Kinetics of the Alkaline Hydrolysis of *cis*- and *trans*-Diacetatobis-(1,2-propanediamine)cobalt(III) Cations

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Abstract

The alkaline hydrolysis of *cis*- and *trans*-diacetatobis(1,2-propanediamine)cobalt(III) cations appears to follow a substitution nucleophilic unimolecular conjugate base mechanism. In these cations, the acetate ligands are replaced by hydroxide ion in a stepwise manner. Both isomers undergo complete hydrolysis without configurational change.

Introduction

Literature results [1–3] indicate that alkaline hydrolysis of acidopentaamminecobalt(III) complexes proceeds by an S_N1CB mechanism (substitution, nucleophilic, unimolecular, conjugate base) involving an intermediate of reduced coordination number (eqn. (1) - (3)) [4, 5].

$$Co(NH_3)_5X^{2+} + OH^- \overset{K_a/K_w}{\rightleftharpoons} Co(NH_3)_4(NH_2)X^+ + H_2O \quad \text{(fast)} \quad (1)$$

$$Co(NH_3)_4(NH_2)X^+ \xrightarrow{k_2} Co(NH_3)_4(NH_2)^{2+} + X^- \quad \text{(slow)} \quad (2)$$

$$Co(N_3)_4(NH_2)^{2+} + H_2O \longrightarrow Co(NH_3)_5OH^{2+} \quad \text{(fast)} \quad (3)$$

If $K_a < K_w$, the kinetics obey the rate law given by the expression

$$-d[\text{complex}]/dt = k_2K_a/K_w[\text{complex}][OH] \quad (4)$$

Studies of alkaline hydrolysis of *cis*- and *trans*-dicarboxylatobis(ethylenediamine)cobalt(III) complexes indicate that the reaction proceeds by a dissociative mechanism involving essentially Co–O bond breaking to yield the corresponding *cis*- and *trans*-acidohydroxo intermediates [6–9]. It has been emphasized that, in the alkaline hydrolysis of the diacetato complexes, both *cis*- and *trans*-acetatohydroxo cations react further to produce mainly *cis*-dihydroxo products and that the isomerization accompanies and does not precede hydrolysis [9].

In the present study, the kinetics of alkaline hydrolysis of *cis*- and *trans*-diacetatobis(1,2-propanediamine)cobalt(III) cations are reported and compared with those of the ethylenediamine analogs in terms of reactivities, C-methylation, stereochemical course and steric effects.

Experimental

Materials

cis- and *trans*-$[Co(pn)_2(AcO)_2]ClO_4 \cdot H_2O$ [10] and *trans*-$[Co(pn)_2(AcO)(H_2O)](AcO)_2 \cdot H_2O$ [11] were prepared by literature procedures. *cis*-$[Co(pn)_2(AcO)(H_2O)](ClO_4)_2$ was prepared, *in situ*, by time-controlled hydrolysis of *cis*-$[Co(pn)_2(AcO)_2]ClO_4$ in dilute acid solution, at room temperature. *cis*-$[Co(pn)_2(H_2O)_2](ClO_4)_3$ was prepared by dissolving $[Co(pn)_2(CO_3)]ClO_4$ in 0.1 M $HClO_4$, at room temperature. *trans*-$[Co(pn)_2(OH)(H_2O)](ClO_4)_2$ was prepared by adding a solution of 0.125 g of NaOH, in 1.0 ml of water, dropwise with continuous stirring, to a solution of 1.0 g of *trans*-$[Co(pn)_2(AcO)_2]ClO_4 \cdot H_2O$, in 2.0 ml of water. The reaction was carried out at 55 °C for 20 min. After cooling to 0 °C, the reaction mixture was treated with 1.0 ml of 60% $HClO_4$ and 0.8 g of $NaClO_4$, and then placed in the refrigerator for 24 h. Upon addition of 60% $HClO_4$, a dark purple precipitate formed which was subsequently filtered, washed with absolute ethanol, ether and dried under vacuum. *Anal.* Calc. for $CoC_6H_{23}N_2ClO_{10}$: Co, 13.36; C, 16.34; N, 12.70; H, 5.26. Found: Co, 13.48; C, 16.27; N, 12.37; H, 5.39%. *trans*-$[Co(pn)_2(H_2O)_2](ClO_4)_3$ was prepared, *in situ*, by adding the appropriate amount of $HClO_4$ to an aqueous solution of *trans*-$[Co(pn)_2(H_2O)OH](ClO_4)_2$, at room temperature.

