Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. VIII. Carbon Dioxide Uptake and Intramolecular Carbonato Ligand Chelation in Aqueous Solution of Diaquo-(β,β',β''-triaminotriethylamine)cobalt(III) Perchlorate[1,2]

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Abstract: The reaction of the title compound with dissolved carbon dioxide was studied by stopped-flow spectrophotometry within the acidity range $7 < \mathrm{pH} < 9$ between 15 and 25° and at an ionic strength of 0.5 M (NaCl). Under these conditions the aquo complex ion consists of a pH-dependent mixture of only two species, $R(H_2O)(OH)^{2+}$ and $R(OH)_2^+$ (R symbolizes the specified cobalt(III) tetramine grouping). Each of these ions undergoes CO_2 uptake and subsequent intramolecular carbonato ligand chelation independently at rates which are readily distinguishable and are governed by the uptake rate constants k_1 and k_2 and the chelation rate constants k_3 and k_4, respectively (see scheme in text below). The magnitudes of k_1 and k_2 are 30 and 97 M^{-1} sec^{-1} at 20°, with $\Delta H_1^\ddagger$ and $\Delta H_2^\ddagger$ values of 14.7 ± 0.1 and 32 ± 6 kcal/mol and $\Delta S_1^\ddagger$ and $\Delta S_2^\ddagger$ values of −1.9 ± 0.2 and 53 ± 22 eu, respectively. The constant k_1 and its temperature parameters differ little from those previously reported for CO_2 uptake by hydroxypentaamminecobalt(III)[11] and hydroxotetraethylenepentaminecobalt(III)[13] complexes, where the products are also monodentate carbonato species but which undergo no ring closure process. The ring-closure rate constant for $R(OH)(HCO_3)^+$ is $k_3 = 0.036$ sec^{-1} at 20° with $\Delta H_3^\ddagger = 12.5 \pm 0.5$ kcal/mol and $\Delta S_3^\ddagger = -22.7 \pm 1.6$ eu. Chelation of $R(OH)(CO_3)$ is too slow to be measurable by our technique but an estimate based on earlier studies yields the figure $k_4 = 1.3 \times 10^{-4}$ sec^{-1} at the given temperature. A survey of all other relevant previous investigations has been made, and the available data are discussed in the context of the present work.

There is as yet very limited direct evidence relative to the kinetics of the ring-closure step in the reaction of bifunctional ligands with polyaquo complex ions, since this second step is in general much more rapid than the initial ligand entrance step.[3] Some indirect evidence concerning the kinetics of chelation in the formation of carbonato complexes is afforded by studies of the base hydrolysis of species of the type $CoN_4CO_3^+$, where N_4 represents a tetrafunctional amine ligand (or group of amine ligands of lower functionality). For example, Scheidegger and Schwarzenbach[4,5] were able to deduce approximate values for the rate constants at 20° of ring closure in the species CoN_4OHCO_3, where N_4 is cis en$_2$ or tren (en = ethylenediamine, tren = β,β',β''-triaminotriethylamine). They were also able to place an order of magnitude estimate on the corresponding rate constants for $CoN_4(OH)(HCO_3)^+$. Francis and Jordan,[6] using a different approach, made a more definitive study of the en$_2$ system including some temperature variation data and they essentially confirmed the earlier findings.

In a few instances, where ligand entry is relatively rapid or ring closure relatively slow, the two processes can be kinetically separated. Thus, Lincoln and Stranks[7,8] have obtained data for both types of reaction in their studies of the anation of $Co(en)_2(H_2O)_2^{3+}$ by phosphate. Similarly, studies in our laboratory[9,10] of formation and ring closure of the complex ion $Co(en)_2(OH)C_2O_4$ to produce the chelated final product $Co(en)_2C_2O_4^+$ demonstrate that only the conjugate acid form of the ring-opened species, viz., $Co(en)_2(H_2O)C_2O_4^+$, undergoes chelation at an appreciable rate, a rate which is of the same order of magnitude as for the various monodentate phosphato species.

