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Reinvestigation of Decarboxylation Kinetics from the Hydrogencarbonatocobalt(III) Intermediate

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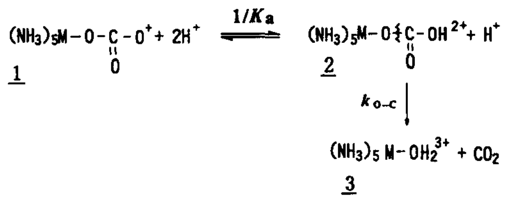
Acid-catalysed hydrolysis has been studied by a stopped-flow method at 25 °C, ionic strength of 2.0 ($NaClO_4$) and oxonium ion concentration of 0.02—1.0 M for monodentate carbonato complexes ($[Co(CO_3)(NH_3)_5]^+$, $[Rh(CO_3)(NH_3)_5]^+$, and $[Ir(CO_3)(NH_3)_5]^+$) and for didentate carbonato complexes ($[Co(CO_3)(NH_3)_4]^+$, $[Co(CO_3)(en)_2]^+$, *α*, *β*-$[Co(CO_3)(trien)]^+$, $[Co(CO_3)(tren)]^+$ and $[Co(CO_3)(nta)]^{2-}$ (M = mol dm^{-3}, en = ethylenediamine, trien = 1,8-diamino-3,6-diazaoctane, tren = tris(2-aminoethyl)amine, and H_3nta = nitrilotriacetic acid)). The experimental first-order rate constant of decarboxylation from the monodentate hydrogencarbonato intermediate depends on the acidity of the solution, which we ascribe to its amphiprotic character. The deprotonation constant depends critically on an aqua ligand *cis* to the hydrogencarbonato ligand: 0.004—0.6 M with it, whereas about 10^{-6} M without it. We interpret that the former strong acidity originates from the stability of the aquacarbonato complex, owing to a strong (21—33 kJ mol^{-1}) intramolecular hydrogen bond. The basicity has been confirmed by the acidity dependent zero-time spectra, the protonation constant being 0.1—0.7 M^{-1}. The hydrolysis rate constant of the monodentate carbonic acid complex has been estimated to be smaller than 0.3 s^{-1} at 25 °C.

It is well known that the acid-catalysed hydrolysis reaction of a carbonatocobalt(III) complex proceeds through decarboxylation from the monodentate hydrogencarbonatocobalt(III) intermediate, whereby not the Co–O(hydrogencarbonato) bond, but one of the O–C bonds in the coordinating hydrogencarbonato ligand, cleaves.[1] For reaction 1 of a monodentate carbonato complex **1**, the current mechanism is based on ^{18}O tracer experiments[2] and the acidity dependence of the experimental rate constant,[3] Scheme 1a.

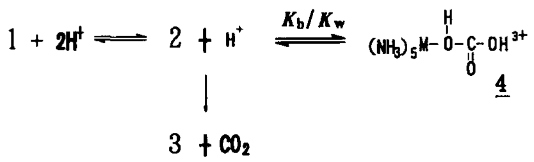
$$\underset{\mathbf{1}}{[M(NH_3)_5(OCO_2)]^+} + 2H^+ \rightarrow \underset{\mathbf{3}}{[M(NH_3)_5(OH_2)]^{3+}} + CO_2, \qquad (1)$$

where M stands for a metal center Co(III), Rh(III) or Ir(III). Preprotonation to the monodentate carbonato ligand in **1** occurs with the equilibrium constant $1/K_a$, following which the O–C bond in the monodentate hydrogencarbonato intermediate **2** cleaves with the first-order rate constant k_{O-C}; a rapid protonation to the resultant hydroxo complex yields the aqua product **3**.[1] A kinetic study of reaction 1 was previously performed at low acidity, an oxonium ion concentration of $h = 10^{-8}$—0.1 M and an ionic strength of $I = 0.5$.[4,5] The experimental first-order rate constants, k_{obs}, have increased significantly with the acidity. Therefrom, the magnitudes of $K_a \approx 10^{-6}$ M and $k_{O-C} \approx 1$ s^{-1} at 25 °C have been estimated.

(a) Current



(b) Modified



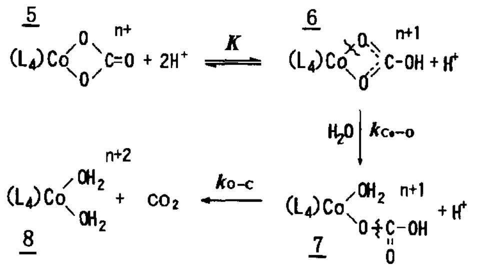
Scheme 1. Mechanism for reaction 1.

Reaction 2 of a didentate carbonato complex **5** proceeds through a carbonato ring opening and following decarboxylation. The current mechanism is based on ^{18}O tracer experiments[6] and the rate acceleration effect in D_2O solvent,[7] Scheme 2a.

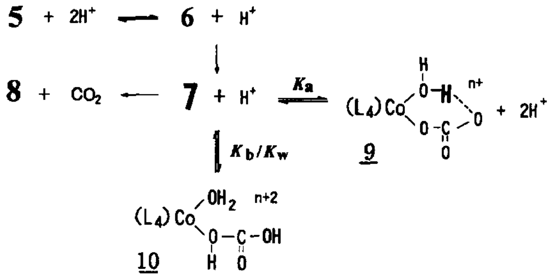
$$\underset{\mathbf{5}}{[Co(L_4)(O_2CO)]^{n+}} + 2H^+ + H_2O \rightarrow \underset{\mathbf{8}}{[Co(L_4)(OH_2)_2]^{n+2}} + CO_2, \qquad (2)$$

where L_4 stands for a ligand or a set of ligands occupying the residual four coordination sites of the coordination octa-

(a) Current



(b) Modified



Scheme 2. Mechanism for reaction 2.

