Photochemical Decomposition of Two μ-Superoxo-dicobalt Ammines in Acidic Aqueous Solutions[1]

Joan S. Valentine[2] **and Donald Valentine, Jr.***

Contribution from the Chemistry Department,
Princeton University, Princeton, New Jersey 08540. *Received September 2, 1969*

Abstract: Near-ultraviolet irradiation ($\lambda > 300$ nm) of μ-superoxo-dicobalt ammines $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ and $[(NH_3)_4Co(NH_2,O_2)Co(NH_3)_4]^{4+}$ in acidic aqueous solutions causes efficient decompositions of those complexes into 1:1:1 mixtures of $[(Co(NH_3)_5(H_2O)]^{3+}$, Co^{2+}, and O_2, independent of temperature, complex concentration, acidity, or ionic strength of the irradiated solutions. Photolysis of either ion in solutions containing chloride ion leads to production of mixtures of $[Co(NH_3)_5(Cl)]^{2+}$ and $[Co(NH_3)_5(H^2O)]^{3+}$; the kinetics of chloride incorporation are very different for the two cations, however. Attempts to scavenge electronically excited O_2, spin-paired Co^{II}, and free-radical intermediates gave negative results. A study of the wavelength dependence of the quantum yield for the photodecomposition reactions showed that the decomposition occurred upon population of ligand-to-cobalt electron-transfer excited states. The mechanisms of these reactions are discussed.

Numerous studies of cobalt(III) ammine photochemistry in acidic aqueous solutions have been reported.[3] Typically, cobalt(III) ammines prove nearly inert to irradiation of the ligand field absorption bands but are decomposed readily upon irradiation of the parity allowed ligand-to-cobalt electron-transfer absorption bands which dominate the ultraviolet absorption spectra of these complexes. The ultimate product of irradiation of the charge-transfer bands is Co^{2+} in quantitative yield, but detailed studies of some of these reactions have revealed bewildering variety in the photochemical primary processes. Known primary photochemistry includes reduction of the cobalt center, aquation, and the related processes of linkage isomerization and possibly geometric isomerization.[3] These processes may occur in competition with each other and as a consequence a second photochemically activated process may be required in some systems to convert cobalt(III) ammines to Co^{2+}. Even systems where reduction to Co^{2+} occurs directly may be complicated by the subsequent chemistry of highly reactive free radicals produced through oxidation of ligands by the cobalt center in the primary process. It is not surprising that it has proved difficult to obtain reliable stoichiometric data for cobalt(III) ammine photochemistry or to relate these data to the primary photochemistry of these systems.[4]

In view of these considerations we were intrigued by Sykes' recent report that upon exposure to sunlight in acidic aqueous solutions, μ-superoxo-bis(pentaamminecobalt) (5+), **1**, underwent the apparently very simple reaction 1.[5] It seemed to us that **1** and related complexes might afford cobalt photochemical substrates more convenient to study than simple cobalt ammines.

$$[(NH_3)_5CoO_2Co(NH_3)]_5^{5+} \xrightarrow[\text{sunlight}]{H^+} [Co(NH_3)_5(H_2O)]^{3+} + Co^{2+} + O_2 + 5NH_4^+ \quad (1)$$

Complex **1** and the related complex μ-amido-μ-superoxo-bis(tetraamminecobalt(III)) (4+), **2**, are known from X-ray and electron spin resonance studies to be best formulated as derivatives of the chromophoric system $[Co^{III}O_2^{-}Co^{III}]$ containing two electronically equivalent trivalent cobalt centers bridged by superoxide.[6] Essentially the same chromophore is found in a number of other complexes. All of these complexes offer the same advantages of thermal kinetic stability and thermodynamic instability with respect to reduction of the cobalt center which are found with cobalt(III) ammines. Moreover, the essential photochemical transformation in reaction 1 is simply reaction 2.

$$[Co^{III}O_2^{-}Co^{III}] \longrightarrow Co^{III} + Co^{2+} + O_2 \quad (2)$$

This reaction could be expected for a superoxide-to-cobalt electron-transfer excited state of the μ-superoxo-dicobalt chromophore. Since O_2, the one-electron oxidation product of superoxide, is not especially reactive and since in most μ-superoxo-dicobalt complexes the O_2^{-}-to-Co^{III} electron-transfer transition lies at considerably lower energies (near 33,000 cm^{-1}) than other electron-transfer transitions, reaction 2 could reasonably be expected to be general and probably free from side reactions. Finally, an attractive feature of reaction 1 or 2 for photochemical studies was the fact that methods existed to test for various likely intermediates such as excited singlet O_2, spin-paired Co^{II}, and coordinatively unsaturated Co^{III} species.

Our studies of the photochemistry of μ-superoxo-dicobalt ammine derivatives have included the fairly detailed investigation of the photochemistry of **1** and **2** which is described in this paper, a study of the effects of substitution of chelating organic ammines for NH_3 on their photochemistry, and a study of the effects of other acido ligands upon the photochemistry of the μ-superoxo-dicobalt chromophore. The latter two parts will be reported elsewhere.[7]

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[1] For preliminary reports of this work, see D. Valentine, Jr., and J. S. Valentine, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. L-19; J. S. Valentine and D. Valentine, Jr., "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, paper B-05.

[2] National Science Foundation Trainee, 1967–1968.

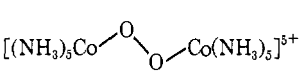
[3] For recent reviews of cobalt(III) systems, see D. Valentine, Jr., *Advan. Photochem.*, **6**, 123 (1968); V. Balzani, L. Moggi, and V. Carassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

[4] For instance, compare the data presented for $Co(NH_3)_6^{3+}$ in J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965); M. F. Manfrin, G. Variani, L. Moggi, and V. Balzani, *Mol. Photochem.*, **1**, 245 (1969).

[5] A. G. Sykes, *Trans. Faraday Soc.*, **59**, 1325 (1963).

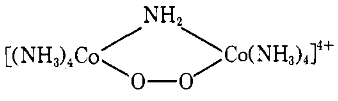
[6] *Cf.* A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, **13**, 1 (1970).

