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Kinetics of Some Oxidation Reactions of Diaquocob(II)aloxime[1a]

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Cobalt(III) complexes of the family $Co(NH_3)_5X^{2+}$ are rapidly reduced by $Co(dmg)_2(H_2O)_2$ resulting, by transfer of group X, in the formation of $Co(dmg)_2(H_2O)(X)$. Kinetic measurements were made on these reactions, which follow a second-order rate expression after correction for the decomposition of the Co(II) reactant. The reactivity of the family of complexes is discussed in terms of the stabilities of the various X-bridged inner-sphere transition states.

Introduction

Considerable interest in the bis(dimethyglyoximato) complexes of cobalt has been expressed in the last few years with the discovery that their chemical properties closely resemble those of vitamin B_{12}. Schrauzer[2] has recently reviewed the chemistry of these dmg complexes,[3] often called "cobaloximes," pointing out their similarities to vitamin B_{12}.

We have studied the rates of oxidation of $Co^{II}(dmg)_2(H_2O)_2$ by a related series of oxidants. We felt it important to examine a B_{12} model system that might provide some assessment of the rates and mechanism of the Co(II)–Co(III) interconversions.

The particular system chosen was the reduction of Co(III) complexes of the type $Co(NH_3)_5X^{2+}$ by $Co^{II}(dmg)_2(H_2O)_2$. The likely oxidation products are $Co^{III}(dmg)_2(H_2O)X$ if the reactions proceed by the inner-sphere mechanism or $[Co^{III}(dmg)_2(H_2O)_2]^+$ from the outer-sphere mechanism. Both of these Co(III) products are kinetically inert toward substitution,[4,5] which adds to the attractiveness of this system because the ease of their isolation and characterization permits a positive determination of the mechanism of the redox reactions.

Aqueous solutions of aquocob(II)aloxime are stable in the absence of acids and oxygen. In the present work the reactions were carried out with the strict exclusion of oxygen; the complex is reported to be a partially reversible oxygen carrier.[6] The decomposition in the presence of hydrogen ion, with concomitant loss of dmg, must be contended with in any aqueous reaction system. The decomposition process can be controlled, at least for a short time, by appropriate buffers, although it limits the oxidizing systems that can be studied to nonhydrolyzable compounds such as the pentaamminecobalt(III) ions.

A related reaction is the oxidation of pentacyanocobaltate(II) ions by the same family of cobalt(III)–ammine complexes.[7]

Experimental Section

Materials.—Diaquocob(II)aloxime was prepared by the method of Schrauzer[8] in an apparatus which allowed the formation, filtration, washing, and drying of the product under nitrogen. The complex was stored over calcium chloride in a vacuum desiccator. Purity was checked by analysis of the Co(II) released by heating a sample of the solid with concentrated nitric acid. *Anal.* Calcd for $Co(C_4N_2O_2H_7)_2(H_2O)_2$: Co, 18.2. Found: Co, 17.6. This complex shows a distinctive absorption maximum at λ 460 nm in organic or aqueous solvents. Aqueous solutions are stable for at least 1 hr after rapid initial reactions with traces of oxygen or acid. The extinction coefficient at 460 nm was found to be 3.84×10^3 M^{-1} cm^{-1}, measured from the decrease in absorbance upon addition of a known but stoichiometrically deficient quantity of $Co(NH_3)_5Br^{2+}$, with allowance made for the absorbance of the products.

The Co(III) complexes $Co(dmg)_2Br(H_2O)$ and $Co(dmg)_2Cl(H_2O)$ were prepared by the method of Ablov and Samus.[9] The acidopentaamminecobalt(III) complexes were prepared by references cited in earlier publications and were generally converted to the perchlorate salts except for $Co(NH_3)_5Br^{2+}$ which was used as the bromide.[10,11]

Lithium perchlorate was prepared from the carbonate and recrystallized twice. Analytical grade sodium acetate, sodium bromide, and glacial acetic acid were used without further purification. Conductivity water was used throughout.