hedron. Preprotonation to the didentate carbonato ligand in **5** occurs with the equilibrium constant K, following which one of the Co–O(hydrogencarbonato) bonds in the didentate hydrogencarbonato intermediate **6** cleaves with the first-order rate constant, k_{Co-O}. The O–C bond in the aquahydrogencarbonato intermediate **7** cleaves with the first-order rate constant, k_{O-C}, and a rapid protonation to the resultant aquahydroxo complex yields the diaqua product **8**.[1] A kinetic study of reaction 2 was recently performed at a high acidity of $h = 0.1$—1.0 M ($I = 1.0$) and 25 °C; $K \approx 1\ M^{-1}$, $k_{Co-O} = 0.01$—$85\ s^{-1}$ and $k_{O-C} \approx 1\ s^{-1}$.[8,9] It was reported that the experimental first-order rate constant of the decarboxylation was independent of the acidity. We have studied later reaction 2 with analogous complexes at an extended acidity of $h = 0.02$—1.0 M ($I = 2.0$) and 25 °C; $K \approx 1\ M^{-1}$, $k_{Co-O} = 0.2$—$126\ s^{-1}$.[10] However, we have found that the experimental rate constant of the decarboxylation is dependent on the acidity of the solution. It increases monotonically for L_4 = *fac*(*N*)-5-dptma, *mer*(*N*)- *i*-dtma and *trans*(*O*)-aeida, while for L_4 = *mer*(*N*)-5-dptma it changes with the acidity, attaining a flat maximum at $h \approx 0.2$ M. Our results contrast with previous ones and are incompatible with the current mechanism predicating an acidity-independent decarboxylation velocity, Scheme 2a. We have interpreted these in terms of our modified mechanism, as illustrated in Scheme 2b; $K_a = 0.004$—0.3 M, $K_b/K_w = 0.1\ M^{-1}$ and $k_{O-C} \approx 1\ s^{-1}$.

In the present report, we intend to clarify the acidity dependence of the experimental rate constant of the decarboxylation reaction and to reinvestigate at an extended acidity of $h = 0.02$—1.0 M ($I = 2.0$) and 25 °C reaction 1 with $[Co(CO_3)(NH_3)_5]^+$, $[Rh(CO_3)(NH_3)_5]^+$, and $[Ir(CO_3)(NH_3)_5]^+$,[4,5] as well as reaction 2 with $[Co(CO_3)(NH_3)_4]^+$, $[Co(CO_3)(en)_2]^+$, α-, β-$[Co(CO_3)(trien)]^+$, $[Co(CO_3)(tren)]^+$, and $[Co(CO_3)(nta)]^{2-}$.[8,9] We are especially interested in the acidity range where the measurement was lacking in previous studies: $0.1\ M < h$ for reaction 1 where the effect of $K_a \approx 10^{-6}$ M is negligible and $h < 0.1$ M for reaction 2 where the effect of $K_b/K_w \approx 0.3\ M^{-1}$ is negligible.

Experimental

Analytical grade reagents and distilled water were used. The samples of the complex were prepared according to published methods and identified by elemental analyses and UV-visible absorption spectra, Table 1. *Caution! Although we experienced no difficulty with the complexes reported here, they should be treated as potentially explosive and handled accordingly.* Perchloric acid was used to adjust the acidity of the solution. The acidic D_2O solution was prepared from 99.8% D_2O (Uvasol, Merck) and aqueous 11.8 M $HClO_4$. At low acidity, McIlvaine buffers were used with 10^{-5} M carbonic anhydrase for a kinetic run.[5,11] The pH value was measured with a Horiba F-22 instrument, of which the reference electrode was filled with 3 M NaCl to prevent the possible precipitation of $KClO_4$ in the solution. The h value was calculated by $h = 10^{-pH}$. A Unisoku RS-450 stopped-flow apparatus and a Unisoku USP-500 rapid-scan spectrophotometer were used (optical path length = 1 cm, dead time ≈ 2 ms). The reaction temperature was controlled within ±0.1 °C. The kinetic measurements were carried out as described in a previous report.[10] The time course of the absorbance, A_t, was recorded at a relevant UV wavelength, where a substantial change of A_t was observed during the reaction. It was recorded at 501 points from $t = 0$ to the 98% completion time. For reaction 1, it was analyzed according to the equation for a single first-order process with an experimental rate constant, k_{obs}, using a calculating soft Unisoku kinetic analysis program, version 1.1. For reaction 2, it was analysed according to the following equation for two consecutive first-order reactions with faster and slower experimental rate constants, k_{fast} and k_{slow}, using the above-mentioned program through previously described procedures:[10]

$$|A_t - A_\infty| = m\exp(-k_{fast}t) + n\exp(-k_{slow}t), \qquad (3)$$

where m and n are constants independent of the reaction time, t. The reliability of the derived rate constant was checked by the correlation coefficient, γ, of the linear Guggenheim's plot, generally being 0.999. In the case of $[Co(CO_3)(nta)]^{2-}$, it was additionally analyzed using the Unisoku nonlinear least-squares fitting routine ANALYSIS EXE according to Eq. 3.

