

the ion pair, obtained estimates of the rate of Co(III)-Me<sub>2</sub>SO bond fission in the transition states formed from the free and from the ion-paired complex ion, concluded that the presence of Br<sup>-</sup> had only a small effect, at most, on the rate of bond fission, and observed that anation occurs more frequently than

solvent exchange as a result of this bond fission. Since the rate of solvent exchange is relatively small for the ion pair, so is the rate of internal return.

Registry No. Co(NH<sub>3</sub>)<sub>5</sub>(Me<sub>2</sub>SO)<sup>3+</sup>, 44915-85-7; Br<sup>-</sup>, 24959-67-9.

Contribution from the Department of Chemistry,  
State University of New York at Buffalo, Buffalo, New York 14214

## Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes.

### 17. Carbon Dioxide Uptake by and Decarboxylation of the *cis*-Bis(ethylenediamine)rhodium(III) System in Aqueous Solution<sup>1</sup>

D. A. PALMER,<sup>2</sup> R. VAN ELDIK,<sup>3</sup> H. KELM,<sup>2</sup> and G. M. HARRIS\*

Received October 17, 1979

In acidic solution *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>)<sup>+</sup> slowly loses carbonate in accordance with the two-term rate law  $k_{\text{obsd}} = k_0 + k_1[\text{H}^+]$ , for which the rate parameters are as follows:  $k_0 = 9.33 \times 10^{-6} \text{ s}^{-1}$  at 25 °C,  $\Delta H^*_0 = 22.8 \pm 1.5 \text{ kcal mol}^{-1}$ ,  $\Delta S^*_0 = -5 \pm 5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ;  $k_1 = 1.00 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C,  $\Delta H^*_1 = 25.0 \pm 3.6 \text{ kcal mol}^{-1}$ ,  $\Delta S^*_1 = 2 \pm 11 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . The decarboxylation of the intermediate species *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>H)(OH<sub>2</sub>)<sup>2+</sup> could be independently studied:  $k = 0.72 \pm 0.02 \text{ s}^{-1}$  at 25 °C,  $\Delta H^* = 19.4 \pm 0.3 \text{ kcal mol}^{-1}$ ,  $\Delta S^* = 5.8 \pm 0.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . Carbon dioxide uptake by *cis*-Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)<sup>2+</sup> yielded *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>)(OH<sub>2</sub>)<sup>+</sup> with  $k = 69 \pm 18 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C,  $\Delta H^* = 15.9 \pm 0.5 \text{ kcal mol}^{-1}$ , and  $\Delta S^* = 3.9 \pm 1.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . At higher pH the corresponding dihydroxo complex gave exclusively *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>)(OH), with the rate parameters  $k = 215 \pm 29 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C,  $\Delta H^* = 14.6 \pm 0.2 \text{ kcal mol}^{-1}$ , and  $\Delta S^* = 1.1 \pm 0.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . These results are compared with existing rate data on analogous cobalt(III) systems, with emphasis being placed on the relative metal-ligand bond strengths.

#### Introduction

The kinetics of carbon dioxide uptake and release by a wide variety of cobalt(III) complexes have been studied<sup>4-6</sup> in considerable detail, and the mechanism of reaction now seems to be well understood. All this kinetic evidence indicates that CO<sub>2</sub> can only add to a hydroxo ligand and, conversely, carbon-oxygen bond breaking takes place in the decarboxylation of the bicarbonato complex. Furthermore, a linear free energy relationship exists<sup>6</sup> between the rates of CO<sub>2</sub> uptake and the dissociation constants of the corresponding conjugate aquo acids, which establishes that the nucleophilicity of the hydroxide bound to the cobalt(III) center determines the rate of CO<sub>2</sub> uptake.

The rates of ring opening of the chelated carbonate ligand have also been thoroughly investigated<sup>7-9</sup> and shown to obey a two-term rate expression,  $k_{\text{obsd}} = k_0 + k_1[\text{H}^+]$ , where the latter term involves a rapid protonation preequilibrium followed by the rate-determining cleavage of the cobalt-oxygen bond to form a monodentate bicarbonato intermediate.<sup>9</sup>

Limited kinetic data are available for other transition-metal complexes, namely, for the (carbonato)pentaammine com-

plexes of rhodium(III) and iridium(III)<sup>10</sup> and for the ring-closed species *cis*-(carbonato)bis(oxalato)chromate(III) ion.<sup>11</sup> Nevertheless, these results generally do comply with the accepted behavioral patterns of the cobalt(III) compounds.

We now report a complete kinetic study of the (carbonato)bis(ethylenediamine)rhodium(III) system. One reason for initiating this research was that the known strength of rhodium-oxygen bonds should allow us to observe the monodentate (carbonato)aquo complex as a relatively stable species because ring closure requires the breaking of the Rh-OH<sub>2</sub> bond and must therefore be an extremely slow process. Consequently, at high pH, the possibility arises that two CO<sub>2</sub> molecules may be independently taken up by the *cis*-Rh(en)<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> ion. In addition, in the absence of intense light,<sup>12</sup> no detectable isomerization of the *cis* isomer occurs, eliminating a complicating factor which prevails in the analogous cobalt(III) system.<sup>13</sup> Finally, it is of interest to see whether the increased strength of the metal-oxygen bond plays a role in determining the nucleophilicity of the hydroxo ligand, as was proposed for the Rh(NH<sub>3</sub>)<sub>5</sub>OH<sup>2+</sup> complex.<sup>10</sup>

#### Experimental Section

**Preparation of Compounds.** *cis*-Dichlorobis(ethylenediamine)rhodium(III) perchlorate was prepared by the method of Johnson and Basolo<sup>14</sup> for the corresponding nitrate salt. Using excess base during the refluxing period and reducing the final volume of solution to 25% of its original volume resulted in yields of 30% or more of the *cis* isomer. It should be noted that it is essential that the solution be maintained at its boiling point during the addition of the aliquots of NaOH

- (1) Preceding paper in this series: Inoue, T.; Harris, G. M. *Inorg. Chem.*, in press.
- (2) Institute for Physical Chemistry, University of Frankfurt, 6 Frankfurt am Main 1, West Germany.
- (3) Department of Chemistry, Potchefstroom University, Potchefstroom 2520, South Africa.
- (4) Chaffee, E.; Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4169.
- (5) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1975**, *97*, 1733.
- (6) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 2490.
- (7) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1971**, *93*, 91.
- (8) van Eldik, R.; Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* **1975**, *14*, 2573.
- (9) Harris, G. M.; Hyde, K. E. *Inorg. Chem.* **1978**, *17*, 1892.