Rate Measurements.—The reactions between $Co(NH_3)_5X^{2+}$ complexes and $Co(dmg)_2(H_2O)_2$ were so rapid that the use of the stopped-flow method was required. The instrument used has been previously described.[10] To avoid interference from the acid decomposition of $Co(dmg)_2(H_2O)_2$, the reactions were carried out in an acetic acid–acetate buffer. Even at pH 5, however, the acid decomposition slowly occurs. To prevent deterioration of the solution, only the sodium acetate component of the buffer was added to the $Co(dmg)_2(H_2O)_2$ stock solution, effectively preventing any decomposition. Only the acetic acid buffer component was present in the $Co(NH_3)_5X^{2+}$ solutions which also served to arrest decomposition of the complexes by base hydrolysis which can be appreciable over long times at pH 5.

The kinetics were followed using the 460-nm absorption maximum of $Co(dmg)_2(H_2O)_2$ in most experiments. All runs were carried out at 24.9 ± 0.1°. The ionic strength was maintained at 0.1 M using lithium perchlorate, and the hydrogen ion concentration was regulated by an acetate buffer with a total concentration of 0.010 M. The pH of each solution from the kinetic runs was measured using a Beckman expanded-scale pH meter.

Product Analysis.—Blank experiments on mixtures of Co^{2+} and the Co(III) complexes deemed the most likely products such as $Co(dmg)_2(H_2O)X$ and $[Co(dmg)_2(H_2O)_2]^+$ were carried out. It was found that adequate separations could be achieved using a chromatographic technique with Dowex 50W-X8 cation-exchange resin. The resin was in the H^+ form for all complexes except for $X^- = F^-$ and NCS^-, where Na^+ resins were necessary. In the blank experiments it was demonstrated that the cationic species Co^{2+}, $[Co(dmg)_2(H_2O)_2]^+$, and excess $Co(NH_3)_5X^{2+}$ were held in the resin column while the uncharged $Co(dmg)_2(H_2O)X$ species was washed through the resin by water.

The wavelength maxima of the authentic $Co(dmg)_2(H_2O)X$ complexes were measured. Their molar absorptivities were also determined from a cobalt analysis made by prior reduction to Co^{2+} with excess Cr(II) and a spectrophotometric analysis with thiocyanate. These $Co(dmg)_2(H_2O)X$ complexes have λ_{max} 240–250 nm, with molar absorptivities determined in this manner of $(2–2.5) \times 10^4$ M^{-1} cm^{-1}. The solutions from the kinetic

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[1] (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 3048. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

[3] The monoanion of dimethylglyoxime is abbreviated dmg.

[4] D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967).

[5] H. G. Tsiang and W. K. Wilmarth, *ibid.*, **7**, 2535 (1968).

[6] G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, **92**, 1551 (1970).

[7] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).

[8] G. N. Schrauzer, *Inorg. Syn.*, **11**, 61 (1968).

[9] A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.*, **4**, 410 (1960).

[10] R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, **93**, 380 (1971).

[11] O. J. Parker and J. H. Espenson, *ibid.*, **91**, 1968 (1969).

studies were passed through the resin column, and the spectra of the water eluents were determined to establish the identity and the yield of any $Co(dmg)_2(H_2O)X$ product.

Results

Decomposition of $Co(dmg)_2(H_2O)_2$.—Cob(II)aloxime is subject to acid decomposition as shown in the reaction

$$Co(dmg)_2(H_2O)_2 + 2H^+ \xrightarrow{H_2O} Co_{aq}^{2+} + 2Hdmg \qquad (I)$$

The reaction rate is strongly acid dependent; in 0.001 *F* perchloric acid, for example, it proceeds to completion at a rate too high for the stopped-flow method. Decomposition proved to proceed slowly in acetate buffers of pH 4.8–6.1.

Reaction I follows a pseudo-first-order rate expression, and is highly pH dependent with half-times between 2.9 sec at pH 4.9 and 68 sec at pH 6.0. The data are summarized in Figure 1 in the form of a plot of k_{dec} *vs.* pH.

