is almost exclusively associative. Most previous studies of five-coordinate systems report dissociative mechanisms.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Fe(S_2C_2Ph_2)_2 \cdot PPh_3$, 14375-89-4; $Fe(S_2C_2Ph_2)_2 \cdot P(OBu)_3$, 51108-62-4; $Co(S_2C_2Ph_2)_2 \cdot PPh_3$, 15636-21-2; $Co(S_2C_2Ph_2)_2P(OBu)_3$, 51154-94-0; $P(p\text{-tolyl})_3$, 1038-95-5; $P(OBu)_3$, 102-85-2; $P(OEt)_3$, 122-52-1; PBu_3, 998-40-3; PPh_2OMe, 4020-99-9.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. VII. Acid-Catalyzed Aquation of Carbonato(nitrilotriacetato)cobaltate(III) Ion[1,2]

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The aquation of the title compound has been studied over the range $-0.03 < \mathrm{pH} < 4.8$ and $15° < T < 30°$ at $I = 2\,M$ by means of stopped-flow technique. The pseudo-first-order rate constants are directly proportional to $[H^+]$ for $1 < \mathrm{pH} < 2.5$, above which pH the rate tends to independence of acidity. The results have been interpreted in terms of a duality of mechanism involving both water- and acid-catalyzed dechelation which leads to a rate expression $k_{\mathrm{obsd}} = k_0 + k_1[H^+]$. At high acid concentration ($[H^+] > 1.5\,M$) the observed pseudo-first-order rate constant readily attains the limiting condition $k_{\mathrm{obsd}} = k_2$, where k_2 is the decarboxylation rate of the aquobicarbonato ring-opened intermediate species. At 25°, $k_0 = 3.0 \times 10^{-3}$ sec^{-1}, $k_1 = 41.9\,M^{-1}$ sec^{-1}, and $k_2 = 57.1$ sec^{-1}, and the temperature-variation parameters describing these constants are respectively $\Delta H^\ddagger = 12.6 \pm 2.7$, 15.8 ± 0.5, and 15.3 ± 1.0 kcal/mol and $\Delta S^\ddagger = 28.1 \pm 9.0$, -1.5 ± 1.5, and -0.8 ± 3.2 cal/deg mol. The high reactivity of this anionic carbonato complex relative to the cationic carbonato complexes reported upon earlier is explained in terms of charge and entropy differences.

Introduction

It is now firmly established[3-5] that the cationic carbonatotetramine complexes of cobalt(III) undergo aquation *via* a mechanism consisting of ring opening of the chelated carbonato group catalyzed both by water and by hydronium ion, followed by a rapid decarboxylation of the monodentate intermediate, as shown in the reaction sequence (1)-(5).

$$CoN_4CO_3^+ + H_2O \xrightarrow{k_0} CoN_4(OH)(CO_3H)^+ \tag{1}$$

$$CoN_4CO_3^+ + H_3O^+ \xrightarrow{k_1} CoN_4(OH_2)(CO_3H)^{2+} \tag{2}$$

$$CoN_4(OH_2)(CO_3H)^{2+} + H_2O \overset{K_1}{\rightleftharpoons} CoN_4(OH)(CO_3H)^+ + H_3O^+ \tag{3}$$

$$CoN_4(OH_2)(CO_3H)^{2+} \xrightarrow{k_2} CoN_4(OH_2)(OH)^{2+} + CO_2 \tag{4}$$

$$CoN_4(OH_2)_2{}^{3+} + H_2O \rightleftarrows CoN_4(OH_2)(OH)^{2+} + H_3O^+ \tag{5}$$

