when

(3) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **2**, 171 (1946).

(4) We thank Dr. H. G. Tennent of Hercules Research Center, Wilmington, Del., for this sample.

(5) H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.*, **75**, 281 (1953). Reasonable yields of this acid were obtained only if the reaction mixture was melted and kept at 270° for 10 min., rather than the recommended 5 min. at 250°. Success in converting this acid to the pentaamminecobalt(III) complex was achieved only when the acid was free of yellow contaminating matter.

(6) H. Gilman and K. Oita, *ibid.*, **79**, 339 (1957).

(7) F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 2111 (1905).

(8) C. F. Allen and D. D. McKay, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 580.

(9) C. Hansch and H. G. Lindwall, *J. Org. Chem.*, **10**, 383 (1945).

(10) We are indebted to Dr. Reuben G. Jones of Eli Lilly and Co. for generous gift samples of furan-3,4-dicarboxylic ester and diethyl 1-formyl-2-diethoxymethylsuccinate.

(11) E. C. Kornfeld and R. G. Jones, *J. Org. Chem.*, **19**, 1674 (1954).

(12) H. Meyer, *Monatsh.*, **24**, 199 (1903).

slightly damp. The most troublesome impurity was the parent carboxylic acid, which often persisted, even after several recrystallizations but, fortunately, was shown not to affect our kinetic measurements. To remove the last traces of parent acid, the complex was dissolved in hot water, saturated NaHCO₃ solution added dropwise to pH 8, and the solution quickly cooled; this procedure was not applicable to complexes of dibasic acids. Yields tend to be small (often less than 20%), with the greatest losses occurring during the final recrystallization(s); somewhat higher yields, sometimes as great as 50%, were obtained from complexes derived from furan-, thiophene-, and pyridinecarboxylic acids.

The general procedure was modified in a number of instances. For acids having basic nitrogen atoms (an amino group or a pyridine ring), the complex was precipitated with saturated NaClO₄, rather than HClO₄, unless the hydroperchlorate was desired. If the acid or its salt was easily oxidized by air or by tripositive cobalt (aniline and phenol derivatives), reaction conditions were milder (60° heating for 3 hr., keeping pH below 5). The anions of a number of the acids (o-iodobenzoic, 2,2'-diphenic, and 2 2'-thiodibenzoic acids) formed insoluble salts with the Co(NH₃)₅H₂O³⁺ cation; in such cases, the mixture was heated at 100° for 3 hr., then worked up in the usual fashion. With very insoluble acids (e.g., anthraquinone-2-carboxylic, p-bromobenzoic, and 4,4'-thiodibenzoic acids), treatment with NaOH yielded solutions having pH above 7, and heating such solutions with the aquocobalt complex resulted in precipitation of brown cobaltic oxide and release of ammonia; in these instances, reaction was carried out at 55° for 16 hr., the mixture filtered to remove the cobalt oxides which inevitably formed, and the filtrate acidified and repeatedly extracted with ether before precipitating the complex. With a number of the dicarboxylic acids, 16 ml., rather than 10 ml., of 1.75 N NaOH was used, converting the acid to a mixture of its mono- and disodium salts; the complexes formed from such solutions often precipitate from the hot reaction mixture as sparingly soluble carboxylate salts, but may be converted to perchlorates by heating with 2 M HClO₄. In preparing complexes from 1,3,5-benzenetricarboxylic and 1,2,4,5-benzenetetracarboxylic acids, enough NaOH was added to neutralize all but one of the carboxyl groups, and after treatment with the aquocobalt complex, the solution was passed through an anion-exchange column (BioRad AG1-X4) to remove the unreacted carboxylate anion. Removal was incomplete, however for subsequent acidification precipitated significant quantities of the carboxylic acid (anion-exchange resins did not appear to be effective in removing anions of dicarboxylic acids).

For very soluble complexes (e.g., those derived from levulinic acid, anthraquinone-2-carboxylic acid, pyrrolecarboxylic acid, and proline), treatment of the reaction mixture with HClO₄ and ether was omitted; instead, the mixture was evaporated (at 60–65°) to a volume of 3–5 ml., an equal volume of saturated NaClO₄ solution added, and the solution cooled to −5°. In a few cases (complexes from sebacic acid and the benzoylbenzoic acids) a second liquid phase, purple and viscous, separated from the reaction mixture. This contained the desired complex and much unchanged carboxylic acid, and was dissolved in hot 90% methanol, quickly filtered, then added to the water–ether–HClO₄ mixture in the usual way.

Special care should be used in working up benzoato complexes having an aldehyde or keto group *meta* or *para* to the carboxylate, for these undergo hydrolysis surprisingly rapidly. After the excess of parent acid was removed, the preparations were cooled rapidly, and the subsequent recrystallizations were carried out quickly so that the solutions did not remain above 30° for more than a few minutes; the solid complexes, however, are quite stable when dry. The 2,5-dihydroxybenzoato complex is less stable, the crystalline solid becoming black after standing in air a few minutes at room temperature; for this complex, drying and weighing steps were omitted, and kinetic measurements were carried out on solutions immediately after preparation.

Table I lists 38 complexes giving satisfactory analyses. In only one case, the complex of 1,2,4,5-benzenetetracarboxylic acid, did the analysis indicate that a dinuclear complex had been isolated. In addition, mononuclear complexes from the following 12 acids were prepared, but were contaminated with from 5 to 15% of the parent acid: p-aminobenzoic, o-thiomethylbenzoic, 1,3,5-benzenetricarboxylic, 4,4'-oxydibenzoic, 2-o-cresoxybenzoic, anthraquinone-2-carboxylic, 3,4-furandicarboxylic, 3,4-thiophenedicarboxylic, 2-pyrrolecarboxylic, glycine, proline, and sebacic. Kinetic studies of the reductions of these impure acids were carried

out, but final purifications were not, either because the quantity remaining was too small or because the complexes exhibited uninteresting kinetic behavior. Several attempts were made to prepare complexes from each of the following acids but without success: anthranilic, N-acetylanthranilic, terephthalic, 4,4'-diphenic, 3,4-dihydroxybenzoic, oxaloacetic (this decarboxylated), 2,6-dihydroxypyridine-4-carboxylic, γ-pyrone-2,6-dicarboxylic, 3-acetyl-2,4-dimethylpyrrole-5-carboxylic, 3-indoleacetic, and ferrocene-1,1'-dicarboxylic.

