in consonance with the postulates of absolute reaction rate theory, we have

$$R = \frac{k_{\mathrm{R1}}}{k_{\mathrm{R2}}}e^{\Delta G_{12}/kT} = \frac{e^{-G_{\mathrm{R1}}^{\ddagger}/kT}}{e^{-G_{\mathrm{R2}}^{\ddagger}/kT}e^{-\Delta G_{12}/kT}}$$

Multiplying top and bottom by $e^{-G_0^{\ddagger}/kT}$ gives us

$$R = \frac{e^{-G_{\mathrm{R1}}^{\ddagger}/kT}e^{-G_0^{\ddagger}/kT}}{e^{-G_{\mathrm{R2}}^{\ddagger}/kT}e^{-\Delta G_{12}/kT}e^{-G_0^{\ddagger}/kT}} = \frac{k_1}{k_2}$$

Thus the relative rates of formation of the experimentally distinct products (in our case, stereospecifically labeled as axial or radial) are determined *only* by the relative rates of formation of the intermediates.

In particular, it does not depend on whether the intermediates are a single species or two distinct species. It also does not depend on whether the intermediates are capable of rapid interconversion in the event they are distinct, nor does it matter whether they have the same or different free energies.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Kinetic Study of the Oxygen Exchange of Sodium Bicarbonate and Carbonatopentaamminecobalt(III)[1]

By D. J. FRANCIS[2] and R. B. JORDAN*

Received September 15, 1971

The kinetics of oxygen-18 exchange between water and the carbonate species obtained by dissolving $NaHCO_3$ in water and by dissolving $(NH_3)_5CoCO_3^+$ in water have been measured. Both systems were studied in the pH range 7.2–8.5 at 20, 26, and 30° at an ionic strength of 1 *M* ($NaClO_4$). The results of this study confirm a previous proposal that the rate of exchange in the complexed system is controlled by the hydration rate of carbon dioxide.

The kinetics of the exchange of carbon-14-labeled carbonate ion and carbonatopentaamminecobalt(III) has been studied by Stranks[3] and by Lapidus and Harris.[4] The results were interpreted assuming that the rate-controlling equilibrium was

$$(NH_3)_5CoCO_3H^{2+} + H_2O \rightleftarrows (NH_3)_5CoOH_2^{3+} + HCO_3^- \quad (1)$$

This interpretation has been reexamined recently by Dasgupta and Harris[5] by using the rate and equilibrium data which are now available for reaction 1, and it was found that the rate of reaction 1 was about 66 times greater than the observed exchange rate. It was suggested then by Dasgupta and Harris that the rate-controlling reaction involves hydration of CO_2, according to the reactions

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \quad (2)$$

$$CO_2 + OH^- \rightleftarrows HCO_3^- \quad (3)$$

By using the known rate constants for these reactions Dasgupta and Harris compared calculated exchange rates to those measured by Stranks. The calculated and observed rates agreed well at the higher pH values but the experimental rate appears to increase more rapidly with increasing acidity than predicted by the CO_2 hydration rate. It was suggested[5] that the original pH measurements may be in error. The only alternative would be that the pentaamminecobalt(III) species catalyzes the hydration of CO_2.

In order to test the CO_2 hydration mechanism, the rate of oxygen-18 exchange of $(NH_3)_5CoCO_3^+$ and of uncomplexed carbonate species has been measured under the same conditions in this work. If the same CO_2 hydration step is rate controlling in both systems, then the same rate constants should describe the oxygen-18 exchange in both.

Experimental Section

Reagents.—The preparation and characterization of the carbonatopentaamminecobalt(III) nitrate have been described previously.[6] Reagent grade sodium bicarbonate, 70% perchloric acid, sodium perchlorate, and 2-amino-2-(hydroxymethyl)-1,3-propanediol (THM) were used as supplied. The oxygen-18-enriched water, initially 1.58 atom % oxygen-18, was obtained from Bio-Rad Laboratories. This water was used as supplied and was recovered for reuse by vacuum distillation, followed by distillation from alkaline potassium permanganate at atmospheric pressure in an all-glass apparatus. Deionized water of normal isotopic content also was distilled from alkaline permanganate.

