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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. IX. Aquation of α- and β-*cis*-Carbonato(ethylenediaminediacetato)cobaltate(III) Ions in Strongly Acidic Solution[1]

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In an earlier paper[2] we demonstrated that the anionic carbonato complex $Co(NTA)CO_3^{2-}$, where NTA is nitrilotriacetate ion, undergoes acid-catalyzed ring opening and subsequent decarboxylation at a much greater rate than that of analogous cationic complexes.[3] This enhancement of rate has been explained in terms of charge and entropy differences. In order to see whether this type of labilization occurs with other anionic carbonato complexes, we have extended our studies to the $Co(EDDA)CO_3^-$ ion where EDDA stands for ethylenediaminediacetate ion. While our work was in progress, Garnett and Watts[4] reported on the synthesis, stereochemistry, and aquation kinetics of α-*cis*- and β-*cis*-$Co(EDDA)CO_3^-$ complexes. However, they studied the aquation in the limited acidity range $1 < pH < 5$, where the ring-opening step is always rate determining. We now report[5a] aquation studies of both α- and β-*cis*-$Co(EDDA)CO_3^-$ over the extended range $-0.3 \leq pH \leq 4.5$ at a constant ionic strength of 2 *M*, and this enables us to compare both decarboxylation and ring-opening rates of these complexes[5b] with our previously reported data[2] for $Co(NTA)CO_3^{2-}$.

Experimental Section

α-$K[Co(EDDA)CO_3]\cdot 4H_2O$ was prepared starting from $K_3[Co(CO_3)_3]\cdot 3H_2O$ following methods described in the literature.[6,7] This compound was also prepared later by the reaction of H_2EDDA with $Na_3[Co(CO_3)_3]\cdot 3H_2O$ as reported by Garnett and Watts.[4] The purity of the compound was checked by chemical analysis.[8] Anal. Calcd for α-$K[Co(C_6N_2H_{10}O_4)CO_3]\cdot 4H_2O$: C, 20.8; H, 4.50; N, 6.90. Found: C, 21.0; H, 4.46; N, 7.09.

β-$K[Co(EDDA)CO_3]\cdot H_2O$ was isolated from the filtrate left after separating out the other isomer by the addition of excess alcohol as described previously.[4] The violet compound was crystallized twice from water by cooling and adding absolute alcohol and was analyzed.[9] Anal. Calcd for β-$K[Co(C_6N_2H_{10}O_4)CO_3]\cdot H_2O$: C, 24.00; H, 3.45; N, 7.99. Found: C, 24.02; H, 3.75; N, 8.15. Ethylenediaminediacetic acid was obtained from K & K Laboratories, Inc., and was used without further purification. All other chemicals were of reagent grade. Degassed water was used in preparing all solutions. Special precautions[2] were taken in making standard nitric acid solutions for the high-acid runs. The rates of aquation were measured on a Durrum Model 110 stopped-flow assembly as described previously.[2] The pH of the solution was maintained constant by using phosphate–citric acid buffer[10] and potassium nitrate was used to establish an ionic strength of 2.0 *M*. The pH measurements of the buffer solution were made by means of a Model 26 Radiometer device. The rate measurements were done at 545 and 385 nm for α-$K[Co(EDDA)CO_3]$ whereas 540 nm was chosen for β-$K[Co(EDDA)CO_3]$. These wavelengths offer the largest absorbance changes between reactants and products.[11] Pseudo-first-order rate constants were derived in the usual manner from semilogarithmic plots of $(A_\infty - A_t)$ vs. time *t*.