[7] (a) J. S. Valentine and D. Valentine, Jr., *Inorg. Chem.*, **10**, 393 (1971); (b) D. Valentine, Jr., and J. S. Valentine, manuscript in preparation.



$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$

1



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Experimental Section

Materials. Sodium perchlorate hydrate was prepared following Olin.[8] Mononuclear Co^{III} ammines were prepared following standard procedures.[9] Samples of **1** acid sulfate prepared following Gleu and Rehm[10] were converted to the perchlorate following Ebsworth and Weil.[11] The nitrate was prepared using Werner's method[12] with substitution of ozone (2% in O_2) for air in the initial oxidation step. Samples of **2** nitrate were prepared similarly[13] or by the method of Mori, *et al.*[14] A perchlorate salt was prepared by successive precipitations of the nitrate from dilute $HClO_4$ with $NaClO_4$. The μ-superoxo-dicobalt cyanides $K_5[(CN)_5CoO_2Co(CN)_5]$ and $Ba_2[(CN)_4Co(NH_2, O_2)Co(CN)_4]$ were prepared following Mori, *et al.*[15] Diamagnetic binuclear cobalt ammines were prepared following Werner.[13]

Analytical Procedures. Cobaltous ion was determined using the method of Gould and Taube.[16] The extinction coefficient of the $[CoCl_4]^{2-}$ ion at 692 nm was determined for each set of conditions and for each sample of concentrated HCl. With these precautions, the precision of determinations was ±2% under most conditions.

Photochemical decomposition of μ-superoxo-dicobalt ammines typically gave rise to 1:1 mixtures of Co^{2+} and Co^{III} products, the latter consisting of one or more components. The number of components and their identities were determined by spectrophotometric analysis of photolyzed solutions and by ion-exchange chromatography on a Dowex 50W-X8 cation-exchange resin. Cobaltous ion and divalent Co^{III} ammines were eluted with 1.00 *M* $NaClO_4$ containing 10^{-3} *M* $HClO_4$, while trivalent species were eluted with 3 *M* HCl. Most quantitative analyses reported in this paper were obtained by spectrophotometric analysis of photolyzed solutions in the 350–600-nm region of the spectrum. All analyses of experiments with cyano complexes and other binuclear cobalt ammines were done spectrophotometrically. This procedure invites the obvious objections that precise determinations of wavelength are very important and that absorption spectra of Co^{III} ammines are very similar in this wavelength region. In fact, with most systems we found that absorbances at wavelengths shorter than 350 nm were 5–10% higher than predicted on the basis of stoichiometric equations consistent with visible absorption data. However, there was no strong anomalous short-wavelength absorption which could be attributed to ligand-to-cobalt electron-transfer absorption, except that expected from visible results, and ion-exchange chromatography of the solutions in question revealed no additional products. We inferred that unexplained short-wavelength absorption was due to small amounts of undecomposed μ-superoxo-dicobalt complex.[17]

Photochemical Procedures. In preliminary experiments identical results were obtained whether or not solutions were purged with a fast stream of inert gas during photolysis, and subsequently solutions were not purged. Photolyses were carried out in clean, loosely stoppered cylindrical Pyrex vessels in solutions containing sufficient acid to protonate NH_3 released during the reaction.

Stoichiometric studies were made using a 450-W Hanovia mediumpressre muercury arc, housed in a quartz immersion well and water cooled, whose output was filtered through cylindrical sleeve filters either of Pyrex (wavelengths longer than 300 nm transmitted) or uranium glass (wavelengths longer than 345 nm). No attempt was made to eliminate infrared or visible lamp emission, because in preliminary experiments it was found that neither **1** nor **2** was decomposed at an appreciable rate by visible or infrared irradiation. The intensity of the source used in stoichiometric experiments was *ca.* 10^{17}–10^{19} photons/sec. Solutions were irradiated in a large water bath thermostated to the desired temperature. The usual procedure was to irradiate a freshly prepared solution of the μ-superoxo-dicobalt ammine until there was no residual 700-nm absorption, then analyze as describe above. To avoid secondary photolysis of products, which were in some instances appreciably sensitive to light of the wavelengths used to decompose the μ-superoxo-dicobalt complex, dilute solutions were employed so that optical densities of product solutions were very low at wavelengths longer than 300 nm.

Some experiments using 254-nm exciting light were carried out using a Srinivasan–Griffin reactor.[18]

Comparative rate studies were made using the Hanovia lamp and a quantum yield merry-go-round,[19] while quantum yields were measured for monochromatic exciting light of wavelengths 406 nm, obtained with the Hanovia lamp and a chemical filter solution,[20] 350 nm, and 320 nm, obtained with a specially constructed monochromator.[21] The emitted intensities of these sources were found using potassium ferrioxalate actinometry to be in the range from 1.8–5.4 einsteins/(l. min)' assuming the quantum yields for production of Fe^{2+} from $[Fe(C_2O_4)_3]^{3-}$ to be 1.14 at 406 nm, 1.21 at 350 nm, and 1.25 at 320 nm.[22,23] All quantum yield measurements except those at 405 nm were made in optically dense solutions, and quantum yields obtained with 405-nm exciting light were corrected for failure to absorb all of the light.

Results

Spectral Properties of Complexes. Spectral data for complexes **1** and **2**, their cyanide analogs, and various possible product complexes are given in Table I. The characteristic 700-nm absorption bands in the spectra of **1** and **2** were used in this work to determine concentrations of those ions.[24]

Table I. Spectral Properties of μ-Superoxo-dicobalt Ammine Derivatives[a]

Complex	λ_{max}[b] (ϵ_{max})
$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ (**1**)	670 (835), 480 (255), 299 (2.90 × 10^4), 340 (sh)
$[(NH_3)_4Co(NH_2,O_2)Co(NH_3)_4]^{4+}$ (**2**)	700 (305), 477 (368), 306 (4.50 × 10^3)
$[(CN)_5CoO_2Co(CN)_5]^{5-}$	485 (375)
$[(CN)_4Co(NH_2,O_2)Co(CN)_4]^{4-}$	514 (300[c])
$[Co(NH_3)_5(H_2O)]^{3+}$	533[d] (32.0) 492 (47.3) 346 (43.7)
$[Co(NH_3)_5Cl]^{2+}$	533 (48.5), 492[d] (36.5)
$[Co(NH_3)_5(NO_3)]^{2+}$	500 (56.7)
$[Co(NH_3)_5(CF_3CO_2)]^{2+}$	500 (63.5)
trans-$[Co(NH_3)_4(H_2O)_2]^{3+}$	511 (50.8)
cis-$[Co(NH_3)_4(H_2O)_2]^{3+}$	500 (47.9)
$[Co(CN)_5(H_2O)]^{2-}$	370 (280)

[a] All spectra were recorded in 0.1 *M* $HClO_4$. [b] Wavelengths are reported in nanometers. [c] This complex may have been contaminated with $[(CN_3)(NH_3)Co(NH_2,O_2)Co(CN)_4]^{3-}$ and related systems. [d] Not a maximum in absorption.

