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Mechanistic Information from the Effect of Pressure on the Formation and Acid-Catalyzed Aquation Reactions of (Carbonato)pentaamminecobalt(III), -rhodium(III), and -iridium(III) Ions in Aqueous Solution[1]

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The formation and decarboxylation kinetics of the complexes $M(NH_3)_5OCO_2^+$ (M = Co(III), Rh(III), and Ir(III)) have been studied as a function of pressure up to 1000 bar. The volumes of activation for CO_2 uptake are -10.1 ± 0.6, -4.7 ± 0.8, and -4.0 ± 1.0 $cm^3\ mol^{-1}$, whereas the corresponding values for decarboxylation are $+6.8 \pm 0.3$, $+5.2 \pm 0.3$, and $+2.5 \pm 0.4$ $cm^3\ mol^{-1}$, respectively. Combined with partial molar volume measurements, these values enable the construction of overall reaction volume profiles. It follows that bond formation during CO_2 uptake and bond breakage during decarboxylation are approximately 50% completed in the transition state of these processes.

Introduction

Harris and co-workers[2-7] have demonstrated in an extensive series of papers that transition-metal hydroxo complexes are in general capable of reacting with CO_2 to produce the corresponding carbonato complexes. These CO_2 uptake reactions are fast (stopped-flow rate) and proceed via oxygen-carbon bond formation without breakage of the metal-oxygen bond. The rate of CO_2 uptake was shown[7,8] to depend on the nucleophilicity of the bound hydroxide ion and therefore correlates with the O-H bond strength (i.e., acid dissociation constant) of the corresponding aquo complex. On acidification the carbonato complexes undergo decarboxylation which is also a fast reaction and in general found to be independent of $[H^+]$ at pH ≤4. Tracer experiments,[9,10] utilizing ^{18}O labeling, have proved conclusively that decarboxylation of monodentate carbonato complexes also takes place without metal-oxygen bond breakage. The rate-determining step involves breakage of the oxygen-carbon bond on the carbonate ligand.

In this study we investigated the pressure dependence of the formation and decarboxylation reactions of the species $M(NH_3)_5OCO_2^+$ (M = Co(III), Rh(III), and Ir(III)) in aqueous solution using a high pressure stopped-flow instrument.[11] In addition, we measured the partial molar volumes of the various species involved in these reactions and, combined with the volumes of activation, constructed overall reaction volume profiles for the studied processes.

Table I. Analytical Data

complex		%C	%N	%H	%O
$[Co(NH_3)_5OH_2](ClO_4)_3$	calc		15.2	3.7	45.2
	found		15.1	3.9	45.0
$[Co(NH_3)_5CO_3]ClO_4$	calc	4.0	23.1	5.0	36.9
	found	3.9	23.3	4.7	36.1
$[Rh(NH_3)_5OH_2](ClO_4)_3$	calc		13.9	3.4	41.2
	found		13.7	3.4	40.8
$[Rh(NH_3)_5CO_3]ClO_4$	calc	3.5	20.2	4.4	32.2
	found	3.4	19.9	4.4	31.7
$[Ir(NH_3)_5OH_2](ClO_4)_3$	calc		11.8	2.9	35.0
	found		12.0	2.8	34.7
$[Ir(NH_3)_5CO_3]ClO_4$	calc	2.8	16.0	3.5	25.6
	found	2.6	16.1	3.3	25.7

Table II. UV-Visible Spectral Data for a Series of Pentaammineaquo and -carbonato Complexes

complex ion	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	ref
$Co(NH_3)_5OH_2^{3+}$	491, 343	49.0, 47.0	19
	491	48.0	3
	490, 345	48.5, 45.0	this work
$Co(NH_3)_5CO_3^+$	505	94	2
	510	95	this work
$Rh(NH_3)_5OH_2^{3+}$	316, 264	105, 94	20
	315, 262	105, 95	21
	314	112	4
	314, 261	112, 101	this work
$Rh(NH_3)_5CO_3^+$	325	178	4
	324	178	this work
$Ir(NH_3)_5OH_2^{3+}$	258	87	4
	258	88	this work
$Ir(NH_3)_5CO_3^+$	262	125	4
	262	125	this work