Our recent investigations[11-13] of carbon dioxide uptake by several types of aquo complexes indicate that these reactions can be very rapid. In the work so far completed, all the aquo complexes are of the type $MN_5H_2O^{3+}$, where M = Co(III),[11] Rh(III),[12] or Ir(III)[12] and $N_5 = (NH_3)_5$, or where M = Co(III) and N_5 = tetraethylenepentamine.[13] In such reactions, there is no subsequent intramolecular chelation step, unlike systems in which a cis NH_3 group becomes part of the chelated product, as in the intramolecular formation of imines at Co(III) centers.[14] With chromium(III) complexes, the situation is quite different. Thus, in the anation of $Cr(NH_3)_5H_2O^{3+}$ by oxalate[15] or nitrate,[16] a cis NH_3 ligand is totally expelled by the chelation step even when the latter step is of transient occurrence[16] only.

In the present work, we have commenced a series of studies of carbon dioxide uptake by various diaquo complex ions of the type $MN_4(H_2O)_2^{3+}$ where N_4 is as defined earlier. In such complexes, chelation of the initially formed aquo carbonato species does occur, and should be much less rapid than the CO_2 uptake process since total ligand water replacement is not involved in the latter reaction.[11] One expects an opportunity to be thus afforded to study the kinetics of each step in sequence. In many species of the N_4 type, cis/trans isomerization contributes an additional complication to the system, so the problem is avoided in this first study by selecting the quadridentate ligand β,β',β''-triaminotriethylamine (tren) for which only the cis diaquo cobalt(III) complex is sterically possible. It turns out that carbon dioxide uptake by this complex is indeed many times more rapid than intramolecular carbonato ligand chelation, enabling a complete investigation of the kinetics and mechanism of each of the two steps separately.

Experimental Section

Preparation of Compounds. β,β',β''-Triaminotriethylamine trihydrochloride (tren·3HCl) was prepared starting from commercially available N-(2-bromoethyl)phthalimide as described earlier.[17] Carbonato(tren)cobalt(III) perchlorate was obtained by following the method of Scheidegger.[5] In this procedure, an ice-cold solution of 9.5 g of $CoCl_2$ in 40 ml of H_2O is added slowly and with constant stirring to a suspension of 19.1 g of PbO_2 in 150 ml of ice-cold aqueous solution containing 10.2 g of tren·3HCl, and 16.8 g of $NaHCO_3$. After mixing is complete, the solution is heated in step-wise manner to 70° (1 hr at 25°, 3 hr at 60°, 30 min at 70°), cooled again to ice-bath temperature, and treated with 46 g of $AgClO_4$. The resultant mixture is filtered and the carbonato

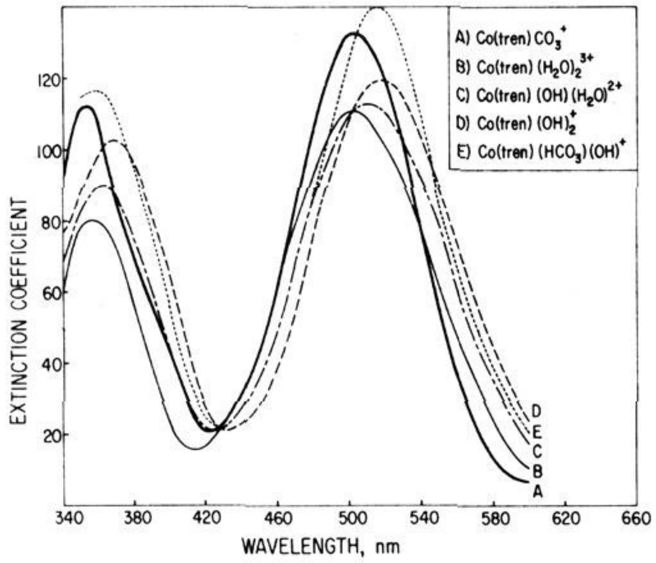


Figure 1. Spectra of the aquo- and carbonato(tren)cobalt(III) complexes relevant to this study.

complex precipitated from the filtrate by addition of 3 volumes of alcohol. The purity of the compound was checked by comparing its visible spectrum with that reported earlier.[5,17]

To prepare diaquo(tren)cobalt(III) perchlorate, 3 ml of 5 *M* perchloric acid was added dropwise to 2 g of solid carbonato(tren)cobalt(III) perchlorate cooled in ice. After complete addition of acid the solution was kept in the ice bath until all effervescence had subsided. The solution was then stored in a vacuum desiccator for 2 days, during which time deep red crystals formed. The crystals were filtered off, washed with ether, and stored in a vacuum desiccator. The purity was checked by microanalysis. Anal. Calcd for $[Co(C_6H_{18}N_4)(H_2O)_2](ClO_4)_3 \cdot H_2O$: C, 12.92; H, 4.34; N, 10.05. Found:[18] C, 13.08; H, 4.19; N, 10.22.

