Reaction of Pentaammineaquarhodium(III) with Carbonate in Strongly Basic Solution: A Multiple Choice of Potential Interactions

Edu Cloete,[a] **Ernst Breet***,[a] **and Rudi van Eldik***,[b]
[a] *Department of Chemistry, Potchefstroom University, Private Bag X6001, 2520 Potchefstroom, South Africa*
[b] *Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany*

The reaction of pentaammineaquarhodium(III) with carbonate to produce pentaamminecarbonatorhodium(III) was studied in strongly basic solution to ascertain whether under such conditions ligand substitution *via* metal–oxygen bond rupture is favoured over carbon dioxide uptake which leaves the metal–oxygen bond intact. The kinetic data are consistent with two opposing reaction paths, the rate constants of which exhibit pH dependencies which permit identification of the species interacting under the extreme conditions considered. The temperature and pressure dependencies of the rate constants facilitated disclosure of the intimate nature of the mechanism.

The uptake of carbon/sulfur dioxide by pentaammine complexes of the type $[M(NH_3)_5X]^{n+}$ (M = Co^{III}, Cr^{III}, Rh^{III}, Ir^{III} or Ru^{III}; X = H_2O or OH^-) readily occurs at $8 < pH < 11$ under conditions where, according to the pK_a values of carbonic/sulfurous acid, finite concentrations of the gaseous species are still available in solution. The metal–oxygen bond remains intact under such conditions, since the uptake of carbon/sulfur dioxide proceeds *via* secondary carbon–oxygen bond formation.[1,2] This feature makes these complexes attractive for utilisation in air-pollution-control applications and novel synthetic routes for O-bonded carbonato/sulfito complexes. At $11 < pH < 13$, however, ligand substitution by carbonate/sulfite or hydrogencarbonate/sulfite ion *via* metal–oxygen bond rupture becomes more likely, since almost no carbon/sulfur dioxide is present in solution under such conditions. Moreover, deprotonation of the co-ordinated ammine could, by way of the conjugate-base mechanism, facilitate ligand substitution in such circumstances. The study of a selected reaction at extreme pH thus seemed essential to confirm possible ligand substitution and to identify the species involved in such a reaction.

The intimate mechanism of the selected reaction is equally unpredictable, since the substitution reactions of the pentammine complexes of the transition metals mentioned predominantly follow an interchange mechanism positioned somewhere on a $I_a \longleftrightarrow I_d$ mechanistic continuum.[3] The reactions of $[Co(NH_3)_5(OH_2)]^{3+}$ are mainly I_d[4] and those of $[Rh(NH_3)_5(OH_2)]^{3+}$ I_a[5] in nature, but a shift between these mechanisms may be effected by replacing the ammine groups with spectator ligands having different steric/electronic effects.[6] A study of the temperature and pressure dependence of the selected reaction was thus needed to disclose the intimate nature of the mechanism by virtue of the resulting activation parameters.

Experimental

The complex $[Rh(NH_3)_5(OH_2)][ClO_4]_3$ was synthesised according to a standard procedure.[7] The product $[Rh(NH_3)_5(OCO_2)]ClO_4{\cdot}H_2O$ was obtained by direct addition of lithium carbonate to a saturated solution of the aqua complex in water and subsequent isolation from an ice-cold solution with absolute ethanol. The microelemental (C, H, N performed by a national laboratory) and spectrophotometric (UV/VIS spectra recorded in 2 mol dm^{-3} $NaClO_4$) analyses of the two compounds gave the following results: $[Rh(NH_3)_5(OH_2)][ClO_4]_3$ [Found (Calc.): H, 3.35(3.40); N, 13.80 (13.90)%]; λ_{max} 315 (ε_{max} 10.5; lit.,[8] 10.5) and 263 nm (ε 9.5, lit.,[8] 9.4 m^2 mol^{-1}); $[Rh(NH_3)_5(OCO_2)]ClO_4{\cdot}H_2O$ [Found (Calc.): C, 3.25 (3.30); H, 4.70 (4.70); N, 18.95 (19.15)%], λ_{max} 325 nm (ε_{max} 17.6; lit.,[9] 17.8 m^2 mol^{-1}).

