The interactions with thioxane ($S(CH_2CH_2)_2O$), a sulfur-oxygen base which shows no steric preferences, were observed and found to involve exclusively sulfur coordination. It appears, therefore, that I, II, and III are all "soft"[15] in the sense of preference for sulfur coordination over oxygen. It also appears that the relative order of this preference in conjunction with the observed stabilities of aquo complexes and measured rates of base exchange is I > II > III, consistent with an order of electron donation by the equatorial chelate of $(dh)_2$ > tmed > tim.

Experimental Section

Materials. Complexes were prepared following established procedures or modifications of such procedures. All adducts unless otherwise stated were found to be stable in the solid state and were characterized by nmr and elemental analysis. Analytical results for adducts used in nmr studies are given in the microfilm edition.

Solvents and Bases. All solvents were distilled and stored over freshly activated Linde 4A molecular sieves. The observed boiling range of the nitrobenzene was 207–209° and for methylene chloride 39.5–40.5°. 3-Fluoropyridine was generously donated by the Chemical Division of the Olin Corp., Stanford, Conn. 06904, and was used without further purification. 1-(2-Trifluoromethylphenyl)imidazole was prepared following a published procedure.[16] Trimethyl phosphite was freshly distilled (111–112°). All other bases were reagent grade and stored over molecular sieves.

Syntheses. Adducts of methylatobis(dimethylglyoximato)cobalt(III) were prepared from the ligand-free dimer, which in turn was prepared by removal of water from methylaquocobaloxime by heating *in vacuo* at 80° for several hours. The methylaquocobaloxime was prepared by previously described procedures.[17] To prepare the adducts, base was added either to the dimer itself, and excess base evaporated off, or to a benzene solution of the dimer, followed by removal of the solvent to give crystalline solids. Details regarding syntheses of several tmed and (tim) complexes are given in the microfilm edition,[18] as are the analytical results for all compounds studied.

(15) R. G. Pearson, *J. Amer. Chem. Soc.*, 85, 3533 (1963).
(16) A. L. Johnson, J. C. Kauer, D. C. Sharma, and R. I. Dorfman, *J. Med. Chem.*, 12, 1024 (1969).
(17) G. N. Schrauzer, *Inorg. Syn.*, 11, 61 (1968).
(18) See paragraph at end of paper regarding supplementary material.

Nmr spectra were obtained and line shape analyses performed as described elsewhere.[4,19,20]

(19) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 88, 4134 (1966).
(20) R. J. Guschl, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1973.

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. VI. Rhodium(III) and Iridium(III) Carbonatopentaammine Complex Ions[1]

D. A. PALMER and G. M. HARRIS*

Preparative procedures have been devised for the previously unreported complex salts $[Rh(NH_3)_5CO_3]ClO_4 \cdot H_2O$ and $[Ir(NH_3)_5CO_3]ClO_4$. Kinetic studies have been made of the acid-catalyzed decarboxylation of these compounds in aqueous solution. The kinetics of carbon dioxide uptake by the hydroxo ions $Rh(NH_3)_5OH^{2+}$ and $Ir(NH_3)_5OH^{2+}$ to form carbonato complex ions has also been investigated. At 25° and $I = 0.5$ M, the aquation rate constants k_1 (see eq 1 below) are 1.13 and 1.45 sec^{-1} for the Rh(III) and Ir(III) carbonato species, respectively, while the rate constants k_2 for CO_2 uptake by the corresponding hydroxo complexes are 470 and 590 M^{-1} sec^{-1}, respectively. Temperature-dependence parameters have been determined and mechanistic conclusions drawn on the basis of comparisons with previously published data concerning the kinetics of various reactions of Co(III), Rh(III), and Ir(III) complex ions.

