Table II. Formal Charges of Group 5 Borane Ligands Employed in This Study

ligand	charge	ligand	charge
$B_{10}H_{10}As$	3–	$B_9H_9As_2$	2–
$B_{10}H_{10}P$	3–	$B_9H_{10}CP(CH_3)$	1–

to a reversible one-electron transfer. The dianion produced in this reduction appears to be the first evidence of a metallacarborane in a formal Co(0) oxidation state.

Conclusions. These results reveal that group-5-substituted cobaltaboranes are capable of extensive electron-transfer reactions. Accessibility of a particular cobalt oxidation state appears to depend largely on the formal ligand charge (Table II) which, of course, determines the overall charge of the complex in a particular metal oxidation state. In the complexes studied, the actual charge varies from 3– for **1** to 1+ for **6** in the formal Co(III) complexes. The electron-transfer reactions of these compounds involve a composite of five separate one-electron steps.

$$? \rightleftarrows \mathrm{Co(IV)} \rightleftarrows \mathrm{Co(III)} \rightleftarrows \mathrm{Co(II)} \rightleftarrows \mathrm{Co(I)} \rightleftarrows \mathrm{Co(0)}$$

The number observed for any particular complex depends on its charge, which shifts the $E°$ potentials. A minimum of two waves (for trinegative **1**) and a maximum of four waves (for mononegative **2**) were found.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant CHE80-04242). We thank Dr. L. J. Todd for providing a sample of **6**.

Registry No. **1**, 65036-28-4; **2**·$N(CH_3)_4$, 65036-33-1; **3**, 65015-72-7; **4**, 65036-34-2; **5**, 57091-19-7; **6**, 81245-18-3.

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242, and the Ruhr-Universität Bochum, D4630 Bochum-Querenburg, Federal Republic of Germany

Electron Transfer. 54. Remote Attack in the Reductions of Carboxylato-Bridged Dicobalt(III) Complexes[1]

VANGALUR S. SRINIVASAN,[2a] A. N. SINGH,[2b] KARL WIEGHARDT,[2c] N. RAJASEKAR,[2b] and E. S. GOULD*[2b]

Received November 10, 1981

Twelve carboxylato-bridged dicoalt(III) complexes of type I have been prepared and their reductions with the metal centers V^{2+}, Eu^{2+}, Cr^{2+}, $Ru(NH_3)_6^{2+}$, and U^{3+}, as well as with the radical (Rb·) and the dihydro derivative (RbH_2) of riboflavin, have been examined. In each of the dimeric oxidants, the carbonyl of the carboxyl group has been tied off by coordination, blocking off inner-sphere reduction of the type often encountered with monomeric carboxylato oxidants, but seven of the dimers feature a pendent carbonyl group in conjugation with the bridging carboxyl. Specific rates in each case appear to be determined by the reduction of the first of the two Co(III) centers. For those dimeric oxidants having no free carbonyl function, rate patterns for reactions with the five metal-center reductants correspond closely to those observed for other systems where only outer-sphere paths are possible. Incorporation of the conjugated carbonyl group enhances the rates of reduction with $Ru(NH_3)_6^{2+}$, Rb·, and RbH_2 (all outer-sphere reductants) only modestly (<10-fold) but accelerates reductions by Cr^{2+}, Eu^{2+}, and U^{3+} by 10^2–10^7, indicating strongly that a second (remote inner-sphere) path has come into play with these metal-center reductants. These experiments provide the first reported evidence for remote attack by U^{3+}. Reductions, using Eu^{2+}, of the carbonyl-substituted dimers yield considerably less than 1:1 Co^{2+}:Eu^{2+} even when the oxidant is taken in excess, indicating that reduction of the carbonyl group (and subsequent dimerization of the derived radical) competes with reduction of bound Co(III); this side reaction appears to occur both with the original dimer and with the monomeric Co(III) intermediate. In contrast, 1:1 stoichiometry is observed in reductions with $Ru(NH_3)_6^{2+}$ (which is too weak a reductant to reduce the carbonyl group) and with Cr^{2+} and U^{3+}, the oxidized forms of which (Cr^{III} and U^{IV}) presumably remain bound to the carbonyl function after the initial act of electron transfer. Rate comparisons between reductions of the dimers and carbonyl-substituted monomeric oxidants of the type $RCO_2Co(NH_3)_5^{2+}$ have been used to estimate the distribution between alternate reaction paths when carbonyl substitution in the monomers allows reduction, in part, by remote attack. It has thus been calculated that the remote path for Cr^{2+} reduction of the monomeric pyruvato complex comprises only 0.2% of the total reaction whereas that for the 2-formylbenzoato complex constitutes 15%.

Among the concepts contributing to the current picture of inner-sphere electron-transfer reactions, that of remote attack (the passage of an electron from one metal center to another through an extended portion of an organic molecule) has proved fascinating both to experimentalists and theoreticians but, at the same time, has suffered a rather checkered history. Early evidence in support of this concept[3] has been subjected to doubt[4] or to reinterpretation,[5] and the systems ultimately used to demonstrate this phenomenon[6] have, in some instances, been quite different from those to which it was originally meant to apply. An important difficulty was that much of the early work dealt with carboxylato derivatives of cobalt(III) having an unsaturated donor group (e.g., an aldehyde, ester, or pyridine function) lying in conjugation with $-COOCo^{III}$, which was presumed to offer a second (remote) path for electron transfer. It is now recognized, however, that such groups can greatly facilitate the more usual mode of transfer through the "adjacent" carboxyl,[4c,7] thus complicating the disentangling of the two competing inner-sphere contributions, unless, as in

---

(1) Sponsorship of this work by the National Science Foundation (Grant CHE 8022881) is gratefully acknowledged.

(2) (a) On leave from Vivekananda College, Mylapore, Madras, India. (b) Kent State University. (c) Ruhr-Universität Bochum.

(3) See, for example: (a) Fraser, R. T. M.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 2239. (b) Sebera, D. K.; Taube, H. *Ibid.* **1961**, *83*, 1785. (c) Gould, E. S.; Taube, H. *Ibid.* **1963**, *85*, 3706.

(4) See, for example: (a) Hurst, J. K.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1178. (b) Gould, E. S. *Ibid.* **1965**, *87*, 4730.

(5) Thamburaj, P. K.; Loar, M. K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1946.

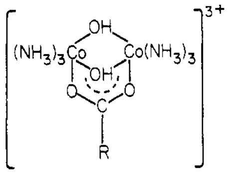
(6) (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929. (c) Balahura, R. J.; Purcell, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4457. (d) Hyde, M. R.; Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1976**, 690.

(7) See, for example: (a) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1. (b) Heh, J. C.-K.; Gould, E. S. *Ibid.* **1978**, *17*, 3138.

