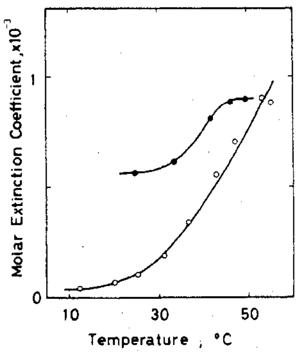

Figure 6. Thermochromism of cupric bromide (○) in 0.20 M CTABr/0.56 M water/chloroform reversed micelles as monitored at 470 nm and of cupric chloride (●) in 0.20 M CTACl/0.83 M water/chloroform reversed micelles as monitored at 408 nm.

halogens in solutions containing water. The amount of water present in the overall system was always sufficient enough to hydrate the copper(II) ion. Nevertheless, in the range where the concentration ratio of water to detergent is relatively small, solubilized water is predominantly interacting with detergents even if other polar solutes are cosolubilized in the system.[4,7] The specific phenomenon is explained in terms of "the two-step hydration mechanism" in the reversed micellar system.[4,7] In addition, the copper(II) halides are encapsulated into a very small polar domain surrounded by bulk nonpolar phase, which causes the increase in the local concentration of the complex.

Masui et al. were the first to investigate the behavior of paramagnetic metal complexes in reversed micelles by means of EPR spectroscopy.[29] In their work the cupric chloride/dodecylpyridinium chloride/chloroform system was adopted. However, the EPR spectrum of copper(II) determined at a relatively low water concentration (the actual concentration was not given) is different from ours. Considering that the electronic spectra of their system showed an absorption band at 406 nm, very close to ours (408 nm), chloride ion must be the most probable ligand also in their system. Therefore, the EPR spectral difference between their and our systems should be interpreted in terms of the microscopic viscosity in the micellar core, which governs the ease of molecular motion of the complex cosolubilized therein.

Acknowledgment. The authors are indebted to Kao Soap Co. for a supply of the starting materials needed for the synthesis of surfactants.

Registry No. $CuCl_2$, 7447-39-4; $CuBr_2$, 7789-45-9.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 18. Carbon Dioxide Uptake by and Decarboxylation of the *trans*-Bis(ethylenediamine)rhodium(III) System in Aqueous Solution[1]

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The new (carbonato)bis(ethylenediamine) complexes of rhodium(III) *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ and *trans*-$Na[Rh(en)_2(OCO_2)_2]$ have been prepared, the former in the pure solid state and the latter in solution containing excess carbonate. The rate parameters for acid-catalyzed decarboxylation of the *trans*-aquocarbonato species are $k_1 = 2.92 \pm 0.08$ s^{-1} at 25 °C. $\Delta H_1^{\ddagger} = 10.9 \pm 0.1$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -19.6 \pm 0.4$ cal deg^{-1} mol^{-1}. The *trans*-dicarbonato analogue undergoes complete decarboxylation at pH ≤ 6 in a one-step process to produce the expected equilibrium mixture of *trans*-diaquo and *trans*-aquohydroxo species, with $k_5 = 2.26 \pm 0.05$ s^{-1} at 25 °C, $\Delta H_5^{\ddagger} = 16.3 \pm 0.2$ kcal mol^{-1}, and $\Delta S_5^{\ddagger} = -2.1 \pm 0.8$ cal deg^{-1} mol^{-1}. At higher pH (>6.5), only one of the carbonato groups is eliminated to produce a mixture of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *trans*-$Rh(en)_2(OCO_2)(OH)$, with $k_3 = 1.3 \pm 0.1$ s^{-1} at 25 °C, the only temperature at which this constant was determined. Carbon dioxide uptake by *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ and *trans*-$Rh(en)_2(OCO_2)(OH)$ yield *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *trans*-$Rh(en)_2(OCO_2)_2^-$, respectively, with second-order rate constants at 25 °C of $k_2 = 81 \pm 3$ and $k_4 = 330 \pm 80$ M^{-1} s^{-1} and the activation parameters $\Delta H_2^{\ddagger} = 12.9 \pm 0.9$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -5.5 \pm 3.1$ cal deg^{-1} mol^{-1} and $\Delta H_4^{\ddagger} = 15.4 \pm 0.7$ kcal mol^{-1} and $\Delta S_4^{\ddagger} = 4.6 \pm 2.4$ cal deg^{-1} mol^{-1}. An unusual aspect of this study is the finding that CO_2 uptake by *trans*-$Rh(en)_2(OH)_2^+$ is a third-order process which yields the dicarbonato species *trans*-$Rh(en)_2(OCO_2)_2^-$ in a single step, with $k_6 = (1.4 \pm 0.2) \times 10^4$ M^{-2} s^{-1}, $\Delta H_6^{\ddagger} = 16.3 \pm 0.9$ kcal mol^{-1}, and $\Delta S_6^{\ddagger} = +16.4 \pm 3.0$ cal deg^{-1} mol^{-1}. These and the other results of this investigation are compared and discussed in relation to previous findings for analogous Co(III) and Rh(III) systems.

Introduction

In the preceding paper in this series[1] we reported on the carbon dioxide uptake by and decarboxylation of the analogous *cis*-bis(ethylenediamine)rhodium(III) system in aqueous solution. Two new carbonato complexes were reported, viz., the bidentate carbonate species *cis*-$Rh(en)_2(CO_3)^+$ and the monodentate species *cis*-$Rh(en)_2(OCO_2)(OH_2)^+$. Acid-catalyzed decarboxylation of the ring-closed species, which necessitates metal–oxygen bond breaking, is very slow due to the strength of the Rh–O bond in this complex. On the other hand, the *cis*-$Rh(en)_2(OCO_2)(OH_2)^+$ species undergoes rapid decarboxylation for which the kinetic parameters are very

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[1] Part 17: Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 1009.

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similar to those reported earlier for closely related monodentate carbonato complexes.[4-7] CO_2 uptake by *cis*-$Rh(en)_2(OH)(OH_2)^{2+}$ and *cis*-$Rh(en)_2(OH)_2^+$ results in the formation of *cis*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *cis*-$Rh(en)_2(OCO_2)(OH)$, respectively, of which only the former can undergo a slow ring-closure reaction. No evidence for the formation of dicarbonato species could be found.