Absorption Spectra. The visible absorption spectra of the various complex species of significance to this work are presented in Figure 1. Those of the carbonato-, diaquo-, aquohydroxo-, and dihydroxo(tren)cobalt(III) complexes were obtained with a Cary Model 15 recording spectrophotometer using a pair of matched 2-cm quartz cells at room temperature. However, the spectrum of the unstable intermediate species, assumed to be hydroxobicarbonatocobalt(III) ion (see Results and Discussion section below), was obtained from the oscillograms of the reaction between solutions of diaquo(tren)cobalt(III) complex and of carbon dioxide, buffered at pH 7.2, by means of the stopped-flow apparatus at various wave lengths in the range 360–600 nm.

Kinetics. The kinetics of carbon dioxide uptake by diaquo(tren)cobalt(III) species were investigated by the acidification method with the Durrum stopped-flow spectrophotometer as described earlier.[11] The reaction was monitored at 503 nm, where the absorbance difference between the aquo and carbonato species is at a maximum. Fortunately, it is also the isosbestic point of the diaquo, aquohydroxo, and dihydroxo species as well as of the carbonato and hydroxobicarbonato species (Figure 1), so that changes in the relative amounts of the aquo species or of the carbonato species have no effect on the absorbance change during reaction. The rate of ring closure of the hydroxocarbonato(tren)cobalt(III) species was followed at 540 nm, utilizing the stopped-flow technique, except that above pH 7.5, where the reactions become quite slow, a Cary 15 spectrophotometer with a time-drive chart recorder could be used.

The ionic strength of the reacting solutions was maintained at 0.5 *M* (NaCl). For pH values less than 8, the pH of the reactant solutions was maintained constant by using a McIlvaine phosphate-citric acid buffer[19] whereas at higher pH boric acid-borax[20] was used. All pH measurements were made either with a Beckman Research Model or a Radiometer Model 26 pH meter. The p*K*'s of $Co(tren)(OH_2)_2^{3+}$ were determined at 15, 20, and 25° by titrating 2×10^{-3} *M* complex solution with 0.02 *M* sodium hydroxide solution, maintaining a total ionic strength of 0.5 *M* by NaCl. The K_1 and K_2 values so obtained are recorded in Table III. The figures at 20° are seen to be in reasonable agreement with earlier measurements made under somewhat different conditions.[5]