Electronic spectra of all complexes were measured with a Cary-14 recording spectrophotometer using matching 1-cm quartz cells. Spectral data are collected in Table I.

Analytical Methods

The method of Hughes *et al.* [12] was employed for cobalt analysis. The remaining elements were

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TABLE I. Spectral Data for Diacetato-, Acetatoaqua- and Diaquabis(1,2-propanediamine)cobalt(III) Ions

Complex ion	λ (nm)	ε (M^{-1} cm^{-1})
trans-$Co(pn)_2(AcO)_2^+$ [a]	535, 460, 356	62.8, 35.0, 77.2
cis-$Co(pn)_2(AcO)^{2+}$ [a]	507, 362	114.1, 85.9
trans-$Co(pn)_2(AcO)(H_2O)^{2+}$ [a]	538, 450, 354	62.2, 33.8, 78.3
cis-$Co(pn)_2(AcO)(H_2O)^{2+}$ [a]	494, 356	106.4, 80.4
trans-$Co(pn)_2(H_2O_2)^{3+}$ [b]	540, 435, 360	45.9, 37.0, 55.1
cis-$Co(pn)_2(H_2O)_2^{3+}$ [b]	490, 360	71.3, 47.7
trans-$Co(pn)_2OH(H_2O)^{2+}$ [c]	513, 470sh, 365	82.6, 89.2

[a]Values are taken from ref. 11. [b]This work, in 0.1 M $HClO_4$, at 20 °C. [c]This work, in water at 20 °C.

determined by M-H-W Microanalytical Laboratories, Phoenix, Ariz. Isomeric purities of all complexes, including those generated in solution, were checked by chromatography [7].

Kinetics

Reactions of *cis*- and *trans*-$Co(pn)_2(AcO)_2^+$ cations with OH^- ion were followed by potentiometry. A known weight of the complex was dissolved in CO_2-free water, in a 100-ml dark brown flask fitted with a ground stopper and maintained at the desired temperature in a water bath whose temperature was thermostatically controlled to ±0.1 °C. After thermal equilibration, the calculated amount of 0.1 M NaOH solution was added so as to maintain the final concentrations at 4.5×10^{-3} M in complex and 9.0×10^{-3} M in NaOH. Samples of 5.0 ml each were withdrawn, at convenient time intervals, and the reaction arrested with known excess of 0.1 M $HClO_4$. The solution was back-titrated with CO_2-free 0.1 M NaOH using a Beckman Zeromatic pH-meter equipped with glass and calomel electrodes.

The end-points of the titrations were obtained from plots of $\Delta^2pH/\Delta V^2$ *versus* volume of NaOH. Concentrations of NaOH, in moles/liter, at different reaction times, were determined at 25, 35 and 45 °C. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained from a weighted least squares fitting of rate data to the equation $\ln(K/T) = \Delta H^{\neq}/T$ + intercept, where $\Delta H^{\neq}$ was evaluated from the gradient and $\Delta S^{\neq}$ from intercept.

