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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 pK'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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(2) Institute for Physical Chemistry, University of Frankfurt, 6 Frankfurt/Main, West Germany.

(3) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

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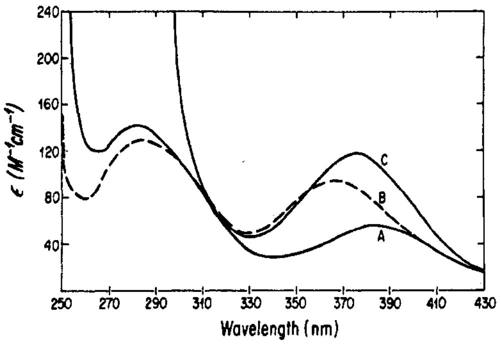

Figure 1. UV–visible absorption spectra: A, *trans*-$Rh(en)_2(Cl)(OH_2)^{2+}$; B, *trans*-$Rh(en)_2(Cl)(OH)^+$; C, *trans*-$Rh(en)_2(Cl)(OCO_2)$.

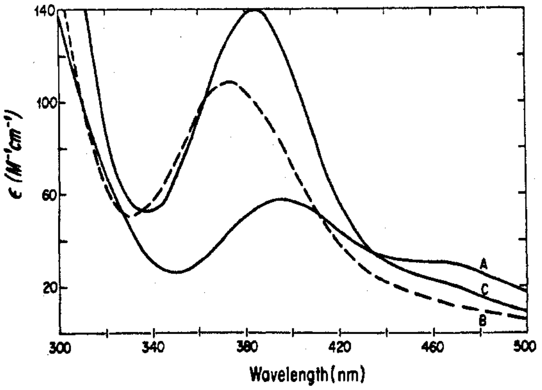

Figure 2. UV–visible absorption spectra: A, *trans*-$Rh(en)_2(Br)(OH_2)^{2+}$; B, *trans*-$Rh(en)_2(Br)(OH)^+$; C, *trans*-$Rh(en)_2(Br)(OCO_2)$.

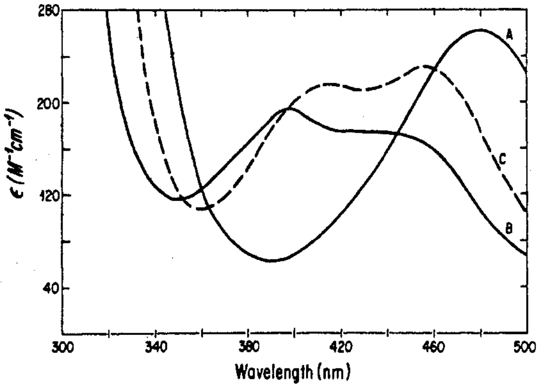

Figure 3. UV–visible absorption spectra: A, *trans*-$Rh(en)_2(I)(OH_2)^{2+}$; B, *trans*-$Rh(en)_2(I)(OH)^+$; C, *trans*-$Rh(en)_2(I)(OCO_2)$.

an ionic strength of 0.5 M ($NaClO_4$) by titrating a 2×10^{-3} M complex solution against 0.1 M NaOH. The pH measurements were made with a Beckman Research Model pH meter. The reference electrode was filled with saturated NaCl solution. The p*K*'s of the three complexes are 6.12, 6.35, and 6.80, for X = Cl, Br, and I, respectively.

Rate Measurements. The various decarboxylation and CO_2 uptake reactions were studied at an ionic strength of 0.5 M ($NaClO_4$) over the acidity and temperature ranges indicated in the Results and Discussion. The "acidification method", described in detail elsewhere,[11] was employed during the CO_2 uptake studies. The reactions were monitored at wavelengths where the difference in absorption between reactant and product is a maximum (see Figures 1–3). The rate measurements were made on a Durrum Model 110 stopped-flow assembly. At pH ≥2, several buffer systems were used to control the pH of the solutions: McIlvaine phosphate–citric acid,[12] phosphate–NaOH, and Tris–HCl,[13,14] depending on the pH range concerned. pH measurements were made on the above-mentioned pH meter by using a water-jacketed sample holder thermostated at the reaction temperature. The observed pseudo-first-order rate constants were calculated in the usual way by using a standard least-squares analysis and are reported in the Results and Discussion as the mean of a least six kinetic runs. Additions of micromolar concentrations of carbonic anhydrase,[15] which catalyzes the hydration of CO_2, were made during the decarboxylation rate studies at pH >6.5, as discussed before.[4]

