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The Volume of Activation for the Mercury Catalyzed Aquation of $Rh(NH_3)_5I^{2+}$

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The aquation of $Rh(NH_3)_5I^{2+}$, as well as the analogous chloro-, bromo- and thiocyanato complexes, in acidic solution has been studied by Poë *et al.* [1]. Based on the activation parameters for both the aquation and anation reactions, the reaction mechanism was thought to be dissociative with very little contribution from bond making in the transition state. The assignment of an I_d mechanism to these reactions of rhodium(III) has also been made more recently [2, 3].

However an I_a mechanism was proposed for the water exchange reaction of $Rh(NH_3)_5OH_2^{3+}$ based on its activation volume [4], this assignment supports the arguments of Chan and Chan [5] who favored an associative mechanism for the spontaneous aquations of the chloro and bromo species. The activation volume for the aquation of the corresponding nitrato complex was interpreted simply in terms of an I mechanism [6]. Thus the mechanism for the aquation/anation reactions of pentaamminerhodium(III) complexes remains a controversial issue.

On the other hand, the mercury induced aquation reactions are generally believed to involve the rate-determining dissociation of a bridged intermediate, $Rh(NH_3)_5XHg^{4+}$ where X = Cl, Br or I, although it could only be detected in the latter case. The iodo complex was therefore chosen for study to allow a comparison to be made with our earlier investigation of the chloro complex [7] and with our recent work about the mercury catalyzed aquation of mer-$RhCl_3(OH_2)_3$ [8].

Experimental

$[Rh(NH_3)_5Cl]Cl_2$ was synthesized [9] and converted to the iodo complex by dissolving it in boiling water and adding sufficient NaI to make the solution 10% in iodide. The solution was refluxed until orange crystals began to form at which time the mixture was allowed to cool to room temperature and the precipitate, $[Rh(NH_3)_5I]I_2$, filtered off. It was converted to the perchlorate salt by recrystallizing twice from a weak $HClO_4/NaClO_4$ solution. Microanalysis confirmed the purity of the complex and its UV/visible absorption spectrum is in close agreement with literature values, *viz.* ϵ_{max} (417 nm) = 275, ϵ_{max} (276 nm) = 3230, *cf.* ϵ_{max} (419 nm) = 270, ϵ_{max} (276 nm) = 3200 M^{-1} cm^{-1} [10].

Solutions containing mercury(II) perchlorate were prepared and analyzed as described previously [11]. The water used to make up the solutions was first passed through a mixed-bed ion-exchange column and then distilled twice. The ionic strength was maintained at 0.3 *M* by using equal concentrations of $NaClO_4$ and $HClO_4$, while the complex concentration was kept at 10^{-4} *M.*

The reaction was monitored *in situ* at 235 nm using a modified Zeiss PMQ II spectrophotometer. The pressure vessel [12], containing a quartz cell [13], was thermostatted to within ±0.1 K.

Solution densities were measured using a DMA 02 densimeter which was maintained at 298.2 K (±0.001 K). These were conducted over a wide range of concentration of $Hg(NO_3)_2$ and the mean value of the apparent molar volumes was assumed to be equal to the partial molar volume of the salt, *i.e.* 43.8 ± 0.5 cm^3 mol^{-1}. By adding known amounts of KI to these solutions and redetermining the densities, the approximate volume of the HgI^+ species could be calculated from the formation constant [14], and the partial ionic molar volumes of K^+ and I^-, 4.50 and 40.8 cm^3 mol^{-1}, respectively [15].

Results and Discussion

The observed pseudo-first-order rate constant is shown in Table I as a function of $[Hg^{2+}]$ at four temperatures. The usual double-reciprocal plots of $1/k_{obs}$ *versus* $1/[Hg^{2+}]$ were linear at each temperature and gave slopes and intercepts corresponding to 1/kK and 1/k, respectively, as defined by eqns. (1) and (2).

$$Rh(NH_3)_5I^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} Rh(NH_3)_5IHg^{4+} \quad (1)$$

$$Rh(NH_3)_5IHg^{4+} + H_2O \xrightarrow{k} Rh(NH_3)_5OH_2^{3+} + HgI^+ \quad (2)$$

A similar treatment of the data in Table II at each pressure gave the values of k and K at various pressures. Plots of the natural logarithm of both quantities *versus* pressure were linear within experimental error limits, although it must also be pointed out

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TABLE I. Temperature Dependence of the Observed Rate Constant as a Function of Mercury(II) Concentration. (Ionic Strength = 0.3 *M*).

