poured slowly into 30 ml of petroleum ether (30–60°) with stirring. Deuterated indene was recovered by extraction with petroleum ether followed by distillation. The nmr spectrum of the recovered indene revealed that only the C-1 and C-3 protons were deuterated, to an equal extent of 89%. This fact is rationalized by the rapid interconversion of the carbon–copper bond between C-1 and C-3 atoms, and it is quite compatible with nmr spectrum of *2*.

Reactions of Cyclopentadiene and Indene with Acetone Catalyzed by 1 and 2. A mixture of cyclopentadiene (or indene), **1** (or **2**), and acetone was stirred at room temperature for 24 hr. In one experiment, *tert*-BuNC (equimolar to **1**) was also added in the reaction mixture. As the reaction proceeded, an aqueous layer separated out. The organic layer was subjected to fractional distillation under reduced pressure. 6,6-Dimethylfulvene (**3a**), bp 60° (25 mm), was obtained from cyclopentadiene and acetone, and 1-isopropylideneindene (**3b**), bp 83–84° (0.5 mm), was formed from indene and acetone. The yields of **3a** and **3b** were determined by glpc using the peak area method to ensure accuracy. Identification of **3a** and **3b** was by ir and nmr spectra as well as elemental analysis. The identification data are summarized in Table V.

Reaction of Cyclopentadiene with Carbonyl Compounds Catalyzed by the Cu_2O–*tert*-BuNC System. A mixture of cyclopentadiene, carbonyl compound, Cu_2O, and isocyanide was stirred at room temperature for an indicated time (Table III). In some cases, the reaction was carried out in the presence of a solvent. The reaction mixture was worked up by a similar procedure to the reaction with **1** as catalyst, and the products were isolated by fractional distillation. The identification data are shown in Table V.

Reaction of Indene (or Fluorene) with Carbonyl Compounds Catalyzed by the Cu_2O–*tert*-BuNC System. An example follows. A mixture of 2.3 g (20 mmol) of indene, 48 mg (0.3 mmol) of Cu_2O, and 0.83 g (10 mmol) of *tert*-BuNC was heated at 60° for 1 hr with stirring under nitrogen. Cu_2O dissolved in the liquid reaction mixture to give a reddish purple solution. To this solution, 1.74 g (30 mmol) of acetone was added slowly. The reaction mixture was stirred at room temperature for 24 hr, and then was worked up by a procedure similar to that of the reaction with **2** as catalyst. The identification data of the products from several carbonyl compounds are summarized in Table V. Product **3g** of the table was purified by recrystallization from EtOH–benzene and **3h** was purified from EtOH.

Reaction of Diethyl Malonate with Isobutyraldehyde Catalyzed by the Cu_2O–*tert*-BuNC System. A mixture of reaction components was heated in a sealed test tube at 80° for 24 hr. Then the reaction mixture was distilled, and a fraction boiling at 70–80° (0.5 mm) was collected. By preparative glpc, the main product was isolated, which was identified as diethyl isobutylidenmalonate: yield 47%; nmr (in CCl_4) τ 8.90 (d, $(CH_3)_2CH-$, $r_i = 6$), 8.70 (t, CH_3CH_2-, $r_i = 6$), 7.60–7.10 (m, $\geqslant CH$, $r_i = 1$), 5.78 (q, CH_3CH_2-, $r_i = 4$), and 3.38 (d, $-CH=$, $r_i = 1$). *Anal.* Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.51, H, 8.73.

Dimerization of Crotononitrile and a Michael-Type Reaction Catalyzed by 1. A mixture of 1.34 g (20 mmol) of crotononitrile and 0.4 ml (0.4 mmol) of a 1 *M* solution of **1** in benzene was heated at 80° for 5 hr under nitrogen. The yield of dimer was determined by glpc analysis using an authentic sample.[4a] The yield of dimer was increased by the addition of an equimolar amount of *tert*-BuNC (see Table IV). The Michael-type addition reaction was carried out similarly and the reaction mixture was worked up according to the procedure of our previous study.[4c]

Electron Transfer through Organic Structural Units. IX. Reductions of Carboxylatopentaamminecobalt(III) Complexes with Copper(I)[1a]

Edward R. Dockal,[1b] E. Thomas Everhart, and Edwin S. Gould*

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44240.

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Abstract: Specific rates for reductions of carboxylatopentaamminecobalt(III) complexes with Cu(I) are only 10^{-7}–10^{-2} times as great as the corresponding rates for reduction with Cr(II), which is more strongly reducing by 0.56 V. Reductions, with Cu^+, of benzoato and ordinary aliphatic derivatives are so slow ($k < 0.01\ M^{-1}\ sec^{-1}$) that precipitation of copper metal from solution generally prevents quantitative measurements; for these, it is impossible to say whether reduction occurs by an inner- or outer-sphere mechanism. Neighboring hydroxyl groups are without apparent effect on rates, but reductions are enhanced by neighboring –SR. No evidence for Cu^+ reduction *via* remote attack is obtained with the aldehydobenzoato, nitrobenzoato, pyruvato, maleato, or 4-pyridinecarboxylato complexes, all of which are reduced rapidly by Cr^{2+}. Rapid reductions are observed with pyridine and pyrazine complexes in which $-COOCo^{III}$ lies α to a basic nitrogen; these almost certainly are inner-sphere reactions, proceeding through chelated transition states, for they no longer occur if the nitrogen is protonated or methylated. A first-order acid dependence for reduction of the pyrazine derivatives indicates that the tripositive forms of these complexes, in which the 4 nitrogen is protonated, are reduced somewhat more rapidly than the nonprotonated form. The 4-cinnolinecarboxylato complex V is the only complex in this series rapidly reduced by Cu^+ for which chelation is structurally excluded, and thus appears to be the sole example of reduction by remote attack. It is suggested that, because of the low reducing potential of Cu^+, remote attack requires a more basic lead-in atom and a more reducible mediating path than is the case for Cr^{2+} reductions.

Studies of bridging action by organic ligands in redox reactions have dealt principally with reductions by Cr^{II}.[2] This direction of emphasis has been advantageous in that the substitution-inert character of the resulting Cr(III) complexes has often provided critical information about reaction mechanism; however, the question remains as to whether the various effects observed require the presence of chromium or whether they are properties principally of the organic ligands.