As a follow-up to this investigation[1] we now report the results of a similar study on the *trans*-bis(ethylenediamine)rhodium(III) system. These complexes are known to be stereochemically inert so that no ring closure of a *trans*-aquocarbonato complex can occur. We were particularly interested to see if it were possible to form a doubly monodentate *trans*-dicarbonato complex. This type of carbonato complex has not been prepared before, although Wan[8] reported some indirect kinetic evidence for the formation of a *trans*-bis(carbonato)bis(ethylenediamine)cobalt(III) complex.

Experimental Section

Preparation of Compounds. *trans*-$[Rh(en)_2Cl_2]NO_3$ was prepared by following the method of Johnson and Basolo.[9] Addition of concentrated $HClO_4$ to a warm concentrated solution of the nitrate salt resulted in the precipitation of *trans*-$[Rh(en)_2Cl_2]ClO_4$. The latter complex was converted to *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$ according to a modified version of the methods described in the literature.[10,11] In our procedure a warm concentrated solution of 3 g of *trans*-$[Rh(en)_2Cl_2]ClO_4$ is treated with 15.5 mL of 1 M NaOH (slightly more than 1:2 ratio) and refluxed for 15 min. The solution is then cooled to room temperature, and the pH is adjusted to 5.8 by the slow addition of (1:1) $HClO_4$. The pH is monitored on a pH meter, since this is a critical value (see Results and Discussion). At this point the desired complex crystallizes, and the yield is approximately 80%. The product is recrystallized by dissolving it in warm 0.01 M NaOH, heating it to boiling, cooling it, and isolating it in the manner outlined above at pH 5.8. The crystals are washed with alcohol and ether and dried in a desiccator under vacuum. Microanal.[12] Calcd for *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$: C, 10.5; H, 4.2; N, 12.3. Found: C, 10.4; H, 3.9; N, 12.5.

trans-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ was prepared by dissolving *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$ in a minimum amount of 0.01 M $HClO_4$ and slowly adding $NaHCO_3$ under constant stirring. At pH ~4 the desired product started to precipitate from the reaction mixture, and the addition of $NaHCO_3$ was continued until a pH of 5.8 was reached. More product precipitated on cooling of the solution. The mixture was then filtered, washed with alcohol and ether, and dried in a desiccator under vacuum. Anal. Calcd for *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$: C, 15.0; H, 4.5; N, 14.0. Found: C, 15.7; H, 4.8; N, 13.3.

trans-$Rh(en)_2(OCO_2)_2^-$ was prepared in solution by dissolving *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$ in dilute NaOH, adjusting the pH to approximately 9, and adding an excess of $NaHCO_3/Na_2CO_3$. The formation of the product was followed spectrophotometrically, and the addition of $NaHCO_3/Na_2CO_3$ (at pH ~9) was continued until no further spectral changes could be observed. The final spectrum differs significantly from that for either *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ or *trans*-$[Rh(en)_2(OCO_2)(OH)]$ (see Table I) and can reasonably be ascribed to the formation of the dicarbonato species under these conditions. The slow evaporation of this solution produced a yellow-white solid which was contaminated with $NaHCO_3/Na_2CO_3$. The spectrum of this impure solid was obtained in slightly basic medium (pH ~9). A spectrum of the *trans*-diaquo species resulting from acidification of a sample of the same solid was also obtained. With use of the known extinction coefficients for the latter complex (Table I), it was determined that the spectrum of $Na[Rh(en)_2(OCO_2)_2]$ obtained from a solution of the solid sample was in exact agreement with that found above for the synthetic mixture in solution.

Table I. UV-Visible Absorption Spectra of Some *trans*-Bis(ethylenediamine)rhodium(III) Complexes

complex species	λ_{max}, nm	ϵ, M^{-1}/cm^{-1}	ref
trans-$Rh(en)_2Cl_2^+$	406, 286	75, 130	9
	406, 286	84, 130	16
	407, 286	75, 125	17
	407, 287	82.5, 126.4	10
	406, 289	79.4, 123	18
	410, 289	82, 121	19, 20
	406, 286	82, 134	21
	407, 287	82.5, 120	this work
trans-$Rh(en)_2(OH_2)_2^{3+}$	342, 272	66, 125	16
	342, 262	64, 148	11
	351, 274	61.6, 130	10
	350, 274	60, 130	this work[a]
trans-$Rh(en)_2(OH)(OH_2)^{2+}$	337, 270	88, 158	11
	343, 282	89, 154	this work
trans-$Rh(en)_2(OH)_2^+$	338, 290	136, 136	16
	336, 289	94, 154	11
	346, 297	98, 130	19
	344, 296	99, 134	this work[b]
trans-$Rh(en)_2(OCO_2)(OH_2)^+$	345	101	this work
trans-$Rh(en)_2(OCO_2)(OH)$	346	121	this work[c]
trans-$Rh(en)_2(OCO_2)_2^-$	347	146	this work[d]

[a] Prepared in solution by dissolving *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$ in 0.01 M $HClO_4$. [b] Prepared in solution by dissolving *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$ in 0.01 M NaOH. [c] Prepared in solution by dissolving *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ in 0.01 M NaOH. [d] Prepared in solution. See Experimental Section.

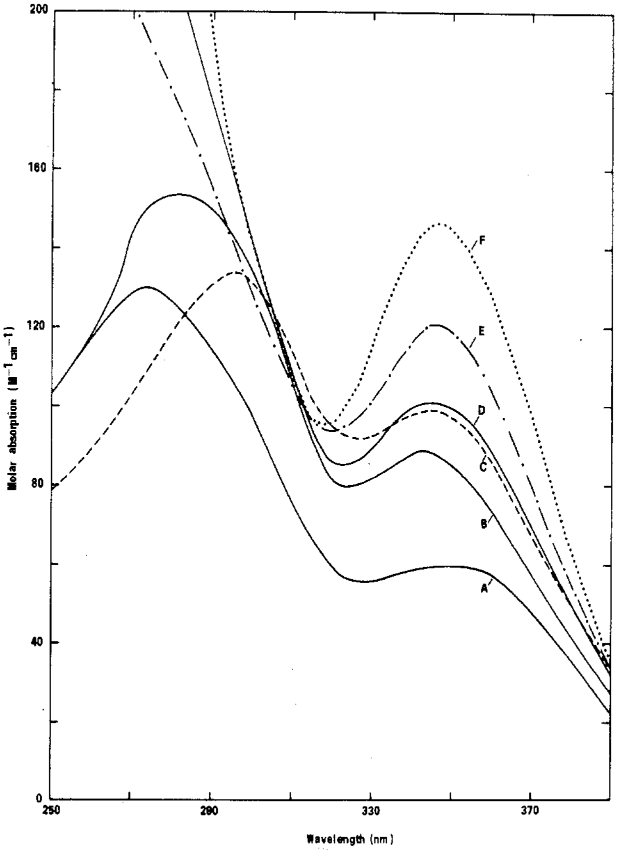

Figure 1. UV-visible absorption spectra of some Rh(III) complexes: A, *trans*-$Rh(en)_2(OH_2)_2^{3+}$; B, *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$; C, *trans*-$Rh(en)_2(OH)_2^+$; D, *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$; E, *trans*-$Rh(en)_2(OCO_2)(OH)$; F, *trans*-$Rh(en)_2(OCO_2)_2^-$.