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[8] A. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957), and references therein.

[9] G. Brauer, "Handbuch des Preparativen Anorganische Chemie," F. Enke, Stuttgart, 1954.

[10] K. Gleu and K. Rehm, *Z. Anorg. Allg. Chem.*, **237**, 79 (1938).

[11] E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

[12] A. Werner and A. Mylius, *Z. Anorg. Allg. Chem.*, **16**, 245 (1898).

[13] A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910). We are most grateful to Drs. J. Weil and G. G. Christoph for sending us a copy of a translation of this article into English. The use of ozone in these preparations is mentioned by A. G. Sykes, *Trans. Faraday Soc.*, **58**, 540 (1962).

[14] M. Mori, J. A. Weil, and M. Ishiguro, *J. Amer. Chem. Soc.*, **90**, 615 (1968).

[15] M. Mori, J. K. Kinnaird, and J. A. Weil, *J. Phys. Chem.*, **71**, 103 (1967).

[16] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

[17] Analysis of this region was made difficult also by absorbance due to various anions, particularly nitrate.

[18] We thank Professor E. C. Taylor for the use of this apparatus.

[19] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

[20] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold, New York, N. Y., 1941, p 69.

[21] P. A. Cerutti, N. Miller, M. G. Pleiss, J. F. Remsen, and W. J. Ramsey, *Proc. Nat. Acad. Sci. U. S.*, **64**, 731 (1969).

[22] J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1965, p 784.

[23] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

[24] This must be done with care as the absorption intensities, especially of **1**, are medium dependent; see ref 6.

Table II. Photochemical Disproportionation Stoichiometries for μ-Superoxo-dicobalt Ammines **1** and **2**

Complex	Filter system	[Complex], $M \times 10^4$	[H$^+$], M	Temp, °C	[Photochemical products], $M \times 10^4$ Co^{2+}	Co^{III}	Co^{III} products
1(NH_3)	*a*	8.82	0.2	22	8.8	8.7	$[Co(NH_3)_5(H_2O)]^{3+}$
1(NH_3)	*b*	8.82	0.2	22	9.1	9.3	$[Co(NH_3)_5(H_2O)]^{3+}$
1(NH_3)	*b*	8.3	0.1[c]	18	8.3	8.2	$[Co(NH_3)_5(H_2O)]^{3+}$
1(NH_3)	*b*	8.3	0.1[d]	18	8.3	8.2	$[Co(NH_3)_5(H_2O)]^{3+}$
2(NH_3)	*b*	5.0	0.002	13	5.0	4.9	$[Co(NH_3)_5(H_2O)]^{3+}$
2(NH_3)	*b*	5.0	0.1	13	5.0	5.0	$[Co(NH_3)_5(H_2O)]^{3+}$
2(NH_3)	*a*	5.0	0.1	13	5.0	5.0	$[Co(NH_3)_5(H_2O)]^{3+}$
2(NH_3)	*b*	5.0	0.1[e]	13	5.0[f]	5.0	$[Co(NH_3)_5(H_2O)]^{3+}$
2(NH_3)	*b*	20.0	0.1	13	19.8	19.8	$[Co(NH_3)_5(H_2O)]^{3+}$
2(NH_3)	*b*	500	0.25	18	505	495	$[Co(NH_3)_5(H_2O)]^{3+}$

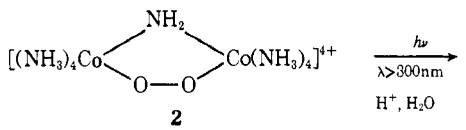
[a] Transmitted light of wavelengths longer than 300 nm. [b] Transmitted light of wavelengths longer than 345 nm. [c] Contains 0.1 M H_2O_2. [d] Contains 0.1 M $(NH_4)_2(S_2O_8)$. [e] Contains 0.9 F $NaClO_4$. [f] Presumed.

Thermal Decomposition. Thermal decomposition of **1** in 0.1 M $HClO_4$ at 25° was found to be first order with $k = 1.4 \times 10^{-5}$ min^{-1}. In 2 M $HClO_4$ at 25°, Sykes[5] found $k = 1.42 \times 10^{-5}$ min^{-1}. The products were Co^{2+} and $[Co(NH_3)_5(H_2O)]^{3+}$ in 1:1 ratio and (we presume) molecular oxygen. Decomposition of **1** under our conditions was not accelerated by purging the solution with N_2, in contrast to the report by Vlcek,[25] who advanced his finding of acceleration by N_2 as evidence that O_2 was in equilibrium with μ-superoxo-dicobalt ammine. The dibridged complex **2** underwent very slow first-order decomposition at 25° with $k = 3 \times 10^{-7}$ min^{-1}. At 85° complete decomposition of **2** required *ca.* 10 hr and gave a 1:1 mixture of Co^{2+} and Co^{III} products consisting of roughly equimolar amounts of $[Co(NH_3)_5(H_2O)]^{3+}$ and the equilibrium mixture of *cis-* and *trans-*$[Co(NH_3)_4(H_2O)_2]^{3+}$.[26] From the singly bridged cyano complex was obtained 2 mol of $[Co(CN)_5(H_2O)]^{2-}$/mol of $[(CN)_5CoO_2Co(CN)_5]^{5-}$ decomposed, with a first-order rate constant $k = 1.2 \times 10^{-4}$ min^{-1} in 0.1 M $HClO_4$ at 25°. The dibridged complex $[(CN)_4Co(NH_2,O_2)Co(CN)_4]^{4-}$ was almost indefinitely stable in dilute acid solutions.