Results and Discussion

The reaction of OH^- with *cis*- and *trans*-$Co(pn)_2(AcO)_2^+$ ions was found to be first order in $[OH^-]$ and first order in [complex]. The kinetics obey a second order law, identical to that of expression (4), where [complex] = $[OH^-]$ (experimental conditions); the integrated rate law is given by the expression

$$\frac{1}{a-x} - \frac{1}{a} = k_2 t \qquad (5)$$

where a is either $[OH^-]$ or [complex] at time, $t = 0$, x its value at $t = t$, and the other terms have their usual significance. Plots of $1/(a-x)$ *versus* t were linear for over 5 half-lives. Values of k_2, for *cis*- and *trans*-$Co(pn)_2(AcO)_2^+$ (Table II) were obtained from a weighted least-squares fitting of concentration–time data to eqn. (5). Values of intercept, $1/a$, obtained by this treatment, were in a fair agreement (5–7%) with experimental values. A correlation coefficient exceeding 0.99 was obtained for all runs.

Previous studies [3b-c, 6, 8, 9] on alkaline hydrolysis of acido ligands of Co(III) amine complexes have indicated that ionization of amine protons proceeds via a conjugate base, S_N1CB, mechanism [13]. The stereochemical data were rationalized in terms of a dissociative process involving a common intermediate of, possibly, trigonal bipyramidal structure [3b], which, generally, leads to

TABLE II. Rate Date for Alkaline Hydrolysis of *cis*- and *trans*-$Co(AA)_2(AcO)_2^+$ (AA = en, pn)

T (°C)	10^2k_2 (M^{-1} s^{-1})			
	cis		*trans*	
	en	pn[a]	en	pn[a]
25	2.41 ± 0.05[b](2.40)[c]	2.10 ± 0.09[d]	5.06 ± 0.11[b](5.1)[c]	4.19 ± 0.61[d]
35	10.3 ± 0.22[b]	7.75 ± 0.54[d]	23.5 ± 0.49[b]	18.5 ± 0.92[d]
45	38.0 ± 0.80[b]	34.4 ± 0.39[d]	81.8 ± 1.7[b]	70.2 ± 1.4[d]

[a]Each entry is the average of three measurements. [b]Ref. 9. [c]Ref. 8. [d]This work.

TABLE III. Products of Alkaline Hydrolysis of *cis*- and *trans*-$Co(en)_2AX^+$ and $Co(pn)_2AX^+$

Reactant	Product	*cis* (%)	Reference
trans-$Co(en)_2ClBr^+$	*trans*-$Co(en)_2ClOH^+$	5 ± 5	18
trans-$Co(en)_2Cl_2^+$	*trans*-$Co(en)_2ClOH^+$	5 ± 2	18
trans-$Co(en)_2ClSCN^+$	*trans*-$Co(en)_2OHSCN^+$	82	19
trans-$Co(en)_2BrSCN^+$	*trans*-$Co(en)_2OHSCN^+$	81	19
trans-$Co(en)_2(AcO)_2^+$	*trans*-$Co(en)_2(AcO)OH^+$	0	7
trans-$Co(pn)_2(AcO)_2^+$	*trans*-$Co(pn)_2(AcO)OH^+$	0	this work
cis-$Co(en)_2N_3NCS^+$	*cis*-$Co(en)_2N_3OH^+$	100	20
cis-$Co(en)_2(N_3)_2^+$	*cis*-$Co(en)_2N_3OH^+$	55	21
cis-$Co(en)_2NO_2Cl^+$	*cis*-$Co(en)_2NO_2OH^+$	67	21
cis-$Co(en)_2(AcO)_2^+$	*cis*-$Co(en)_2(AcO)O^+$	100	7
cis-$Co(pn)_2(AcO)_2^+$	*cis*-$Co(pn)_2(AcO)OH^+$	100	this work

