

Volumes of Activation for the Mercury(II) Induced Aquation Reactions of Halopentaamminecobalt(III), Rhodium(III) and Chromium(III) Ions in Acidic Aqueous Solution

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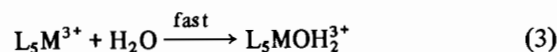
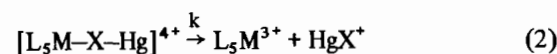
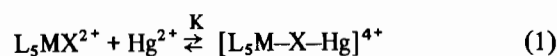
The pressure dependencies of the rates of Hg(II) induced aquation of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$, and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ were studied at 15 °C, with the exception of the latter which was investigated at 25 °C, and a $[\text{H}^+]$ of 0.31 M with $\mu = 0.6$ M. The respective volumes of activation were found to be -1.7 ± 1.0 , $+0.8 \pm 0.5$, $+0.7 \pm 0.4$, and -1.0 ± 0.4 $\text{cm}^3 \text{ mol}^{-1}$. These results are discussed with reference to the numerous conventional kinetic data in the literature, further establishing a D-mechanism for the rate-determining step.

Introduction

The spontaneous and Hg(II) induced aquation reactions of haloammine complexes of transition metals in their third oxidation state have been investigated by numerous authors [4]. Work was originally performed on the pentaamminecobalt(III) complexes [5–12], later to be expanded to include other ammine ligands such as ethylenediamine [13–19] and triethylenetetramine [20]. Similar studies were also reported for the corresponding complexes of rhodium(III) [21–23], chromium(III) [24–29], and ruthenium(III) [30].

A general feature of the suggested reaction mechanisms for these induced aquation reactions is the existence of a bridged intermediate of the type $[\text{L}_5\text{M}-\text{X}-\text{Hg}]^{4+}$, where L = ammine, M = Co, Rh, Cr, or Ru, and X = Cl^- , Br^- , I^- , CN^- , or NCS^- . These intermediates have been visualized either as transition state species or as chemically stable intermediates based on kinetic and/or spectroscopic evidence. Formation constants are recorded for the latter type, e.g. $\text{L}_5\text{CoNCSHg}^{n+}$, $(\text{L}_5\text{CoNCS})_2\text{Hg}^{m+}$ [18], $\text{Co}(\text{NH}_3)_5\text{NCSHg}^{4+}$ [12], $\text{Rh}(\text{NH}_3)_5\text{IHg}^{4+}$ [23], $\text{Cr}(\text{OH}_2)_5\text{CNHg}^{4+}$ [25, 26], $\text{Cr}(\text{OH}_2)_5\text{NCSHg}^{4+}$ [27], and $\text{Ru}(\text{NH}_3)_5\text{ClHg}^{4+}$ [30]. Indeed, the complex $[(\text{Co}(\text{NH}_3)_5\text{NCS})_2\text{Hg}](\text{ClO}_4)_6$ has been recently isolated [31]. It has been observed [15] that HgX^+ is also an efficient catalyst in these reactions, with a reactivity similar to the parent Hg^{2+} .

A general reaction sequence, which is consistent with most of the available data at high $[\text{Hg}^{2+}]$, is as follows:



The rate-determining step, eq. (2), involves cleavage of the M–X bond to produce a five-coordinate intermediate L_5M^{3+} which is scavenged by the solvent (water) to give $\text{L}_5\text{M}(\text{OH}_2)^{3+}$. In other words, the mechanism of reaction is dissociative of the $\text{S}_{\text{N}}1$ or D type, and is governed by the rate law:

$$k_{\text{obs}} = - \frac{d \ln [\text{L}_5\text{MX}^{2+}]}{dt} = \frac{kK[\text{Hg}^{2+}]}{1 + K[\text{Hg}^{2+}]}$$

This equation ignores contributions from the HgX^+ species and is valid under the conditions of a high $[\text{Hg}^{2+}]$ and the absence of added X^- ions. In those cases where K is small, k_{obs} is a linear function of $[\text{Hg}^{2+}]$, with eq. (4) simplifying to:

$$k_{\text{obs}} = kK[\text{Hg}^{2+}]$$

In some of the systems referred to above, large K values were, in fact, found (even of the order of 10^4 M^{-1}) such that plots of k_{obs} versus $[\text{Hg}^{2+}]$ deviate markedly from linearity, in agreement with the given rate equation.