The impetus for the present work was a report by Parker and Espenson,[3] who studied the rates of reduc-

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[1] (a) From the Ph.D. Thesis of E. R. Dockal, Kent State University, 1971. This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 2878-A3; (b) NSF Trainee, 1969–1971.

[2] (a) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969); see, however, (b) R. T. M. Fraser, *J. Amer. Chem. Soc.*, **84**, 3436 (1962); (c) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968).

tion of a number of inorganic cobalt(III) complexes with Cu^+, described methods for preparing, handling, and storing solutions of $CuClO_4$, and presented evidence that such reactions occurred, in some cases, by an inner-sphere mechanism (but not necessarily by ligand transfer).[4] Several obvious differences between Cr^{2+} and Cu^+ make this extension of interest. In aqueous acid, Cu^+ is less strongly reducing (by about 0.56 V) than Cr^{2+}, but the smaller charge on Cu^+ should result in a smaller electrostatic barrier to reaction with a positively charged oxidant. Since the coordination number of Cu^+ is lower (probably four), we might anticipate steric effects to be less important than in Cr(II) reductions. Moreover, in contrast to Cr(II), which undergoes oxidation with no change in coordination number, the oxidation of copper(I) almost certainly involves an increase in covalency, although this need not occur during activation.

This investigation, the results of which supersede those presented in an earlier preliminary report,[5] points both to similarities and differences when the reactivity patterns for Cu^+ reductions are compared to those for reductions by Cr^{2+}.[6] In particular, although a number of instances arise in which Cu^+ reductions, like Cr^{2+} reductions, are accelerated by chelation, evidence for remote attack all but disappears from the Cu^+ series.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,[6b,7] chloropentaamminecobalt(III) perchlorate,[6b] and chromous solutions[6b] were prepared as described. Concentrations of Cr(II) solutions were determined by adding an excess of chloropentaamminecobalt(III) perchlorate under N_2, diluting the solution tenfold with concentrated HCl, and reading the absorbance of $CrCl_4^{2-}$ at 692 nm.[6b] Lithium perchlorate was prepared by neutralizing reagent grade $HClO_4$ with reagent grade Li_2CO_3 and was recrystallized from water before use. Copper(II) perchlorate solution was prepared by dissolving $CuCO_3$ in $HClO_4$, filtering, boiling off the CO_2 formed, then diluting to the desired concentration. Those cobalt(III) complexes not available from previous studies[6a] were, for the most part, prepared from the aquopentaammine perchlorate in aqueous media as described.[6b]

A newer and, in our hands, more widely applicable procedure was used in preparation of the pyruvato, acetylenedicarboxylato, and aldehydobenzoato derivatives. The carboxylic acid (20 mmol) is dissolved or suspended in 8 ml of diethylene glycol at 70–80°. Stirring is maintained while 750 mg of powdered carbonatopentaamminecobalt(III) nitrate[7] is added, then continued while the preparation is heated at 70° for 25 min. The mixture is added to a separatory funnel containing 10 ml of water, 1 ml of concentrated $HClO_4$, and 200 ml of ether, then shaken, and the ether layer, which contains much of the unreacted carboxylic acid and some diethylene glycol, is discarded. After two additional extractions with 150-ml portions of ether, the aqueous layer is separated, air is drawn through it for 10 min to remove dissolved ether, and 3 ml of concentrated $HClO_4$ is added. The preparation is allowed to stand for 2 hr at −5°, after which the precipitated complex perchlorate is filtered off, pressed dry, and recrystallized from 5–10 ml of hot water. This procedure is more rapid than the more usual preparation from the aquo perchlorate in water;[6b] it is more convenient and results in much higher yields than the preparation from the aquo perchlorate and the carboxylato salt in dimethylformamide.[6a] It is particularly suited to complexes derived from very lipophilic carboxylic acids, from aminobenzoic acids having high values of pK_A, from amido-substituted acids, or from oxidizable acids which do not survive treatment with Co(III) species in hot aqueous solutions. The preparation, as described, proceeds through the aquopentaamminecobalt(III) complex, which may be isolated in good yield if the heating period is shortened to only 5 min, but does not work well if the purified aquo perchlorate is used as starting material.[8]

Kinetic Studies. In very nearly all kinetic experiments a 5- to 20-fold excess of Cu(I) was used; Cu(I) was generated in the reaction cell by addition of $Cr(ClO_4)_2$ to oxygen-free $Cu(ClO_4)_2$.[3] It was necessary to maintain more than a threefold excess of Cu^{2+} over Cr^{2+} to avoid formation of copper metal. Although Cu^+ solutions are thermodynamically unstable to disproportionation, solutions of concentration below 0.001 *M* could be kept from one to several hours at 25° when care was taken to avoid metallic surfaces, and solutions in which (Cu^+) fell between 10^{-3} and 10^{-2} *M* could be kept from 10 to 60 min.[9] Initial concentrations of Co(III) were 7×10^{-5}–1×10^{-3} *M*. Reactions having specific rates less than 1 M^{-1} sec^{-1} were generally carried out in a 1.0-cm cylindrical cell, those with specific rates greater than unity in a 10.0-cm cell. Wherever acid dependency was suspected, rates were followed at three or more acidities in the range 0.1–1.0 *M*. For most runs, ionic strength was kept near 1.1 *M* by addition of $LiClO_4$. Reaction temperatures were 25.0 ± 0.1°.

The progress of reactions was followed at 502 nm by using the 0–0.2 absorbance unit slidewire of the Cary 14 spectrophotometer. Reactions were first order in both Cu(I) and Co(III) and were not observably affected by changes in (Cu^{2+}). Provided precipitation of copper did not occur, rate constants evaluated from points during a single run generally agreed to within 4%, whereas those obtained from different runs agreed to better than 8%. When copper precipitated after partial reduction of Co(III), specific rates were estimated from initial slopes; such values are reliable only to a single significant figure. Finally, for a considerable number of slow reactions where precipitation occurred before a measurable drop in absorbance, only upper limits to specific rates could be estimated.

Results and Discussion

Representative kinetic data are given in Table I. Specific rates for Cu^+ reductions are compared to values for Cr(II) reductions in Table II, and complexes for

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(3) O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 1968 (1969).

