CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
OHIO UNIVERSITY, ATHENS, OHIO 45701

The Kinetics of the Acid Hydrolysis of *trans*-Nitroaquobis(2,4-pentanedionato)cobalt(III)

BY ROBERT J. KLINE AND RANCE A. VELAPOLDI

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trans-Nitroaquobis(2,4-pentanedionato)cobalt(III) undergoes hydrolysis in neutral or acidic media at 20–40° to give diaquobis(2,4-pentandionato)cobalt(III) cations which are rapidly reduced to cobalt(II) species. A spectrophotometric study of the hydrolysis reaction has provided the following kinetic parameters: $E_a = 26.8 \pm 0.5$ kcal mol^{-1}, $\Delta G^{\ddagger} = 22.4 \pm 0.8$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 12.5 \pm 1.5$ cal deg^{-1} mol^{-1}. The pseudo-first-order reaction is found to be unaffected by changes in ionic strength or acidity or the substitution of deuterium oxide for solvent water.

Introduction

Sodium *trans*-dinitrobis(2,4-pentanedionato)cobaltate(III) undergoes rapid hydrolysis in dilute aqueous solution to *trans*-nitroaquobis(2,4-pentanedionato)cobalt(III).[1] The ease of displacement of one nitro group has been attributed to the strong *trans*-labilizing effect of the other nitro ligand. The nitroaquo complex is relatively stable in basic solution or in solutions that contain excess nitrite ions, but in neutral or slightly acid solutions the second nitro group is displaced to give, ultimately, a cobalt(II) solution.[2] The reduction reaction results in characteristic spectral changes at 227 and 333 nm which may be used to follow the rate of formation of the reducible diaquocobalt(III) cation from the nitroaquo complex. A spectrophotometric study of the kinetics of this reaction has been made and is reported herein.

Experimental Section

Materials.—Sodium *trans*-dinitrobis(2,4-pentanedionato)cobaltate(III) monohydrate was prepared by the partial dehydration over sulfuric acid of the pentahydrate obtained from the reaction between hexanitrocobaltate(III) ions and 2,4-pentanedionato ions in water solution as described by Rosenheim and Garfunkel.[3] Because of the lability of the nitro ligands the compound was not recrystallized. It was triturated thoroughly with benzene and acetone to remove tris(2,4-pentanedionato)cobalt(III). *Anal.* Calcd for $Na(Co(C_5H_7O_2)_2(NO_2)_2) \cdot H_2O$: Co, 15.10; C, 30.78; H, 3.62; N, 7.19. Found: Co, 14.91; C, 30.87; H, 3.69; N, 8.06.

Sodium perchlorate was prepared from reagent grade sodium carbonate and perchloric acid. Other common chemicals were of reagent grade and were used directly as received. Conductivity water, redistilled from alkaline permanganate, was used to prepare the solutions for spectrophotometric analysis.

Kinetic Studies.—The rate of solvolysis was followed at 227 and 333 nm which are characteristic absorption bands of the 2,4-pentanedionatocobalt(III) chromophore.[2] Correction for the absorbance by liberated nitrite ions was required at 227 nm. A Cary Model 14 recording spectrophotometer was used.

Solutions of the proper ionic strength (held constant at 0.500 *M* with sodium perchlorate) containing any desired chemicals other than the dinitro salt were added to a spectrophotometric cell which was equipped with a mixing chamber. The cell and its contents were placed in the reservoir of a constant-temperature circulator bath and allowed to reach the temperature of the cell block of the spectrophotometer. At time zero, a previously weighed quantity of the *trans*-dinitro salt was added to the cell solution, and, after complete dissolution of the salt had been achieved, the cell was placed in the spectrophotometer. First readings of the optical density were obtained within 3 or 4 min. The temperature of the cell block was found to remain constant to ±0.05°.

The absorption *vs.* time data were subjected to a least-squares analysis using a program written for an IBM Model 1620 computer by Dr. James Y. P. Tong of this university.

