$(CH_3)_3N$ should be progressively harder bases than ammonia. If preference for $BF_3$ over $BH_3$ is taken as a measure of hardness, our results indicate that both $CH_3NH_2$ and $(CH_3)_2NH$ are hard bases since both produce larger equilibrium constants with $BF_3$ than with $BH_3$. However, methylamine shows a greater preference for the hard fluoroborane acceptors than does dimethylamine, while a slight reverse preference is observed for the soft borane acceptor. These observations suggest that methylamine behaves as a harder base than dimethylamine in this system. Only a qualitative comparison is justified, however, in view of the relatively small differences observed and the numerous factors which can affect the equilibrium constants.

**Acknowledgment.** We gratefully acknowledge the support of this work by the Robert A. Welch Foundation under Grant No. E-439.

**Registry No.** $(CH_3)_3N{\cdot}BH_3$, 75-22-9; $(CH_3)_3N{\cdot}BH_2F$, 35449-24-2; $(CH_3)_3N{\cdot}BHF_2$, 35237-72-0; $(CH_3)_3N{\cdot}BF_3$, 420-20-2; $(CH_3)_3P{\cdot}BH_3$, 1898-77-7; $(CH_3)_3P{\cdot}BH_2F$, 67226-44-2; $(CH_3)_3P{\cdot}BHF_2$, 67194-37-0; $(CH_3)_3P{\cdot}BF_3$, 420-21-3; $(C_6H_5)_3P{\cdot}BH_3$, 2049-55-0; $(C_6H_5)_3P{\cdot}BH_2F$, 67194-38-1; $(C_6H_5)_3P{\cdot}BHF_2$, 67194-39-2; $(C_6H_5)_3P{\cdot}BF_3$, 850-07-7; $(CH_3)_2NH{\cdot}BH_3$, 74-94-2; $(CH_3)_2NH{\cdot}BH_2F$, 67194-40-5; $(CH_3)_2NH{\cdot}BHF_2$, 42525-42-8; $(CH_3)_2NH{\cdot}BF_3$, 811-59-6; $CH_3NH_2{\cdot}BH_3$, 1722-33-4; $CH_3NH_2{\cdot}BH_2F$, 67194-41-6; $CH_3NH_2{\cdot}BHF_2$, 42525-40-6; $CH_3NH_2{\cdot}BF_3$, 373-56-8.

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Contribution from the Departments
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# Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 13. Acid-Catalyzed Aquation of ($\alpha\beta S$)-Carbonato(tetraethylenepentamine)cobalt(III) Ion and Carbon Dioxide Uptake by ($\alpha\beta S$)-Aquo(tetraethylenepentamine)cobalt(III) Ion[1]

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*Received May 25, 1978*

Previous studies in this series dealing with complexes of the pentaammine type have embraced the acid-catalyzed decarboxylation kinetics of the species $M(NH_3)_5(CO_3)^+$ ($M \equiv$ Co(III),[2] Rh(III),[3] and Ir(III)[3]) and the carbon dioxide uptake kinetics[4] of $Co(NH_3)_5(OH)^{2+}$. Other studies have dealt with the acid-catalyzed carbonato ring-opening and decarboxylation reactions of various chelated carbonato complex ions of the general type $Co(N)_4(CO_3)^+$, where $(N)_4$ represents a tetrafunctional grouping of amine ligands. Large variations have been noted in the rate of the ring-opening process, depending on the nature of the "nonparticipating" tetraamine grouping.[5,6] While no ring opening is involved in the acidic hydrolysis of carbonatopentaamine complexes, it was of interest to us to examine the effect of a drastic change in the pentaamine grouping on both the decarboxylation process and on its reverse, the carbon dioxide uptake by the corresponding aquopentaamine species. As our first study of this nature, we have examined the reactions of the carbonato cobaltic complexes containing the straight-chain pentadentate species tetraethylenepentamine.