Table I

ANALYSES OF CARBOXYLATOPENTAAMMINECOBALT(III) PERCHLORATES, RCo(NH₃)₅(ClO₄)₂

R	Calcd.	Found
o-Fluorobenzoato	12.2	12.3
o-Chlorobenzoato	11.8	11.4
o-Bromobenzoato	10.9	10.8
o-Iodobenzoato	10.0	9.5
Salicylato	12.3	12.1
m-Hydroxybenzoato	12.3	11.8
p-Hydroxybenzoato	12.3	11.9
o-Methoxybenzoato	11.9	12.0
m-Methoxybenzoato	11.9	11.5
p-Methoxybenzoato	11.9	11.7
2,4 Dihydroxybenzoato	11.9	11.8
2,6-Dihydroxybenzoato	11.9	11.5
o-Phenoxybenzoato	10.7	11.1
p-Nitrobenzoato	11.6	11.4
p-Carbomethoxybenzoato	11.3	11.3
m-Aminobenzoato	12.3	12.0
o-Acetylbenzoato	11.7	11.5
o-Benzoylbenzoato	10.4	10.3
p-Benzoylbenzoato	10.4	10.5
p-Formylbenzoato	12.0	12.1
2-Hydroxy-5-formylbenzoato	11.7	11.4
2,2'-Oxydibenzoato	9.9	9.5
2,2'-Thiodibenzoato	9.6	9.5
2,2'-Dicarboxydiphenyl	10.1	9.6
2-Furoato	13.0	12.9
2-Thiophenecarboxylato	12.6	12.4
3-Thiophenecarboxylato	12.6	12.5
2-Pyridinecarboxylato	12.7	12.5
3-Pyridinecarboxylato	12.7	12.0
4-Pyridinecarboxylato	12.7	12.6
2,6-Dicarboxypyridine	11.7	11.6
2,5-Dicarboxypyridine (HClO₄ adduct)	9.6	9.7
(ClO₄)	53.0	53.1
N-Methyl-2-carboxypyridine[a]	10.1	10.0
N-Methyl-3-carboxypyridine[a]	10.1	10.1
N-Methyl-4-carboxypyridine[a]	10.1	10.0
N-Methyl-2,5-dicarboxypyridine[a]	9.5	9.7
(ClO₄)	48.8	48.2
Levulinato	12.9	12.8
4,4'-Thiodibenzoato (H)	3.9	4.1
(C)	27.4	26.6
1,2,4,5-Benzenetetracarboxylato (binuclear)		
(H)	3.6	3.1
(C)	12.8	12.9

[a] Triperchlorates.

Spectra.—Each pure complex that was examined showed an absorption maximum at 502–503 mμ. The ε-value for this peak lay very close to 80, irrespective of the nature of the substituents (phthalato, 79.5; p-methoxybenzoato, 78.0; p-phenoxybenzoato, 80.5; p-nitrobenzoato, 78.8; 4-pyridinecarboxylato, 77.9), the two exceptions being the p-hydroxybenzoato complex (ε 90.0) and the 2,2'-dicarboxybiphenyl complex (ε 55.0). A

second peak, near 350 mμ, present in the spectra of the phthalato and isophthalato complexes, is absent from the spectra of most benzenemonocarboxylato complexes, but is observed in the pyridinecarboxylato complexes (ϵ 64). A striking and reversible change occurs when a complex having a hydroxy group *ortho* or *para* to the coordinated carboxy group is treated with base. The color changes from pink to bright orange, and two of the absorption maxima (lying, for example, at 503 (ϵ 76.0) and 235 mμ (ϵ 22,000) in the *o*-hydroxybenzoato complex) disappear. The extinction coefficient for a third peak, near 298 mμ, is little changed on addition of base (ϵ 4400 in acid, 3900 in base), but the peak is much broader in base. No such effect is observed with *m*-hydroxy compounds.

Analyses.—Cobalt analyses were carried out by adding 2.5 ml. of 0.1 N NaOH to a 10–30 mg. sample of the complex. The mixture was boiled, allowed to cool, then brought to a boil once more. It was then diluted to 25.00 ml. with concentrated HCl, any residue removed by pressure (not suction) filtration, the solution transferred to a 1-cm. cell, and the absorbance at 692 mμ read. The extinction coefficient for Co(II) in this medium is about 560, but is a rather sensitive function of the exact concentration of HCl used. The procedure was therefore standardized internally for each set of runs, using a pure sample of the aquo complex. This method was exceedingly rapid and, with internal standardization, gave values reproducible to better than 1%.

For perchlorate analysis, a 15-mg. sample of complex was dissolved in 15 ml. of a solution 2.5 M in NaCl and 0.1 M in HCl. The mixture was heated to 90°, and a twofold excess of tetraphenylarsonium chloride in water was added slowly with vigorous stirring. The mixture was cooled, allowed to stand 2 hr., and the precipitated tetraphenylarsonium perchlorate filtered off, washed with 10 ml. of ice water in small portions, dried 2 hr. at 110°, and weighed.

Kinetic Experiments.—Rates were evaluated by following the decrease of absorbance at 502 mμ. Samples were dissolved in 5.0 ml. of warm water or hot methanol, diluted to 25.0 ml. with 3.2 M NaClO$_4$, with 3.2 M HClO$_4$, or with mixtures of the two, and transferred to a 10.0-cm. cylindrical cell. Nitrogen was bubbled through for 10 min., and a known excess of Cr(II) was added. Generally, good pseudo-first-order plots were obtained, and in those cases where successive runs with different Cr(II) concentrations were made, first-order dependence on Cr(II) was confirmed. Rate constants from several points in a single run were reproducible to better than 5%, whereas those obtained from different runs checked to within about 8%. When an acid dependence was suspected, runs were carried out at at least three acidities lying between 0.01 and 3.0 M. Rate experiments were generally carried out with $\mu = 3.0$, but a number of complexes (particularly those difficultly soluble in 3 M perchlorate) were examined at $\mu = 1.0$. For those complexes studied at both ionic strengths, increasing μ from 1.0 to 3.0 was found to increase the specific rate of reduction by 15 ± 2%. The presence of 5 ml. of methanol in 27 ml. of solution lowered the rate only slightly (about 4%).

The reduction of the *p*-benzoylbenzoato complex at concentrations greater than 8×10^{-4} M resulted in precipitation of a white crystalline solid, which was filtered off and dried. This melted at 193° and did not depress the melting point of the pure parent acid.

Stoichiometry Experiments.—A sample (15 to 30 mg.) of the complex was dissolved in 2.5 ml. of boiled distilled water or 1 M HClO$_4$, the solution purged with nitrogen, and 0.50 ml. of a solution 0.9 M in HClO$_4$ and 0.046 M in Cr(II) was added. After 20 min., the solution was diluted to 25.0 ml. with concentrated HCl, the absorbance read at 692 mμ, and the amount of Co(III) reduced calculated from the amount of Co(II) released.

Reduction of Acids.—Samples (8 mg.) of organic acids were dissolved in 2 ml. of boiled water ori n methanol; nitrogen was bubbled through the solutions to remove O$_2$, and 0.50 ml. of 0.046 M Cr(II) added as above. The solutions were allowed to stand 40 min., after which a 0.50 M solution of chloropentaamminecobalt(III) perchlorate was added through the cap (syringe) until the maroon color persisted. The solutions were then uncapped and diluted to 25.00 ml. with concentrated HCl; the absorbance at 692 mμ was read and the quantity of Cr(II) not consumed by the organic acid calculated from the Co(II) produced. Some air oxidation of Cr(II) always occurred, for even when no organic acid was used, the Co(II) measured corresponded to only 85–90% of the Cr(II) added. The figures summarized in Table VII are corrected for this loss.