configurational change in the hydrolysis product. Data in Table III, show reaction products of alkaline hydrolysis of *cis*- and *trans*-$Co(en)_2AX^+$ (A and X are either different or identical acido groups). It is quite interesting to note, in certain cases (*trans*-isomers of $Co(en)_2Cl_2^+$, $Co(en)_2ClBr^+$, $Co(en)_2(AcO)_2^+$ and *cis*-isomers of $Co(en)_2N_3NCS^+$, $Co(en)_2(AcO)_2^+$), that first-stage hydrolysis takes place, essentially without configurational change. Illuminati *et al.* [9] have reported that both *cis*- and *trans*-$Co(en)_2(AcO)(OH)^+$, in alkaline solutions, hydrolyzed further to yield mainly *cis*-dihydroxo products, indicating that isomerization accompanied hydrolysis. In this study, however, the final products of alkaline hydrolysis retained the original configurations of their diacetato parents; no isomerization was observed. The isolation of *trans*-$Co(pn)_2(OH)(H_2O)^{2+}$ as perchlorate salt supports this finding; acidifying the third fraction, isolated chromatographically in alkaline hydrolysis of *trans*-$Co(pn)_2(AcO)_2^+$, produced a spectrum identical to that of *trans* diaqua cation. Similarly, no isomerization was observed in the course of alkaline hydrolysis of *cis* diacetato cation. These observations lead to the conclusion that, in the pn system, isomerization does not accompany hydrolysis.

Oxygen-18 tracer studies on alkaline hydrolysis of $Co(NH_3)_5OCOR^{2+}$ ($R = CH_3$) [14] and $Co(en)_2(OCOR)_2^+$ ($R = C_6H_4X$; X = substituent) [6], indicated that Co–O is the bond being broken. More recently, Taube *et al.* [15], have reported that both Co–O and C–O bond breaking modes occur during the hydrolysis of $Co(NH_3)_5OCOCF_3$. The C–O bond breaking was attributed to a second order dependence of hydrolysis rate on $[OH^-]$ and that the attack by hydroxide ion occurs at the carbonyl carbon of the carboxylate ligand due to the electron withdrawing effect of $-CF_3$ group.

Steric crowding, in *cis* complexes of the type $Co(AA)_2X_2^+$ (AA = en, pn; X is an adico group), on one hand, has an accelerating effect on a dissociative process. On the other hand, *cis* complexes are more basic [11, 16] than their *trans* counterparts; amine protons, in *cis* complexes, are less acidic and hence their ionization in the pre-equilibrium step (eqn. (1)), is rather slow. The latter effect, generally, counterbalances the steric rate-accelerating effects and the end result of the interplay of the two opposing effects would be in favor of the less hindered trans complexes. In the studies of alkaline hydrolysis of $Co(en)_2X_2^+$, where X varied from formato, acetato, substituted acetate [8, 9], to Cl and NO_2 [9], the rate constant ratio k_t/k_c was found to be always greater than 1. Our results, here, are consistent with the above arguments and the ratio $k_t/k_c > 2$, at all temperatures. Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, shown in Table IV, are positive and of the same magnitude for both isomers. However, differences in $\Delta S^{\neq}$ ($\Delta\Delta S^{\neq} = 4.8$ e.u.), indicate that differences in reactivities between the two isomers are essentially steric in nature and slightly in favor of the *trans* isomer. This, again, might indicate that, N–H in *trans* isomers which is less sterically crowded, is more available for attack by the hydroxide ion, as required in the pre-equilibrium step.

Steric effects due to C-alkyl substituent on the en ring have a decelerating or small accelerating influence on alkaline hydrolysis of Co(III) amine complexes [17]. A comparison of rate constants for *cis* and *trans* isomeric pairs shows that, on the average,

TABLE IV. Activation Enthalpies and Entropies for Alkaline Hydrolysis of $Co(AA)_2(AcO)_2^+$ (AA = en, pn)

Complex	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
cis-pn	109 ± 6	87.3 ± 2.0
cis-en[a]	107 ± 3	77.0 ± 8.4
trans-pn	108 ± 2	92.1 ± 4.5
trans-en[a]	110 ± 3	89.5 ± 8.4

[a]Ref. 9.

the en system is ~20% more reactive than the pn analog. Differences in their activation parameters $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ are, respectively, 3 kJ mol^{-1} and 7.3 e.u., for *cis* and 5 kJ mol^{-1} and 11 e.u., again respectively, are in favor of the en system. Again, the comparison points to the fact that the hydrolysis is dominated by steric effects and also that the *trans* isomers are more reactive than their *cis* counterparts.

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