The corresponding rate law which describes the variation of the observed pseudo-first-order rate constant with acidity is given by (6). This rate law fits the data well at acidities

$$k_{\mathrm{obsd}} = k_0 + k_1[H^+] \tag{6}$$

above pH 2, where k_2 greatly exceeds $k_1[H^+]$. There is, however, evidence that at high acid concentrations[5] k_{obsd} approaches a limiting value, indicative of the situation in which $k_1[H^+] > k_2$, and $k_{\mathrm{obsd}} \rightarrow k_2 =$ constant. Also, recent photochemical studies[6] further support the proposed appearance of the dechelated aquobicarbonato intermediate, which is the actual species involved in the decarboxylation step (reaction 4). There are, however, no data concerning the decarboxylation of anionic carbonatocobalt(III) complexes with the exception of some as yet unpublished studies of carbonato(ethylenediaminediacetato)cobalt(III) complexes.[7] The role that charge plays in the substitution reactions of amine complexes of cobalt(III) is not easily predictable,[8] but generally the rates observed increase as charge decreases. As is apparent from this work as well as from Garnett's study, the reactivity of anionic carbonatocobalt(III) complexes is considerably greater than that of cationic complexes.

This paper now reports in detail the kinetic investigation of the acid-catalyzed aquation of $Co(NTA)CO_3^{2-}$ (NTA ≡ nitrilotriacetate ion) and offers a possible explanation for the high lability of the complex. Also presented is evidence that at high acid concentration the pseudo-first-order rate constant for the acid hydrolysis of $Co(NTA)CO_3^{2-}$ readily reaches the limiting condition where $k_{\mathrm{obsd}} = k_2$. This enables accurate evaluation of the decarboxylation rate constant k_2 completely independent of the ring-opening rate constant k_1, an aim which we were only partially successful in accomplishing in our earlier studies of cationic carbonatocobalt(III) species.[5]

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[1] A preliminary report of this investigation was presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972; see Abstracts, No. INORG 123.

[2] Part VI: D. A. Palmer and G. M. Harris, *Inorg. Chem.*, 13, 965 (1974).

[3] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 91, 3207 (1969).

[4] V. S. Sastri and G. M. Harris, *J. Amer. Chem. Soc.*, 92, 2943 (1970).

[5] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 93, 91 (1971).

[6] V. W. Cope, S. Chen, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 95, 3116 (1973).

[7] P. J. Garnett, Ph.D. Thesis, The University of Western Australia, 1972, private communication.

[8] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 3, p 66; C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature* (*London*), 187, 477 (1960).

Experimental Section

Potassium carbonato(nitrilotriacetato)cobaltate(III) was prepared according to the method of Mori, *et al.*[9] The pure product was obtained only after recrystallizing the crude material 4 times by dissolving it in cold water and adding absolute alcohol slowly. The purity was checked by chemical analysis.[10] *Anal.* Calcd for $K_2[Co(NC_6H_6O_6)CO_3]H_2O$: C, 20.85; H, 2.00; N, 3.47. Found: C, 21.20; H, 2.05; N, 3.61.

Potassium hydroxoaquo(nitrilotriacetato)cobaltate(III)[11] was also prepared according to the published method.[9] The product was crystallized twice from hot water (50-60°) and the purity of the complex was checked by microanalysis.[12] *Anal.* Calcd for $K[Co(NC_6H_5O_6)(OH)(H_2O)]$: C, 22.44; H, 2.82; N, 4.36. Found: C, 22.93; H, 2.83; N, 4.33.

Diaquo(nitrilotriacetato)cobalt(III) ion was produced in solution by treating potassium hydroxoaquo(nitrilotriacetato)cobaltate(III) with an equivalent amount of nitric acid. This can also be accomplished by adding dilute nitric acid to potassium carbonato(nitrilotriacetato)cobaltate(III). The visible spectrum of the final solution is shown in Figure 1.

The infrared spectra of the potassium carbonato- and hydroxoaquo(nitrilotriacetato)cobaltate(III) salts were obtained by means of the KBr disk technique with a Beckman IR5A instrument. The carbonato complex has a strong peak at 1605 cm^{-1} and a shoulder at 1670 cm^{-1} whereas two strong bands, one at 1620 cm^{-1} and an other at 1670 cm^{-1}, appear for the hydroxoaquo complex. These bands of NTA complexes can be assigned to the coordinated carboxylate groups[9,13] as similar spectral characterizations have been made by Busch and coworkers[14] with EDTA complexes. The C–O stretching frequencies of the bidentate carbonate of the NTA complex appear at 1010 and 765 cm^{-1} as compared to 1030 and 760 cm^{-1} reported for a series of carbonatocobalt(III) species by Nakamoto.[15] The C–O stretching frequency at 1593 cm^{-1} for CO_3^{2-} is masked by the strong band of the coordinated carboxylate group.