- (10) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965.
- (11) Palmer, D. A.; Dasgupta, T. P.; Kelm, H. *Inorg. Chem.* **1978**, *17*, 1173.
- (12) Muir, M. M.; Huang, W. L. *Inorg. Chem.* **1973**, *12*, 1831.
- (13) Wan, W. K.; DeJovine, J. M.; Harris, G. M., to be submitted for publication.
- (14) Johnson, S. A.; Basolo, F. *Inorg. Chem.* **1962**, *1*, 925.

Table I. The Respective  $pK_3$  and  $pK_5$  Values for the Acid Dissociation of  $cis\text{-Rh(en)}_2(\text{OH})_2^{3+}$  and  $cis\text{-Rh(en)}_2(\text{OH})(\text{OH}_2)^{2+}$

ionic strength, M	$pK_3$	$pK_5$	ref
0.5	6.09	8.08	this work
0.01	5.82	7.98	this work
0.02	5.85	7.95	15

solution; otherwise more  $trans\text{-[Rh(en)}_2\text{Cl}_2]\text{ClO}_4$  is formed at the expense of the  $cis$  form. The absorption spectrum ( $\lambda_{\text{max}}$  ( $\epsilon$ ) 352 nm (198), 295 nm (192)) is in good agreement with the reported values.<sup>15-19</sup>

$cis\text{-Hydroxoquoobis(ethylenediamine)rhodium(III) perchlorate}$  was prepared by adding 2.07 g of  $cis\text{-[Rh(en)}_2\text{Cl}_2]\text{ClO}_4$  (5.5 mmol) to a solution containing 0.3 g of LiOH in ca. 60 cm<sup>3</sup> of water which was then heated to 70 °C and maintained at this temperature for 1 h with continuous stirring. The solution was then cooled in ice,<sup>20</sup> and 2.5 g of AgClO<sub>4</sub> was added (theoretically 2.27 g would be sufficient for complete precipitation of the free Cl<sup>-</sup>). After the AgCl was filtered off, the pH of the filtrate was raised to ca. 12 by the addition of LiOH, whereupon the excess silver precipitated in the form of Ag<sub>2</sub>O. The pH of the filtered solution was lowered to ca. 1 by using 70% HClO<sub>4</sub> and the volume reduced on a hot plate to 8–10 cm<sup>3</sup>. After cooling of the solution in ice, solid LiOH was slowly added to the well-stirred solution until a pH of 7 was reached, during which time a pale yellow precipitate formed. The filtered crystals were washed with a large volume of ethanol followed by ether and finally dried at 60 °C for 1 h. The complex was recrystallized by dissolving it in a minimum amount of a warm (40 °C) solution of LiOH and repeating the procedure outlined above. The yield was 1.36 g, or 57%. Anal. Calcd for  $cis\text{-[Rh(en)}_2(\text{OH})(\text{OH}_2)](\text{ClO}_4)_2$ : C, 10.5; N, 12.3; H, 4.2; Cl, 15.5. Found: C, 10.5; N, 12.1; H, 4.3; Cl, 15.3. This method is similar to that described by Pavelich<sup>21</sup> for the synthesis of the less soluble  $trans\text{-[Rh(en)}_2(\text{OH})(\text{OH}_2)](\text{ClO}_4)_2$ .

The visible/UV absorption spectra of the respective diaquo, hydroxoquo, and dihydroxo species show the following maxima: 318 (174), 271 (148); 323 (199), 283 (155 sh); 329 (184), 280 nm (179 M<sup>-1</sup> cm<sup>-1</sup>). The only spectral data available in the literature<sup>15,16,22</sup> refer to the products in solution of base hydrolysis reactions of the  $cis$ -dihalogeno parent compound. However, the reported maxima are in reasonable agreement with those of the dihydroxo complex recorded here. In addition, the product of the acid-catalyzed aquation of  $\text{Rh(en)}_2\text{C}_2\text{O}_4^+$  was reported<sup>17</sup> to exhibit an extinction coefficient of 123 M<sup>-1</sup> cm<sup>-1</sup> at 340 nm, which is in excellent agreement with our value for  $cis\text{-Rh(en)}_2(\text{OH})_2^{3+}$  of 122 M<sup>-1</sup> cm<sup>-1</sup> at this wavelength.

$cis\text{-Aquo(carbonato)bis(ethylenediamine)rhodium(III) cation}$  was prepared by dissolving 0.5 g of  $cis\text{-[Rh(en)}_2(\text{OH})(\text{OH}_2)](\text{ClO}_4)_2$  in ca. 20 cm<sup>3</sup> of 0.1 M HClO<sub>4</sub> and adding sufficient solid Li<sub>2</sub>CO<sub>3</sub> to bring the pH up to 7. Attempts to isolate this compound in the solid state invariably yielded a product contaminated with various amounts of the ring-closed carbonato complex. A single peak in the absorption spectrum was found at 332 nm (224 M<sup>-1</sup> cm<sup>-1</sup>).