Results and Discussion

The runs with the β-carbonato species gave clean-cut first-order plots of several half-times duration over the whole acidity range of this study ($-0.3 < pH < 4.5$). The values derived for k_{obsd} from these experiments at various pH's and temperatures are recorded in Table I. However, for the α complex, a complication was apparent under conditions of higher acidity (pH $\leq$1.3). This showed up as a subsequent slow *decrease* in absorbance at 545 nm after the initial rapid *increase* ascribable[11] to the formation of the α-diaquo product complex. For example, at 20° and 0.05 *M* acid concentration, the linear plot of the increasing absorbance portion gave $k_{obsd} = 5.0$ sec^{-1}, while the subsequent decreasing absorbance curve yielded $k_{obsd} \approx 0.5$ sec^{-1}, of the same order of magnitude as the value obtained for pure β-carbonato complex. Our experimental procedure required a minimum of a 20-min waiting period for temperature equilibration after loading the reactant syringes, and it was soon recognized that partial isomerization of α- to β-carbonato complex can occur during this necessary period of delay.[12] This interpretation was confirmed by a series of runs in which the delay period was successively lengthened to a maximum of 425 min, during which the spectrum of the reactant complex solution slowly changed from that of pure α-carbonato to nearly pure β complex,[13] while the spectrum of the product obtained changed from that of pure α-diaquo to nearly pure β-diaquo complex. However, in all runs made with the minimum waiting period, there was no difficulty in obtaining reproducible values of k_{obsd} for aquation of the α-carbonato complex, and these data are recorded in Table I at the same temperatures and pH range as for the β-carbonato species.

Scheme I

$$Co(EDDA)CO_3^- + H_2O \rightarrow Co(EDDA)(OH)(CO_3H)^- \qquad k_0$$

$$Co(EDDA)CO_3^- + H_3O^+ \rightarrow Co(EDDA)(OH_2)(CO_3H) \qquad k_1$$

$$Co(EDDA)(OH_2)(CO_3H) + H_2O \rightleftarrows Co(EDDA)(OH)(CO_3H)^- + H_3O^+ \qquad K_1$$

$$Co(EDDA)(OH_2)(CO_3H) \rightarrow Co(EDDA)(OH_2)(OH) + CO_2 \qquad k_2$$

$$Co(EDDA)(OH_2)_2^+ + H_2O \rightleftarrows Co(EDDA)(OH_2)(OH) + H_3O^+ \qquad K_2$$

It is apparent from the tabulated data that in the high-acid region ($[H^+] > 1.5$ *M*), k_{obsd} values for both isomers approach a limiting value, whereas at lower acidities (pH >2) the observed rate constants are strongly dependent on hydrogen ion concentration as noted previously.[4] A mechanism which can explain all the data is as proposed in the earlier studies[2–4] and can be written as in Scheme I. Since the limiting value $k_{obsd} = k_2$ is indeed reached in the high-acid region (pH $\leq$0.0), the average k_2 values were derived from these observed pseudo-first-order rate constants at the various temperatures and are shown in Table II, together with the relevant activation parameters. The corresponding values[2] for the Co(NTA)-CO_3^{2-} species are $k_2 = 57.1$ sec^{-1} (25°), $\Delta H_2^\ddagger = 15.3 \pm 1.0$ kcal/mol, and $\Delta S_2^\ddagger = 1 \pm 3$ cal/(deg mol). It is seen that the decarboxylation rate constant for $Co(NTA)(H_2O)(CO_3H)$ is very similar to that for the α-EDDA species, but both these are greater than the rate constant for the β-EDDA complex by a factor of over 20. The latter is in fact close to the value for bicarbonatopentaamminecobalt(III) complex decarboxylation[14,15] ($k = 1.1$ sec^{-1} (25°), $\Delta H^\ddagger = 16.8 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -2 \pm 1$ cal/(deg mol)), or for Co(tren)-$(OH_2)(CO_3H)^{2+}$, which is stereochemically similar to the NTA analog and which has a k_2 estimated[3] also to be $\sim$1 sec^{-1} at 25°. Apparently the presence of an amido group cis to the bicarbonato, which is possible in the β-EDDA complex but not in the α congener, somewhat hinders the decarboxylation process in the same manner as occurs in the pentaammine and tren species. It is interesting, however, that decarboxylation of the NTA and α-EDDA species is even more facile than that of carbonic acid[16] ($k = 20$ sec^{-1}, $\Delta H^\ddagger \approx 15$ kcal/mol, $\Delta S^\ddagger \approx 0$ eu) though our high ionic strength medium may possibly account for some of this difference.[17]