Exchange Kinetics.—For each kinetic run an isotopically enriched solution and an unenriched buffer solution were prepared by dissolving 0.17 g of THM in 5 ml of either oxygen-18-enriched water or unenriched water. Each solution was titrated to the required pH with 1.0 *M* $HClO_4$ and then diluted to volume (10 ml) with either enriched or unenriched water.

For the carbonate exchange studies the reaction solution was prepared by dissolving 1.08 g of $NaClO_4$ and a weighed sample (about 0.015 g) of $NaHCO_3$ in 1 ml of unenriched buffer solution in a 10-ml volumetric flask.[7] This solution and the appropriate enriched buffer solution were equilibrated at the required temperature before diluting the sample to volume with enriched buffer solution. At appropriate times 0.8-ml samples of the reaction solution were syringed into a nitrogen bubbler containing 0.5 ml of 70% $HClO_4$. The CO_2 evolved was dried and collected as described elsewhere.[8]

---

[1] Financial support from the National Research Council of Canada is gratefully acknowledged.

[2] This work represents part of the dissertation of D. J. Francis presented to the Faculty of Graduate Studies of the University of Alberta in partial fulfillment of the requirements for the Ph.D. degree.

[3] D. R. Stranks, *Trans. Faraday Soc.*, **51**, 505 (1955).

[4] G. Lapidus and G. M. Harris, *J. Amer. Chem. Soc.*, **85**, 1223 (1963).

[5] T. P. Dasgupta and G. M. Harris, *ibid.*, **90**, 6360 (1968).

[6] D. J. Francis and R. B. Jordan, *ibid.*, **89**, 5591 (1967).

[7] The contribution of the buffer to the ionic strength actually changes with pH so that the ionic strength of the reactant solution varied from 1.0 *M* at pH 7 to 0.89 *M* at pH 9.

[8] D. J. Francis and R. B. Jordan, *Inorg. Chem.*, **11**, 461 (1972).

During each run a 1-ml sample of the reaction solution was withdrawn for pH measurement. This sample was also used to determine the isotopic content of the reaction medium by transferring the water, under vacuum, to an appropriate sample tube. The water was equilibrated isotopically with a known amount of normal carbon dioxide at 80° for 10–20 hr. Then the CO_2 was dried and transferred to a sample tube for mass spectrometric analysis. Since the amount of CO_2 was 10^3 times less than the amount of water, no isotope dilution correction was applied.

The oxygen-18-exchange rate of $(NH_3)_5CoCO_3^+$ was studied by essentially the same procedure. In this case 1.06 g of $NaClO_4$ was added to both the enriched and unenriched buffer solutions, rather than putting all the $NaClO_4$ in the latter. This modification facilitated the dissolution of the cobalt complex salt in the unenriched buffer. The reaction solution was prepared by dissolving a weighed amount of $(NH_3)_5CoCO_3(NO_3)\cdot 1.5H_2O$ (about 0.04 g) in 1 ml of unenriched buffer solution and then diluting the solution to 10 ml with enriched buffer, after temperature equilibration. The sampling procedure was the same as that used previously.

In general nine or ten samples were taken for each kinetic run covering the time for the reaction to reach about 80% completion. Good linear kinetic plots, of the function given in the next section, were obtained with only 3–4% method-induced exchange apparent from the zero-time extrapolation of these plots. The pH measurements were made on a Beckman Expandomatic pH meter using a combination microelectrode. The pH meter was calibrated against a standard voltage source following the manufacturer's instructions. A 2.0 *M* NaCl solution was used in place of saturated KCl as the electrode electrolyte in order to avoid precipitation of $KClO_4$. Fisher Certified buffer solutions were used to standardize the system (±0.02 pH unit).

The ratio (R) of $C^{16}O^{18}O$ to $C^{16}O^{16}O$ was determined on a CEC Model 21-614 low-resolution mass spectrometer from the heights of the mass 46 and mass 44 peaks. For a sample of normal CO_2 the ratio (R_0) was found to be $(4.01 \pm 0.05) \times 10^{-3}$, where the error represents the reproducibility and is largely due to uncertainty in reading the peak heights.