Results

Spectra of the Products.—Normally, the products formed from reduction of a carboxylatopentammine-cobalt(III) complex with Cr(II) in acid are Co^{2+}, NH$_4^+$, and the carboxylato complex of Cr(III). When there was reason to suspect that this was not so, a spectrum of the resulting solution was taken, and the spectrum of the chromium(III) product obtained by subtraction of the known absorbencies of Co^{2+} and (excess) Cr^{2+}. Table II compares the spectra of a number of these products with the spectra of known Cr(III) complexes. Data for two of the maxima, one

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
Aquo[a]	406	15.6	571	13.4
Acetato[b]	406	20.7	568	21.6
Lactato[b]	409	31.2	563	25.7
Malonato[b]	416	27.2	559	32.4
Salicylato	415	36	555	35.0
m-Hydroxybenzoato	417	43.8	569	37.4
p-Hydroxybenzoato	411	40.5	572	38.7
2,4-Dihydroxybenzoato	420	38.5	560	36.5
o-Methoxybenzoato	410	31.2	568	26.4
Phthalato	417	21.7	573	20.5
Isophthalato	414	30.4	567	30.8
2,2'-Thiodibenzoato			580	25.2
2,2'-Biphenyldicarboxylato	417	13.0	573	20.6
o-Acetylbenzoato	412	25.2	575	22.6
o-Benzoylbenzoato	412	30.5	575	21.4
2-Hydroxy-5-formylbenzoato			555	54.1
Pyridine-4-carboxylato	410	23.6	579	19.5
Pyridine-3-carboxylato	410	22.6	577	21.2
N-Methylpyridine-4-carboxylato	408	28.5	600	20.0
Pyridine-2-carboxylato	406	50.8	553	32.8
Pyridine-2,6-dicarboxylato	428	44	577	102
Pyridine-2,5-dicarboxylato	403	40.9	562	29.2
Pyrrole-2-carboxylato			543	21.6

[a] R. I. Colemar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54**, 3204 (1932). [b] R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *ibid.*, **80**, 4469 (1958).

near 410 mμ, the other near 575 mμ, are included, but the second of these peaks is often very broad and considerable difficulty is encountered in estimating the position of λ_{max}. The extinction coefficients, however, allow a clear choice between the aquo- and a carboxylatochromium(III) complex and appear to indicate, for the pyridine derivatives, whether the product is chelated. In cases most favorable for coordination through nitrogen, one or both of the ϵ-values exceed 40. For substituted benzoato complexes, the picture is less clear. Products thought, on the basis of other evidence, to be chelated (*e.g.*, the salicylato and the 2,4-dihydroxybenzoato Cr(III) derivatives) have higher extinction coefficients than some of the nonchelated products, but absorb less intensely than other complexes (*e.g.*, the *m*- and *p*-hydroxybenzoato compounds) which clearly cannot be chelated. In general, no serious

inconsistency is introduced by assuming nonchelation in products for which both ϵ-values are less than 35, but reserving judgment when one or both values exceed this.

Range of Rates.—The specific rates for reduction of pentaamminecobalt(III) complexes with Cr^{2+} (adjusted to 0% methanol and $\mu = 3.0$) are summarized in Tables III–V. Over two-thirds of the values lie

TABLE III

SPECIFIC RATES FOR CHROMOUS REDUCTION OF CARBOXYLATO-
PENTAAMMINECOBALT(III) IONS DERIVED FROM MONOBASIC
ACIDS[a]

Ligand	k
o-Fluorobenzoato	0.15
o-Chlorobenzoato[b]	0.11
o-Bromobenzoato	0.096
o-Iodobenzoato[b]	0.095
o-Methoxybenzoato	0.28
m-Methoxybenzoato	0.22
p-Methoxybenzoato	0.19
o-Phenoxybenzoato	0.17
2-o-Cresoxybenzoato	0.11
o-Thiomethylbenzoato	0.38
2-Furoato	0.43
2-Thiophenecarboxylato	0.30
3-Thiophenecarboxylato	0.23
p-Carbomethoxybenzoato	0.20
o-Acetylbenzoato	0.80
o-Benzoylbenzoato	5.4
2-Anthraquinonecarboxylato	5.0
p-Benzoylbenzoato	$0.32 + 1.5[H^+]$
p-Formylbenzoato (0°)	$29 + 5.4 \times 10^2[H^-]$
Trifluoroacetato[c]	0.052
Levulinato	$0.35 + 0.008/[H^+]$

[a] In l. mole^{-1} sec.$^{-1}$, at 25°; $\mu = 3.0$; $(H^+) = 0.16$–2.90 F. [b] Our value for the p-iodo complex is in good agreement with that reported by Fraser[2b] (0.083 at $\mu = 1.0$). However, his value for the o-chloro compound (0.074) is less than that for the iodo compound, whereas we observe the reverse trend in the o-halogenobenzoato series. [c] The authors are indebted to Mr. Robert Jordan for a sample of this complex.

between 0.08 and 0.30. Thus, the rates of reactions in this series are strikingly insensitive to the usual inductive, conjugative, and steric effects which so often influence reactivity in organic compounds. In the extreme case, replacement of the three α-hydrogens in the acetate group with fluorines retards the reduction of the pentaamminecobalt(III) derivatives only by a factor of 3, whereas such a replacement in the parent acid increases its dissociation constant by over five powers of 10. Although one hesitates to rationalize small rate differences in the present series on a structural basis, it is probably safe to assume that a rate constant greater than 0.5 indicates the operation of one or more special effects.

Remote Attack through p-Carbonyl Substituents.— The "special effect" which rests, at present, on firmest experimental ground is remote attack, i.e., reduction of Co(III) by attack by the reducing agent at a noncoordinated carboxyl or carbonyl, which is separated from the coordinated carboxyl by a system of conjugated double bonds.[2c] In the present series, this type of attack is exemplified by the reduction of the p-

TABLE IV

SPECIFIC RATES FOR CHROMOUS REDUCTION OF CARBOXYLATO-
PENTAAMMINECOBALT(III) IONS DERIVED FROM DIBASIC ACIDS[a]

Ligand	pK_{HA}	k_{HA} (acid path)	k_{A^-} (basic path)
Sebacato		0.28	
Salicylato	9.77	0.15	2×10^5
m-Hydroxybenzoato	8.80	0.20	
p-Hydroxybenzoato[b]	9.91	0.23	
2,4-Dihydroxybenzoato	7.75	0.16	3×10^6
2,5-Dihydroxybenzoato	(7.7)[c]	0.29	$0.016/K_{HA}$ ($\approx 10^6$)
2,6-Dihydroxybenzoato	7.72	0.095	5×10^5
2-Hydroxy-5-formylbenzo-ato	(9.4)[c]	0.55	$0.27/K_{HA}$ ($\approx 10^9$)
2,2'-Oxydibenzoato	2.28	0.20	
2,2'-Thiodibenzoato	2.45	0.19	14
4,4'-Oxydibenzoato		0.19	
4,4'-Thiodibenzoato		0.22	
Furan-3,4-dicarboxylato	(2.8)[c]	0.16	$0.022/K_{HA}$ (≈ 10)
Thiophene-3,4-dicarboxylato	2.94	0.075	9
Biphenyl-2,2'-dicarboxylato[b]	2.97	0.078	21
1,3,5-Benzenetricarboxylato		0.23	
1,2,4,5-Benzenetetracarboxylato (binuclear)		0.38	

[a] In l. mole^{-1} sec.$^{-1}$ at 25°; $\mu = 3.0$; $(H^+) = 0.06$–2.90 F. [b] Our data for these complexes are not in agreement with those of Fraser,[2b] who reports a value of 0.13 for the p-hydroxy complex, and, for the biphenyl derivative, an acid independent term of 0.10, a first-order acid term having a specific rate of 3.4, but no inverse acid term. [c] Estimated value.