Nitrilotriacetic acid was obtained from Eastman Kodak Co. and used without further purification. All other chemicals used were of reagent grade. Deionized and degassed water was used in preparing all solutions. Concentrated nitric acid[16] was diluted to double the volume and then aerated for 2 hr to remove any dissolved oxides of nitrogen. The acid was stored in a Pyrex bottle in the dark and the strength of the acid was determined by titrating with standard alkali using a mixed indicator. Above pH 2, the pH determinations were made with either a Beckman Research Model pH meter or a Model 26 Radiometer pH meter, using a water-jacketed sample holder thermostated at the reaction temperature. The rate measurements below pH 3 were made on a Durrum Model 110 stopped-flow assembly equipped with a Tektronix Model 5103-N oscilloscope as described previously.[17] The record of a typical stopped-flow run is shown in Figure 2.

The runs at higher pH values were made on a Cary 15 spectrophotometer with a time-drive chart recorder. All runs were followed at 410 nm which offers the largest absorbance difference between reactant and product.[18] Temperature control of the solution inside the optical cells was maintained to within ±0.1° by circulating water through a metal block cell holder. The pH of the reactant solution was maintained constant by using McIlvaine phosphate-citric acid buffer,[19] and an ionic strength of 2.0 *M* was maintained by addition of potassium nitrate. Pseudo-first-order rate constants were derived in the conventional manner from semilogarithmic plots of the fraction of reactant remaining as a function of time.

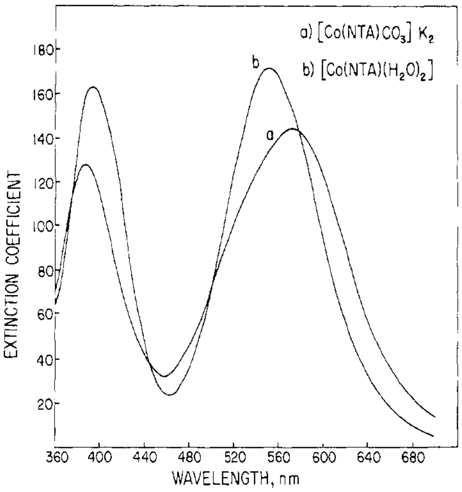

Figure 1. Visible absorption spectra of (a) $[Co(NTA)CO_3]K_2$ and (b) $[Co(NTA)(H_2O)_2]$ in aqueous solution at room temperature.

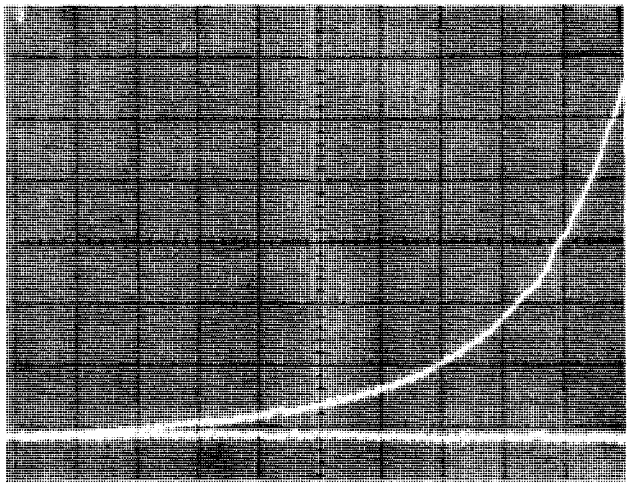

Figure 2. Typical oscilloscope trace of acid hydrolysis of $[Co(NTA)CO_3]^{2-}$ at 20° $[H^+] = 0.1\,M$, and $I = 2\,M$ (KNO_3). Time scale on abscissa, 0.2 sec/div; absorbance on ordinate, arbitrary units.