Results

Reaction 1. The k_{obs} of reaction 1 are summarized in Table S1. For $[Co(CO_3)(NH_3)_5]^+$, our results at low acidity, $h < 0.001$ M, confirm the earlier results.[4,5] In high acidity, the k_{obs} decreases with increasing acidity, Fig. 1. This is incompatible with the current mechanism for reaction 1, predicating an acidity-independent k_{obs}, Scheme 1a. We assume the basicity of **2**: A protonation with the equilibrium constant K_b/K_w giving rise to a carbonic acid complex **4**, Scheme 1b. Neglecting the contribution of $K_a \approx 10^{-6}$ M at high acidity, $0.01\ M < h$, k_{obs} are expressed by

Table 1. Samples of the Complex Used in This Work

	C%	H%	N% [a]	λ_{max}/nm (ε)
$[Co(CO_3)(NH_3)_5]NO_3\cdot H_2O$[17]	4.2	5.8	29.9	509 (97.7)[b]
	(4.2)	(6.0)	(29.6)	505 (94)[4]
$[Rh(CO_3)(NH_3)_5]ClO_4\cdot 4H_2O$[5]	2.4	4.0	16.7	323 (173)
	(2.9)	(3.9)	(16.7)	325 (178)[5]
$[Ir(CO_3)(NH_3)_5]ClO_4\cdot 2H_2O$[5]	2.7	3.2	14.6	262 (125)
	(2.5)	(3.2)	(14.8)	262 (125)[5]
$[Co(CO_3)(NH_3)_4]NO_3\cdot 0.5H_2O$[18]	4.8	4.6	27.9	359 (122), 522 (98)
	(4.8)	(4.8)	(28.1)	364 (105), 523 (102)[18]
$[Co(CO_3)(en)_2]ClO_4$ [8]	18.1	4.9	16.2	358 (115), 511 (126)
	(17.7)	(4.8)	(16.6)	360 (122), 510 (133)[8]
α-$[Co(CO_3)(trien)]ClO_4\cdot H_2O$[19]	21.9	5.1	14.7	356 (104), 503 (120)
	(21.9)	(5.2)	(14.7)	357 (102), 503 (120)[19]
β-$[Co(CO_3)(trien)]ClO_4\cdot H_2O$[19]	21.9	5.1	14.7	358 (145), 506 (183)
	(21.9)	(5.2)	(14.7)	358 (140), 507 (178)[19]
$[Co(CO_3)(tren)]ClO_4\cdot H_2O$[20]	22.2	5.2	14.5	353 (107), 503 (129)
	(22.0)	(5.3)	(14.6)	—
$K_2[Co(CO_3)(nta)]\cdot 2H_2O$[21]	19.8	1.8	3.4	388 (151), 571 (170)
	(20.0)	(2.4)	(3.3)	388 (150), 564 (165)[21]

a) In parenthesis calculated values are shown. b) In 1 mM NaOH.

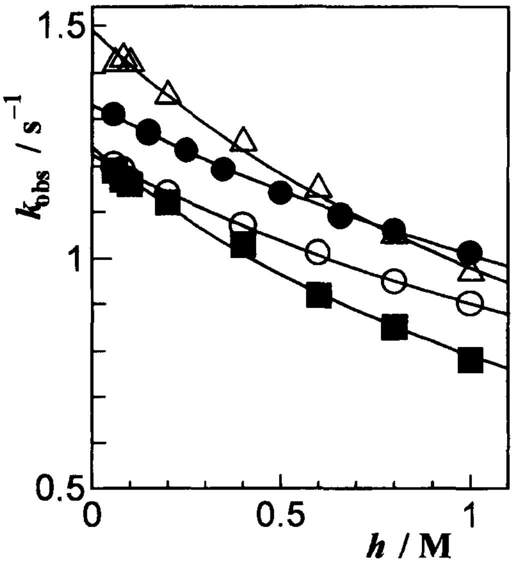


Fig. 1. Plots of k_{obs} at 25 °C and $I = 2.0$ ($NaClO_4$) versus h for the reaction of $[Co(CO_3)(NH_3)_5]^+$ in H_2O(●) and D_2O-(○); $[Rh(CO_3)(NH_3)_5]^+$ (■); and $[Ir(CO_3)(NH_3)_5]^+$ (△). Curve fittings were achieved using Eq. 4.

$$k_{obs} = k_{O\text{–}C} \;/\; \{1 + (K_b/K_w)h\} \qquad (4)$$

The k_{obs} well fit to Eq. 4, the correlation coefficient of the linear relation between $1/k_{obs}$ and h being greater than 0.997. In the case of $[Co(CO_3)(NH_3)_5]^+$, we have obtained temperature-independent K_b/K_w values of 0.32 ± 0.01 M^{-1} at 15 °C and 0.28 ± 0.01 M^{-1} at 35 °C, as well as temperature-dependent $k_{O\text{–}C}$ values. From the latter, we estimate $\Delta H^{\ddagger} = 79.7\pm0.2$ kJ mol^{-1}, being similar to the previous value, and $\Delta S^{\ddagger} = 24.6\pm0.6$ J K^{-1} mol^{-1}, differing from the previous value -2.1 or -8.4 J K^{-1} mol^{-1}.[4,5] Equal volumes of $[M(CO_3)(NH_3)_5]^+$ solution {0.01 or 0.1 M NaOH, $I = 2.0$ ($NaClO_4$)} and an $HClO_4$ or McIlvaine buffer solution {$I = 2.0$ ($NaClO_4$)} were mixed and the zero-time absorption spectrum of the mixture was recorded. Using one and the same solution of a complex, spectra **A′** or **A**, **B** and **C** were recorded in this time order, and finally the reproducibility of **A′** or **A** was checked. The hydrolysis of $[M(CO_3)(NH_3)_5]^+$ during the 20 min for one series of runs was suppressed by the addition of NaOH.[12] In the cases of $[Co(CO_3)(NH_3)_5]^+$ and $[Rh(CO_3)(NH_3)_5]^+$, **B** differs significantly from **A′** or **A**, while **C** differs slightly from **B**, Fig. 2a—d. **A′** or **A** and **B** should correspond to the spectra of **1** and **2**, while the spectrum **C** should correspond to the spectrum of a mixture of **2** and **4**, Scheme 1b. In the case of $[Ir(CO_3)(NH_3)_5]^+$, spectrum **B** differs from **A**, while **C** overlaps **B**, Fig. 2f. We have estimated the K_a and K_b/K_w values from the acidity dependent zero-time absorbance, A_{obs}, at a relevant wavelength by Eqs. 5 and 6, Figs. 3 and 4. We checked the agreement of the final A_{obs} values at $h = 0$ M with the initial one and confirmed that the change in A_{obs} is not caused by the base hydrolysis of $[M(CO_3)(NH_3)_5]^+$ during the time (< 35 min) for one series of runs.

