Short Communication

Ammonia Photoaquation in Bromopentaamminerhodium(III). Product Stereochemistry and Excited State Rearrangement

L. H. Skibsted

Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40,
DK-1871 Frederiksberg C, Denmark


In aqueous solution, ammine ligand aquration is the major photo-reaction resulting from ligand field excitation of bromopentaamminerhodium

\[ \text{hv} \rightarrow [\text{Rh(NH}_3\text{)}_5\text{Br}]^{2+} + \text{H}_3\text{O}^+ \]

[\text{Rh(NH}_3\text{)}_4\text{(H}_2\text{O})\text{Br}]^{2+} + \text{NH}_4^+ \]

(III)\textsuperscript{1–3} and the photoprodut \( [\psi_{\text{NH}_3} = 0.18(1), 25^\circ\text{C}] \) is mainly, although not exclusively, the \textit{trans} isomer. Product stereochemistry cannot be taken as evidence for the stereochemical origin of photosubstituted ligands, owing to the high stereomobility of such excited-state reactions.\textsuperscript{4,5} However, \textsuperscript{15}N-labelling has proved to be a valuable tool in tracing photoaquated ammonia,\textsuperscript{6,7} and in order to establish whether axial or equatorial ammonia is substituted in this octahedral \( d^8 \) pentammine complex with a weak-field heteroligand, \textit{trans}-NH\textsubscript{3} has been \textsuperscript{15}N-labelled and the ammonia released during photoaquation of [\text{Rh(NH}_3\text{)}_5\text{Br}]^{2+} has been subjected to isotopic analysis.

Stereocchemical selection rules, which have enjoyed considerable success in rationalizing the stereocchemical consequences of photosolvolysis of \( d^8 \) low-spin octahedral complexes,\textsuperscript{5,8} have largely been based on experiments with rhodium (III) amines. The results communicated here on the photostereochemistry of [\text{Rh(NH}_3\text{)}_5\text{Br}]^{2+} are of interest in this connection, since the work represents an extension of the previous work\textsuperscript{7} on [\text{Rh(NH}_3\text{)}_5\text{Cl}]^{2+} to a pentammine complex in which the field difference between the ammonia ligand and the heteroligand is more substantial.

[\text{Rh(NH}_3\text{)}_5\text{Br}]^{2+} was labelled in the \textit{trans}-position using the same strategy as employed previously for [\text{Rh(NH}_3\text{)}_4\text{(H}_2\text{O})\text{Cl}]^{2+};\textsuperscript{7} \textit{trans}-[\text{Rh(NH}_3\text{)}_4\text{(H}_2\text{O})\text{Cl}_2]_2(\text{ClO}_4)_2(100 \text{ mg}) was heated in 10 ml of a \textsuperscript{15}N-enriched 0.9 M \text{NH}_3/\text{NH}_4\text{ClO}_4 buffer with pH = 9.5 \textsuperscript{15}\text{NH}_4\text{ClO}_4 prepared from 99% \textsuperscript{15}\text{NH}_4\text{Cl}, (Amersham Int.) by precipitation with Li\text{ClO}_4 in a sealed ampoule at 85°C for 6 h. From the reaction mixture, a product mixture of \textit{trans}-[\text{Rh(NH}_3\text{)}_4(\text{15}\text{NH}_3)\text{Br}]\text{Br}_2 and \textit{trans}-[\text{Rh(NH}_3\text{)}_4(\text{15}\text{NH}_3)(\text{H}_2\text{O})]\text{Br}, was precipitated (by the addition of 10 ml of 65% \text{HBr}). The product was heated overnight at 90°C, and the \textit{trans}-[\text{Rh(NH}_3\text{)}_4(\text{15}\text{NH}_3)\text{Br}]\text{Br}_2 was reprepated as \textit{trans}-[\text{Rh(NH}_3\text{)}_4(\text{15}\text{NH}_3)\text{Br}]\text{Cl}_2 and finally con-