In the region $2 \leq pH \leq 4.5$ the results for both the isomers fit the expected rate expression,[2,4] which has the form

$$k_{obsd} = k_0 + k_1[H^+]$$

Table I. Values of the Observed Rate Constants for Acid-Catalyzed Aquation of α- and β-Co(EDDA)CO_3^- Complex Ions[a] ([Complex] = 1×10^{-3} *M*; *I* = 2 *M* (KNO_3))

	α-Co(EDDA)CO_3^-			β-Co(EDDA)CO_3^-		
	k_{obsd}			k_{obsd}		
pH	15°	20°	25°	15°	20°	25°
−0.30	29	41	58	0.91 (0.90^b)	1.40 (1.41^b)	2.30 (2.31^b)
−0.25	29	41	59	0.90	1.38	2.28
−0.20	29	37	48	0.92 (0.95^b)	1.45 (1.36^b)	2.35 (2.23^b)
−0.18	27	39	55	0.89	1.36	2.30
−0.08	24	31	51	0.86	1.24	2.04
0.00	25	33	59			
0.30	17	27	40	0.48	0.81	1.14
0.52	13	20	30	0.33	0.51	0.85
1.00	5.0	9.0	14.0	0.14	0.20	0.31
1.30	2.5	5.2	7.7	0.06	0.10	0.16
2.00	0.5	2.0	1.2			
2.02				0.012	0.016	0.023
2.20				0.0079	0.012	0.018
2.25		0.43				
2.30	0.30		0.60			
2.40				0.0055	0.0089	0.012
2.43	0.21		0.43			
2.44		0.27				
2.61			0.29			
2.62	0.12					
2.63		0.18		0.0034	0.0058	0.0077
2.74		0.12				
2.79				0.0022	0.0034	0.0047
2.80			0.19			
2.82	0.082					
2.96		0.075				
2.97				0.0014	0.0025	0.0031
3.00	0.049					
3.02			0.11			
3.15		0.051				
3.17				0.0010	0.0015	0.0024
3.18			0.075			
3.19	0.034					
3.33				0.0009	0.0013	0.0019
3.35		0.035				
3.36			0.056			
3.39	0.025					
3.49		0.027				
3.50	0.019		0.04			
3.60				0.00054	0.00084	0.0012
3.71		0.017				
3.75	0.011					
3.76			0.023			
3.89				0.00047	0.00064	0.00079
3.97		0.0086				
4.01	0.0064					
4.02			0.014			
4.11		0.0074				
4.19	0.0048		0.011			
4.33			0.0082			
4.34		0.0063				
4.35	0.0038					

[a] Units of k_{obsd} are sec^{-1}. [b] Ionic strength 3 *M*.

However, since the acid-catalyzed path plays the dominant role, particularly in the case of the α isomer, a least-squares analysis of the k_{obsd} vs. [H^+] plot of all the data in the above-mentioned acidity range gives almost a zero intercept and very reliable k_1 values. The less reliable k_0 values are evaluated from similar plots in the range $3.5 \leq pH \leq 4.5$ where acid catalysis is not so pronounced. The values for k_0 and k_1 with their standard deviations at the various temperatures are presented in Table II, together with the corresponding activation parameters. These are seen to agree reasonably well with the earlier data,[4] also included in Table II, bearing in mind that the earlier results were more limited in scope, at a lower ionic strength (1.0 *M*) and with a different neutral salt ($NaClO_4$).