0020-1669/82/1321-2531$01.25/0

favorable cases,[8] demonstrably different products arise from the two routes.

The extension of electron-transfer studies to μ-carboxylato-dicobalt(III) complexes of type I has added insight into this area.[6d,9] In such oxidants, the C═O group (the site for adjacent attack by reducing metal centers on monomeric $-COOCo^{III}$ complexes) has been blocked off by coordination to the second metal center, and reduction of Co^{III} must occur either by a (slow) outer-sphere path or by attack at a remote "lead-in" site on group R if available. Thus, Hyde and coworkers[6d] have reported that Cr^{2+} reductions of the dimeric carboxylato-bridged 2- and 4-formylbenzoato complexes (I, R = 2- and 4-C_6H_6CHO) proceed about 10^5 times as rapidly as reductions of the analogous μ-benzoato complex[10] (I, R = C_6H_5), strongly indicating that the aldehyde groups lying in conjugation with the carboxyl bridge have provided an additional (remote) path for electron transfer.



I

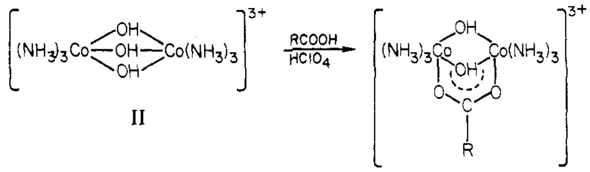
The present paper deals with additional examples of carboxylato-bridged oxidants bearing a remote carbonyl funciton; moreover, our study has been extended to include the action of several additional reducing centers, allowing us to observe a number of subsidiary variations in patterns of redox behavior.

Experimental Section

Materials. Lithium perchlorate[11] and solutions of $Eu(ClO_4)_2$,[12] $V(ClO_4)_2$,[13] $Cr(ClO_4)_2$,[14] $Ru(NH_3)_6Cl_2$,[15] and $U(ClO_4)_3$[16] were prepared as described. Riboflavin, an Aldrich product, was used as received; master solutions, 0.001 M in this compound, were prepared in deaerated 1.0 M $HClO_4$ just before use and were converted either to the cation radical, Rb·,[17] or to the dihydro derivative, RbH_2,[18] by reduction with V^{2+} or Eu^{2+} as described. α-Keto acids not available commercially were prepared by oxidations of the appropriate methyl ketones with alkaline $KMnO_4$.[7a,19] Other carboxylic acids were Aldrich products and were used as received.

Monomeric carboxylato derivatives of $(NH_3)Co^{III}$ were available from previous studies[4b,12b] or were prepared from aquopentaamminecobalt(III) perchlorate as described.[11,12b,14]

Carboxylato-bridged dimeric cobalt(III) complexes were prepared by treatment[20] of the parent carboxylic acid with the tri-μ-hydroxo complex, II. The latter was prepared by an adaptation of the sequence of Siebert and co-workers.[21] A solution of 540 g of $CoCl_2{\cdot}6H_2O$ in 1500 mL of water was added to 600 g of NH_4Cl and 810 g of $NaNO_2$ in 4500 mL of water. After addition of 3000 mL of 20% ammonia, air was passed through the mixture for 5 h. The solution was then reduced by one-third of its volume by evaporation at 30 °C. The precipitate which formed, *mer*-$(NH_3)_3Co(NO_2)_3$,[21c] was filtered and washed successively with cold water, ethanol, and ether; it was then dissolved in a mixture of 4500 mL of water and 30 mL of glacial acetic acid at 85 °C, filtered, cooled to 0 °C, and the yellow-brown needles (240 g) were separated by filtration. The latter product was added to 1920 mL of concentrated HCl at 25 °C and kept for 24 h with occasional stirring. The precipitate formed was filtered off and washed successively with 20% HCl, ethanol, and ether. It was then dissolved in 3000 mL of 1% HCl, treated with 10 mL of saturated $NaClO_4$, and filtered, and 3000 mL of concentrated HCl was added to the filtrate. Cooling to 0 °C yielded 167 g of dark brown crystals, $(NH_3)_3Co(H_2O)Cl_2{}^+Cl^-$. The dichloro chloride was then dissolved in 167 mL of water and cooled to 0 °C and 1000 mL of 1 M NH_3 added dropwise, with stirring, over a period of 2 h. To the mixture was then added 417 mL of saturated $NaClO_4$, the mixture cooled again to 0 °C, and the precipitated tri-μ-hydroxy perchlorate $(NH_3)_3Co(OH)_3Co(NH_3)_3(ClO_4{}^-)_3{\cdot}2H_2O$ filtered off and washed successively with 50% ethanol, absolute ethanol, and ether. The crude dihydrate (120 g) was then dissolved in 1330 mL of 0.1 M acetic acid at 30 °C, treated with 310 mL of saturated $NaClO_4$, and kept at 0 °C overnight, and the purified crystalline tri-μ-hydroxo compound (II) (80 g) was filtered off and dried.



II

I

So that the tri-μ-hydroxo compound could be converted to the desired carboxylato-brided dicobalt complexes (I), 0.003 mol of the carboxylic acid was dissolved in 20 mL of 1 M $HClO_4$ at 60 °C, 1.0 g of the tri-μ-hydroxo perchlorate was added, and the solution stirred for 30 min and then cooled to 0 °C for 30 min. Addition of 10 mL of 70% $HClO_4$, followed by chilling at 0 °C for 12 h, generally precipitated the μ-carboxylato-dicobalt(III) perchlorate.[22,23] Analyses of dimeric complexes appear in Table I, together with summaries of spectral features. Values of extinction coefficients have been adjusted in accord with observed departures from calculated cobalt content.

Rate Measurements. Rates were measured from absorbance changes on the Beckman Model 5260 recording spectrophotometer or the Durrum-gibson stopped-flow spectrophotometer as described.[4b,14,24] Reductions of the μ-carboxylato dimeric complexes by Cr^{2+}, V^{2+}, Eu^{2+}, $Ru(NH_3)_6{}^{2+}$, and U^{3+} were monitored at 524 nm, whereas those of the monomeric Co(III) oxidants were followed at 502 nm. Slower reductions by the metal centers were carried out in a 1-cm cell with $[(Co^{III})_2]$ near 10^{-3} M; more rapid reactions were run in a 10-cm cell with $[Co^{III}{}_2] = 10^{-4}$ M. Reductions by the cation radical (Rb·) and the dihydro derivative (RbH_2) of riboflavin were studied at 495 nm, the low-energy maximum of Rb· in 1 M $HClO_4$. The order with respect to the reagent in excess was determined throughout by at least a twofold variation in this reagent. Reactions were found to be first order each in oxidant and reductant but were generally carried out under pseudo-first-order conditions; the mole ratio reductant/oxidant exceeded 10 for reductions with metal centers,

---

[8] Zanella, A.; Taube, H. *J. Am. Chem. Soc.* **1972**, *94*, 6403. Note that in this work, which dealt, in part, with the Cr^{2+} reduction of the $(NH_3)_5Co^{III}$ derivative of 4-$HOOCC_6H_4CHO$, differentiation of Cr(III) products resulting from the two contributing paths was possible because of the substitution-inert nature of the Cr(III) center. Such a distinction is generally not feasible for reductions by V(II), Eu(II), or U(III), for the resulting oxidation products undergo rapid equilibration in aqueous media.