TABLE V

SPECIFIC RATES FOR REDUCTION OF CARBOXYLATOPENTAAM-
MINECOBALT(III) IONS DERIVED FROM NITROGEN-CONTAINING
ACIDS[a]

Ligand	pK_{HB^+}	k_{BH^+} (acid path)	k_B (basic path)	k_{Me} (N-methyl deriv.)
p-Aminobenzoato		0.14		
m-Aminobenzoato		0.12		
Prolinato		0.027		
Pyridine-2-carboxylato	4.49		2×10^5	0.87
Pyridine-3-carboxylato	4.73	0.11		0.13
Pyridine-4-carboxylato	4.79	1.3	1.5×10^3	1.4
Pyridine-2,5-dicarboxylato	<0[b]		>200	8
Pyridine-2,6-dicarboxylato	<0[b]		>150	
Pyrrole-2-carboxylato	2.70	0.28	2.6	

[a] In l. mole^{-1} sec.$^{-1}$ at 25°; $\mu = 3.0$; $(H^-) = 0.03$–2.90 F. [b] This upper limit refers to the N-protonated (tripositive) form of the complexes. Second acid dissociation constants (for the dipositive forms) have been found to be 3.45 (for the 2,6-complex) and 3.80 (for the 2,5).

benzoyl and p-formyl (p-aldehydo) derivatives, the latter being reduced "immeasurably rapidly" at room temperature.[13] In addition to the high rates, there are two other indications of remote attack: The rate laws for these complexes include large terms which are first order in hydrogen ion, a characteristic which has

(13) R. T. M. Fraser, J. Am. Chem. Soc., **83**, 4920 (1961).

been found in the pentaammine complexes only in cases where remote attack greatly predominates over adjacent attack.[2b,14] Moreover, we have observed that reduction of the p-benzoyl complex yields aquo-chromium(III) and the free parent acid, and Fraser[15] has made the corresponding observation with the p-formyl derivative. Release of the free acid, which has never been reported for cases involving the more usual adjacent attack, occurs because the "remote" carbonyl group, although it must come into contact with Cr^{2+} to accept the reducing electron, is too weakly basic to remain bonded to it in an aqueous environment.

Chelation and Possible Electron Transfer Through o-Carbonyl Groups.—The rates for the o-benzoyl and 2-anthraquinone derivatives, and, to a lesser extent, the o-acetyl derivative, indicate that a carbonyl group lying *ortho* to the coordinated carboxylate group may also accelerate reduction. Remote attack might be expected here as well, for, classically speaking, the *ortho* and *para* positions are conjugatively equivalent. Nevertheless, important differences appear. *No term first order in hydrogen ion has been observed in the rate laws, and the reduction yields the carboxylatochromium-(III) product, rather than the free parent acid* (Table II). The identity of the product tells us that chromium is bound to the carboxyl group in the activated complex for reduction, and we may infer that the *ortho* carboxyl group serves to stabilize the transition state through chelation
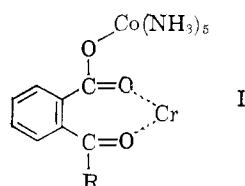
although, once again, the weakly basic carbonyl oxygen cannot remain bound to chromium, and a chelated product would not be expected (nor is it observed). However, this cannot be the entire story, for the phthalato complex, which may form a chelate in just the manner shown, is reduced with a specific rate of 0.075 at $25°$,[2c] *i.e.*, more slowly than virtually all other benzoato complexes in the series, including the *m*- and *p*-$NH_3{}^+$ substituted complexes (Table V) having an additional unit of positive charge. It is suggested, therefore, that conductivity associated with the carbonyl linkage is important here (as is the case with the p-benzoyl and p-formyl compounds), and that electron transport takes place, at least in part, into the keto group, through the ring, and thence into the carboxyl group. Since both carboxyl oxygens in the transition state are already attached to positive centers (one to Co(III), the other to Cr(II)), hydrogen ion catalysis is not observed.

Duality of Paths for Complexes of Dibasic Acids.—Reductions of the complexes of dibasic acids (Table IV) may be expressed as the sum of two terms, pertaining, respectively, to the acid form of the complex (designated Ro-A-H), and to its conjugate base (Ro-A$^-$)

(14) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).
(15) R. T. M. Fraser, Ph.D. Thesis, University of Chicago.

$$-\frac{d(Co(III))}{dt} = k_{HA}(Cr^{2+})(Ro\text{-}A\text{-}H) + k_{A^-}(Cr^{2+})(Ro\text{-}A^-) \quad (1)$$

where k_{HA} and k_{A^-}, the specific rates for the acidic and basic forms of the complex, may be evaluated from the dependence of reaction rate on acidity and from K_{HA}, the acidity constant of Ro-A-H. The second term, representing the basic path, does not always appear, particularly when the acidic centers in the complex are far apart, in which case the specific rate is independent of acidity. It is evident that the observed rate constants for the basic paths fall into two distinct groups. Those associated with the complexes of dicarboxylic acids cluster near 10, whereas those from the o-hydroxy-benzoic acids lie well above 10^5.

Reductions of Dicarboxylato Complexes.—The magnitude of the rate constants associated with the basic paths for reduction of our dicarboxylato complexes, and, more particularly, comparison of molecular models of complexes which exhibit this path with those of complexes that do not, suggests that the basic path proceeds through a chelated transition state, although the low absorbancies of the resulting solutions in such cases (Table II) indicate that chelation does not persist in the products. Strainless models of chelated transition states have been constructed for each dicarboxylato complex displaying an inverse acid term in its reduction (with the rings for the biphenyl-2,2'-dicarboxylato and 2,2'-thiodibenzoato complexes having eight and nine atoms, respectively), whereas those complexes for which such models cannot be made (*e.g.*, the isophthalato, the 4,4'-thiodibenzoato, and the 1,3,5-benzenetricarboxylato complexes) are reduced at rates independent of (H$^+$).

The alternative interpretation, that the k_{A^-} values for the dicarboxylato complexes in this series exceed the k_{HA} values by a factor of about 10^2 because of the extra unit of negative charge associated with the bridging group, seems less satisfactory, for there is other evidence that reactions in this series are strikingly insensitive to the charge type of the electron-transfer bridge. Thus, it may be noted that the protonated and methylated forms of the complexes in Table V (in which the ligand bears a net charge of zero) are reduced about as rapidly as many of the substituted benzoato complexes in Table III (in which the ligand bears at net charge of -1).

When formation of a six-membered chelate is possible, k_{A^-} increases significantly, being near 100 for the dimethylmalonato complex[16] and 2500 for the malonato complex.[14] It nevertheless remains well below the K_{A^-} values noted here for the hydroxybenzoate complexes.
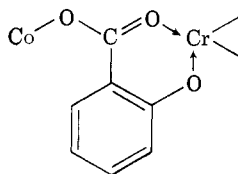
Chelation of Reduction of o-Hydroxybenzoate Derivatives.—Incorporation of a hydroxy group *ortho* to the carboxylato group in this series should greatly favor chelation in the transition state, for here the chelate would be an almost planar, conjugated, six-membered ring.

Although the spectra of the resulting solutions (Table II) do not easily distinguish a chelated Cr(III) product from a nonchelated one and, in any event, say nothing

(16) R. Butler and H. Taube, unpublished results.

about occurrence of chelation in the activated complex, comparison of the specific rates for the acidic and basic paths is instructive.

The K_{HA} values for reduction of the isomeric hydroxybenzoato complexes are not greatly different from each other and fall well within the range characteristic of the "ordinary" benzoato complexes in Table III, indicating that the activated complexes for reduction of the acid forms of the o-hydroxybenzoato complexes are not stabilized significantly by chelation.

