CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

Kinetics of Formation of Propylenediaminetetraacetatocobaltate(III) from the Corresponding Pentadentate Complexes

BY K. SWAMINATHAN AND DARYLE H. BUSCH

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The rates of conversion of $[Co(HPDTA)Cl]^-$, $[Co(HPDTA)Br]^-$, $[Co(HPDTA)H_2O]$, $[Co(PDTA)H_2O]^-$, and $[Co(PDTA)OH]^{2-}$ into the hexadentate complex $[Co(PDTA)]^-$ have been measured as functions of temperature, *p*H, and nature of the supporting electrolyte. All rate processes conform to the simple first-order rate law. The results are compared to those obtained earlier with the corresponding EDTA complexes. The methyl group on the periphery of the NCCN chelate ring in the PDTA complexes serves to accelerate most of these reactions. In those cases in which the leaving group is an anion, an SN1 mechanism is suggested.

Introduction

The hexadentate complex of cobalt(III) with propylenediaminetetraacetic acid (H_4PDTA) was prepared and resolved into optical isomers by Dwyer and Garvan.[1] That early study revealed that of the four possible isomers, D*l*, D*d*, L*d*, L*l*, only two, D*l* and L*d*, appear to exist. The subject of isomer distribution in this system has been discussed further in subsequent work.[2,3] It has been concluded that the relative orientation of the methyl group on the NCCN chelate ring of the coördinated PDTA is the source of this extreme stereospecificity. The two isomers which exist contain the methyl group in an equatorial orientation.[4] Recently, the pentadentate complexes of the general formula $M^I[Co(HPDTA)X]$ have been reported.[3,5]

The closely related hexadentate and pentadentate complexes of ethylenediaminetetraacetic acid (H_4EDTA) have been subjected to detailed study,[6-9] culminating in the structure determination of Smith and Hoard.[10] The conversion of the pentadentate complexes into the common product, $[Co(EDTA)]^-$, containing hexadentate $EDTA^{4-}$, has been the subject of kinetic studies

$$[Co(EDTA)X]^{2-} \longrightarrow [Co(EDTA)]^- + X^- \quad (1)$$

(eq. 1).[11-13] A number of aspects of these conversions are of particular interest. The multiply connected nature of the chelate rings greatly restricts rearrangements. The incoming group, the fourth carboxyl group, is a part of the polydentate ligand. Base catalysis of the substitution reaction by an SN1cb mechanism,[14,15] is very unlikely since the donor atoms are not attached to replaceable hydrogen atoms. It has been suggested that the reactions of $[Co(EDTA)Br]^{2-}$, $[Co(HEDTA)Br]^-$, $[Co(EDTA)OH]^{2-}$, $[Co(EDTA)Cl]^{2-}$, and $[Co(HEDTA)H_2O]$ all proceed by SN1 mechanisms, on the basis of kinetic and related data. Among the principal supporting observations are: (1) The rates are clearly first order. (2) The reactions of the optically active starting materials proceed with complete retention of configuration. (3) The reactions producing anionic leaving groups are associated with negative entropies of activation. (4) The rate of loss of Cl^- or Br^- from the corresponding starting materials is accelerated by metal ions of high affinity for halide ions. (5) Bromide ion is lost more rapidly than chloride ion.

The rates of the analogous processes for the complexes $[Co(HPDTA)Cl]^-$, $[Co(PDTA)Cl]^{2-}$, $[Co(HPDTA)Br]^-$, $[Co(PDTA)Br]^{2-}$, $[Co(HPDTA)H_2O]$, $[Co(PDTA)H_2O]^-$, and $[Co(PDTA]$-

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TABLE I

RATE CONSTANTS[a] FOR THE CONVERSION OF $[Co(HPDTA)Cl]^-$ AND $[Co(HPDTA)Br]^-$ INTO $[Co(PDTA)]^-$

Compound	pH	Ionic strength	$k \times 10^3$, min.$^{-1}$			
			25°	35°	44°	60°
Na[Co(HPDTA)Br]	2.2	0.4	...	...	4.35	...
1.931×10^{-3} *M*	3.0	.4	...	...	4.44	...
	4.0	.4	...	...	3.98	...
	5.0	.4	...	1.92	3.83	...
					4.22	
	6.0	.4	0.744	...	3.46	...
					4.48	
	2.9[b]	.4	.699	2.24	4.15	...
			.691	1.87	3.92	
	2.9[b]	.1	...	...	3.84	...
Na[Co(HPDTA)Cl]	6.0	.4	...	...	0.833	...
1.901×10^{-3} *M*	2.9[b]	.4	.132	0.362	.800	8.23
			.124	0.384	.883	7.44
$Ba[Co(HPDTA)Cl]_2$	2.9[b]	.4	...	...	.940	...
1.000×10^{-3} *M*					.973	

[a] The average value for the mean deviation for duplicate experiments is 4.9% of the observed rate constant. [b] No buffer added.