Results and Discussion

The pseudo-first-order rate constants k_{obsd} (including both stopped-flow and Cary 15 results) are recorded in Table I along with the calculated second-order rate constants $k' = k_{obsd}/[H^+]$. The data clearly indicate three important regions to be considered so far as the acid dependency is concerned. In the high-acid region where $[H^+] > 1.5\,M$, the pseudo-first-order rate constants are essentially invariant and thus seem to have attained the limiting condition of $k_{obsd} \rightarrow k_2$ mentioned earlier. The average values of k_2 determined from the pseudo-first-order rate constants over this high acid concentration range at four different temperatures are shown in Table II. The activation parameters obtained by analyzing these data according to conventional transition-state theory are $\Delta H^{\ddagger} = 15.3 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -0.8 \pm 3.2$ cal/deg mol. In the central

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[9] M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, *Bull. Chem. Soc. Jap.*, 31, 940 (1958).

[10] Microanalysis was done by Instranal Laboratory, Inc., Rensselaer, N. Y. 12144.

[11] Mori, *et al.*,[9] claimed that they had isolated two types of $K[Co(NTA)(OH)(H_2O)]$, one α and one β form. We failed to reproduce his preparative method for the β species. The difference between α and β forms, according to Mori, is whether the OH is trans or cis to the tertiary nitrogen, but this kind of distinction probably is not feasible, since proton transfer between OH and OH_2 should be very rapid.

[12] Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

[13] Y. Tomita and K. Ueno, *Bull. Chem. Soc. Jap.*, 36, 1069 (1963).

[14] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, 75, 4574 (1953); 78, 716 (1956); M. L. Morris and D. H. Busch, *ibid.*, 78, 5178 (1956).

[15] K. Nakamoto, "Infra-red Spectra of Inorganic Co-ordination Compounds," Wiley, New York, N. Y., 1970, p 170.

[16] Nitric acid is used in all of the runs instead of perchloric acid since the complex is used as a K salt which would give insoluble potassium perchlorate.

[17] E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Amer. Chem. Soc.*, 95, 4169 (1973).

[18] The molar absorbance of $Co(NTA)CO_3^{2-}$ is 93 at 410 nm whereas $Co(NTA)(H_2O)_2$ has a molar absorbance of 145 at the same wavelength.

[19] P. J. Ewing, J. M. Markwitz, and I. Rosenthal, *Anal. Chem.*, 28, 1179 (1956).

Table I. Pseudo-First-Order Rate Constants for the Acid Hydrolysis of $Co(NTA)CO_3$ ($I = 2.0\ M\ (KNO_3)$)[a]