$cis\text{-Carbonato}bis(ethylenediamine)rhodium(III) perchlorate$  was prepared by refluxing a solution of  $cis\text{-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)^+$ , prepared in the above manner, for 1 h. During this time the pH was monitored approximately every 10 min and readjusted to 7 if necessary. After cooling of the solution in ice, 10% HClO<sub>4</sub> was added dropwise until the pH  $\approx$  3. The dropwise addition of ethanol eventually resulted in the formation of a fine, cream-colored precipitate which was then filtered off, washed with ethanol and ether, and dried at 60 °C for 1 h. Anal. Calcd for  $cis\text{-[Rh(en)}_2\text{CO}_3]\text{ClO}_4$ : C, 15.7; N, 14.6; H, 4.2. Found: C, 15.3; N, 14.6; H, 4.7. The absorption spectrum showed

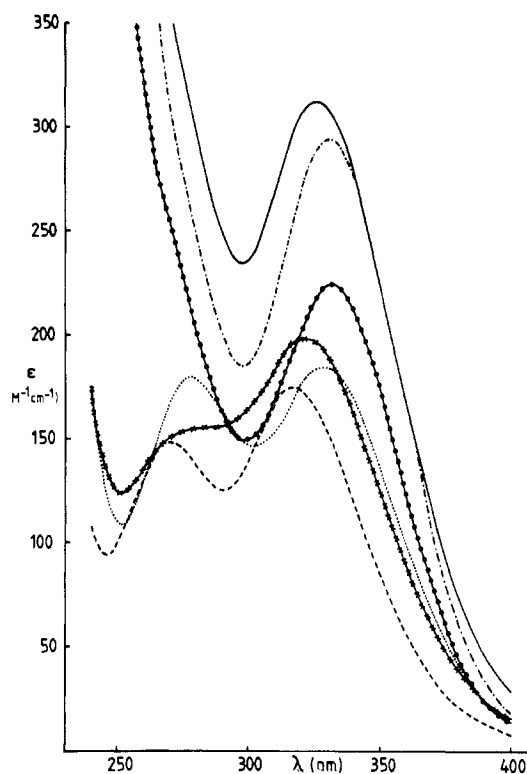


Figure 1. UV/visible absorption spectra of the complexes relevant to this research: —,  $cis\text{-Rh(en)}_2\text{CO}_3^+$ ; -●-●-,  $cis\text{-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)^+$ ; - - - -,  $cis\text{-Rh(en)}_2(\text{CO}_3)(\text{OH})$ ; - - - - -,  $cis\text{-Rh(en)}_2(\text{OH})_2^{3+}$ ; -x-x-x-,  $cis\text{-Rh(en)}_2(\text{OH})(\text{OH}_2)^{2+}$ ; ···,  $cis\text{-Rh(en)}_2(\text{OH})_2^+$ .

a peak at 327 nm (312 M<sup>-1</sup> cm<sup>-1</sup>).

All other chemicals used were of reagent grade. The UV/visible absorption spectra were obtained by using a Cary 118 recording spectrophotometer. The spectra of the various complexes of significance to this research are presented in Figure 1.

**Determination of Acid-Dissociation Constants.** The  $pK$  values for the acid dissociation of  $cis\text{-Rh(en)}_2(\text{OH})_2^{3+}$  were obtained at 25 °C by titration using a Beckman Research Model pH meter. A  $2 \times 10^{-3}$  M complex solution was titrated against a 0.1 M NaOH solution. The  $pK$ 's at virtually zero ionic strength and in 0.5 M NaClO<sub>4</sub> solution are given in Table I together with the only available literature values. The agreement between the corresponding values at low ionic strength is very satisfactory.

The acid dissociation constant of the  $cis\text{-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)^+$  ion was determined spectrophotometrically at 330 nm where this species has an extinction coefficient of 221 M<sup>-1</sup> cm<sup>-1</sup>, while the deprotonated form has a value of 300 M<sup>-1</sup> cm<sup>-1</sup>. As the accuracy of the spectrophotometric technique is generally quite poor, no attempt was made to maintain constant ionic strength or to thermostat the solutions. Under these conditions a value of  $8.45 \pm 0.16$  for the  $pK$  was obtained.

**Rate Measurements.** The kinetics of decarboxylation and CO<sub>2</sub> uptake were followed by using a Durrum Model 110 stopped-flow spectrophotometer. The techniques utilized in conducting such experiments have been adequately described elsewhere.<sup>1,4,6</sup> The kinetics of these reactions were always studied under pseudo-first-order conditions. The observed first-order rate constants recorded here represent the mean value of at least six kinetic runs. A wide range of buffer systems were used to cover the entire range of pH values: phosphate/citrate, 2.2–6.2; phosphate/NaOH, 5.8–7.2; Tris-base/HCl, 7.0–9.0; boric acid/NaOH, 8.6–10.2.

The rates of ring opening of the chelated carbonate in  $\text{Rh(en)}_2\text{CO}_3^+$  were determined on a Cary Model 118 spectrophotometer fitted with a thermostated cell compartment containing 2-cm quartz cells.

In all cases, the kinetics were followed at 330 nm, while the ionic strength was maintained at 0.5 M by the addition of appropriate amounts of NaClO<sub>4</sub>.

## Results and Discussion

The mechanism for the decarboxylation reactions of a series of (carbonato)pentaamminecobalt(III), -rhodium(III), and

(15) Klabunde, U. Ph.D. Dissertation, Northwestern University, 1967.

(16) Poë, A.; Vuik, C. *J. Chem. Soc., Dalton Trans.* **1976**, 661.

(17) Rowan, N. S.; Milburn, R. M.; Dasgupta, T. P. *Inorg. Chem.* **1976**, *15*, 1477.

(18) Jakse, F. P.; Paukstelis, J. V.; Petersen, J. D. *Inorg. Chim. Acta* **1978**, *27*, 225.