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

complex species	λ_{max}, nm	ϵ_{max}, $M^{-1}\,cm^{-1}$	ref
trans-$Rh(en)_2(Cl)(OH_2)^{2+}$	383, 283	46, 143	8
	386, 282	55, 147	16
	380–350, 280	26, 73	17
	384, 283	56, 143	this work
trans-$Rh(en)_2(Cl)(OH)^+$	363, 285	123, 172	8
	~360, 280	52, 76	17
	370, 293	94, 134	18
	367, 285	94, 129	this work
trans-$Rh(en)_2(Cl)(OCO_2)^a$	376	118	this work
trans-$Rh(en)_2(Br)(OH_2)^{2+}$	470, 405, 280	32, 55, 520	8
	~465, ~395	26, 48	17
	465 (sh), 396, 252 (sh)	31, 58, 603	this work
trans-$Rh(en)_2(Br)(OH)^+$	370, 275 (sh)	138, 1066	8
	370, 290 (sh)	103, ~200	17
	376, 290 (sh)	105, 148	18
	373, 295 (sh)	109, 146	this work
trans-$Rh(en)_2(Br)(OCO_2)^a$	384	141	this work
trans-$Rh(en)_2(I)(OH_2)^{2+}$	476, 332 (sh), 300 (sh)	150, 760, 1240	8
	475, 300	95, 1000	17
	480, 298	263, 1417	this work
trans-$Rh(en)_2(I)(OH)^+$	445, 390 (sh), 338, 270	149, 120, 1195, 6072	8
	450–400, 270	71, 2150	17
	446, 402, 274	150, 160, 4000	19
	440 (sh), 397	175, 196	this work
trans-$Rh(en)_2(I)(OCO_2)^a$	456, 415	232, 216	this work

[a] Prepared in solution. See the Experimental Section.

Results and Discussion

The UV–visible absorption spectra of the species *trans*-$Rh(en)_2(X)(OH_2)^{2+}$ and *trans*-$Rh(en)_2(X)(OH)^+$ are, according to the data in Table I, in satisfactory agreement with those reported elsewhere.[8,16–19] The uncertainty in the extinction coefficients has been referred to in the past.[8,16] Acidification of basic solutions of the carbonato complexes gave the spectra of the corresponding aquo complexes. Addition of sufficient $NaHCO_3$ to raise the pH to approximately 8.5 regenerates the spectra of the carbonato complexes, illustrating the quantitative reversibility of this process. The p*K* values of the aquo complexes show an increase in basicity along the series Cl < Br < I. This is in the order of increasing

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

temp, °C	pH	k_{obsd}, s^{-1}
25.0	0.30	1.19 ± 0.04
	0.60	1.25 ± 0.05
	1.30	1.24 ± 0.06
	1.60	1.27 ± 0.03
	2.32	1.30 ± 0.05
	2.66	1.29 ± 0.06
	3.63	1.29 ± 0.06
	4.68	1.27 ± 0.05
	5.54	1.06 ± 0.04
	5.65	1.06 ± 0.05
	5.74	0.99 ± 0.04
	6.20	0.72 ± 0.04
	6.26	0.64 ± 0.02
	6.49	0.51 ± 0.01
	6.72	0.39 ± 0.02
	7.15	0.11 ± 0.01
	7.45	0.069 ± 0.003
	7.85	0.035 ± 0.003
7.67	0.30	0.162 ± 0.01
9.75		0.20 ± 0.01
13.10		0.28 ± 0.01
13.57		0.31 ± 0.01
19.40		0.66 ± 0.01
19.85		0.70 ± 0.01
25.0		1.08 ± 0.01
30.3		1.68 ± 0.04
34.9		2.75 ± 0.12
$\Delta H^{\ddagger}$, kcal mol^{-1}		17.4 ± 0.5
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		−0.1 ± 1.6

[a] $[Rh(III)]^b = 1.25 \times 10^{-3}$ M, wavelength = 380 nm, ionic strength = 0.5 M. [b] Weighed as *trans*-$Rh(en)_2(Cl)(OCO_2)$ or *trans*-$[Rh(en)_2(Cl)(OH_2)](ClO_4)_2$.

trans effectiveness[20] for weakening of the M–O bond and consequently strengthening of the O–H bond of the aquo ligands.