15°			20°			25°			30°		
pH	k_{obsd}, sec^{-1}	k', M^{-1} sec^{-1}	pH	k_{obsd}, sec^{-1}	k', M^{-1} sec^{-1}	pH	k_{obsd}, sec^{-1}	k', M^{-1} sec^{-1}	pH	k_{obsd}, sec^{-1}	k', M^{-1} sec^{-1}
−0.30	23.5	11.8	−0.30	38.9	19.5	−0.30	55.4	27.7	−0.30	94.6	47.3
−0.26	26.8	14.9	−0.30	33.0	16.5	−0.26	60.0	33.3	−0.30	98.6	49.3
−0.18	24.4	16.3	−0.18	37.0	24.7	−0.18	56.0	37.3	−0.26	93.1	51.7
−0.18	23.0	15.3	−0.18	32.7	21.8	0.00	37.0	37.0	−0.26	92.5	51.4
0.00	16.6	16.6	−0.26	33.0	18.3	0.30	22.7	45.4	−0.18	94.9	63.3
0.30	9.30	18.6	0.00	24.4	24.4	0.92	5.1	42.5	−0.18	96.6	64.4
1.00	1.56	15.6	0.30	14.0	28.0	0.92	5.0	41.6	−0.08	82.0	68.3
1.20	1.10	17.5	0.60	7.3	29.2	1.20	2.7	42.9	−0.08	81.1	67.6
1.20	1.00	15.9	1.00	2.53	25.3	1.40	1.71	42.8	0.00	59.4	59.4
1.22	1.03	17.2	1.20	1.74	27.6	1.26	2.83	41.3	0.00	64.9	64.9
1.30	0.78	15.6	1.40	1.13	28.3	1.52	1.38	46.0	0.22	48.8	80.3
1.40	0.63	15.8	1.40	0.92	23.0	1.60	1.13	45.2	0.22	48.1	79.1
1.60	0.25	10.0	1.60	0.63	25.2	1.79	0.67	41.9	0.31	44.7	92.0
2.00	0.16	16.0	1.60	0.66	26.4	2.00	0.43	43.0	0.31	44.0	90.5
2.00	0.18	18.0	1.46	0.92	26.3	2.48	0.21	63.6	0.39	27.2	67.2
2.16	0.13	18.8	1.80	0.35	21.9	2.55	0.116	41.4	0.39	26.6	65.7
2.35	0.10	22.4	2.00	0.19	19.0	2.62	0.086	35.8	0.69	16.3	80.3
2.62	0.041	17.1	2.00	0.23	23.0	2.84	0.064	44.1	0.69	15.5	76.4
2.85	0.027	19.2	1.97	0.37	34.6	2.96	0.046	41.8	0.92	8.06	67.2
2.89	0.027	21.0	1.97	0.40	36.4	3.00	0.051	50.5	1.05	6.26	70.3
2.96	0.021	19.2	2.50	0.087	27.2	3.02	0.046	48.4	1.00	6.54	65.4
3.62	0.0079	32.8	2.89	0.045	34.9	3.24	0.031	53.4	1.30	3.53	70.6
3.59	0.0063	24.0	2.90	0.043	34.1	3.28	0.028	53.8	1.30	3.29	65.8
4.40	0.0014	35.0	2.93	0.046	39.0	3.82	0.010	66.2	1.60	1.73	69.2
4.00	0.0016	16.0	2.90	0.036	28.6	3.82	0.011	72.8	1.60	1.78	71.2
4.19	0.0032	49.2	2.95	0.034	30.4	3.85	0.0081	57.9	2.00	0.64	64.0
4.85	0.00085	60.7	3.12	0.025	32.9	3.85	0.0089	63.6	2.00	0.62	62.0
			3.10	0.027	34.0	4.70	0.0032	160	2.00	0.63	63.0
			3.40	0.017	41.4	4.70	0.0035	175	2.89	0.083	63.8
			3.40	0.020	48.5	4.22	0.0048	80	2.89	0.086	66.2
			3.60	0.012	48.0	4.30	0.0046	92	3.24	0.039	67.2
			3.66	0.084	38.2				3.24	0.042	72.4
			3.92	0.064	53.3				3.70	0.015	75.0
			4.80	0.0016	106				3.70	0.017	85.0
			4.70	0.0022	110				4.22	0.0079	132.0
									4.70	0.0054	270.0
									4.80	0.0040	250.0

[a] Below pH 2, the acidities were adjusted by conventional volumetric procedures.

Table II. Rate Constants for the Ring Opening of $Co(NTA)CO_3^{2-}$ and Decarboxylation of $Co(NTA)(HCO_3)(H_2O)^-$

Temp, °C	$10^3 k_0$, sec^{-1}	k_1, M^{-1} sec^{-1}	k_2, sec^{-1}
15	1.18 ± 0.60	16.5 ± 0.7	24.4 ± 1.7
20	2.37 ± 0.60	26.4 ± 0.6	34.3 ± 2.9
25	3.00 ± 0.80	41.9 ± 0.8	57.1 ± 2.5
30	3.80 ± 0.60	67.3 ± 1.0	95.1 ± 2.3