[9] (a) Scott, K. L.; Wieghardt, K.; Sykes, A. T. *Inorg. Chem.* **1973**, *12*, 655. (b) Bertram, H.; Bolsing, E.; Spieker, H.; Wieghardt, K. *Ibid.* **1978**, *17*, 221.

[10] Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 651.

[11] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[12] (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fan, F. R.-F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

[13] (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.*, **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.

[14] Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

[15] Fan, F. R.-F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

[16] Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

[17] Singh, A. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 1232.

[18] Singh, A. N.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 1236.

[19] (a) Businelli, N. Italian Patent 475964 (1952); *Chem. Abstr.* **1955**, *49*, 12539*d*. (b) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942.

[20] Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1973**, 2548.

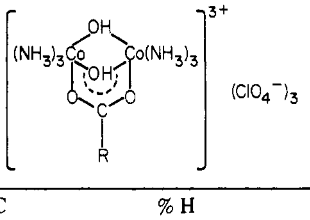
[21] (a) Linhard, M.; Siebert, H. *Z. Anorg. Allg. Chem.* **1969**, *364*, 24. (b) Siebert, H.; Tremmel, G. *Ibid.* **1972**, *390*, 292. (c) Siebert, H. *Ibid.* **1978**, *441*, 47.

[22] Slight modifications of this ligation procedure were necessary in a number of instances. The reaction temperature was 50 °C for the μ-pyruvato complex and 80 °C for the μ-(4-formylbenzoato) complex. The pyruvato complex was subjected to further purification, first by treatment with "Tris" buffer[7b] and then by passage through Bio-Rad Bio-Gel P-2,[23] followed by elution with dilute $HClO_4$, after which the eluate was concentrated by rotary evaporation and twice crystallized from 1 μ $HClO_4$.

[23] Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289.

[24] Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373.

Table I. Analysis of μ-Carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorates



RCOO	%C calcd	%C found	%H calcd	%H found	%Co calcd	%Co found[a]	λ_{max}, nm	ϵ_1, M^{-1} cm^{-1}	λ_{max}, nm	ϵ_2, M^{-1} cm^{-1}
			Dimeric Complexes							
formato	2.00	1.98	3.58	3.51	20.7	19.5	364[b]	312	522	119
acetato	3.92	3.75	3.75	3.56	19.0	18.2	357[b]	298	522	111
trifluoroacetato	3.60	3.94	3.00	3.60	17.7	16.5	366[b]	276	523	110
benzoato	12.44	12.23	3.70	3.86	17.5	16.5	364[b]	352	521	136
p-nitrobenzoato	11.67	11.50	3.33	3.51	16.4	15.2	364[b]	560	523	129
pyruvato (III)	5.61	5.72	3.73	3.48	18.4	18.2	357[b]	333	522	109
phenylglyoxylato (IV)	13.65	13.58	3.56	3.63	16.8	16.0	368[b]	308	526	116
(4-methoxyphenyl)glyoxylato	14.73	15.01	3.68	4.04			370[b]	1550	531	116
(2,4-dimethoxyphenyl)glyoxylato	15.73	15.95	3.80	4.00	15.5	14.7			527	122
(2,4,6-trimethoxyphenyl)glyoxylato	16.64	16.71	3.90	4.10	14.9	14.2			525	130
4-formylbenzoato (V)	13.65	13.19	3.56	3.70	16.8	15.8	357[b]	322	521	111
2-formylbenzoato	13.65	13.43	3.56	3.75	16.8	15.4	365[b]	280	524	111
			Monomeric Complexes[c]							
(4-methoxyphenyl)glyoxylato	20.65	20.83	4.21	4.15	11.3	10.9			502[d] 490[e]	85[d] 96[e]
4-acetylbenzoato	21.30	21.02	4.34	4.41	11.7	10.6			502	

[a] See ref 14. [b] Shoulder. [c] $RCOOCo(NH_3)_5(ClO_4)_2$. [d] In 0.1 M $HClO_4$. [e] In water.

whereas the mole ratio oxidant/reductant exceeded 8 for the reactions of Rb· and RbH_2. Reductions with Cr^{2+}, V^{2+} and Eu^{2+} were run both in 1.0 M $HClO_4$ and in a solution 0.1 M in $HClO_4$ and 0.9 M in $LiClO_4$. Reactions of U^{3+} were carried out in 0.2 M $HClO_4$, whereas those of $Ru(NH_3)_6^{2+}$ were carried out in 0.5 M LiCl in the presence of 0.1 M HCl. Modifications in procedure needed to study the reactions of Rb· and RbH_2 have been detailed.[17,18]

With a single exception, rates for the metal-center reductants were independent of $[H^+]$ in this series.[25] The activity dependences of the reactions of Rb· and RbH_2 with substitution-inert cobalt(III) complexes, reflecting partial protonation of the reductants, have been previously established.[17,18] Kinetic data were generally taken for at least 4 half-lives, and an "infinity reading" taken after 6 half-lives. In the case of reductions by metal centers constants evaluated from successive half-life values within a single run agreed to within 6%, and specific rates obtained from replicate runs on the Beckman spectrophotometer checked to better than 8%, whereas successive oxidations on the Durrum (with the same pair of master solutions) were repeated until kinetic curves for three consecutive runs were superimposable. Specific rates obtained by stopped flow from different master solutions agreed to better than 6%. Data for reductions by Rb· and RbH_2 were significantly less precise, reflecting the special difficulties associated with use of these reductants.[17,18] Reductions, using Eu^{2+} and U^{3+}, of a number of the carbonyl-substituted complexes exhibited a second kinetic component, very probably due to reaction of the OH-substituted complex formed from reduction of the ligand, which could be shown (see below) to compete with the primary reaction; this second component was slow enough not to interfere seriously with measurement of the rate constant of the primary reaction. Chromium(II) reductions of the complexes of substituted phenylglyoxylic acids were complicated by the intervention of strongly absorbing intermediates[12b] and, in addition, by secondary reactions of Cr^{2+} (if in excess) with the Cr(III) products to form intensely green Cr^{II}–Cr^{III} species. Further study of these facets is proceeding. Aside from the rapid reductions by U^{3+}, which were monitored at 21 °C, temperatures were kept at 25.0 ± 0.2 °C during this series of experiments.