Introduction

It has frequently been found that comparisons of the ki-

(1) (a) This research was reported in preliminary form at the Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 11-13, 1971. (b) Part V: E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Amer. Chem. Soc.*, 95, 4169 (1973).

netics of reactions of complex ions which differ only in the identity of the central metal ion provide valuable insights into their properties. Such studies have been made, for example, of various reactions of complex ions of the type $M(NH_3)_5X^{n+}$, where M = Co(III), Rh(III), or Ir(III), and X is a ligand which differs from NH_3. A classic comparison

of this type is provided as a result of some very early work[2] on the acidic hydrolysis (aquation) of the halopentaammine ions where X = Cl or Br. Subsequent studies concern the formation, isomerization, and aquation of the nitrosopenta-ammine series[3,4] and the aquation of the nitro,[4] acetato,[5] fluoroacetato,[5] and isocyanatopentaammine[6] complexes. Basic hydrolysis of the fluoroacetato series[7] and solvent water exchange with the aquopentaammine series[8] have also been examined. Two general conclusions as to the kinetics of such reactions may be drawn from this body of work: When metal-ligand bond making or bond fission is not direct-ly involved in the process, there is little variation in the rate constants in proceeding along the series Co(III), Rh(III), and Ir(III) complexes. However, when the metal-ligand bond is made or broken, the rate constants for the reactions of the complexes fall in the order Co(III) $\geqslant$ Rh(III) $\gg$ Ir(III).

In view of the proposed mechanism for the aquation-for-mation equilibration of the $Co(NH_3)_5CO_3^+$ ion,[1,9] one would expect the corresponding process for the Rh(III) and Ir(III) congeners to be governed by rate constants of a mag-nitude very similar to those of the Co(III) system. The pres-ent study was undertaken to test this assumption. Procedures have been devised to prepare the previously unsynthesized compounds $[Rh(NH_3)_5CO_3]ClO_4 \cdot H_2O$ and $[Ir(NH_3)_5CO_3]$-ClO_4, and the results of the rate studies confirm the propos-ed mechanism of uptake and release of carbon dioxide in systems of the stoichiometry $M(NH_3)_5OH^{2+} + CO_2 \rightleftarrows M(NH_3)_5CO_3^+ + H^+$.

Experimental Section

Materials. All chemicals used were of reagent grade.

$[Rh(NH_3)_5OH_2](ClO_4)_3$ was prepared by the method of Cunning-ham, House, and Powell[10] and $[Ir(NH_3)_5OH_2](ClO_4)_3$ by the method of Borghi and Monacelli.[8]

Carbonatopentaamminerhodium(III) Perchlorate. Solid Li_2CO_3 was added to a stirred solution containing 1 g of $[Rh(NH_3)_5OH_2]$-$(ClO_4)_3$ in 20 ml of water until a pH of 8.5 was attained. After stir-ring for 10 min the solution was evaporated to dryness at room temp-erature using a rotatory evaporator. The solid residue was washed thoroughly with ethanol. The complex was recrystallized twice from a minimum volume of water saturated with CO_2 and then precipitated with ethanol. The pale yellow crystals were washed with ethanol and ether and vacuum-dried at 40°. *Anal.*[11] Calcd for $[Rh(NH_3)_5CO_3]$-$ClO_4 \cdot H_2O$: C, 3.28; H, 4.69; N, 19.15; Cl, 9.70. Found: C, 3.27; H, 4.74; N, 18.95; Cl, 9.73.

Carbonatopentaammineiridium(III) Perchlorate. This compound was prepared by the same method described for the preparation of $[Rh(NH_3)_5CO_3]ClO_4 \cdot H_2O$. *Anal.*[11] Calcd for $[Ir(NH_3)_5CO_3]ClO_4$: C, 2.75; H, 3.46; N, 16.03; Cl, 8.12. Found: C, 2.68; H, 3.31; N, 15.74; Cl, 7.96.

Determination of Acid Dissociation Constants. The pK values for the acid dissociation of both $Rh(NH_3)_5OH_2^{3+}$ and $Ir(NH_3)_5OH_2^{3+}$ were determined at 25° by titration with 0.02 M NaOH, with com-

(2) D. R. Stranks, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 2, Table IX, p 128, and references quoted therein.

(3) F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1, 1 (1962).

(4) (a) B. E. Crossland and P. J. Staples, *J. Chem. Soc. A*, 2853 (1971); (b) D. L. Klimek, B. Grossman, and A. Haim, *Inorg. Chem.*, 11, 2382 (1972).

(5) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 1241 (1962).

(6) (a) R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 9, 1567 (1970); (b) P. C. Ford, *ibid.*, 10, 2153 (1971).

(7) (a) R. B. Jordan and H. Taube, *J. Amer. Chem. Soc.*, 88, 4406 (1966); (b) F. Monacelli, *J. Inorg. Nucl. Chem.*, 29, 1079 (1967).

(8) (a) E. Borghi and F. Moncelli, *Inorg. Chim. Acta*, 5, 211 (1971); (b) T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 94, 8357 (1972).