(4) This distinction arises from the difference between Co^{II}–X–Cu^{II}, the dinuclear metal species formed directly after the act of internal electron transfer in inner-sphere Cu^+ reductions, and Co^{II}–X–Cr^{III}, formed in Cr^{2+} reductions. Since chromium(III) is substitution inert, dissociation of the latter intermediate gives Cr^{III}–X and Co^{2+}, whereas, as pointed out by Parker and Espenson,[3] Cu(II) centers are more substitution labile than Co(II). Hence, dissociation of the copper species should yield principally Co^{II}–X and Cu^{2+} as initial products.

(5) S. A. Kazmi and E. S. Gould, Abstracts of the Second Central Regional Meeting, American Chemical Society, Columbus, Ohio, June 4, 1970, p 47.

(6) (a) E. S. Gould, *J. Amer. Chem. Soc.*, **87**, 4730 (1965); **88**, 2983 (1966); (b) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964); (c) R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

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

(8) This preparation is a modification of that described briefly by M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, **92**, 5533 (1970), in which the same reagents are allowed to react in dimethylformamide. We find that although reaction in this solvent sometimes gives the desired carboxylato complex, it more often yields, as the main product, the DMF–pentaammine complex.

A preparation of carboxylatopentaammine complexes from the corresponding carboxylic anhydrides has been described by L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968). In comparing this method with the more usual preparations from the parent carboxylic acids, we find that reaction through the anhydride works best for anhydrides of just those carboxylic acids of low molecular weight which react without complication in water. We have found no case as yet where reaction through the anhydride is successful and reaction through the acid fails, but have observed a number of examples of the reverse situation (*e.g.*, preparations of the complexes of 2- and 4-aldehydobenzoic and 2- and 4-benzoylbenzoic acids.)

(9) These time limits refer to solutions 0.1–1.2 *M* in $HClO_4$; precipitation was much more rapid from solutions of higher pH. Use of hypodermic syringe needles with chrome-plated hubs for addition of acidic $Cr(ClO_4)_2$ to Cu(II) led almost invariably to the precipitation of a brown solid, almost certainly metallic copper, during the kinetic runs; needles with plastic hubs largely eliminated this problem. Since metal surfaces catalyze the disproportionation of Cu^+, it was necessary to avoid contact of the needle with the solution when Co(III) solutions were added to the optical cell. Premature precipitation of copper metal was invariably observed when cells having slightly scratched inner surfaces were used. Moreover, cells were observed to become increasingly capricious with respect to such precipitation with repeated use, even when no surface scratches were visible. These difficulties, presumably reflecting nucleation phenomena, could be eliminated only in part by prolonged cleaning of cells with concentrated HNO_3 between kinetic runs.

Table I. Kinetic Data for Copper(I) Reductions of Carboxylatopentaamminecobalt(III) Complexes

Organic ligand	(Cu^{2+}), $M \times 10^3$	(Cu^+), $M \times 10^3$	(H^+)	k[a]
Formato	26.0	8.9	2.0[b]	0.029
	26.0	8.9	1.0	0.034
S-Benzylthioglycolato	26.0	7.8	2.0[b]	0.074
	25.0	8.5	1.17	0.070
	26.0	7.1	0.25	0.073
Oxalato	18.6	2.23	1.0	0.084
	18.6	2.23	0.5	0.12
	18.6	2.23	0.25	0.19
	19.6	1.11	0.10	0.36
2-Pyridinecarboxylato	39.4	6.4	1.0	0.12
	19.6	1.12	0.5	0.23
	26.0	6.9	0.24	0.44
	19.5	1.02	0.10	1.1
2,3-Pyridinedicarboxylato	18.1	1.92	1.0	1.2
	17.8	2.23	0.50	1.6
	17.9	2.14	0.25	2.6
	17.8	2.23	0.10	3.1
2,4-Pyridinedicarboxylato	17.8	2.20	1.0	0.60
	18.2	1.79	0.50	1.06
	19.9	0.86	0.25	1.39
	19.9	0.86	0.10	2.4
2,5-Pyridinedicarboxylato	18.6	2.14	1.0	1.3
	19.8	0.95	0.75	1.5
	19.9	0.86	0.50	1.6
	19.7	1.07	0.25	2.0
	19.9	0.86	0.10	2.0
	19.7	1.17	0.10	2.3
2,6-Pyridinedicarboxylato	19.9	0.89	1.0	26
	19.9	0.89	0.50	29
	19.9	0.89	0.25	31
	19.9	0.89	0.10	38
Pyrazinecarboxylato	20.0	0.40	1.0	36
	19.9	0.87	0.25	18
	19.8	0.90	0.10	16
2,3-Pyrazinedicarboxylato	19.9	0.89	1.0	3.3
	19.9	0.89	0.50	2.0
	19.2	0.86	0.25	1.3
	19.2	0.86	0.10	1.03
4-Cinnolinecarboxylato	19.9	0.89	2.0[b]	29
	19.9	0.89	1.0	44
	19.9	0.89	0.75	53
	19.9	0.89	0.50	77
	19.9	0.89	0.10	>250
Pyruvato	18.6	2.23	1.0	0.03[c]
S-Phenylthioglycolato	26.0	7.1	1.0	0.02[c]
	25.0	6.9	0.25	0.02[c]
Acetylenecarboxylato	18.6	2.23	1.0	0.01[c]
	18.6	2.23	0.25	0.01[c]
Acetylenedicarboxylato	16.3	4.4	1.0	0.01[c]
	19.7	1.1	0.1	0.01[c]
β-(3-Pyridyl)acrylato	19.7	1.1	1.0	0.007[c]
	19.7	1.1	0.1	0.007[c]

[a] Specific rates in M^{-1} sec^{-1} at 25°; $(Co^{III})_0 = 8 \times 10^{-5}$–$1 \times 10^{-3}$ *M;* Co^{III} added to Cu^I; $\mu = 1.1$, unless otherwise indicated. [b] Reactions in strongly acid solution; ionic strength very nearly equal to (H^+). [c] Specific rates estimated from initial rates.