(19) Ogino, H.; Bailar, J. C., Jr. *Inorg. Chem.* **1978**, *17*, 1118.

(20) If the original dichloro complex contained some of the  $trans$  isomer, cooling of the solution in ice at this point will result in the complete precipitation of  $trans\text{-[Rh(en)}_2\text{Cl}_2]\text{ClO}_4$ .

(21) Pavelich, M. J. *Inorg. Chem.* **1975**, *14*, 982.

(22) Gillard, R. D.; Tipping, L. R. H. *J. Chem. Soc., Dalton Trans.* **1977**, 1241.

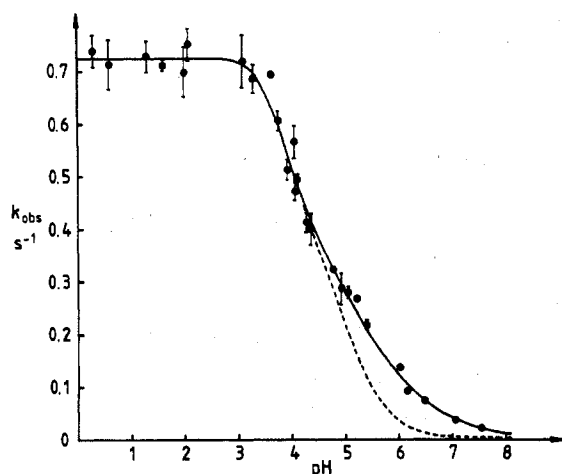


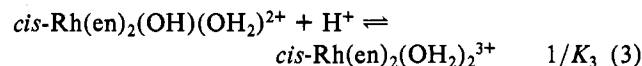
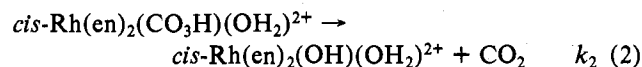
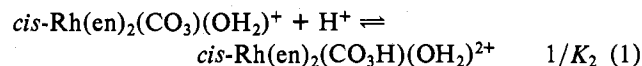
Figure 2. Plot of  $k_{\text{obsd}}$  vs. pH for the acid-catalyzed aquation of  $\text{cis-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)^+$  at 25 °C and  $\mu = 0.5 \text{ M}$ . The dashed curve represents the theoretical results for complete aquation.

Table II. Pseudo-First-Order Rate Constants for the Acid Hydrolysis of  $\text{cis-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)^+$  ( $[\text{Complex}] = 10^{-3} \text{ M}$ ;  $\mu = 0.5 \text{ M}$ ; 25 °C)

pH	$k_{\text{obsd}}^{a,b}$ $\text{s}^{-1}$	pH	$k_{\text{obsd}}^{a,c}$ $\text{s}^{-1}$	pH	$k_{\text{obsd}}^{a,d}$ $\text{s}^{-1}$
0.30	0.737	3.92	0.513 <sup>b</sup>	5.40	0.218
0.60	0.713	4.06	0.566 <sup>b</sup>	6.02	0.138
1.30	0.728	4.07	0.472 <sup>b</sup>	6.15	0.093
1.60	0.711	4.11	0.491 <sup>b</sup>	6.25	0.133 <sup>b</sup>
2.00	0.699	4.29	0.413	6.48	0.072
2.04	0.751	4.30	0.409 <sup>b</sup>	7.05	0.037
3.09	0.719	4.37	0.400	7.53	0.021
3.28	0.686	4.72	0.324	0.30	0.411 <sup>b,c</sup>
3.43	0.754	4.90	0.287	0.30	0.234 <sup>b,d</sup>
3.63	0.696	5.05	0.281 <sup>b</sup>	0.30	0.121 <sup>b,e</sup>
3.77	0.606	5.22	0.269		

<sup>a</sup> Average error in  $k_{\text{obsd}}$  is 3.9%. <sup>b</sup> No carbonic anhydrase added. <sup>c</sup> 20 °C. <sup>d</sup> 15.5 °C. <sup>e</sup> 9.9 °C.

-iridium(III) complexes, as well as numerous other monodentate complexes of cobalt(III), has been well established,<sup>1,4,10</sup> such that the following set of reactions can be assumed to be operative in the present system, namely:



Indeed, the plot of  $k_{\text{obsd}}$  vs. pH illustrated in Figure 2 conforms to this concept of a limiting rate-determining loss of  $\text{CO}_2$  and shows the typical falloff at higher pH. It should be noted that identical  $k_{\text{obsd}}$  values were obtained by using either a solution of  $\text{cis-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)\text{ClO}_4$  (contaminated with the chelated carbonato complex which is kinetically stable within the reaction times encountered here, as will be shown later in the text) in water at  $\text{pH} \approx 7$  in one syringe of the stopped-flow or a solution of  $\text{cis-Rh(en)}_2(\text{OH})(\text{OH}_2)(\text{ClO}_4)_2$  with an equivalent amount of  $\text{NaHCO}_3$ , adjusted to a final pH of 7.

The rate equation for the decarboxylation process which is compatible with eq 1–3 is as follows

$$k_{\text{obsd}} = k_2[\text{H}^+]/([\text{H}^+] + K_2) \quad (4)$$

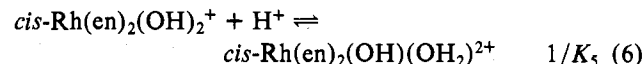
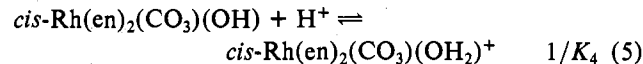
and can be rearranged to the form where a plot of  $1/k_{\text{obsd}}$  vs.  $1/[\text{H}^+]$  should be linear, with a slope of  $K_2/k_2$  and an intercept of  $1/k_2$ . Treating the pseudo-first-order rate constants given