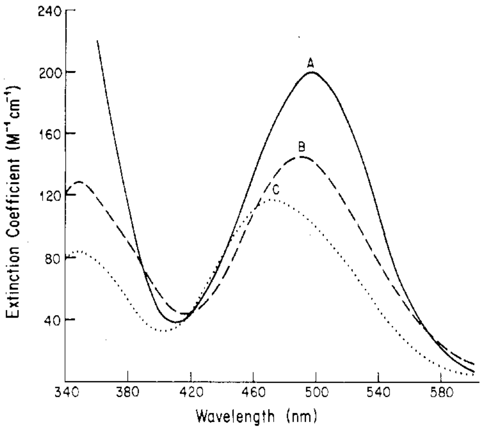

**Figure 1.** UV–visible spectra of some (tetraethylenepentamine)cobalt(III) complexes: (A) $\alpha\beta S$-$[Co(tetren)(CO_3)]ClO_4$; (B) $\alpha\beta S$-$[Co(tetren)(OH)](ClO_4)_2$; (C) $\alpha\beta S$-$[Co(tetren)(OH_2)](ClO_4)_3$.

## Experimental Section

**Materials.** Tetraethylenepentamine(tetren) was used as obtained from Matheson Coleman and Bell. All other chemicals were of reagent grade. Deionized and degassed water was used in preparing all solutions.

**Preparation and Characterization.** ($\alpha\beta S$)-Hydroxo- and ($\alpha\beta S$)-aquo(tetraethylenepentamine)cobalt(III) perchlorates were prepared and characterized as described by House and Garner.[7-9] ($\alpha\beta S$)-Carbonato(tetraethylenepentamine)cobalt(III) perchlorate was prepared as follows. Solid $Li_2CO_3$ is slowly added to a stirred solution containing 2 g of $[Co(tetren)(OH)](ClO_4)_2$ in a minimum amount of water until a pH of 8–8.5 is attained. The solution is stirred for 5 min and cooled in an ice bath, and an equal volume of absolute ethanol is added. The mixture is allowed to stand for a few minutes in the ice bath, filtered, and washed thoroughly with ethanol. The filtrate is then evaporated to dryness. Bright red platelike crystals are obtained. Anal. Calcd for $[Co(tetren)(CO_3)](ClO_4){\cdot}3H_2O$: C, 23.40; H, 6.29; N, 15.18. Found:[10] C, 23.56; H, 6.16; N, 15.28.

**Spectra.** The absorption spectra in the UV–visible region were obtained by use of a Cary 15 spectrophotometer. The spectrum of the carbonato complex was determined in dilute sodium bicarbonate solution to avoid hydrolysis and is very similar to that of the $Co(NH_3)_5CO_3^+$ complex ion. (A steep charge-transfer absorbance increase near 350 nm for both complexes is diagnostic of the presence of monodentate carbonato ligand.) After treatment with acid, the carbonato complex solution gave a spectrum identical with that of $\alpha\beta S$-$Co(tetren)(OH_2)^{3+}$, confirming that the geometry of the carbonato species is $\alpha\beta S$. The electronic spectra of aquo, hydroxo, and carbonato complexes are presented in Figure 1. The infrared spectrum of the carbonato complex was measured on a Beckman IR5A spectrometer using the KBr disk technique and exhibits two CO stretching frequencies at 1458 and 1340 $cm^{-1}$ to be compared with 1453 and 1373 $cm^{-1}$ for the $Co(NH_3)_5CO_3^+$ complex ion.[11]

**Kinetic Runs.** The kinetics of acid-catalyzed aquation of the carbonato species were studied between 15 and 30 °C at an ionic strength of 0.5 M (NaCl) and over an acidity range of $1 \le pH \le$