Results and Discussion

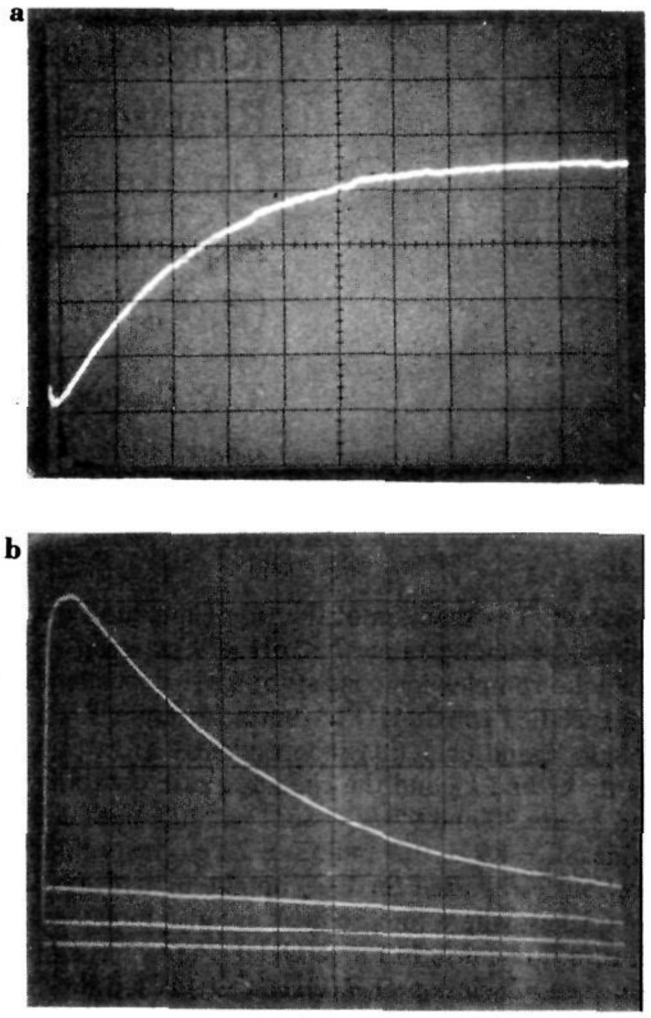


Figure 2. (a) Stopped-flow oscilloscope trace of reaction of diaquo(tren)cobalt(III) complex with carbon dioxide: [complex] = 1.0×10^{-3} *M*; $[CO_2] = 0.01$ *M*; pH 7.45; *t* = 25°; ordinate (proportional to absorbance at 503 nm), 50 mV/division; abscissa, 0.5 sec/division. (b) Conditions same as for Figure 2a except run at 540 nm with time-base of 5.0 sec/division. Sweep repeated several times to determine "infinite time" absorbance.

Preliminary stopped-flow experiments were carried out at 25°, pH 7.5, $I = 0.5$ *M* (NaCl) and $[CO_2] = 0.01$ *M* to establish that the two sucessive reactions could be distinguished kinetically. Our earlier studies[11-13] indicated that CO_2 uptake to form a monodentate carbonato species should have a half-time of the order of magnitude of 0.5 sec under the specified conditions. The first runs were therefore made employing a total oscilloscope sweep time of 5 sec and at 503 nm, the isosbestic point for the various aquo species present ($\epsilon = 111$) and for the two types of carbonato products involved ($\epsilon = 134$) (see Figure 1). As shown in Figure 2a, a cleanly exponential rise in absorbance is observed, with a half-time of about 0.8 sec. Figure 2b illustrates what occurs with total sweep times of 50 sec at 540 nm where the absorbance decrease for disappearance of the unstable intermediate is at a maximum (see Figure 1). It is seen from these experiments that an unequivocal time-scale distinction is possible between the rising absorbance resulting from CO_2 uptake and the fall-off in absorbance as ring closure is completed. The clearly exponential nature of this absorbance decrease is quite obvious on the 50-sec time scale (Figure 2b).

Series of runs were then carried out at several temperatures and over the acidity range $7 < pH < 9$, utilizing the 5-sec time scale at 503 nm and the 50-sec time scale at 540 nm. The data are recorded in Tables I and II in the form of pseudo-first-order rate constants at various pH's and temperatures. The magnitude of k'_{obsd} was obtained from the 5-sec time scale data by means of a least-squares analysis of conventional $\ln |A_\infty - A_t|$ vs. time data, using the observed maximum[21] in absorbance as A_∞, while k''_{obsd} is similarly obtained from the 50-sec time scale data where the final product is solely $Co(tren)CO_3^+$. Interpretation of the results may be accomplished on the basis of the proposed mechanism (R = Co(tren)) shown in (Scheme I). Since the

Table I. Rate Constants for the Carbon Dioxide Uptake by $Co(tren)(H_2O)_2^{3+}$ Ion ($[CO_2]$, 0.01 *M*; *I*, 0.5 *M* (NaCl))

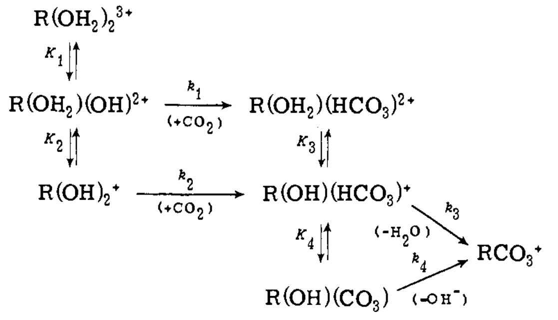
15°		20°		25°	
pH	k'_{obsd}, sec^{-1}	pH	k'_{obsd}, sec^{-1}	pH	k'_{obsd}, sec^{-1}
6.70	0.24	7.04	0.41	6.90	0.54
6.92	0.13	7.08	0.36	7.10	0.59
7.00	0.15	7.10	0.37	7.28	0.66
7.20	0.19	7.19	0.34	7.32	0.74
7.45	0.20	7.19	0.32	7.32	0.76
7.55	0.17	7.28	0.44	7.42	0.64
7.55	0.18	7.40	0.52	7.42	0.77
7.55	0.18	7.40	0.50	7.45	0.85
7.60	0.21	7.48	0.49	7.45[a]	0.88
7.65	0.22[a]	7.48	0.48	8.30	1.15
8.63	0.38	7.65	0.58	8.30	1.19
8.63	0.44	8.14	0.72	8.40	1.25
8.81	0.62	8.14	0.69	8.52	1.22
8.81	0.68	8.40	0.75	8.60	1.31
		8.41	0.70	8.78	1.64
		8.42	0.73	8.78	1.60
		8.52	0.74	9.00	1.74
		8.72	0.86	9.00	1.91
		8.72	0.91	9.00	1.62