$$K_a = (A_{obs} - A_2)\,h/(A_1 - A_{obs}) \qquad (5)$$

$$1/(A_2 - A_{obs}) = 1/(K_b/K_w)(A_2 - A_4)h + 1/(A_2 - A_4) \qquad (6)$$

A_1, A_2 and A_4 stand for the absorbances due to species **1**, **2**, and **4**, respectively. We have regarded the A_{obs} at $[OH^-] = 0.005$ or 0.05 M to be A_1 and the A_{obs} at $h = 0.01$ M to be A_2.

Reaction 2. An example of the absorbance-time trace is given in Fig. 5, which shows that A_t initially increases and then decreases. The biphasic nature of the process is clearly demonstrated. The experimental rate constants (mean of three or four runs) and A_{obs} are summarized in Table S2. In the case of $[Co(CO_3)(nta)]^{2-}$, we have checked the effects of the wavelength and the analytical method for the trace on the magnitude of the experimental rate constant. When

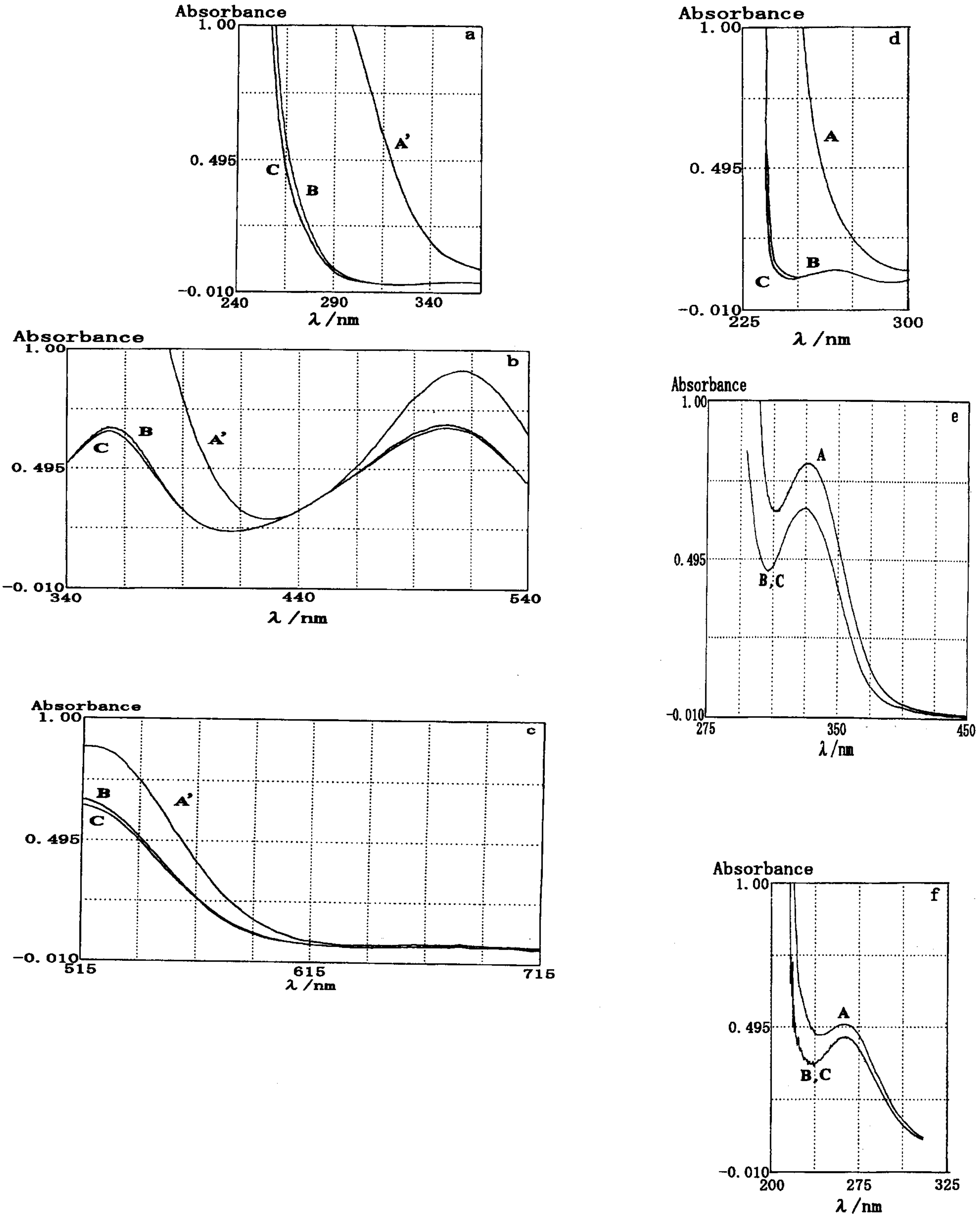


Fig. 2. Zero-time spectra of $[Co(CO_3)(NH_3)_5]\ NO_3$, the concentration of the complex $C = 0.4$ mM (a) or 8 mM (b)(c); $[Rh(CO_3)(NH_3)_5]ClO_4$, $C = 1$ mM (d) or 4.5 mM (e); $[Ir(CO_3)(NH_3)_5]ClO_4$, $C = 4$ mM (f). 25 °C and $I = 2.0$ ($NaClO_4$). A′, 0.005 M NaOH; A, 0.05 M NaOH; B, 0.01 M $HClO_4$; C, 1.0 M $HClO_4$.