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Table II. Acid Dissociation Constants of Some *trans*-Bis(ethylenediamine)rhodium(III) Complexes

complex species	temp, °C	ionic strength, M	pK	ref
trans-$Rh(en)_2(OH_2)_2{}^{3+}$ (K_1)	26.4	1.0	4.37	10
	~20	0.2	4.43	11
	25	0.5	4.33	this work
trans-$Rh(en)_2(OH)(OH_2)^{2+}$ (K_2)	26.4	1.0	7.63	10
	~20	0.2	7.81	11
	25	0.5	7.72	this work
trans-$Rh(en)_2(OCO_2)(OH_2)^+$ (K_4)	25	0.5	7.40	this work

A series of ion-exchange experiments were performed in an effort to find supporting evidence for the formation of the dicarbonato species in solution. Complications arise due to the presence of a large excess of free carbonate/bicarbonate ions in such synthetic mixtures. Studies with an anion-exchange resin in the carbonate form clearly illustrated the partial presence of a negatively charged complex species in solution, which supports the above evidence and the kinetic conclusions reported later on.

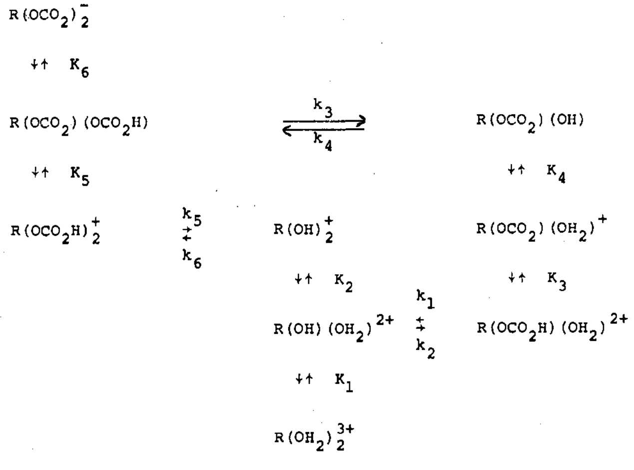
All chemicals used in the syntheses were of reagent grade. Deionized and degassed water was used in preparing all solutions. Absorption spectra in the UV-visible region were measured by using a Cary 118 spectrophotometer, and data for the various species of interest are summarized in Table I and Figure 1.

Determination of the Acid Dissociation Constants. The pK values for the acid dissociation of *trans*-$Rh(en)_2(OH_2)_2{}^{3+}$ and *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ were determined at 25 °C and an ionic strength of 0.5 M ($NaClO_4$) by titrating a 2×10^{-3} M complex solution with 0.1 M NaOH. These and all other pH measurements were made with a Beckman Research Model pH meter and a reference electrode filled with saturated NaCl solution by using a water-jacketed sample holder thermostated at the desired temperature. The pK's of the various species are summarized and compared with literature values in Table II.

Rate Measurements. The decarboxylation and CO_2 uptake reactions were studied at an ionic strength of 0.5 M ($NaClO_4$) and over the acidity and temperature ranges shown in the Results and Discussion. The "acidification method", described in detail elsewhere,[13] was employed during the CO_2 uptake studies. The reactions were monitored at various wavelengths, where the difference in absorbance between reactant and product is at a maximum (see Figure 1). The rate measurements were made on a Durrum Model 110 stopped-flow assembly. For pH ≥2 various buffer systems were used: McIlvaine phosphate-citric acid,[14] phosphate-NaOH,[15] boric acid-NaOH,[15] sodium borate-NaOH,[15] and Tris-HCl,[15,22] depending on the pH range concerned. The observed pseudo-first-order rate constants were calculated in the usual way by using a least-squares program and are reported as the mean of at least six kinetic runs.

Decarboxylation rate studies at pH >6.5 showed deviations in the first-order plots at longer reaction times, an effect which became more pronounced with increasing pH. This apparent deviation can be explained[5] in terms of the formation of CO_2 for which the rate of hydration becomes rate limiting at higher pH. As a consequence the CO_2 uptake reaction becomes significant, and a pseudoequilibrium is reached which slowly decays to the true thermodynamic equilibrium at a rate controlled by the hydration of CO_2. Addition of micromolar concentrations of the CO_2 hydration catalyst carbonic anhydrase[5] to the reaction solution corrected the observed deviations.

Scheme I



(R ≡ trans Rh(en)$_2$)

Results and Discussion

The *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$ complex was prepared at pH 5.8 since this is the most favorable value according to the pK values in Table II. Similarly, the complex *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ was prepared under conditions where mainly *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ exists in solution. The preparation of the carbonato complexes was based on the general principle that a hydroxo species can take up CO_2, without M–O bond cleavage.[13,23] This is in keeping with the inability of an aquo ligand to take up CO_2.[5,13,24] The spectra of the carbonato complexes (Figure 1) show a single absorption maximum near 350 nm and an increasing absorption at lower wavelength, which is typical for monodentate carbonato complexes.[5,13] The pK values of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ (Table II) are very similar, indicating that the carbonato and hydroxo ligands influence the acidity of the trans aquo ligand in a similar way.

A comparison of the spectral data in Figure 1 with that previously reported[1] for the *cis*-bis(ethylenediamine)rhodium(III) system indicates that no trans to cis isomerization nor any ring-closure reactions occur in the present system. It is obvious that the *trans*-carbonatoaquo and -dicarbonato complexes are isomerically stable under the various present experimental conditions.

On the basis of our earlier experience with such systems, the suggested overall reaction mechanism is given in Scheme I. For simplicity, the hydrogen ions participating in the acid-base equilibria are omitted from the scheme, and K_1 to K_6 are considered to be *acid dissociation* constants. The rate constants k_1, k_3, and k_5 refer to decarboxylation reactions, while CO_2 uptake rate constants are given as k_2, k_4, and k_6. It is to be noted that k_5 and k_6 describe processes in which there is simultaneous loss or gain of *two* CO_2 molecules, a phenomenon which will be discussed in detail below.