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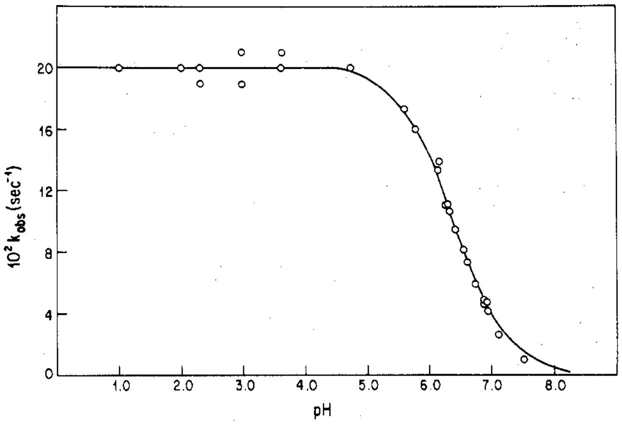

**Figure 2.** Observed decarboxylation rate constant for Co(tetren)-$(CO_3)^+$ ion as a function of pH at 20 °C and $I = 0.5$ M (NaCl).

7.5. The reaction was monitored at a wavelength of 490 nm where the absorbances of the carbonato and aquo complexes are close to a maximum.[12] The rate of carbon dioxide uptake by $\alpha\beta S$-Co(tetren)$(OH)^{2+}$ was measured within the temperature range 15–25 °C by the "equilibrium method" described earlier,[4] the reaction being followed at 500 nm.[13] Most of the rate measurements for decarboxylation and carbon dioxide uptake were made on the Durrum Model 110 stopped-flow assembly,[4] but the slower reactions were followed on a time-drive Radiometer strip-chart recorder synchronized with the oscilloscope. The pH was maintained constant by use of a McIlvaine phosphate–citric acid buffer.[14] All pH determinations were made on a Model 26 Radiometer pH meter using a water-jacketed sample holder thermostated at the reaction temperature. The p$K$ of $\alpha\beta S$-Co(tetren)$(OH_2)^{3+}$ was determined directly by titrating a $2 \times 10^{-3}$ M complex solution with 0.02 M NaOH solution, maintaining a total ionic strength of 0.5 M by NaCl. The first p$K$ for the aquo complex was found to be 6.3 ± 0.1 at 25 °C.

## Results and Discussion

A typical set of data at 20 °C for the decarboxylation reaction is given in Figure 2. The rate data exhibit the same sigmoid pH dependence as was observed in the comparable study of the $Co(NH_3)_5CO_3^+$ ion.[2] Clearly the same type of preprotonation/$CO_2$ release mechanism is operative here, according to the reactions

$$\text{Co(tetren)(CO}_3)^+ + \text{H}^+ \rightleftarrows \text{Co(tetren)(CO}_3\text{H)}^{2+} \quad 1/K_c \tag{1}$$

$$\text{Co(tetren)(CO}_3\text{H)}^{2+} \xrightarrow{\text{r.d.}} \text{Co(tetren)(OH)}^{2+} + \text{CO}_2 \quad k_1 \tag{2}$$

$$\text{Co(tetren)(OH)}^{2+} + \text{H}^+ \rightleftarrows \text{Co(tetren)(OH}_2)^{3+} \quad 1/K_A \tag{3}$$

The corresponding rate equation is

$$k_{\text{obsd}} = k_1[\text{H}^+]/([\text{H}^+] + K_c) \tag{4}$$

which can be plotted in the double-reciprocal linear form to yield a value for $k_1$ at 20 °C as recorded in Table I and a value for p$K_c$ of 6.4. The curve of Figure 2 was constructed by use of these parameters in eq 4. The rate constant values at the other temperatures given in Table I were determined by runs made at pH 1 only, where $k_{\text{obsd}} = k_1$. These data enable determination of the conventional temperature parameters for $k_1$, also given in Table I. The corresponding rate parameters[15] at 25 °C for $Co(NH_3)_5(CO_3)^+$ are $k_1 = 1.10$ s$^{-1}$, $\Delta H_1^\ddagger = 15.8 \pm 0.4$ kcal mol$^{-1}$, and $\Delta S_1^\ddagger = 5.3 \pm 1.3$ cal deg$^{-1}$ mol$^{-1}$. While these are only moderately distinguishable from the values for Co(tetren)$(CO_3)^+$ given in Table I, one notes that the reduction in rate for the pentachelate species by a factor of about 4 is almost entirely due to the reduction in $\Delta S_1^\ddagger$ by about 3 units. A probable explanation is that the degree of solvation of the tetren complex should be somewhat less than that of the $(NH_3)_5$ complex due to the more hydrophobic nature of the multiple methylene groups of the former. An increased ordering of solvent molecules thus must take place in forming the transition state for the tetren than for the $(NH_3)_5$ congener. However, it is obvious that the differences in the decarboxylation chemistry between these two complexes are minor.