Volumes of activation, obtained from the pressure dependence of the rate constants, have been used with considerable success in the elucidation of reaction mechanisms. Not only have such studies been able to substantiate previously proposed mechanisms [32–34], but they have also contributed to a better understanding of the activation process. Furthermore, examples exist in which the volume of activation has provided evidence against previously

accepted mechanisms [35, 36]. To our knowledge only one pressure study of a Hg(II) induced aquation reaction has been reported to date [37]. We now present our results for the pressure dependence of the rates of the Hg(II) induced aquation of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$, and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$.

Experimental

Materials

The compounds used were prepared by standard procedures reported in the given references: $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ [38], $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ [39], $[\text{Cr}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ [40] and $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ [41]. The purity of these complexes was established by microanalysis and from their visible/uv spectra.

The methods for preparing and analyzing solutions of $\text{Hg}(\text{ClO}_4)_2$ have been described in detail elsewhere [15]. The total ionic strength, adjusted with NaClO_4 , and $[\text{H}^+]$ were determined [18] by ion exchange techniques and titration, respectively.

Rate Measurements

The rate of aquation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ was followed spectrophotometrically using a modified Zeiss PMQ II instrument equipped with a conventional thermostatted high pressure cell [42]. For the remaining more labile complexes, a high pressure rapid mixing system [43] was used seated inside a Zeiss DMR 10 spectrophotometer. The observed first order rate constants were calculated in the usual way from the slope of $\ln(A_t - A_\infty)$ versus time plots, where A_t and A_∞ are the absorbances at time t and at infinity, respectively. These plots were linear for at least two half-lives.

Results

The complexes chosen have all been shown to exhibit second-order kinetics over a wide range of $[\text{Hg}^{2+}]$ [23, 24]. As the $[\text{Hg}^{2+}]$ used in this study fall within this range, the rate constants for induced aquation are considered to be second-order and these values are presented in Table I as a function of pressure.

Under pseudo-first-order conditions, which were maintained throughout this investigation, Hg^{2+} was in sufficient excess – factor of 18 – that contributions from HgX^+ as a potential reaction partner may be ignored.

The second-order rate constants shown in Table I at normal pressure are in reasonable agreement with the corresponding values available in the literature, summarized in Table II, especially when the dif-

TABLE I. Second-order Rate Constants for the Mercury Induced Aquation of the Pentaammine Complexes as a Function of Pressure at 15 °C ($[\text{H}^+] = 0.31 \text{ M}$, $[\text{Hg}^{2+}] = 0.088\text{--}0.092 \text{ M}$, Complex Concentration = 0.005 M , $\mu = 0.6 \text{ M}$).

Complex	λ nm	Pressure bar	$10^2 k$ $\text{M}^{-1} \text{s}^{-1}$
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	300	1	2.69 ± 0.09
		250	2.71 ± 0.30
		500	2.59 ± 0.01
		750	2.71 ± 0.15
		1000	2.46 ± 0.05
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	300	1	2.56 ± 0.01
		250	2.53 ± 0.09
		500	2.59 ± 0.03
		750	2.61 ± 0.11
		1000	2.64 ± 0.04
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	530	1	1.36 ± 0.15
		200	1.35 ± 0.01
		400	1.33 ± 0.09
		600	1.30 ± 0.01
		800	1.33 ± 0.09
		1000	1.32 ± 0.07
$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+ \text{ a}}$	350	1	0.0854 ± 0.0004
		250	0.0845 ± 0.0024
		500	0.0890 ± 0.0034
		750	0.0862 ± 0.0012
		1000	0.0905 ± 0.0010
		1250	0.0914 ± 0.0005
		1500	0.0886 ± 0.0011

^a25 °C.

ferences in experimental conditions are taken into account. Ionic strength and the specific nature of the supporting electrolyte are known to significantly affect the rates of reactions of this type [5, 11, 17].

Due to the nature of the rapid mixing device, the maximum pressure which may be exerted on the system is 1 kbar. On the other hand, use of the conventional high pressure cell to study the aquation of the less labile $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ complex allowed the pressure range to be extended to 1.5 kbar. Nevertheless, no curvature of the $\ln k$ versus pressure plots was observed within the given experimental error limits. Therefore, a linear least squares program was used to fit the data shown in Table I, although it should be mentioned that these data represent the mean values of a number of kinetic experiments, and that the total number of individual rate constants was subjected to the least squares treatment. The volumes of activation so obtained are: for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, $\Delta V_{\text{exp}}^{\ddagger} = -1.7 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$; for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, $\Delta V_{\text{exp}}^{\ddagger} = +0.8 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$; for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, $\Delta V_{\text{exp}}^{\ddagger} = +0.7 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ and for $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, $\Delta V_{\text{exp}}^{\ddagger} = -1.0 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$.