Acid-Catalyzed Decarboxylation of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$. The decarboxylation of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ was studied over the acidity range 0.30 ≤ pH ≤ 7.32 and temperature range 11–31 °C. These results are given in Table III. Changing the ionic strength from 0.5 to 1.0 M and the wavelength at which the reaction was followed from 345 to 270 nm is seen to have no significant influence on the value of k_{obsd}. The final product spectra were identical with those of *trans*-$Rh(en)_2(OH_2)_2{}^{3+}$, *trans*-Rh(en)$_2$(OH)-

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Table III. pH and Temperature Dependence of k_{obsd} for the Decarboxylation of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ [a]

temp, °C	pH	k_{obsd}, s^{-1}
25.0	0.30	3.14 ± 0.05,[c] 2.87 ± 0.18
	0.60	2.97 ± 0.23,[c] 2.75 ± 0.15
	1.30	3.03 ± 0.10,[c] 2.94 ± 0.18
	1.60	2.85 ± 0.10,[c] 2.91 ± 0.16
	2.00	2.88 ± 0.07,[c] 2.99 ± 0.10
	3.11	2.88 ± 0.11
	3.76	2.71 ± 0.14
	4.60	2.51 ± 0.09
	5.30	1.95 ± 0.06[d]
	5.42	1.90 ± 0.05
	5.50	1.77 ± 0.07[d]
	5.66	1.48 ± 0.06[d]
	5.71	1.15 ± 0.09
	5.91	0.99 ± 0.02[d]
	5.92	1.11 ± 0.08[d]
	5.93	1.12 ± 0.02[d]
	5.98	1.05 ± 0.03[d]
	6.10	1.02 ± 0.03[d]
	6.35	0.37 ± 0.03[d]
	6.52	0.28 ± 0.02[d]
	6.97	0.136 ± 0.006[d]
	7.32	0.067 ± 0.002[d]
11.02	0.30	1.12 ± 0.04
15.61	0.30	1.54 ± 0.04
19.86	0.30	2.10 ± 0.03
25.0	0.30–3.11	2.92 ± 0.08[e]
30.54	0.30	4.19 ± 0.06
$\Delta H^{\ddagger}$, kcal mol^{-1}		10.9 ± 0.1
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		−19.6 ± 0.4

[a] $[Rh(III)]$[b] = 1.25×10^{-3} M, wavelength = 345 nm, ionic strength = 0.5 M. [b] Prepared by dissolving *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ at pH 8.5. [c] Ionic strength = 1.0 M. [d] Wavelength = 270 nm. [e] Mean of data in top part of table within pH range specified in text.

Table IV. pH and Temperature Dependence of k_{obsd} for the Decarboxylation of *trans*-$Rh(en)_2(OCO_2)_2^-$ [a]

temp, °C	pH	k_{obsd}, s^{-1}
25.0	0.30	2.26 ± 0.03
	0.60	2.29 ± 0.05
	1.30	2.29 ± 0.02
	1.60	2.21 ± 0.05
	2.23	2.29 ± 0.06
	3.22	2.19 ± 0.03
	4.12	2.31 ± 0.04
	5.14	2.07 ± 0.04
	5.70	1.73 ± 0.03
	5.70	1.66 ± 0.02
	5.79	1.65 ± 0.04
	5.91	1.47 ± 0.02
	6.12	1.19 ± 0.02
	6.31	1.10 ± 0.04
	6.41	0.99 ± 0.04
	6.57	0.83 ± 0.02
	6.82	0.34 ± 0.01
	7.11	0.193 ± 0.003
	7.79	0.068 ± 0.005
11.02	0.60	0.56 ± 0.01
15.59	0.60	0.91 ± 0.02
19.88	0.60	1.44 ± 0.03
25.0	0.30–4.12	2.26 ± 0.05[c]
30.54	0.60	3.91 ± 0.08
$\Delta H^{\ddagger}$, kcal mol^{-1}		16.3 ± 0.2
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		−2.1 ± 0.8

[a] $[Rh(III)]$[b] = 1.25×10^{-3}M, wavelength = 347 nm, ionic strength = 0.5 M. [b] *trans*-$Rh(en)_2(OCO_2)_2^-$ was prepared in solution as described in the Experimental Section. [c] Mean of above data at pH ≤4.2.

$(OH_2)^{2+}$, or a mixture of the two, depending on the pH of the solution. Up to a pH of ~6.1, the reactions and equilibria represented by k_1, k_2, K_1, and K_3 (Scheme I) are the only ones of significance since pK_2 and pK_4 are well over 7. The rate law for such a process is therefore closely approximated by eq 1.

$$k_{\mathrm{obsd}} = \frac{k_1[H^+]}{[H^+] + K_3} + \frac{k_2K_1[CO_2]}{[H^+] + K_1} \qquad (1)$$

In the absence of added carbonate, no CO_2 uptake occurs below pH 6.5, and eq 1 simplifies to eq 2. The constants k_1

$$k_{\mathrm{obsd}} = k_1[H^+]/([H^+] + K_3) \qquad (2)$$

and K_3 were estimated by a least-squares analysis of the data treated in the conventional double reciprocal form of eq 2 within the crucial range $2.0 \leq \mathrm{pH} \leq 6.1$. This procedure yielded $k_1 = 2.6 \pm 0.2$ s^{-1} and p$K_3 = 5.8 \pm 0.1$ for the data at 25 °C given in the upper part of Table III with a reasonably good correlation coefficient ($F = 0.956$). The value for k_1 is seen to be in satisfactory agreement with the mean of all values of k_{obsd} for pH <3.2, i.e., 2.92 ± 0.08 s^{-1}, which is as expected since, at high $[H^+]$, eq 2 reduces to $k_{\mathrm{obsd}} = k_1$. The activation parameters, determined at high $[H^+]$ and recorded in the lower part of Table III, therefore refer to the rate constant k_1.