Experimental Section

The following complexes were prepared as described in the literature: $[Co(NH_3)_5OH_2](ClO_4)_3$,[12,13] $[Rh(NH_3)_5OH_2](ClO_4)_3$,[14,15] $[Co(NH_3)_5CO_3]ClO_4$,[12,16] $[Rh(NH_3)_5CO_3]ClO_4$,[4,16] and $[Ir(NH_3)_5CO_3]ClO_4$.[4,16] $[Ir(NH_3)_5OH_2](ClO_4)_3$ was synthesized from $[Ir(NH_3)_5Cl]Cl_2$ according to the procedure of Schmidtke.[17] We found that a considerably higher yield of $[Ir(NH_3)_5Cl]Cl_2$ could be obtained when $IrCl_6^{3-}$ was boiled with $(NH_4)_2CO_3$ under reflux for 12 h. Chemical analyses[18] resulted in the values given in Table I. UV-visible absorption spectra (Table II) are in close agreement with those published elsewhere. Chemicals of analytical reagent grade and

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Table III. Pressure Dependence of the Formation and Decarboxylation Reactions of Complexes of the Type Type $M(NH_3)_5OCO_2^{+}$ [a]

M	P, bar	$k_{obsd}/[CO_2] = k_1$,[b] M^{-1} s^{-1}	$\Delta\overline{V}^{\ddagger}$, cm^3 mol^{-1}	$k_{obsd} = k_2$,[c] s^{-1}	$\Delta\overline{V}^{\ddagger}$, cm^3 mol^{-1}
Co(III)	10	199 ± 20	−10.1 ± 0.6	1.07 ± 0.03	+6.8 ± 0.3
	250	214 ± 10		1.02 ± 0.07	
	500	244 ± 40		0.95 ± 0.02	
	750	263 ± 20		0.87 ± 0.04	
	1000	282 ± 40		0.82 ± 0.08	
Rh(III)	10	335 ± 35	−4.7 ± 0.8	1.09 ± 0.05	+5.2 ± 0.3
	250	344 ± 20		1.05 ± 0.10	
	500	376 ± 50		1.00 ± 0.06	
	750	368 ± 40		0.93 ± 0.08	
	1000	388 ± 50		0.89 ± 0.09	
Ir(III)	10	411 ± 50	−4.0 ± 1.0	1.44 ± 0.07	+2.5 ± 0.4
	250	429 ± 30		1.40 ± 0.08	
	500	427 ± 46		1.35 ± 0.12	
	750	430 ± 50		1.31 ± 0.10	
	1000	474 ± 55		1.31 ± 0.11	

[a] $[M] = 2.5 \times 10^{-3}$ M, temp = 25 °C, ionic strength = 0.5 M, wavelength = 260 nm; values of k_{obsd} are the mean of at least five determinations. [b] CO_2 uptake reaction, pH 8.5 (Tris buffer), $[CO_2] = 0.01$ M at atmospheric pressure and not corrected for the compressibility of the solvent at elevated pressures. [c] Acid-catalyzed decarboxylation reaction; $[H^+] = 0.1$ M.

Table IV. Partial Molar Volume Measurements at 25 °C

complex	$\overline{V}$,[a] cm^3 mol^{-1}	ion	$\overline{V}$,[b] cm^3 mol^{-1}
$[Co(NH_3)_5OH_2](ClO_4)_3$	207.0 ± 0.4	$Co(NH_3)_5OH_2^{3+}$	54.9
$[Rh(NH_3)_5OH_2](ClO_4)_3$	212.6 ± 1.0	$Rh(NH_3)_5OH_2^{3+}$	60.5
$[Ir(NH_3)_5OH_2](ClO_4)_3$	212.0 ± 1.2	$Ir(NH_3)_5OH_2^{3+}$	59.9
$[Co(NH_3)_5OH](ClO_4)_2$[c]	162.6 ± 0.9	$Co(NH_3)_5OH^{2+}$	68.6
$[Rh(NH_3)_5OH](ClO_4)_2$[c]	164.5 ± 1.2	$Rh(NH_3)_5OH^{2+}$	70.3
$[Ir(NH_3)_5OH](ClO_4)_2$[c]	164.4 ± 1.5	$Ir(NH_3)_5OH^{2+}$	70.6
$[Co(NH_3)_5CO_3]ClO_4$	142.2 ± 0.6	$Co(NH_3)_5CO_3^{+}$	91.5
$[Rh(NH_3)_5CO_3]ClO_4$	146.6 ± 0.8	$Rh(NH_3)_5CO_3^{+}$	95.9
$[Ir(NH_3)_5CO_3]ClO_4$	147.9 ± 0.7	$Ir(NH_3)_5CO_3^{+}$	97.2