The overall mechanism for the CO_2 uptake and decarboxylation processes is assumed to be of the form now well-established[4] for monodentate carbonato systems (eq 1–3). The overall rate law for this mechanism is as in eq 4. In the absence of added carbonate, eq 4 simplifies to eq 5 which is the rate law for the decarboxylation process.

$$trans\text{-}Rh(en)_2(X)(OH_2)^{2+} \overset{K_1}{\rightleftharpoons} trans\text{-}Rh(en)_2(X)(OH)^+ + H^+ \quad (1)$$

$$trans\text{-}Rh(en)_2(X)(OH)^+ + CO_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} trans\text{-}Rh(en)_2(X)(OCO_2H)^+ \quad (2)$$

$$trans\text{-}Rh(en)_2(X)(OCO_2H)^+ \overset{K_3}{\rightleftharpoons} trans\text{-}Rh(en)_2(X)(OCO_2) + H^+ \quad (3)$$

$$k_{obsd} = \frac{k_1[H^+]}{[H^+] + K_3} + \frac{k_2K_1[CO_2]}{[H^+] + K_1} \quad (4)$$

$$k_{obsd} = k_1[H^+]/([H^+] + K_3) \quad (5)$$

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

temp, °C	pH	k_{obsd}, s^{-1}
25.0	0.30	1.15 ± 0.03
	0.60	1.10 ± 0.02
	1.30	1.08 ± 0.01
	1.60	1.08 ± 0.01
	2.14	1.17 ± 0.02
	2.52	1.13 ± 0.03
	3.26	1.15 ± 0.02
	4.32	1.12 ± 0.02
	5.04	1.20 ± 0.01
	5.68	0.82 ± 0.01
	5.74	1.05 ± 0.02
	5.76	0.86 ± 0.01
	5.94	1.01 ± 0.02
	6.18	0.97 ± 0.01
	6.27	0.62 ± 0.01
	6.50	0.80 ± 0.02
	6.80	0.31 ± 0.01
	6.87	0.48 ± 0.01
	6.90	0.47 ± 0.02
	7.34	0.14 ± 0.01
4.92	0.60	0.104 ± 0.002
10.32		0.19 ± 0.01
14.88		0.33 ± 0.02
19.80		0.57 ± 0.01
24.36		1.01 ± 0.02
28.80		1.48 ± 0.02
$\Delta H^{\ddagger}$, kcal mol^{-1}		18.2 ± 0.2
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		+2.6 ± 0.8

[a] $[Rh(III)]^b = 3 \times 10^{-3}$ M, wavelength = 385 nm, ionic strength = 0.5 M. [b] Weighed as *trans*-$[Rh(en)_2(Br)(OH_2)](ClO_4)_2$.

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

temp, °C	pH	k_{obsd}, s^{-1}
25.0	0.30	0.48 ± 0.01
	0.60	0.51 ± 0.01
	1.30	0.51 ± 0.01
	1.60	0.52 ± 0.01
	2.00	0.55 ± 0.03
	2.46	0.58 ± 0.02
	3.25	0.58 ± 0.01
	3.90	0.58 ± 0.01
	4.88	0.59 ± 0.01
	5.68	0.54 ± 0.02
	5.80	0.48 ± 0.01
	6.00	0.44 ± 0.01
	6.33	0.36 ± 0.01
	6.45	0.31 ± 0.01
	6.75	0.22 ± 0.01
	6.88	0.17 ± 0.01
	7.28	0.104 ± 0.002
5.67	0.30	0.061 ± 0.002
10.73		0.103 ± 0.004
14.95		0.17 ± 0.01
19.71		0.26 ± 0.01
25.0		0.48 ± 0.01
29.38		0.76 ± 0.01
$\Delta H^{\ddagger}$, kcal mol^{-1}		17.2 ± 0.3
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		−2.3 ± 1.1

[a] $[Rh(III)]^b = 2.5 \times 10^{-4}$ M, wavelength = 300 nm, ionic strength = 0.5 M. [b] Weighed as *trans*-$[Rh(en)_2(I)(OH_2)](ClO_4)_2$.