Acid-Catalyzed Decarboxylation of *trans*-$Rh(en)_2(OCO_2)_2^-$. The above reaction was studied over the ranges $0.3 < \mathrm{pH} < 7.8$ and 11 °C < t < 31 °C, and the rate data are summarized in Table IV. Preliminary experiments showed that with pH <6, the only spectrally identifiable product is a mixture of *trans*-$Rh(en)_2(OH_2)_2^{3+}$ and *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$. Furthermore, there was no spectral evidence for the consecutive loss of the two CO_2 molecules in rate-distinguishable reactions, the plots of the data being rigorously first order throughout this pH range. One notes also (cf. Tables III and IV) that the rate of decarboxylation of the possible monocarbonato intermediate *trans*-$Rh(en)_2(OCO_2H)(OH_2)^{2+}$ differs very little from that of the dicarbonato parent species in the low-pH range. We have therefore postulated in Scheme I that the reaction governed by k_5 results in simultaneous loss of *both* carbonato ligands. This assumption requires that the reverse process, governed by k_6, should involve simultaneous uptake of two CO_2 molecules and should therefore vary with $[CO_2]^2$. Some experiments to be discussed later do in fact confirm the third-order nature of k_6. By contrast, when pH >6.5 the initially identifiable product is a mixture of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *trans*-$Rh(en)_2(OCO_2)(OH)$. Further loss of CO_2 from this species is a somewhat slower process in the high-pH range than is the loss of CO_2 from the dicarbonato parent complex, as is clear by comparison of Tables III and IV.

We return now to consideration of the details of the kinetics of the decarboxylation of the dicarbonato species in the low-pH range. In the absence of added CO_2, the reverse CO_2 uptake processes governed by k_4 and k_6 may be ignored, and the appropriate rate expression is readily seen to be eq 3. At high

$$k_{\mathrm{obsd}} = \frac{k_3K_5[H^+] + k_5[H^+]^2}{K_5K_6 + K_5[H^+] + [H^+]^2} \qquad (3)$$

$[H^+]$, eq 3 reduces to $k_{\mathrm{obsd}} = k_5$, so k_{obsd} should become independent of $[H^+]$ at low pH, as is confirmed by the data of Table IV. From the mean value of k_{obsd} at pH <4.2, $k_5 = 2.26 \pm 0.05$ s^{-1} and the activation parameters determined in this range are those of k_5 (see last entries of Table IV). A double-reciprocal plot method cannot be applied to eq 3, but it may be rewritten as eq 4. From this, values of k_3 and K_6 can

$$\frac{k_5[H^+]^2}{k_{\mathrm{obsd}}} - K_5[H^+] - [H^+]^2 = K_5K_6 - \frac{k_3K_5[H^+]}{k_{\mathrm{obsd}}} \qquad (4)$$

be evaluated by plotting the lhs of eq 4 vs. $[H^+]/k_{\mathrm{obsd}}$, with

Table V. $[CO_2]$ Dependence of k_{obsd} for CO_2 Uptake by *trans*-$Rh(en)_2(OH)_2^+$ [a]

$[CO_2]$,[c] M	k_{obsd}, s^{-1}	$k_{obsd}/[CO_2]^2$, M^{-2} s^{-1}
0.02	1.95 ± 0.14	4880
0.15	1.23 ± 0.02	5470
0.01	0.50 ± 0.02	5000

[a] $[Rh(III)]^b = 5 \times 10^{-4}$ M, temp = 9.1 °C, wavelength = 270 nm, pH 8.82, ionic strength = 0.5 M. [b] Weighed as *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$. [c] As prepared in "acidification method". See ref 5 and 13.

Table VI. pH Dependence of k_{obsd} for CO_2 Uptake by *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ and *trans*-$Rh(en)_2(OH)_2^+$ [a]

pH	k_{obsd}, s^{-1}	k_{CO_2},[d] s^{-1}
6.33	1.37 ± 0.06	0.85 ± 0.07
6.65	1.25 ± 0.09	0.96 ± 0.10
6.72	1.10 ± 0.05	0.86 ± 0.06
6.84	0.84 ± 0.02	0.65 ± 0.03
7.12	0.95 ± 0.02	0.84 ± 0.03
7.19	1.09 ± 0.10	1.01 ± 0.11
7.20	0.76 ± 0.03	0.68 ± 0.03
7.32	0.97 ± 0.02	0.90 ± 0.02
7.52	1.02 ± 0.05	0.98 ± 0.05
7.73	1.02 ± 0.03	0.99 ± 0.03
7.90	1.20 ± 0.02	1.19 ± 0.03
8.00	1.06 ± 0.04	1.05 ± 0.04
8.10	1.25 ± 0.05	
8.18	1.28 ± 0.12	
8.20	1.19 ± 0.05	
8.27	1.25 ± 0.03	
8.54	1.22 ± 0.04	
8.54	1.64 ± 0.18	
8.71	1.30 ± 0.05	
8.73	1.95 ± 0.18	
8.92	2.12 ± 0.08	
9.02	2.47 ± 0.06	

[a] $[Rh(III)]^b = 10^{-3}$ M, temp = 25 °C, $[CO_2]^c = 10^{-2}$ M, ionic strength = 0.5 M. [b] Weighed as *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$. [c] According to "acidification method". See ref 5 and 13. [d] Calculated by subtracting $k_1[H^+]/[H^+] + K_3$ from k_{obsd}.

Table VII. Temperature Dependence of k_{obsd} for CO_2 Uptake by *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ and *trans*-$Rh(en)_2(OH)_2^+$ [a]

pH	temp, °C	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}	$10^{-4}k_6$, M^{-2} s^{-1}
6.74	6.06	0.333 ± 0.010	25.7 ± 0.8	
	10.60	0.446 ± 0.016	34.0 ± 1.2	
	15.25	0.765 ± 0.011	61.9 ± 0.9	
	19.80	1.09 ± 0.05	89.1 ± 4.1	
	24.27	1.29 ± 0.04	103 ± 3	
	29.20	2.02 ± 0.13	166 ± 1	
9.07	5.12	0.371 ± 0.017		0.39 ± 0.02
	10.50	0.503 ± 0.039		0.52 ± 0.04
	15.12	0.986 ± 0.125		1.02 ± 0.13
	19.90	1.48 ± 0.14		1.54 ± 0.15
	25.15	2.64 ± 0.11		2.75 ± 0.11
	29.75	4.10 ± 0.37		4.27 ± 0.39
$\Delta H_6^{\ddagger}$, kcal mol^{-1}			12.9 ± 0.9	16.3 ± 0.9
$\Delta S_6^{\ddagger}$, cal deg^{-1} mol^{-1}			−5.5 ± 3.1	16.4 ± 3.0