$OH]^{2-}$ have been determined and evaluated in terms of the several factors previously considered for the EDTA complexes.

Experimental

The cobalt(III) complexes were prepared as reported earlier.[5] All other materials were reagent grade.

Rate determinations were carried out by a spectrophotometric method. The apparatus consisted of a constant temperature bath, a circulating pump, and a Beckman DU spectrophotometer. The cell compartment was thermostated by a constant flow of water from the temperature bath. The temperature of the cell compartment was constant within ±0.1°.

The samples of reactant and sodium nitrate (to adjust the ionic strength) were weighed on an analytical balance in volumetric flasks. Buffer solutions were added and the solutions were made up to volume. All solutions were prepared at the temperatures at which experiments were to be conducted. Samples of the solutions were transferred immediately to the cells and placed in the cell compartment of the spectrophotometer. Optical densities were measured at appropriate time intervals, and the solutions in the cells were replaced every 6 hr. For measurements at 60°, aliquot portions were drawn from the thermostated volumetric flask, cooled to room temperature, and the optical densities were measured immediately. The condensation of moisture on the cells was minimized at the lower temperatures by keeping magnesium perchlorate in the cell compartment, and by covering the entrance to the cell compartment with cloth bags filled with magnesium perchlorate. The buffer systems used were: potassium hydrogen phthalate–sodium hydroxide, potassium hydrogen phosphate–sodium hydroxide, boric acid–sodium hydroxide. All measurements involving the reactions of $[Co(HPDTA)Br]^-$ and $[Co(HPDTA)Cl]^-$ were made at 540 mμ, while those involving $[Co(HPDTA)H_2O]$, $[Co(PDTA)H_2O]^-$, and $[Co(PDTA)OH]^{2-}$, were carried out at 500 mμ. Since all measurements on systems exhibiting appreciable pH dependence were obtained using buffered solutions, first order or pseudo first order rate constants were calculated from graphs of log $(OD - OD_\infty)$ *vs.* time. OD_∞ was determined by direct measurements at long times. Except as noted in the discussion to follow, the values so obtained agreed within experimental error with those expected for the product assumed. Unless otherwise indicated, the ionic strength was adjusted to 0.4.

Discussion

The Reactions of $[Co(HPDTA)Cl]^-$ and $[Co(HPDTA)Br]^-$.—Rate constants for the conversion of the chloride- and bromide-containing pentadentate complexes of cobalt(III) with propylenediaminetetraacetic acid into the hexadentate complex are summarized in Table I. Over the pH range 2.2 to 6.0, the rates are independent of hydrogen ion concentration. The correspondence of rates measured in distilled water (pH 2.9 as a result of ionization) with those determined in the various buffers obviates the possibility of interferences resulting from reactions with constituents of the buffer systems. Further, the data of Table I reveal that the reaction is relatively insensitive to ionic strength. The rate of loss of bromide from $[Co(HPDTA)Br]^-$ exceeds the rate of loss of Cl^- from $[Co(HPDTA)Cl]^-$.

The several aspects of the rate data on these PDTA complexes agree closely with the behavior previously noted for the analogous complexes of EDTA. Without repeating the detailed arguments presented in that earlier study,[12] it appears appropriate to assign S_N1 mechanisms to the processes of immediate concern. This also is supported by the qualitative observation that

Hg^{2+}, Pb^{2+}, and Ag^+ exert strong catalyzing effects on the conversions of $[Co(HPDTA)Cl]^-$ and $[Co(HPDTA)Br]^-$ into $[Co(PDTA)]^-$. As a consequence of the stereospecificity of the $PDTA^{4-}$, the report[3] that these reactions proceed with complete retention of configuration is of no consequence in deducing the mechanism of the chemical transformation.