The decarboxylation reactions of *trans*-$Rh(en)_2(X)(OCO_2)$, X = Cl, Br, and I, were studied over the acidity range $0.30 \leq pH \leq 7.85$ and temperature range 4–35 °C. These data are summarized in Tables II–IV. Plots of k_{obsd} vs. pH confirm the expected sigmoid type of curve for all three sets of data, in agreement with eq 5. At high $[H^+]$ (pH <5), k_{obsd} is independent of $[H^+]$ and $k_{obsd} = k_1$, so that the reported activation parameters are those for k_1. The values of K_3 can be

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(20) Published data on either thermodynamic or kinetic trans effects for rhodium(III) complexes are sparse. However, kinetic studies of the series of reactions of the type *trans*-$RhL_4X(H_2O) + Y \rightarrow$ *trans*-$RhL_4XY + H_2O$ seem to indicate a strengthening of the Rh–OH_2 bond by the trans ligand X in the order $OH^- > Br > Cl > H_2O$ (Buchacek, R. J.; Harris, G. M. *Inorg. Chem.* **1976**, *15*, 926).

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Table V. Rate Parameters for the Acid-Catalyzed Decarboxylation of *trans*-$Rh(en)_2(X)(OCO_2H)^{n+}$

X	k_1, s^{-1}	pK_3	ref
OH_2	2.92 ± 0.08	5.8 ± 0.1	4b
OCO_2H^-	2.26 ± 0.05	5.8 ± 0.1	4b
OCO_2^{2-}	1.3 ± 0.1	6.4 ± 0.1	4b
Cl^-	1.26 ± 0.04[a]		
	1.24 ± 0.02[b]	6.36 ± 0.01[b]	this work
Br^-	1.12 ± 0.03[a]		
	1.18 ± 0.09[b]	6.42 ± 0.05[b]	this work
I^-	0.55 ± 0.04[a]		
	0.55 ± 0.01[b]	6.58 ± 0.01[b]	this work
NH_2[c]	0.72 ± 0.02	4.7 ± 0.1	4a
NH_3[d]	1.13 ± 0.06	6.95 ± 0.05	15

[a] Mean value of k_{obsd} ($=k_1$) at pH <5. [b] Calculated from double reciprocal plot of data from Tables II–IV. [c] Values for *cis*-$Rh(en)_2(OH_2)(OCO_2H)^{2+}$. [d] Value for $Rh(NH_3)_5(OCO_2H)^{2+}$.

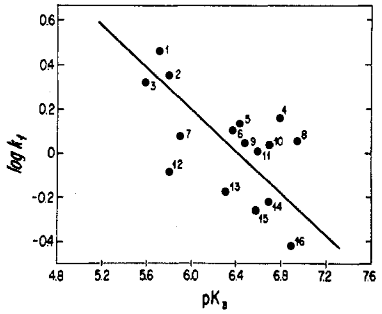

Figure 4. Plot of the log of the rate constant for the decarboxylation of monodentate carbonate complexes vs. the p*K* of the bicarbonate form of the complex at 25 °C: (1), *trans*-$Rh(en)_2(OCO_2H)(OH_2)^{2+}$;[4b] (2), *trans*-$Rh(en)_2(OCO_2H)_2^+$;[4b] (3), *trans*-$Co(en)_2(OCO_2H)(OH_2)^{2+}$;[21] (4), $Ir(NH_3)_5(OCO_2H)^{2+}$;[15] (5), *trans*-$Rh(en)_2(OCO_2H)(OCO)_2$;[4b] (6), *trans*-$Rh(en)_2(Cl)(OCO_2H)^+$ (this work); (7), $Co(tren)(OCO_2H)(OH_2)^{2+}$;[22] (8), $Rh(NH_3)_5(OCO_2H)^{2+}$;[15] (9), *trans*-$Rh(en)_2(Br)(OCO_2H)^+$ (this work); (10), $Co(NH_3)_5(OCO_2H)^{2+}$;[11] (11), *trans*-$Co(en)_2(Cl)(OCO_2H)^+$;[6] (12), *cis*-$Co(en)_2(OCO_2H)(OH_2)^{2+}$;[21] (13), *trans*-$Co(en)_2(NH_3)(OCO_2H)^{2+}$;[23] (14), *cis*-$Co(en)_2(NH_3)(OCO_2H)^{2+}$;[23] (15), *trans*-$Rh(en)_2(I)(OCO_2H)^+$ (this work); (16), *trans*-$Co(NH_3)_4(CN)(OCO_2H)^+$.[5]