TABLE II. A Comparison of the Rate and Activation Parameters^a for the Mercury(II) Induced Aquation of the Pentaamine Complexes at 25 °C.

Substrate	Spontaneous Aquation				Hg ²⁺ Induced Aquation				Ref.
	μ_o <i>M</i>	$10^6 k_o$ <i>s</i> ⁻¹	ΔH_o^\ddagger kJ mol ⁻¹	ΔS_o^\ddagger JK ⁻¹ mol ⁻¹	μ_l <i>M</i>	$10^4 k_l$ <i>M</i> ⁻¹ <i>s</i> ⁻¹	ΔH_l^\ddagger kJ mol ⁻¹	ΔS_l^\ddagger JK ⁻¹ mol ⁻¹	
Co(NH ₃) ₅ Cl ²⁺	0.002–1.0	1.9	94.6	-38	0.3	570			48, 6
					1.0	1160			15
Co(NH ₃) ₅ Br ²⁺	0.002–0.8	7.4	91.3	-37	0.01	1210 ^b	59.0 ^b	-29 ^b	48, 11
Cr(NH ₃) ₅ Cl ²⁺	1.0	3.9	93.4	-36	2.0	871	62.4	-56	49, 24
Rh(NH ₃) ₅ Cl ²⁺	0.1	0.197 ^c	94	-58	0.2	6.1	68	-77	22
	0.01–0.025	0.048	99.7	-51	0.166	9.1 ^c	67.6	-124	50, 23

^aThe subscripts o and l are in keeping with the observed overall rate law $k_{obs} = k_o + k_l [Hg^{2+}]$. ^b[HClO₄] = 0.01 *M*. ^cExtrapolated.

Discussion

The volumes of activation for all four reactions are essentially zero. This similarity strongly suggests that a common mechanism is operating. At first glance, the value of zero indicates the mechanism to be dissociative, although the volume changes associated with the formation of the precursor, or Hg-bound intermediate, must also be considered, even though it was not detected. Thus ΔV_{exp}^\ddagger represents the sum of the volume changes incurred in precursor formation (eq. 1), for which *K* is apparently small, and the true volume of activation associated with the decomposition of the intermediate. If the latter step is indeed dissociative, involving complete M–X bond breakage as represented by eq. 2, then it results in a positive contribution to ΔV^\ddagger . The volume effect for the pre-equilibrium is essentially determined by a bond formation (Hg–X) and possibly a release of a water molecule. Thus a negative volume quantity of $\Delta \bar{V}$ should be expected.

Additional contributions to both $\Delta \bar{V}$ and ΔV^\ddagger from solvation changes should be minimal as no overall change of the charge is incurred. During the formation of the intermediate, as shown in eq. 1, the charge density is probably the same as in the two individual ions. Charge separation, as accompanying the rate determining step of eq. 2, is possibly compensatory since one charge center increases and the other one decreases. The lack of any measurable pressure dependence of ΔV_{exp}^\ddagger tends to support the claim of negligible solvation changes. Therefore, qualitatively, a ΔV_{exp}^\ddagger value of approximately zero as a result of cancellation between $\Delta \bar{V}$ and ΔV^\ddagger is consistent with a D mechanism.

At this point it is perhaps of interest to compare the Hg²⁺ induced aquation of M(NH₃)₅X²⁺ complexes with the redox reaction [44] between Co(NH₃)₅X²⁺ and Fe²⁺. Such comparisons have been previously