Investigations on systems involving $[Co(HEDTA)Br]^-$ led to the suggestion that the complex might exist as a mixture of geometric isomers, since the simple first-order rate law was not obeyed, but the data correspond closely to the function derived for two parallel reactions. The chloro complex, prepared by the method of Dwyer and Garvan,[9] behaved as a single isomeric constituent.[12,13] Since the bromo complexes cannot be prepared by this procedure, the chloro complex $[(Co(HPDTA)Cl]^-$ was prepared by both available synthetic schemes[5,6,9] and the rates were determined on both products. In both cases, the simple first order rate law was obeyed and the rates constants varied only slightly: *k* for Na[Co(HPDTA)Cl] prepared by Schwarzenbach's method,[5,6] 0.84 $min.^{-1}$; *k* for $Ba[Co(HPDTA)Cl]_2$ prepared by Dwyer and Garvan's method,[5,9] 0.96 $min.^{-1}$. The fact that the dipositive barium ion is present in the second case may account for the somewhat higher rate.[12] It also should be pointed out that the rate behavior of $[Co(HPDTA)Br]^-$ also is in keeping with the simple first-order law. The more extreme selectivity of $PDTA^{4-}$ (as compared to $EDTA^{4-}$) in determining which of the several carboxyl groups is replaced by a monodentate group has been considered in detail elsewhere.[16] On that basis, it is not surprising that no evidence is found for geometric isomers. It should be pointed out that whereas only three geometric isomers are conceivable for $[Co(EDTA)X]^-$,[12] the complex $[Co(PDTA)X]^-$ might have six isomeric forms if the thermodynamic relationships permitted this permutation of the monodentate group. This follows from the fact that all four of the carboxyl groups in $[Co(PDTA)]^-$ are geometrically non-equivalent.

Activation energies and frequency factors are reported in Table II. These are compared with the appropriate values for the corresponding EDTA complexes. The low values of the frequency factors imply negative entropies of activation in all cases, in agreement with the postulated SN1 mechanism.[12] The values for the activation energies are lower for both the PDTA complexes of immediate concern. It is logical to assume (models) that the presence of the methyl group on the periphery of the complex produces an internal crowding which serves to facilitate dissociation. Thus, this result also supports the suggestion that bond breaking is of primary importance in these reactions. The antithetical SN2 mechanism should be associated with a retardation in the PDTA case.

Table II

Activation Energies and Frequency Factors for the Conversion of $[Co(HY)Cl]^-$ and $[Co(HY)Br]^-$ into $[Co(Y)]^-$

Compound	E_a, kcal./mole	*A*, $min.^{-1}$
$[Co(HPDTA)Br]^-$	17.2	2.8×10^9
$[Co(HEDTA)Br]^-$ [12]	20.3	1.4×10^{11}
$[Co(HPDTA)Cl]^-$	20.9	5.4×10^{12}
$[Co(HEDTA)Cl]^-$ [12]	24.1	2.4×10^{13}

The Reactions of $[Co(HPDTA)H_2O]$, $[Co(PDTA)H_2O]^-$, and $[Co(PDTA)OH]^{2-}$.—The pseudo first order rate constants obtained with solutions prepared from $Na_2[Co(PDTA)OH] \cdot 4H_2O$, at various *p*H and temperature values, are summarized in Table III. The *p*H dependence

Table III

Pseudo First Order Rate Constants[a] for Solutions of $Na_2[Co(PDTA)OH] \cdot 4H_2O$

2.000×10^{-3} *M*, Ionic strength = 0.4

	$k_{obs} \times 10^2$, $min.^{-1}$		
*p*H	7.9°	15°	25°
1.0	0.111	0.406	1.61
		0.409	1.53
2.2	...	1.13	4.15
			3.76
3.0	...	1.80	7.85
			7.64
4.0	...	2.97	9.21
		2.99	10.7
5.0	1.02	2.82	11.5
	1.02		10.8
6.0	...	2.87	12.3
			12.6
7.0	...	3.22	11.5
			10.6
8.0	0.683	1.81	6.39
	.678		
	.631		
9.0	...	...	1.46
			1.48

[a] The average value for the mean deviation for duplicate and triplicate experiments is 2.5% of the observed rate constant.