[a] "Tris" buffer used instead of phosphate–citrate.

Table II. Rate Constants for the Ring Closure of $Co(tren)(OH)(HCO_3)^+$ (*I*, 0.5 *M* (NaCl))

15°		20°		25°	
pH	$10^2k''_{obsd}$, sec^{-1}	pH	$10^2k''_{obsd}$, sec^{-1}	pH	$10^2k''_{obsd}$, sec^{-1}
7.17	2.3	7.19	3.3	7.35	4.5
7.30	2.4	7.34	3.6	7.52	4.1
7.51	2.2	7.74	3.3	7.64	4.6
7.75	1.6	7.90	3.0	7.78	3.3
8.00	1.9	8.03	3.3	7.85	4.1
8.45	1.4	8.05	2.6	8.15	3.5
8.82	1.1	8.20	1.6	8.55	0.66
		8.50	1.5	8.74	0.89
		9.04	0.54	8.88	0.77

Scheme I



value of pK_1 is close to 5.3 (see Table III), a negligible amount of the diaquo species will be present in the experimental pH range. Similarly, the $R(OH_2)(HCO_3)^{2+}$ species will be instantaneously converted as formed[22] into the $R(OH)(HCO_3)^+$ species,[23] since the value[5] of pK_3 is also about 5.3. For the relatively rapid reactions described by k_1 and k_2, the mechanism requires that

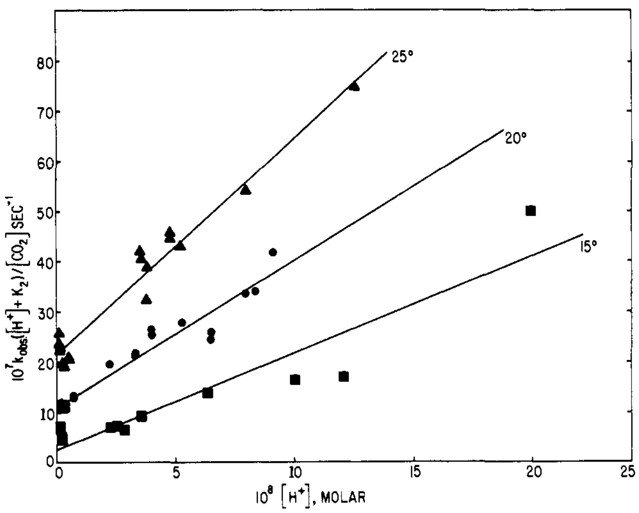


Figure 3. Plot of values of lhs of eq 4 vs. $[H^+]$ at various temperatures. Solid line is least-squares fit to data.

$$-\frac{d}{dt}\{[R(OH_2)(OH)^{2+}] + [R(OH)_2{}^+]\} = \{k_1[R(OH_2)(OH)^{2+}] + k_2[R(OH)_2{}^+]\}[CO_2] \quad (1)$$

Thus

$$-\frac{d}{dt}[\text{total aquo complex}] = \left\{\frac{k_1[H^+] + k_2K_2}{[H^+] + K_2}\right\}[\text{total aquo complex}][CO_2] \quad (2)$$

whence

$$k'_{obsd} = \frac{k_1[H^+] + k_2K_2}{[H^+] + K_2}[CO_2] \quad (3)$$

Since the value of K_2 is known at the various temperatures (see Table III), the data may be analyzed according to a modified form of eq 3, viz

$$k'_{obsd}\frac{\{[H^+] + K_2\}}{[CO_2]} = k_1[H^+] + k_2K_2 \quad (4)$$

Plots are made of the quantity on the lhs of eq 4 vs. $[H^+]$, yielding straight lines of slope k_1 and intercept k_2K_2, as illustrated in Figure 3.