[a] $[Rh(III)]^b = 1 \times 10^{-3}$ M, wavelength = 345 nm, $[CO_2]^c = 0.01$ M, ionic strength = 0.5 M. [b] Weighed as *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$. [c] As prepared in "acidification method". See ref 5 and 13.

use of the known value of k_5 and various assumed values of K_5. Such calculations were performed for a series of pK_5 values between 4.5 and 6.5, by using the data of Table IV at pH >5. An excellent fit of the data ($F = 0.996$) is obtained when the difference between pK_5 and pK_6 is made rather small—i.e., when $pK_5 = 5.8 \pm 0.1$ and $pK_6 = 6.4 \pm 0.1$, with $k_3 = 1.3 \pm 0.1$ s^{-1}. It is worth noting that the magnitude of pK_5 is the same as the value of pK_3 obtained earlier, showing the close correspondence in the acidities of the fully protonated mono- and dicarbonato species. There is, however, a substantial difference between the second-stage acidities of the two species, with pK_4 having a value of 7.4 (Table II) as compared to 6.4 for K_6. It is, in fact, this one-unit difference in the magnitude of pK_4 and pK_6 which causes the enhanced stability of the monocarbonato complex at high pH as compared to the dicarbonato as mentioned above, even though k_1 and k_5 are not very different. The magnitude of k_3 is more or less as one might expect, being approximately half of k_5, since the latter relates to the simultaneous loss of both protonated carbonato groups. Differences in the trans effect of the second carbonato group[4,25] or in the net charge of the complex ions[26,27] may also play a role, though obviously not a very substantial one, in determining the relative magnitude of k_3 and k_5.

Carbon Dioxide Uptake by *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ and *trans*-$Rh(en)_2(OH)_2^+$. It was noted above that CO_2 uptake by the dihydroxo species has been assumed to depend on $[CO_2]^2$, as proposed in Scheme I. Some preliminary experiments were carried out to test this hypothesis. In these the rate of CO_2 uptake was measured at pH 8.82, where the dihydroxo complex is the major reactant, and at three different CO_2 concentrations, other experimental conditions being fixed. As summarized in Table V, it is obvious that k_{obsd} is in fact proportional to $[CO_2]^2$ with a considerable degree of precision. We next studied the kinetics of the system in detail in the range $6.3 < pH < 9.1$ and $5\ °C < t < 30\ °C$, determining the rate constants at $\lambda = 345$ nm as recorded in Tables VI and VII. In the analysis of these data, account must be taken of some contribution to k_{obsd} by decarboxylation reactions. As is clear from eq 1 and the data of Table III, decarboxylation of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ will not contribute significantly toward k_{obsd} unless pH ≤8, while the dicarbonato species will not be formed in appreciable amounts unless the pH substantially exceeds this figure. One can thus determine "corrected" k_{obsd} figures in Table VI by subtracting the value of $k_1[H^+]/([H^+] + K_3)$ from each k_{obsd} value up to pH 8, above which the correction becomes negligible and may be ignored. The appropriate rate equation applicable to the corrected k_{obsd} values, k_{CO_2}, then takes the form (see Scheme I) of eq 5. Since $[CO_2]$ is constant at 0.01 M in all runs

$$k_{CO_2} = \frac{k_2[CO_2][H^+] + k_6K_2[CO_2]^2}{[H^+] + K_2} \tag{5}$$

recorded, the quantity $k_{CO_2}([H^+] + K_2)$ should be a linear function of $[H^+]$, with a slope of $k_2[CO_2]$ and intercept $k_6K_2[CO_2]^2$. A least-squares analysis of the data for pH <9.1 in this form[28] confirms the linearity ($F = 0.990$) and yields the values $k_2 = 81 \pm 3$ M^{-1} s^{-1} and $k_6 = (1.4 \pm 0.2) \times 10^4$ M^{-2} s^{-1}. The temperature dependences of these two rate constants were determined by performing the series of experiments recorded in Table VII. For those at pH 6.74, where the major product is *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$, the k_{obsd} values include a contribution from the reverse decarboxylation process as already explained. After correction for this to yield k_{CO_2} the values of k_2 are effectively estimated from the equality $k_{CO_2} = k_2[CO_2][H^+]/([H^+] + K_2)$. When the correction is made, it is assumed that K_3 is constant over the experimental temperature range, and the k_1 values at each temperature are determined from the data of Table III. For the data at pH 9.07, the major product is *trans*-$Rh(en)_2(OCO_2)_2^-$, and no decarboxylation corrections are required. With K_2 assumed to be constant, one readily evaluates k_6 from the relation $k_{CO_2} = k_6K_2[CO_2]^2/([H^+] + K_2)$. These latter values tend to be

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

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Table VIII. pH and Temperature Dependence of k_{obsd} for CO_2 Uptake by *trans*-$Rh(en)_2(OCO_2)(OH)$[a]

temp, °C	pH	k_{obsd}, s^{-1}	k_4,[d] $M^{-1}\ s^{-1}$
25.0	7.95	2.52 ± 0.25	323 ± 32
	8.12	3.85 ± 0.34	458 ± 40
	8.54	2.39 ± 0.12	256 ± 13
	8.87	2.47 ± 0.14	255 ± 14
	9.21	3.18 ± 0.24	323 ± 24
	9.46	3.87 ± 0.32	390 ± 32
			av 334 ± 79
5.66	9.40	0.569 ± 0.005	57.4 ± 0.5
10.68	9.40	0.779 ± 0.043	78.6 ± 4.3
15.38	9.40	1.24 ± 0.07	125 ± 7
20.45	9.40	2.16 ± 0.26	218 ± 26
25.0	7.95–9.46		334 ± 79[e]
29.47	9.40	5.18 ± 0.24	523 ± 24
$\Delta H^{\ddagger}$, kcal mol^{-1}			15.4 ± 0.7
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}			+4.6 ± 2.4

[a] $[Rh(III)]^b = 1 \times 10^{-3}$ M, wavelength = 345 nm, $[CO_2]^c = 0.01$ M, ionic strength = 0.5 M. [b] Weighed a *trans*-$[Rh(en)_2(OCO_2)(OH_2)ClO_4$. [c] As prepared in "acidification method". See ref 5 and 13. [d] Calculated from eq 6. [e] Mean value of data reported above at this temperature.

somewhat higher than they should be because of the high-pH difficulties already mentioned.[28] However, it is assumed that the errors are a constant fraction of each rate constant over the whole temperature range, so they should not greatly affect the precision of the temperature parameters. The latter are also quoted in Table VII for both k_2 and k_6.