It is of interest to compare the rather accurately known acid-catalyzed ring-opening rate constants (k_1) for the two EDDA complexes with several of those previously studied, and the relevant data are presented in Table III. One sees that k_1 varies by a factor of over 10^7 between the complex most resistant to aquation (Co(py)$_4CO_3^+$) and that least resistant (α-Co(EDDA)CO_3^-), reemphasizing the very large influence of the "nonparticipating" ligands on the reactivity of the chelated carbonato group. Further, the α-EDDA species is somewhat more reactive than the NTA complex and notably more reactive than its β congener, similar to the previous finding for the α- and β-trien[3] and the α- and β-dmtr[20] pairs of complexes. However, the EDDA complexes are much more reactive than the corresponding trien species, in both cases a result of lower $\Delta H^{\ddagger}$ values. This contrasts with the NTA analog, where the increased reactivity appears to be mainly because of an increased $\Delta S^{\ddagger}$. The best comparison of the EDDA complexes seems to be with Co(tren)CO_3^+, the rate

Table II. Rate Parameters for the Acid-Catalyzed Aquation Reactions of α- and β-Co(EDDA)$\mathrm{CO_3}^-$ Ions[a] ([Complex] = 10^{-3} *M*; $I = 2.0$ *M* ($\mathrm{KNO_3}$))

A. α-Co(EDDA)$\mathrm{CO_3}^-$

Temp, °C	10^3k_0, $\mathrm{sec^{-1}}$		k_1, M^{-1} $\mathrm{sec^{-1}}$		k_2, $\mathrm{sec^{-1}}$
15	1.1 ± 0.1		58 ± 1		28.5
20	1.7 ± 0.8	(1.1)	76 ± 1	(50)	39.5
25	2.9 ± 0.2	(2.2)	118 ± 1	(83)	55.0
30.3	.....	(3.9)	.....	(136)	. . .
$\Delta H^\ddagger$, kcal/mol	17 ± 2	(21 ± 3)	12 ± 1	(16 ± 1)	11.1 ± 0.6
$\Delta S^\ddagger$, eu	−14 ± 7	(0 ± 12)	−8 ± 8	(5 ± 3)	−13 ± 2

B. β-Co(EDDA)$\mathrm{CO_3}^-$

Temp, °C	10^4k_0, $\mathrm{sec^{-1}}$		k_1, M^{-1} $\mathrm{sec^{-1}}$		k_2, $\mathrm{sec^{-1}}$
15	2.8 ± 0.8		1.25 ± 0.02		0.90
20	7.3 ± 2.9	(1.9)	1.73 ± 0.07	(1.82)	1.40
25	9.8 ± 4.3	(3.8)	2.44 ± 0.11	(3.04)	2.31
30.3	. . .	(6.9)	. . .	(5.23)	. . .
$\Delta H^\ddagger$, kcal/mol	21 ± 6	(21 ± 3)	10.8 ± 0.3	(17 ± 1)	16.3 ± 1.5
$\Delta S^\ddagger$, eu	−2 ± 20	(2 ± 12)	−20 ± 1	(2 ± 3)	−2 ± 5

[a] Parenthesized values are from ref 4; $I = 1.0$ *M* ($\mathrm{NaClO_4}$).

Table III. Rate Parameters for Acid-Catalyzed Ring-Opening Reactions of Some Chelated Cobalt(III) Carbonato Complexes at 25°

Complex ion[a]	k_1, M^{-1} $\mathrm{sec^{-1}}$	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, eu	Ref
$\mathrm{Co(py)_4CO_3}^+$	8.9×10^{-6}	24.0	−1	18
$\mathrm{Co(phen)_2CO_3}^+$	1.5×10^{-4}	20.4	−9	19
$\mathrm{Co(bpy)_2CO_3}^+$	2.2×10^{-4}	22.3	−2	19
α-Co(dmtr)$\mathrm{CO_3}^+$	1.8×10^{-2}			20
β-Co(dmtr)$\mathrm{CO_3}^+$	5.6×10^{-4}			20
$\mathrm{Co(en)_2CO_3}^+$	0.6	13.8	−7	3
Co(tren)$\mathrm{CO_3}^+$	2.0	11.1	−20	3
α-Co(trien)$\mathrm{CO_3}^+$	5.2	15.0	−5	3
β-Co(trien)$\mathrm{CO_3}^+$	0.2	17.0	−5	3
Co(NTA)$\mathrm{CO_3}^{2-}$	47	18.6	+11	2
α-Co(EDDA)$\mathrm{CO_3}^-$	118	12	−8	This work
β-Co(EDDA)$\mathrm{CO_3}^-$	2.4	10.8	−20	This work