The data for the slower reactions described by k_3 and k_4 can be interpreted in a closely analagous fashion to that indicated by eq 1-4. The proposed mechanism leads to the relation

$$k''_{obsd}\{[H^+] + K_4\} = k_3[H^+] + k_4K_4 \quad (5)$$

Since a reasonable estimate can be made[24] of the magnitude of pK_4, plots can be made of the lhs of eq 5 vs. $[H^+]$ to yield k_3 and k_4K_4. As it turns out, the magnitude of k_4K_4

Table III. Rate Parameters for the Uptake of Carbon Dioxide by Diaquo(tren)cobalt(III) Complex

Temp, °C	k_1 (M^{-1} sec^{-1})	k_2 (M^{-1} sec^{-1})	10^2k_3 (sec^{-1})	$10^{11}k_4K_4$ (sec^{-1})	10^6K_1[a] (*M*)	10^9K_2[a] (*M*)
15	19.3 ± 2.1	28 ± 16	2.47 ± 0.09	(0.2 ± 3.0)	4.0	8.9
20	29.5 ± 1.9	97 ± 8	3.61 ± 0.12	(2.5 ± 3.4)	4.5[b]	11.2[b]
25	43.8 ± 2.2	170 ± 10	4.97 ± 0.20	(−2.9 ± 4.2)	5.0	12.5
	$\Delta H_1^{\ddagger}$ = 14.7 ± 0.1 kcal/mol		$\Delta S_1^{\ddagger}$ = −1.9 ± 0.2 eu			
	$\Delta H_2^{\ddagger}$ = 32 ± 6 kcal/mol		$\Delta S_2^{\ddagger}$ = 53 ± 22 eu			
	$\Delta H_3^{\ddagger}$ = 12.5 ± 0.5 kcal/mol		$\Delta S_3^{\ddagger}$ = −22.7 ± 1.6 eu			

[a] Estimated error approximately ±0.05 p*K* units. [b] Scheiddeger reports[5] values for K_1 and K_2 of 3.8×10^{-6} and 16×10^{-9} *M*, respectively, at 20° and $I = 0.1$ *M* ($NaClO_4$).

Table IV. Rate Parameters for Intramolecular Oxyanion Chelation Reactions of Some Aquoaminecobalt(III) Complexes at 20°

No.	Complex	k (sec^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)	Ref
1	$Co(tren)(OH)(HCO_3)^+$	0.036[a]	12.5 ± 0.5	−22.7 ± 1.6	This work
2	$Co(tren)(OH)(CO_3)$	1.3×10^{-4}			5
3	$Co(en)_2(OH)(HCO_3)^+$	0.13[a,b]	14 ± 2	−16 ± 5	6
4	$Co(en)_2(OH)(CO_3)$	2.5×10^{-5} [c]	28 ± 3	17 ± 9	6
5	$Co(en)_2(OH)(PO_4)^-$	$\leqslant 2 \times 10^{-5}$			7[d]
6	$Co(en)_2(OH)(HPO_4)^+$	8×10^{-4}			7[d]
7	$Co(en)_2(OH_2)(HPO_4)^+$	2×10^{-4}			7[d]
8	$Co(en)_2(OH_2)(C_2O_4)^+$	5×10^{-5}	23.0 ± 0.5	−6.5 ± 1.0	10

[a] Values for this constant were estimated to be between 0.01 and 0.7 sec^{-1} in the earlier study (ref 5). [b] The authors recorded their rate constant in the form kK_W/K, where K_W is the water dissociation constant (1.5×10^{-14}) and K is the acid dissociation constant of the complex ion, for which we have adopted the figure of 1.8×10^{-9} (determined[4] at 20° and $I = 0.1$) in making our estimate of k. Since ΔH for K_W is 13.6 kcal/mol and that for K can be assumed to be rather small, one can estimate the approximate values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ as given above. [c] A value of 6×10^{-5} sec^{-1} was obtained for this constant in the earlier study (ref 5). [d] Measurements made at 22.5°; no values available for $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