Analysis of Results

The isotope-exchange results have been treated in a standard manner; however, because of the number of species involved, an outline of the method will be given. If the free carbonate species H_2CO_3, HCO_3^-, CO_3^{2-}, and CO_2 are designated as 1, 2, 3, and 4, respectively, and X_i is the concentration of oxygen-18 in the ith species in gram-atoms per liter, then

$$\frac{d(X_1 + X_2 + X_3 + X_4)}{dt} = F - D \qquad (4)$$

where F is the rate of formation of ^{18}O-containing free carbonate species and D is the rate of destruction of ^{18}O-containing free carbonate species. Then, following the usual method,[9] it can be shown that

$$\log \frac{X_\infty - X_t}{X_\infty - X_0} = -\frac{R_T}{2.303}\left(\frac{a + b}{ab}\right)t \qquad (5)$$

where $a = \Sigma_{i=1}^{4} a_i$ and a_i is the total concentration of oxygen in the ith carbonate species; b is the total oxygen concentration in the water; $X_t = \Sigma_{i=1}^{4} X_i$ at time t; X_∞ and X_0 are the values at complete and zero reaction times, respectively; and R_T is the total number of reactions of all carbonate species with water per unit time. The total concentration of oxygen (gram-atoms per liter) in the carbonate species (a) can be expressed in terms of the known total concentration of carbonate species (T) by

$$\begin{aligned} a &= 3[H_2CO_3] + 3[HCO_3^-] + 3[CO_3^{2-}] + 2[CO_2] \qquad (6) \\ &= GT \end{aligned}$$

where G will be a function of the equilibrium constants relating the various species and the hydrogen ion concentration. It may be noted that G will be nearly 3 except when significant amounts of CO_2 are present.

It can be shown readily that the 46/44 mass ratio at time t, R_t, is equal to X_t/a if $^{16}O \gg {}^{18}O$ as is the case in this study. Therefore the experimental R_t, R_0, and R_∞ may be substituted for X_t, X_0, and X_∞, respectively, in eq 5. Then substitution into eq 5 and noting that $b \gg a$ give

$$\log \frac{R_\infty - R_t}{R_\infty - R_0} = -\frac{k_{obsd}}{2.303}t \qquad (7)$$

and k_{obsd} is determined from the appropriate semilogarithmic plot and is equal to R_T/GT.

The chemical reactions and equilibria which have been considered in relation to k_{obsd} are

$$K_{C1} = [H^+][HCO_3^-]/([CO_2] + [H_2CO_3]) \qquad (8)$$

$$K_{C2} = [H^+][HCO_3^-]/[HCO_3^-] \qquad (9)$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (k_3,\ k_4) \qquad (10)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (k_5,\ k_6) \qquad (11)$$

By considering these equations and by noting that the last two produce oxygen atom exchange, it can be shown that

$$k_{obsd} = \frac{1}{G}\left\{\frac{\frac{k_3k_4}{k_3 + k_4}[H^+] + k_6K_{C1}}{K_{C1} + [H^+] + \frac{K_{C1}K_{C2}}{[H^+]}}\right\} \qquad (12)$$

The results of previous studies[10] indicate that $k_4 \gg k_3$ and, under our experimental conditions $(K_{C1} + [H^+]) \gg K_{C1}K_{C2}/[H^+]$. Therefore eq 12 simplifies to

$$k_{obsd} = \frac{1}{G}\left\{\frac{k_3[H^+] + k_6K_{C1}}{K_{C1} + [H^+]}\right\} \qquad (13)$$

It should be noted that G is a function of K_{C1}, K_{C2}, $[H^+]$, and k_4. Therefore the value of k_4 must be known to calculate G. However k_4 is not very important in this context because it controls only the concentration of CO_2, which is a minor species in the present experiments.