in Table II in this manner results in an initial straight line up to a pH of 4.94. The cause of the curvature at higher pH can be traced to the advent of the reverse reaction— $\text{CO}_2$  uptake by  $\text{cis-Rh(en)}_2(\text{OH})(\text{OH}_2)^{2+}$ , as will be demonstrated later in the discussion—under these conditions, despite the fact that carbonic anhydrase was added to the initial complex solution to ensure that the liberated  $\text{CO}_2$  rapidly hydrolyses. However, it must be remembered that the  $\text{p}K$  for the hydrolysis of  $\text{CO}_2$  is 6.06,<sup>4</sup> thereby ensuring that the bulk of the “free carbonate” is present as  $\text{CO}_2$  at pH 5. Thus, in those cases where carbonic anhydrase was not present (see Table II) the  $k_{\text{obsd}}$  values are only slightly larger than the rest. Nevertheless, the linearity of the plot at lower pH values provides for reasonably accurate values of  $k_2$  and  $K_2$  of  $0.68 \pm 0.02 \text{ s}^{-1}$  and  $(2.0 \pm 0.2) \times 10^{-3} \text{ M}$ , respectively. The former compares favorably with the limiting value of  $k_{\text{obsd}}$ , viz.,  $0.72 \pm 0.02 \text{ s}^{-1}$ . The dashed line in Figure 2 represents the theoretical curve obtained by substituting the above values for  $k_2$  and  $K_2$  in eq 4 and clearly shows that decarboxylation does not go to completion above a pH of ca. 5. This point will be brought forward later in the paper.

From the temperature dependence of  $k_{\text{obsd}}$  at 0.5 M  $\text{HClO}_4$  (see Table II), the following activation parameters for  $k_2$  were obtained:  $\Delta H^\ddagger_2 = 19.4 \pm 0.3 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger_2 = 5.8 \pm 0.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . These values are compatible with the general range of values found for the various analogous cobalt(III) reactions,<sup>13</sup> as well as those of the pentaammine complexes of  $\text{Co(III)}$ ,<sup>4</sup>  $\text{Rh(III)}$ ,<sup>10</sup> and  $\text{Ir(III)}$ ;<sup>10</sup> i.e.,  $\Delta H^\ddagger_2 = 14\text{--}19 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger_2 = -6$  to  $+6 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . Although these energy differences are appreciable, the rate constants only vary by a factor of 7.5 at 25 °C indicating that the trends in  $\Delta H^\ddagger_2$  and  $\Delta S^\ddagger_2$  more or less cancel out. Thus it can be concluded that changes in bond energies result in compensating changes in solvation, particularly in hydrogen bonding of the solvent to the carbonate ligand.<sup>1</sup> However, the overriding point is that only C–O bond breakage is involved in all of these reactions.

One surprising aspect of this reaction is the low  $\text{p}K_2$  value of 4.70. Although it may be attributed to hydrogen bond interaction between the cis oriented aquo and carbonate ligands, no enhancement of the acidity of the cis isomer relative to the trans isomer, or the cis-diaquo analogue, was observed for the corresponding cobalt(III) complex.<sup>13</sup>

At higher pH, where the rate of decarboxylation tends to zero (naturally, in strongly basic solution base hydrolysis of the carbonate group becomes important<sup>10</sup>), two additional protonation equilibria must be taken into account:



In previous publications,<sup>1,6,7,11,23–26</sup>  $K_2$  and  $K_4$  were assumed to relate to the deprotonation of the two bicarbonate species implying the existence of  $\text{cis-Rh(en)}_2(\text{CO}_3\text{H})(\text{OH})^+$  as a nonreactive entity rather than  $\text{cis-Rh(en)}_2(\text{CO}_3)(\text{OH}_2)^+$ . Although these two possibilities are kinetically indistinguishable, we now tend to prefer the equilibria in the form given above. On the basis of the considerable amount of kinetic data available on decarboxylation reactions,<sup>1,4,6,7,10,11,13,23–26</sup> it is apparent that once a monodentate carbonate ligand is protonated, carbon dioxide is then liberated at a rate which is virtually independent of the nature of the metal center and

(23) Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* 1974, 13, 1275.

(24) Dasgupta, T. P. *Inorg. Chim. Acta* 1976, 20, 33.

(25) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* 1969, 91, 3207.

(26) Hyde, K. E.; Fairchild, G. H.; Harris, G. M. *Inorg. Chem.* 1976, 15, 2631.

**Table III.** Observed Pseudo-First-Order Rate Constants for Carbon Dioxide Uptake Reactions of *cis*-Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)<sup>2+</sup> and *cis*-Rh(en)<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> ([Complex] = 10<sup>-3</sup> M; [CO<sub>2</sub>] = 10<sup>-2</sup> M, μ = 0.5 M; 25 °C)

run no.	pH	k <sub>obsd</sub> , s <sup>-1</sup>	run no.	pH	k <sub>obsd</sub> , s <sup>-1</sup>
1	5.45	0.348	18	8.32	1.22
2	5.76	0.336	19	8.40	1.25
3	5.82	0.340	20	8.52	1.89
4	5.88	0.338	21	8.55	1.38
5	6.13	0.353	22	8.65	1.69
6	6.31	0.343	23	8.67	1.51
7	6.31	0.344	24	8.80	1.61
8	6.53	0.435	25	8.91	2.07
9	6.66	0.379	26	8.96	1.69
10	6.81	0.650	27	9.11	2.18
11	7.06	0.906	28	9.13	2.00
12	7.17	0.643	29	9.14	2.55
13	7.33	1.01	30	9.24	2.48
14	7.53	1.30	31	9.31	2.28
15	7.62	1.55	32	9.40	3.57
16	7.94	1.34	33	9.49	3.64
17	8.26	1.32	34	9.90	5.49

the surrounding ligands. Therefore, it seems unlikely that a  $-(\text{CO}_3\text{H})(\text{OH})^+$  species would not also be equally reactive, even though it may be suggested that intramolecular hydrogen bonding between these two ligands could reduce the lability of the bicarbonato ligand. This point will be discussed further in a forthcoming publication.<sup>27</sup> Moreover, the similarity between the respective values of pK<sub>4</sub> and pK<sub>5</sub> (8.45 and 7.98) tends to add further support to the idea that both processes involve the deprotonation of an aquo ligand, especially when the difference in charge is taken into account.