analyzed by Guggenheim's method, data at 580 nm gave unreliable k_{fast} values with the low correlation coefficients at $0.4\ \text{M} \le h$. When analyzed by a non-linear least squares method, data at 580 nm gave slightly smaller k_{fast} values compared to that obtained at 312.4 nm. The k_{fast} values at $h \le 0.2$ M and the k_{slow} values are essentially independent of the wavelength used and of the analytical method. For the nta complex, we use the k_{fast} and k_{slow} values obtained

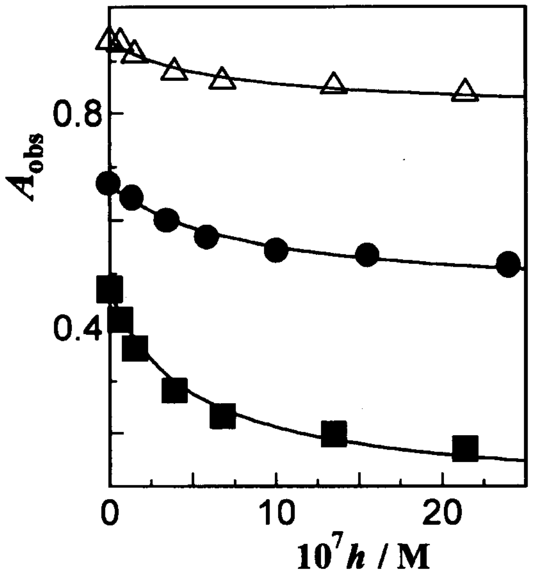


Fig. 3. Acidity dependence of A_{obs} at 250 nm for $[Co(CO_3)(NH_3)_5]^+$ (0.2 mM, ●), $[Rh(CO_3)(NH_3)_5]^+$ (0.7 mM, ■) and $[Ir(CO_3)(NH_3)_5]^+$ (8 mM, △). 25 °C and $I = 2.0$ ($NaClO_4$). Curve fittings were achieved using Eq. 5.

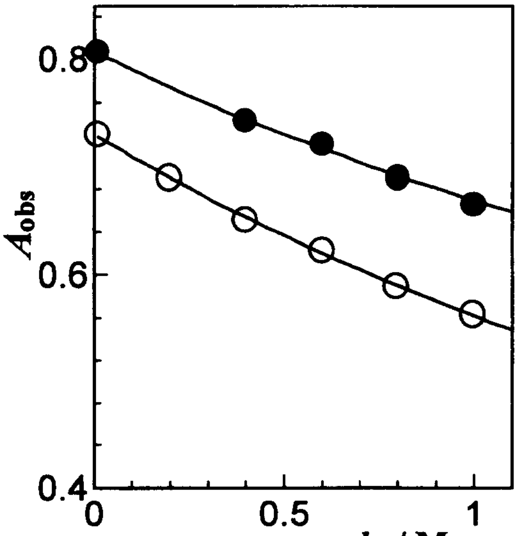


Fig. 4. Acidity dependence of A_{obs} at 250 nm for $[Co(CO_3)(NH_3)_5]^+$ $C = 0.4$ mM in H_2O(●) and in D_2O(○). 25 °C and $I = 2.0$ ($NaClO_4$). Curve fittings were achieved using Eq. 6.

at 312.4 nm and analyzed by Guggenheim's method. For the tetraammine complex, the acidity dependence of the experimental rate constants is shown in Fig. 6. For the other complexes, the acidity dependences of k_{fast} or k_{slow} corresponding to the decarboxylation are shown in Fig. 7. We interpret our results according to our modified mechanism, where an amphiproticity of the intermediate **7** is assumed: a deprotonation (K_a) to a monodentate carbonato complex **9** and a protonation (K_b/K_w) to a monodentate carbonic acid complex **10**, Scheme 2b. We derive the constant values by Eqs. 7—10 by applying a least-squares fitting routine to the quadratic or linear relation between h/k_{fast} or h/k_{slow} and h.

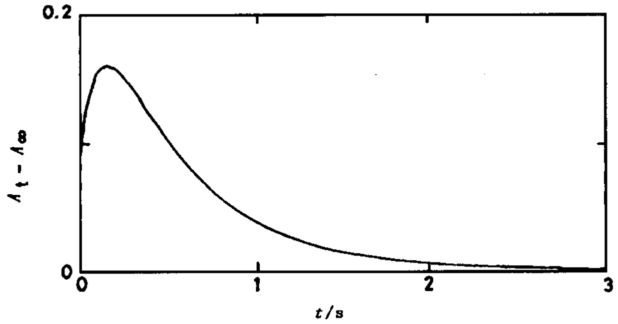


Fig. 5. Observed absorbance—time trace at 312.4 nm for the reaction of 2 mM $[Co(CO_3)(nta)]^{2-}$ in 0.06 M $HClO_4$. 25 °C and $I = 2.0$ ($NaClO_4$).

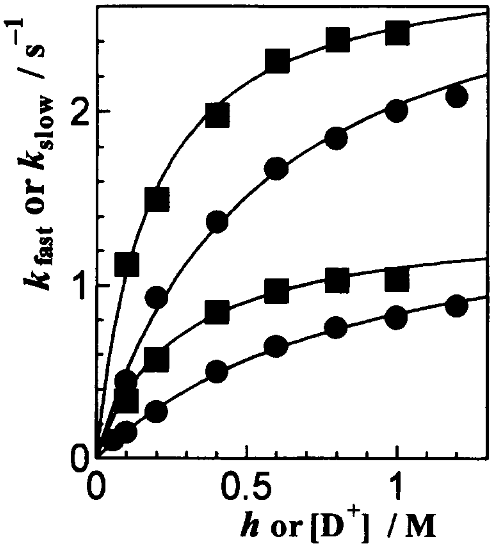


Fig. 6. Plots of k_{fast} and k_{slow} versus h (●) or $[D^+]$ (■) for the reaction of $[Co(CO_3)(NH_3)_4]^+$ in H_2O and in D_2O solutions at 25 °C and $I = 2.0$ ($NaClO_4$). Curve fittings were achieved using Eqs. 7 and 8.