The values of k_4 at 20, 26, and 30° were estimated from a log (k_4/T) *vs.* $1/T$ plot of the results in ref 11 at 25 and 37°. The ionic strength (μ) dependence of k_4 was estimated using the equation[12]

$$\log k_4 = C - 0.187\mu \qquad (14)$$

where the constant C was calculated from the value of k_4 at 25° in 0.11 *M* KCl.[11] The effect of changing the medium from KCl to $NaClO_4$ was neglected.

The value of K_{C1} in 1 *M* $NaClO_4$[13] is known and the temperature dependence of K_{C1} in 1 *M* $NaClO_4$ was assumed to be the same as that in 1 *M* NaCl.[14]

Since the experiments were all in the range of pH <9, there is very little carbonate ion present and the analysis is insensitive to the value of K_{C2}. Therefore the

---

(9) A. C. Wahl and N. A. Bonner, Ed., "Radioactivity Applied to Chemistry," 1st ed, Wiley, New York, N. Y., 1951, p 8.

(10) D. M. Kern, *J. Chem. Educ.*, **37**, 14 (1960).

(11) L. Rossi-Bernardi and R. L. Berger, *J. Biol. Chem.*, **243**, 1297 (1968).

(12) R. L. Berger, private communication. The value of k_4 decreases with increasing ionic strength as indicated in Figure 5 of ref 11 and not in the opposite way as stated in the text of ref 11.

(13) M. Frydman, G. Nilsson, T. Rengemo, and L. G. Sillén, *Acta Chem. Scand.*, **12**, 878 (1958).

(14) H. S. Harned and F. T. Bonner, *J. Amer. Chem. Soc.*, **67**, 1026 (1945).

same value of K_{C2}, 2.75×10^{-10},[6] was used at all three temperatures.

The variation of k_{obsd} with $[H^+]$ was fitted to eq 12 to obtain least-squares best fit values[15] of k_3 and k_6. It may be noted from eq 13 that the data can also be analyzed graphically, since a plot of $k_{obsd}G(K_{C1} + [H^+])$ *vs.* $[H^+]$ should have a slope k_3 and an intercept k_6K_{C1}.

In the treatment of the oxygen-18 exchange in the $(NH_3)_5CoCO_3^+$ system it is assumed that CO_2 hydration is the rate-controlling process. The results can be used to determine if this assumption is correct by comparing the values of k_3 and k_6 obtained from the free carbonate and $(NH_3)_5CoCO_3^+$ systems. Two additional equilibria must be considered (eq 15 and 16).

$$(NH_3)_5CoOCO_2H^{2+} \rightleftharpoons (NH_3)_5CoOCO_2^+ + H^+ \quad K_1 \qquad (15)$$

$$(NH_3)_5CoOH^{2+} + HCO_3^- \rightleftharpoons (NH_3)_5CoOCO_2H^{2+} + OH^- \quad K_f \qquad (16)$$

The general treatment is the same as that outlined above, except that now the complexed carbonate species must also be considered so that eq 6 becomes

$$a' = 2[(NH_3)_5CoOCO_2^+] + 2[(NH_3)_5CoOCO_2H^{2+}] + 3[H_2CO_3] + 3[HCO_3^-] + 3[CO_3^{2-}] + 2[CO_2] = G'T' \qquad (17)$$

where T' is the initial complex concentration since the complex is the only source of carbonate species. A factor of 2 is used in front of the cobalt(III) complexes in eq 17 because the acid hydrolysis is known to proceed with carbon–oxygen bond cleavage.[16] Previous studies[17] have shown that the oxygen atom coordinated to cobalt does not undergo intramolecular exchange with the other two oxygens of the coordinated carbonate ion in $(NH_3)_5CoOCO_2^+$.

If CO_2 hydration is the rate-controlling process for the complexed carbonate system, then it can be shown that

$$k'_{obsd} = \frac{1}{G'T'}\left\{\frac{\dfrac{k_3k_4}{k_3 + k_4}[H^+] + k_6K_{C1}}{K_{C1} + [H^+] + \dfrac{K_{C1}K_{C2}}{[H^+]}}\right\}[T] \qquad (18)$$

where [T] is the total uncomplexed carbonate species and T' is the total carbonate, complexed plus uncomplexed.