Due to the relatively poor solubility of *cis*-[Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> in solutions containing NaClO<sub>4</sub>, the rates of CO<sub>2</sub> uptake were determined by using the "pH-jump method";<sup>6</sup> i.e., one syringe of the stopped-flow spectrophotometer contained a solution of the complex in 0.02 M CO<sub>2</sub> (pH ~ 3.5) while the other contained the appropriate amount of NaClO<sub>4</sub> dissolved in a solution of the buffer. The resulting observed pseudo-first-order rate constants are shown in Table III as a function of pH. It is immediately apparent that significant CO<sub>2</sub> uptake occurs at pH 5.45, although, as will be shown later in the text, the reaction does not proceed to completion. Nevertheless, this confirms the suggested explanation that the curvature of the double reciprocal plot of the acid hydrolysis data at pH > 5 results from an equilibration of the system, even in the presence of carbonic anhydrase.

From a knowledge of the values of pK<sub>3</sub> and pK<sub>5</sub> it can be assumed that within the pH range 5.45–7.17 the only kinetically significant complex species present in solution is *cis*-Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)<sup>2+</sup>. Thus the reverse reaction in eq 2 represents the rate-determining step (*k*<sub>2</sub>) for CO<sub>2</sub> uptake in this pH region leading, in turn, to the rate expression

$$k_{\text{obsd}} = k_{-2}K_3[\text{CO}_2]/([\text{H}^+] + K_3) + k_2[\text{H}^+]/([\text{H}^+] + K_2) \quad (7)$$

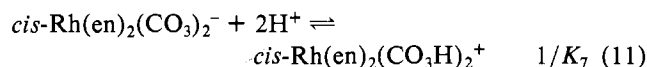
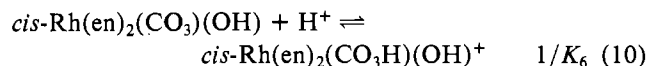
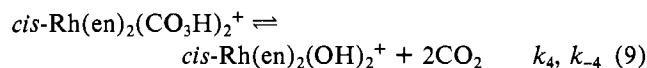
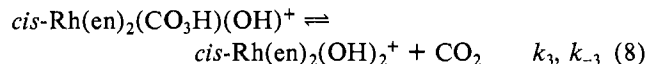
By use of the values given above for *k*<sub>2</sub> and *K*<sub>2</sub> and the measured value of *K*<sub>3</sub> at μ = 0.5 M in Table I, *k*<sub>-2</sub> may be determined for each set of *k*<sub>obsd</sub>/pH data. The mean value of *k*<sub>-2</sub> for runs 3–12 is 69 ± 18 M<sup>-1</sup> s<sup>-1</sup>. For runs 1 and 2, *k*<sub>-2</sub> values of 125 and 87, respectively, were obtained indicating that the value of *K*<sub>2</sub> may be underestimated. However, under these conditions, the change in absorbance is rather small due to the unfavorable equilibrium, such that these values are less reliable. At pHs greater than 7.2 "*k*<sub>-2</sub>" increases, undoubtedly due to the appearance of the dihydroxo species which is significantly more reactive. Although the deviations in *k*<sub>-2</sub> are

**Table IV.** Rate Constants for Carbon Dioxide Uptake by *cis*-Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)<sup>2+</sup> ([Complex] = 10<sup>-3</sup> M; [CO<sub>2</sub>] = 10<sup>-2</sup> M; μ = 0.5 M)

temp, °C	k <sub>obsd</sub> , s <sup>-1</sup>	k <sub>-2</sub> , M <sup>-1</sup> s <sup>-1</sup>
7.1	0.148 ± 0.005	15.9
10.2	0.197 ± 0.003	21.3
15.3	0.309 ± 0.003	33.4
19.9	0.488 ± 0.001	52.8
25.0	0.829 ± 0.009	89.5
29.6	1.35 ± 0.07	146.

quite large, for a given buffer solution the reproducibility is vastly improved (ca. ±2%), and reliable activation parameters can be obtained. The temperature dependence of *k*<sub>obsd</sub>, shown in Table IV, was determined at pH 7.17 because the contribution of the reverse reaction is minimal and [H<sup>+</sup>] is relatively small compared to *K*<sub>3</sub>, thus providing optimal conditions for estimating *k*<sub>-2</sub>. The resulting activation parameters, Δ*H*<sup>‡</sup><sub>-2</sub> = 15.9 ± 0.5 kcal mol<sup>-1</sup> and Δ*S*<sup>‡</sup><sub>-2</sub> = 3.9 ± 1.6 cal deg<sup>-1</sup> mol<sup>-1</sup>, are virtually identical with those of a number of hydroxo-aquocobalt(III) complexes, suggesting a common mechanism for CO<sub>2</sub> uptake in which the nature of either the metal center or the inert ligands plays only a secondary role in dictating the rate of reaction. However, it is perhaps surprising that *k*<sub>-2</sub> is significantly slower than the rate of the corresponding reaction involving Rh(NH<sub>3</sub>)<sub>5</sub>OH<sup>2+</sup> (69 and 490 M<sup>-1</sup> s<sup>-1</sup>, respectively), especially as the latter is less basic.<sup>6</sup>

In the higher pH region (8.0–9.2), the following series of equations must be considered together with eq 6:



It is important to note that within the time scale of these reactions, as well as those at lower pH, no detectable ring closure by the monodentate carbonate ligand was observed. Furthermore, the oscilloscope traces showed that decarboxylation was significantly slower than CO<sub>2</sub> uptake for runs 3–31 so as not to interfere with the kinetics of the latter. Presumably, the subsequent loss of CO<sub>2</sub> by the complex is a consequence of the slow hydrolysis of the free CO<sub>2</sub>, and its rate is determined by the latter, which is itself a function of pH.