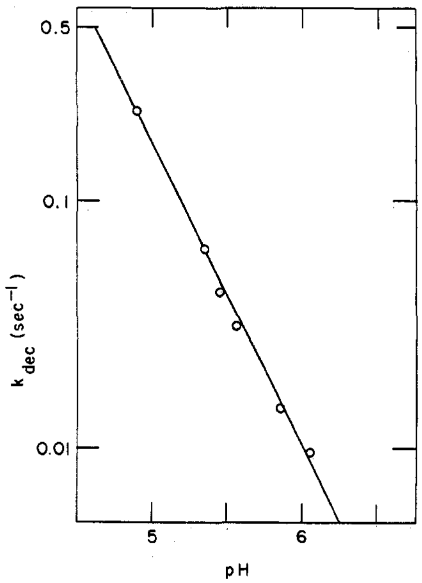

Figure 1.—The apparent first-order rate constant for the decomposition of $Co^{II}(dmg)_2(H_2O)_2$ as in reaction I as a function of pH at 25° in 0.01 *M* acetate buffer.

In order to correct for reaction I during the slower redox reactions, the decomposition rate was evaluated as a function of pH under conditions identical with those of the main reaction.

Reaction Products.—Using authentic samples of the monosubstituted Co(III) complexes, $Co(dmg)_2(H_2O)X$, and of the diaquo complex, the ion-exchange procedure outlined above was used to demonstrate that, in every case, the redox reaction resulted in transfer of X

$$Co(NH_3)_5X^{2+} + Co(dmg)_2(H_2O)_2 \longrightarrow Co_{aq}^{2+} + Co(dmg)_2(H_2O)X + 5NH_3 \qquad (II)$$

The exclusive products resulting from these reactions under the conditions of the kinetic studies were the $Co(dmg)_2(H_2O)X$ species.

Kinetic Studies.—Most kinetic experiments were carried out in the presence of a fairly substantial excess of the Co(III) complex, except in the case of the $Co(NH_3)_5Br^{2+}$ reaction where the high rate necessitated the use of second-order conditions. The kinetic data were evaluated using the integrated pseudo-first-order or second-order rate expression in the form presented previously.[11] For the slower reactions a correction for the simultaneous decomposition of the $Co(dmg)_2(H_2O)_2$ reactant was applied to the data, subtracting the value of k_{dec} at the pH in question from the experimental pseudo-first-order constant.

After such correction, all the kinetic data were in accord with the second-order rate expression

$$-d[Co(dmg)_2(H_2O)_2]/dt = k_2[Co(NH_3)_5X^{2+}][Co(dmg)_2(H_2O)_2] \qquad (1)$$

The kinetic data for each complex are summarized in Table I. The value of k_2 proved to be independent of $[H^+]$ except for the complex $Co(NH_3)_5H_2O^{3+}$ as discussed below. The reactions of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$ were also studied to learn the effect of certain other variables. The rate constant for the former complex proved to be independent of added free bromide ion, and that of the latter was unchanged when ionic strength was raised from 0.1 to 0.2 *M*, when the reaction was followed at 265 rather than 460 nm, and when the acetate buffer was omitted. Consistent values of k_2 for the slowly reacting $Co(NH_3)_5F^{2+}$ complex were obtained, despite a substantial correction, up to 50%, for the decomposition of the $Co(dmg)_2(H_2O)_2$ reactant.