Table II. Yields of Co^{2+} from Reductions of Dimeric and Monomeric (Carboxylato)cobalt(III) Complexes with Metal-Center Reductants[a]

complex	yield of Co^{2+}, % V^{2+}	Cr^{2+}	Eu^{2+}	Ru^{II}[b]	U^{3+}
		Bridged Dimers (I)			
formato				98	98
acetato				100	97
trifluoroacetato				100	94
pyruvato	94	100	47	99	
phenylglyoxylato	74	100	53	100	97
(4-methoxyphenyl)glyoxalato	86	100	44	100	
(2,4-dimethoxyphenyl)-glyoxylato	100	100	75 63[c]	96	
(2,4,6-trimethoxyphenyl)-glyoxylato	95 83[c]	100	69 54[c]	100	99
4-formylbenzoato		100		99	94
2-formylbenzoato		97		101	96
p-nitrobenzoato	23	20	32	102	
		Monomers ($RCOOCo(NH_3)_5^{2+}$)			
pyruvato		100[d]	100[e]	94	
phenylglyoxylato	58[c]	90	37	98	
(4-methoxyphenyl)glyoxylato	69	90	42	98	
(2,4-dimethoxyphenyl)-glyoxylato	67 85[c]	100	43	100	
(2,4,6-trimethoxyphenyl)-glyoxylato	85 100[c]	100	48	100	
4-formylbenzoato		100[f]	100[e]	96	
2-formylbenzoato		100[g]	100[e]	97	

[a] $[H^+]$ = 1.0 M, unless otherwise indicated; [oxidant] = 0.0050 M; [reductant] = 0.0020 M; reductant was added to Co(III). [b] Reductions by $Ru(NH_3)_6^{2+}$ were carried out in a solution 0.5 M in LiCl and 0.01 M in HCl. [c] $[H^+]$ = 0.10 M. [d] Reference 7a. [e] Reference 12b. [f] Reference 14. [g] Reference 4b.

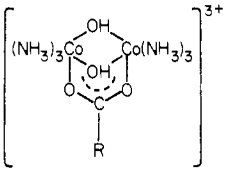
Stoichiometry Studies. Stoichiometry experiments,[14] in which cobalt(III) and a ligand bound to it were allowed to compete for a deficient quantity of metal-center reducing agent, were carried out as described.[6b,14] The procedure was standardized with the Cr^{2+} reduction of the maleato derivative of $(NH_3)_5Co^{III}$, which is known to act rapidly and, with Cr^{2+} in deficiency, to yield Co^{2+} quantitatively.[26] Results are summarized in Table II. For the reductions with $Ru(NH_3)_6^{2+}$, which are slow, mixtures were allowed to stand

---

(25) Preliminary kinetic data (VSS) for the Cr^{2+} reduction of the tri-μ-hydroxo dimer, II, in the range 0.1–1.0 M $HClO_4$ are in accord with the rate law rate = $[Cr^{2+}]$[dimer]$(0.30 + 1.0/[H^+])$ (M^{-1} s^{-1}) (25 °C, μ = 1.0). Interpretation here is complicated by the known[21a] slow interconversion between Co^{III}_2 species in this system.

(26) Olson, M. V.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2072.

Table III. Specific Rates for Reductions of Bridged Dimeric Cobalt(III) Complexes[a]



bridging ligand, RCOO	$k_{V(II)}$	$k_{Eu(II)}$	$k_{Cr(II)}$	$k_{Ru(II)}$[b]	$k_{U(III)}$[c]	$k_{Rb\cdot}$[d]	k_{RbH_2}[e]
formato	0.12	0.015	0.0027[j]	0.177	4.1	0.43	
acetato	0.053	0.0086	0.0014	0.062	1.26	0.28	10.0
trifluoroacetato	0.41	0.060	0.0059	0.72[i]	11.8		
benzoato	0.067	0.0102	0.0017[k]	0.117	2.8		
p-nitrobenzoato	0.069	0.0163	*f*	0.153			
pyruvato (III)	0.30	1.53	4	0.34	1.5×10^5 [h]	5.7	34
phenylglyoxylato (IV)	0.83	86	1.6×10^4	0.73	1.2×10^5 [h]	5.0	72
(4-methoxyphenyl)glyoxylato	1.07	57	1.1×10^4	0.60	1.7×10^5 [h]	94	
(2,4-dimethoxyphenyl)glyoxylato	1.00	10.1	6×10^2	0.68	1×10^5 [h]		
(2,4,6-trimethoxyphenyl)glyoxylato	0.88	22		0.64	8×10^4 [h]		
4-formylbenzoato (V)	0.15[g]	0.69	123[g]	0.182	4.5×10^2 [h]	6.7	86
2-formylbenzoato	0.24[g]	0.054	32[g]	0.28	7.3×10^4 [h]		36

[a] Specific rates in M^{-1} s^{-1} at 25 °C ($\mu = 1.0$) unless otherwise indicated. Rates with metal-center reductants are independent of $[H^+]$. Values pertain to disappearance of dimeric oxidant. [b] Reductions with $Ru(NH_3)_6^{2+}$ were carried out in 0.5 M LiCl; $[H^+] = 0.01$ M. [c] Reactions were carried out in 0.2 M $HClO_4$. [d] Specific rates are proportional to $[H^+]^{-1}$. Given values are for 1.3 M $HClO_4$.[17] [e] Specific rates vary with $[H^+]$ in accord with eq 2 of ref 18. Values given for 1.3 M $HClO_4$. [f] Formation of a strongly absorbing intermediate was too rapid to measure. [g] Reference 6d. [h] Reactions at 21 °C. [i] Reaction in 0.15 M LiCl. [j] Huck, H.-M.; Wieghardt, K. *Inorg. Chem.* 1980, *19*, 3688. [k] A small acid dependency has been reported for this reaction (see ref 10).