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(16) D. H. Busch and K. Swaminathan, *J. Inorg. & Nuclear Chem.*, in press.

has been treated quantitatively by the method utilized by Shimi and Higginson[11] in analyzing the similar EDTA system. These rapid equilibria are assumed

$$[Co(PDTA)OH]^{2-} \overset{K_1}{\rightleftharpoons} [Co(PDTA)H_2O]^{-} \overset{K_2}{\rightleftharpoons} [Co(HPDTA)H_2O]$$

It also is assumed that the sum of the concentrations of these three substances corresponds to the amount of $[Co(PDTA)OH]^{2-}$ dissolved. If these three substances, $[Co(HPDTA)H_2O]$, $[Co(PDTA)H_2O]^-$, and $[Co(PDTA)OH]^{2-}$, individually transform into $[Co(PDTA)]^-$ at characteristic rates denoted respectively as k_1, k_2, and k_3, then the observed pseudo first order rate constants may be expressed as

$$k_{obs} = (k_1[H^+]^2 + k_2K[H^+] + k_3K_1K_2)/([H^+]^2 + K_1[H^+] + K_1K_2)$$

In order to facilitate calculation, the values of K_1 and K_2 found for the EDTA complexes were assumed for those of PDTA; *i.e.*, $K_1 = 10^{-8}$, $K_2 = 10^{-3}$ (for acidic dissociation). The rate constants k_1, k_2, and k_3 then were calculated from sets of three simultaneous equations. The fit of all the data was demonstrated by applying these constants to calculate those values of k_{obs} not utilized in their derivation. Agreement was within the uncertainties of the data. The values of these rate constants are given in Table IV.

TABLE IV

RATE CONSTANTS FOR THE CONVERSION OF $[Co(HPDTA)H_2O]$, k_1; $[Co(PDTA)H_2O]^-$, k_2; AND $[Co(PDTA)OH]^{2-}$, k_3; INTO $[Co(PDTA)]^-$

T, °C.	$k_1 \times 10^2$, min.$^{-1}$	$k_2 \times 10^2$, min.$^{-1}$	$k_3 \times 10^2$, min.$^{-1}$
7.9	0.11	1.0	0.31
15.0	0.41	2.8	0.78
25.0	1.6	12.0	1.5

As was true of the bromo and chloro complexes, the reactions of the PDTA complexes are uniformly more rapid than those of their EDTA counterparts; however, the difference is significant only in the case of the complexes of the form $[Co(Y)OH]^{2-}$. In this case, the acceleration in the PDTA case is associated with a decreased activation energy (Table V), although it must be emphasized that these values are only approximate. The information at hand is consistent with the assumption that the OH^- ion is eliminated by the same kind of mechanism that pertains in the case of Cl^- and Br^- eliminations (Table II).

TABLE V

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR THE CONVERSION OF $[Co(HY)H_2O]$, $[Co(Y)H_2O]^-$, AND $[Co(Y)OH]^{2-}$ INTO $[Co(Y)]^-$

Compound	E_a, kcal./mole	A, min.$^{-1}$
$[Co(HPDTA)H_2O]$	26	1.5×10^{17}
$[Co(HEDTA)H_2O]$[13]	26	7.9×10^{16}
$[Co(PDTA)H_2O]^-$	24	4.1×10^{16}
$[Co(EDTA)H_2O]^-$[11]	25	3.2×10^{17}
$[Co(PDTA)OH]^{2-}$	15	1.2×10^{9}
$[Co(EDTA)OH]^{2-}$[11]	19	3.6×10^{11}

The reaction of $[Co(PDTA)OH]^{2-}$ at *p*H values greater than 9 yields products having optical densities that do not conform to that of $[Co(PDTA)]^-$. In fact, as subsequent reports will show,[17] $[Co(Y)OH]^{2-}$ undergoes further base hydrolysis in both the EDTA and the PDTA systems at high *p*H (>9). In view of this, the constants given by Shimi and Higginson[11] for the conversion of $[Co(EDTA)OH]^{2-}$ into $[Co(EDTA)]^-$ (derived at a *p*H of 10.5) may, as those authors suggest, actually contain contributions from these competitive rate processes. The results presented here for the reaction of $[Co(PDTA)OH]^{2-}$ are derived from data confined to the *p*H range within which $[Co(PDTA)]^-$ is clearly the predominant product (within a very few per cent.).