Kinetic runs were performed with test solutions containing either the aqua or the carbonato complex as starting material and such that $[Rh] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} (adjusted with standardised $NaClO_4$ solution), $0 < [CO_3]_T < 0.3$ mol dm^{-3} (using standard Na_2CO_3 solution) and $11 < pH < 13$ (using standard NaOH solution according to $pK_1 = 6.03$ and $pK_2 = 9.80$[1] for an aqueous solution of CO_2 at 25 °C and 0.5 mol dm^{-3} ionic strength) after mixing prethermostatted and deoxygenated complex and ligand solutions for *in situ* spectrophotometric measurement (Unicam SP1800, Zeiss PMQII) in sealed cuvettes. The pH was adjusted analytically and, where possible ($pH \leqslant 12$), checked by physical measurement (Metrohm E520). The temperature was kept constant (Techne C100, Lauda TUK30) within 0.2° over the range 40–60 °C, while the pressure was varied over the range 0.1–150 MPa using a high-pressure optical cell described elsewhere.[10] The quoted pK_a values were assumed to remain practically unchanged under the above-mentioned conditions under which kinetic measurements were performed and literature data measured at different ionic strengths were extrapolated.

The pseudo-first-order rate constants were determined at a 10-fold excess of ligand by utilising both integral [$\ln (A_\infty - A_t)$ *versus* t] and initial rate [$\Delta c/\Delta t = \Delta A/(\varepsilon_2 - \varepsilon_1)\ \Delta t$ *versus* c] methods. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated from a plot based on the equation $\ln (kh/k_BT) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R$,[11] whereas $\Delta V^\ddagger$ was obtained by plotting $\ln k$ *versus* p according to the frequently used equation $\ln k = \text{constant} - (\Delta V^\ddagger p/RT)$.[12]

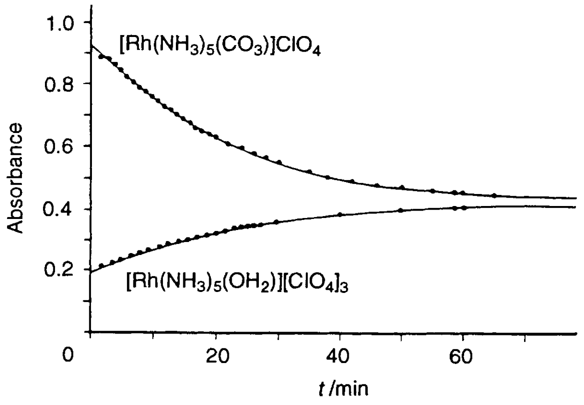


Fig. 1 Equilibrium attainment through the competitive anation and aquation reactions $[Rh(NH_3)_5(OH)]^{2+} + HCO_3^- \rightleftharpoons [Rh(NH_3)_5(OCO_2)]^+ + H_2O$ at $[Rh^{III}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, $[CO_3]_T = 0.3$ mol dm^{-3}, pH 11.5, 50 °C, and atmospheric pressure

Results and Discussion

Repetitive scans of the UV/VIS spectra of solutions of $[Rh(NH_3)_5(OH_2)][ClO_4]_3$ and $[Rh(NH_3)_5(OCO_2)]ClO_4$ respectively mixed with an excess of Na_2CO_3 at high pH allow the overall reaction to be depicted as an equilibrium between concomitant forward and reverse reaction steps as shown in Fig. 1. A similar result was obtained previously[13] for the conversion between $[Rh(NH_3)_5(OH_2)]Br_3$ and $[Rh(NH_3)_5Br]Br_2$ by measuring the change in conductance with time.