Results

The sequence of reactions occurring when the *trans*-dinitro salt is dissolved in neutral or dilute acid solution is believed to be (acac is used to represent the 2,4-pentanedionate ion)

$$Co(acac)_2(NO_2)_2^- + H_2O = Co(acac)_2(NO_2)(H_2O) + NO_2^- \quad (1)$$

$$Co(acac)_2(NO_2)(H_2O) + H_2O = Co(acac)_2(H_2O)_2^+ + NO_2^- \quad (2)$$

$$Co(acac)_2(H_2O)_2^+ + e^- = Co(acac)_2 \cdot 2H_2O \quad (3)$$

Cotsoradis and Archer concluded that reaction 1 is fast when they observed nmr peaks characteristic of the nitroaquo complex of intensity corresponding to 17–50% hydrolysis of the dinitro salt *immediately* after the dissolution of the dinitro complex in deuterium oxide.[1]

The ultimate fate of the cobalt is shown in eq 3. A transient shoulder observed at approximately 290 nm during the rate runs probably corresponds to the strong absorption band of $Co(acac)_2 \cdot 2H_2O$ at 287 nm.[4] However a solution that had been allowed to age 72 hr at room temperature gave only bands at 205 and 270 nm which probably correspond to free nitrite (207 nm) and free 2,4-pentanedione (274 nm), respectively. The expected extensive hydrolysis of $Co(acac)_2 \cdot 2H_2O$ in dilute solutions accounts for these results.

A sensitive color test for the presence of free 2,4-pentanedione is available which depends on the formation of $Fe(acac)_2^+$ which absorbs strongly at 489 nm.[5] Although a quantitative comparison of the rates could not be made, a solution of the dinitro salt to which iron(III) nitrate had been added showed an increased absorbance at 489 nm which paralleled the

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(1) B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967).

(2) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

(3) A. Rosenheim and A. Garfunkel, *Ber.*, **44**, 1865 (1911).

(4) S. Basu and K. K. Chatterji, *Z. Chem.*, **209**, 360 (1958).

(5) J. Badoz-Lambling, *Ann. Chim.* (Paris), **8**, 586 (1953).

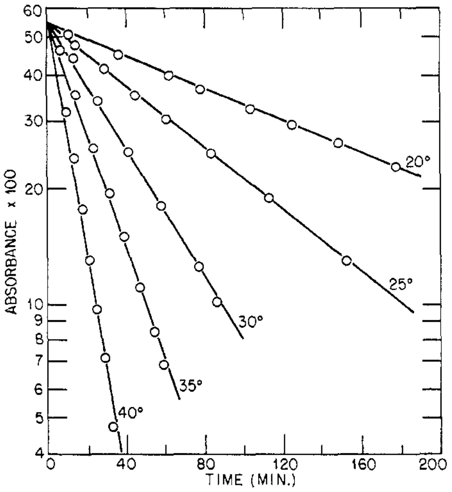

Figure 1.—Pseudo-first-order plot of log (absorbance) *vs.* time at 333 nm (μ = 0.500, $NaClO_4$).

decrease in absorbance at 333 nm. This shows that the free 2,4-pentanedione concentration increased as the cobalt(III) complex was reduced to the easily dissociated cobalt(II) complex.

It was found possible to separate a 2,4-pentanedione–cobalt(II) species from an "infinity-time" solution of the dinitro salt that had an R_f value identical with the R_f value of a known solution of bis(2,4-pentanedionato)-cobalt(II). Using a 12:6:1 acetone–water–nitric acid solution as the developing solvent, cobalt-containing spots were observed which had R_f values of 0.54 from both sources.

The source of the electron in eq 3 is not known. A search for the presence of nitrate ions by infrared studies of freeze-dried solutions failed. Owing to the strong absorption by 2,4-pentanedione in the 270-nm region and the similarity of the spectra of nitrite and nitrate in the 250-nm region, the uv region could not be used. A material balance for 2,4-pentanedione based on the $Fe(acac)_2^+$ indicator ion method in several solutions always failed to account for all the diketone added. It is possible that this is the reducing agent but no oxidation products of it were ever detected.

