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Pressure Dependence of the Photoaquation Quantum Yields of some Rhodium(III) Ammine Complexes in Solution

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The effect of pressures up to 200 MPa was studied for the photoaquation reactions of a series of complexes of the type $Rh(NH_3)_5X^{(3-n)+}$, *where* $X = NH_3$ $(n = 0)$, I $(n = 1)$ *and* SO_4 $(n = 2)$. *The quantum yields for the photo-labilization of* NH_3 *on the first two complexes decrease with increasing pressure, resulting in volumes of activation of* $+3.9 \pm 0.5$ *and* $+1.4 \pm 0.9$ cm^3 mol^{-1}, *respectively. The* $Rh(NH_3)_5SO_4^+$ *species undergoes photolabilization of* SO_4^{2-} *and the corresponding volume of activation is* -3.9 ± 0.6 cm^3 mol^{-1}. *Partial molar volume data on the ground state reactant and product species allowed the estimation of the overall reaction volumes, which along with the activation volume data support the view that the photoaquation processes are dissociatively activated.*

Introduction

We recently reported the effect of pressure on the physical and chemical properties of the ligand field photolysis of complexes of the type $Rh(NH_3)_5X^{2+}$, where X = Cl and Br, in weakly acidic aqueous solution [1]. From a combination of the pressure dependencies of the photochemical quantum yields for the various aquation reactions and of the lifetimes of the excited states, we were able to estimate the volumes of activation for all reaction paths responsible for the deactivation of the lowest energy excited state. These turned out to be significantly negative for the photoaquation of the halide ions compared to significantly positive values for the photoaquation of an ammonia ligand. Nevertheless, the results were discussed in terms of a dissociative reaction mechanism, the difference in sign being ascribed to contributions from solvational effects when Cl^- and Br^- are the leaving groups. In an effort to investigate this phenomenon in more detail we studied the effect of pressure on the photoaquation reactions of a series of differently charged complexes, *viz.* $Rh(NH_3)_6^{3+}$, $Rh(NH_3)_5I^{2+}$ and $Rh(NH_3)_5SO_4^+$.

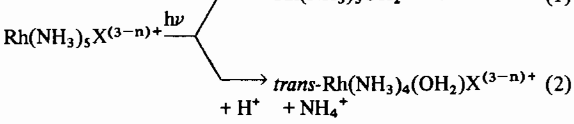
Experimental

The complexes $[Rh(NH_3)_6](ClO_4)_3$ [2], $[Rh(NH_3)_5I](ClO_4)_2$ [3] and $[Rh(NH_3)_5SO_4]ClO_4$ [4] were prepared according to published procedures. *trans*-$[Rh(NH_3)_4(OH_2)I]S_2O_6$ was isolated by irradiating a solution of $Rh(NH_3)_5I^{2+}$ until complete photoaquation occurred, followed by the addition of an excess of $Na_2S_2O_6$. UV-visible absorption spectra (Perkin-Elmer 555 spectrophotometer) and chemical analyses (Hoechst Analytical Laboratory, Frankfurt) were in agreement with those published elsewhere [4, 7, 8] and those expected theoretically. Complex solutions were irradiated under pressures up to 200 MPa using earlier described equipment [5]. The photolyses were carried out in 10^{-3} to 10^{-2} *M* $HClO_4$ at 25 ± 1 °C, except for $Rh(NH_3)_5SO_4^+$ where the temperature was kept at 14 ± 1 °C to decrease the rate of the competing thermal aquation process [6].

Photochemical conversions were determined from pH measurements in the case of $Rh(NH_3)_6^{3+}$ and $Rh(NH_3)_5I^{2+}$, and also from UV-visible spectral changes for the latter complex. In the case of the $Rh(NH_3)_5SO_4^+$ complex the amount of substituted sulfate was determined using ion-exchange chromatography (Dionex). Partial molar volumes were determined from density measurements on an Anton Paar DMA 02/c digital precision densimeter at 25 ± 0.002 °C.