The pseudo-first-order rate constants measured with the integral method [selected example shown in Fig. 2(*a*)] strictly obey the rate equation (1) according to linear plots of k_{obs} *versus*

$$k_{obs} = k_1[CO_3]_T + k_2 \qquad (1)$$

$[CO_3]_T$ obtained under all conditions. The rate constants k_1 (second order) and k_2 (first order) for the forward and reverse reaction steps were obtained from the slope and intercept of these plots and are listed (first entries) in Tables 1 and 2 as a function of pH and temperature. These rate constants were also obtained separately (second entries) by using the initial-rate method [selected example shown in Fig. 2(*b*)] with either the aqua complex (k_1 path) or the carbonato complex (k_2 path) as reagent.

The values of both k_1 and k_2 decrease significantly with increasing pH. The best way to interpret these pH dependencies is to compare for each reaction path, at an appropriate temperature (*e.g.* 50 °C), the expected rate constants of all possible contributing reactions within Scheme 1 (protons omitted for simplicity) with those measured in this investigation. For the k_1 path, possible reactions could be (a)–(c). Reaction

$$[Rh(NH_3)_5(OH)]^{2+} + CO_2 \xrightarrow{k_a} \qquad (a)$$

$$[Rh(NH_3)_5(OH_2)]^{3+} + HCO_3^-/CO_3^{2-} \xrightarrow{k_b} \qquad (b)$$

$$[Rh(NH_3)_5(OH)]^{2+} + HCO_3^-/CO_3^{2-} \xrightarrow{k_c} \qquad (c)$$

(a) stems from the possibility that, at the extreme pH values of this investigation, a finite fraction of CO_2, however small, may still prevail in solution. This fraction is given by $f_{CO_2} = [H^+]^2/([H^+]^2 + K_1[H^+] + K_1K_2)$, with the values of K_1 and K_2 mentioned in the experimental section for conditions at which k_a was previously measured by other authors.[9] The value $k_a = 6.4 \times 10^3$ dm^3 mol^{-1} s^{-1} at 50 °C, extrapolated from the average of their measured (through employing two different methods) and predicted (by using their activation parameters) values at 25 °C, can be used along with the values of f_{CO_2} at $11 < pH < 13$ to calculate $k_1 = f_{CO_2}k_a$ measured in this investigation at 50 °C. The calculated values $k_1 = 4.1 \times 10^{-3}$, 4.2×10^{-4}, 4.3×10^{-5}, 4.3×10^{-6} and 4.3×10^{-7} dm^3 mol^{-1} s^{-1} at pH 11.0, 11.5, 12.0, 12.5 and 13.0, respectively, are in agreement with the experimental values in Table 1 at pH

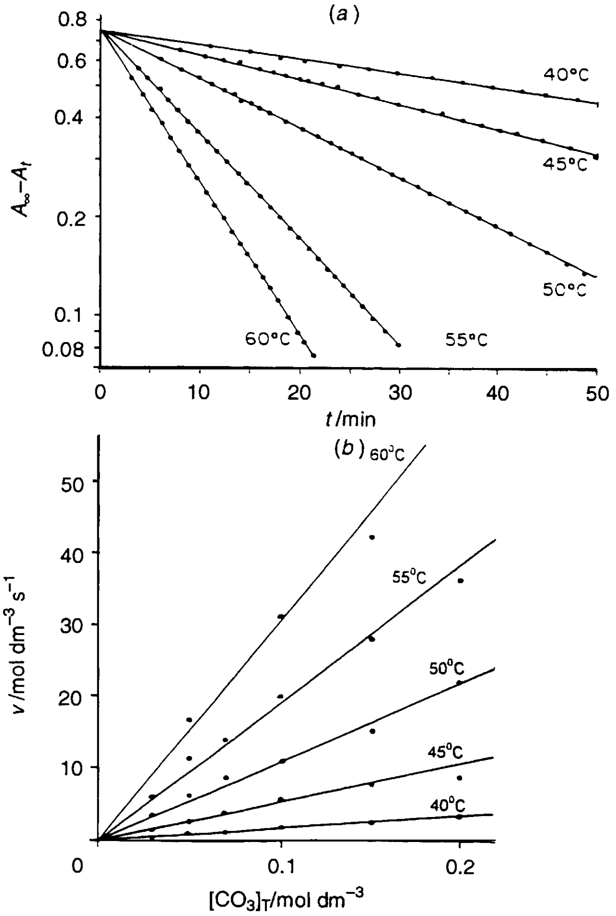
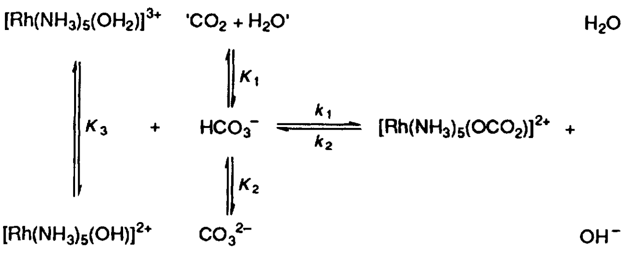