Photochemical Decomposition Stoichiometries. Stoichiometric studies of photochemical decompositions of **1** and **2** were carried out in various acidic aqueous media using (in effect) either 300–400-nm ($\lambda > 300$ nm) or 345–400-nm ($\lambda > 345$ nm) exciting light. Irradiation produced only very slow decomposition of **2** and no decomposition of **1** when the exciting light was of wavelengths longer than 440 nm. Irradiations with light in the wavelength ranges 300–400 or 345–400 nm led to smooth decomposition reactions in which O_2 was evolved. These decompositions were studied in this work. Irradiations with 254-nm light of solutions of **1** or **2** in 0.1 M $HClO_4$ led eventually to production of 2 mol of Co^{2+}/mol of μ-superoxo-dicobalt complex taken. A study of 254-nm irradiation of **1** by Barnes, *et al.*,[27] led them to conclude that the photochemical decomposition observed is the result of free-radical processes. In contrast we present here evidence that the photochemical decompositions of **1** and **2** upon irradiation with light of wavelengths longer than 300 nm involve solely molecular processes.

The only cobalt-containing products detected in solutions of **1** or **2** irradiated at 25° in 0.1 M $HClO_4$ with light of $\lambda > 300$ nm until the 700-nm absorption had disappeared were Co^{2+} and $[Co(NH_3)_5(H_2O)]^{3+}$ in 1:1 ratio. Representative stoichiometric data are given in Table II to illustrate the precision of our measurements. The ultimate source of the electron used to reduce the Co center was established when it was found that the oxygen gas yields in these reactions were essentially quantitative (*vide infra*). The stoichiometric equations 3 and 4 can thus be written.

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+} \xrightarrow[\lambda>300\text{nm}]{h\nu} \underset{H^+,\ H_2O}{} [Co(NH_3)_5(H_2O)]^{3+} + Co^{2+} + O_2 + 5NH_4^+ \quad (3)$$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$$[Co(NH_3)_5(H_2O)]^{3+} + Co^{2+} + O_2 + 4NH_4^+ \quad (4)$$

The stoichiometric equations 3 and 4 were obeyed exactly, independent of complex concentration, irradiating light intensity in the range 10^{16}–10^{19} photons/(sec cm^2), acidity in the range pH 0–4, temperatures in the range 0–30°, or the presence of 0.1 M H_2O_2 or 0.1 M $Na_2S_2O_8$ in the photolysis solutions. Photochemical decompositions of **1** or **2** in solutions containing sufficient concentrations of various anions resulted in production of the corresponding $[Co(NH_3)_5(X)]^{2+}$ complexes in addition to $[Co(NH_3)_5(H_2O)]^{3+}$, but the ratio of Co^{2+} to Co^{III} products remained 1.00 ± 0.03. Irradiation of solutions of **1** in concentrated H_2SO_4 and in 85% H_3PO_4 gave, respectively, $[Co(NH_3)_5(SO_4H)]^{2+}$ and $[Co(NH_3)_5(PO_4H_2)]^{2+}$ in 1:1 mixture with Co^{2+}. It was found that NO_3^-, Cl^-, $CF_3CO_2^-$, and $CCl_3CO_2^-$ could all be incorporated as $[Co(NH_3)_5X]^{2+}$ in photolyses of **1** and **2**.

Identification of the Co^{III} ammine product from **2** as $[Co(NH_3)_5(H_2O)]^{3+}$ rather than $[Co(NH_3)_4(H_2O)_2]^{3+}$ rests on spectral investigations of product solutions and also of the trivalent fractions isolated by ion-exchange chromatography of photolyzed solutions. At most, less than 2–3% of the diaquo cation can have been formed in this reaction. The photochemical decomposition of **2** at 25° thus leads to different Co^{III} products

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(25) A. Vlcek, *Collect. Czech. Chem. Commun.*, **25**, 3036 (1960).

(26) R. D. Mast and A. G. Sykes, *J. Chem. Soc. A*, 1031 (1968).

(27) J. E. Barnes, J. Barrett, R. W. Brett, and J. Brown, *J. Inorg. Nucl. Chem.*, **30**, 2207 (1968).

than thermal decomposition at 85°, suggesting that the two processes involve different intermediates. Since it was possible that observed differences in thermal and photochemical decompositions of **2** were due to similar intermediates giving different reactions at different temperatures, **2** was decomposed photochemically at 65°. All the Co^{III} appeared as $[Co(NH_3)_5(H_2O)]^{3+}$. The formation of $[Co(NH_3)_5(H_2O)]^{3+}$ from **2** implies that during photochemical decomposition protonation of the μ-amido group is more rapid than its removal from the remaining Co^{III} center.

Gas evolved in photochemical decompositions of **1** and **2** in 0.1 *M* $HClO_4$ solutions which had been carefully degassed and sealed under vacuum before photolysis was trapped and shown volumetrically to be produced in stoichiometric amounts, as demanded by reactions 3 and 4, and by mass spectroscopy to be almost entirely pure oxygen. In a typical experiment **1** gave 96 mol % of O_2 which was more than 99% pure with slightly greater than background N_2 (*m/e* 28) and N_2O (*m/e* 44). The latter are known products of the oxidation of coordinated NH_3 during photochemical decomposition of Co^{III} ammines induced by 254-nm irradiation and may be due either to a small component of the photolysis reaction or to photolysis of impurities in the μ-superoxo-dicobalt complex. It is certain that the N_2 did not arise from product $[Co(NH_3)_5(H_2O)]^{3+}$ since this complex is not decomposed with a significant quantum yield upon irradiation with the light source used in these experiments. Irradiations of **1** and **2** in solutions containing up to 0.1 *M* H_2O_2, 0.1 *M* $Na_2S_2O_8$, or 80% ethanol were accompanied by normal gas evolution. Irradiation of **2** in 70% aqueous ethanol in the presence of an organic phase consisting of a 1:5 mixture of 1,3-cyclohexadiene and benzene, in an apparatus similar to that used by Waters[28] to trap excited singlet oxygen generated chemically, followed by flash evaporation of the dried organic layer left at most a few per cent of polymeric residue, and the amount of residue was decreased substantially upon rigorous purification of the cyclohexadiene. Norascaridole, the product of reaction of cyclohexadiene with excited singlet oxygen,[29] was not detected. It was found similarly that the vigorous thermal decomposition of the diamagnetic cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ in acidic solutions did not give rise to intermediates capable of oxygenating cyclohexadiene.