estimated from the conventional least-squares analysis of the double reciprocal plot of k_{obsd}^{-1} vs. $[H^+]^{-1}$. As discussed previously,[4] serious difficulties appear in the interpretation of k_{obsd} at high pH, so that the data points above pH 6.8 were omitted in obtaining the k_1 and K_3 values recorded in Table V, together with their standard deviations. The k_1 values obtained in this manner and those calculated as the mean value of K_{obsd} at pH <5.0 agree well within the experimental error limits. The decrease in k_1 along the series Cl > Br > I is accompanied by a parallel decrease in the value of K_3 (increase in pK_3). This is consistent with the general behavior found for the decarboxylation of nearly all the monodentate carbonato complexes studied so far, as illustrated by the "linear free energy relationship" of Figure 4. The two most seriously deviant species (not included in the plot) are the (carbonato)tetraethylenepentaminecobalt(III) complex ion and *cis*-$Rh(en)_2(OCO_2H)(OH_2)^{2+}$. The former has an unusually low rate constant k_1, probably ascribable to its usually low level of solvation,[24] while the latter has an exceptionally high acid dissociation constant K_3, which may result from exceptionally effective interactions between the adjacent aquo and bicarbonato groups such as to reduce substantially the basicity of the latter group. While there is much scatter in Figure 4, the strong positive correlation between the acidity of the parent species and its rate of decarboxylation is obvious. This illustrates how the strength of the primary M–O bond of the carbonato ligand can have a parallel effect on reducing the strength of both of its secondary bonds, O–C and O–H. As for the various rhodium(III) trans species, it is clear that the labilizing effect of the ligand trans to the bicarbonato group decreases k_1 in the order $H_2O > OCO_2H^- > OCO_2^{2-} > Cl^- > Br^- \approx NH_3 > I^-$, as illustrated in Table V.

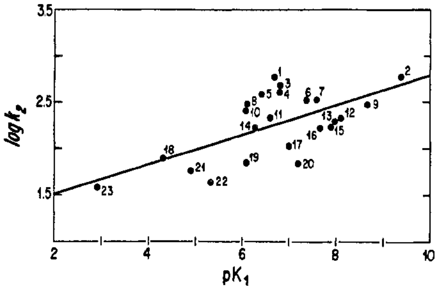

Figure 5. Plot of the log of the rate constant for CO_2 uptake by various hydroxo metal complexes vs. the p*K* of the corresponding aquo form of the complex at 25 °C: (1), $Ir(NH_3)_5(OH)_2^+$;[15] (2), Cu(glygly)(OH);[25] (3), $Rh(NH_3)_5(OH)^{2+}$;[15] (4), *trans*-$Rh(en)_2(I)(OH)^+$ (this work); (5), *trans*-$Rh(en)_2(Br)(OH)^+$ (this work); (6), *trans*-$Rh(en)_2(OCO_2)(OH)$;[4b] (7), *trans*-$Co(NH_3)_4(CN)(OH)^+$;[5] (8), *cis*-$Co(en)_2(OH)(OH_2)^{2+}$;[21] (9), $Zn(CR)(OH)^+$;[27] (10), *trans*-$Rh(en)_2(Cl)(OH)^+$ (this work); (11), $Co(NH_3)_5(OH)^{2+}$;[11] (12), *cis*-$Rh(en)_2(OH)_2^+$;[4a] (13), *cis*-$Co(cyclam)(OH)_2^+$;[25] (14), (α,βS)-$Co(tetren)(OH)^{2+}$;[24] (15), $Co(tren)(OH)_2^+$;[28] (16), *trans*-$Rh(en)_2(OH))_2^+$[4b] [The rate constant for CO_2 uptake for this species is third order. For comparison purposes in this figure, it is plotted as $K[CO_2]$, with $[CO_2] = 0.01$ M, a typical value in a large proportion of the data reported.]; (17), *cis*-$Cr(C_2O_4)_2(OH)(OH_2)^{2-}$;[29] (18), *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$;[4b] (19), *cis*-$Rh(en)_2(OH)(OH_2)^{2+}$;[4a] (20), *trans*-$Co(cyclam)(OH)_2^+$;[25] (21), *cis*-$Co(cyclam)(OH)(OH_2)^{2+}$;[25] (22), $Co(tren)(OH)(OH_2)^{2+}$;[28] (23), *trans*-$Co(cyclam)(OH)(OH_2)^{2+}$.[25]