$$k_{fast} = k_{O\text{–}C}h/\{(K_b/K_w)h^2 + h + K_a\} \tag{7}$$

$$k_{slow} = k_{Co\text{–}O}Kh/(Kh + 1) \tag{8}$$

$$k_{fast} = k_{Co\text{–}O}Kh/(Kh + 1) \tag{9}$$

$$k_{slow} = k_{O\text{–}C}h/\{(K_b/K_w)h^2 + h + K_a\} \tag{10}$$

In the cases of $[Co(CO_3)(NH_3)_4]^+$, $[Co(CO_3)(en)_2]^+$, and β-$[Co(CO_3)(trien)]^+$, we cannot conclusively assign k_{fast} and k_{slow} to the two kinetic processes in Scheme 2b, because either increase monotonically with increasing acidity. However, we prefer to assign the processes on the basis of the similarity between the kinetically and spectrophotometrically determined acidity constants, K, Table 3: k_{fast} to the decarboxylation with $[Co(CO_3)(NH_3)_4]^+$ and $[Co(CO_3)(en)_2]^+$ while k_{slow} with β-$[Co(CO_3)(trien)]^+$. We neglect the K_b/K_w in these cases because the supposed basicity is dormant: $(K_b/K_w)h^2 \approx 0.3\times0.5^2$ M $\ll K_a = 0.24$—0.63 M. In the cases of α-$[Co(CO_3)(trien)]^+$, $[Co(CO_3)(tren)]^+$, and $[Co(CO_3)(nta)]^{2-}$, the k_{fast} values increase monotonically

Table 2. Rate and Equilibrium Constants at 25 °C for the Decarboxylation

Hydrogencarbonato Intermediate[a)]	Ref.	I[b)]	k_{O-C}/s^{-1}	K_a/M	$(K_b/K_w)/M^{-1}$
$[Co(HCO_3)(NH_3)_5]^{2+}$	c)	2.0	1.3±0.0	$(7.5\pm1.0)\times10^{-7}$ e)	0.33±0.01, 0.26±0.10[e)]
	c)	2.0 (KCl)	1.6±0.0	—	0.35±0.01
	c)	2.0	1.2±0.0[d)]	—	0.36±0.00,[d)] 0.25±0.04[d,e)]
	c)	0.5	1.3±0.0	$(3.0\pm0.6)\times10^{-7}$	—
	4	0.5	1.3	4×10^{-7}	—
	5	0.5 (NaCl)	1.1	2×10^{-7}	—
$[Rh(HCO_3)(NH_3)_5]^{2+}$	c)	2.0	1.2±0.0	$(4.8\pm1.1)\times10^{-7}$ e)	0.57±0.01
	5	0.5 (NaCl)	1.1	1.1×10^{-7}	—
$[Ir(HCO_3)(NH_3)_5]^{2+}$	c)	2.0	1.5±0.0	$(6.8\pm1.2)\times10^{-7}$ e)	0.52±0.01
	5	0.5 (NaCl)	1.5	1.6×10^{-7}	—
$[Co(HCO_3)(NH_3)_4(H_2O)]^{2+}$	c)	2.0	3.1±0.2	0.52±0.00	—
	c)	2.0	2.9±0.1[d)]	0.17±0.01[d)]	—
	9	1.0	1.5	—	—
$[Co(HCO_3)(en)_2(H_2O)]^{2+}$	c)	2.0	1.3±0.0	0.24±0.00	—
	8	1.0	0.9	—	—
α-$[Co(HCO_3)(trien)(H_2O)]^{2+}$	c)	2.0	0.8±0.2	0.04±0.03	0.4±0.2 <
	9	1.0	0.6	—	—
β-$[Co(HCO_3)(trien)(H_2O)]^{2+}$	c)	2.0	0.25±0.01	0.63±0.00	—
	9	1.0	0.5	—	—
$[Co(HCO_3)(tren)(H_2O)]^{2+}$	c)	2.0	0.5±0.1	0.1±0.0	0.6±0.1 <
	9	1.0	0.3	—	—
fac(*N*)-$[Co(HCO_3)(5\text{-dptma})(H_2O)]^{+1}$	10	2.0	0.47	0.15	—
mer(*N*)-$[Co(HCO_3)(5\text{-dptma})(H_2O)]^{+1}$	10	2.0	0.18	0.004	0.11 <
fac(*N*)-$[Co(HCO_3)(i\text{-dtma})(H_2O)]^{+1}$	10	2.0	1	—	—
mer(*N*)-$[Co(HCO_3)(i\text{-dtma})(H_2O)]^{+1}$	10	2.0	2.2	0.2	—
mer(*N*)-$[Co(HCO_3)(i\text{-2,3ma})(H_2O)]^{+1}$	10	2.0	0.3	—	—
cis(*O*)-$[Co(aeida)(HCO_3)(H_2O)]$	10	2.0	2	—	—
trans(*O*)-$[Co(aeida)(HCO_3)(H_2O)]$	10	2.0	4.4	0.3	—
$[Co(HCO_3)(nta)(H_2O)]^-$	c)	2.0	3.1±0.1	0.05±0.00	0.7±0.0
	9	1.0	2.0	—	—
cis-$[Rh(HCO_3)(en)_2(H_2O)]^{2+}$	14	0.5	0.72	2×10^{-5}	—

a) The abbreviations for ligands are: H(5 – dptma) = *N*,*N*-bis(3-aminopropyl)glycine, H(*i* – dtma) = *N*,*N*-bis(2-aminoethyl)glycine, H(*i*-2,3-ma) = *N*-(2-aminoethyl)-*N*-(3-aminopropyl)glycine and H_2aeida = *N*-(2-aminoethyl)-*N*-(carboxymethyl)glycine. In the *fac*(*N*) or the *mer*(*N*) coordination mode, the three nitrogen atoms of the tetradentate reside on a face or a meridian of the coordination octahedron. In the *cis*(*O*) or the *trans*(*O*) coordination mode the two oxygen atoms of the quadridentate reside in a *cis* or a *trans* position of the coordination octahedron. b) $NaClO_4$ unless indicated. c) This work. d) In D_2O. e) Estimated from the acidity dependence of A_{obs}.