For the basic path, it is quite another matter. The very high k_{A^-} values in Table IV appear only when one or two hydroxyls lie *ortho* to the coordinated carboxyl, strongly suggesting chelation in the basic paths. The effect (corresponding to a rate increase of three to six powers of 10 over the reduction of the malonato complex) is striking, particularly since it is substantially a reflection merely of the difference in stability between a conjugated planar ring system and one that is nonconjugated and puckered. Although the magnitude is not out of line with observed differences in stabilities between malonato and salicylato complexes,[17] it is not unreasonable to ask whether an additional mode of reduction, *i.e.*, electron transfer through phenolic oxygen, has come into play in the basic path. The data at hand give scant support to such an alternate mechanism, although they do not rule it out. For it may be argued that the *para* and *ortho* positions are conjugatively equivalent and that any mode of electron transfer through an o-O$^-$ substituent should occur also through a p-O$^-$ group, although the effect might be attenuated. We find no evidence for a basic path in reduction of the p-hydroxy complex, but such a path might easily pass undetected if it constituted less than 5% of the entire reduction. Because of the very high pK_{HA} value for the *para* compound, this "upper limit" corresponds to a k_{A^-} value of about 10^6 in our range of acidity. The question thus remains open, and extension of these measurements to lower acidities is highly desirable.

Nontransmission through Sulfur.—Values in Table IV for the sulfur-containing dicarboxylato complexes derived from 4,4'-thiodibenzoic (II), 2,2'-thiodibenzoic (III), and thiophene-3,4-dicarboxylic (IV) acids are
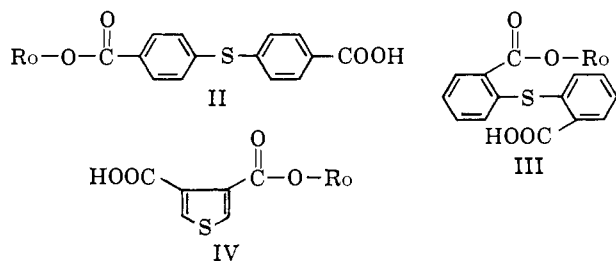
(Ro = "roseo" = Co(NH₃)₅)

of some interest, not because they are large, but rather because they are very similar to their respective oxygen analogs. In these complexes, the coordinated carboxyl is separated from the noncoordinated carboxyl by conjugated carbon systems which are, in turn, separated from each other by sulfur atoms. To the extent that these sulfur atoms can transmit electronic effects from one conjugated carbon system to the other by "d-orbital resonance,"[18] the two carboxyl groups may be considered to be conjugated with each other, although there is considerable variation, both in steric relationships and detailed electronic distribution within this triad. Since there is no evidence that the reduction of these complexes occurs by remote attack, as has been observed for the fumarato and terephthalato complexes,[2c] we may infer that the sulfur atom, however similar it may be to a pair of doubly-bonded carbons in other respects,[19] does not easily transmit a reducing electron from one conjugated system to another.[20]

Electron Transfer through Nitrogen. Pyridinecarboxylato Complexes.[21]—Each of the ligands listed in Table V has a basic nitrogen atom, although the basicity of the pyridinedicarboxylato complexes is too weak to be detected in dilute aqueous solution. Again, rates of reduction may be expressed as the sum of two terms, involving specific rates for the acidic (k_{BH^+}) and basic (k_B) forms of the complex. In this group, reductions of the pyridinecarboxylato complexes provide what appears to be the first strong evidence for remote attack involving electron transfer through nitrogen. As with other conjugation-related effects exhibited by pyridine derivatives, this path has been observed for α- and γ-, but not for β-substituents.

In reduction of the pyridine-2-carboxylato complex, only the basic path was detected, even in 3 M HClO₄. Both paths were observed with the 4-carboxylate com-

(18) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(19) For a recent summary of the evidence that sulfur, like C=C, but unlike oxygen, may stabilize adjacent free-radical or carbanion centers, see C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, pp. 26–60.

(20) Remote attack does not appear to be involved in reduction of the binuclear complex of 1,2,4,5-benzenetetracarboxylic acid. It is found to react substantially more rapidly than the phthalato complex (ref. 2c) and the binuclear terephthalato complex (D. K. Sebera, Ph.D. Thesis, University of Chicago), both of which have structural features in common with it. However, no first-order acid term was observed, even in 2.5 M HClO₄. This observation does not tell us whether the complex has structure V, VI,
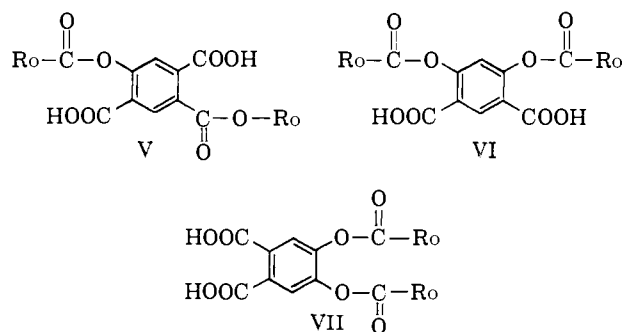
or VII (where Ro = "roseo" = Co(NH₃)₅), although VII would be considered unlikely on a steric basis. Remote attack would not be expected in the reduction of V, since no –COOH group lies *para* to a –COORo group. It would, as well, be unlikely in reductions of VI and VII, for the –COORo groups are pushed out of the plane of the benzene ring by "*ortho* interference."

(21) A brief report, summarizing the results in this and the following section, has appeared (E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, 85, 3706 (1963)).

(17) For example, the pK values (25°) for the monomalonato and monosalicylato complexes of Cu(II) are reported as 5.60 (R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, 28, 609 (1932)) and 10.60 (A. K. Babko, *Zh. Obsch. Khim.*, 17, 443 (1947)), respectively.

plex, whereas only the acidic path appears with the 3-isomer, which reacts at a rate comparable not only to its N-methylated derivative, but also to the many "normal" carboxylato complexes in Tables III–V. Rates corresponding to these basic paths are surprisingly high, considering particularly that the basic forms of these complexes have one more positive charge than the basic forms of the complexes in Table IV.

The marked structural similarity between the pyridine-4-carboxylato (VIII) and the fumarato (IX) complexes

VIII   IX
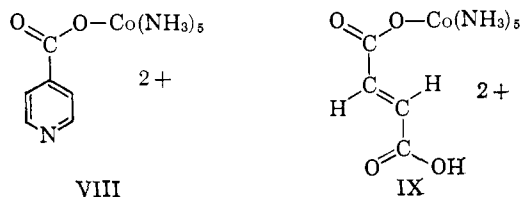
suggests to us that the basic path for reduction of the 4-carboxylato complex is associated with remote attack, in this case at nitrogen. However, the spectrum of the product is very similar to that obtained from the isomeric 3-carboxylato complex, and similar also to that of the acetato complex (Table II). Apparently, then, the N–Cr bond does not survive, but the N-coordinated Cr(III) complex is rapidly re-equilibrated to the more stable carboxylato-coordinated complex.

If this picture is true, reduction of the pyridine-4-carboxylato complex is similar to reduction of the p-benzoyl- and p-formylbenzoato complexes in that chromium does not remain bound to the site of attack in the Co(III) complex, but the two types of reduction differ with respect to the ultimate fate of the Cr(III) product. The aquochromium(III) complex, resulting from reductions of p-carbonylbenzoato derivatives, is not observed as a product from reduction of the pyridine derivative, nor is it at all likely that the observed carboxylato-coordinated product is formed from the aquo, for such conversions at room temperature are known to be extremely slow.[22] We propose instead that the N-coordinated product is converted directly to the carboxylato-coordinated product by action of the unreacted Cr(II), again by electron transfer through the pyridine-carboxylato system.
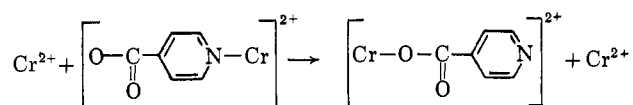
The fact that no spectral irregularities attributable to an N-coordinated Cr(III) product could be detected, even when an excess of Co(III) complex was used in the reaction, suggests that the specific rate of such a "follow-up reaction" compares with that for the initial reduction and may be greater. A similar exchange, leading to a carboxylatochromium(III) product, may be imagined for a —C=O—Cr(III) intermediate resulting from reduction of a p-carbonyl complex, but it is not observed. Thus, it may be presumed that such a step, in this case, does not compete favorably with hydrolysis to $Cr(H_2O)_6^{3+}$.