| \text{Table 1. Fraction of axial ammonia photoaquated}\textsuperscript{a} in [\text{Rh(NH}_3\text{)}_5\text{Br}]^{2+} in aqueous 0.010 M \text{HClO}_4, calculated from isotopic analysis of \text{NH}_3 released from 6.71% \textsuperscript{15}\text{N} \text{trans-enriched [Rh(NH}_3\text{)}_5\text{Br}]^{2+}. | \\
|----------------|----------------|----------------|----------------|
| \[\text{[Rh(NH}_3\text{)}_5\text{Br}]^{2+}\] | \text{NH}_3\text{/mol} | \text{15}\text{N}\%/ | \text{Axial NH}_3\textsuperscript{d} | \\
| 23.3 | 12.9 | 5.81 | 0.86 |
| 24.0 | 15.0 | 5.92 | 0.88 |
| 23.9 | 14.7 | 5.91 | 0.87 |

\textsuperscript{a}\lambda_{\text{max}} = 366 \text{ nm.} \textsuperscript{b}Amount of complex photolyzed. \textsuperscript{c}Amount of released \text{NH}_3 separated from photolysis solution. \textsuperscript{d}Axial \text{NH}_3 released as a fraction of total released \text{NH}_3.
Table 2. Photoisomerization quantum yields for aquabromotetramminerhodium(III) in acidic solution at 25°C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \Phi_c )</th>
<th>( \Phi_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>0.457(1)⁶</td>
<td>0.018(1)⁶</td>
</tr>
<tr>
<td>[Rh(NH₃)₄(D₂O)Br]²⁺</td>
<td>0.417(3)</td>
<td>0.034(2)</td>
</tr>
</tbody>
</table>

⁴10⁻³ M HClO₄/H₂O: \( \lambda_m = 366, 405 \) and 438 nm; a total of 10 experiments. ⁵10⁻² M DClO₄/D₂O:
\( \lambda_m = 436 \) nm; a total of 4 experiments. ⁶Previously reported as 0.50(4) (Ref. 11).

Verted into trans-[Rh(NH₃)₄(¹⁵NH₃)Br](ClO₄)₂ by precipitation with 70% HClO₄; the latter salt had the expected UV-absorption spectrum (10⁻³ M HClO₄): \( \lambda_{max} \approx 359 \) nm, 122 l mol⁻¹ cm⁻¹; 424, 26; Cary 219 spectrophotometer).

Solutions of trans-[Rh(NH₃)₄(¹⁵NH₃)Br](ClO₄)₂ (1.63% ¹⁵N total enrichment, corresponding to 6.71% ¹⁵N trans-enrichment; 13.8 ml of ca. 2 mM aqueous 0.010 M HClO₄ solutions) were irradiated with monochromatic light of wavelength 366 nm (ca. 7 μ einstein min⁻¹, 5 cm light path) at 25°C for 2 h, and the photoaquated ammonia was separated from the reaction mixture by the distillation and trapping procedure described previously.⁶ The amount of NH₃ thus separated was determined by titration, and the ¹⁵N/¹⁴N ratio was subsequently determined by optical emission spectroscopy.⁰ Experimental results are summarized in Table 1. With the present experimental design, a natural ¹⁵N/¹⁴N ratio corresponding to 0.36% ¹⁵N is expected for exclusively equatorial photolabilization, whereas 6.71% is indicative of axial labilization. The observed ¹⁵N/¹⁴N ratios correspond to 87±4% axial labilization.