(9) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 90, 6360 (1968).

(10) A. J. Cunningham, D. A. House, and H. K. J. Powell, *Aust. J. Chem.*, 23, 2375 (1970).

(11) Microanalyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

Table I. Spectral Data for Various Rh(III) and Ir(III) Complex Ions

Complex ion	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	λ_{min}, nm	ϵ_{min}, M^{-1} cm^{-1}
$Rh(NH_3)_5CO_3^+$	325	178	294	118
$Rh(NH_3)_5OH^{2+}$	319	132	292	109
$Rh(NH_3)_5OH_2^{3+}$	314	112	283	76
$Ir(NH_3)_5CO_3^+$	262	125	247	109
$Ir(NH_3)_5OH^{2+}$	238	298	270 sh	97
$Ir(NH_3)_5OH_2^{3+}$	258	87	242	75

plex concentrations of about 6×10^{-3} M and with both reactants at an ionic strength of 0.5 M. The pK's for $Rh(NH_3)_5OH_2^{3+}$ and $Ir(NH_3)_5OH_2^{3+}$ were found to be 6.78 ± 0.03 and 6.70 ± 0.03 respec-tively. They are independent of the nature of the anion (*i.e.*, chlo-ride, nitrate, or perchlorate) used to make up the ionic strength. Previous reports indicate the pK of the aquorhodium complex[12] to be 6.39 at 25° and an ionic strength of 0.2 M, while that for Ir-$(NH_3)_5OH_2^{3+}$ is quoted as 6.5 at virtually zero ionic strength.[8]

The pK of $Rh(NH_3)_5CO_3H^{2+}$ was determined by rapidly dis-solving 0.0914 g of the carbonato complex (2.5×10^{-4} mol) in 50 ml of 2.5×10^{-3} M $HClO_4$ or HNO_3 (1.25×10^{-4} mol), thermo-stating at 25° and then following the resulting pH change over a period of *ca.* 25 sec on a high-speed recorder. Back-extrapolation of pH to zero time gave the same result in both acids, *i.e.*, pK = 6.9 ± 0.1. No attempt was made to fix the ionic strength in these determinations, which are at best only approximate.

Spectra. Infrared spectra were measured on a Beckman IR5A spectrometer using KBr disks. Both the rhodium and iridium car-bonato complexes exhibit CO stretches at 1455 ± 5 and 1370 ± 5 cm^{-1}, which are characteristic of unidentate coordinated carbonate.[13]

Absorption spectra in the uv-visible range were measured using a Cary 15 spectrophotometer. The spectra of the carbonato com-plexes were measured in a sodium bicarbonate solution at pH 8.5 to inhibit hydrolysis. The observed maximum and minimum values of the molar absorption coefficients of the various complexes at the ap-propriate wavelengths are given in Table I.

Rate Measurements. The kinetics of the aquation of the car-bonato species were investigated at 25° and at an ionic strength of 0.5 M ($NaNO_3$) with complex concentrations generally of the order of 2.5×10^{-3} M. Reactions of the rhodium and iridium complexes were monitored at the wavelengths of 340 and 260 nm, respectively. The majority of the results were obtained using a Durrum stopped-flow spectrophotometer in the manner previously described.[1,9] How-ever, for pH >9 a Cary 15 spectrophotometer was generally used, since the reactions became quite slow in this range.

For pH values less than 7 a McIlvaine phosphate-citric acid buf-fer[14] was used, while at higher pH a number of different buffer sys-tems[15] were used: boric acid-borax-NaOH, Tris base-Tris maleate, Tris base-Tris hydrochloride, bicarbonate-carbonate. All pH measurements were made with a Beckman Research Model pH meter.

For runs in which carbonic anhydrase was added (usually in 2-5 micromolar amounts) NaCl was substituted for $NaNO_3$ as the inert electrolyte because nitrate ion has an inhibiting effect on the en-zyme's activity.[16]

The rate of CO_2 uptake by $Rh(NH_3)_5OH^{2+}$ was determined by means of the previously described techniques.[1] The "*equilibration method*" involves mixing equivolumes of a 0.1 M $NaNO_3$ solution containing carbonic anhydrase and a solution of the aquo complex and the desired buffer. In the "*acidification method*," a weighed amount of $NaHCO_3$ is "titrated" with 1 M HCl to pH $\simeq$3 and the reaction is initiated by mixing the resulting CO_2 solution with a solution containing aquo complex and a relatively concentrated buf-fer.