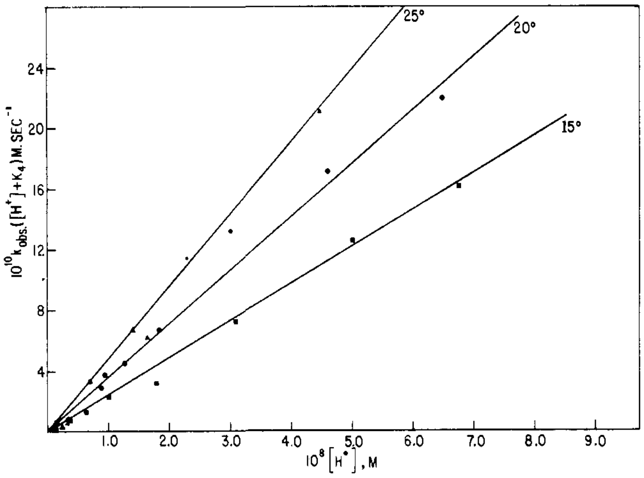
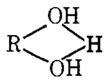


Figure 4. Similar to Figure 5, plotting lhs of eq 5 vs. [H$^+$].

is so small that the intercepts of these plots are indistinguishable from zero (see Table III and Figure 4). The rate parameters obtained in the manner just described are collected together in Table III, together with the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ figures derived by least-squares analysis of the temperature variation of the k's in the usual manner.

The rate constants for CO_2 addition, k_1 and k_2, might be expected on statistical grounds to differ by a constant factor of about 2, since the significant center for CO_2 uptake reactivity is the OH ligand.[11] This expectation is seen to be approximately fulfilled over the temperature range studied, but the divergence in the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values is difficult to explain, since the processes should be mechanistically very similar. However, in the $R(OH_2)(OH)^{2+}$ species, there is the possibility of a shared-proton structure of the type

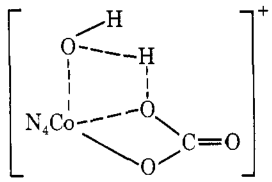


which can have a substantial effect on the nature of the activated complex for CO_2 reaction as compared to its dihydroxo congener. Nevertheless, the k_1 values are quite "normal" in terms of a direct comparison with the rate of CO_2 uptake by CoN_5OH^{2+} complexes. Thus, for $Co(NH_3)_5OH^{2+}$ and Co(tetraethylenepentamine)OH^{2+}, k_1 has values[11,13] at 25° of 220 and 167 M^{-1} sec^{-1}, respectively, only a few times greater than for the tren species. The corresponding $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ values are 15.3 and 15.6 kcal/mol and 3.6 and 4.1 eu, respectively. The latter constants are seen to be very close to the values of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ for $Co(tren)(OH_2)(OH)^{2+}$ (Table III).

In order to facilitate discussion of the second-step reactions, we have collected in Table IV all the currently published data relative to oxyanion chelation rates of a number of aquoaminecobalt(III) complexes. One notes that the ring-closure rate for the $CoN_4(OH)(HCO_3)^+$ type of complex (compounds **1** and **3**) is about two orders of magnitude more rapid than any of the other processes. In the case of the phosphato complexes, all three of which chelate slowly, it has been argued convincingly[8] that the monodentate species are in the trans configuration, so that the ring closure rate is limited by the trans → cis isomerization rate. For the complex $Co(en)_2(H_2O)(OH)^{2+}$, trans → cis isomerization occurs with a rate constant[25] of 4×10^{-3} sec^{-1} at 25°, only a few times greater than the chelation of the protonated phosphato species (compounds **6** and **7**) if allowance is made for the small temperature difference. The conclusion drawn previously[8] concerning the stereochemistry of these two phosphato species is thus supported. One must also conclude that very rapid ring-closures cannot be rate limited by isomerization. This is of course predetermined for the tren species (**1**), since it is permanently in the cis form. For the en$_2$ congener, however, it is obvious that the ring-opened compound (**3**) exists only in the cis form, at least under the conditions adopted by Francis and Jordan[6] in determining the rate constant. On the other hand, the aquooxalato species (**8**), though superficially very similar to the hydroxobicarbonato analog (**3**), is one of the group which is slow to chelate. If it is in the cis form, it may well be that ring formation by the four-atom oxalato grouping is inherently much slower than by the three-atom carbonato species. However, it is also possible that the trans → cis isomerization is rate limiting for compound **8** as it is for the phosphato complexes **6** and **7**, inasmuch as the rate constants are only a small factor apart.