Table II. Specific Rates for Copper(I) and Chromium(II) Reductions of Pentaamminecobalt(III) Complexes, $RCo(NH_3)_5$[a]

R	k_{Cu^+}	$k_{Cr^{2+}}$
Aquo[b]	0.003	
Hydroxo[b]	800	1.5×10^5
Chloro[b]	7.5×10^4	6×10^5
β-(3-Pyridyl)acrylato (I)	0.007	1.1[c]
Acetylenecarboxylato	0.01	1.0
Acetylenedicarboxylato	0.01	
S-Phenylthioglycolato	0.02	0.91
Pyruvato (II)	0.03	1×10^4
Formato	0.034	7.2
S-Benzylthioglycolato (III)	0.072	5.2
Oxalato	$0.058 + [0.03/(H^+)]$	$100 + [40/(H^+)]$[d]
2-Pyridinecarboxylato	$0.12/(H^+)$	$36/(H^+)$[e]
2,3-Pyridinedicarboxylato	3.6[f]	
2,4-Pyridinedicarboxylato	3.4[f]	$>4 \times 10^3$
2,5-Pyridinedicarboxylato	2.5[f]	$>2 \times 10^2$
2,6-Pyridinedicarboxylato	25[g]	210[g]
Pyrazinecarboxylato (IV)	$13 + 23(H^+)$	$>1 \times 10^3$
2,3-Pyrazinedicarboxylato	$0.7 + 2.5(H^+)$	$>7 \times 10^2$
4-Cinnolinecarboxylato (V)	$12 + [33/(H^+)]$	$>1 \times 10^3$

[a] Specific rates in M^{-1} sec^{-1} at 25°, $\mu = 1.1$. Rates for Cr(II) reductions taken from ref 2 and 6; rates for Cu(I) reductions of organic complexes taken from this work. [b] See ref 3. [c] A. Liang, unpublished results, Kent State University, 1971. [d] See ref 2c. [e] In the present study, we find the specific rate of reduction of the 2-pyridinecarboxylato complex by Cr(II) to be 36 M^{-1} sec^{-1} in 1.0 *M* $HClO_4$, 76 in 0.5 *M* $HClO_4$, and 155 in 0.25 *M* $HClO_4$ (25°, $\mu = 1.1$). The coefficient of the inverse-acid term here recorded is taken as preferred over a lower value reported in an earlier paper in this series (ref 6b), which was obtained under conditions where less than one-third of the total reaction was followed. [f] Specific rate for the dipositive (monoprotonated) form(s) of these complexes, obtained from extrapolation of a Hofstee-type plot (see text). [g] Value for 1.2 *M* $HClO_4$, $\mu = 1.2$.

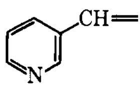
Table III. Pentaamminecobalt(III) Complexes, $RCo(NH_3)_5$, Reduced Immeasurably Slowly with Cu(I)[a]

R	$k_{Cu^+} <$	$k_{Cr^{2+}}$
N-Methyl-2-pyridinecarboxylato	0.01	0.087
Benzoato	0.002	0.15
Salicylato	0.004	$0.11 + [0.03/(H^+)]$
Acetato	0.004	0.35
3-Pyridinecarboxylato	0.007	0.10
N-Methyl-4-pyridinecarboxylato	0.004	1.4
Glycolato	0.006	3.1
Lactato	0.005	6.7
4-Pyridinecarboxylato	0.007	$1.1 + [0.01/(H^+)]$
o-Aldehydobenzoato	0.01	46
o-Nitrobenzoato	0.003[b]	60[c]
p-Aldehydobenzoato	0.01	$40 + [400(H^+)]$
Mucochlorato (VI)	0.01	
Maleato (VII)	0.02	200
5-Uracilcarboxylato (VIII)	0.01	>600

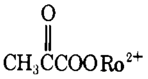
[a] Specific rates and upper limits in M^{-1} sec^{-1} at 25°, $\mu = 1.1$. Rates for Cr(II) reductions taken principally from ref 2 and 6; upper limits for Cu(I) reductions taken from this work. [b] This upper limit applies also to reductions of the meta and para nitro complexes. [c] Estimated value for reduction in 1.2 *M* $HClO_4$, obtained by combining data on rates of absorbance changes with data for distribution of reducing capacity between Co(III) and ligand.[6a]

which only upper limits for Cu(I) reductions could be obtained are listed in Table III. Variations between these upper limits cannot be taken as significant, for they reflect, in large part, irreproducible[9] variations in the time interval between the mixing of reagents and the precipitation of elemental copper.

General Trends. Evidence for Inner-Sphere Reductions. The specific rate for Cu^+ reduction of $Co(en)_3{}^{3+}$, where a bridge mechanism is structurally excluded, has been reported as $\leqslant 4 \times 10^{-4}$.[3] Upper limits listed for the complexes in Table III (each of which reacts with Cr^{2+} by an inner-sphere path in one or more of its variants) lie close enough to this figure so that we cannot, with confidence, choose between possible paths for Cu^+ reductions of members of this group. The Cu^+ reductions of many of the organic complexes in Table II are much more rapid (by one to five powers of ten) than the upper limit for $Co(en)_3{}^{3+}$. Although rate increases of this magnitude have, in the past,[6a] been taken as evidence of inner-sphere reduction, such indications can be treacherous.[10] We suggest that a more convincing case for bridging emerges from certain similarities in patterns between the Cr(II) and Cu(I) series; in particular, the occurence of an inverse-acid term in the reduction of the oxalato complex, the kinetic predominance of such a term for the 2-pyridinecarboxylato complex, and the acceleration of reduction by incorporation of an *S*-benzylthio group α to the bound carboxyl (III). Moreover, the acid dependencies observed for reductions of the various pyridinedicarboxylato complexes (Table I) are difficult to reconcile with an outer-sphere path.