Results and Discussion

The overall carboxylation-decarboxylation process for

(12) A. J. Poe, K. Shaw, and M. J. Wendt, *Inorg. Chim. Acta*, 1, 371 (1967).

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordina-tion Compounds," 2nd ed, Wiley, New York, N. Y., 1970, pp 169-171.

(14) P. J. Elving, J. M. Markovitz, and J. Rosenthal, *Anal. Chem.*, 28, 1179 (1956).

(15) R. M. C. Dawson, W. H. Elliott, and K. M. Jones, Ed., "Data for Biochemical Research," Oxford University Press, London, 1959, pp 205, 207. (Note that "Tris" $\equiv$ tris(hydroxymethyl)amino-methane.)

(16) S. Lindskog, *J. Biol. Chem.*, 238, 945 (1963).

the pentaamminecarbonatocobalt(III) species is well described by the mechanism previously proposed,[1b] which can be restated in the more general form

$$M(NH_3)_5OH^{2+} + CO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(NH_3)_5CO_3H^{2+}$$

(1)
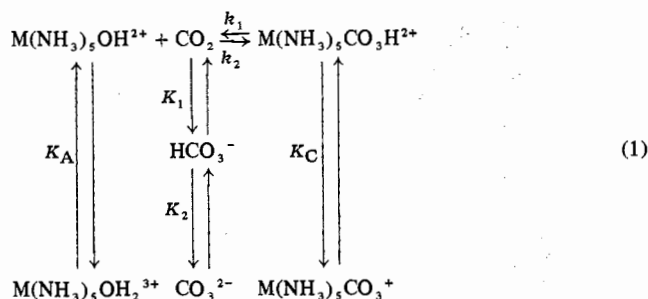
For present purposes, M is taken to represent Rh(III) and Ir(III) as well as Co(III). The K's are the acid dissociation constants of the various species identified, and k_1 and k_2 are the rate constants for CO_2 elimination and uptake, respectively. In buffered solutions containing excess carbonate, the observed rate constant corresponding to the above mechanism is given by (h = hydrogen ion concentration, b = total carbonate concentration)

$$k_{obsd} = k_1\left(\frac{h}{h + K_C}\right) + k_2b\left(\frac{K_A}{h + K_A}\right)\left(\frac{h^2}{h^2 + K_1h + K_1K_2}\right)$$

(2)

In the absence of added carbonate ($b = 0$), only decarboxylation of the pentaamminecarbonato complexes is observable up to pH 9, and the observed pseudo-first-order rate constant is described by the first term on the right of eq 2.

An accurate analysis of the data was achieved by least-squares procedure, using the linear reciprocal form of the appropriate rate law, *viz.*

$$1/k_{obsd} = 1/k_1 + K_C/k_1h$$

(3)

The data obtained for the hydrolysis of the Rh(NH_3)_5-CO_3^+ and Ir(NH_3)_5CO_3^+ species at 25° is presented in this reciprocal form in Figure 1. These plots yield the values of k_1 and K_C recorded in Table II, the error limits of each being indicated in the table. A series of runs at pH ⩽3 (where $k_{obsd} = k_1$) over a range of temperatures enabled estimation of the activation parameters for k_1, which also appear in Table II, together with values of their standard deviations. The corresponding data for the previously studied cobalt(III) analog[9,17] are also included for comparison purposes.

It is abundantly clear from the data presented in Figure 1 and Table II that the three acid-catalyzed decarboxylation reactions under consideration are all equally well described by the same mechanism, one which involves no metal–oxygen bond scission. In this respect, the reactions are analogous to the hydrolyses of the corresponding nitrosopentaammine complexes,[4] where the rate constants for the three complexes are within a factor of 4 of one another. In direct contrast, however, the release of nitrite from the nitritopentaammine complexes exhibits a large decrease in rate constant[4] in going from Rh to Ir, in keeping with the concept of metal–oxygen bond breakage in the rate-determining step in these reactions.