Table IV. Specific Rates for Reductions of Monomeric Cobalt(III) Complexes, $RCOOCo(NH_3)_5^{2+}$ [a]

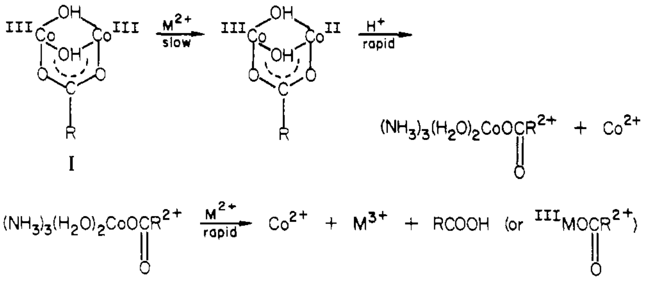
ligand, RCOO	$k_{V(II)}$	$k_{Eu(II)}$	$k_{Cr(II)}$	$k_{Ru(II)}$[b]
formato[c]	3.5	16	7.2	0.092
trifluoroacetato[c]	0.86	1.30	0.034	0.18
glyoxylato	8.4[c]	80	$>7 \times 10^3$ [d]	0.059
pyruvato	10.0[e]	1.15×10^3 [f]	10×10^3 [c]	0.117
phenylglyoxylato	2.6	3.7×10^4 [f]	*g*	0.31[c]
(4-methoxyphenyl)glyoxylato	3.5	1.2×10^4	*g*	0.38
(2,4-dimethoxyphenyl)glyoxylato	3.5	7.4×10^2	*g*	0.39
(2,4,6-trimethoxyphenyl)glyoxylato	3.4	3.0×10^2	*g*	0.41
4-formylbenzoato	1.12[e]	$1.08 + 0.31[H^+]$[h]	$53 + 380[H^+]$[h]	0.048
2-formylbenzoato	1.24[c]	1.8[f]	94[c]	0.131
4-acetylbenzoato	0.83	1.16	$0.73 + 1.15[H^+]$	

[a] Specific rates in M^{-1} s^{-1} at 25 °C ($\mu = 1.0$) unless otherwise indicated. [b] Reductions with $Ru(NH_3)_6^{2+}$ were carried out in 0.5 M LiCl; $[H^+] = 0.01$ M. [c] Data from ref 15. [d] Lower limit for dehydrated (aldehydo) form. See: Price, H. J.; Taube, H. *J. Am. Chem. Soc.* 1967, *89*, 269. [e] Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5539. [f] Reference 12b. [g] Reactions initiated by the very rapid formation of a strongly absorbing intermediate. [h] Reference 8.

for several hours before analyzing for Co^{2+}; in such cases, the results represent lower limits since the reductant was undoubtedly partially consumed by traces of O_2 diffusing into the vessel. For the still slower reductions of those dimeric complexes having neither a carbonyl nor a nitro group, the procedure used did not give consistent values, but in these instances, reduction of the ligand may reasonably assumed to be negligible.

Results and Discussion

The reactions of dimeric complexes of type I with one-electron reductants necessarily occur in steps. Reduction of one Co^{III} center yields a Co^{III}–Co^{II} intermediate, which would be expected to undergo very rapid hydrolysis at the substitution labile Co(II) center in the acidic medium used, yielding Co^{2+} and a monomeric Co(III) complex, the latter of which is then reduced.



Since the second act of electron transfer, involving the monomeric $(H_2O)_2Co^{III}$ species, may be considered to be much more rapid than reduction of the dimer,[27] the initial reduction may be taken to be rate determining in our systems.

Kinetic data for reactions of dimeric oxidants with five metal-center oxidants, and with the radical cation[17] (Rb·) and the dihydro derivative[18] (RbH_2) of riboflavin, are assembled in Table III. Note that the rate constants which are given refer to disappearance of the dimeric species rather than to the formation of Co^{2+} (values for the latter process would be twice those entered). Data pertaining to the reductions of

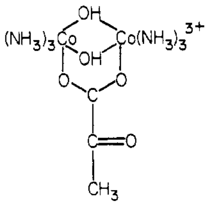
---

(27) No studies of reductions of complexes of the type $RCOOCo(NH_3)_3(H_2O)_2^{2+}$ appear to have been reported. With $Ru(NH_3)_6^{2+}$ as a reductant, we find dimeric complexes of type I to be reduced 1.5–10 times as rapidly as (carboxylato)pentaammine complexes, $RCOOCo(NH_3)_5^{2+}$, derived from the same carboxylic acid (compare Tables III and IV). However, Linck[13a] has shown that replacement of a single NH_3 by H_2O in the coordination sphere of Co(III) increases the rate of reduction by a factor of at least 20; hence, the diaquo monomers would be expected to react with $Ru(NH_3)_6^{2+}$, and with the riboflavin-derived reductants, at least 400 times as rapidly as the corresponding Co(III) pentaammines, or at least 40 times as rapidly as their dimeric precursors. The latter expectation is in accord with our observation that reductions of the dimers with excess Ru(II) exhibit no indication of a second (slow) kinetic component. With the other metal center reductants, the kinetic advantage enjoyed by the diaquo monomers should be even more marked since these may utilize an inner-sphere (carboxyl) route which is denied to the dimer.

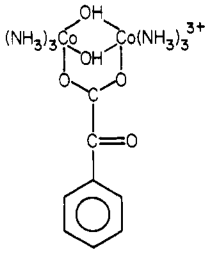
monomeric pentaammines derived from some of the same carboxylic acids appear in Table IV.

The most pronounced regularities are observed with the metal-center reductions of the first five dimeric oxidants, none of which possesses a "lead-in- carbonyl function. In this portion of the series, log *k* values pertaining to a given reductant are very nearly linearly related to those for the other reductants. As shown in Figure 1, log–log plots comparing rate constants for V^{2+} (k_V values) with those for Eu^{2+} (k_{Eu}) and for Cr^{2+} (k_{Cr}) have slopes near unity, in accord with the model of Marcus for outer-sphere series,[28] whereas k_{Ru} values are perceptibly more sensitive than the others to structural alteration of the oxidant, a point that has been noted both by Linck[13a] and by Hua.[29]

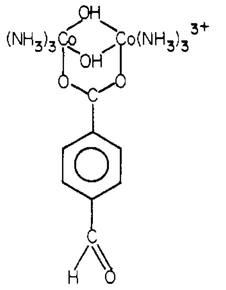
The final seven dimeric oxidants in Table III feature a carbonyl group conjugated with the bridging carboxyl.



III



IV



V

Values of k_{Ru} for the pyruvato(III) and substituted glyoxylato dimers lie appreciably above those for the μ-acetato and μ-benzoato dimers (but below that for the μ-(trifluoroacetato) derivative), very probably reflecting electron attraction (and consequent outer sphere rate enhancement)[15,30] by the α-carbonyl substituent. The modest increases in $k_{\mathrm{Rb}\cdot}$ and k_{RbH_2} attending the incorporation of a carbonyl function, as well as the corresponding enhancements in k_{Ru} within the monomeric series (Table IV), may reasonably be attributed to the same effect.[31]

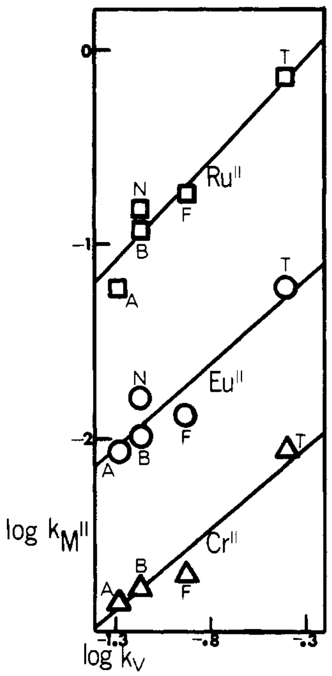


Figure 1. log–log plots comparing the specific rates of reduction of μ-carboxylato-dicobalt(III) complexes (of type I) by V^{2+}, Cr^{2+}, Eu^{2+}, and $Ru(NH_3)_6{}^{2+}$. Oxidants included have no pendent carbonyl group. Reaction conditions are specified in Table III. Individual oxidants are (A) μ-acetato, (B) μ-benzoato, (N) μ-(4-nitrobenzoato), (F) μ-formato, and (T) μ-(trifluoroacetato). The least-squares lines shown correspond to the equations $\log k_{Cr} = 0.89 \log k_V - 1.76$, $\log k_{Eu} = 0.89 \log k_V - 0.92$, and $\log k_{Ru} = 1.05 \log k_V + 0.26$.