The fact that the aquo complexes $[Co(HY)H_2O]$ containing pentadentate EDTA and PDTA react at very similar rates appears to be significant. As pointed out by Dyke and Higginson,[18] it is not unreasonable to suppose that bond formation and bond breaking contribute to comparable extents in the formation of the transition state in this reaction. The appealing aspect of this suggestion arises from the expectation that bond breaking should cause the PDTA complex to react more rapidly than the EDTA complex, while the formation of bonds in the transition state should retard the sterically more hindered PDTA complex in its transformation, as compared to that of EDTA. It follows that appropriate contributions of the two types might produce processes of nearly equivalent rate. As the discussion in the preceding section shows, processes which are logically assigned SN1 mechanisms are accelerated to a small extent in

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(17) D. W. Cooke, K. Swaminathan, and D. H. Busch, unpublished results.

the PDTA case. On the other hand, results obtained on the kinetics of base hydrolysis of the hexadentate complexes suggest that a greater contrast in the behaviors of the two groups of complexes is to be expected when the rate-determining steps are most probably SN2 in character.[17] From this vantage point, the reactions of the aquo complexes containing pentadentate EDTA and PDTA appear to be associated with relatively strong contributions from the breaking of bonds in proceeding to the transition state. These comments are equally appropriate to the complexes $[Co(Y)H_2O]^-$ and $[Co(HY)H_2O]$.

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CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

Stereochemistry and Mechanism of the Reactions of Ethylenediamine with Ethylenediaminetetraacetatocobaltate(III) and Propylenediaminetetraacetatocobaltate(III)

BY DARYLE H. BUSCH, K. SWAMINATHAN, AND DEAN W. COOKE

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The kinetics of the reactions of ethylenediamine with $Co(PDTA)^-$ and $Co(EDTA)^-$ have been studied over extensive ranges of *p*H and ethylenediamine concentration. All data were obtained under pseudo first order conditions. At *p*H values greater than 9, the rate constants have the form $k_{obs} = k_1(k_2K/k_{-1})(OH^-)(en)/[1 + (k_2K/k_{-1})(OH^-)]$. This expression is derivable for the series of reactions

$$Co(Y)^- + en \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Co(Y)en^-]^*$$

$$[Co(Y)en^-]^* + OH^- \overset{K}{\rightleftarrows} [Co(Y)(en\text{-}H)^{2-}]^* + H_2O$$

$$[Co(Y)(en\text{-}H)^{2-}]^* \xrightarrow{k_2} \text{5-coördinate intermediate}$$

$$\text{5-coördinate intermediate} \xrightarrow{\text{fast}} Co(Y)(en\text{-}H)^{2-}$$

$$Co(Y)(en\text{-}H)^{2-} + H_2O \rightleftarrows Co(Y)en^- + OH^-$$

where the bracketed and starred formulas imply species containing monodentate en. This scheme involves the intervention of the SN1cb mechanism after the coördination of the first NH_2 group. All subsequent steps in the displacement of the hexadentate ligand by two additional en molecules are rapid (not rate determining), and $Co(en)_3{}^{3+}$ is the sole product. The isomer yields and enantiomorphic configurations of the reactants and products are completely explainable in terms of this process. Optically active $Co(EDTA)^-$ reacts to form $Co(en)_3{}^{3+}$ with partial *retention* of configuration, while $Co(PDTA)^-$ reacts with essentially complete *inversion*. The stereospecificity in the first case arises from statistical effects associated with the low symmetry of the complex. In the second case, $Co(PDTA)^-$, a steric effect produces the observed extreme stereospecificity. The absolute configurations of $Co(EDTA)^-$, $Co(EDTA)Br^{2-}$, $Co(EDTA)Cl^{2-}$, $Co(PDTA)^-$, $Co(PDTA)Br^{2-}$, and $Co(PDTA)Cl^{2-}$ constitute the first examples of unequivocal deduction of configuration from the kinetics and stereochemistry of a reaction of an octahedral ion.

Introduction

The most remarkable reactions observed in the chemistry of the cobalt(III) complexes of ethylenediaminetetraacetic acid (H_4EDTA) and propylenediaminetetraacetic acid (H_4PDTA) are those with ethylenediamine (eq. 1).[1-3] These reactions proceed with some retention of optical activity when active starting materials are used, even though every bond to the central cobalt(III) ion is replaced. In 50% aqueous ethyl-

$$Co(Y)^- + 3en \longrightarrow Co(en)_3{}^{3+} + Y^{4-} \quad (1)$$

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