Results and Discussion

It is generally known that Rh(III) ammine complexes undergo aquation reactions during ligand-field excitation according to



$$Rh(NH_3)_5X^{(3-n)+} \xrightarrow{h\nu} Rh(NH_3)_5OH_2^{3+} + X^{n-} \quad (1)$$

$$Rh(NH_3)_5X^{(3-n)+} + H^+ \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(OH_2)X^{(3-n)+} + NH_4^+ \quad (2)$$

For $X^{n-} = NH_3$, reactions (1) and (2) are identical and occur with a quantum yield of 0.075 mol/

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einstein at 313 nm [7]. For $X^{n-} = I^-$, only reaction (2) occurs and $\phi = 0.87$ mol/einstein at 435 nm [8]. The photoaquation reaction of $Rh(NH_3)_5SO_4^+$ has not been reported before, and we found aquation of the coordinated sulfate on irradiation at 313 nm with $\phi = 0.31 \pm 0.02$ mol/einstein. No significant change in pH accompanied the latter reaction, indicating that no aquation of coordinated ammonia occurs. In addition, spectrophotometric analyses confirmed that $Rh(NH_3)_5OH_2^{3+}$ is the only photoaquation product within the experimental error limits concerned.

The studied complexes are all weak emitters and no data concerning the pressure dependence of the excited state lifetimes are available. However, it can be assumed that excitation into singlet ligand field absorption bands is followed by efficient internal conversion and intersystem crossing ($\phi \approx 1$) to the lowest energy excited triplet state, from which the primary photoreaction (k_p) and radiationless deactivation to the ground state (k_n) occur. In addition, our earlier studies clearly demonstrated that radiationless deactivation is almost independent of pressure [1,9], *i.e.* $\Delta V_n^{\#} \approx 0$, such that

$$\frac{\partial}{\partial P}\left(\ln\frac{\phi}{1-\phi}\right) = \frac{\partial}{\partial P}(\ln k_p) = -\frac{\Delta V_p^{\#}}{RT} \qquad (3)$$

The pressure dependencies of ϕ are summarized in Table I, and the corresponding plots of $\ln \phi/(1-\phi)$ *versus* pressure are linear for all three systems, within the experimental error limits concerned. The resulting values of $\Delta V_p^{\#}$ are summarized in Table II, along with overall reaction volumes ($\Delta\bar{V}$) calculated from the partial molar volumes of all reactant and product species in the ground state.

TABLE I. Pressure Dependence of the Photoaquation Quantum Yields for the Ligand Field Photolysis of some Rh(III) Ammine Complexes[a].

Complex	P (MPa)	ϕ (mol einstein^{-1})
$Rh(NH_3)_6^{3+}$ [b]	1	0.071 ± 0.003
	50	0.069 ± 0.002
	100	0.060 ± 0.003
	150	0.056 ± 0.003
	200	0.054 ± 0.002
$Rh(NH_3)_5I^{2+}$ [b]	1	0.87 ± 0.02
	50	0.88 ± 0.02
	100	0.87 ± 0.02
	150	0.86 ± 0.02
	200	0.85 ± 0.02
$Rh(NH_3)_5SO_4^+$ [c]	1	0.31 ± 0.02
	50	0.33 ± 0.02
	100	0.33 ± 0.03
	150	0.36 ± 0.03
	200	0.39 ± 0.03

[a] 10^{-3} to 10^{-2} *M* $HClO_4$. [b] Temp. = 25 ± 1 °C. [c] Temp. = 14 ± 1 °C.

The slightly positive values of $\Delta V_p^{\#}$ for the photoaquation of ammonia in $Rh(NH_3)_6^{3+}$ and $Rh(NH_3)_5I^{2+}$ are in close agreement with our earlier findings for the $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$ complexes [1]. The absolute magnitude of these values, however, is such that the dissociative aquation process is probably of the I_d type. In the case of the sulfato complex, the aquation of the sulfate ligand results in a small, negative volume of activation. The overall reaction volume is strongly negative in this case (see

TABLE II. Volumes of Activation and Overall Volume Changes for a Series of Photoaquation Reactions.