with the acidity, while the k_{slow} values increase with the acidity at $h < 0.2$ M, attain a flat maximum at $h \approx 0.2$ M, but decrease slightly with acidity at $0.2M < h$, Fig. 7. These k_{slow} should be treated by Eq. 10 compatible with the maximum appearance. The resultant constant values are summarized in Tables 2 and 3 with the previous ones.

Discussion

Concerning the carbonato ring-opening process in reaction 2, we have no special addition to the previous discussion, because our values of K and k_{Co-O} are more or less the same as those given earlier, Table 3.[9] Our k_{O-C} values for reactions 1 and 2 are also similar to previous ones, Table 2. The newly found aspect in this work is that the hydrogencarbonato intermediates, **2** and **7**, have an amphiprotic character. For reaction 1, the K_a values determined spectrophotometrically in this work agree satisfactorily well with the corresponding ones determined kinetically in previous studies, thus justifing the existence of an equilibrium between **1** and **2**.[4,5] By analogy with this, an equilibrium between **7** and **9** is reasonable.

The rather strong acidic character, K_a = 0.004—0.63 M, of **7** has been demonstrated by the increasing experimental rate constant with increasing acidity at $h < 0.2$ M, where a measurement is lacking in the previous studies, Figs. 6 and 7. Although these K_a values for species **7** are rather dependent on the variation of L_4, their magnitudes are in strong contrast to those, $(3—8)\times10^{-7}$ M, for species **2**. We ascribe the difference to the effect of an aqua ligand in **7**, and believe that the aquacarbonato complex **9** is stabilized by the intramolecular hydrogen bond between the monodentate carbonato ligand and the *cis* aqua ligand, Scheme 2b. Delocalization of the carbonyl π-electrons onto the six-membered plane involving the hydrogen bond should contribute to the stability. This stability is the cause of the rather strong acidity of species **7**. In contrast, a possible hydrogen bond between the carbonato and a *cis* amine or ammonia ligands is weak, partly because the nitrogen atom is less electronegative and partly because the fixed direction of an amine N–H bond is against the plane formation, or the two ammonia hydrogen atoms out of the plane may hinder the π-electron delocalization. It is conceiv-

Table 3. Rate and Equilibrium Constants at 25 °C for the Carbonato Ring Opening in Reaction 2

Complex	Ref.	I(NaClO$_4$)	k_{Co-O}/s^{-1}	K/M^{-1} a)
$[Co(CO_3)(NH_3)_4]^+$	b)	2.0	1.6±0.1$^{c)}$	1.1±0.0$^{c)}$ (0.8±0.1)
	9	1.0	1.7	1.0
	b)	2.0	1.4±0.1$^{c,d)}$	3.7±0.2$^{c,d)}$
$[Co(CO_3)(en)_2]^+$	b)	2.0	1.0±0.1$^{c)}$	1.2±0.0$^{c)}$ (0.8±0.0)
	8	1.0	0.9	1.2 (0.9)
α-$[Co(CO_3)(trien)]^+$	b)	2.0	5.6±0.6$^{e)}$	3±1$^{e)}$
	9	1.0	9.7	0.7
β-$[Co(CO_3)(trien)]^+$	b)	2.0	1.3±0.6$^{e)}$	0.6±0.2$^{e)}$ (0.8±0.1)
	9	1.0	0.3	0.8
$[Co(CO_3)(tren)]^+$	b)	2.0	2.6±0.1$^{e)}$	2.1±0.1$^{e)}$
	9	1.0	4.3	0.6
fac(*N*)-$[Co(CO_3)(5\text{-dptma})]$	10	2.0	0.21	(1.6)
mer(*N*)-$[Co(CO_3)(5\text{-dptma})]$	10	2.0	126	(1.0)
fac(*N*)-$[Co(CO_3)(i\text{-dtma})]$	10	2.0	3.9	(1.2)
mer(*N*)-$[Co(CO_3)(i\text{-dtma})]$	10	2.0	0.8	(1.4)
mer(*N*)-$[Co(CO_3)(i\text{-}2,3\text{ma})]$	10	2.0	12	(0.9)
cis(*O*)-$[Co(aeida)(CO_3)]^-$	10	2.0	3.4	(1.3)
trans(*O*)-$[Co(aeida)(CO_3)]^-$	10	2.0	2.8	(1.0)
$[Co(CO_3)(nta)]^{2-}$	b)	2.0	78±10$^{e)}$	1.8±0.0$^{e)}$
	9	1.0	85	(0.9)

a) In parenthesis, values estimated from the acidity dependence of A_{obs} are shown. b) This work. c) Estimated by Eq. 8. d) In D$_2$O. e) Estimated by Eq. 9.