---

(17) At pH 3 and I = 0.5 M (NaNO_3), k_1 has values of 0.42, 0.65, and 1.10 sec⁻¹ at 15, 20, and 25°, respectively: K. Hyde and D. A. Palmer, unpublished work. The quoted temperature parameters were obtained by a least-squares analysis of all our data between 7 and 37° on this reaction (see ref 9).
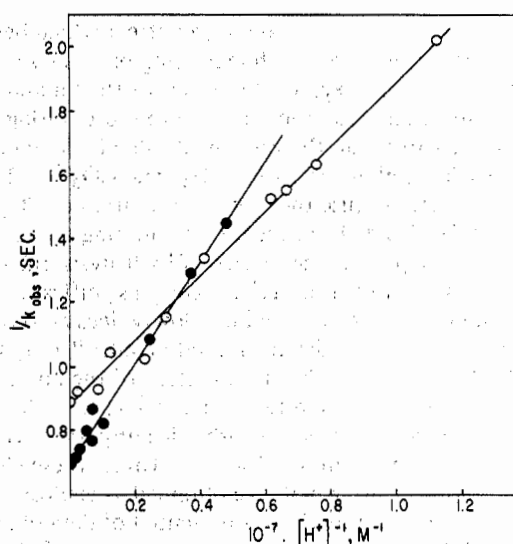
Figure 1. Double-reciprocal plot of variation of observed rates of aquation of rhodium(III) and iridium(III) carbonato complexes with hydrogen ion concentration at 25° and I = 0.5 M: ○, Rh(NH_3)_5-CO_3^+; ●, Ir(NH_3)_5CO_3^+.

Table II. Rate Parameters for Decarboxylation of M(NH_3)_5CO_3^+ at 25° and I = 0.5 M

M	k_1, sec⁻¹	$10^7K_C, M$	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, cal/deg mol
Co(III)	1.10 ± 0.05	2.0 ± 0.1	16.8 ± 0.2	−2 ± 1
Rh(III)	1.13 ± 0.06	1.1 ± 0.1	17.0 ± 0.5	−1 ± 1
Ir(III)	1.45 ± 0.07	1.6 ± 0.1	19.0 ± 0.5	6 ± 1

It is noted that the rate constants of aquation for both the carbonatopentaammine and nitrosopentaammineiridium(III) complexes are slightly larger than for the corresponding rhodium(III) congeners. This may be an indirect effect of the expected strengthening of the metal–oxygen bond in changing from rhodium(III) to iridium(III), as evidenced by the much slower release of ligand bound to Ir(III) as compared to Rh(III) when metal–oxygen bond cleavage is involved.[8] It is well known[18] that the symmetrical COO infrared stretching frequency of unidentate carbonato ligand decreases as the strength of the metal–oxygen bond increases, indicating a weakening of the acyl oxygen–carbon bond and thereby facilitating the dissociation of the CO_2 fragment from the carbonato ligand.

Some runs were made at 25° and pH 3.12 (where $k_{obsd} = k_1$) to determine the effects of ionic strength variation and the nature of added salt on this rate parameter for the Rh(III) complex. The results were as given below.

Ionic strength, M	0.1	0.2	0.5	1.0	0.5	0.5
Salt used	NaNO_3	NaNO_3	NaNO_3	NaNO_3	NaCl	NaClO_4
Obsd rate const, sec⁻¹	1.10	1.12	1.13	1.15	1.14	1.12

All the values of k_1 are seen to be identical within experimental error, as is to be expected, since this constant describes the unimolecular decomposition of the fully protonated intermediate M(NH_3)_5CO_3H^{2+}. It may well be, however, that this independence of ionic strength would not be observed at higher pH's where K_C is an important factor in the rate expression (see eq 2), since this latter constant describes an equilibrium between charged species. However, this possibility has not been put to test at this time.

During the present study, it was noted that at pH >6.5, the semilogarithmic absorbance *vs.* times plots were no longer

(18) Reference 13, pp 222–223, 233.