[a] Experimentally measured value. [b] Calculated value from $V_{ClO_4^-} = 50.7$ cm^3 mol^{-1}.[31] [c] Prepared in solution by dissolving the corresponding aquo complexes in 0.03 M NaOH. The measured density was corrected for the small change in $[OH^-]$ due to the neutralization of the aquo species and for the presence of the third perchlorate ion in solution.

doubly distilled water were used throughout this study.

Absorption spectra in the UV–visible region were recorded on a Perkin-Elmer 555 spectrophotometer. Partial molar volumes were determined with a digital density apparatus, DMA 02 (Anton Paar KG, Austria), thermostated at 25.000 ± 0.002 °C. In general, densities were measured for at least six concentrations in the range 5×10^{-3}–5×10^{-2} M.

Kinetic studies were performed on a high-pressure stopped-flow instrument for pressures up to 1000 bar. The "acidification method", described in detail elsewhere,[3] was employed during the CO_2-uptake studies. The reactions were monitored at wavelengths where the difference in absorption between reactants and products is a maximum. Tris buffers[22] were used to control the pH of the solutions during the CO_2-uptake studies. pH measurements at normal pressure were performed on a Radiometer PHM 64 meter. The observed pseudo-first-order rate constants were calculated in the usual way by using a standard least-squares analysis.

Results and Discussion

The suggested mechanism[2-4] common for the formation and decarboxylation reactions of complexes of the type $M(NH_3)_5OCO_2^+$ can be summarized as in eq 1. The overall

$$M(NH_3)_5OH_2^{3+} \overset{K_A}{\rightleftharpoons} M(NH_3)_5OH^{2+} + H^+$$

$$M(NH_3)_5OH^{2+} + CO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(NH_3)_5OCO_2H^{2+} \qquad (1)$$

$$M(NH_3)_5OCO_2H^{2+} \overset{K_B}{\rightleftharpoons} M(NH_3)_5OCO_2^+ + H^+$$

rate expression for this mechanism is given by eq 2 (decarb

$$k_{obsd} = k_{CO_2\,uptake} + k_{decarb} = \frac{k_1K_A[CO_2]}{[H^+] + K_A} + \frac{k_2[H^+]}{[H^+] + K_B} \qquad (2)$$

= decarboxylation). Under the experimental conditions employed during the CO_2-uptake measurements, no decarboxylation occurs and $K_A >> [H^+]$[23] such that eq 2 reduces to $k_{obsd} = k_1[CO_2]$. Similarly, the experimental conditions for the decarboxylation studies were chosen such that no CO_2 uptake occurs and $[H^+] >> K_B$[24] with the result that $k_{obsd} = k_2$. These two limiting forms of rate law 2 allow a direct measurement of the rate-determining steps in mechanism 1. In addition, if the $[H^+]$ of the test solutions varies as a function of pressure due to the compressibility of the solution and the influence of pressure on the acid/base equilibrium of the buffer, it will still not influence the limiting forms of rate law 2. The obtained results are summarized in Table III.

The values of k_1 and k_2 at 10 bar are in close agreement with those reported in the literature[2-4] for the corresponding reactions at atmsopheric pressure. The experimental error limits on the values of k_1 and k_2 are very similar to those observed for such measurements at normal pressure in general.[2-4,7] Plots of ln k_1 and ln k_2 vs. pressure are linear within the experimental error limits and enable the estimation of the volume of activation ($\Delta\overline{V}^{\ddagger}$) in the usual way. The sign of $\Delta\overline{V}^{\ddagger}$ is in agreement with bond formation and bond breakage reactions, respectively, and represents the intrinsic change in volume in both cases. No major contributions from changes in solvation are expected to influence the magnitude of $\Delta\overline{V}^{\ddagger}$ since neither the uptake nor loss of CO_2 involves any changes in charge. The absolute magnitude of $\Delta\overline{V}^{\ddagger}$ is surprisingly small, especially if one considers that the processes involve the uptake or release of a CO_2 molecule, for which the partial molar volume is of the order of 35 cm^3 mol^{-1} (see further discussion). Furthermore $|\Delta\overline{V}^{\ddagger}|$ decreases significantly along the series Co(III) > Rh(III) > Ir(III), that is, with increasing size of the central metal atom. $\Delta\overline{V}^{\ddagger}$ for CO_2 uptake (k_1) seems to parallel the corresponding values for $\Delta S^{\ddagger}$, whereas a completely opposite tendency is observed when $\Delta\overline{V}^{\ddagger}$ for decarboxylation (k_2) is compared to the corresponding $\Delta S^{\ddagger}$ values.[3,4]