made of the conventional activation parameters of these two reactions [6, 15, 24]. Candlin and Halpern [45] measured the volumes of activation for the redox reaction, where X = F⁻, Cl⁻, Br⁻ and N₃⁻, confirming that it is of the inner sphere type. For X = Cl⁻ and Br⁻, ΔV_{exp}^\ddagger was found to be +8 cm³ mol⁻¹. Stranks [46] rationalized these results by ascertaining that the volume increase of ca. +14 cm³ mol⁻¹ resulting from the release of water in the transition state – presumably a water molecule from the first coordination sphere of Fe²⁺(aq) – more than compensates for the negative volume effects originating from electrostatic repulsion and solvent electrostriction. In this case the transition state is generally considered to be the X-bridged species so that the associated volume change of +8 cm³ mol⁻¹ may well be similar to that anticipated for step 1 of the Hg²⁺ induced aquation process. However, it must be remembered that the effects of solvent rearrangement are likely to be smaller for Hg²⁺ complex formation than for that involved in the rate-determining electron transfer step of the redox process. Thus, the actual activation step in eq. 2, which involves the dissociation of the intermediate (or, in other words, virtually the reverse of eq. 1), should involve a decrease in volume of at least 8 cm³ mol⁻¹ to yield the observed ΔV_{exp}^\ddagger of approximately zero.

Another approach to this problem is to use the quantitative treatment which was developed to correlate the existing volume data [32, 51] for the aquation of Co(NH₃)₅Xⁿ⁺ and Cr(NH₃)₅Xⁿ⁺ complexes [33]. This involves measuring the partial molar volumes of the individual complex species. Fortunately, these data are conveniently available in the literature. Thus, the volume of activation can be defined in terms of the partial molar volumes of all the species taking part in eqs. 1 and 2, assuming that *K* is small [23, 24], i.e., $\Delta V_{exp}^\ddagger = \Delta \bar{V}_1 + \Delta V_2^\ddagger = \bar{V}(HgX^+) + \bar{V}(L_5M^{3+}) - \bar{V}(L_5MX^{2+}) - \bar{V}(Hg^{2+})$.

TABLE III. Complete Volume Data for the Hg^{2+} Induced Aquation of $\text{M}(\text{NH}_3)_5\text{X}^{2+}$ (units: $\text{cm}^3 \text{mol}^{-1}$).

$\text{M}(\text{NH}_3)_5\text{X}^{2+}$	$\bar{V}(\text{L}_5\text{MX}^{2+})$ at 25 °C	$\bar{V}(\text{X}^-)$ [33]	$\Delta V_{\text{exp}}^{\ddagger}$	$\bar{V}(\text{L}_5\text{M}^{3+})$ at 25 °C	$\Delta \bar{V}_4$
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	85.8 ± 0.4 [33]	21.75	-1.7 ± 1.0	54.9 ± 0.9	-7.5 ± 2.3
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	95.0 ± 1.1 [33]	29.4	$+0.8 \pm 0.5$	54.9 ± 0.9	-11.5 ± 2.5
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	83.2 ± 1.0 [33]	21.75	$+0.7 \pm 0.4$	$(54.9 \pm 0.9)^{\text{a}}$	-7.3 ± 2.3
$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$	82.3 ± 0.5 [47]	21.75	-1.0 ± 0.4	$(54.9 \pm 0.9)^{\text{a}}$	-4.7 ± 1.8

^aThese values are approximated, see Discussion.

Although the partial molar volumes were all determined at 25 °C and $\mu = 0$, whereas $\Delta V_{\text{exp}}^{\ddagger}$ values refer to $\mu = 0.6 M$ and, in most cases, 15 °C, these differences in experimental conditions should only lead to insignificant errors (temperature), or at worst, a constant deviation (ionic strength) for all four systems, so that it is indeed justified to equate these different volume quantities.

Now, consider the independent equilibrium



which can be expressed in terms of the corresponding volume quantities

$$\Delta \bar{V}_4 = \bar{V}(\text{Hg}^{2+}) + \bar{V}(\text{X}^-) - \bar{V}(\text{HgX}^+)$$

Rearrangement with the above expression for $\Delta V_{\text{exp}}^{\ddagger}$ gives the following:

$$\Delta \bar{V}_4 = \bar{V}(\text{L}_5\text{M}^{3+}) - \bar{V}(\text{L}_5\text{MX}^{2+}) + \bar{V}(\text{X}^-) - \Delta V_{\text{exp}}^{\ddagger}$$