**Table I.** Rate Parameters for the Decarboxylation of Co(tetren)$CO_3^+$ and the $CO_2$ Uptake of Co(tetren)$(OH)^{2+}$

| temp, °C | decarboxylation[a] $k_1$, s$^{-1}$ | $CO_2$ uptake[b] $k_2$, M$^{-1}$ s$^{-1}$ |
|---|---|---|
| 15 | 0.12 ± 0.01 | 68 ± 16 |
| 20 | 0.20 ± 0.01 | 115 ± 9 |
| 25 | 0.28 ± 0.03 | 166 ± 15 |
| 30 | 0.51 ± 0.03 | |
| $\Delta H^\ddagger$, kcal mol$^{-1}$ | 15.6 ± 1.9 | 15.4 ± 1.2 |
| $\Delta S^\ddagger$, cal deg$^{-1}$ mol$^{-1}$ | −8.6 ± 4.4 | 3.3 ± 4.1 |

[a] [Complex] = 1 mM; $I = 0.5$ M (NaCl). [b] [Complex] = 1 mM; [carbonate] = 0.05 M; [carbonic anhydrase] = 1 μM; $I = 0.5$ M (NaCl).

**Table II.** Rate of $CO_2$ Uptake by $\alpha\beta S$-Co(tetren)$OH^{2+}$ [a]

| pH | $k_{\text{obsd}}$, s$^{-1}$ | $10^{-2}k_2$, M$^{-1}$ s$^{-1}$ | pH | $k_{\text{obsd}}$, s$^{-1}$ | $10^{-2}k_2$, M$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| | | $T$ = 20 °C | | | |
| 7.34 | 0.26 | 1.06 | 7.84 | 0.09 | 1.06 |
| 7.35 | 0.31 | 1.31 | 7.88 | 0.085 | 1.10 |
| 7.50 | 0.20 | 1.14 | 8.11 | 0.052 | 1.14 |
| 7.55 | 0.18 | 1.38 | 8.11 | 0.056 | 1.23 |
| 7.56 | 0.16 | 1.03 | 8.20 | 0.043 | 1.16 |
| 7.58 | 0.18 | 1.22 | 8.25 | 0.043 | 1.31 |
| 7.59 | 0.16 | 1.10 | 8.30 | 0.034 | 1.16 |
| 7.60 | 0.14 | 0.97 | 8.30 | 0.036 | 1.23 |
| 7.62 | 0.14 | 1.02 | 8.34 | 0.032 | 1.26 |
| 7.65 | 0.14 | 1.09 | 8.38 | 0.031 | 1.28 |
| 7.70 | 0.14 | 1.23 | | | |
| | | $T$ = 15 °C | | | |
| 7.20 | 0.18 | 0.51 | 7.36 | 0.19 | 0.76 |
| 7.30 | 0.17 | 0.59 | 7.67 | 0.11 | 0.86 |
| | | $T$ = 25 °C | | | |
| 7.35 | 0.32 | 1.42 | 7.50 | 0.28 | 1.73 |
| 7.40 | 0.34 | 1.70 | 7.52 | 0.28 | 1.81 |
| 7.50 | 0.27 | 1.66 | | | |

[a] [Carbonate] = 0.05 M; [complex] = $1 \times 10^{-3}$ M; [carbonic anhydrase] = 1 μM; $I = 0.5$ M (NaCl).