The CO_2 uptake reactions of the *trans*-$Rh(en)_2(X)(OH)^+$ species were studied under pH conditions where the reverse decarboxylation reactions would not interfere. Eq 4 then simplifies to eq 6 from which k_2 can be calculated since the

$$k_{obsd} = k_2K_1[CO_2]/([H^+] + K_1) \qquad (6)$$

K_1 values are known from pH titrations of the aquo complexes. The pH and temperature dependences of k_{obsd} and k_2, along with the mean value for k_2 at 25 °C and its activation parameters, are summarized in Table VI. The increase in k_2 along the series Cl < Br < I is accompanied by steady increases in $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The nucleophilicity of the oxygen in the hydroxo ligand depends on the M–O bond strength, which, in turn, is governed by the trans-labilizing effect of the halide ion as discussed above. The observed sequence in k_2 and its activation parameters is in agreement with this pattern.

In a previous paper in this series[25] it was demonstrated that a reasonable correlation between log k_2 and pK_1 could be obtained for 14 different CO_2 uptake reactions, in agreement with earlier suggestions.[26] Since then, nine additional CO_2 uptake reactions have been studied,[4,5] and an updated plot of log k_2 vs. pK_1 is presented in Figure 5. The slope (0.16 ± 0.04) and intercept (1.2 ± 0.3) of the calculated line are in very close agreement with the values reported earlier.[25] In the earlier plot[25] only one data point (no. 3) for CO_2 uptake by Rh(III) complexes was included, and it seemed to deviate from the rest of the data (mainly for Co(III)). The inclusion of eight additional data points for various Rh(III) systems illustrates

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Table VI. pH and Temperature Dependence of k_{obsd} and k_2 for the CO_2 Uptake by *trans*-$Rh(en)_2(X)(OH)^+$ [a]

X = Cl, $[Rh(III)]^c = 1 \times 10^{-3}$ M, λ 380				X = Br, $[Rh(III)]^c = 1 \times 10^{-3}$ M, λ 385				X = I, $[Rh(III)]^c = 2.5 \times 10^{-4}$ M, λ 300			
temp, °C	pH	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}	temp, °C	pH	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}	temp, °C	pH	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}
25.0	7.06	2.27 ± 0.14	253 ± 16	25.0	7.29	3.79 ± 0.24	422 ± 27	25.0	7.56	4.22 ± 0.07	496 ± 8
	7.39	2.58 ± 0.05	272 ± 5		7.49	4.09 ± 0.18	439 ± 19		7.80	4.22 ± 0.05	464 ± 5
	7.57	2.62 ± 0.03	271 ± 3		7.74	4.16 ± 0.22	432 ± 23		8.02	3.91 ± 0.07	414 ± 7
	7.74	2.64 ± 0.22	271 ± 22		7.96	3.95 ± 0.24	404 ± 24		8.25	4.06 ± 0.24	420 ± 25
	7.95	2.54 ± 0.21	258 ± 21		8.18	3.73 ± 0.17	378 ± 17		8.38	3.88 ± 0.15	398 ± 15
	8.17	2.47 ± 0.09	249 ± 9		8.35	3.70 ± 0.13	373 ± 13		8.57	3.72 ± 0.18	378 ± 18
	8.33	2.45 ± 0.11	246 ± 11		8.49	3.55 ± 0.20	357 ± 20		8.72	3.82 ± 0.27	386 ± 27
	8.50	2.49 ± 0.09	250 ± 9		8.67	3.57 ± 0.07	358 ± 7				
	8.66	2.75 ± 0.07	275 ± 7								
			mean 260 ± 12				mean 395 ± 33				mean 422 ± 43
6.06	8.66	0.65 ± 0.02	66 ± 2	10.57	8.18	1.01 ± 0.01	102 ± 1	6.19	8.25	0.39 ± 0.01	41 ± 1
9.82		0.88 ± 0.02	88 ± 2	15.18		1.27 ± 0.03	129 ± 3	10.39		0.65 ± 0.02	67 ± 2
14.06		1.06 ± 0.06	106 ± 6	19.80		2.15 ± 0.08	219 ± 9	15.15		1.13 ± 0.04	117 ± 4
19.17		2.09 ± 0.05	209 ± 5	24.80		3.77 ± 0.08	382 ± 8	19.82		1.69 ± 0.04	175 ± 4
25.00		2.75 ± 0.07	275 ± 7	29.46		5.19 ± 0.15	527 ± 15	24.05		2.48 ± 0.08	257 ± 8
								25.00		3.65 ± 0.14	378 ± 14
								29.67		4.93 ± 0.22	510 ± 23
$\Delta H^{\ddagger}$, kcal mol^{-1}		12.5 ± 1.3				15.1 ± 1.1				17.6 ± 0.8	
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		−5.3 ± 4.4				+3.9 ± 3.9				+11.9 ± 2.7	