T	10^3 [Hg^{2+}] *M*	10^3 k_{obs} s^{-1}	10^3 k s^{-1}	10^3 K M^{-1}
284.9	0.537	1.79	6.22 ± 0.4	733 ± 56
	0.725	2.12		
	1.08	2.75		
	1.61	3.50		
	2.15	3.80		
	2.69	4.08		
291.5	0.725	4.53	14.0 ± 0.4	643 ± 22
	1.08	5.76		
	1.61	7.18		
	2.15	8.14		
	2.69	8.67		
294.8	0.725	6.70	22.3 ± 1.4	583 ± 47
	1.08	8.89		
	1.61	10.8		
	2.15	12.2		
	2.69	13.6		
300.2	0.725	9.44	34.2 ± 1.6	512 ± 29
	1.08	12.3		
	1.61	15.8		
	2.15	17.6		
	2.69	19.6		

TABLE II. Pressure Dependence of the Observed Rate Constant as a Function of the Mercury(II) Concentration at 284.9 K. (Ionic Strength = 0.3 *M*).

Pressure bar	10^3 [Hg^{2+}] *M*	10^3 k_{obs} s^{-1}	10^3 k s^{-1}	10^3 K M^{-1}
1	0.537	1.79	6.22 ± 0.4	733 ± 56
	0.725	2.12		
	1.08	2.75		
	1.61	3.50		
	2.15	3.80		
	2.69	4.08		
250	0.537	1.89	6.00 ± 0.6	826 ± 97
	0.725	2.15		
	1.08	2.91		
	1.61	3.59		
	2.15	3.80		
	2.69	4.05		
500	0.537	1.90	5.81 ± 0.5	866 ± 63
	0.725	2.14		
	1.08	2.87		
	1.61	3.47		
	2.15	3.86		
	2.69	3.89		

(continued on facing page)

TABLE II. *(continued)*

Pressure bar	10^3 $[Hg^{2+}]$ M	10^3 k_{obs} s^{-1}	10^3 k s^{-1}	10^3 K M^{-1}
750	0.537	1.90	5.73 ± 0.5	886 ± 98
	0.725	2.14		
	1.08	2.91		
	1.61	3.40		
	2.15	3.76		
	2.69	4.04		
1000	0.537	1.88	5.70 ± 0.5	884 ± 106
	0.725	2.13		
	1.08	2.90		
	1.61	3.50		
	2.15	3.77		
	2.69	3.85		
1250	0.537	1.80	5.74 ± 0.4	835 ± 67
	0.725	2.15		
	1.08	2.74		
	1.61	3.52		
	2.15	3.61		
	2.69	3.91		
1500	0.537	1.83	5.69 ± 0.3	855 ± 63
	0.725	2.15		
	1.08	2.71		
	1.61	3.45		
	2.15	3.61		
	2.69	4.01		

that neither quantity showed a large pressure dependence so that the pressure range would need to be significantly extended – beyond the capability of our apparatus – to really justify the claim that the activation volume is independent of pressure. The activation parameters calculated from all the given data are listed in Table III together with the parameters for the spontaneous aquation reaction.

The slightly negative value of ΔV for equation (1) is not consistent with our earlier prediction [7] of a value of *ca.* +8 cm^3 mol^{-1} which indicates that the volume increase resulting from the release of a coordinated water molecule from the Hg^{2+} center is not the dominant effect, but is instead compensated by increased electrostriction, and/or contractional rearrangement of the bridged species. The latter may be at least partially due to stronger bonding between the mercury ion and the iodide as compared to chloride in $Rh(NH_3)_5Cl^{2+}$ studied previously [7].