linear over an extended time interval, an effect which became more and more pronounced with increasing pH. This apparent anomaly can be explained in terms of the building up of the concentration of carbon dioxide produced during the hydrolysis to greater than the very small value it should have if completely in equilibrium with HCO_3^- and CO_3^{2-}. This buildup is possible because the rates of hydration of CO_2 by reaction with OH^- and H_2O become rate limiting at high pH.[19] As a consequence, the reverse of hydrolysis, the reaction of CO_2 with $M(NH_3)_5OH^{2+}$, becomes significant and a pseudoequilibrium is reached which slowly decays to the true thermodynamic equilibrium at a rate controlled by the rate of CO_2 hydration. This interpretation of the nonlinearity of the rate plots was tested by making runs in the presence of micromolar quantities of carbonic anhydrase, which catalyzes CO_2 hydration dramatically.[20] Under these circumstances, normal linear plots are obtained as is illustrated in Figure 2, where a comparison is presented of data obtained for $Co(NH_3)_5CO_3^+$ hydrolysis in the presence and absence of enzyme. Additional runs conducted at pH <6 in the presence of enzyme demonstrated that it does not itself catalyze the hydrolysis of the carbonato complex ion. It therefore now seems reasonable to conclude that part of the discrepancy between the hydrolysis rate constants derived from the data on the hydrolytic equilibration of $Co(NH_3)_5$-CO_3^+ at pH 8.5–9.4 obtained by Francis and Jordan[21] and the lower pH data from this laboratory[9] can be ascribed to the fact that the former workers did not utilize the enzyme so that their measured rates were determined at least to some extent by the rate of CO_2 hydration.

At pH 11, base hydrolysis of the carbonato complexes becomes the only observable process, and some runs were made at 25° and $I = 1.0 M$ using the Rh(III) species and Ir(III) species in order to permit a comparison with similar experiments previously reported for the Co(III) analog.[21] The value of the second-order rate constant, for the Ir(III) complex k_{OH}, is negligible under these conditions, indicating an upper limit of about $10^{-7} M^{-1}$ sec^{-1}. For the Rh(III) and Co(III) cogeners, k_{OH} has values of 2.4×10^{-6} and $2.3 \times 10^{-3} M^{-1}$ sec^{-1}, respectively. The difference in k_{OH} values between the Rh(III) and Co(III) complexes is of the same order of magnitude as has been observed for complexes of the type $M(NH)_5X^{2+}$, where X = Cl, Br, or I.[22] However, the corresponding factor for the fluoroacetatopentaammine complexes, which, like the carbonato species, involve metal-oxygen bonding to the reactive ligand, is only about 20 in favor of the Co(III) compound.[7]

Recently, a study has been completed of the kinetics of uptake of carbon dioxide by the aquopentaamminecobalt-(III) complex ion over a broad pH range.[1b] Similar experiments have now been performed at 25° with the rhodium-(III) complex within the pH range 7.8–10.2, yielding the data shown in Table III. For most of the runs, the conventional "equilibration method" starting with aquopentaammine salt was employed (see Experimental Section), while for several runs (as indicated in the table), the starting material was the carbonato complex (*i.e.*, the equilibration was
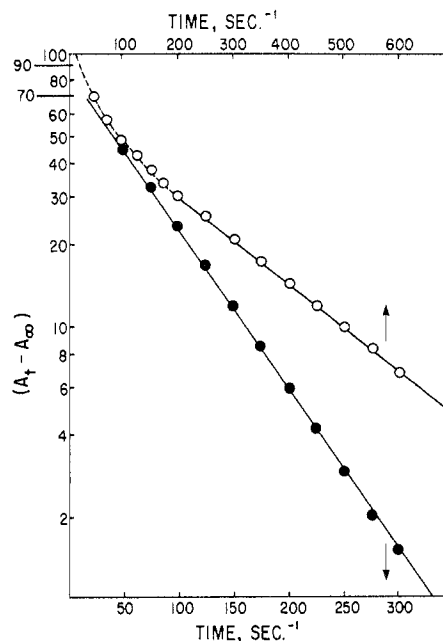
(19) R. E. Forster, J. T. Edsall, A. B. Otis, and F. J. W. Roughton, Ed., "CO$_2$: Chemical, Biochemical, and Physiological Aspects," National Aeronautics and Space Administration, Washington, D. C., 1969, pp 20–21. (Obtainable from U. S. Government Printing Office, Washington, D. C.)

(20) Reference 19, p 101 ff.

(21) D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, **89**, 5591 (1967).

(22) C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, **89**, 3141 (1967).

Figure 2. Hydrolysis of $Co(NH_3)_5CO_3^+$ at pH 8.35, 25°, and $I = 0.5 M$. A_t and A_∞ are the relative absorbances at time t and at "infinite" time, respectively: ○, without enzyme; ●, with enzyme.