Data for the carbon dioxide uptake study are summarized in Table II. These have been analyzed exactly as outlined previously[4] for the "equilibrium method". One utilizes a mechanism consisting of the reverse of reactions 1–3 (with the reverse of reaction 2 having a second-order rate constant $k_2$), plus the additional equilibria

$$\text{CO}_2 + \text{H}_2\text{O} \overset{K_1}{\rightleftarrows} \text{H}^+ + \text{HCO}_3^- \overset{K_2}{\rightleftarrows} \text{H}^+ + \text{CO}_3^{2-} \tag{5}$$

The rate expression derived from this mechanism has been given previously.[4] This takes the form

$$k_{\text{obsd}} = k_1\left(\frac{[\text{H}^+]}{[\text{H}^+] + K_c}\right) + k_2 b\left(\frac{K_A}{[\text{H}^+] + K_A}\right)\left(\frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}\right) \tag{6}$$

where $b$ is the total carbonate concentration and the other constants are as already defined. One way this equation can be used is to calculate $k_2$ directly at the various [H$^+$]'s, using the known values of $k_1$ and the equilibrium constants. Such calculated $k_2$ values are recorded in Table II, and the averages of these with their standard deviations at the three experi-

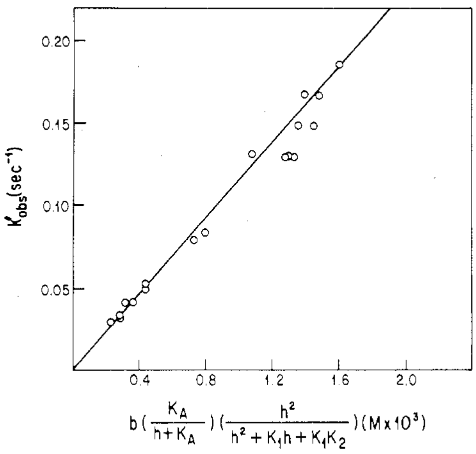

**Figure 3.** Linear plot of rate data for $CO_2$ uptake by $Co(tetren)(OH)^{2+}$ at 20 °C and $I = 0.5$ M (NaCl).

mental temperatures are given in Table I. The alternative procedure, given enough data (as is true at 20 °C), is to plot $k'_{obsd} = k_{obsd} - k_1([H^+]/[H^+] + K_c)$ vs. $b(K_A/[H^+] + K_A)\cdot([H^+]^2/[H^+]^2 + K_1[H^+] + K_1K_2)$, which should yield a straight line through the origin of slope $k_2$. Such a plot is presented in Figure 3, and a least-squares analysis gives an intercept indistinguishable from zero (0.006 ± 0.053) and a slope of $k_2 = 113 \pm 4$ $M^{-1}$ $s^{-1}$. This latter figure is in excellent agreement with the "average" value of $k_2 = 115 \pm 9$ $M^{-1}$ $s^{-1}$ already determined at 20 °C and recorded in Table I, along with the data at the other temperatures and the activation parameters calculated therefrom. One notes that these parameters are barely distinguisable from the corresponding figures[4] for $Co(NH_3)_5OH^{2+}$, for which $k_2 = 220$ $M^{-1}$ $s^{-1}$ at 25 °C, $\Delta H_2^\ddagger = 15.3 \pm 0.9$ kcal mol$^{-1}$, and $\Delta S_2^\ddagger = 3.6 \pm 3.0$ cal deg$^{-1}$ mol$^{-1}$. In fact, most of the diaquotetraamine-cobalt(III) complexes also have rate parameters rather similar to these, with slight differences seemingly related to differences in the $pK_A$ values of the various aquo species.[16] Since the $pK_A$'s for $Co(tetren)(OH_2)^{3+}$ (6.3, as measured above) and for $Co(NH_3)_5(OH_2)^{3+}$ (6.6[4]) differ but little, no significant contrasts in carbon dioxide uptake kinetics are to be expected, as confirmed herewith.