The fully deprotonated hydroxocarbonato or hydroxophosphato complexes (**2**, **4**, and **5**) appear to fall into a different category, since even the tren species (**2**), which is constrained into the cis form, chelates rather slowly. With these compounds, the rate limitation is probably provided by the difficulty of replacing OH (as compared to H_2O) by the oxyanion chelate. This concept is supported by the fact that oxygen exchange between solvent water and the species *cis*-$Co(en)_2(OH)_2^+$ has a rate constant[26] at 20° of about 10^{-5} sec^{-1}, somewhat less rapid than ring closure for compound **2** but very close to the speed of the chelation reactions of **4** and **5**.

The relatively rapid ring-closure rate for the $Co(tren)(OH)(HCO_3)^+$ complex already commented upon is somewhat surprising. Some early oxygen-18 tracer studies[27] of the acid-catalyzed ring opening and decarboxylation of $Co(NH_3)_4CO_3^+$ ion show that the former process involves scission of a Co-O bond while the latter does not. The ring opening probably involves concerted protonation of the chelated carbonato group and insertion of a water molecule to form the highly unstable aquobicarbonato intermediate, according to the mechanism suggested by recent kinetic studies[28] of this type of reaction. While the hydroxobicarbonato tren congener is not entirely identical with the intermediate proposed as a result of acid-catalyzed ring opening, there is sufficient parallelism to visualize the ring-closure transition state for $Co(tren)(OH)(HCO_3)^+$ in the following form:



This requires that there be replacement of the departing OH_2 group by the entering free end of the chelating CO_3 group. This necessitates $Co-OH_2$ bond fission, a process which usually occurs at a considerably slower rate than what is observed here. For example, the highly accelerated solvent water exchange with the ion *cis*-$Co(en)_2(H_2O)(OH)^{2+}$ (as compared to its diaquo or dihydroxo congeners) has a rate constant[26] at 20° of not greater than 10^{-3} sec^{-1}, less than 0.03 as great as the tren carbonato ring-closure process under discussion. It seems likely that the considerable enhancement of the rate of water replacement by the potentially bidentate adjacent carbonato ligand is a result of a large decrease in enthalpy of activation, though the effect may be partially negated by a similarly large decrease in entropy of activation.[29] In the absence of definitive information on the temperature parameters for a more directly comparable water exchange process, further discussion of these factors is inappropriate at this time.

References and Notes

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(21) The final absorbance value A_∞ at 503 nm is constant since the ring-closure reaction involves no absorbance change at this wavelength (see Figure 1).
(22) Only proton transfer is involved in the various acid-base equilibria, all of which are instantaneous as compared to the processes under investigation.
(23) This complex has also been symbolized[5] in the form Co(tren)$(OH_2)(CO_3)$. We prefer the hydroxobicarbonato formulation on the basis of arguments previously given (see, for example, K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, **70**, 171 (1970), footnote 268).
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Reactivity of Coordinated Nitrosyls. V. Generation and Characterization of a Ruthenium(II) Alkylnitroso Complex[1,2]

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Abstract: The radiolysis of $Ru(NH_3)_5NO^{3+}$ in aqueous *tert*-butyl alcohol solution generates the species $[Ru(NH_3)_5\{(N-O)CH_2C(CH_3)_2OH\}]^{2+}$ which can be formally viewed as a Ru(II) alkylnitroso complex with a C-N bond. The complex has been isolated as the tetraphenylborate salt and has been characterized by elemental microanalysis, ion exchange chromatography, and uv-visible, ir, and nmr spectroscopy. The product can be envisioned as resulting from the attack of the carbon-radical derived from the reaction of OH radicals with *tert*-butyl alcohol, $\cdot CH_2C(CH_3)_2OH$, with $Ru(NH_3)_5NO^{2+}$ generated by the reaction of H atoms and e_{aq}^- with the Ru(III) substrate. This stable, air-insensitive radical adduct can also be formulated as a Ru(III) nitroxide complex (valence tautomer).

The multielectron reduction of coordinated nitrosyls results in a variety of products including free or coordinated NH_2OH[3] and NH_4^+[4] and coordinated nitrides.[5] Fast kinetics stopped-flow studies of the reaction of $Ru(NH_3)_5NO^{3+}$ with Cr^{2+} in aqueous solution indicate the presence of at least four successive transient intermediates[6] in the course of the formation of $Ru(NH_3)_6^{3+}$ and these transient species have been observed using cyclic voltammetry