(22) See, for example, R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, J. Am. Chem. Soc., **80**, 4469 (1958).

The high absorbance of the product derived from reduction of the pyridine-2-carboxylato complex indicates that a chelated product, having a Cr(III)–N bond, has been formed. Moreover, the extreme rapidity of the basic path points to chelation in the activated complex, but the Cr atom in the product is bound both to oxygen and nitrogen, and the direction of electron flow, as in the case of reduction of the salicylato complex, has not been determined. However, to the extent that the data on reduction of the 4-carboxylato compound suggest remote attack through nitrogen, electron transfer through nitrogen must be considered also in reduction of the 2-carboxylato isomer. In view of the long recognized similarities in conjugative relationships between the 2- and 4-positions of pyridine derivatives,[23] it is difficult to see why electron transfer would be permitted in one case but prohibited in the other.
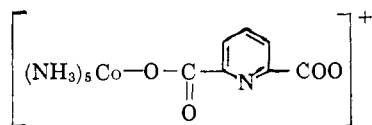
The reduction of the pyrrole-2-carboxylato complex contrasts with that of its counterpart in the pyridine series. The low value of ϵ_{max} at 543 mμ for Cr(III) species in the resulting solution indicates that the predominant product is not chelated. The basic path for reduction, although kinetically detectable, is slower than that for the pyridine-2-carboxylato complex by a factor of 10^5, but still significantly faster than reduction of the corresponding furan and thiophene derivatives. A chelated transition state is not ruled out for the small portion of the reduction of the pyrrole derivative proceeding through the basic path, but because of the tetrahedral configuration about the pyrrole nitrogen, the chelate ring would not approach planarity and any Cr–N bond should, in contrast to the case of the pyridine complex, lie well out of the plane of the heterocyclic ring. Interestingly, the specific rate for the basic path for the pyrrole complex approximates those for the dicarboxylato complexes in Table IV which, we believe, are reduced through nonplanar chelated activated complexes.

Reductions of Pyridinedicarboxylato Complexes.— Reductions of the complexes of pyridine-2,5-dicarboxylic and -2,6-dicarboxylic acids, even in 3 M HClO$_4$, are immeasurably fast under our conditions and may be presumed to proceed predominantly by the basic path. Our lower limits for the rate constants fall so much below the values for the 2- and 4-pyridinemonocarboxylato complexes because the dicarboxylato complexes are much the weaker bases. The Cr(III) products formed in these reductions are chelates, as indicated by their spectra (Table II), the color of the 2,6-product being unusually intense for this series. It is likely that the 2,6-derivative is reduced in the same manner as the 2-carboxylato complex; the ambiguity with respect to direction of electron flow is here also.
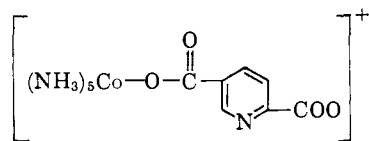
Discussion of the mode of reduction of the 2,5-derivative requires that we know whether, in the preparation, cobalt(III) has become attached to the 2- or the 5-carboxyl group. Although we cannot be sure, comparing its base strength with that of the 2,6-derivative allows a resonable choice. The complexes themselves are immeasurably weak bases in water, but the basicities of their nonprotonated forms (X and XI) are measurable. As indicated, the monopositive ion derived from the 2,5-complex is about twice as strong a base

(23) See, for example, G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 484-486.
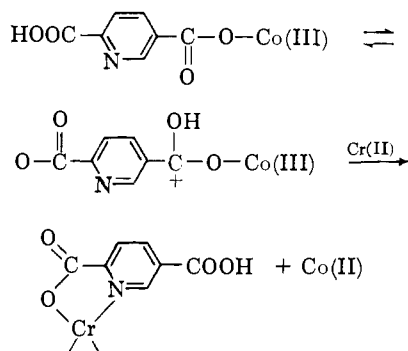
$$\left[(NH_3)_5Co\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!\underset{N}{\bigcirc}\!-\!COO \right]^+$$

X

$pK_B = 10.55$

$$\left[(NH_3)_5Co\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!\underset{N}{\bigcirc}\!-\!COO \right]^+$$

XI

$pK_B = 10.20$

$(25°, \mu = 0.0075)$ as its 2,6-isomer, indicating that in the 2,5-isomer the base-weaking Co(III) center is coordinated to the 5-, rather than the 2-, carboxyl group. Since the coordinated and noncoordinated carboxy groups lie *"para"* to each other, remote attack, as thought to occur in reduction of the terephthalato complex, may occur here also. If, as we suspect, the cobalt is bound to the 5- rather than the 2-carboxyl group, formation of a chelated product suggests that chelation may facilitate remote attack as well as adjacent attack.

$$HOOC\!-\!\underset{N}{\bigcirc}\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\!-\!Co(III) \quad \rightleftharpoons$$

$$\underset{\underset{O}{\|}}{O\!-\!C}\!-\!\underset{N^+}{\bigcirc}\!-\!\underset{\underset{+}{|}}{\overset{OH}{\underset{|}{C}}}\!-\!O\!-\!Co(III) \quad \xrightarrow{Cr(II)}$$

$$\underset{O}{\overset{O}{\underset{\diagdown}{\bigcirc}}}\!\underset{Cr}{\overset{C}{\diagup}}\!\!\!\!-\!\underset{N}{\bigcirc}\!-\!COOH \; + \; Co(II)$$

The position of Co(III) in the N-methylated 2,5-dicarboxylato complex is also undetermined, although we suggest that formation of the complex is more likely at the 5- rather than at the more hindered 2-position. In any event, remote attack, but not chelation, is possible in the reduction of this complex, and the observed specific rate is significantly greater than for reductions of the other N-methylated complexes in the series. It is, however, only one-tenth as rapid as the reduction of the terephthalato complex,[2c] probably because the α-carboxyl group (be it "adjacent" or "remote" with respect to cobalt) is kept out of the plane of the pyridine ring by interference with the N-methyl group.

When the 2,5-dicarboxylato complex or its N-methyl derivative was treated with an excess of Cr^{2+}, more deeply colored species were slowly formed. A blue-purple product (ϵ_{max} 63.0 (404 mμ), 47.0 (540 mμ)) was obtained from the nonmethylated complex and a deep green product (ϵ_{max} 71.5 (570 mμ), 12,000 (284 mμ)) from the methylated complex. These are almost certainly Cr(III) complexes also, possibly with the rings reduced to dihydropyridine or related structures, for the 2,5-dicarboxypyridine system (both methylated and nonmethylated) has been found to be readily reduced by Cr(II) in the absence of Co(III) (Table VII). Moreover, when the product obtained from the

N-methyl compound was exposed to air for 3 days, the color faded, and a maximum appeared at 406 mμ, the expected wave length for an N-methylated carboxylatochromium(III) derivative (Table II), indicating partial re-oxidation to the pyridine ring.

Competition for Cr(II).—Experiments in which a deficiency of Cr(II) was treated with (a) a number of carboxylato complexes and (b) the corresponding parent acids are summarized in Tables VI and VII.