The most striking accelerations encountered in this study are associated with the reductions, using Cr^{2+}, Eu^{2+}, and U^{3+}, of the carbonyl-substituted dimers. The magnitudes of the rate enhancements (10^3–10^7 for Cr^{2+}, 10^2–10^3 for Eu^{2+}, and 10^3–10^4 for U^{3+}), in conjunction with the structural features common to the rapid oxidants, indicate strongly that reaction by a second (remote) path has come into play. Hyde and co-workers[6d] have presented evidence supporting such a path for the Cr^{2+} reductions of the μ-(formylbenzoato) dimers, although the rate increases reported by these investigators are considerably less marked than those observed here for the μ-(phenylglyoxylato) oxidants. With Eu(II) and U(III), there is less precedent. Earlier evidence[12b] that the lanthanide reductant may utilize a carbonyl function as a lead-in group, although suggestive, is open to question,[32] whereas data pointing to remote attack of any kind in reductions by U^{3+} has not yet appeared.[33-35]

Vanadium(II) rates for reductions of the α-keto dimeric complexes hint that even this reducing center may react in part through a remote path. In the absence of carbonyl groups, k_V values for the dimeric oxidants (as well as for other slow outer-sphere oxidants[15]) are generally about half of the corresponding k_{Ru}'s, whereas with the α-keto dimers, the ratio k_V/k_{Ru} may reach 1.5. If the ratio of outer-sphere rates is taken to be nearly constant,[15,28] it may be inferred that the more rapid V^{2+} reductions in this series are utilizing an inner-sphere path having a magnitude half to two-thirds the observed specific rate. The mode of partition between reaction paths thus appears to resemble that indicated for V^{2+} reductions of acylpyridine derivatives of $(NH_3)_5Co^{III}$.[6b]

The rapid Eu^{2+} reductions of the carbonyl-substituted dimeric oxidants are seen to yield considerably less than 1 mol of Co^{2+}/mol of reductant, even when the oxidant is taken in

---

(28) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(29) Hua, L. H.-C.; Balahura, R. J.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3692.

(30) Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945.

(31) The unusually high $k_{\mathrm{Rb}\cdot}$ values observed for the dimeric (4-methoxyphenyl)gloxylato complex continue to puzzle us. The direction of the effect suggests intervention of an additional (inner-sphere) path. However, the search for a reaction product in which the flavin ring has undergone modification is complicated by the circumstance that reductions by Rb· must be carried out with riboflavin (the oxidized form) in excess.[17]

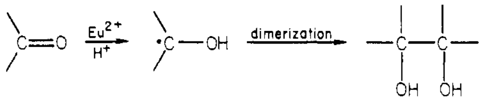
(32) The high rates reported by Fan[12b] for Eu^{2+} reductions of the monomeric $(NH_3)_5Co^{III}$ complexes of pyruvic, phenylglyoxylic, and mucochloric acids must be interpreted with caution in light of evidence[5,7] that effective remote lead-in groups may also facilitate reduction by adjacent attack in monomeric systems.

(33) The very high specific rates for U^{3+} reductions of monomeric (carboxylato)cobalt(III) complexes (10^2–10^4 M^{-1} s^{-1})[16] tend to obscure kinetic indications of remote attack in such systems.

(34) Since the k_U values for the more rapid dimeric oxidants (Table IV) are quite similar and appear to approach 1.8×10^5 M^{-1} s^{-1}, it may be reasonably asked whether this value lies near a limit imposed by substitution at the U(III) center. The report[35] of a higher rate (1.1×10^6) for U(III) reduction of $Co(NH_3)_5N_3{}^{2+}$ under similar conditions weighs against this suggestion.

(35) Wang, R. T.; Espenson, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 380.

excess (Table II). The observed departures from 1:1 stoichiometry indicate that reduction of the carbonyl group competes with reaction at the Co(III) center. This carbonyl reduction may involve the dimeric oxidant, the monomeric Co(III) intermediate, the liberated carboxyl ligand (this is much less likely),[36] or a combination of these. In analogy with earlier work[6b,37] on related systems, it is taken to be a reduction to radical VI, followed by dimerization to a pinacol-like product



In the case of the pyruvato-bridged oxidant, ligand reduction appears to occur only on the dimer since reduction of the monomeric pentaammine complex (which is closely similar to the monomeric triammine intermediate) is found to yield Co^{2+} quantitatively. With the several phenylglyoxylato-bridged oxidants, it is likely that ligand reduction occurs at both stages. These "secondary reactions" should not seriously affect the reliability of the specific rates here recorded for the primary electron-transfer reactions (which are measured with the reductant in large excess), for their net result is simply to block the "lead-in group" in the Co(III) complexes, converting them in part to much more slowly reduced species, the reactions of which are easily distinguished from the transformations of principal interest.

The highly variable stoichiometries of the Eu(II) reactions contrast markedly with the nearly quantitative yields of Co^{2+} observed here for the corresponding reductions by Cr(II), U(III), and Ru(II).[38,39] The results with $Ru(NH_3)_6^{2+}$ may be attributed to the relatively weak reducing potential (E_0 = +0.214 V) of this reagent,[40] which may rule out electron transfer to the carbonyl group but not to the more strongly oxidizing Co(III) center.[41] With Cr^{2+}, on the other hand, we believe that initial transfer occurs to the carbonyl but that the substitution-inert Cr(III) center which is formed remains bound to the radical intermediate (yielding a radical cation of type $\cdot COCr^{III}$), thus inhibiting (electrostatically) the dimerization which, in the absence of ligation to Cr(III), would compete with internal electron transfer to Co(III). If this reasoning be correct, the quantitative yields of Co^{2+} found to be formed in the U(III) reductions may be taken to indicate that reactions with this reductant likewise proceed through an analogous U(IV)-bound radical cation. Substitutions at U(IV) centers, which in this case would lead to aquation of such a radical cation, have been shown to be much more rapid than those at Cr(III),[42] but the evidence at hand suggests that they are significantly slower than those at Eu(III). For reductions with V^{2+}, departures from 1:1 stoichiometry are appreciable but less severe than those observed with Eu^{2+}, hinting at the intervention of a V(III)-bound radical ion which persists somewhat longer than that bound to Eu(III) but is more labile than that bound to U(IV).