The photoproduct [Rh(NH₃)₄(H₂O)Br]²⁺, which notably is also the major photoproduct resulting from ligand field excitation of both cis- and trans-[Rh(NH₃)₃Br]⁺,¹¹ was previously believed to be exclusively the trans isomer. However, a careful spectral analysis of exhaustively photolyzed solutions revealed this photoproduct to be in a cis/trans photostationary state, although with a strong trans preference:

\[
\text{cis-[Rh(NH₃)₄(H₂O)Br]²⁺} \xrightarrow{\Phi_c} \xrightarrow{\Phi_e} \text{trans-[Rh(NH₃)₄(H₂O)Br]²⁺}
\]

The quantum yields for the interconversion of the aquabromotetramminerhodium(III) ions (Table 2) in acidic aqueous solution and in acidic deuterium oxide (Norsk Hydro, 99.8%) were determined by irradiation of solutions of either isomer of [Rh(NH₃)₃(H₂O)Br]S₂O₇¹¹ (monitored spectrophotometrically;¹²,¹³ ferrioxalate actinometry). The composition of the cis/trans photostationary state, calculated from the isomerization quantum yields and the molar absorption coefficients at the wavelength of irradiation, is compared in Table 3 with the composition calculated from the

Table 3. Photostationary states for cis- and trans-aquabromotetramminerhodium(III) at 25°C in aqueous 10⁻³ M perchloric acid.

<table>
<thead>
<tr>
<th>( \lambda_m/\text{nm} )</th>
<th>Reacting complex</th>
<th>cis/trans photostationary state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% trans obsd.⁶</td>
<td>% trans calc.⁸</td>
</tr>
<tr>
<td>366</td>
<td>trans-[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>cis-[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>97.6</td>
</tr>
<tr>
<td>405</td>
<td>trans-[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>95.9</td>
</tr>
<tr>
<td></td>
<td>cis-[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>95.6</td>
</tr>
<tr>
<td>436</td>
<td>trans-[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>94.0</td>
</tr>
<tr>
<td></td>
<td>cis-[Rh(NH₃)₄(H₂O)Br]²⁺</td>
<td>92.3</td>
</tr>
<tr>
<td></td>
<td>trans-[Rh(NH₃)₄(D₂O)Br]²⁺</td>
<td>93.6</td>
</tr>
<tr>
<td></td>
<td>cis-[Rh(NH₃)₄(D₂O)Br]²⁺</td>
<td>89.7</td>
</tr>
</tbody>
</table>

⁶Calculated from spectral analysis of exhaustively photolyzed solution. ⁸Calculated from % trans = 100/(1 + r), where \( r = (\Phi_e/\Phi_c)^{\epsilon_{\text{trans}}/\epsilon_{\text{cis}}} \); cf. Ref. 12. ¹⁰⁻² M DClO₄, D₂O.

190
absorption spectra ("observed"), and the agreement confirms that the photoproduct is in a photostationary state. The relative insensitivity to deuteration of the water ligand (only coordinated H2O is deuterated in acidic D2O, owing to the vast difference in D/H exchange rate for this ligand and for coordinated NH3) is consistent with observations made for [Rh(NH3)4(H2O)Cl]2+ and with a dissociative water-exchange mechanism for the photoisomerization.14

Two results have been obtained in the present study. Firstly, the ammonia which is preferentially photoaquated in [Rh(NH3)3Br]3+ has been identified as the axial ammonia, although ca. 10% originates from the four equatorial positions, implying that axial ammonia is labilized ca. 30 times as efficiently as the equatorial ammonia ligands. Secondly, the photoproduct [Rh(NH3)4(H2O)Br]2+ has been shown to form a photostationary state with a strong trans preference. The selection rules based on the angular overlap model5,8,11 correctly predict axial ammonia to be photolabilized in [Rh(NH3)3Br]3+ and the photoproduct [Rh(NH3)4(H2O)Br]2+ to have the trans geometry. However, the important conclusion that can be drawn is that, although these selection rules lead to predictions which are qualitatively correct, finer details remain to be discovered for these excited-state reactions.4

Acknowledgements. This research was supported by grants from the Danish Natural Science Research Council. The author wishes to thank the Physics Laboratory of the Royal Veterinary and Agricultural University, in particular Dr. H. Saaby Johansen, for carrying out the isotopic analyses, and Bodil Øby for technical assistance.

References

Received December 4, 1987.