TABLE I

KINETIC DATA FOR THE REACTION[a] BETWEEN $Co(NH_3)_5X^{2+}$ COMPLEXES AND $Co(dmg)_2(H_2O)_2$

	Concn ranges, *M*		
X	10^4 $[Co(NH_3)_5X^{2+}]$	$10^6[H^+]$	k_2, M^{-1} sec^{-1}
Br	0.4–1.55	0.24–1.4	$(3.2 \pm 0.3) \times 10^5$
Cl	0.3–26.5	0.20–1.3	$(1.40 \pm 0.08) \times 10^4$
N_3	5.4–51	0.20–1.51	$(6.4 \pm 0.3) \times 10^3$
NCS	5–50	0.20–2.2	$(2.5 \pm 0.1) \times 10^2$
OH[b]	14–70	0.15–0.74	$(7.7 \pm 1.5) \times 10^2$ [c]
F	48–202	0.09–0.37	10.5 ± 0.9

[a] At 24.9° in HOAc–OAc⁻ buffer (0.01 *M*) with $\mu = 0.10$ *M* ($LiClO_4$). [b] The concentration cited is $[Co(NH_3)_5H_2O]_{tot}$. [c] Corrected for the protonation of $Co(NH_3)_5OH^{2+}$ as described in the text.

At pH ≥5 an appreciable proportion of $Co(NH_3)_5H_2O^{3+}$ is converted to the hydroxo form in accord with the equilibrium

$$Co(NH_3)_5H_2O^{3+} = Co(NH_3)_5OH^{2+} + H^+ \quad K_a \qquad (III)$$

for which the reported equilibrium constant is 6.0×10^{-7} *M* at 25° and $\mu = 0.30$ *M*.[12] Because an accurate value of K_a was not available under these present conditions, the data were treated in a fashion which regards K_a as an unknown.

Assuming both the aquo and hydroxo complexes react with $Co(dmg)_2(H_2O)_2$, the apparent rate constant k_2 would depend on $[H^+]$ as given by

$$k_2\{K_a + [H^+]\} = k_{OH}K_a + k_{H_2O}[H^+] \qquad (2)$$

It was not possible by varying K_a to make the left-hand side of eq 2 increase regularly with $[H^+]$. This suggests that the reactivity of the aquo complex is negligible relative to that of the hydroxo species; under this assumption expression 3 is obtained. The data conformed well with this relation, leading to the values $k_{OH} = 7.7 \times 10^2$ M^{-1} sec^{-1} and $K_a = 8.1 \times 10^{-7}$ *M*.

$$1/k_2 = 1/k_{OH} + [H^+]/K_ak_{OH} \qquad (3)$$

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[12] R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 897 (1968).

This value of K_a agrees well with the literature value[12] under similar conditions.

Discussion

The decomposition of diaquocob(II)aloxime in 0.01 *M* acetate buffer occurs in a first-order process showing a dependence on $[H^+]$ slightly greater than first-order (*ca.* 1.1–1.2 order) between pH 4.8 and 6.1. The likely role of H^+ in this process is the protonation of *both* oxygens of the dimethylglyoxime ligands thereby destroying the O---H---O hydrogen bonding which lends such great stability to these complexes. Independent evidence exists for the importance of such protonation in $Co^{III}(dmg)_2$ complexes.[13,14]

The rate of reduction of RCl^{2+} was found to be the same whether or not acetate was present, suggesting that any interaction between ~0.01 *M* acetate and cob(II)aloxime is slight.

The rate constants summarized in Table I show a wide range ($\sim 3 \times 10^4$) in reactivity between the different $Co(NH_3)_5X^{2+}$ complexes. The very slow reaction rate of $Co(NH_3)_5H_2O^{3+}$ was referred to previously, and we have also found that $Co(NH_3)_6^{3+}$ reacts too slowly to measure (*i.e.*, decomposition of $Co(dmg)_2(H_2O)_2$ is the only process seen).

Except for $Co(NH_3)_5OH^{2+}$, the product determinations referred to above establish that all the reactions proceed by an inner-sphere mechanism; we presume the hydroxo complex reacts in the same fashion. The basis of this claim rests on the assumption that anation of $Co(dmg)_2(H_2O)_2^+$ by X^- in a medium similar to the present one does not occur rapidly. The kinetics of the anation reactions were not studied, but inappreciable quantities of the complex $Co(dmg)_2(H_2O)X$ were found in the control experiments.