Table V. Estimated Distribution between Reaction Paths in Reductions of Monomeric Carbonyl-Substituted (Carboxylato)pentaamminecobalt(III) Complexes, $RCOOCo(NH_3)_5^{2+}$

	k^{remote}-(calcd)[a]		fraction remote attack[b]	
ligand (RCOO)	Cr^{2+}	Eu^{2+}	Cr^{2+}	Eu^{2+}
pyruvato	17		0.0017	
2-formylbenzoato	14		0.150	
phenylglyoxylato		37		0.0010
(4-methoxyphenyl)glyoxylato		25		0.0021
(2,4-dimethoxyphenyl)glyoxylato		4.3		0.0058
(2,4,6-trimethoxyphenyl)glyoxylato		9		0.030

[a] Specific rates (in M^{-1} s^{-1} at 25 °C) estimated as 0.43 times the measured specific rates (Table III) for reductions of the corresponding carboxylato-bridged dimeric cobalt(III) complexes (see text). [b] Obtained by division of k^{remote} by k^{obsd} (Table IV).

Finally, the present results may be used, albeit tentatively, to estimate the distribution between reaction paths in the reductions of certain of the monomeric carbonyl-substituted cobalt(III) complexes. Zanella has shown that reduction, by Cr^{2+}, of the monomeric $(NH_3)_5Co^{III}$ complex of 4-formylbenzoic acid ($k = 53 + 380[H^+]$ M^{-1} s^{-1} at 25 °C) proceeds almost exclusively by remote attack,[8] as does reduction of the dimeric complex of the same acid (V) in this and in Hyde's[6d] study (k = 123). If the ratio of the acid-independent rate constants, 0.43, is taken to be characteristic of the two series of oxidants when a remote path is operative, we may calculate specific rates that would apply to reductions of a number of the monomeric complexes if only the remote path were available. The ratio of the latter (k^{remote}) values to the observed specific rates (Table IV) may then be considered to represent the fraction of the Co(III) reduction proceeding via remote attack. Such estimated fractions are listed in Table V. Although values of k^{remote} fall significantly above the specific rates characteristic of reductions of carboxylato complexes in the absence of rate-enhancing substituents (about 0.15 M^{-1} s^{-1} for reductions by Cr^{2+},[14] 1 M^{-1} s^{-1} for Eu^{2+} [12b,43]), the remote path is seen to constitute only a minor fraction in each case. Hence, it is not at all astonishing that attempts to characterize carbonyl-bound Cr(III) products in the Cr^{2+} reductions of the monomeric pyruvato[7a,24] and 2-formylbenzoato[24] oxidants have been unsuccessful.[44]

Registry No. III, 81572-38-5; IV, 81572-39-6; V, 52375-31-2; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-formato})Co(NH_3)_3](ClO_4)_3$, 38258-08-1; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-trifluoroacetato})Co(NH_3)_3](ClO_4)_3$, 38266-36-3; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-benzoato})Co(NH_3)_3](ClO_4)_3$, 52362-70-6; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-acetato})Co(NH_3)_3](ClO_4)_3$, 38258-09-2; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}p\text{-nitrobenzoato})Co(NH_3)_3](ClO_4)_3$, 58482-17-0; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-(4-methoxyphenyl)glyoxylato})Co(NH_3)_3](ClO_4)_3$, 81572-41-0; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-(2,4-dimethoxyphenyl)glyoxylato})Co(NH_3)_3](ClO_4)_3$, 81572-43-2; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-(2,4,6-trimethoxyphenyl)glyoxylato})Co(NH_3)_3](ClO_4)_3$, 81572-45-4; $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-2-formylbenzoato})Co(NH_3)_3](ClO_4)_3$, 52362-80-8; $[(NH_3)_5Co((4\text{-methoxyphenyl)glyoxylato})](ClO_4)_2$, 81572-47-6; $[(NH_3)_5Co(4\text{-acetylbenzoato})](ClO_4)_2$,

---

(36) Note that two Co(III) centers must be reduced by Eu(II) before a molecule of ligand is released. It therefore follows that if only the carbonyl group on the free ligand undergoes reduction (assumed to be a 1e transaction), the yield of Co^{2+} cannot fall below 66%.

(37) (a) Liu, C.-L.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1831. (b) Konstantatos, J.; Vrachnou-Astra, E.; Katsaros, N.; Katakis, D. *J. Am. Chem. Soc.* **1980**, *102*, 3035.

(38) The single exception (Table II) is the Cr^{2+} reduction of the bridged *p*-nitrobenzoato complex. Electron transfer to the nitro group of a nitro-substituted cobalt(III) oxidant, with only partial transmittal to the Co(III) center, has been described in earlier reports.[39]

(39) (a) Gould, E. S. *J. Am. Chem. Soc.* **1966**, *88*, 2983. (b) Reid, R.; Fan, F.-R. F.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 2766.

(40) Endicott, J. F.; Taube, H. *Inorg. Chem.* **1965**, *4*, 437.

(41) It may be asked whether the substitution-inert character of the Ru(II) center militates against preliminary electron transfer to the carbonyl function, i.e., whether such transfer requires coordination of the carbonyl group to the reducing center. Reid[39b] has presented evidence that reduction by such a two-step path (the so-called "chemical mechanism") may proceed without alteration of the ligand environment of the reductant.

(42) Loar, M. K.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3689.

(43) Thamburaj, P. K.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 15.

(44) In the case of reductions by Eu^{2+} equilibration about the highly labile Eu(III) center constituting the product is very rapid. Hence, even if a carbonyl-bound Eu(III) species were a primary product, the latter would almost certainly not be detected.