Assuming, for the moment, that reaction 9 is not operative under the prevailing experimental conditions, the following rate equation can be derived for eq 6 and 8:

$$k_{\text{obsd}} = k_{-3}K_5[\text{CO}_2]/([\text{H}^+] + K_5) + k_3[\text{H}^+]/([\text{H}^+] + K_6) \quad (12)$$

which under the experimental conditions (pH range) concerned reduces to *k*<sub>obsd</sub> = *k*<sub>-3</sub>*K*<sub>5</sub>[CO<sub>2</sub>]/([H<sup>+</sup>] + *K*<sub>5</sub>). If the reaction is indeed second order in CO<sub>2</sub>, *k*<sub>-3</sub> must be replaced by *k*<sub>-4</sub>[CO<sub>2</sub>]. Application of eq 12 to the raw data in runs 17–29 in Table III results in a mean value for *k*<sub>-3</sub> of 215 ± 29 M<sup>-1</sup> s<sup>-1</sup>. In order to determine the exact molecularity of this reaction, we varied [CO<sub>2</sub>] over the range 0.004–0.02 M, while the complex concentration was maintained at 3 × 10<sup>-4</sup> M. These results are presented in Table V. With the exception of the value obtained at [CO<sub>2</sub>] = 0.004 M, the second-order rate constants, *k*<sub>-3</sub>, are very consistent, with a mean value of 52.6 ± 2.3 M<sup>-1</sup> s<sup>-1</sup> at 9 °C, thereby establishing the reaction to be first order in [CO<sub>2</sub>], or, in other words, eq 9 and 11 need not be considered here. At the lowest [CO<sub>2</sub>], the change in

(27) van Eldik, R.; Palmer, D. A.; Harris, G. M., to be submitted for publication.

Table V. The Dependence of the Rate Constant for Carbon Dioxide Uptake by *cis*-Rh(en)<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> on Carbon Dioxide Concentration ([Complex] = 3 × 10<sup>-4</sup> M; 9.0 °C; μ = 0.5 M)

[CO <sub>2</sub> ], M	pH	k <sub>obsd</sub> , s <sup>-1</sup>	k <sub>-3</sub> , <sup>a</sup> M <sup>-1</sup> s <sup>-1</sup>
0.004	9.04	0.209 ± 0.018	57.9
0.008	9.00	0.359 ± 0.019	50.3
0.010	8.86	0.431 ± 0.021	50.2
0.012	8.97	0.591 ± 0.004	52.9
0.016	8.95	0.747 ± 0.036	55.6
0.020	8.89	0.930 ± 0.012	53.8

<sup>a</sup> Calculated according to eq 12.

Table VI. Rate Constants for Carbon Dioxide Uptake by *cis*-Rh(en)<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> ([CO<sub>2</sub>] = 10<sup>-2</sup> M; [Complex] = 10<sup>-3</sup> M; pH 8.86; μ = 0.5 M)

temp, °C	k <sub>obsd</sub> , s <sup>-1</sup>	k <sub>-3</sub> , M <sup>-1</sup> s <sup>-1</sup>
9.0	0.431 ± 0.021	50.2
14.2	0.685 ± 0.009	79.8
19.0	1.06 ± 0.03	124
25.0	1.76 ± 0.07	205
30.0	2.81 ± 0.05	327

absorbance was considerably smaller than in the other experiments. This suggests that the [CO<sub>2</sub>] of 0.004 M is not sufficient to force the reaction to go to completion, which accounts for the significantly higher value of "k<sub>-3</sub>"; i.e., k<sub>obsd</sub> = k<sub>3</sub> + k<sub>-3</sub>[CO<sub>2</sub>].

The temperature dependence of k<sub>-3</sub> was studied at a pH of 8.86 and at [CO<sub>2</sub>] = 0.01 M. The results are given in Table VI. The activation parameters are as follows: ΔH<sup>‡</sup><sub>-3</sub> = 14.6 ± 0.2 kcal mol<sup>-1</sup> and ΔS<sup>‡</sup><sub>-3</sub> = 1.1 ± 0.7 cal deg<sup>-1</sup> mol<sup>-1</sup>. These parameters are virtually identical with corresponding values for the analogous reaction with *cis*-Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)<sup>2+</sup>. The ratio k<sub>-3</sub>/k<sub>-2</sub> is ca. 4, whereas the statistical factor is only 2. However, the similarity in the activation parameters does not allow one to draw any definite conclusions as to the significance of the larger factor involved.

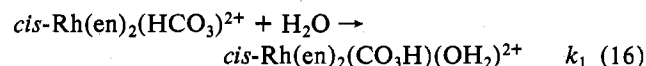
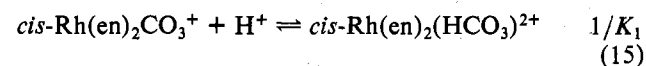
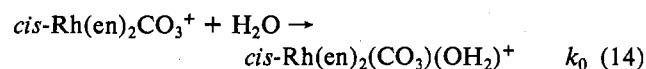
A final comment on this reaction concerns the CO<sub>2</sub> uptake data at pH > 9.2, i.e., runs 32–34. Here the absorbance increase becomes progressively smaller, while the secondary step—a decrease in absorbance—becomes faster such that no real "infinity value" for the CO<sub>2</sub> uptake reactions is obtained. Thus the apparent k<sub>-3</sub> values become increasingly larger. This effect may be traced to the rapid rate of base hydrolysis of CO<sub>2</sub> which competes with the CO<sub>2</sub> uptake by the dihydroxo complex.