Photochemical decomposition of $[(CN)_5CoO_2Co(CN)_5]^{5-}$ in neutral and acidic aqueous solutions was investigated briefly using exciting light of λ >345 nm. In H_2O and 0.1 *M* $HClO_4$ solutions this complex gave approximately 2 mol of $[Co(CN)_5(H_2O)]^{2-}$ and 0.43 ± 0.02 mol of H_2O_2 per mol of complex decomposed. Traces of Co^{2+} (up to about 4%) were also detected. Some O_2 was evolved, but although quantitative studies gave erratic results it was clear that less O_2 was evolved than predicted by reaction 5.[30] Nevertheless, the principal stoichiometric result of irradiation of this system is presumably that indicated by reaction 5. The dibridged complex $[(CN)_4Co(NH_2,O_2)Co(CN)_4]^{4-}$ proved very resistant to irradiation having λ >300 nm in neutral or acidic solutions.

$$2[(CN)_5CoO_2Co(CN)_5]^{5-} + 2H^+ + 4H_2O \xrightarrow{h\nu} 4[Co(CN)_5(H_2O)]^{2-} + H_2O_2 + O_2 \quad (5)$$

Rapid photochemical decomposition upon irradiation with light of λ >300 nm was observed in the binuclear cobalt ammine series only with complexes containing μ-superoxo bridges. Only very slow decompositions were observed upon >300 nm irradiation of 0.1 *M* $HClO_4$ solutions of the complexes with X = OH, NO_2, SO_4, and C_2O_4 in the series $[(NH_3)_4Co(NH_2,X)Co(NH_3)_4]^{n+}$, or of $[(en)_2Co(NH_2,OOH)Co(en)_2]^{4+}$ and $[(en)_2Co(NH_2,NO_2)Co(en)_2]^{4+}$.

Kinetic Studies of the Photochemical Decompositions. The stoichiometries determined above for photochemical decompositions of **1** and **2** are consistent with several different mechanisms for these reactions. For instance, either primary photochemical aquation of $[Co^{III}O_2^-{-}Co^{III}]$ leading to products of the type $[Co^{III}O_2^-] + [Co^{III}]$ or primary photoreduction leading to $[Co^{III}O_2] + [Co^{II}]$ could give the observed products. It is even conceivable that the first photon absorbed by $[Co^{III}O_2^-{-}Co^{III}]$ produces an intermediate which can only be converted to the final products photochemically. Accordingly, kinetics studies were carried out to provide evidence concerning various mechanistic possibilities.

Basically two types of studies were undertaken. Quantum yields for disappearance of **1** and **2** upon near-ultraviolet irradiation were measured with monochromatic 405-, 350-, and 320-nm light using potassium ferrioxalate actinometry. Comparative rates for disappearance of **1** and **2** under various conditions were obtained using the same light sources employed in determining stoichiometries.

Quantum yields and comparative rates were obtained for disappearance of μ-superoxo complex rather than appearance of products for analytical reasons. Disappearance of μ-superoxo complex and appearance of final products cannot be assumed *a priori* to have identical quantum efficiencies and we have, therefore, obtained evidence to show that these two processes are coupled to each other. First, rates of disappearance of **1** and **2** in 0.1 *M* $HClO_4$ solutions, after correction for failure to absorb all the incident light, were independent of complex concentration to over 95% disappearance of characteristic 700-nm absorption. Second, spectra of solutions of either complex irradiated for a period of time sufficient to produce only partial decomposition were identical with spectra expected for mixtures of μ-superoxo complex and final products defined by eq 3 and 4. For example, a solution of 0.002 *M* **2** perchlorate in 0.1 *M* $HClO_4$ was irradiated with light of λ >345 nm until the apparent 700-nm extinction coefficient had decreased from 306 to 267 (13% conversion). A difference spectrum of the irradiated solution, obtained by subtracting the spectrum of a 0.00174 *M* solution of **2** from the observed spectrum, was identical with the spectrum expected for a mixture of 0.00026 *M* Co^{2+} and 0.00026 *M* $[Co(NH_3)_5(H_2O)]^{3+}$ in the range 250–550 nm. These findings eliminate mechanisms requiring more than one photochemically activated step in conversion of **1** or **2** to final products. Moreover, the absence of strong 300-nm absorption

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[28] E. McKeown and W. A. Waters, *J. Chem. Soc. B*, 1040 (1966).

[29] G. O. Schenck and K. Gollnick, *Pure Appl. Chem.*, **9**, 507 (1964).

[30] The nature of gas evolution from $[(CN)_5CoO_2Co(CN)_5]^{5-}$ appears to have been stated incorrectly by J. Barrett, *Chem. Commun.*, 874 (1968).

Table III. Summary of Quantum Efficiencies for Photochemical Decompositions of **1** and **2**

Complex	λ, nm: 700	480	405	365[a]	350	320[b]	310[a]	254[a]
	Quantum yield							
1	$<10^{-3}$	$\ll 0.01$	0.1[c]	0.65	0.24	0.30	0.83	0.30
2	$<10^{-3}$	~ 0.01	0.1		0.40	0.49[e] 0.48[f] 0.50[g]		
$[(CN)_5CoO_2Co(CN)_5]^{5-}$	*d*	~ 0.01	0.05		0.20	0.20		
$[(CN)_4Co(NH_2,O_2)Co(CN)_4]^{4-}$	*d*	$<10^{-3}$	$<10^{-3}$		$<10^{-3}$	$<10^{-3}$		

[a] Quantum yields for 365- and 310-nm irradiation are from ref 27 and were said to be obtained in 0.2 *M* HCl (see text). [b] In 0.1 *M* $HClO_4$ solutions. Quantum yields for 320-nm excitation were measured at two intensities of absorbed light, 3.34 and 9.01 × 10^{-5} einstein/(l. min); the absorbed intensity of 350-nm light was 1.11 × 10^{-4} einstein/(l. min). [c] Precision limits are ±20% of reported value at 405 nm and ±10% of the reported value at 350 and 320 nm. [d] Complex does not absorb. [e] Absorbed intensity = 3.34 × 10^{-5} einstein/(l. min). Concentration of **2** = 0.0020 *M*. [f] Absorbed intensity = 9.01 × 10^{-5} einstein/(l. min). Concentration of **2** = 0.0020 *M*. [g] Concentration of **2** = 0.0010 *M*.

suggests that long-lived complexes of the type $[Co(NH_3)_5O_2]^{3+}$ and $[Co(NH_3)_5O_2]^{2+}$ are not formed since such species, especially the latter, would be expected to absorb strongly near 300 nm.