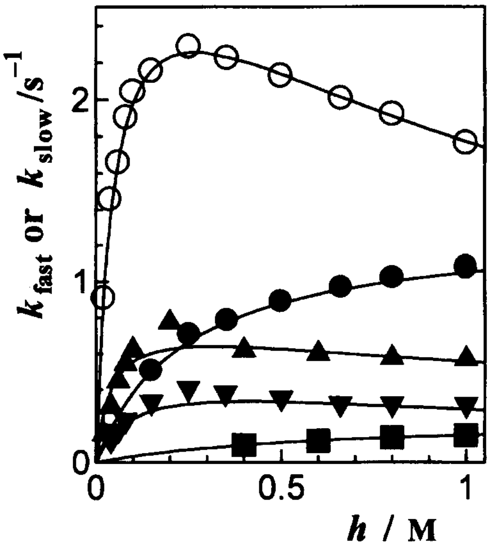


Fig. 7. Plots of k_{fast} or k_{slow} versus h corresponding to the decarboxylation in reaction 2 at 25 °C and I = 2.0 (NaClO$_4$). The k_{fast} with L$_4$ = (en)$_2$ (●) and the k_{slow} with L$_4$ = α-trien (▲), β-trien (■), tren (▼), and nta (○) are shown. Curve fittings were achieved using Eqs. 7 and 10.

able that the variation of L$_4$ influences the solvation sphere around **7** or **9** and, accordingly, the stability of this hydrogen bond.[13] We estimate the free energy gain at 21—33 kJ mol^{-1} from the terms $-RT\ln K_a$ with $K_a = 10^{-6}$, 0.004 and 0.63 M. This magnitude is appropriate to a strong hydrogen-bond energy. The small magnitude, $K_a = 2\times10^{-5}$ M, reported for *cis*-$[Rh(HCO_3)(en)_2(H_2O)]^{2+}$ is reasonable since a weak (7 kJ mol^{-1}) hydrogen bond forms because the ionic radius, 0.081 nm, of Rh(III) is large compared to the 0.069 nm of Co(III).[14] The basic characters of intermediates **2** and **7** have been demonstrated by a decrease of the experimental rate constants of decarboxylation at high acidity, Figs. 1 and 7. The differences between spectra **B** and **C** justify the existence of species **4**, Fig. 2. In the case of $[Ir(CO_3)(NH_3)_5]^+$, we ascribe the observed overlap of spectra **B** and **C** to the similarity of the absorption spectra of **2** and **4**, Fig. 2f. In the case of $[Co(CO_3)(NH_3)_5]^+$, the effect of an electrolyte variation has been checked. The k_{O-C} = 1.6 s^{-1} and K_b/K_w = 0.35 M^{-1} in KCl+HCl are essentially the same as the 1.3 s^{-1} and the 0.33 M^{-1} in NaClO$_4$+HClO$_4$. This unfavors a conception to ascribe the rate decrease to some solution medium effect. In reaction 2 with L$_4$ = (NH$_3$)$_4$, (en)$_2$ and β-trien, the rate decrease is unobservable at high acidity because the strong acidity overwhelms the basicity. One can not know which one of the carbonyl and hydroxyl oxygen atoms of the carbonic acid ligand coordinates to the metal in the species **4** and **10**. We have tentatively assumed a coordination through the latter. In either case, **4** and **10** should not be a very stable one on account of the reduced basicity of the carbonic acid ligand or on an analogy of the acid-catalysed hydrolysis of the acetatopentaamminecobalt(III).[15] However, in the cases of $[Co(HCO_3)(NH_3)_5]^{2+}$, $[Rh(HCO_3)(NH_3)_5]^{2+}$, $[Ir(HCO_3)(NH_3)_5]^{2+}$, and $[Co(HCO_3)(nta)(H_2O)]^-$, we estimate that the first-order rate constant for the hydrolysis of **4** or **10** should be smaller than one tenth of the corresponding k_{O-C} on the basis that the k_{obs} or the k_{slow} fits satisfactorily well to Eq. 4 or to Eq. 10; < 0.3 s^{-1}. In the case of $[Co(HCO_3)(NH_3)_5]^{2+}$, the agreement of the kinetic K_b/K_w = 0.33 or 0.36 M^{-1} with the spectrophotometric one 0.26 or 0.25 M^{-1} supports this reduced lability of **4** or **10**. The K_b/K_w value for α-$[Co(HCO_3)(trien)(H_2O)]^{2+}$, $[Co(HCO_3)(tren)(H_2O)]^{2+}$, or *mer*(*N*)-$[Co(HCO_3)(5\text{-dptma})(H_2O)]^+$ should be larger than that estimated by assuming species **10** to be a dead-end species. In the case of $[Co(CO_3)(NH_3)_4]^+$, it is reasonable that the rate constants $k_{Co\text{–}O} = 1.4\ s^{-1}$ and $k_{O\text{–}C} = 2.9\ s^{-1}$ in D_2O are similar to the 1.6 and 3.1 s^{-1}, respectively, obtained for a reaction in H_2O. The equilibrium constants $K = 3.7\ M^{-1}$ and $K_a = 0.17$ M in D_2O may be compared to the corresponding values in H_2O, $K = 1.1\ M^{-1}$ and $K_a = 0.52$ M and are consistent with the expected effects for specific acid-catalysed processes.[16] This justifies the protonation equilibrium between **5** and **6** and the deprotonation equilibrium between **7** and **9**, Scheme 2. In the case of $[Co(HCO_3)(NH_3)_5]^{2+}$, the $k_{O\text{–}C} = 1.2\ s^{-1}$ in D_2O is close to the $k_{O\text{–}C} = 1.3\ s^{-1}$ in H_2O, while the $K_b/K_w = 0.36$ or $0.25\ M^{-1}$ in D_2O is similar to the 0.33 or $0.26\ M^{-1}$ in H_2O. Although this is rather strange, the absence of the expected solvent isotope effect on the magnitude of K_b/K_w may be understood on the account that there are many exceptional protonation equilibria showing no such effect.[16]

Supporting Information Available: Experimental rate constants for reaction 1 (Table S1); and experimental rate constants and zero-time absorbances for reaction 2 at 25 °C and $I = 2.0(NaClO_4)$ (Table S2) are deposited as Document No. 73046 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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