The observed pseudo-first-order rate constants for the hydrolysis of *cis*-Rh(en)<sub>2</sub>CO<sub>3</sub><sup>+</sup> in acidic solution are listed in Table VII. This results can be adequately described by the two-term rate equation

$$k_{\text{obsd}} = k_0 + \bar{k}_1[\text{H}^+] \quad (13)$$

The temperature dependence of k<sub>obsd</sub> yields the following activation parameters: ΔH<sup>‡</sup><sub>0</sub> = 22.8 ± 1.5 kcal mol<sup>-1</sup>; ΔS<sup>‡</sup><sub>0</sub> = -5 ± 5 cal deg<sup>-1</sup> mol<sup>-1</sup>; ΔH<sup>‡</sup><sub>1</sub> = 25.0 ± 3.6 kcal mol<sup>-1</sup>; ΔS<sup>‡</sup><sub>1</sub> = 2 ± 11 cal deg<sup>-1</sup> mol<sup>-1</sup>, respectively.

The recently established mechanism<sup>9,26</sup> for ring opening is illustrated by the equations



whereby the protonated complex in eq 15 remains six-coordinate. As the linear rate equation (13) holds for the data in

Table VII. Rate Constants for the Acid-Catalyzed Aquation of *cis*-Rh(en)<sub>2</sub>CO<sub>3</sub><sup>+</sup> ([Complex] = 10<sup>-3</sup>; μ = 0.5 M)

temp, °C	[H <sup>+</sup> ], M	10 <sup>4</sup> k <sub>obsd</sub> , s <sup>-1</sup>	10 <sup>4</sup> k <sub>0</sub> , s <sup>-1</sup>	10 <sup>4</sup> k <sub>1</sub> , M <sup>-1</sup> s <sup>-1</sup>
49.0	0.50	3.18	1.65 ± 0.06	3.1 ± 0.2
	0.40	2.96		
	0.25	2.35		
54.5	0.10	2.04	3.8 ± 0.5	4.7 ± 1.6
	0.05	1.77		
	0.50	6.36		
	0.40	4.92		
	0.25	5.52		
60.0	0.10	4.44	5.6 ± 0.3	6.4 ± 1.0
	0.05	3.61		
	0.50	8.95		
	0.40	7.99		
	0.25	6.94		
65.0	0.10	6.83	11.3 ± 2.0	17.7 ± 6.6
	0.05	5.65		
	0.50	18.8		
	0.40	18.2		
	0.25	19.4		
70.3	0.10	13.2	16.2 ± 2.4	36.3 ± 7.8
	0.05	10.2		
	0.50	31.4		
	0.40	34.1		
	0.25	25.9		
	0.10	21.1		
	0.05	15.9		

Table VII, one must conclude K<sub>1</sub> is a large quantity, with the bulk of the total carbonato complex being in the deprotonated form within the [H<sup>+</sup>] range studied. This is in keeping with earlier findings.<sup>26</sup>

The extremely slow rate of ring opening found for both reaction paths is due to the fact that Rh–O bond breaking is now involved. Thus, a value of 9.33 × 10<sup>-6</sup> s<sup>-1</sup> for k<sub>0</sub> (extrapolated to 25 °C from the data in Table VII) is similar in magnitude to rate constants found for the hydrolysis of other oxygen bound ligands, e.g., NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, as well as for the water exchange of Rh(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>3+</sup>.<sup>28</sup> The resistance of *cis*-Rh(en)<sub>2</sub>CO<sub>3</sub><sup>+</sup> to acid catalysis, compared to most analogous cobalt(III) complexes,<sup>23</sup> can be assigned<sup>9,26</sup> to a higher value expected for K<sub>1</sub> which is also the consequence of stronger Rh–O bonding. In keeping with this assignment, ΔH<sup>‡</sup><sub>1</sub> is considerably larger than the corresponding values generally reported for similar cationic cobalt(III) complexes, viz., 10–18 kcal mol<sup>-1</sup>.<sup>23,24</sup> The ΔS<sup>‡</sup><sub>1</sub> values for these cobalt(III) reactions are usually negative but vary significantly in magnitude.<sup>23,24</sup> The resulting variations in k<sub>1</sub> have been ascribed to the effects of the different charges on the cobalt(III) substrates and their related solvation changes, as well as to the degree of steric hindrance imposed on the carbonate ligand by the "inert" ligand/s.<sup>23,24</sup>

**Acknowledgment.** The authors gratefully acknowledge financial support from the John D. and Frances H. Larkin Foundation of the State University of New York at Buffalo. R.v.E. wishes to thank Potchefstroom University for an extended sabbatical leave and the S.A. Council for Scientific and Industrial Research for support. D.A.P. and H.K. acknowledge financial support from the Fonds der Chemischen Industrie.

**Registry No.** *cis*-[Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>, 72709-24-1; *cis*-[Rh(en)<sub>2</sub>CO<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, 72709-23-0; *cis*-Rh(en)<sub>2</sub>(OH<sub>2</sub>)(CO<sub>3</sub>)<sup>+</sup>, 72709-22-9; *cis*-Rh(en)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup>, 41188-56-1; *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>)(OH), 72709-21-8; *cis*-Rh(en)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, 72748-20-0; CO<sub>2</sub>, 124-38-9; *cis*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 67047-30-7; *cis*-Rh(en)<sub>2</sub>(OH)(OH<sub>2</sub>)<sup>2+</sup>, 53368-50-6; *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>)<sup>+</sup>, 72709-20-7; *cis*-Rh(en)<sub>2</sub>(CO<sub>3</sub>H)(OH<sub>2</sub>)<sup>2+</sup>, 72709-19-4.