I

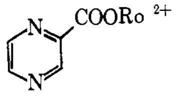


$CH_3\overset{O}{\overset{\|}{C}}COORo^{2+}$

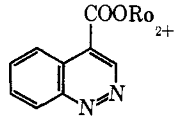
II

$C_6H_5CH_2SCH_2COORo^{2+}$

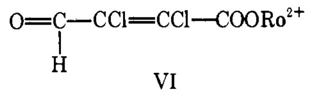
III



IV

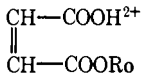


V



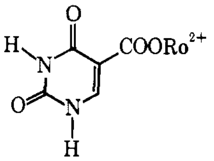
$O{=}\underset{H}{\underset{|}{C}}{-}CCl{=}CCl{-}COORo^{2+}$

VI



$\begin{array}{l} CH{-}COOH^{2+} \\ \| \\ CH{-}COORo \end{array}$

VII



VIII

Ro = "roseo" = $(NH_3)_5Co^{III}$

In all cases where direct comparison between the two series is possible, Cu^+, thermodynamically the weaker reducing agent, is, as expected, oxidized the more slowly. In the absence of complicating factors, values of the ratio $k_{Cr^{2+}}/k_{Cu^+}$ appear to cluster about 10^2, but this ratio may be modified sharply by structural features which favor reduction by one reducing center, but not by the other.

One searches in vain, within the Cu^+ series, for substantial acceleration of reductions of complexes having a carbonyl group in conjugation with the bound carboxylate. Such accelerations, observed, for example, for the Cr^{2+} reductions of the *o*- and *p*-formylbenzoato and pyruvato complexes, were taken, in at least some cases correctly,[2a] as early evidence for electron transfer through an extended section of an organic ligand, *i.e.*, remote attack. It is now generally recognized that a ligand allowing remote attack must itself be reducible, although its reduction need not occur during reaction of its Co(III) complex.[6a,b] The standard reduction potentials of such carbonyl-substituted ligands approach 0.2 V,[11] *i.e.*, very near that for the Cu^{II}/Cu^{I} couple in an aqueous solution where the $(Cu^{2+})/(Cu^+)$ ratio is 10. With potentials balanced this closely, the apparent erosion of remote attack as a path for these Cu^+ reductions occasions no astonishment. For such carbonyl complexes, the ratio $k_{Cr^{2+}}/k_{Cu^+}$ greatly exceeds the "normal" value of 10^2.

Acceleration by Neighboring Oxygen, Sulfur, and Nitrogen. There is a growing array of evidence that reductions in the Cr^{2+} series may be facilitated by chelation. In a number of instances, a primary Cr(III) product has been identified as a chelate,[6b,c,12] indicating a chelated transition state, both in such cases and, by analogy, in reactions of related oxidants having chelating substituents and exhibiting similarly enhanced reaction rates. With but a single exception, each of the faster Cu^+ reductions in Table II involves a Co(III) complex having a group in a position which allows chelation of Cu(I) as it attacks carboxyl. The implication here is that acceleration *via* chelation is a mechanistic feature common to the two reduction series. However, chelation with Cu^+ appears to be significantly more selective. Neighboring hydroxyl which, whether alcoholic[6c] or phenolic[12a] in character, opens a rapid chelated path for Cr(II) reduction, is without apparent effect in the Cu^+ reductions; moreover, the very striking accelerations associated with neighboring –COOH in the Cr(II) reduction of the maleato complex VII[12b] and with neighboring C=O in reduction of the uracilcarboxylato complex VIII[6a] appear to have no counterpart in the Cu^+ series. For complexes in this group, values of the ratio $k_{Cr^{2+}}/k_{Cu^+}$ fall in the range 10^3–10^5.

On the other hand, we observe enhancement of Cu^+ reduction by neighboring sulfur with the *S*-benzylthioglycolato complex III, by neighboring $-COO^-$ in the inverse-acid term for the oxalato complex, and, most dramatically, by neighboring nitrogen with the various pyridine- and pyrazinecarboxylato complexes. If, as is reasonable, we associate these accelerations with chelation in the activated complex, participation by α-SR, but not α-OH, in the Cu^+ reductions is of particular interest since it is in accord with Pearson's classification[13] of sulfur-containing donors and Cu^+ as complementary "soft" reagents.[14] In general, it appears that participation in inner-sphere reduction requires a more basic center for Cu^+ reactions than for Cr^{2+}.[15]

Evidence for chelation during reduction by Cu^+ is strongest for the pyridine- and pyrazinecarboxylato derivatives in Table I. Note that, in contrast to the Cr(II) series, Cu^+ reductions of complexes in these classes are slow unless the bound carboxyl lies α to a basic nitrogen; in particular, no accelerations are observed for γ-carboxy complexes[16] or for complexes in which the nitrogen has been blocked by methylation.

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[10] See, for example, E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968).

[11] For a summary of reduction potentials of carbonyl systems, including pyruvate (E_0 = 0.23 V), see W. M. Clark, "Oxidation-Reduction Potentials of Organic Systems," Williams and Wilkins, Baltimore, Md., 1960, pp 497–505. No potentials for aldehydobenzoic acids appear to have been reported, but as aldehydes, they may be assumed to have values slightly greater than 0.2 V at 25°.

[12] (a) A. Liang and E. S. Gould, *J. Amer. Chem. Soc.*, **92**, 6791 (1970); (b) M. V. Olson and H. Taube, *Inorg. Chem.*, **9**, 2072 (1970).

[13] See, for example, R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[14] Measurable, but less intense, acceleration of Cr(II) reductions resulting from incorporation of α- or β-SR groups in aliphatic carboxylatopentaamminecobalt(III) derivatives[6a] has likewise been attributed to chelation in the activated complex, but this has not yet been satisfactorily demonstrated. For more dramatic effects of neighboring sulfur in related electron-transfer systems, see R. H. Lane and L. E. Bennett, *ibid.*, **92**, 1090 (1970).

[15] The lack of evidence for remote attack in the Cu^+ reduction of the *o*- and *p*-nitrobenzoato complexes (Table III), despite the ease with which nitro compounds are reduced,[11] is in agreement with this generalization.