TABLE VI

YIELDS OF Co(II) FROM REDUCTION OF CARBOXYLATOPENTAAM-
MINECOBALT(III) COMPLEXES

Ligand	$-(H^+) = 0.15-$		$-(H^+) = 1.0$	
	$\dfrac{Co(III)}{Cr(II)}$	Yield Co(II)	$\dfrac{Co(III)}{Cr(II)}$	Yield Co(II)
Aquo	3.0	0.99		
p-Nitrobenzoato	3.0	0.0		
2-Furoato	3.0	0.91	3.0	0.94
p-Formylbenzoato	1.5	1.00	3.0	1.00
p-Benzoylbenzoato	{ 3.0	{ 1.00		
	{ 1.25	{ 0.93		
o-Benzoylbenzoato	1.25	1.00	3.0	0.98
o-Acetylbenzoato	1.25	0.89	3.0	0.94
2-Anthraquinonecarboxylato	1.5	0.90		
Levulinato	3.0	0.87		
2-Hydroxy-5-formylbenzoato	1.5	0.99		
Pyridine-2-carboxylato	1.25	1.00		
Pyridine-3-carboxylato	3.0	0.82		
Pyridine-4-carboxylato	1.5	1.00	3.0	0.92
Pyridine-2,5-dicarboxylato[a]	1.5	0.95	3.0	0.97
N-Methylpyridine-4-carboxylato	1.5	0.96	3.0	0.88
N-Methylpyridine-2,5-dicarboxylato	1.5	0.99	3.0	0.95
Pyrrole-2-carboxylato	3.0	1.00	3.0	0.73

[a] A similar determination with the complex of pyridine-2,6-dicarboxylic acid could not be carried out since the color of the Cr(III) product interfered with that of Co(II) in HCl.

A Co(II) yield substantially below unity in Table VI signifies that some entity is competing with coordinated Co(III) for Cr(II). Behavioral extremes in this series are exemplified, on one hand, by the p-nitrobenzoato complex and, on the other, by the p-formylbenzoato complex. The nitro group quickly takes up all reducing electrons from Cr^{2+}, is itself reduced, and transmits none through the ring to Co(III), whereas the p-CHO group accepts reducing electrons but transmits virtually all of them through the ring to Co(III). Many of the intermediate values may be rationalized by assuming that Cr(II) reduces the organic portion of the Cr(III) product formed in the main reaction. This supposition is consistent with the decreased yields of Co(II) (insofar as these changes lie outside of experimental error), as (H^+) is raised from 0.15 to 1.0; the competing reduction, to a more nearly saturated organic product, almost certainly requires protons.

Since the p-benzoyl derivative yields the free parent acid, rather than the Cr(III) complex, on reduction, the observed discrepancy here between Cr(II) consumed and Co(II) produced cannot be attributed to partial reduction of a Cr(III) complex. In this case,

Table VII

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

Acid	(H⁺)	Cr(II) consumed, %	Color produced
2-Furoic	0.40	10	
p-Formylbenzoic	0.15	0	
p-Benzoylbenzoic	0.15	5	
o-Benzoylbenzoic	0.40	10	
o-Acetylbenzoic	0.15	0	
	0.40	20	
Anthraquinone-2-carboxylic	0.15	5	Dark brown
Levulinic	0.15	24	
2-Pyridinecarboxylic	0.15	b	Red-brown
3-Pyridinecarboxylic	0.15	20	
4-Pyridinecarboxylic	0.15	>40	Purple
	0.40	20	
2,5-Pyridinedicarboxylic	0.15	80	Purple
2,6-Pyridinedicarboxylic	0.15	>85	Dark blue
N-Methyl-2-pyridinecarboxylic	0.15	5	
N-Methyl-3-pyridinecarboxylic	0.15	0	
N-Methyl-4-pyridinecarboxylic	0.15	23	Purple
N-Methyl-2,5-pyridinedicarboxylic	0.15	>64	Green
2-Pyrrolecarboxylic	0.40	0	

[a] 40 min.; 25°; concentration of acid, 4.0 g./l. [b] Intense color prevented estimation of Cr(II) consumed.

about 7% of the Cr(II) is oxidized by the free parent acid, by a radical-like intermediate, or by a combination of both. As shown in Table VII, p-benzoylbenzoic acid does indeed oxidize Cr(II), but the reaction is slow; after 40 min. (twice the reaction period for the competition experiments), and in the absence of Co(III), only 5% of the Cr(II) is oxidized by the free acid. Intervention of a radical-like intermediate, which may either form the predominant products or react with a second Cr(II), is thus a distinct possibility here, although the differences are too small to be anything but suggestive. Likewise, analogous intermediates cannot be ruled out for reduction of other complexes in Table VI for which yields of Co(II) lie well below unity; rate data on the reduction of carboxylatochromium(III) complexes with Cr(II) would be pertinent here.

Relevance of Reducibility of Ligands to Reduction of Complexes. Evidence for Radical-Ion Intermediates. —The values in Table VII may be taken as rough indications of the relative rates at which the various parent carboxylic acids are reduced by Cr^{2+}, since concentrations of Cr^{2+} and carboxylic acid, temperature, and reaction period are kept nearly constant throughout the series. These figures emphasize an important distinction between the manner in which the carbonylbenzoato groups, on one hand, and the pyridinecarboxylato groups, on the other, facilitate reduction of coordinated Co(III) by Cr^{2+}.

As Conant has shown,[24] ordinary aldehydes and ketones are reduced extremely slowly by Cr^{2+} at room temperature, and our figures reveal little, if any, difference in reducibilities among the various carbonylbenzoic acids. This suggests that the ligand in such

(24) J. B. Conant and H. B. Cutter, *J. Am. Chem. Soc.*, **48**, 1025 (1926).

cases serves largely to transmit the electron deficiency associated with Co(III) to another (possibly more accessible) site, for without Co(III), no transfer would occur. In this respect, it is interesting that the levulinato complex reacts at a "normal" rate, although its parent acid (γ-ketovaleric acid) is more easily reduced than any other carbonyl acid in our series. The keto group apparently has some capacity for accepting a reducing electron, but this electron cannot find its way through the $-CH_2-CH_2-$ chain to the coordinated carboxyl.

The same sort of "conduction" through the ligand almost certainly occurs in reduction of certain of the pyridinecarboxylato complexes (particularly the basic forms of the 2- and 4-carboxylato derivatives); but for the series as a whole, reducibility of the ring system appears to have assumed increased importance, for it is to be noted that those acids which are reduced most easily with Cr^{2+} form complexes which are, in turn, reduced easily. We suggest that certain of the pyridinecarboxylato ligands may facilitate electron transfer by accommodation of the reducing electron on the pyridine ring itself, forming a radical-ion intermediate. The electron may enter the system through a noncoordinated carboxyl group, or through the ring nitrogen, if it is neither protonated nor alkylated. If neither route is open, the more usual mode of reduction, in which the incoming electron attacks the coordinated carboxyl, is to be expected,[25] but even here, in favorable cases, the pyridine ring may facilitate reduction by conjugative stabilization of the intermediate radical ion, e.g., XII.