Calculation of G' and [T] requires a knowledge of K_1 and K_f. Values for K_1 at 20, 26, and 30° were calculated from the values of k_1/K_1 in 1.0 *M* $NaClO_4$[6] and k_1 in 0.5 *M* $NaClO_4$.[5] The values of k_1/K_1 were calculated from the transition state theory equation with $\Delta H^{\ddagger} = 17.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 28.9$ cal mol^{-1} deg^{-1}.[18] Similarly k_1 was calculated using $\Delta H^{\ddagger} = 16.7\ (5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.9\ (3)$ cal mol^{-1} deg^{-1}, calculated from the data of Dasgupta and Harris.

The original value of K_f[6] has been revised in view of the values of K_1 now available and is found to be 5.5×10^{-6} at 25°. It has been assumed that this value is independent of temperature, as seems reasonable in view of the small temperature dependence observed for the formation constants of similar complexes.[19,20]

The experimental values of k'_{obsd} as a function of $[H^+]$ were fitted to eq 18 with k_4 fixed and using k_3 and k_6 as fitting parameters in a method analogous to that applied to the results from the free carbonate system. Equation 18 may also be reduced to obtain a form equivalent to eq 13 and the results can be treated graphically as described previously.

Results and Conclusions

The results of the oxygen-18-exchange study of the free carbonate system under various conditions are summarized in Table I. It should be noted that over the pH range studied the dominant species is bicarbonate ion. For example at 26°, the percentages of CO_2, HCO_3^-, and CO_3^{2-} at the lowest acidity studied are 0.32, 91.6, and 8.07, respectively, while at the highest acidity the values are 2.62, 96.3, and 1.07, respectively. The best fit values of k_3 and k_6 are given in Table II. A comparison of the experimental and calculated k_{obsd} values in Table I shows that the results are fitted very well by eq 13.

TABLE I

KINETIC RESULTS FOR THE EXCHANGE OF OXYGEN BETWEEN FREE CARBONATE SPECIES AND WATER

Temp, °C	10^2T, *M*	$10^3[H^+]$, *M*	10^4k_{obsd}, sec^{-1}	
			Exptl	Calcd[a]
20	2.60	0.872	0.72	0.75
20	2.32	1.55	1.12	1.11
20	2.80	2.34	1.56	1.53
20	1.84	3.56	2.13	2.16
26	2.19	0.310	0.99	0.99
26	1.94	0.662	1.52	1.43
26	2.07	0.768	1.47	1.55
26	2.22	1.26	2.16	2.13
26	2.72	1.89	2.83	2.85
26	2.44	3.46	3.43	2.97
30	2.64	0.310	1.93	1.92
30	1.97	0.538	2.35	2.39
30	2.28	0.829	2.95	2.94
30	2.44	1.35	4.01	3.90
30	2.12	1.78	4.62	4.68

[a] These values are determined for a least-squares best fit to eq 16 using fixed values at 20, 26, and 30° for $10^{-1}k_4$ of 1.016, 1.806, and 2.602 sec^{-1} and 10^7K_{C1} of 8.15, 8.79, and 9.22 *M*, respectively, while K_{C2} was 2.75×10^{-10} *M* at all temperatures.

TABLE II

BEST FIT PARAMETERS FOR EXCHANGE OF OXYGEN IN THE SYSTEMS CONTAINING FREE[a] AND COMPLEXED[b] CARBONATE SPECIES

Temp, °C	10^2k_3,[c] sec^{-1}		10^4k_6,[c] sec^{-1}	
	Free[a]	Complexed[b]	Free[a]	Complexed[b]
30	5.12 ± 0.80	4.10 ± 0.70	4.58 ± 0.90	3.63 ± 0.70
26	3.11 ± 0.38	2.86 ± 0.11	2.16 ± 0.60	2.55 ± 0.52
20	1.33 ± 0.30	1.61 ± 0.07	0.93 ± 0.85	0.85 ± 0.30

[a] Free refers to the system derived from $NaHCO_3$. [b] Complexed refers to the system derived from $(NH_3)_5CoCO_3^+$. [c] Error limits are 95% confidence limits calculated by the least-squares program with statistical parameters suitable to the number of degrees of freedom for each fit: D. J. Francis, Ph.D. Thesis, University of Alberta, 1970.