Fig. 2 Determination of pseudo-first-order rate constants for the reaction $[Rh(NH_3)_5(OH)]^{2+} + HCO_3^- \rightleftharpoons [Rh(NH_3)_5(OCO_2)]^+ + H_2O$ using (*a*) the integral method, (*b*) the initial-rate method; $[Rh^{III}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, {$[CO_3]_T = 0.2$ mol dm^{-3} for (*a*)}, pH 12.0, $40 < T < 60$ °C, atmospheric pressure



Scheme 1

Table 1 Rate constant k_1 as a function of pH and temperature at $[Rh^{III}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, $0 < [CO_3]_T < 0.3$ mol dm^{-3}, atmospheric pressure

	k_1/dm^3 mol^{-1} s^{-1}						
pH	40	45	50	55	60 °C	$\Delta H_1^‡$/ kJ mol^{-1}	$\Delta S_1^‡$/ J K^{-1} mol^{-1}
11.0			$(3.9 \pm 0.2) \times 10^{-3}$			75 ± 11	−60 ± 35
	1.16×10^{-3}		3.68×10^{-3}		6.93×10^{-3}		
11.5						88 ± 2	−27 ± 6
	6.24×10^{-4}		1.76×10^{-3}		5.01×10^{-3}		
12.0	$(8 \pm 2) \times 10^{-5}$		$(5.7 \pm 0.4) \times 10^{-4}$			117 ± 13	51 ± 40
	8.48×10^{-5}	2.62×10^{-4}	5.69×10^{-4}	8.66×10^{-4}	1.19×10^{-3}		
12.5	$(1.75 \pm 0.03) \times 10^{-5}$	3.60×10^{-5}	$(8.5 \pm 0.9) \times 10^{-5}$	$(2.1 \pm 0.2) \times 10^{-4}$	4.45×10^{-4}	132 ± 9	85 ± 28
	1.39×10^{-5}		9.14×10^{-5}		2.42×10^{-4}		
13.0	7.00×10^{-6}		$(4.5 \pm 0.5) \times 10^{-5}$	$(7 \pm 2) \times 10^{-5}$	$(5.5 \pm 0.9) \times 10^{-5}$	120 ± 17	39 ± 55
	9.03×10^{-6}		2.41×10^{-5}		7.28×10^{-5}		

Table 2 Rate constant k_2 as a function of pH and temperature at $[Rh^{III}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, $0 < [CO_3]_T < 0.3$ mol dm^{-3}, atmospheric pressure

	k_2/s^{-1}						
pH	40	45	50	55	60 °C	$\Delta H_2^‡$/ kJ mol^{-1}	$\Delta S_2^‡$/ J K^{-1} mol^{-1}
11.0			$(1.78 \pm 0.04) \times 10^{-3}$				
12.0	$(2.01 \pm 0.04) \times 10^{-4}$		$(4.56 \pm 0.08) \times 10^{-4}$			76 ± 7	−73 ± 22
	1.64×10^{-4}		4.73×10^{-4}	9.45×10^{-4}	9.75×10^{-4}		
12.5	$(4.71 \pm 0.01) \times 10^{-5}$	3.06×10^{-4}	$(1.88 \pm 0.02) \times 10^{-4}$	$(3.41 \pm 0.04) \times 10^{-4}$	6.78×10^{-4}	113 ± 2	32 ± 5
13.0	1.90×10^{-5}	9.12×10^{-5}	$(7.31 \pm 0.09) \times 10^{-5}$	$(1.09 \pm 0.05) \times 10^{-4}$	$(2.37 \pm 0.02) \times 10^{-4}$	104 ± 7	−4 ± 21