Complex	Leaving group	$\Delta V_p^{\#}$ [a] cm^3 mol^{-1}	$\Delta\bar{V}$ [b] cm^3 mol^{-1}
$Rh(NH_3)_6^{3+}$	NH_3	+3.9 ± 0.5	−1.8 ± 1.3
$Rh(NH_3)_5I^{2+}$	NH_3	+1.4 ± 0.9	+5.3 ± 1.8
$Rh(NH_3)_5SO_4^+$	SO_4^{2-}	−3.9 ± 0.6	−45.5 ± 1.4

[a] Calculated from the data in Table I using eqn. (3). [b] $\Delta\bar{V} = \Sigma\bar{V}(\text{Products}) - \Sigma\bar{V}(\text{Reactants})$; the following $\bar{V}$ values were used (in cm^3 mol^{-1}):

$Rh(NH_3)_6^{3+}$	63.2 ± 0.9 [11]
$Rh(NH_3)_5OH_2^{3+}$	60.7 ± 0.9 [11]
$Rh(NH_3)_5I^{2+}$	94.1 ± 0.3 [11]
trans- $Rh(NH_3)_4(OH_2)I^{2+}$	98.7 ± 1.7 [c]
$Rh(NH_3)_5SO_4^+$	111.2 ± 0.6 [c]
H_2O	18.0
NH_4^+	14.2 [12]
H^+	−4.5 [12]
SO_4^{2-}	23.0 [12]

[c] Determined in this study.

Table II), demonstrating that electrostriction plays a significant role during the generation of $Rh(NH_3)_5OH_2^{3+}$ and SO_4^{2-} from the singly-charged sulfato complex. On the basis of these results a significantly more negative $\Delta V_p^{\#}$ value is expected in case the photoaquation of $Rh(NH_3)_5SO_4^+$ follows a pure dissociative mechanism. As a comparison the $\Delta V_p^{\#}$ values for the aquation of the halide ions in $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$ were found to be -8.6 ± 1.6 and -6.8 ± 1.6 cm^3 mol^{-1}, respectively [1]. A possible explanation may be the partial formation of ion-pairs during the dissociatively-activated photoaquation process, *i.e.* $Rh(NH_3)_5^{3+}\cdot SO_4^{2-}$, for which $\Delta V_p^{\#}$ will be significantly more positive than in the case of separated ions. A very similar result was recently found for the thermal base hydrolysis reactions of a series of pentaamminecobalt(III) complexes [10]. These all proceed via the formation of a five-coordinate intermediate $Co(NH_3)_4NH_2^{2+}$ (Sn1CB mechanism) for which a fairly constant partial molar volume, independent of the nature of the leaving group, could be estimated. In the case of the sulfato complex however deviations were observed in the volume profile of the process, which were ascribed to the presence of ion-pairs of the type $Co(NH_3)_4NH_2^{2+}\cdot SO_4^{2-}$. It follows that the value of $\Delta V_p^{\#}$ for the photoaquation of $Rh(NH_3)_5SO_4^+$ can be considered to be in line with a dissociative mechanism, most probably of the interchange type.

Finally, we comment that negative values for $\Delta V_p^{\#}$ in this and our earlier study [1] have been interpreted in terms of dissociative reaction modes in which volume decreases due to changes in electrostriction outweigh the volume increases due to bond breakage. The earlier-mentioned base hydrolysis study [10] clearly demonstrated that the volume of activation for the dissociation of the conjugate base species $Co(NH_3)_4(NH_2)X^{(2-n)+}$ decreases with increasing charge on X. Furthermore, this value remained positive in all cases, indicating that intrinsic volume changes always outweighed the changes due to electrostriction. However, effects due to charge creation are more significant in the photoaquation reactions of $Rh(NH_3)_5X^{(3-n)+}$ than in the base hydrolysis reactions of $Co(NH_3)_4(NH_2)X^{(2-n)+}$ due to the formation of $Rh(NH_3)_5^{3+}$ and X^{n-}, as compared to $Co(NH_3)_4(NH_2)^{2+}$ and X^{n-}, which can account for the overall negative volumes of activation. It is therefore quite understandable why $\Delta V_p^{\#}$ for the photoaquation of *trans*-$Rh(NH_3)_4X_2^+$ to produce *trans*-$Rh(NH_3)_4(OH_2)X^{2+}$ has values of $+2.8 \pm 0.6$ and $+2.9 \pm 0.7$ cm^3 mol^{-1} for X = Cl and Br, respectively [5]. These values are certainly in line with a dissociative photosubstitution mode and demonstrate the effect of the charge on the complex ion.

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