Table III. Rate of Uptake of CO_2 by $Rh(NH_3)_5OH^{2+}$ at 25° Using the Equilibration Method ([Total Carbonate] = 0.05 M; $I = 0.5 M$; Tris Buffer)

Run no.	pH	k_{obsd}, sec^{-1}	$10^{-2}k_2, M^{-1}$ sec^{-1}
1	7.06	2.1_3	5.8
2	7.11	1.7_0	4.6
3	7.35	1.2_6	5.1
4	7.50	0.85_2	4.4
5^a	7.71	0.57_5	4.4
6^a	7.87	0.43_9	4.9
7^b	8.09	0.30_2	7.3
8^a	8.10	0.26_2	4.7
9	8.13	0.19_4	3.3
10	8.16	0.22_3	4.5
11^c	8.23	0.13_7	2.7
12^a	8.37	0.13_9	4.5
13^a	8.56	0.09_3	4.8
14^a	8.67	0.069	4.5
15	8.99	0.036	5.3
16^b	9.09	0.050	6.0
17^b	9.18	0.020	3.8
18^b	9.91	0.0046	7.7
		Mean	4.9 ± 1.2

^{a} Starting material was $Rh(NH_3)_5CO_3^+$. ^{b} Carbonate self-buffering only. [Total carbonate] was 0.50, 0.096, 0.06, and 0.08 M in runs 7, 16, 17, and 18, respectively. ^{c} No enzyme added. k_{obsd} estimated from initial slope of plot (see text).

carried out in the direction of carbon dioxide release). In both types of experiment, k_{obsd} is determined by the complete expression already given (eq 2), by means of which the values of k_2 can be calculated by use of the appropriate known constants.[23] Run 7 again illustrates the modest accelerating influence of high concentration of added carbonate, previously observed in the Co(III) study,[1b] and run 11 gives a low value for k_2 as to be expected in a situation where the CO_2–HCO_3^-–CO_3^{2-} equilibrium is not rapidly maintained due to absence of enzyme. Otherwise the rate

(23) For these calculations we employed the following known values of the constants: $k_1 = 1.13$ sec^{-1} (Table II), $K_C = 1.1 \times 10^{-7}$ (Table II), $K_A = 1.7 \times 10^{-7}$ (see Experimental Section), $K_1 = 8.7 \times 10^{-7}$ (ref 1b), and $K_2 = 1.6 \times 10^{-10}$ (ref 1b).

Table IV. Rate of Uptake of CO_2 by $Rh(NH_3)_5OH^{2+}$ at 25° Using the Acidification Method ($[CO_2] = 0.01\ M; I = 0.5\ M$; Tris Buffer)

Run no.	pH	k_{obsd}, sec^{-1}	$10^{-2}k_2, M^{-1}$ sec^{-1}
1	6.76	1.2_9	2.7
2^a	7.19	4.5_0	3.1
3^a	7.29	4.8_6	3.2
4	7.40	2.9_2	3.6
5	7.67	3.5_1	3.9
6	7.72	2.9_3	3.3
7^b	7.99	3.8_7	2.8
8	8.03	3.5_4	3.7
9	8.67	3.9_0	4.0
			Mean 3.4 ± 0.5

^{a} Initial $[CO_2] = 0.02\ M$. ^{b} Saturated CO_2 solution used as one reactant. Concentration ($\sim0.015\ M$) estimated from gas solubility data.

data are quite consistent, and one derives a mean value for the rate constant for uptake of carbon dioxide by hydroxopentaamminerhodium(III) complex ion of $k_2 = (4.9 \pm 1.2) \times 10^2\ M^{-1}$ sec^{-1} at 25° and $I = 0.5\ M$. It is noted (Table III) that even at pH $\sim$10, where the CO_2 concentration is down to a very low and somewhat indefinite value,[24] the figures deduced for k_2 are quite consistent with those obtained at higher acidities. This suggests that possible direct reactions of HCO_3^- or CO_3^{2-} with the aquopentaammine complex are negligibly slow as compared to CO_2 uptake. This conclusion is further supported by an additional experiment in which $Rh(NH_3)_5OH^{2+}$ was treated with 0.5 $M\ Na_2CO_3$ (pH $\sim$12) where only a slight initial change in absorbance was noted,[25] with no evidence of further reaction over a period of 1 hr at 25°.