The order of effectiveness of the halide ions as bridging ligands ($Br^- > Cl^- \gg F^-$) is reflected in the respective values of the second-order rate constants or more precisely by the relative stabilities of the respective transition states according to Haim.[15] Both these observations demonstrate the "soft acid" or "class b" character of $Co(dmg)_2(H_2O)_2$ in the transition states and also presumably in the free complex.

Generally, a high rate ratio for reduction of an azido complex compared to the N-bonded thiocyanato complex can be expected,[16] provided the reductant exhibits hard-acid character. For example, the rate constant ratio is 1.5×10^4 for the reductions of $(NH_3)_5CoN_3^{2+}$ and $(NH_3)_5CoNCS^{2+}$ by Cr^{2+}.[17] The ratio for the reduction of the same two complexes by the soft acid $Co(CN)_5^{3-}$ is 1.5.[7] For $Co^{II}(dmg)_2(H_2O)_2$ the ratio is 26, again indicating a tendency toward soft-acid character.

Considering the rate constants found for certain other Co(II)–Co(III) reactions, the present reactions appear rather rapid. We note that $Co(dmg)_2(H_2O)_2$ is a low-spin complex,[17] and the electron is transferred from and into an e_g orbital.

Indeed it has been observed[18] that $Co(dmg)_2(H_2O)$ reacts very rapidly with $Fe(CN)_6^{3-}$, at a specific rate $\geq 3 \times 10^7\ M^{-1}\ sec^{-1}$. This reaction produces a new anionic species which we presume to be $[(NC)_5FeCN\text{-}Co(dmg)_2H_2O]^{3-}$ by analogy with $Co(CN)_5^{3-}$ reactions.[19] The observation of this reaction and the importance of the inner-sphere mechanism for the $Co(NH_3)_5X^{2+}$ reactions necessarily implicate rapid axial ligand exchange for the complex $Co(dmg)_2(H_2O)_2$.

One practical benefit of the present reactions should also be noted. They can provide a convenient synthetic method for $Co(dmg)_2(H_2O)X$ complexes. This is particularly useful for the fluoro complex, which is difficult to prepare by other methods.

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(14) A. Adin and J. H. Espenson, *Chem. Commun.*, 753 (1971).

(15) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

(16) J. H. Espenson, *ibid.*, **4**, 121 (1965).

(17) J. P. Candlin, J. Halpern, and D. Z. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

(18) A. Adin, unpublished experiments.

(19) A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

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Importance of Asymmetric Nitrogens to the Circular Dichroism of Alkyl-Substituted Ethylenediaminediacetic Acid Complexes of Cobalt(III)[1]

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Four Co(III) complexes containing *N*-alkyl-substituted ethylenediaminediacetic acid have been completely resolved, and their absorption and circular dichroism spectra are reported. Two of the complexes, *trans*-[Co(DMEDDA)en]I and *trans*-[Co(DEEDDA)en]I (containing, respectively, the *N,N'*-dimethyl- and *N,N'*-diethylethylenediamine-*N,N'*-diacetate ion), have been reported previously. The two corresponding complexes containing oxalate ion in place of ethylenediamine are new. Both ethylenediamine complexes give very similar absorption and circular dichroism spectra, as do the two oxalate complexes. The CD peak intensities of all the complexes, however, are less than half those of the corresponding unsubstituted-EDDA complexes. This reduction in intensities is attributed to a lower contribution to the asymmetry of the complexes from nitrogens in the *N*-alkyl-substituted EDDA's as compared to unsubstituted EDDA.

Introduction

In the course of recent studies to determine factors responsible for variations in intensities of circular dichroism (CD) bands within and between series of related complexes, a series of cobalt(III) complexes containing the tetradentate ligand ethylenediamine-*N,N'*-diacetate (EDDA) was prepared.[2,3] The geometrical

[1] This work was supported by a research grant (GM-10829) from the Division of General Medical Studies, U. S. Public Health Service.

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(3) C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969).