Using the known partial molar volumes of the iodo complex substrate (94.1 ± 0.3 cm^3 mol^{-1}) [6] and the Hg^{2+} ion (the volume of the dehydrated mercuric ion is –22.8 ± 0.5 cm^3 mol^{-1}), the approximate volume of the bridged complex ion can be calculated from eqn. (3).

$$V\{Rh(NH_3)_5IHg(OH_2)^{4+}_{x-1}\} = \Delta V + V\{Rh(NH_3)_5I^{2+}\} + V\{Hg(OH_2)^{2+}_x\} - V\{H_2O\} \qquad (3)$$

for x = 6: $V\{Hg(OH_2)^{2+}_6\} = 85.2 \pm 0.5$ cm^3 mol^{-1}.

Thus, $V\{Rh(NH_3)_5IHg(OH_2)^{4+}_5\} = 160.0 \pm 1.2$ cm^3 mol^{-1}.

The fully hydrated form of the mercury(II) cation represented in the above equation by $Hg(OH_2)^{2+}_x$ is identical to the abbreviated form, Hg^{2+}, used in the text until now.

From eqn. (2), the volume of the transition state is given by:

$$V^{\neq} = \Delta V^{\neq} + V\{Rh(NH_3)_5IHg(OH_2)^{4+}_5\} + V\{H_2O\} \qquad (4)$$

$= 179.2 \pm 1.7$ cm^3 mol^{-1}.

If this step does involve complete dissociation of the HgI^+ group, then

$$V^{\neq} = V\{Rh(NH_3)^{3+}_5\} + V\{HgI(OH_2)^{+}_5\} + V\{H_2O\} \qquad (5)$$

If one were to assume $V\{Rh(NH_3)^{3+}_5\} = V\{Rh(NH_3)^{3+}_6\} = 63.2 \pm 0.9$ cm^3 mol^{-1} [7, 16], $V^{\neq} = 63.2 + 131.6 + 18.0 = 212.8 \pm 3.9$ cm^3 mol^{-1}.

TABLE III. Summary of the Activation Parameter for the Spontaneous and Mercury Catalyzed Aquation of $[Rh(NH_3)_5I](ClO_4)_2$.

Parameter	Catalyzed Aquation	Spontaneous Aquation	Ref.
K (M^{-1})	583 ± 47 (294.8 K)		this work
	225 ± 16 (284.6 K)		16
ΔH (kJ mol^{-1})	−16.7 ± 1.3		this work
ΔS (J K^{-1} mol^{-1})	−5.0 ± 3		this work
ΔV (cm^3 mol^{-1})	−1.7 ± 1.0		this work
k (s^{-1})	$(2.23 \pm 0.14) \times 10^{-2}$ (294.8 K)		this work
	2.05×10^{-2} [a]		16
		4.2×10^{-9} [a]	1
$\Delta H^{\neq}$ (kJ mol^{-1})	78.3 ± 5.4		this work
		109.6 ± 0.9	1
		106.3	17
		111.7	18
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−12.0 ± 19		this work
		−33.0 ± 3	1
		−43.0	
		−18.0	17
			18
$\Delta V^{\neq}$ (cm^3 mol^{-1})	1.2 ± 0.3		this work

[a] Extrapolated to 294.8 K from the data in references 1 and 16 at ionic strengths of 0.2 and 0.17 *M*, respectively.

The difference between the two values of $V^{\neq}$ is therefore 33.6 ± 5.6 cm^3 mol^{-1} which, on face value, would indicate that a purely dissociative D-mechanism is not operative. However, if the other extreme value for $V\{Rh(NH_3)_5^{3+}\}$ is assumed (*i.e.* $V\{Rh(NH_3)_6^{3+}\} - V\{NH_3\} = 63.2 - 24.5 = 38.7$ cm^3 mol^{-1}), the difference between the $V^{\neq}$ values is reduced to 9.1 ± 5.6 cm^3 mol^{-1}, which is less significant. Nevertheless, it is larger than the sum of the experimental errors involved. As it is very unlikely that the real situation corresponds to the latter approximation, equation (2) must involve an interchange step with considerable $Rh{-}OH_2$ bond making in the transition state. If the first approximation is correct, then one can calculate that bond making and breaking are equally advanced given a maximum contribution from bond formation of −18 cm^3 mol^{-1}. The assignment of an interchange mechanism is borne out to a certain extent by the similarity in the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values shown in Table III for the spontaneous and catalyzed reactions.

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