[a] $[CO_2]^b = 0.01$ M, ionic strength = 0.5 M. [b] From acidification method. See ref 11. [c] Weighed as *trans*-$[Rh(en)_2(X)(OH_2)](ClO_4)_2$.

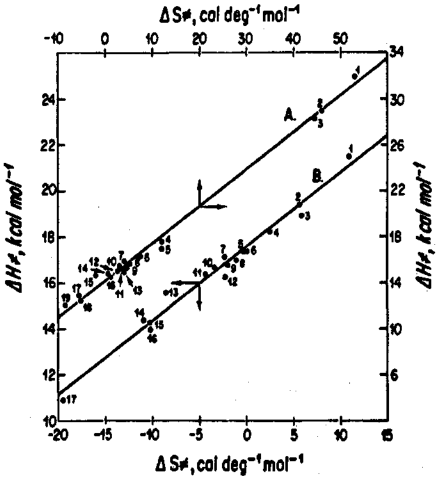

Figure 6. Plots of ΔH^* vs. ΔS^* for the formation and decarboxylation of various transition-metal monodentate carbonate complexes. (A) CO_2 uptake reactions: (1), $Co(tren)(OH)_2^+$;[28] (2), *trans*-$Co(cyclam)(OH)(OH_2)^{2+}$;[25] (3), *trans*-$Co(cyclam)(OH)_2^+$;[25] (4), *trans*-$Rh(en)_2(I)(OH)^+$ (this work); (5), $Rh(NH_3)_5(OH)^{2+}$;[15] (6), *trans*-$Rh(en)_2(OH)_2^+$;[4b] (7), *cis*-$Rh(en)_2(OH)(OH_2)^{2+}$;[4a] (8), *trans*-$Co(NH_3)_4(CN)(OH)^+$;[5] (9), *trans*-$Rh(en)_2(OCO_2)(OH)^+$;[4b] (10), $(\alpha,\beta S)$-$Co(tetren)(OH)^{2+}$;[24] (11), $Co(NH_3)_5(OH)^{2+}$ [11] and *cis*-$Co(en)_2(OH)(OH_2)^{2+}$;[21] (12), *cis*-$Co(cyclam)(OH)_2^+$;[25] (13), *trans*-$Rh(en)_2(Br)(OH)^+$ (this work); (14), *cis*-$Co(cyclam)(OH)(OH_2)^{2+}$;[25] (15), $Co(tren)(OH)(OH_2)^{2+}$;[28] (16), *cis*-$Rh(en)_2(OH)_2^+$;[4a] (17), *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$;[4b] (18), *trans*-$Rh(en)_2(Cl)(OH)^+$ (this work); (19), *cis*-$Cr(C_2O_4)_2(OH)(OH_2)^{2-}$.[29] (B) Decarboxylation reactions: (1), *trans*-$Co(NH_3)_4(CN)(OCO_2H)^+$;[5] (2), *cis*-$Rh(en)_2(OCO_2H)(OH_2)^{2+}$;[4a] (3), $Ir(NH_3)_5(OCO_2H)^{2+}$;[15] (4), *trans*-$Rh(en)_2(Br)(OCO_2H)^+$ (this work); (5), *trans*-$Rh(en)_2(Cl)(OCO_2H)^+$ (this work); (6), *trans*-$Co(en)_2(Cl)(OCO_2H)^+$;[6] (7), *trans*-$Rh(en)_2(I)(OCO_2H)^+$ (this work); (8), $Rh(NH_3)_5(OCO_2H)^{2+}$;[15] (9), $Co(NH_3)_5(OCO_2H)^{2+}$;[11] (10), *trans*-$Co(en)_2(NH_3)(OCO_2H)^{2+}$;[23] (11), *cis*-$Co(en)_2(NH_3)(OCO_2H)^{2+}$;[23] (12), *trans*-$Rh(en)_2(OCO_2H)_2^+$;[4b] (13), $Co(tetren)(OCO_2H)^{2+}$;[24] (14), *cis*-$Co(en)_2(OCO_2H)(OH_2)^{2+}$;[21] (15), $Co(tren)(OCO_2H)(OH_2)^{2+}$;[22] (16), *trans*-$Co(en)_2(OCO_2H)(OH_2)^{2+}$;[21] (17), *trans*-$Rh(en)_2(OCO_2H)(OH_2)^{2+}$.[4b]