The loss of absorbance at 227 and 333 nm is a result of the reduction reaction 3 but the rate-controlling step is believed to be reaction 2. The main evidence for this is the magnitude of the activation energy which is within the range of values expected for the acid hydrolysis of cobalt(III) complexes.[6] The activation energies for redox reactions of cobalt(III) are usually about 10 kcal mol^{-1} smaller.

Plots of log (absorbance) *vs.* time are shown in Figure 1. It is seen from the linearity of the plots that the data may be treated as a pseudo-first-order process. The same quality of rate plots was obtained at 227 nm after correction for the absorbance by liberated nitrite ions. The rate constants obtained for the reactions in neutral solutions are given in Table I. The average rate constants at the various temperatures gave an excellent Arrhenius plot from which the energy of activation was found to be 26.8 ± 0.5 kcal mol^{-1}. The other activation parameters are $\Delta G^{\ddagger} = 22.4 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = +12.5 \pm 1.5$ cal deg^{-1} mol^{-1}.

TABLE I

RATE CONSTANTS FOR THE HYDROLYSIS OF $Co(acac)_2(NO_2)(H_2O)$ IN NEUTRAL SOLUTIONS,[a]

Temp, °C	10^4C_0,[b] *M*	10^5k(333 nm), sec^{-1}	10^5k(227 nm), sec^{-1}	10^5k(av),[c] sec^{-1}
20	0.250	6.11	5.96	6.73 ± 0.72
	1.000	7.62	7.55	
	2.500	6.28	6.85	
25	0.250	12.5	12.4	14.1 ± 1.2
	0.500	15.3	15.1	
	1.000	15.0	15.2	
	2.500	14.2	13.3	
	5.000	14.1	14.1	
30	0.250	30.7	32.3	31.5 ± 1.1
	1.000	32.5	32.9	
	1.294	31.8	31.5	
	2.500	29.9	30.3	
35	0.250	62.0	62.6	61.7 ± 2.2
	1.000	61.5	64.3	
	2.500	59.2	60.8	
40	1.000	120	122	115 ± 7.3
	2.267	114	118	
	2.500	106	109	

[a] At μ = 0.5 *M*, $NaClO_4$. [b] C_0 is the initial concentration of $Na(Co(acac)_2(NO_2)_2) \cdot H_2O$. [c] Errors are standard deviations.

The effects of various substances on the rate of the reaction at 25° are shown in Table II. It is seen that the rate is insensitive to the substitution of D_2O for H_2O as the solvent. Essentially the same rate constant is obtained whether measured in solutions of 0.500 *M* ionic strength or at an ionic strength of approximately zero. The substitution of perchloric acid for sodium perchlorate at constant ionic strength gave somewhat lowered rate constants but no trend was observed. Therefore, an acid-dependent pathway is not believed to be of significance.

TABLE II

RATE CONSTANTS FOR THE HYDROLYSIS OF $Co(acac)_2(NO_2)(H_2O)$ UNDER VARIOUS CONDITIONS AT 25.0°

Conditions	Ionic strength,[a] *M*	10^4C_0,[b] *M*	10^5k(333 nm), sec^{-1}
H_2O soln	~0	2.539	14.5
H_2O soln	~0	2.529	14.7
D_2O soln	~0	3.381	13.3
0.010 *M* $HClO_4$	0.500	2.423	12.0
0.010 *M* $HClO_4$	0.500	2.568	12.1
0.250 *M* $HClO_4$	0.500	2.765	13.3
0.500 *M* $HClO_4$	0.500	1.229	12.4

[a] Ionic strength maintained with $NaClO_4$. [b] C_0 is the initial concentration of $Na(Co(acac)_2(NO_2)_2) \cdot H_2O$.

Discussion

As has been mentioned earlier, the high value of the activation energy, 26.8 kcal mol^{-1}, is within the range of values expected for the acid hydrolysis of a cobalt(III) complex.[6] For this reason we contend that the hydrolysis reaction (2) is slower than the redox reaction (3).