11.0 only. This means that the value of k_1 at this pH largely represents the uptake of CO_2 [reaction (a)], and that the other possibilities [(b) and (c)] are negligible. The measured k_1 values at higher pH are significantly larger than the calculated values, implying that under such conditions reactions other than the uptake of CO_2 must also contribute.

Reaction (b) represents substitution (*i.e.* anation) of $[Rh(NH_3)_5(OH_2)]^{3+}$ by HCO_3^-/CO_3^{2-}. It requires $f_{HCO_3^-} = K_1[H^+]/([H^+]^2 + K_1[H^+] + K_1K_2)$, $f_{CO_3^{2-}} = K_1K_2/([H^+]^2 + K_1[H^+] + K_1K_2)$ and $f_{Rh-OH_2} = [H^+]/(K_3 + [H^+])$ ($pK_3 = 6.6$ measured experimentally in this investigation at 25 °C and 1.0 mol dm^{-3} ionic strength) to be calculated at $11 < pH < 13$ to obtain k_b' and k_b'' in the rate equation (2) by

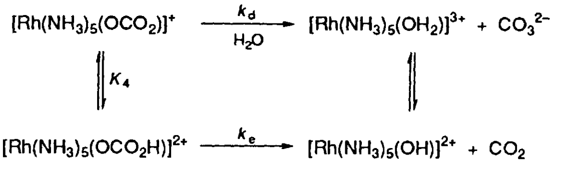
$$k_b = (k_b' f_{HCO_3^-} + k_b'' f_{CO_3^{2-}}) f_{Rh-OH_2} \qquad (2)$$

solving four linear equations (pH 11.5, 12.0, 12.5 and 13.0) in which k_b is taken as the measured k_1 less the contribution of CO_2 uptake at the selected pH value. The rate constants $k_b' = 1.1 \times 10^3$ dm^3 mol^{-1} s^{-1} and $k_b'' = 1.3 \times 10^2$ dm^3 mol^{-1} s^{-1} so obtained for 50 °C are much too high for substitution of Rh^{III} by a weak nucleophile, yielding calculated values $k_1 \approx 10^2$ dm^3 mol^{-1} s^{-1} for $11 < pH < 13$ totally incomparable to the experimental values in Table 1. This means that reaction (b) is not a realistic possibility to account for the measured k_1 values.

Reaction (c) entails substitution of $[Rh(NH_3)_5(OH)]^{2+}$ by HCO_3^-/CO_3^{2-}, for which the rate equation simplifies to (3)

$$k_c = k_c' f_{HCO_3^-} + k_c'' f_{CO_3^{2-}} \qquad (3)$$

since all Rh^{III} is assumed to be present as the hydroxo complex at $pH \geqslant 11.5$. Using $f_{HCO_3^-}$, $f_{CO_3^{2-}}$ and the corrected k_1 values as outlined above, $k_c' = 6.9 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $k_c'' \approx 0$ at 50 °C are obtained by solving the four available linear equations. These values are quite realistic for the proposed reaction, the calculated values $k_1 = 1.8 \times 10^{-3}$, 4.8×10^{-4}, 1.4×10^{-4} and 4.4×10^{-5} dm^3 mol^{-1} s^{-1} at pH 11.5, 12.0, 12.5 and 13.0, respectively, being in good agreement with the experimental values in Table 1. Moreover, a similar value $k_c' = 4.7 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at 50 °C had been measured[14] for the same substitution reaction of $[Co(tren)(OH)_2]^+$ [tren = tris(2-aminoethyl)amine] and for this complex it was also found that $k_c' \approx 10^2 k_c''$. The k_1 values measured at $pH > 11$ thus represent substitution of $[Rh(NH_3)_5(OH)]^{2+}$ by HCO_3^- (not CO_3^{2-}), the reaction probably being facilitated by internal transfer of H^+ such that HCO_3^- acts as a general acid and protonates $[Rh(NH_3)_5(OH)]^{2+}$ to produce the more labile $[Rh(NH_3)_5(OH_2)]^{3+}$, which undergoes anation by CO_3^{2-}.