The kinetic results for the system containing com-

---

(15) L. L. Rines, J. A. Plambeck, and D. J. Francies, "ENLLSQ Reprogrammed," Program Library, Department of Chemistry, University of Alberta, 1970.

(16) J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Amer. Chem. Soc.*, **74**, 268 (1952).

(17) L. L. Po and R. B. Jordan, unpublished work using $(NH_3)Co{}^{18}OC^{16}O^{16}O^+$ equilibrated under various conditions and recovered after acidification as $((NH_3)_5CoOH_2)Br_3$ showed that the labeled oxygen originally bound to cobalt(III) was recovered without isotopic dilution in the aquo product.

(18) The value of 30.0 cal mol^{-1} deg^{-1} reported in ref 6 is incorrect due to an arithmetic error.

(19) C. G. Barraclough and R. S. Murray, *J. Chem. Soc. A*, 7047 (1965).

(20) S. Sheel, D. T. Meloon, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962).

TABLE III
KINETIC RESULTS FOR THE EXCHANGE OF OXYGEN IN THE CARBONATOPENTAAMMINECOBALT(III) SYSTEM

Temp, °C	$10^2T'$,[a] M	10^2T,[b] M	G'	$10^8[H^+]$, M	10^4k_{obsd}, sec^{-1} Exptl	10^4k_{obsd}, sec^{-1} Calcd[c]
20	1.160	0.581	2.49	1.10	0.577	0.582
20	1.402	0.656	2.46	1.38	0.666	0.654
20	1.356	0.636	2.46	2.50	1.04	1.06
20	1.090	0.550	2.49	2.82	1.26	1.24
20	1.140	0.562	2.47	4.27	1.72	1.74
20	1.188	0.572	2.45	6.03	2.33	2.32
26	1.012	0.636	2.63	0.279	0.78	0.75
26	0.910	0.577	2.63	0.903	1.23	1.27
26	0.783	0.515	2.65	1.15	1.49	1.50
26	0.728	0.484	2.65	2.22	2.42	2.36
26	0.578	0.400	2.65	6.18	5.41	5.49
26	0.716	0.466	2.60	8.29	6.78	6.73
30	1.500	0.925	2.62	0.339	1.10	1.12
30	1.348	0.847	2.63	0.604	1.44	1.44
30	1.385	0.859	2.61	0.914	1.78	1.75
30	1.295	0.813	2.62	1.48	2.35	2.36

[a] The total carbonate species present. [b] The free carbonate produced from hydrolysis of $(NH_3)_5CoCO_3^+$. [c] Determined from a least-squares fit to eq 18 using fixed values for 10^7K_1 of 3.47, 3.30, and 3.20 M at 20, 26, and 30°, respectively, and other constants given in footnote *a* of Table I.

plexed carbonate are given in Table III. A typical set of species concentrations can be derived from the kinetic run at 30° with $[H^+] = 1.48 \times 10^{-8}$ M, for which the percentages of $(NH_3)_5CoCO_3^+$, $(NH_3)_5CoCO_3H^{2+}$, H_2CO_3, HCO_3^-, CO_3^{2-}, and CO_2 are 35.6, 1.6, 0.04, 60.7, 1.1, and 1.0, respectively. Clearly the major species are $(NH_3)_5CoCO_3^+$ and HCO_3^-. The experimental k'_{obsd} values were fitted to eq 18 to obtain the best fit values of k_3 and k_6 which are given in Table II.

There has been considerable variation in the values of k_3 and k_6 in previous work as discussed in ref 10, 21, and 22. The results of this study (Table II) are in good agreement with the recent literature values.[21,22] An interpolation of the data of Poulton and Baldwin[21] to an ionic strength (μ) of 1.0 gives $k_3 = 3.1 \times 10^{-2}$ sec^{-1} at 25°. Welch, *et al.*,[22] have shown that their value for k_6 of 2.3×10^{-4} sec^{-1} (25°, $\mu < 0.1$) is consistent with the results of Poulton and Baldwin and it is also in agreement with the value found here.