Quantum yields for photochemical decomposition of several binuclear cobalt complexes upon monochromatic 405-, 350-, and 320-nm irradiations in 0.1 *M* $HClO_4$ are given in Table III. The μ-superoxo-dicobalt complexes **1** and **2** undergo efficient photochemical decompositions only upon 350- and 320-nm irradiations, and the principal photochemical reactivity of these systems is thus associated with the absorption bands having maxima near 300 nm which have been assigned to oxygen-to-cobalt electron-transfer transitions. At 320 nm the quantum yield for decomposition of **2** in $HClO_4$ solutions was 0.48 ± 0.03, independent of complex concentration, acidity, ionic strength, and per cent conversion at two different intensities.

Kinetic and Stoichiometric Studies of Anion Incorporations in Photochemical Decomposition of 1 and 2. Formation of both $[Co(NH_3)_5(Cl)]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ in photolyses of **1** and **2** with light of λ >345 nm in solutions containing chloride ion has already been mentioned. Kinetic and stoichiometric analyses of the incorporation reaction gave rather different results for the two μ-superoxo complexes. In photolyses of **1**, the fraction *f* of Co^{III} products in the final product mixture appearing as $[Co(NH_3)_5(Cl)]^{2+}$ depended on the concentration of chloride as shown in Figure 1: *f* increased with increasing chloride concentration for $[Cl^-] \leq 0.5$ *M* and then became essentially independent of chloride concentration. For $[Cl^-] = 0.30$ *M* we found $f = 0.15$; for $[Cl^-] = 0.53$ *M*, $f = 0.23$; and for $[Cl^-] = 0.80$ *M*, $f = 0.25$. It was found that addition of chloride ion also increased the quantum efficiency for decomposition of **1** upon >345-nm irradiation.[31] For solutions containing 0.1 *M* $HClO_4$ the relative quantum yields for photochemical decomposition of **1** were found to be: $\phi_{rel} = 1.00$ for $[Cl^-] = 0$, $\phi_{rel} = 1.7$ for $[Cl^-] = 0.50$ *M*, $\phi_{rel} = 3.5$ for $[Cl^-] = 1.05$ *M*, and $\phi_{rel} = 3.8$ for $[Cl^-] = 1.50$ *M* as NaCl. The kinetic and stoichiometric behaviors of these systems are not strongly coupled; that is, values of *f* approach a constant value of about 0.25 at chloride concentrations at which increases in chloride concentration still produce increases in relative quantum yield.

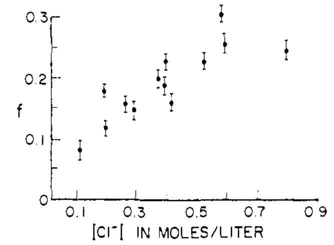
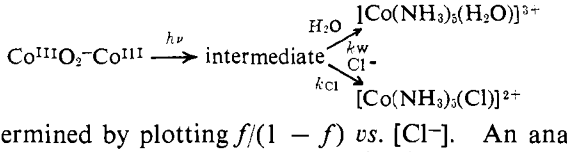


Figure 1. Incorporation of chloride as $[Co(NH_3)_5(Cl)]^{2+}$ in photolyses of **1** in solutions containing chloride ion. The parameter *f* is the fraction of Co^{III} product appearing as $[Co(NH_3)_5(Cl)]^{2+}$.

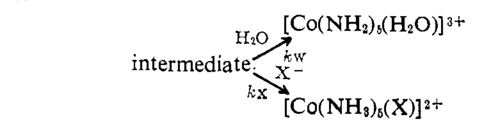
Rather different results were obtained in the system **2** + Cl^- irradiated with light of λ >345 nm. Here it was found that added chloride did not affect the quantum yield for decomposition of the μ-superoxo cation, suggesting that chloride incorporation took place *after* the primary photochemistry of **2** had occurred. For this system, we relate *f* to reactions of a (presumed) common precursor to both $[Co(NH_3)_5(Cl)]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ by eq 6, where k_{Cl}/k_W has the units liters per mole and the pseudo-first-order rate constant k_W and the second-order rate constant k_{Cl} are defined by reaction 7.[32] The ratio k_{Cl}/k_W can thus be

$$k_{Cl}/k_W = \frac{f}{(1 - f)[Cl^-]} \qquad (6)$$



$$Co^{III}O_2^-Co^{III} \xrightarrow{h\nu} \text{intermediate} \begin{array}{l} \xrightarrow[k_W]{H_2O} [Co(NH_3)_5(H_2O)]^{3+} \\ \xrightarrow[k_{Cl}]{Cl^-} [Co(NH_3)_5(Cl)]^{2+} \end{array} \qquad (7)$$

determined by plotting $f/(1 - f)$ *vs.* $[Cl^-]$. An analogous analysis has been applied to anion incorporations in the decomposition of $[Co(NH_3)_5(N_3)]^{2+}$ upon reaction with NO^+ as in[32,33]



$$[Co(NH_3)_5(N_3)]^{2+} + NO^+ \longrightarrow \text{intermediate} \begin{array}{l} \xrightarrow[k_W]{H_2O} [Co(NH_2)_5(H_2O)]^{3+} \\ \xrightarrow[k_X]{X^-} [Co(NH_3)_5(X)]^{2+} \end{array} \qquad (8)$$

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(31) This was reported incorrectly, on the basis of preliminary experiments, in ref 1. Part of the discrepancy between the data of Barnes, *et al.* (ref 27), and this work (*cf.* Table III) may have been due to their use of 0.2 *M* HCl as solvent for quantum yield measurements. However, it should also be noted that we have consistently found the chloride salt of **1** to give erratic results in quantitative experiments.