Scheme 2

To summarise, the forward reaction or k_1 path represents carbon dioxide uptake at pH 11 and substitution of the hydroxo complex by hydrogencarbonate ion at all remaining pH values in the range 11–13.

For the k_2 path, two possible reverse reactions, *viz.* aquation (k_d) and decarboxylation (k_e), according to Scheme 2 (protons omitted for simplicity) may be considered. The corresponding rate can be written as in (4) with $K_4 = 10^{-7} \gg [H^+]$ under

Table 3 Comparative aquation data for $[Rh(NH_3)_5X]^{2+}$ taken from ref. 15

X^-	k_2 (25 °C)/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	k_2 (50 °C)/s^{-1}
NO_3^-	1.2×10^{-5}	97.4	−12.5	2.5×10^{-4}
SO_4^{2-}	1.6×10^{-6}	89.5	−55.6	2.7×10^{-5}
$CF_3CO_2^-$	2.0×10^{-7}	105	−25.1	4.0×10^{-6}
Br^-	3.4×10^{-8}	103	−41.4	1.0×10^{-6}
Cl^-	3.8×10^{-8}	101	−46.4	1.1×10^{-6}
I^-	6.2×10^{-9}	110	−32.6	2.5×10^{-7}

Table 4 Equilibrium constant K as a function of pH and temperature at $[Rh^{III}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, $0 < [CO_3]_T < 0.3$ mol dm^{-3}, atmospheric pressure

	K/dm^3 mol^{-1}						
pH	40	45	50*	55	60	$\Delta H^⊖$/kJ mol^{-1}	$\Delta S^⊖$/J K^{-1} mol^{-1}
12.0	0.47 ± 0.08	0.86	1.22 ± 0.04	0.92	1.22	35 ± 15	−148 ± 45
12.5	0.33 ± 0.06	0.39	0.47 ± 0.03	0.63 ± 0.07	0.5 ± 0.2	24 ± 8	−187 ± 24
13.0	0.42 ± 0.08		0.5 ± 0.2	0.6 ± 0.2	0.27 ± 0.06	22 ± 11	−191 ± 33

* $K = 2.1 \pm 0.1$ dm^3 mol^{-1} at pH 11.0.

Table 5 Values of k_1 and k_2 as a function of pressure at $[Rh^{III}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, $0 < [CO_3]_T < 0.3$ mol dm^{-3}, pH 12, 50 °C

p/MPa	$10^4 k_1$/dm^3 mol^{-1} s^{-1}	$10^4 k_2$/s^{-1}
1	8.53 ± 0.06	3.9 ± 0.2
50	8.63 ± 0.01	4.1 ± 0.2
100	8.80 ± 0.10	4.2 ± 0.1
150	9.50 ± 0.02	4.5 ± 0.1

$\Delta V_1^‡ = -1.8 \pm 0.6$, $\Delta V_2^‡ = -2.4 \pm 0.5$ cm^3 mol^{-1}.