[a] py = pyridine; phen = *o*-phenanthroline; bpy = bipyridine; dmtr = 4,7-dimethyl-triethylenetetramine; en = ethylenediamine; tren = β,β',β''-triaminotriethylamine; trien = triethylenetetramine.

parameters for which are almost identical with those for the β-EDDA complex and differ from the α-EDDA species mainly in the increased $\Delta S^\ddagger$ for the latter.

Clearly, the overall ionic charge of the complex ion is not a factor of prime significance, as is illustrated by rate comparisons of β-EDDA with tren species and of α-EDDA with NTA. Neither do considerations of ligand basicity nor diaquo complex acidity afford clean-cut correlations of reactivities including the anionic species, contrary to a previous suggestion with respect to the tetraammine complexes.[19] One notes that the average pK_a's of the ligands dmtr, tren, trien, NTA, and EDDA are 6.3,[20] 9.5,[21a] 7.3,[21a] 4.7,[21a] and 5.9,[21b] respectively. Similarly, the first p*K*'s of the various diaquo complexes $\mathrm{CoL(H_2O)_2}^{3+}$ are 5.4,[22] 5.4,[23] 5.3,[23] 6.2,[24] 7.4,[25] and 6.0[25] for L = tren, α-trien, β-trien, NTA, α-EDDA, and β-EDDA, respectively. The factors which govern the relative magnitudes of the rate constants for acid-catalyzed ring opening of chelated carbonato complexes obviously include a stereochemical component, as outlined before.[3] The influence of the electronic structure of the ligand, however, at least as evidenced by the type of pK_a data quoted, is not yet clearly delineated for this type of reaction. Indeed, the contrasts in k_1 as between the dmtr and trien complexes or between the tren and NTA species, for example, might perhaps better be ascribed to differences in solvation resulting from methyl substitution in the first case and ionic charge reversal in the second.

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Registry No. α-K[Co(EDDA)$\mathrm{CO_3}$], 56144-83-3; β-K[Co(EDDA)$\mathrm{CO_3}$], 53029-88-2.

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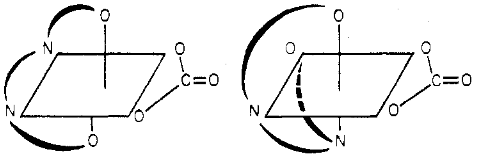

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(11) The extinction coefficients of α-Co(EDDA)$\mathrm{CO_3}^-$ at 545 and 385 nm are 96 and 138 M^{-1} $\mathrm{cm^{-1}}$, respectively, while for the α-diaquo complex at the same wavelengths, these coefficients are 140 and 78 M^{-1} $\mathrm{cm^{-1}}$, respectively. The corresponding coefficients for the β-carbonato and β-diaquo complexes at 540 nm are 214 and 163 M^{-1} $\mathrm{cm^{-1}}$, respectively.
(12) The rate constant for this isomerization is reported to be 3×10^{-4} $\mathrm{sec^{-1}}$ at 29.3°: P. J. Garnett and D. W. Watts, personal communication. This suggests a half-time of the order of magnitude of 100 min at room temperature.
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Synthesis and Acid Hydrolysis of *trans*-Dichlorobis(ethylenediamine)ruthenium(III) and Related Compounds

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Further to our studies on the reactions of ruthenium(III) ethylenediamine complexes[1-3] we report the synthesis of the new *trans*-dichlorobis(ethylenediamine)ruthenium(III) complex