Carbon Dioxide Uptake by *trans*-Rh(en)$_2$(OCO$_2$)(OH). This reaction was studied over the acidity range $7.9 < \text{pH} < 9.5$ where no interference by the decarboxylation reactions already discussed occurs. These results and those of a temperature-dependence study are summarized in Table VIII. The reaction and equilibrium governed by k_4 and K_4 (Scheme I) are the only ones requiring consideration under the conditions specified. The appropriate rate law is eq 6. Since K_4

$$k_{\text{obsd}} = k_4K_4[CO_2]/([H^+] + K_4) \qquad (6)$$

is known (Table II), k_4 can be calculated for each experiment. The experimental errors involved in such measurements have been discussed previously.[5,13,23] It is seen that k_4 is reasonably constant over the given pH range and is more than 3 times greater than k_2 at the same temperature. It is apparent that the OH ligand trans to a CO_3 grouping is somewhat more nucleophilic than when H_2O is its trans partner. However, the magnitudes of both of these second-order CO_2 uptake rate constants and their activation parameters are well within the range of values of those reported for other Co(III) and Rh(III) systems.[1,5,24] This is also true for the various rate constants and activation parameters of the decarboxylation processes reported here and elsewhere.[1,5,8,29] A more detailed comparison and discussion of CO_2 uptake and decarboxylation rate parameters will be given in a forthcoming paper,[30] so as to include another series of *trans*-$Rh(en)_2$ complexes investigated subsequently to this work.

The outstanding aspect of this study is the first direct evidence presented for the formation of a trans monodentate dicarbonato complex. In our earlier study of the corresponding *cis*-bis(ethylenediamine)rhodium(III) system,[1] our inability to form the *cis*-dicarbonato species must now be ascribed to steric hindrance and/or some interaction between the first-formed carbonato ligand and the hydroxo ligand in the cis position, which prevents the entry of the second CO_2 molecule. Some indirect evidence for the presence of a *trans*-dicarbonato complex in the *trans*-bis(ethylenediamine)cobalt(III) system[8] does exist, although no evidence was reported for the formation of such a species in the corresponding (cyclam)cobalt(III) system.[25] The kinetic study shows that formation of the trans monodentate dicarbonato species takes place by simultaneous CO_2 uptake by the trans OH groups, apparently reacting as entirely independent entities though attached to a common $Rh(en)_2^{3+}$ center. This results in a third-order process unlike any previously observed for CO_2 uptake, with a rate constant of about 1.4×10^4 $M^{-2}\ s^{-1}$ at 25 °C. While this seems to be a rather large rate constant for such a process, it is several orders of magnitude smaller than the theoretical predictions for an encounter-controlled reaction of this type[31] (about 10^9 $M^{-2}\ s^{-1}$).

Finally, we should comment on the chosen notation for the species *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ in Scheme I. In earlier work in this series,[24,32,33] similar cobalt(III) ammine complexes in the cis configuration were assumed to exist in the $(OCO_2H)(OH)$ form, rather than in the $(OCO_2)(OH_2)$ form. From the pH dependence of the decarboxylation[33] and ring-closure[24,32] rate constants, it was concluded that cis species in the form $(OCO_2H)(OH)$ decarboxylate[33] much more slowly than the protonated form $(OCO_2H)(OH_2)$ but undergo ring closure[24,32] much faster than the deprotonated form $(OCO_2)(OH)$. We have pointed to these arguments previously[1] and find it difficult to understand the general nature of such species based on the $(OCO_2H)(OH)$ notation. The $(OCO_2)(OH_2)$ formulation would be a more acceptable and easier to understand notation, since protonation of the carbonato ligand would then result in a rapid loss of CO_2,[4-7] whereas deprotonation of the aquo ligand would slow up the ring-closure process significantly since it involves its replacement by a hydroxo ligand. It is important to note that it is difficult to locate the proton in cis systems since it may be shared by the carbonato and hydroxo ligands. In the present study, however, we isolated the carbonatoaquo (or bicarbonatohydroxy) intermediate as a solid complex. By titrating with NaOH (Table II) and from the pH dependence of the acid-catalyzed decarboxylation of this species (Table III), two significantly different p*K* values were obtained (7.4 and 5.8, respectively). Since we are dealing with trans isomers in this study, the only reasonable explanation for these and previously mentioned observations must be based on the notation *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ for the isolated intermediate. The p*K* values indicate that the aquo ligand is indeed more basic than the carbonato ligand, presumably due to a trans-labilizing effect[25] of the latter ligand[4] by which the weakening of the M–O bond is accompanied by the strengthening of the O–H bond on the aquo ligand. Furthermore, the trans configuration of these ligands does not permit direct sharing of a proton, as suggested for the cis configuration.

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(28) For pH >9.1, the k_{obsd} values show a continuing increase accompanied by smaller absorbance changes. A similar effect was reported in the study of the CO_2 uptake reactions of the cis analogues of the present complexes, and can be ascribed to the increasingly rapid base hydrolysis both of CO_2 and of the carbonato product itself. These processes compete with the uptake reaction and prevent total carboxylation of the aquorhodium(III) center in the high-pH runs, resulting in the apparent increases in the k_{obsd} values.

(29) Table III. Reference 27.

(30) van Eldik, R.; Palmer, D. A.; Kelm, H.; Harris, G. M., companion paper in this issue.

(31) The standard collision theory of third-order reactions yields a value for the collision frequency of $\geq 10^9$ $M^{-2}\ s^{-1}$ (Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; p. 75). It has been pointed out that theoretical collision frequencies in the liquid phase differ little from those in the gas phase, at least for second-order reactions (Entelis, S. G.; Tiger, R. P. "Reaction Kinetics in the Liquid Phase"; Keter Publishing House: Jerusalem, **1976**; p 24).