$$k_2 = k_d\{K_4/([H^+] + K_4)\} + k_e\{[H^+]/([H^+] + K_4)\} \approx k_d + (k_e[H^+]/K_4) \quad (4)$$

the prevailing experimental conditions.[9] A linear plot of k_2 *versus* $[H^+]$ from Table 2 yields $k_d = (1.6 \pm 0.8) \times 10^{-4}$ s^{-1} and $k_e = 16 \pm 2$ s^{-1} at 50 °C. The value of k_d seems realistic for aquation when compared to aquation data at 50 °C for similar complexes in Table 3. These data were extrapolated from published data at 25 °C,[15] using the listed activation parameters. The k_d values for $[Rh(NH_3)_5(OCO_2)]^+$ and $[Rh(NH_3)_5(ONO_2)]^{2+}$ are very similar, as one would expect for leaving groups which are both weak nucleophiles. The remaining O-bonded leaving groups are all stronger nucleophiles and thus responsible for the smaller aquation rate constants reported. The value of $k_e = 1.1$ s^{-1} reported in literature[9] for the decarboxylation of $[Rh(NH_3)_5(OCO_2)]^+$ at 25 °C becomes 13 s^{-1} on conversion to 50 °C with activation parameters reported by the authors. Our k_e value is close to this, suggesting that decarboxylation is also a realistic possibility to account for the observed pH dependence of the reverse reaction step.

To summarise, the reverse reaction or k_2 path represents parallel aquation (substitution by water) and decarboxylation (loss of carbon dioxide) of the carbonato complex over the entire $11 < pH < 13$ range.

The pH dependence of k_1 and k_2 is accompanied by similar tendencies for $\Delta H^‡$ and $\Delta S^‡$ in Tables 1 and 2. The change in $\Delta H_1^‡$ and $\Delta S_1^‡$ with pH is more significant for $11 < pH < 12$ to coincide with the shift from CO_2 uptake to HCO_3^- substitution, two processes with quite different energy profiles. The values of $\Delta H_2^‡$ and $\Delta S_2^‡$ lie within the scope of values reported for decarboxylation {*e.g.* $\Delta H^‡ = 71$ kJ mol^{-1}, $\Delta S^‡ = -4$ J K^{-1} mol^{-1} for $[Rh(NH_3)_5(OCO_2)]^+$ [9]}, a process which is acid catalysed and may be favoured towards lower pH, and spontaneous aquation {*e.g.* $\Delta H^‡ = 97$ kJ mol^{-1}, $\Delta S^‡ = -13$ J K^{-1} mol^{-1} for $[Rh(NH_3)_5(NO_3)]^{2+}$ [15]}, a process which may be favoured towards higher pH.

The ratio $K = k_1/k_2$ represents the equilibrium constant for the overall process. Its values as a function of pH and temperature are listed in Table 4. The decrease with increasing pH (close to a factor 5 over the range $11 < pH < 13$ at 50 °C) illustrates to what extent the equilibrium is perturbed towards higher pH as a result of a shift from the forward to the reverse reaction step as the more dominant path. This shift is readily accomplished since the extent of reaction, represented by the reaction enthalpies $\Delta H^⊖$ in Table 4, is quite small and K is numerically close to unity at the intermediate values of the selected pH range.

The values of $\Delta V^‡$ in Table 5, calculated from the pressure dependencies of k_1 and k_2 at selected conditions, are both small and negative, and thus suggest an associative interchange mechanism for both reaction steps.

The k_1 path features charge neutralisation, which means that $(\Delta V_1^‡)_{solvolysis}$ is positive. The small negative value of $\Delta V_1^‡$ therefore implies an even more negative value for $(\Delta V_1^‡)_{intrinsic}$, emphasising the associative nature of the k_1 path. The absence of any curvature in plots of k_{obs} *versus* $[CO_3]_T$ within the chosen concentration range suggests that the associative nature does not involve significant ion-pair formation and can be understood in terms of an associatively activated transition state.

Considering the k_2 path, one would expect the spontaneous aquation to be associatively and the decarboxylation to be dissociatively activated, though the latter reaction may be less dissociative than expected as a result of the retention of the metal–oxygen bond. The small negative value of $\Delta V_2^‡$ suggests that the aquation reaction may slightly outweigh the decarboxylation reaction, a possibility not too far-fetched under the extreme pH conditions concerned. The explanation of small or near-zero activation volumes in terms of a competition between positive and negative contributions[6,16] is equally well acceptable.

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