Thus, if the results are consistent with a D mechanism, a value of $\Delta \bar{V}_4$ should be obtainable. The appropriate partial molar volumes are listed in Table III. In the previous study [33], mentioned above, the postulate [46] that $\bar{V}(\text{Co}(\text{NH}_3)_5^{3+}) = \bar{V}(\text{Co}(\text{NH}_3)_6^{3+})$ was validated as the mean volume of the proposed five coordinate transition state, calculated from the volume data for a series of leaving groups, was found to be $54.9 \pm 0.9 \text{ cm}^3 \text{mol}^{-1}$ which is in excellent agreement with the directly accessible partial molar volume of $\text{Co}(\text{NH}_3)_6^{3+}$ of $55.0 \pm 1.1 \text{ cm}^3 \text{mol}^{-1}$. In view of the apparent insensitivity of the partial molar volumes of these pentammine complexes [33, 47] to the nature of the central metal atom, as also shown by the values of $\bar{V}(\text{L}_5\text{MX}^{2+})$ in Table III, it seems reasonable to assume that $\bar{V}(\text{L}_5\text{M}^{3+}) = 54.9 \text{ cm}^3 \text{mol}^{-1}$ for the Cr(III) and Rh(III) complexes. The resulting values of $\Delta \bar{V}_4$ for $\text{X} = \text{Cl}^-$ are reasonably similar, with a mean value of $-6.5 \pm 2.7 \text{ cm}^3 \text{mol}^{-1}$. The sign and magnitude of $\Delta \bar{V}_4$ is consistent with a wide variety of volume changes for ion pair dissociation involving ions carrying charges of equal magnitude (e.g. Rb^+NO_3^- , $\Delta \bar{V}_0 = -5$ [52]. Ti^+NO_3^- , $\Delta \bar{V}_0 =$

-12 [52]; $\text{Ni}^{2+}\text{SO}_4^{2-}$, $\Delta \bar{V}_0 = -8.6$ [53]; $\text{Zn}^{2+}\text{SO}_4^{2-}$, $\Delta \bar{V}_0 = -8.0$ [54]; $\text{Mg}^{2+}\text{SO}_4^{2-}$, $\Delta \bar{V}_0 = -7.3$ [55]; $\text{Ca}^{2+}\text{SO}_4^{2-}$, $\Delta \bar{V}_0 = -10.2$ [55] $\text{cm}^3 \text{mol}^{-1}$). Unfortunately corresponding values are not available for ion-pairs containing chloride ions in aqueous solution. However, the magnitude of $\Delta \bar{V}_0$ does appear relatively insensitive to the types of ions involved and the charges they carry. A similar conclusion was reached from a study [56] of lithium chloride and bromide ion-pairs in a wide range of alcohols. In addition, using high pressure temperature jump techniques, Jost [57] was able to measure the volume change associated with the dissociation of the $\text{Fe}(\text{OH}_2)_5\text{NCS}^{2+}$ complex ion ($\Delta \bar{V}_0 = -8.9 \text{ cm}^3 \text{mol}^{-1}$ at $\mu = 0.2 M$ and 25 °C), which is in keeping with the above values. Finally, earlier in the discussion, a $\Delta \bar{V}$ value for the formation of the $(\text{NH}_3)_5\text{M-X-Hg}^{4+1}$ intermediate was estimated at ca. $+8 \text{ cm}^3 \text{mol}^{-1}$ based on data for the $\text{Co}(\text{NH}_3)_5\text{X}^{2+}/\text{Fe}^{2+}$ redox reaction. Thus the volume equation is fully consistent with an essentially dissociative process as defined by eqs. 1 to 3.

The only other pressure study of an induced aquation involved the reaction of Pb^{2+} with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in the presence of sodium polyethylenesulfonate in acidic aqueous medium [37]. The authors report a value for $\Delta V_{\text{exp}}^{\ddagger}$ of $+2.5 \pm 0.5 \text{ cm}^3 \text{mol}^{-1}$. Although a comparison between this value and the $\Delta V_{\text{exp}}^{\ddagger}$ reported in this work for the same substrate must be treated with caution, it is interesting that they are very similar in magnitude, tending to suggest a similarity of mechanism. Therefore, the dehydration [37, 58] (chelation by the polyelectrolyte) of the $\text{Pb}^{2+}(\text{aq})$ ion must be virtually complete prior to the activation process.

The rates and activation parameters, which are summarized in Table II, are difficult to rationalize, especially in view of the large discrepancies between the values reported by the various workers for the same reaction. Generally, the ΔS^{\ddagger} values for the spontaneous and induced aquation reactions are similar, so that the differences in the rates of these two processes are reflected in the ΔH^{\ddagger} terms. ΔH_1^{\ddagger} is considered to stem mainly from the energy required to break the M-X bond [22], which explains the

comparatively slow rates of induced aqueation of the Rh(III) complexes, and provides further evidence for a D mechanism.

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