[16] Unpublished experiments by J. Barber, Kent State University, 1969–1971, indicate that the relatively small inverse-acid term for the

Pyridine Derivatives. Several distinct types of acid dependency appear among the heterocyclic entries in Table II. The simplest is the one-term inverse-acid rate law observed for the reductions of the 2-pyridinecarboxylato derivative, both by Cu^+ and by Cr^{2+}. This implies not only that observable reduction requires the deprotonated form of this complex, but also that the (small) concentration of this form is, in the acidity range studied, inversely proportional to (H^+); that is, that it is derived from an acid having a pK value well above 2. The estimated pK_A, 4.0, for the protonated form of this complex[17] is consistent with the observed behavior. The tabulated rate constant for this Cu^+ reduction, 0.12 sec^{-1}, corresponds to a specific rate of 1200 M^{-1} sec^{-1} for reduction of the complex in its basic form.[18]

Reductions, by Cu^+, of the pyridinedicarboxylato complexes (Tables I and II) vary in a more complicated fashion with acidity. These do not conform to a two-term acid rate law, frequently governing Cr(II) reductions, in which reaction rates increase sharply at low acidities but approach a constant (acid-independent) rate at high acidity. Instead, specific rates appear to approach a constant value at the low-acid limit of the range studied, but fall sharply with increased acidity at the high-acid end. This mode of variation indicates, again, that the oxidant is present in (at least) two forms, an unreactive acidic species and its reactive conjugate base; however, for these complexes, the two species exist in comparable concentrations in the acidity range studied. For this situation, which corresponds to the rate law

$$\text{rate} = \frac{k(\text{Cr}^{\text{II}})(\text{Co}^{\text{III}})}{1 + (\text{H}^+)/K_A} \qquad (1)$$

both the limiting rate, k, and an acidity constant K_A of the protonated species may be obtained conveniently by plotting (rate)(H^+) *vs.* rate.[19] Such plots are shown in Figure 1. Values for limiting specific rates (obtained as intercepts of such plots) are included in Table II, whereas acidity constants (obtained from the slopes) are listed, as pK_A's, in Table IV. The negative pK_A values for the 2,5- and 2,6-dicarboxy derivatives are in accord with the upper limit of 0.0 reported for these complexes.[6b]

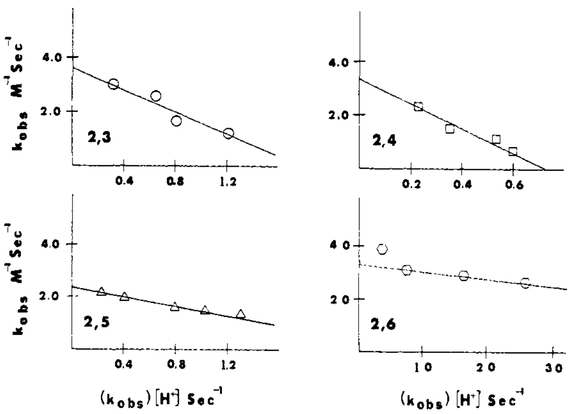


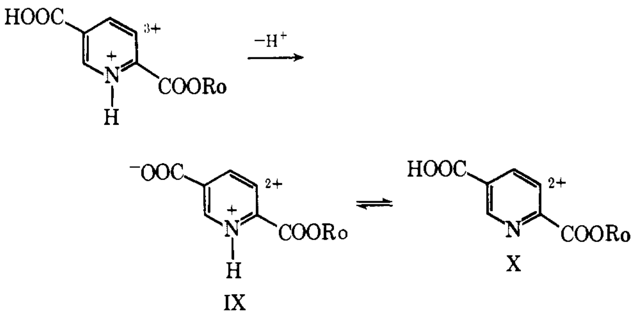
Figure 1. Hofstee-type plots, (H^+)k_{obsd} *vs.* k_{obsd} (Cu^+ reductions of 2,3-, 2,4-, 2,5-, and 2,6-pyridinedicarboxylato complexes; 25°; μ = 1.1; see Table I). The slopes of the lines shown lead to the acidity constants listed in Table IV for these $Co(NH_3)_5$ complexes. Intersections of the lines with the ordinate give the limiting specific rates for reduction of these complexes (Table II).

Note that the extrapolated specific rates for the pyridinedicarboxylato entries fall well below the value 1200 M^{-1} sec^{-1} calculated for the basic form of the 2-monocarboxylato species. The differences are far too great to be attributed reasonably to steric effects associated with the second carboxyl; nor is it likely that they are due, in the main, to basicity differences, for the 2,6 compound, the least basic of the group, reacts more rapidly than its isomers. Our data, however, appear to confirm the partition of the deprotonated (dipositive) dicarboxy complexes into two forms, *i.e.*, a zwitterion-like species, IX, which is reduced with difficulty, in rapid equilibrium with its tautomer, X, which may participate in chelation and is therefore reduced with ease. The specific rates, obtained by extrapolation, of the deprotonated forms of the dicarboxy complexes indicate that equilibria of the type IX $\rightleftharpoons$ X greatly favor the less active zwitterionic species, in analogy with the known distribution between microspecies of the isomeric noncoordinated pyridinecarboxylic acids in water.[20] The

Table IV. Acidity Constants for Pyridinedicarboxylatopentaamminecobalt(III) Complexes, $RCo(NH_3)_5$[a]

R	pK_A[b]
2,3-Pyridinedicarboxylato	0.28
2,4-Pyridinedicarboxylato	0.70
2,5-Pyridinedicarboxylato	−0.15
2,6-Pyridinedicarboxylato	−0.56

[a] Values refer to acidities of the O-coordinated, N-protonated tripositive forms of the complexes. For evidence that Co^{III} is bound to the 2-COOH group in each case, see ref 22. [b] 25°; μ = 1.1; obtained from the slopes of Hofstee plots derived from variation, with acidity, of rates of reduction by Cu^+ (see text).



Cr(II) reduction of the 4-pyridinecarboxylato complex should be revised downward. The inverse-acid dependence which was originally taken[6b] as a basis for calculation of this term has been shown to be due, in part, to an inverse-acid-dependent autocatalysis which appears to be confined to a small number of γ-substituted pyridine derivatives. However, even when correction is made for this effect, the inverse-acid term in the rate law does not disappear.

(17) This pK_A, which refers to μ = 1.1, is obtained by downward correction of the pK_A value 4.5, recorded for μ = 3.0,[6b] by 0.5 unit, in accord with the variation in apparent pK_A with ionic strength observed for carboxylato complexes of this type: E. S. Gould and H. Taube, unpublished experiments, Stanford University, 1963.