A comparison of the best fit values of k_3 and k_6 from the free and complexed carbonate systems given in Table II shows that within the 95% confidence limits k_3 and k_6 are the same from the two studies as expected if the rate-controlling step is the same in both. Although the confidence limits are about ±20%,[23] the results show that the complexed system certainly is not exchanging twice as fast as the free system, as would be required in order to explain the results of Stranks.

It can be seen more easily that the rate-controlling steps are the same in the two systems if one considers Figure 1 which shows the appropriate plots indicated by eq 13. It is apparent from this graph that the predicted rate law is obeyed and that the values of k_3 and k_6 obtained from the two systems are indistinguishable. Similar behavior is found at 20°; however at 30° the results from the complexed system are consistently 10–15% lower than those from the free system. This is also indicated by the fact that both k_3 and k_6 in Table II are lower at 30° for the complexed system. In view of the agreement at 20 and 26° it is believed that there may be some systematic error in the complexed system at 30°. The latter was studied several months after the free system and it is possible that either the temperature or the pH readings are somewhat in error.[24]

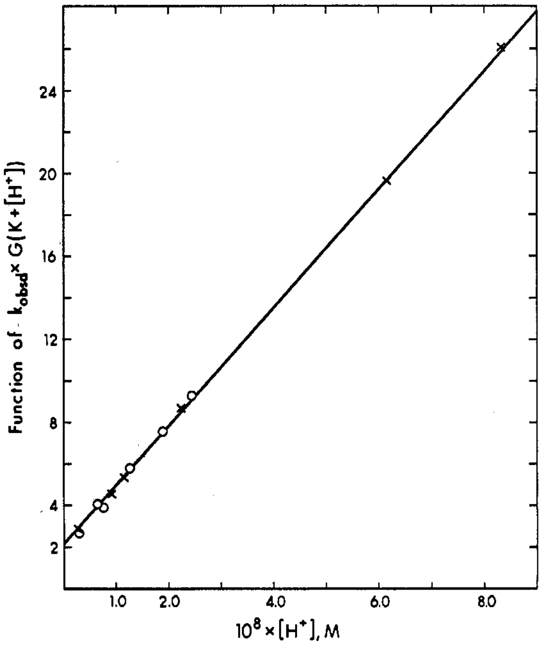

Figure 1.—Variation of the oxygen-18-exchange rate with acidity at 26°, $\mu = 1.0$ M: ○, $k_{obsd}G(K_{C1} + [H^+])$ *vs.* $[H^+]$ for the free carbonate system; ×, $k_{obsd}G'T'(K_{C1} + [H^+])/T$ *vs.* $[H^+]$ for the complexed carbonate system.

It is concluded that, within the experimental error on the measured rate constants, the rates of oxygen-18 exchange of carbonate complexed to $(NH_3)_5Co^{3+}$ and of free carbonate species are controlled by the normal hydration rate of carbon dioxide, consistent with the mechanism proposed by Dasgupta and Harris.[5] The present study shows that this mechanism is operative at around pH 8 and the calculations of Dasgupta and Harris, using Strank's results, indicate that it is operative near pH 10. Therefore it seems very probable that the deviations noted in Stranks' data at intermediate pH values[5] are due to experimental error as has been suggested by Dasgupta and Harris and cannot be attributed to any catalytic effects of cobalt(III) species on the CO_2 hydration rate.

---

(21) D. J. Poulton and H. W. Baldwin, *Can. J. Chem.*, **45**, 1045 (1967).

(22) M. J. Welch, J. F. Lipton, and J. A. Seck, *J. Phys. Chem.*, **73**, 3351 (1969).

(23) The confidence limits are large mainly because of the small number of runs (4–6) at each temperature, rather than a poor fit of the experimental results to the rate law.

(24) The possibility that neglect of the temperature dependence of K_f causes the discrepancy was tested, but K_f would have to change by a factor of 2 between 26 and 30° to bring the 30° results into agreement. This requires a very unreasonable $\Delta H°$ of ~25 kcal mol^{-1} for K_f.