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**Registry No.** $\alpha\beta S$-[Co(tetren)($CO_3$)]$ClO_4$, 67772-78-5; $\alpha\beta S$-Co(tetren)($CO_3$)$^+$, 67738-27-6; $\alpha\beta S$-Co(tetren)($OH_2$)$^{3+}$, 67738-28-7; $\alpha\beta S$-[Co(tetren)(OH)]($ClO_4$)$_2$, 67738-30-1; $H^+$, 12408-02-5.

## References and Notes

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# Oxidation of Hydrazine by Iodine in Aqueous Perchloric Acid

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The oxidation of aqueous hydrazine by iodine solutions is a well-known reaction that has been used as a basis for the iodometric determination of hydrazine.[1] The kinetics have been repeatedly studied with conflicting results, particularly in the [$I^-$] dependence of the rate law: Berthoud and Perrot[2] report an inverse second-order dependence of the rate law on [$I^-$] in chloride media, [$I^-$] = 0.05–0.20 M; in hydrogen sulfate media, Arora et al.,[3] in [$I^-$] = 0.008–0.046 M, Sen Gupta and Sen Gupta,[4] in [$I^-$] = 0.011–0.046 M, and Hasty,[5] in [$I^-$] = 0.02–0.12 M, all report different, complex inverse dependences on [$I^-$]. Hasty's work, while more recent, exhibits large experimental scatter, large uncertainties in his derived rate parameters, and a complex hydrogen ion dependence that is not substantiated by his published data. To resolve these discrepancies we undertook an investigation of this reaction in constant ionic strength, noncomplexing perchlorate media at 25 °C.[6] We report here the conclusions of this study which establish a well-defined rate law.

## Experimental Section

**Reagents.** All solutions were prepared with water redistilled from alkaline permanganate. Sodium perchlorate and sodium iodide were recrystallized from redistilled water, and stock NaI solutions were stored under $N_2$ in brown bottles in the dark. Iodine solutions were prepared by dissolving resublimed $I_2$ in dilute NaI containing a trace of dilute $HClO_4$ to inhibit $I_2$ hydrolysis and were stored similarly. Hydrazinium perchlorate was prepared as described previously.[7] Perchloric acid was doubly distilled, and other reagents were of analytical quality.

**Stoichiometry.** The stoichiometry[1,6] was reconfirmed over the pH range 1.5–9.0 using $HClO_4$ and acetate, phosphate, and borate buffers. The ratio $\Delta[I_2]/\Delta[N_2H_5^+]$ was found to be 2.01 ± 0.02, consistent with eq 1 in the acidic media.

$$2I_2 + N_2H_5^+ \rightarrow N_2 + 4I^- + 5H^+ \qquad (1)$$

**Kinetics.** Runs were performed by flooding with $I^-$, $H^+$, and $N_2H_5^+$, at 25 °C and at $\mu = 0.35$ M, maintained with $NaClO_4$, unless otherwise noted. Kinetic solutions were deoxygenated with a stream of $N_2$ prior to addition of the $I_2$ solution, and kinetics were followed continuously in a thermostated spectrophotometer at λ 467 nm, an isosbestic point of the $I_2$–$I_3^-$ system, at which other species in the mixture are essentially transparent. The ln $(A_t - A_\infty)$ vs. time data were linear over at least 2 half-lives and the pseudo-first-order rate parameters $k_{obsd} = -d \ln (A_t - A_\infty)/dt$ were independent of initial [$I_2$].

## Results and Discussion

The $k_{obsd}$ values were proportional to [$N_2H_5^+$] and inversely proportional to [$H^+$], as shown by the constancy of $k' = {}^1/_2k_{obsd}[H^+]/[N_2H_5^+]$ at [$I^-$] = 0.102 ± 0.001 M. For

0020-1669/78/1317-3306$01.00/0