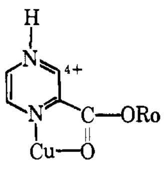
(18) Reservations associated with high apparent specific rates obtained in this way have been discussed by M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, 91, 6977 (1969); and by Liang and Gould.[12a]

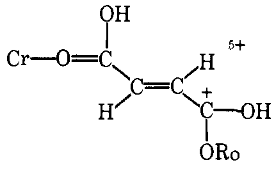
(19) B. H. J. Hofstee, *Nature (London)*, **184**, 1296 (1959); see also M. Dixon and E. C. Webb, "Enzymes," 2nd ed, Academic Press, New York, N. Y., 1964, p 69.

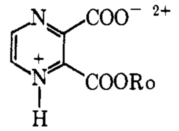
(20) R. W. Green and K. H. Tong, *J. Amer. Chem. Soc.*, **78**, 4896 (1956), report that 90–95% of the molecules of pyridinecarboxylic acids exist in aqueous solution at 25° as the zwitterionic forms. The pyridinedicarboxylato complexes in the present study may, in principle, be derived from these by incorporation of a $-COOCo(NH_3)_5^{2+}$ substituent, and

recorded pK_A's refer to loss of H^+ from the tripositive forms of the dicarboxy complexes. As expected, the 2,6 complex, in which the -COOH group lies α to NH^+, is the strongest acid of the group, whereas the 2,4 complex, in which -COOH lies γ to NH^+, is the weakest.[21] The Hofstee plot for the 2,6-dicarboxylato complex curves upward at the highest pH studied. The effect, although slight, lies well outside of experimental error and suggests reduction of an additional Co(III) species, possibly the unipositive cation formed by removal of two protons. Similar deviations for the (less acidic) dicarboxylato isomers would occur at still lower acidities and would not be observed under our experimental conditions.[22]

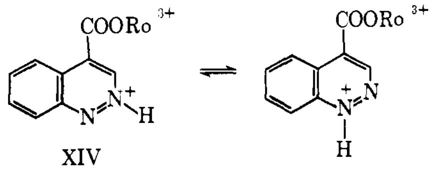
Pyrazine and Cinnoline Derivatives. Evidence for Remote Attack. A third acidity relationship governs the reduction kinetics of the pyrazinecarboxylato derivatives (*e.g.*, IV), the only complexes in this series for which rates increase with (H^+). Reductions of both the mono- and dicarboxylato species conform to a two-term rate law which contains, in addition to an acid-independent term, a term first order in (H^+). There are thus two kinetic paths for these reductions, with the protonated path being somewhat the more rapid. In the absence of pK_A data for these complexes, the value for the monocarboxylato complex is estimated as -0.5,[23] and the dicarboxylato complex may be assumed to be an even stronger acid.[6b] The predominant form of the monocarboxylato derivative in the acidity range studied is then the nonprotonated cation, IV, which, as expected, is reduced readily *via* a chelated route, corresponding to the observed acid-independent contribution. The first-order acid term, indicating additional rapid reduction *via* the protonated transition state, XI, brings to mind the type of protonated precursor complex (*e.g.*, XII) suggested specifically for the acid-dependent Cr(II) reductions of a number of carboxylato complexes thought to proceed *via* remote attack.[2a,24] To the extent that such a protonated path is symptomatic of electron transfer through extended systems, the behavior of the pyrazine systems suggests that the preferred path for such transfer is through neighboring nitrogen, which is thus acting as a "lead-in" atom,[2a] as well as in a chelating capacity. Combination of the rate constant for the H^+-dependent path, 23 M^{-2} sec^{-2}, with the estimated acidity constant for the monoprotonated complex yields a specific rate near 10^2 M^{-1} sec^{-1} for reduction of this tripositive species. The picture here proposed for reduction of the pyrazinecarboxylato complex probably applies also to the dicarboxylato complex, for which, however, both observed paths are significantly slower. As in the pyridine series, the retarding action of the second carboxyl may be attributed, at least in part, to the distribution of both the dipositive and protonated tripositive Co(III) species between reactive chelating cations and inactive tautomers (*e.g.*, XIII).[25]


XI


XII


XIII

A fourth type of hydrogen ion dependence is observed for the 4-cinnolinecarboxylato complex V. The reduction, with Cu^+, of this derivative is immeasurably rapid (under our conditions) at pH 1 but in 0.5–2.0 M $HClO_4$ follows a binomial rate law, containing both an inverse-acid and an acid-independent term, thus resembling the type found for the oxalato and aquopentaammine[3] complexes and, in the Cr(II) series, for a large number additional species having acidic centers. More important, this cinnoline derivative is the only complex rapidly reduced by Cu^+ for which a chelated transition state is structurally excluded. From the manner in which the reduction behavior of this complex stands apart from that of the other nonchelating oxidants examined, it is difficult to avoid the conclusion that here, and only here, reduction is occurring *via* remote attack. The observed rate law points to two active species, the nonprotonated complex V, which predominates at low acidities, and the monoprotonated (at N-2) cation XIV, which would be expected to be


XIV XV

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it would not be surprising if such a substitution, together with appropriate modification of the medium to accommodate the necessary counterions, favored the zwitterionic forms to an even greater degree.

(21) For a similar, but more detailed, analysis of pyridinecarboxylato systems, see I. D. Hansen, E. A. Lewis, J. J. Christensen, R. M. Izatt, and D. P. Wrathall, *J. Amer. Chem. Soc.*, **93**, 1099 (1971).

(22) The observed rapid reductions of the pyridinedicarboxylato complexes in Table II confirm an earlier suggestion[6a] that during the preparations of these complexes, Co(III) becomes attached to the 2-carboxyl group. Except in the case of the 2,6 complex, they do not rule out the formation of a mixture of mononuclear derivatives, of which only the 2-$COOCo(NH_3)_5$ complex would be expected to be reduced at a measurable rate under our conditions. However, since the absorbance changes occurring in the reductions of the 2,3, 2,4, and 2,5 complexes are not measurably less than those for the 2,6- and the 2-monocarboxy complexes, it appears that in each case we are dealing predominantly, if not exclusively, with a 2-$COOCo(NH_3)_5$ derivative.