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Registry No. *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$, 75081-59-3; *trans*-$Na[Rh(en)_2(OCO_2)_2]$, 75030-42-1; *trans*-$[Rh(en)_2(OH)(OH_2)](ClO_4)_2$, 75030-43-2; *trans*-$[Rh(en)_2Cl_2]^+$, 18539-17-8; *trans*-$[Rh(en)_2(OH_2)_2]^{3+}$, 21863-10-5; *trans*-$[Rh(en)_2(OH)(OH_2)]^{2+}$, 27842-81-5; *trans*-$[Rh(en)_2(OH)_2]^+$, 55683-53-9; *trans*-$[Rh(en)_2(OCO_2)(OH_2)]^+$, 75081-58-2; *trans*-$[Rh(en)_2(OCO_2)(OH)]$, 75109-61-4; *trans*-$[Rh(en)_2(OCO_2)_2]^-$, 75030-44-3; CO_2, 124-38-9; *trans*-$[Rh(en)_2Cl_2]ClO_4$, 41367-59-3.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 20. Carbon Dioxide Uptake by and Decarboxylation of *trans*-Halogenobis(ethylenediamine)rhodium(III) Complexes in Aqueous Solution[1]

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The formation and decarboxylation reactions of *trans*-$Rh(en)_2(X)(OCO_2)$, where X = Cl, Br, and I, were studied kinetically. The rate parameters for the decarboxylation of *trans*-$Rh(en)_2(X)(OCO_2H)^+$ are, for X = Cl, Br, and I, respectively, $k = 1.26 \pm 0.04$, 1.12 ± 0.03, and 0.55 ± 0.04 s^{-1} at 25 °C $\Delta H^* = 17.4 \pm 0.5$, 18.2 ± 0.2, and 17.2 ± 0.3 kcal mol^{-1}, and $\Delta S^* = -0.1 \pm 1.6$, $+2.6 \pm 0.8$, and -2.3 ± 1.1 cal deg^{-1} mol^{-1}. CO_2 uptake by *trans*-$Rh(en)_2(X)(OH)^+$ produces *trans*-$Rh(en)_2(X)(OCO_2)$ for which the rate parameters are, for X = Cl, Br, and I, respectively, $k = 260 \pm 12$, 395 ± 33, and 422 ± 43 M^{-1} s^{-1} at 25 °C, $\Delta H^* = 12.5 \pm 1.3$, 15.1 ± 1.1, and 17.6 ± 0.8 kcal mol^{-1}, and $\Delta S^* = -5.3 \pm 4.4$, $+3.9 \pm 3.9$, and $+11.9 \pm 2.7$ cal deg^{-1} mol^{-1}. A complete survey is made of the existing rate data for the aquation and formation reactions of cobalt(III) and rhodium(III) carbonato complexes. Some general conclusions are drawn therefrom concerning the trans-labilizing influence of a number of ligands and of the relationships between the various p*K*'s and rate constants involved.

Introduction

In preceding studies in this series[4] we reported on the formation and decarboxylation reactions of the complexes *cis*-$Rh(en)_2(OCO_2)(OH_2)^+$, *cis*-$Rh(en)_2(CO_3)^+$, *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$, and *trans*-$Rh(en)_2(OCO_2)_2^-$, where en = ethylenediamine. Substitution trans to the hydroxo or carbonato groups seems to have a significant influence on the basicity of these ligands. This effect is also seen in studies of the formation and decarboxylation reactions[5] of *trans*-$Co(NH_3)_4(CN)(OCO_2)$ and in the decarboxylation[6] of *trans*-$Co(en)_2(Cl)(OCO_2)$. The purpose of the present investigation was to extend our knowledge of the properties of trans rhodium(III) carbonato complexes and has included studies of CO_2 uptake by *trans*-$Rh(en)_2(X)(OH)^+$ and acid-catalyzed decarboxylation of *trans*-$Rh(en)_2(X)(OCO_2)$ for the series X = Cl, Br, and I. We have related these findings to the large body of previous data concerning the kinetic properties of carbonato complexes.

Experimental Section

Materials. *trans*-$[Rh(en)_2Cl_2]NO_3$ was prepared according to standard procedures[7] and converted to *trans*-$[Rh(en)_2Cl_2]ClO_4$ as described previously.[4b,8] *trans*-$[Rh(en)_2Br_2]ClO_4$ was prepared by following the published procedure for the corresponding nitrate salt,[7] except for the addition of a few milliliters of concentrated $HClO_4$ instead of concentrated HNO_3. *trans*-$[Rh(en)_2I_2]I$ was prepared by following Johnson and Basolo's method[7] and was used in this form. The complexes *trans*-$[Rh(en)_2(X)(OH_2)](ClO_4)_2$, X = Cl, Br, and I, were prepared by refluxing the appropriate dihalide complex with 1 equiv of 0.1 M $AgClO_4$ for X = Cl and Br and with 2 equiv for X = I according to the method reported elsewhere.[8] These conversions were found to be more efficient in dilute perchloric acid solutions. Analyses[9] for *trans*-$[Rh(en)_2(X)(OH)_2](ClO_4)_2$ are as follows. Anal. Calcd for X = Cl: C, 10.1; H, 3.8; N, 11.8; Cl, 22.4. Found: C, 10.3; H, 3.4; N, 11.6; Cl, 22.4. Calcd for X = Br: C, 9.2; H, 3.5; N, 10.8. Found: C, 9.4; H, 3.5; N, 10.8. Calcd for X = I: C, 8.5; H, 3.2; N, 9.9; I, 22.4. Found: C, 8.7; H, 3.0; N, 10.0; I, 22.5.

The *trans*-$Rh(en)_2(X)(OCO_2)$ complexes were prepared in solution by the addition of $NaHCO_3$ to aqueous solutions of the *trans*-$Rh(en)_2(X)(OH_2)^{2+}$ complexes as described for the general preparation of monodentate carbonate complexes.[10] Various procedures were followed to isolate *trans*-$Rh(en)_2(Cl)(OCO_2)$. The best yield was obtained by adding an excess of alcohol to the synthetic solution, which then precipitates the excess of free carbonate in solution, followed by the addition of anhydrous ether to the filtrate which results in the precipitation of the wanted product. In some cases an oil was produced, and the desired product could only be isolated with great difficulty in very low yields. Analyses indicated that the obtained solid was slightly contaminated with some of the aquo (or hydroxo) chloro complex. No effort was made to isolate the bromo and iodo carbonato complexes since they are very similar in nature to the chloro complex, as can be seen from the acid-catalyzed decarboxylation studies reported later on. All chemicals were of reagent grade. Deionized and degassed water was used in preparing all solutions.

Spectra. Absorption spectra in the UV–visible region were recorded on a Cary 118 spectrophotometer. The spectra of the various species involved in this study are summarized in Table I and illustrated in Figures 1–3. The hydroxo species were prepared in solution by dissolving the corresponding aquo species in basic medium.

Determination of Acid Dissociation Constants. The acid dissociation constants of *trans*-$Rh(en)_2(X)(OH_2)^{2+}$ were determined at 25 °C and

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