A series of nine runs with the aquorhodium complex by means of the "acidification method" (see Experimental Section) was carried out at 25°, with the results given in Table IV. The values of k_2 obtained in this manner (average $k_2 = (3.4 \pm 0.5) \times 10^2\ M^{-1}$ sec^{-1}) are somewhat lower than those recorded in Table III but not significantly so. Since the reactant in these later experiments is pure CO_2, rather than CO_2 in equilibrium with HCO_3^- and CO_3^{2-}, the slightly different rate constant may be the result of an ion-pairing effect in solutions containing appreciable concentrations of ionic carbonate, as suggested above in connection with the "equilibration method" data. A similar small discrepancy was noted in the earlier study utilizing $Co(NH_3)_5OH^{2+}$ as reactant (see Tables I and II, ref 1b). An alternative explanation is that the discrepancy may derive from small losses of CO_2 by escape of a small fraction of the gas from the reactant solution prior to making the run, a difficulty which it was found almost impossible to control.

(24) The data on $\bar{K}_2$ at $I = 0.5\ M$ is not well established (see ref 1b), thus preventing accurate estimation of the CO_2 concentration at high pH (see eq 2).

(25) Possibly this is an indication of ion-pair formation between the doubly charged aquo complex cation and CO_3^{2-} anion.

Table V. Variation of Rate of CO_2 Uptake by $Rh(NH_3)_5OH^{2+}$ with Temperature

Temp, °C	pH	$10^{-2}k_{obsd},^a$ sec^{-1}	$10^{-2}k_2,^b$ M^{-1} sec^{-1}
15.1	8.46	7.82	1.57
19.9	8.33	10.7	2.72
25.0	Various^c		4.90^c
29.9	8.08	33.8	7.91
34.9	7.96	62.7	10.7

^{a} Average of three determinations ($\pm5\%$ error). ^{b} Computed by procedure used for Table III, utilizing values of K_A, K_C, K_1, and K_2 approximately adjusted for the temperature variation (see footnote 20 in ref 1b). ^{c} See data given in Table III.

Activation parameters were estimated for CO_2 uptake by $Rh(NH_3)_5OH^{2+}$ on the basis of the limited temperature dependence study recorded in Table V. The corresponding parameters are $\Delta H^{\ddagger} = 17 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 12 \pm 3$ cal deg^{-1} mol^{-1}, as compared to 15.3 ± 0.9 and 3.6 ± 3.0, respectively, for the Co(III) congener.[1b] The near-equivalence of these constants is good evidence for the previously assumed identity of mechanism for these reactions.

A few runs were made to determine the value of k_2 for the complex ion $Ir(NH_3)_5OH^{2+}$ by the equilibration method at 25° and $I = 0.5\ M$. For pH's of 7.34, 8.08, and 8.68 and total carbonate concentrations of 0.0535, 0.0498, and 0.0536 M, respectively, the k_{obsd} values were 1.53, 0.318, and 0.084 sec^{-1}, respectively. The corresponding mean value of the derived rate constant[26] is $k_2 = 5.9 \times 10^2\ M^{-1}$ sec^{-1}. This is seen to be a little larger than the value for the Rh(III) complex (Table IV) and nearly 3 times that for the Co(III) species[1b] ($2.2 \times 10^2\ M^{-1}$ sec^{-1}). This minor trend in rate constants again reflects the order of the metal–oxygen bond strength in the complexes (Ir > Rh > Co) and may be the result of secondary influences such as a decreasing basicity of the coordinated oxygen of the M–O–H group in parallel with the increasing M–O bond strength.

Registry No. [$Rh(NH_3)_5CO_3$]ClO_4, 50600-90-3; [$Rh(NH_3)_5OH_2$]-($ClO_4)_3$, 15611-81-1; [$Ir(NH_3)_5CO_3$]ClO_4, 50600-92-5; $Ir(NH_3)_5$-OH_2^{3+}, 29589-08-0; $Rh(NH_3)_5OH_2^{3+}$, 15337-79-8; $Rh(NH_3)_5CO_3^+$, 50600-89-0; $Rh(NH_3)_5OH^{2+}$, 26214-91-5; $Ir(NH_3)_5CO_3^+$, 50600-91-4; $Ir(NH_3)_5OH^{2+}$, 44439-82-9; $Co(NH_3)_5CO_3^+$, 15844-68-5; $Rh(NH_3)_5$-CO_3H^{2+}, 50600-93-6.

(26) Using eq 2 and the appropriate values of the other constants, as already explained for the Rh(III) analog.[23]