that this is not the case, and no significant dependence on the nature of the metal ion is observed, including complexes of Ir(III) (no. 1), Cu(II) (no. 2), Zn(II) (no. 9), and Cr(III) (no. 17). The rate of CO_2 uptake depends on the nucleophilicity of the "bound" hydroxide ion[26] and thus correlates with the strength of the O–H bond of the corresponding aquo complex.

Finally, the activation parameters for the formation (CO_2 uptake) and decarboxylation reactions of monodentate carbonato complexes are presented as isokinetic plots in Figure 6. The significance of such plots has been discussed in detail elsewhere[30-33] and the lines fit eq 7,[32] where ΔG_0^* is the intrinsic free energy of activation and β_0 is the isokinetic temperature.

$$\Delta H^* = \Delta G_0^* + \beta_0 \Delta S^* \qquad (7)$$

The slopes of the lines in Figure 6, which give β_0 values of 319 ± 6 and 320 ± 12 K, are identical within experimental error for both the CO_2 uptake (line A) and decarboxylation (line B) processes. The corresponding intrinsic free energies, given by the intercepts, are 14.3 ± 0.1 and 17.5 ± 0.1 kcal mol^{-1}, respectively. Since no significant deviation from lines A or B is observed for any of the data points, we can conclude that a common mechanism is operative in each of the processes.[30] Also, the reaction mechanisms must not involve the formation or breakage of any metal–ligand bonds, since, if such were the case, different isokinetic plots of similar slope but varying intercepts would have been obtained for different metal ions.[32] We are thus provided with a further confirmation of our assumption that all the reactions referred to in Figure 6 must proceed via secondary oxygen–carbon bond formation or breakage.

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Registry No. *trans*-$Rh(en)_2(Cl)(OH_2)^{2+}$, 15337-41-4; *trans*-$Rh(en)_2(Cl)(OH)^+$, 53775-44-3; *trans*-$Rh(en)_2(Cl)(OCO_2)$, 75010-88-7; *trans*-$Rh(en)_2(Br)(OH_2)^{2+}$, 15337-42-5; *trans*-$Rh(en)_2(Br)(OH)^+$, 55683-55-1; *trans*-$Rh(en)_2(Br)(OCO_2)$, 75010-89-8; *trans*-$Rh(en)_2(I)(OH_2)^{2+}$, 15379-03-0; *trans*-$Rh(en)_2(I)(OH)^+$, 38542-37-9; *trans*-$Rh(en)_2(I)(OCO_2)$, 75010-90-1; *trans*-$[Rh(en)_2Cl(OH_2)](ClO_4)_2$, 55683-58-4; *trans*-$[Rh(en)_2Br(OH_2)](ClO_4)_2$, 55683-59-5; *trans*-$[Rh(en)_2I(OH_2)](ClO_4)_2$, 55683-60-8; CO_2, 124-38-9; *trans*-$Rh(en)_2(Cl)(OCO_2H)^+$, 75010-91-2; *trans*-$Rh(en)_2(Br)(OCO_2H)^+$, 75010-92-3; *trans*-$Rh(en)_2(I)(OCO_2H)^+$, 75010-93-4.

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