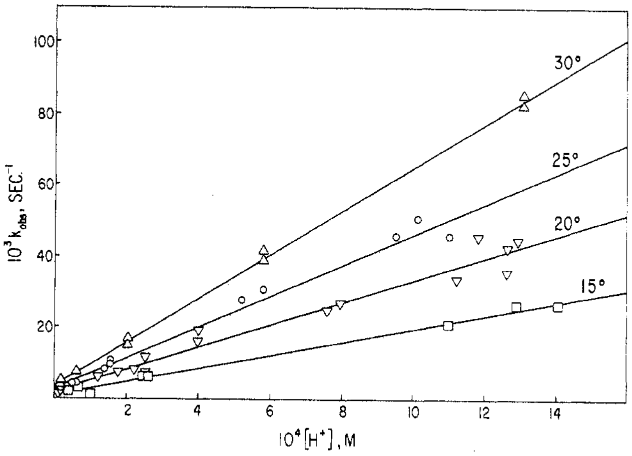

Figure 3. Plot of k_{obsd} *vs.* $[H^+]$ at different temperatures and $I = 2\ M\ (KNO_3)$.

region ($0 < pH < 2$), the acid-catalyzed path makes the dominant contribution to the aquation rate and a clean first-order dependency on $[H^+]$ is observed. This is clearly reflected by the near-constancy of the k' values. However, in the higher pH region the water-catalyzed path makes a significant contribution to the rate and the rate constant k_{obsd} becomes the sum of two rate constants as suggested by eq 6 above. The treatment of the data in the range $2.8 < pH < 4.5$ at four different temperatures is shown in Figure 3 as k_{obsd} *vs.* $[H^+]$ plots. The intercepts of these plots give k_0 values which are recorded in Table II. The k_1 values in Table II were determined by linear least-squares analysis of all k_{obsd} *vs.* $[H^+]$ data in the range $1 < pH < 4.5$. This kind of treatment gives nearly zero intercepts but very reliable k_1 values.[20] Activation parameters were also derived from the k_0 and k_1 data and are recorded in Table III. The results can be interpreted very satisfactorily in terms of the mechanism given earlier, with N_4 replaced by NTA and the ionic charges decreased by 3 units. These reactions yield the two-term rate law eq 6 when $k_2 \gg k_1[H^+]$ which is true in the higher pH range as illustrated by the linear plots with nonzero intercepts (Figure 3). At high acid concentration $k_1[H^+]$ finally surpasses k_2 and the latter becomes the limiting rate constant, as explained earlier.

It is enlightening to compare the ring-opening rate of $Co(NTA)CO_3^{2-}$ with that of $Co(tren)CO_3^+$ (where tren = 2,2′,2″-triaminotriethylamine) since these complexes are isostructural and have similarly restricted stereochemistry.

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(20) Least-squares analysis of the data plotted in Figure 3 yielded k_1 values which were not significantly different from those given in Table III which embrace the wider acidity range.

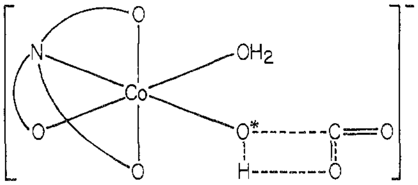
Table III. Rate Parameters for the Ring-Opening Reactions Some Cobalt(III)-Carbonato Complexes at 20°

Complex	$10^4 k_0$, $\sec^{-1}$	$\Delta H_0^{\ddagger}$, kcal/mol	$\Delta S_0^{\ddagger}$, cal/deg mol	k_1, $M^{-1} \sec^{-1}$	$\Delta H_1^{\ddagger}$, kcal/mol	$\Delta S_1^{\ddagger}$, cal/deg mol
$Co(tren)CO_3$[a]	1.0	15 ± 2.0	−25 ± 5	1.4	11.1 ± 1.0	−20.0 ± 4.0
$Co(NTA)CO_3$	23.7	12.6 ± 2.7	+ 28.1 ± 9	26.4[b] (25[c])	15.8 ± 0.5	−1.5 ± 1.5
α-$Co(EDDA)CO_3$[d]	11.3	21.0 ± 3.0	−1.0 ± 12	50.1	16.7 ± 1.0	+ 5.6 ± 3.0
β-$Co(EDDA)CO_3$[d]	1.9	21.5 ± 3.0	−2.66 ± 12	1.8	17.6 ± 1.0	+ 2.4 ± 3.0

[a] Reference 5; $I = 0.5\ M$. [b] This work; $I = 2.0\ M$. [c] This work; $I = 0.5\ M$. [d] Reference 7; $I = 0.5\ M$.