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[6] C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, New York, N. Y., 1966, p 444.

The positive entropy change indicates a greater degree of disorder in the activated complex than in the reactants. Such a result would be expected if a stretching and loosening of bonds occur in forming the activated complex.[7] The lack of a deuterium isotope effect, the insensitivity to changes in ionic strength, and the pseudo-first-order kinetics are all compatible with such an activation process.

Acid catalysis is frequently observed when the displaced ligand is the anion of a weak acid or has a strong tendency to form hydrogen bonds.[8] In the case of nitro complexes, the mechanism is believed to involve the rapid protonation of an oxygen atom of the coordinated nitro group followed by the slower displacement of HNO_2 by water.[9,10]

The absence of an acid-catalyzed pathway in our system may indicate that the nitro ligands are not protonated. The oxygen atoms of the acetylacetonate rings are known to be bridged in the structures of $(Ni(acac)_2)_3$[11] and $(Co(acac)_2)_4$[12] and in the adducts of $Co(acac)_3$ with silver nitrate.[13] Therefore, these basic sites may be preferred to the oxygen atoms of the nitro ligand in forming bonds to the protons.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN 48202

Steric Effects in Chelation Kinetics. II. Role of Alcoholic Oxygen as a Donor Atom and the Internal Conjugate Base Effect in Cobalt(II)–Poly(amino alcohol) Reactions[1]

BY D. B. RORABACHER AND D. B. MOSS

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The kinetics of the aquocobalt(II) ion reacting with two branched poly(amino alcohol) ligands, N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine (THPED), have been studied at 25°, $\mu = 0.1$, over the pH range from 5.7 to 7.2 using the stopped-flow technique. The reaction rates are slower than would be predicted for a simple dissociative mechanism and the kinetic behavior is found to conform to a mechanism in which first-bond formation involves an alcoholic oxygen donor atom followed by second-bond formation to a nitrogen donor atom as the rate-determining step. The data permit an estimation of the rate constant for cobalt(II)–alcoholic oxygen bond rupture equal to 6×10^6 sec^{-1}. In addition, the first evidence is found for an internal conjugate base effect for the aquocobalt(II) ion.

Introduction

For complexation reactions involving an aquometal ion, $M(H_2O)n^{a+}$, and a unidentate ligand, L^{b-}, the general dissociative mechanism[2]

$$M(H_2O)_n{}^{a+} + L^{b-} \overset{K_{os}}{\rightleftharpoons} M(H_2O)_n{}^{a+} \cdots L^{b-} \xrightarrow{k^{M-H_2O}}$$

$$M(H_2O)_{n-1}{}^{a+} \cdots L^{b-} + H_2O \xrightarrow{\text{fast}} ML(H_2O)_{n-1}{}^{a-b} \quad (1)$$

(involving formation of an equilibrated outer-sphere complex, $M(H_2O)_n{}^{a+} \cdots L^{b-}$, preceding metal–water bond rupture, k^{M-H_2O}, as the rate-determining step) has been thoroughly tested and found to be applicable almost without exception.[3] Even for multidentate ligand reactions, where the formation of multiple coordinate bonds to a single metal ion raises the possibility of a more complicated mechanistic behavior, there is much supportive evidence for the applicability of the simple dissociative mechanism. In fact, conformance in the mechanism described by eq 1 can be tested readily by comparing the observed overall second-order rate constant, $k_M{}^L$ (M^{-1} sec^{-1}), to the value predicted by

$$k_M{}^L = K_{os}k^{M-H_2O} \quad (2)$$

where K_{os} (M^{-1}) represents the diffusion-controlled equilibrium constant for formation of the outer-sphere complex and k^{M-H_2O} (sec^{-1}) represents the first-order rate constant for unaided metal–water bond rupture from the aquated metal ions.

Recent studies on multidentate ligand reactions with aquonickel ion, however, have shown evidence of modified behavior resulting in observed rate constants

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[2] M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 373.

[3] M. Eigen and R. G. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.