81572-49-8; $[(NH_3)_5Co(pyruvato)]^{2+}$, 19306-91-3; $[(NH_3)_5Co(phenylglyoxylato)]^{2+}$, 49861-82-7; $[(NH_3)_5Co((2,4\text{-dimethoxyphenyl})glyoxylato)]^{2+}$, 81572-50-1; $[(NH_3)_5Co((2,4,6\text{-trimethoxyphenyl})glyoxylato)]^{2+}$, 81572-51-2; $[(NH_3)_5Co(4\text{-formylbenzoato})]^{2+}$, 19743-65-8; $[(NH_3)_5Co(2\text{-formylbenzoato})]^{2+}$, 42532-71-8; $[(NH_3)_5Co(glyoxylato)](ClO_4)_2$, 15189-50-1; V, 7440-62-3; Cr, 7440-47-3; Eu, 7440-53-1; $Ru(NH_3)_6^{2+}$, 19052-44-9; U, 7440-61-1; $Rb^{+}\cdot$, 78962-23-6; RbH_2, 13345-95-4.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Novel Method for the Chemical Generation of Aliphatic Radicals and Its Application to the Kinetics of Reduction of Cobalt(III)-Amine Complexes by 2-Hydroxy-2-propyl Radicals

JAMES H. ESPENSON,* MAKOTO SHIMURA, and ANDREJA BAKAČ

Received February 17, 1982

Homolytic cleavage of the chromium–carbon bond in the complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$ provides a ready source of the carbon-centered radical $\cdot C(CH_3)_2OH$ in strongly acidic solutions, pH 0–3. The kinetics of reaction of the radical with another substrate present in solution can be studied in competition with the recombination reaction between radical and Cr^{2+}. The method was applied to a study of the reduction of several cobalt(III) complexes, with the following pH-independent rate constants at 25.0 °C: $Co(NH_3)_6^{3+}$, 4.1×10^5 M^{-1} s^{-1}; $Co(ND_3)_6^{3+}$, 3.0×10^5; $Co(en)_3^{3+}$, 1.7×10^5; $Co(tn)_3^{3+}$, 1.9×10^6; $Co(chxn)_3^{3+}$, $<1 \times 10^4$. The mechanism of $Co(NH_3)_6^{3+}$ reduction over the entire pH range 0–14 has been reformulated as consisting of three pathways: (1) outer-sphere electron transfer from $\cdot C(CH_3)_2OH$, dominant at pH 0–3; (2) outer-sphere electron transfer from $\cdot C(CH_3)_2O^-$, dominant at pH >10; (3) reversible formation of a covalent intermediate, $(NH_3)_5CoNH_2C(CH_3)_2OH^{2+}$, whose subsequent decomposition is the prevalent reaction at intermediate pH, pH 5–9. The rate constants for the first of these reactions correlate well with λ_{max} and $E°$ values of the Co(III) complexes and with the rate constants for the corresponding reduction by $Cr(bpy)_3^{2+}$, save for $Co(chxn)_3^{3+}$ whose low reactivity with the free radical is attributed to its conformational inflexibility. Several Cr(III) complexes—$Cr(NH_3)_6^{3+}$, $Cr(urea)_6^{3+}$, and $(H_2O)_5CrCl^{2+}$—failed to react with $\cdot C(CH_3)_2OH$.

Introduction

The 2-hydroxy-2-propyl radical (referred to by Chemical Abstracts as 1-hydroxy-1-methylethyl) is a powerful one-electron reducing agent: $(CH_3)_2CO + H^+ + e^- = \cdot C(CH_3)_2OH$, $E° = -1.2$ V[1] vs. NHE. The rates of its reactions and those of related free radicals are often determined by the pulse-radiolysis technique. The competition between the reaction of the substrate of interest with the free radical and its bimolecular disproportionation poses a limit: only the most reactive substrates, typically those with $k > \sim 3 \times 10^6$ M^{-1} s^{-1}, can be studied.

In the course of studying the reversible homolytic cleavage of organochromium cations,[2] including $(H_2O)_5CrC(CH_3)_2OH^{2+}$, it occurred to us that this reaction could be used for the chemical, rather than radiolytic, generation of the free radical in acidic solution. The experimental conditions can easily be controlled to adjust the rate of radical formation to a range suitable for quantitative kinetic studies of the rates of the radical–substrate reaction.

We describe in this paper the development of the technique and its limitations, chief among which is the requirement that the substrate not react rapidly with Cr^{2+}. The reaction of $\cdot C(CH_3)_2OH$ with $Co(NH_3)_6^{3+}$ and related complexes[3-9] provides an important application since the constants in acidic solution fall to values too low for radiolytic determination. The mechanism is, moreover, of considerable interest in view of the change in rate at a pH well below the pK_a value of the free radical, which has been the basis for suggestions that certain chemical intermediates play a key role in the oxidation–reduction reaction.[4,5]

The notation used for the reactions occurring is given in eq 1–3, with $Co(NH_3)_6^{3+}$ as one example of the complexes under consideration. The values of the forward[2] and reverse[10] rate constants for the first step being known, the results permit the evaluation of k_2.

$$CrC(CH_3)_2OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cr^{2+} + \cdot C(CH_3)_2OH \qquad (1)$$

$$Co(NH_3)_6^{3+} + \cdot C(CH_3)_2OH \xrightarrow{k_2} Co(NH_3)_6^{2+} + (CH_3)_2CO + H^+ \qquad (2)$$

$$Co(NH_3)_6^{2+} + 6H_3O^+ \xrightarrow{\text{fast}} Co(H_2O)_6^{2+} + 6NH_4^+ \qquad (3)$$

Experimental Section

The cobalt(III) and chromium(III) complexes[11] were prepared by standard methods: $[Co(NH_3)_6](ClO_4)_3$,[12] $[Co(ND_3)_6](ClO_4)_3$,[13] $[Co(en)_3](ClO_4)_3$,[14] $[Co(tn)_3](ClO_4)_3$,[15] $[Co(chxn)_3]Cl_3\cdot H_2O$,[16]

---

(1) The value cited is from the estimate made by: Endicott, J. F. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 90–92. It is probably preferred to the experimental determination of $E_{1/2}$ given by: Lilie, J.; Beck, G.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 458.

(2) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(3) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944.

(4) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1977**, 1056.

(5) Olson, K. R.; Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* **1974**, 938.

(6) Hoffman, M. Z.; Simic, M. *J. Am. Chem. Soc.* **1972**, *94*, 1757.

(7) Campano, D. C.; Kantrowitz, E. R.; Hoffman, M. Z.; Weinberg, M. S. *J. Phys. Chem.* **1974**, *78*, 626.

(8) Papaconstantinou, E. *J. Inorg. Chem.* **1978**, *40*, 2071.

(9) Papaconstantinou, E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 115.

(10) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(11) The chelating ligands are abbreviated as follows: en = 1,2-diaminoethane; tn = 1,3-diaminopropane; chxn = *trans*-1,2-diaminocyclohexane; bpy = 2,2′-bipyridine.

(12) Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 216.

(13) Anderson, J. S.; Briscoe, H. V. A.; Spoor, N. *J. Chem. Soc.* **1943**, 361.

(14) Work, J. B. *Inorg. Synth.* **1946**, *2*, 221.

(15) Bailar, J. C., Jr.; Work, J. B. *J. Am. Chem. Soc.* **1946**, *68*, 232.

0020-1669/82/1321-2537$01.25/0