*Short Communication*

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

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In aqueous solution, ammine ligand aquation is the major photoreaction resulting from ligand field excitation of bromopentaamminerhodium

$$[Rh(NH_3)_5Br]^{2+} + H_3O^+ \xrightarrow{hv}$$

$$[Rh(NH_3)_4(H_2O)Br]^{2+} + NH_4^+$$
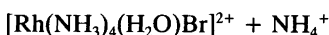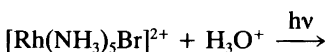
(III)[1-3] and the photoproduct [φ_{NH_3} = 0.18(1), 25 °C][2] is mainly, although not exclusively, the *trans* isomer. Product stereochemistry cannot be taken as evidence for the stereochemical origin of photosubstituted ligands, owing to the high stereomobility of such excited-state reactions.[4,5] However, ^{15}N-labelling has proved to be a valuable tool in tracing photoaquated ammonia,[6,7] and in order to establish whether axial or equatorial ammonia is substituted in this octahedral d^6 pentaammine complex with a weak-field heteroligand, *trans*-NH$_3$ has been ^{15}N-labelled and the ammonia released during photoaquation of [Rh(NH$_3$)$_5$Br]$^{2+}$ has been subjected to isotopic analysis.

Stereochemical selection rules, which have enjoyed considerable success in rationalizing the stereochemical consequences of photosolvolysis of d^6 low-spin octahedral complexes,[5,8] have largely been based on experiments with rhodium (III) amines. The results communicated here on the photostereochemistry of [Rh(NH$_3$)$_5$Br]$^{2+}$ are of interest in this connection, since the work represents an extension of the previous work[7] on [Rh(NH$_3$)$_5$Cl]$^{2+}$ to a pentaammine complex in

which the field difference between the ammonia ligand and the heteroligand is more substantial.

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

Table 1. Fraction of axial ammonia photoaquated[a] in [Rh(NH$_3$)$_5$Br]$^{2+}$ in aqueous 0.010 M HClO$_4$, calculated from isotopic analysis of NH$_3$ released from 6.71 % [15]N *trans*-enriched [Rh(NH$_3$)$_5$Br]$^{2+}$.

[Rh(NH$_3$)$_5$Br]$^{2+}$ [b] /μmol	NH$_3$[c]/μmol	[15]N/%	Axial NH$_3$[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

[a]λ_{irr} = 366 nm. [b]Amount of complex photolyzed. [c]Amount of released NH$_3$ separated from photolysis solution. [d]Axial NH$_3$ released as a fraction of total released NH$_3$.

Table 2. Photoisomerization quantum yields for aquabromotetraamminerhodium(III) in acidic solution at 25°C.

Complex	φ_{ct}	φ_{tc}
$[Rh(NH_3)_4(H_2O)Br]^{2+}$ [a]	0.457(11)[c]	0.018(1)
$[Rh(NH_3)_4(D_2O)Br]^{2+}$ [b]	0.417(3)	0.034(2)

[a] 10^{-3} M $HClO_4/H_2O$: $\lambda_{irr} = 366$, 405 and 436 nm; a total of 10 experiments. [b] 10^{-2} M $DClO_4/D_2O$: $\lambda_{irr} = 436$ nm; a total of 4 experiments. [c] Previously reported as 0.50(4) (Ref. 11).

verted into *trans*-$[Rh(NH_3)_4(^{15}NH_3)Br](ClO_4)_2$ by precipitation with 70% $HClO_4$; the latter salt had the expected UV-absorption spectrum[9] (10^{-3} M $HClO_4$: λ_{max}, $\varepsilon_{max} = 359$ nm, 122 l mol^{-1} cm^{-1}; 424, 26; Cary 219 spectrophotometer).

Solutions of *trans*-$[Rh(NH_3)_4(^{15}NH_3)Br](ClO_4)_2$ (1.63% ^{15}N total enrichment, corresponding to 6.71% ^{15}N *trans*-enrichment; 13.8 ml of ca. 2 mM aqueous 0.010 M $HClO_4$ 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 NH_3 thus separated was determined by titration, and the $^{15}N/^{14}N$ ratio was subsequently determined by optical emission spectroscopy.[10] Experimental results are summarized in Table 1. With the present

experimental design, a natural $^{15}N/^{14}N$ ratio corresponding to 0.36% ^{15}N is expected for exclusively equatorial photolabilization, whereas 6.71% is indicative of axial labilization. The observed $^{15}N/^{14}N$ ratios correspond to 87±4% axial labilization.

The photoproduct $[Rh(NH_3)_4(H_2O)Br]^{2+}$, which notably is also the major photoproduct resulting from ligand field excitation of both *cis*- and *trans*-$[Rh(NH_3)_4Br_2]^+$,[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:

$$cis\text{-}[Rh(NH_3)_4(H_2O)Br]^{2+} \underset{\varphi_{tc}}{\overset{\varphi_{ct}}{\rightleftharpoons}}$$

$$trans\text{-}[Rh(NH_3)_4(H_2O)Br]^{2+}.$$
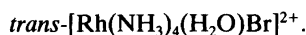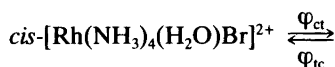
The quantum yields for the interconversion of the aquabromotetraamminerhodium(III) ions (Table 2) in acidic aqueous solution and in acidic deuterium oxide (Norsk Hydro, 99.8%) were determined by irradiation of solutions of either isomer of $[Rh(NH_3)_4(H_2O)Br]S_2O_6$[11] (monitored spectrophotometrically;[12,13] 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*-aquabromotetraamminerhodium(III) at 25°C in aqueous 10^{-3} M perchloric acid.

λ_{irr}/nm	Reacting complex	*cis*/*trans* photostationary state	
		% *trans* obsd.[a]	% *trans* calc.[b]
366	*trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	99.4	99.1
	cis-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	97.6	99.1
405	*trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	95.9	96.3
	cis-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	95.6	96.3
436	*trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	94.0	94.5
	cis-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	92.3	94.5
	trans-$[Rh(NH_3)_4(D_2O)Br]^{2+}$ [c]	93.6	89.4
	cis-$[Rh(NH_3)_4(D_2O)Br]^{2+}$ [c]	89.7	89.4

[a] Calculated from spectral analysis of exhaustively photolyzed solution. [b] Calculated from % *trans* = $100/(1+r)$, where $r = (\varphi_{tc} \varepsilon_{trans}^{irr}/\varphi_{ct} \varepsilon_{cis}^{irr})$; cf. Ref. 12. [c] 10^{-2} M $DClO_4$, D_2O.

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 H_2O is deuterated in acidic D_2O, owing to the vast difference in D/H exchange rate for this ligand and for coordinated NH_3) is consistent with observations made for $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ 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 $[Rh(NH_3)_5Br]^{2+}$ 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 $[Rh(NH_3)_4(H_2O)Br]^{2+}$ has been shown to form a photostationary state with a strong *trans* preference. The selection rules based on the angular overlap model[5,8,11] correctly predict axial ammonia to be photolabilized in $[Rh(NH_3)_5Br]^{2+}$ and the photoproduct $[Rh(NH_3)_4(H_2O)Br]^{2+}$ 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]

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