(32) *Cf.* A. Haim and H. Taube, *Inorg. Chem.*, 2, 1199 (1963).

(33) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *ibid.*, 6, 1027 (1967).

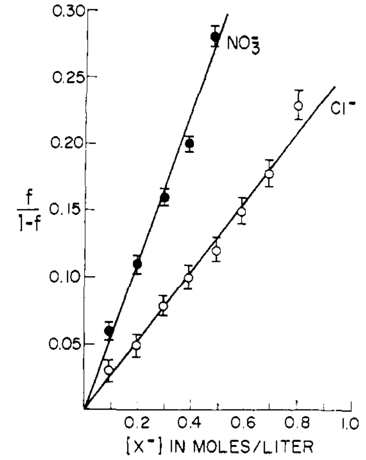

Figure 2. Incorporation of anions as $[Co(NH_3)_5(X)]^{2+}$ in photolyses of **2** in solutions containing chloride (○) and nitrate (●). The parameter f is the fraction of Co^{III} product appearing as $[Co(NH_3)_5(X)]^{2+}$.

A plot of $f/(1 - f)$ *vs.* $[Cl^-]$ for the photochemical system **2** + Cl^- is shown in Figure 2. The slope, which is k_{Cl}/k_W defined by reaction 7, was found to be 0.25 ± 0.03 l./mol. For reaction 8 with $X^- = Cl^-$, Buckingham, *et al.*,[33] found $k_{Cl}/k_W = 0.25$ l./mol at an ionic strength of 1.0 (most closely approximating our conditions). Remarkably good agreement was obtained also between our data for the photochemical system **2** + NO_3^- and the data of Buckingham, *et al.*,[33] for reaction 8 with $X^- = NO_3^-$. For the **2** + NO_3^- system we found $k_{NO_3}/k_W = 0.55 \pm 0.03$ l./mol, while for reaction 8 Buckingham, *et al.*,[33] reported k_{NO_3}/k_W 0.49 l./mol for ionic strength of 1.0. Nitrate ion also was found not to affect the quantum yield for photodecomposition of **2**.

Discussion

Electronic absorption spectra observed for **1** and **2** are similar; there are strong absorption bands with maxima near 700, 480, and 300 nm, and in the spectrum of **1** there is a shoulder near 345 nm. The 300-nm band has $\epsilon > 10^3$ and has been assigned by all authors as a superoxide-to-cobalt electron-transfer band. The 480-nm (and 350-nm) band is generally agreed to be due to cobalt-localized transitions. Much controversy has centered on assignment of the 700-nm band which is observed for **1** and **2**, but not for either of the cyanide analogs $[(CN)_5CoO_2Co(CN)_5]^{5-}$ and $[(CN)_4Co(NH_2,O_2)Co(CN)_4]^{4-}$. The 700-nm band has been variously attributed to the transitions $^2A_1 \rightarrow {}^2E$, derived from the $^1A_1 \rightarrow {}^1E$ transition observed for tetragonally distorted Co^{III} centers;[34,35] to a localized transition of the superoxide anion;[36] and to a transition derived from an ordinary spin-forbidden cobalt-localized transition.[37] None of these assignments is entirely satisfactory. In this work we have shown that for **1** and **2** neither the 700- nor the 480-nm transition is appreciably photochemically active. Our observation that the 700-nm absorption band is unreactive is compatible with each of the suggested assignments above since an O_2^--localized transition might not lead to decomposition and cobalt-localized transitions are known from studies of mononuclear systems to be generally unreactive upon irradiation.[38] The principal photochemical activity of both cations is associated with excitation of the 300-nm O_2^--to-Co^{III} electron-transfer transition. Because the 297- and 345-nm transitions in the spectrum of **1** overlap so strongly, it was not possible to determine whether or not the 350-nm transition was photochemically active.

Our data allow the conclusion that the photochemical reactions 3 and 4 involve molecular and not free-radical processes. Oxygen evolution from both **1** and **2** systems was not quenched by addition of methanol, ethanol, or hydrogen peroxide. Photochemical decomposition of **2** in 80% ethanolic HCl did not give rise to intermediates capable of inducing oxygenation of 1,3-cyclohexadiene. The quantum efficiencies for photochemical decompositions of **1** and **2** were the same at two different intensities and did not depend on the concentration of the μ-superoxo complexes. Finally, Davies, Hagopian, and Sykes[39] report that if complex **1** is labeled with ^{18}O in the bridging O_2^- group, the O_2 obtained from its photodecomposition under conditions similar to ours has the same isotopic composition as that used in preparing the complex. It seems reasonable to conclude that the primary photochemistry responsible for reactions 3 and 4 is electron transfer from O_2^- to Co^{III}.[40]

With this provisional conclusion we may consider elucidation of the detail of converting primary photoproducts to the products finally obtained. Plausible primary products are Co^{II}, O_2, and Co^{III}, where Co^{III} is either a $[Co^{III}O_2]^{3+}$ complex[41] or a coordinatively unsaturated Co^{III} ammine, and Co^{II} is a transient Co^{II} ammine derivative. We sought to trap possible spin-paired Co^{II} ammine derivatives having long lifetimes[42] by introducing as trapped reagents 0.1 *M* quantities of H_2O_2 and $Na_2S_2O_8$. Similarly, 1,3-cyclohexadiene was introduced as a probe for excited singlet states of O_2[43] generated in the photodecompositions. None of the reagents had any measurable effect on the photodecompositions and we can draw no conclusions about the possible production of these species. On the other hand, results of considerable interest were obtained in the anion incorporations which were carried out to test whether coordinatively unsaturated Co^{III} ammines might be intermediates in the photochemical reactions.

The good agreement observed between both k_{Cl}/k_W and k_{NO_3}/k_W values for the photochemical systems **2** + X and the corresponding k_{Cl}/k_W and k_{NO_3}/k_W

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(34) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **308**, 254 (1961).

(35) J. Barrett, *Chem. Commun.*, 874 (1968).