XII
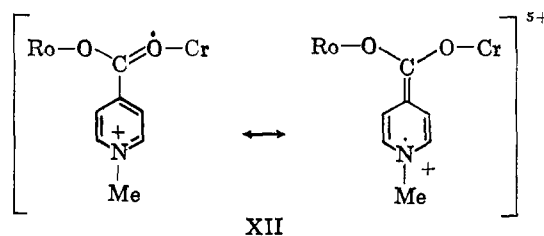
The latter description would seem to apply to the reduction of the N-methylated and the protonated 4-pyridinecarboxylato derivatives, for the rates lie well above those for the corresponding 2- and 3-carboxylato species,[26] being, at the same time, far below those for other reductions in the series in which a noncoordinated carboxyl, or a basic nitrogen (or both), is available. Moreover, as shown in Table VII, the 4-acid and its N-methyl derivative are reduced more easily by Cr(II) than are the corresponding 3-substituted analogs and the methylated 2-analog. Since the initial step in reduction of the pyridinecarboxylic acids with Cr^{2+} is almost certainly the transfer of an electron to the ring, forming a radical, we may infer that the same electronic factors which tend to stabilize radicals derived from the uncoordinated 4-carboxy

(25) Attack by Cr^{2+} on the π-orbital system of the ring is conceivable. The possibility is ruled out here, however, by invariable formation of a carboxylato- rather than an aquochromium(III) product, unless strict, and highly unusual, orientational requirements are associated with such an attack.

(26) Dr. R. T. M. Fraser (private communication) reports specific rates for reduction (0.2 M HClO₄, μ = 1) as 1.2 (methylated) and 0.95 (nonmethylated). His values, if increased by 15% to correct for differences in ionic strength, are in reasonable agreement with ours.

acids (in comparison with those derived from the 2-
and 3-systems) also stabilize radical-ions which inter-
vene in reduction of the respective $(NH_3)_5Co(III)$
complexes.[27]

Stabilization of a radical-ion intermediate, facili-
tating electron transfer by adjacent attack, comes to
light here, largely because other effects which have
been invoked to account for acceleration of electron-
transfer reactions in carboxylatocobalt(III) complexes
(i.e., remote attack, chelation, and increased negative
charge on the bridging group) are ruled out in the re-
duction of the methylated and protonated 4-pyridine-
carboxylato complexes.

The lesson to be learned is that specific rate of re-
duction is a reliable guide neither to the site of attack
nor the direction of electron flow. In particular, the
"fast" reduction of such complexes as the o-benzoyl-
benzoato (Table III) and the pyruvato[16] derivatives
could conceivably be rationalized by considering
stabilization of a radical-ion intermediate in attack on
the carboxylato group (e.g., XIII), rather than by
assuming transient chelation and electron transfer
through the carbonyl group. However, the difficulty

(27) N-Ethyl-4-carbethoxypyridinyl, a stable free radical closely related to
our N-substituted 4-carboxypyridine complexes, has been isolated recently
(E. M. Kosower and E. J. Poziomek, J. Am. Chem. Soc., 85, 2035 (1963)).

XIII
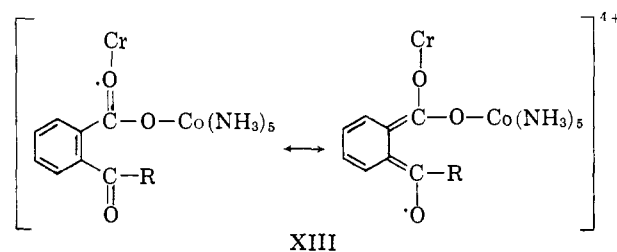
in reducing the carbonylbenzoato acids in our series,
in contrast to the ease in reducing many of the pyridine-
carboxylic acids, leads us to favor the radical-ion in-
termediate in rapid reductions of pyridinecarboxylato
complexes but not in reductions of the carbonyl com-
plexes. With the carbonyl complexes, a low-lying
vacant orbital, while not low enough to accept an
electron from Cr^{2+}, may nevertheless be involved in
the resonance transfer of an electron from the reducing
agent to the Co(III) center.

Tracer Experiments on Alkaline Hydrolysis of Some Oxalate Ammonia Cobalt(III) Complexes

BY CARLOS ANDRADE AND HENRY TAUBE

When $Co(NH_3)_5C_2O_4^+$ releases $C_2O_4^{2-}$ in alkaline solution at 25°, C–O bond breaking takes place in <1%
of the hydrolytic events, but some solvent oxygen is incorporated into the $C_2O_4^{2-}$ by exchange. At 100°. the
total incorporation of solvent oxygen is greatly decreased and the $C_2O_4^{2-}$ formed has very nearly the isotopic
composition of the original oxalate. When $Co(en)_2C_2O_4^+$ hydrolyzes, one C–O bond is broken for the release
of each oxalate, and extensive oxygen exchange accompanies the hydrolytic reaction. The observations made
with $Co(en)_2C_2O_4^+$ are interpreted on the basis that the first act of the hydrolysis, leading to opening of the
chelate, takes place by C–O scission and the second by Co–O scission.

In the course of work we are doing on oxygen ex-
change between oxalatoamminecobalt(III) complexes
and solvent in acid solution, we found it interesting—
and necessary—to do oxygen tracer experiments on the
hydrolysis of these complex ions. These tracer studies
are concerned with issues somewhat different from
those of the exchange experiments; for this reason as
well as the additional one that some of the effects are
quite striking, the results of the tracer experiments
appear to merit separate publication. Our results
would appear to have a bearing on studies which have
been done on the reactions of carboxylate chelate com-
plexes in alkaline solution.[1] They are also of interest
in comparison with results which we have obtained for
the methyl esters of oxalic acid and which will be de-
scribed in a forthcoming publication.

Experimental

Preparation of Complex Salts.—$[Co(NH_3)_5C_2O_4H](ClO_4)_2$ was
prepared[2] by the reaction of $[Co(NH_3)_5OH_2](ClO_4)_3$ with $H_2C_2O_4$

(1) D. H. Busch, D. W. Cooke. K. Swaminathan, and Y. A. Im, "Ad-
vances in the Chemistry of Coordination Compounds," Macmillan Com-
pany, New York, N. Y., 1961; D. H. Busch, K. Swaminathan, and D. W.
Cooke, Inorg. Chem., 1, 260 (1962).

in water. Analysis showed 20.20% oxalate (calcd., 20.37%)
and 46.17% ClO_4^- (calcd., 46.04%). $[Co(en)_2C_2O_4]ClO_4$ (not
necessarily anhydrous) was prepared from the chloride[3] by double
decomposition. The perchlorate salt was not analyzed, but a
report of analysis of $[Co(en)_2C_2O_4]Cl\cdot3H_2O$ showed 16.48% Co
(calcd., 16.52%).).

Procedure.—For all experiments, salts of normal isotopic
composition were used, added to aqueous alkaline solutions en-
riched in O^{18}. With the oxalato complexes as reactants, reaction
is so slow that the product complex undergoes serious deteriora-
tion (as in the case of the pentaammine complex), or it undergoes
exchange (as in the case of the bisethylenediamine complex)
during the course of the reaction, and isotopic analysis of only
the product oxalate is feasible. The solutions after the reaction
were filtered to remove solid material, then acidified to a faint
acid reaction, and a solution of $AgNO_3$ was added to precipitate
$Ag_2C_2O_4$. The $Ag_2C_2O_4$ was collected by filtration, washed with
water of normal isotopic composition and then with CH_3OH, and
dried at 40° for 12 hr. and then in a vacuum desiccator for 12 hr.
The CO_2 released by heating the solid to complete decomposition
was collected and analyzed by mass spectrometer (Atlas Model
M86). The isotopic composition of the solvent was determined
by the Anbar–Guttmann[4] method.

(2) P. Saffir and H. Taube, J. Am. Chem. Soc., 82, 13 (1960).
(3) A. Werner and A. Wilmos, Z. anorg. Chem., 21, 145 (1899).
(4) M. Anbar and S. Guttmann, Intern. J. Appl. Radiation Isotopes, 5,
233 (1959).