(23) The pK_a value of pyrazine itself, 0.7 (A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1968, p 439), has been corrected downward by 1.2 units to take into account the acid-strengthening effect of the -COORo group, obtained from studies in the pyridine series.[6b]

(24) D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961). There has been speculation as to the role of the "extra" hydrogen ion in this path. For a suggested transition state such as XII, it is not clear whether the H^+ facilitates reduction electrostatically by easing the passage of negative charge from the lead-in atom to the oxidizing center, whether it improves conjugation between these centers, whether it lowers the energy of the unoccupied molecular orbital involved in the electron-transfer process, or whether some combination of these effects is operative. The first two of these possibilities would appear to be ruled out for transition state XI, for the added H^+ lies outside of the electron-transfer path and its attachment cannot reasonably be expected to improve conjugation within the system. The third explanation, an effect on the energy of the unoccupied molecular orbital, remains, but at the present stage of development of this subject, it is sufficiently vague so that it cannot be confirmed directly.

(25) The incorporation of a second carboxyl group almost certainly increases steric crowding, and more pronounced departures from planarity in chelated transition states would be expected. Although approach to planarity is thought to affect the rates of a number of Cr(II) reductions,[6a,b] it is doubtful that this factor is important in the present system, for Cu(I) reductions of the 2,3-, 2,4-, and 2,5-pyridinedicarboxylato complexes proceed at very similar rates (Table II).

in equilibrium with its tautomer, **XV**. The latter is protonated at N-1 with the basic nitrogen not conjugated with $-\text{COOCo}^{\text{III}}$; it is therefore much less readily reduced.

Our evidence that remote attack in reduction by Cu^+ is confined, thus far, to a single heterocyclic species appears to reflect the circumstance that of the ligands studied, only the cinnolinecarboxylato system offers the combination of basicity, conjugation, and, most important, ready reducibility now thought to be necessary for electron passage through extended organic systems. Although cinnoline derivatives have long been known to be easily reduced,[26] no standard potentials appear to have been reported; however, as azobenzene-like bases, they may be assumed to have values of about +0.4 V,[11] *i.e.*, more strongly oxidizing than either pyridine systems (by 0.5–1.9 V[27]) or aldehydes and ketones (by at least 0.2 V.)

In summary, these attempts to compare the reducing action of Cu(I) and Cr(II) toward carboxylatocobalt(III) derivatives have met with the difficulty that most Co(III) complexes which are reduced at convenient rates by Cr^{2+} react immeasurably slowly with Cu^+, whereas many of those which react with measurable rates with Cu^+ are, under our conditions, reduced immeasurably rapidly by Cr^{2+}. Nevertheless, it has become clear that inner-sphere reduction paths are important for Cu^+ as well as for Cr^{2+}, and that the reactivity of both reducing centers may be strongly enhanced by chelation. Reduction by remote attack, although rare in the Cu(I) series, may be observed if the bridging ligand is judiciously chosen so that stronger basicity at the lead-in atom and greater ease of reducibility of the mediating path are made to compensate for the lower reducing potential of the metal center.

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[26] See, for example, P. W. Neber, G. Knoller, K. Herbst, and A. Trissler, *Justus Liebigs Ann. Chem.*, **471**, 113 (1929).

[27] J. Volke in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 296.

Oxidation of Mercury(I) by Neptunium(VII)[1]

Mark A. Thompson,[2] J. C. Sullivan,* and Edward Deutsch[3]

Contribution from Argonne National Laboratory, Argonne, Illinois 60439, and the University of Chicago, Chicago, Illinois 60637.

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Abstract: The empirical form of the rate law for the oxidation of Hg(I) by Np(VII) is $-\text{d[Np(VII)]}/\text{d}t = k'\cdot$[Np(VII)][Hg(I)], where $k' = k_1 + k_2[\text{H}^+]$. At 25° and $\mu = 1.0\ M$, $k_1 = 28.1 \pm 0.7\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 13.4 \pm 1.4\ M^{-2}\ \text{sec}^{-1}$. The respective apparent activation energies are 12.2 ± 0.3 and 8.3 ± 0.8 kcal/mol. These results are consistent with Sykes' correlation of Hg(I) oxidation rate laws with the oxidation potential of the oxidant. Arguments are presented which indicate that, at least for the k_2 path, the rate of Np(VII) reduction is not sensitive to the nature of the reductant.

The rate laws determined for the oxidation of mercurous to mercuric ions in perchlorate media have, as noted by Sykes,[4] two forms which seem to correlate with the oxidation potential of the oxidant. The salient difference is the presence of a term in the rate law inverse in mercuric ion concentration when the relatively weak oxidants Tl(III)[5] and Mn(III)[6] are used. No such term appears when the oxidant is Co(III)[7] or Ag(II).[8] Among the considerations that prompted this investigation was the desire to test Sykes' correlation for a stronger oxidizing agent than Co(III) or Ag(III); Np(VII) is such a reagent, previous work having shown that it rapidly and quantitatively oxidizes Co(II) and Ag(I).[9] In addition it was desired to increase the limited amount of information available on the dynamic chemical behavior of the very strong oxidant Np(VII) in acid solution, detailed studies having been reported only for the oxidation of Tl(I)[10] and water[9] by this reagent. Thus, this paper presents the results obtained in a kinetic study of the reaction

$$\text{Hg}_2^{2+} + 2\text{Np(VII)} = 2\text{Hg}^{2+} + 2\text{Np(VI)} \qquad (1)$$

in acidic aqueous media.

Experimental Section

Reagents. Mercuric perchlorate stock solutions were prepared by dissolution of recrystallized $\text{Hg(ClO}_4)_2$ which had been prepared

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* Address correspondence to this author at Argonne National Laboratory.

[1] Investigation conducted under the auspices of the U. S. Atomic Energy Commission.

[2] Participant in the ACM Honors Program from Cornell College, Mount Vernon, Iowa.

[3] Department of Chemistry, University of Chicago.

[4] A. G. Sykes, "Kinetics of Inorganic Reactions," 1st ed, Pergamon Press, Elmsford, N. Y., 1966, p 170–172.

[5] A. M. Armstrong and J. Halpern, *Can. J. Chem.*, **35**, 1020 (1957).

[6] D. R. Rosseinsky, *J. Chem. Soc.*, 1181 (1963).

[7] D. R. Rosseinsky and W. C. E. Higginson, *ibid.*, 31 (1960).

[8] W. C. Higginson, D. R. Rosseinsky, B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, **29**, 49 (1960).

[9] J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Lett.*, **5**, 927 (1969).

[10] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **92**, 3028 (1970).