(36) K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 1725 (1968).

(37) Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 146 (1969).

(38) *Cf.* A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958).

(39) R. Davies, A. K. E. Hagopian, and A. G. Sykes, *J. Chem. Soc. A*, 623 (1969).

(40) It is not possible to rule out aquation-type processes wherein an O_2^--to-Co^{III} bond is broken to give $Co^{III}O_2^-$ and Co^{III} fragments and O_2^--to-Co^{III} electron transfer occurs later to give $Co^{II} + O_2$.

(41) This would presumably be a complex of the $O_2(^3\Sigma_g)$ ground state since $O_2(^1\Delta_g)$ should have a short lifetime under our experimental conditions because of the various paramagnetic ions present in the solution.

(42) W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, **73**, 1941 (1969), gave evidence that spin-paired excited states of Co^{II} may have appreciable lifetimes.

(43) Reaction of 1,3-cyclohexadiene with $^1O_2$ is efficient and yields norascaridole; *cf.* K. Gollnick, *Advan. Photochem.*, **6**, (1968).

values observed for reaction 8 suggests strongly that a common intermediate is precursor to stable Co^{III} products in both the photochemical systems and in reaction 8. We feel the most logical candidate for this intermediate is the coordinatively unsaturated Co^{III} ammine $[Co(NH_3)_5]^{3+}$, obtained in the photochemical systems from $[Co(NH_3)_5(O_2)]^{3+}$ and in reaction 8 from either $[Co(NH_3)_5(N_2)]^{3+}$ or $[Co(NH_3)_5(NNNNO)]^{3+}$. In neither the photochemical systems nor reaction 8 is it likely that the original reactants (*i.e.*, **2** or $[Co(NH_3)_5(N_3)]^{2+}$) are immediate precursors to $[Co(NH_3)_5]^{3+}$. The five-coordinate intermediate can be expected to react with its solvation sphere at a rate at least competitive with reorganization of that solvation sphere. Consequently, $[Co(NH_3)_5]^{3+}$ produced directly from **2** or its excited states (*i.e.*, before the reduced Co center departed) would react with a solvation sphere appropriate to a species having a charge of 4+, while $[Co(NH_3)_5]^{3+}$ produced directly from $[Co(NH_3)_5(N_3)]^{3+}$ after reaction with NO$^+$ would react with a solvation sphere appropriate to a species having a charge of 2+ or 3+. Since anion incorporation is well known to depend on the charge of the incorporating species,[44] it is highly unlikely that k_X/k_W values obtained for photochemical systems and for reaction 8 could be in agreement as close as that observed unless the precursor to $[Co(NH_3)_5]^{3+}$ in both cases had the same charge. It has already been pointed out[32] that species such as $[Co(NH_3)_5(N_2)]^{3+}$ or $[Co(NH_3)_5(NNNNO)]^{3+}$, with lifetimes long compared to the time required for solvent reorganization, probably are formed in reaction 8. There is no evident reason why a $[Co(NH_3)_5(O_2)]^{3+}$ complex should not have a similar lifetime.

In assessing the differences in behavior of the photochemical systems **1** + Cl$^-$ and **2** + Cl$^-$, we note that Sykes has presented convincing kinetic evidence for formation of ion pairs between **1** and Cl$^-$.[45] For this system, Sykes found the formation constant for the ion pair to be approximately unity when the total ionic strength was 2.0. All of the anion-incorporation experiments described here were carried out with solutions having total ionic strengths considerably lower than 2.0. Under our photolysis conditions, therefore, extensive ion pairing between **1** and Cl$^-$ probably occurs, and results obtained with **1** are expected to contain contributions from photolysis of the ion pair as well as photolysis of free **1**. Our stoichiometric incorporation data allow the further conclusion that the role of Cl$^-$ in the photochemistry of the ion pair cannot be restricted simply to promotion of formation of $[Co(NH_3)_5O_2]^{3+}$, because if this were the case the f values obtained for **1** + Cl$^-$ would be identical with those obtained for **2** + Cl$^-$.

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(44) For instance, see G. E. Dolbear and H. Taube, *Inorg. Chem.*, **6**, 60 (1967).

(45) A. G. Sykes, *Trans. Faraday Soc.*, **59**, 1334, 1343 (1963).

Oxidations of Aqueous Chromium(II). II. Chromium–Carbon Bond

Willfred Schmidt, James H. Swinehart, and Henry Taube*

Contribution from the Departments of Chemistry, Stanford University,
Stanford, California 94305, and the University of California at Davis,
Davis, California 95616. Received April 11, 1970

Abstract: An investigation of the formation and kinetic stability of complexes containing a chromium–carbon bond in an aqueous medium is described. Pentaaquochromium(III) ions carbon bonded to small acyclic anions such as are derived from isopropyl alcohol and diethyl ether are formed by the reduction of organic radicals with Cr(II). The organic radicals are produced by hydrogen abstraction with OH radicals. Aquation rates of the Cr(III) complexes when the organic ligands contain hydroxyl groups (alcohols) are described by the differential rate law $-\mathrm{d}\ \ln\,[(H_2O)_5CrL^{2+}]/\mathrm{d}t = k_1 + k_2[H^+]$. The rate laws for complexes having organic ligands which do not have a hydroxyl group (*e.g.*, methyl or the radical derived from diethyl ether) do not show the term independent of hydrogen ion. A mechanism is proposed in which the activated complex contains a solvent molecule in a position so as to take advantage of hydrogen bonding with the organic ligand.

As part of a continuing study of oxidations of aqueous Cr(II),[1] the formation and kinetic stability of complexes formed when radicals of small acyclic molecules oxidize Cr(II) have been studied.

A recent review article[2] has covered the use of Cr(II) as a reducing agent in a variety of organic reactions. Anet[3] first noted and isolated a stable chromium intermediate containing a chromium–carbon bond. This was the benzylchromium ion obtained in the reduction

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* Address correspondence to this author at Stanford University.

(1) W. G. Schmidt, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **7**, 1984 (1968).

(2) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, **7**, 247 (1968).

(3) F. A. L. Anet and E. LeBlanc, *J. Amer. Chem. Soc.*, **79**, 2649 (1957).