The data for these complexes along with corresponding figures for $Co(EDDA)CO_3^-$ are presented in Table III. Although the results were obtained at different ionic strengths for each complex, it can be assumed that ring-opening rates are not greatly affected by ionic strength, as substantiated by some experiments with $Co(NTA)CO_3^{2-}$ at $I = 0.5$ (see Table III). It is apparent that the water-catalyzed ring-opening rate is nearly 10 times as great and the acid-catalyzed rate is nearly 20 times as great as for $Co(tren)CO_3^+$. This can be attributed to the difference in charge of these two complexes, the electrostatic interaction between negatively charged complex and positively charged hydronium ion being more favorable in the NTA case. The neutralization of charge during interaction releases solvent molecules, resulting in a much more positive entropy of activation. The enhanced rate for the water-catalyzed ring opening seems also to be due to the favorable entropy factor. As seen in Table III, similar observations have been made by Garnett[7] on the ring-opening reactions of α-*cis*-$Co(EDDA)CO_3^-$ and β-*cis*-$Co(EDDA)CO_3^-$ (EDDA ≡ ethylenediaminediacetate). The faster rate of acid-catalyzed ring opening for α-$Co(EDDA)CO_3^-$ as compared to $Co(NTA)CO_3^{2-}$ may be due to the added influence of ligand geometry, as observed previously[5] for α- and β-$Co(trien)CO_3^+$, where trien is triethylenetetramine.

Let us now consider the decarboxylation reaction which is independently observed at high acid concentrations. It has been postulated[3-5] for cationic complexes that the decarboxylation occurs only through the decomposition of $CoN_4(HCO_3)(H_2O)^{2+}$ since the pK of reaction 3 is about 6. A similar assumption can be made in the case of the NTA complex, since the pK of $Co(NTA)(HCO_3)(H_2O)^-$ is likely to be more than 6 because of reduction by 3 units of the charge on the complex.[21] It has also been shown[5] that the decarboxylation of $CoN_4(HCO_3)(OH_2)^{2+}$ occurs *via* the mechanism similar to the decarboxylation reaction of $CoN_5HCO_3^{2+}$, including the C-O bond fission. However, it was not possible to reach the limiting rate for the N_4 system even at an acid concentration of $2\ M$.[5] For $Co(NTA)CO_3^{2-}$ the pseudo-first-order rate constants definitely reach the limiting state and one can make a direct comparison of the rates and activation parameters of the decarboxylation of $Co(NTA)(HCO_3)(H_2O)^-$ with that of $Co(NH_3)_5HCO_3^{2+}$. For the latter[2] at 25°, $k = 1.13\ \sec^{-1}$, $\Delta H^{\ddagger} = 16.8 \pm 0.2$ kcal/mol, and $\Delta S^{\ddagger} = -2 \pm 1$ cal/deg mol. It is seen (Table II) that the rate of decarboxylation of $Co(NTA)(HCO_3)(H_2O)^-$ is about 50 times greater than that of the pentaammine complex and that this rate increase is due almost entirely to decreased enthalpy of activation. The enhancement in rate can be explained by the same kind of model as proposed[3] for the transition state of $Co(NH_3)_5HCO_3^{2+}$



In $Co(NTA)(HCO_3)(H_2O)^-$, the increased negative charge on the central cobalt atom arising from the ligand NTA increases the basicity of O* and thereby facilitates H bonding. This will in turn weaken the C-O* bond quite considerably. Alternatively, the residual negative charge on the central Co atom might alone weaken the Co-O* bond to such an extent that decarboxylation occurs through Co-O bond fission. It is noteworthy in this connection that the rate of decarboxylation of carbonic acid[22] is only about one-third of that of $[Co(NTA)(H_2O)(CO_3H)]^-$. Thus, direct dissociation of HCO_3^- from the latter species and subsequent decomposition of the bicarbonate is ruled out as a viable mechanism.

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Registry No. $K_2[Co(NTA)CO_3]$, 50986-61-3; $[Co(NTA)(HCO_3)(H_2O)]^-$, 50986-62-4.

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