The partial molar volumes of the species $M(NH_3)_5OH_2^{3+}$, $M(NH_3)_5OH^{2+}$, and $M(NH_3)_5OCO_2^+$ were measured as described in the Experimental Section, and the results are summarized in Table IV. These values are in good agreement with those reported for some of the species elsewhere.[25,26] In addition, we measured the partial molar volume of dissolved CO_2 by carefully acidifying dilute $NaHCO_3$ solutions and found a value of 34.5 ± 1.4 cm^3 mol^{-1}. The latter falls within the range of values varying between 31.3 and 37.6 cm^3 mol^{-1} reported in the literature.[27-31] For the CO_2-uptake process the volume of activation $\Delta\overline{V}^{\ddagger} = \overline{V}_{\ddagger} - \overline{V}_{MOH} - \overline{V}_{CO_2}$, where $\overline{V}_{\ddagger}$

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(22) Tris = tris(hydroxymethyl)aminomethane.

(23) The pK_A values for $M(NH_3)_5OH_2^{3+}$ are 6.3,[3,19] 6.8,[4] and 6.7[4] for M = Co(III), Rh(III), and Ir(III), respectively.

(24) The pK_B values for $M(NH_3)_5OCO_2H^{2+}$ are 6.7,[3] 6.9,[4] and 6.8[4] for M = Co(III), Rh(III), and Ir(III), respectively.

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Table V. Volume Quantities for the Overall Process[a]

$M(NH_3)_5OH^{2+} + CO_2 \rightleftharpoons [M(NH_3)_5OH^{2+}\text{--}CO_2]^{\ddagger} \rightleftharpoons M(NH_3)_5OCO_2H^{2+}$

M	$\bar{V}_{MOH} + \bar{V}_{CO_2}$	$\bar{V}_{\ddagger}{}^{b}$	$\bar{V}_{MOCO_2H}{}^{c}$
Co(III)	103.1	93.0	86.2
Rh(III)	104.8	100.1	94.9
Ir(III)	105.1	101.1	98.6

[a] All volume quantities are given in $cm^3\ mol^{-1}$. [b] Calculated according to eq 3. [c] Calculated according to eq 4.

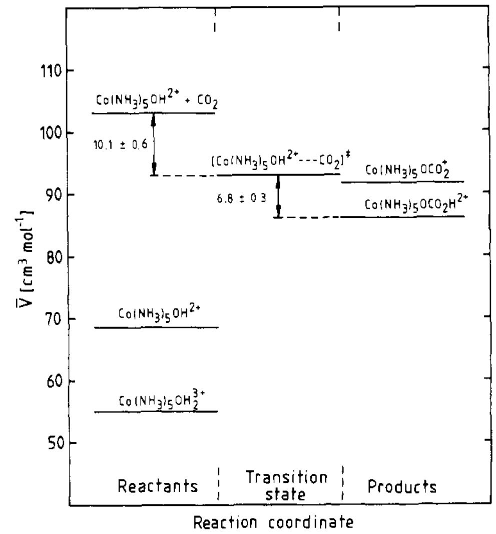

Figure 1. Volume profile diagram for the reaction $Co(NH_3)_5OH^{2+} + CO_2 \rightleftharpoons Co(NH_3)_5OCO_2H^{2+}$.

is the partial molar volume of the transition state. It follows that

$$\bar{V}_{\ddagger} = \Delta\bar{V}^{\ddagger}{}_{CO_2\,\mathrm{uptake}} + \bar{V}_{MOH} + \bar{V}_{CO_2} \qquad (3)$$

For the decarboxylation reaction $\Delta\bar{V}^{\ddagger} = \bar{V}_{\ddagger} - \bar{V}_{MOCO_2H}$ such that the partial molar volume of the unstable bicarbonato complex intermediate, viz., $M(NH_3)_5OCO_2H^{2+}$, can be calculated from eq 4. In this equation it is assumed that both

$$\bar{V}_{MOCO_2H} = \bar{V}_{\ddagger} - \Delta\bar{V}^{\ddagger}{}_{\mathrm{decarb}} = \Delta\bar{V}^{\ddagger}{}_{CO_2\,\mathrm{uptake}} + \bar{V}_{MOH} + \bar{V}_{CO_2} - \Delta\bar{V}^{\ddagger}{}_{\mathrm{decarb}} \qquad (4)$$

processes, i.e., CO_2 uptake and decarboxylation, proceed via the same transition state due to the principle of microscopic reversibility. The estimated values of $\bar{V}_{\ddagger}$ and $\bar{V}_{MOCO_2H}$ are summarized in Table V along with other volume quantities that enable the construction of overall reaction volume profiles. One example of such a profile is given in Figure 1 for the Co(III) system.

A comparison of the data in Table IV for the different central metal ions reveals that the increase in $\bar{V}$ along the series Co(III) < Rh(III) < Ir(III) is rather small and shows no distinct correlation with the charge on the complex ions. The increase in partial molar volumes, $\bar{V}$, along the series $M(NH_3)_5OH_2{}^{3+} < M(NH_3)_5OH^{2+} < M(NH_3)_5OCO_2{}^{+}$ is partially ascribed to the decrease in overall charge, combined with a considerable increase in volume for the formation of the significantly larger carbonato complexes. Inclusion of the $\bar{V}$ values for the $M(NH_3)_5OCO_2H^{2+}$ species (Table V) further illustrates this effect. A comparison of $\bar{V}$ for the $M(NH_3)_5OH^{2+}$ and $M(NH_3)_5OCO_2H^{2+}$ species indicates that for similarly charged ions the bicarbonato complex is between 18 and 28 $cm^3\ mol^{-1}$ larger than the corresponding hydroxo complexes. In addition, $\bar{V}$ for $M(NH_3)_5OCO_2H^{2+}$ shows a significant increase with increasing size of the central metal atom. This may partially be due to some charge separation, i.e., increase in electrostriction, between the metal and bicarbonate center in the case of the smaller metal atoms, viz., Co(III). Protonation of the carbonato complexes results in a volume decrease in the case of the Co(III) species (compare Tables IV and V) but in almost no change for the larger metal species. This may partially account for the relatively small $|\Delta\bar{V}^{\ddagger}|$ values found for the Rh(III) and Ir(III) species in this study.

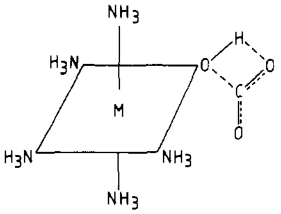

Figure 2. Suggested transition state during CO_2 uptake and decarboxylation reactions.

The values of $\bar{V}_{\ddagger}$ are such that the transition state lies approximately halfway between the reactant and product states. This is further clearly seen in Figure 1. We conclude that bond formation during CO_2 uptake and bond breakage during decarboxylation are approximately 50% completed in the transition state for both processes. This can be considered as direct evidence for a transition state of the type shown in Figure 2, which has been postulated in an earlier study.[32]

Finally, it is interesting to note that the volumes of activation reported for the decarboxylation of carbonato complexes in this study are in good agreement with those reported by Brower and co-workers[33] for the decarboxylation of organic acids in aqueous medium.

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Registry No. $Co(NH_3)_5OH_2{}^{3+}$, 14403-82-8; $Co(NH_3)_5CO_3{}^{+}$, 15844-68-5; $Rh(NH_3)_5OH_2{}^{3+}$, 15337-79-8; $Rh(NH_3)_5CO_3{}^{+}$, 50600-89-0; $Ir(NH_3)_5OH_2{}^{3+}$, 29589-08-0; $Ir(NH_3)_5CO_3{}^{+}$, 50600-91-4; $Co(NH_3)_5OH^{2+}$, 16632-75-0; $Rh(NH_3)_5OH^{2+}$, 26214-91-5; $Ir(NH_3)_5OH^{2+}$, 44439-82-9.

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