

Position-dependent Deuterium Isotope Effect on Photoisomerization of Ammineaquarhodium(III) Complexes: Identification of the Excited-state Vibronic Deactivation Mode

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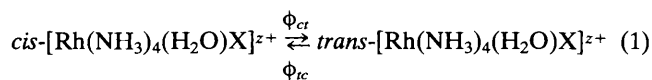
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cis to *trans* Photoisomerization quantum yields are increased by a factor of approximately two by deuteration of co-ordinated water in tetra-ammineaquarhodium(III), but are almost insensitive to deuteration of co-ordinated water in tetra-ammineaquachlororhodium(III) and to deuteration of co-ordinated ammonia in either complex; this identifies the dominating nonradiative deactivation mode (competing with the excited-state rearrangement) as a hydrogen-oxygen vibration in an excited-state intermediate of reduced co-ordination number.

Stereochemical selection rules based on the angular overlap model¹⁻³ have been capable of rationalizing^{4,5} and predicting³ the stereochemical consequences of photosolvolytic of d⁶ low-spin octahedral complexes. A more thorough understanding of these rearrangement processes requires, however, characterization of the individual deactivation path for the ligand field excited states involved, and several photophysical investigations have recently focused on the reaction dynamics of excited-state processes in d⁶ metal centres of which rhodium(III) amines have served as the prototype.⁶⁻⁸ The nonradiative deactivation is, in most cases, the predominant decay pathway, and the coupling between ligand field excited states and the electronic ground state should accordingly play a key role in any detailed mechanistic description of photochemical phenomena such as light-induced isomerization.

Reported here are some striking differences in the effect of deuteration of ammine and aqua ligands in *cis*- and *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ and in *cis*- and *trans*-[Rh(NH₃)₄(H₂O)Cl]²⁺, on *cis* to *trans* and *trans* to *cis* photoisomerization. These differences help to identify the specific relaxation processes and are expected to facilitate the theoretical treatment of the vibronic coupling mechanisms for the dissipation of the excitation energy to the solvent molecules.

In acidic aqueous solution, *cis*- and *trans*-[Rh(NH₃)₄(H₂O)X]^{z+} (X = Cl, H₂O), when subjected to light matching the (t_{2g})⁶ to (t_{2g})⁵(e_g)¹ multiplicity-allowed ligand field transitions (¹T₁ ← ¹A₁ and ¹T₂ ← ¹A₁ in O_h symmetry), have previously been found to exchange co-ordinated and solvent water (¹⁸O-labelling^{9,10}) in the lowest-energy triplet state to initiate isomerization and eventually to form photo-stationary states with a *trans* preference [equation (1)].



The perdeuterio-compounds *cis*- and *trans*-[Rh(ND₃)₄(D₂O)₂](ClO₄)₃ were prepared by repeated heating of the perprotio perchlorates¹⁰ dissolved in D₂O (Norsk Hydro, 99.8%) in a sealed ampoule at 105 °C for 6 h and precipitation by addition of DClO₄ (70%, Merck). The deuteration was followed by i.r. spectroscopy and the isomeric purity was checked by u.v. spectroscopy.¹⁰ The vast difference in the proton exchange rate for co-ordinated ammonia and co-ordinated water in rhodium(III) complexes in acidic solution^{11,12} permitted *in situ* creation of [Rh(ND₃)₄(H₂O)₂]³⁺ by dissolution of [Rh(ND₃)₄(D₂O)₂](ClO₄)₃ in 1 M-HClO₄, H₂O,

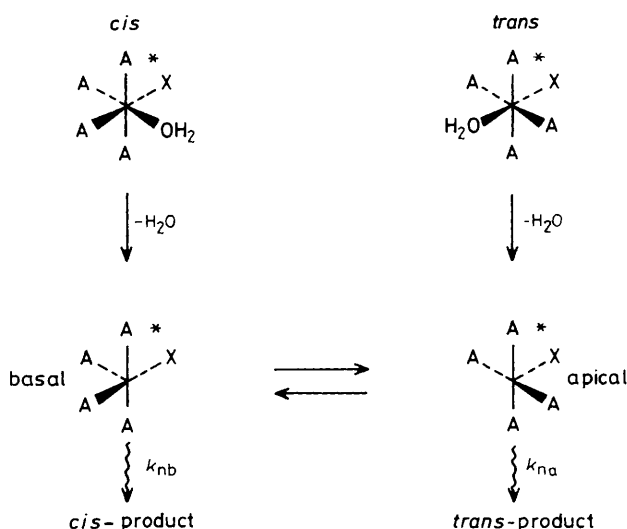


Figure 1. Excited-state photoisomerization reaction mechanism for ammineaquarhodium(III): A = NH₃, X = Cl or H₂O. Only for X = D₂O/H₂O is a deuterium/hydrogen isotope effect on photoisomerization observed.

Table 1. Deuterium/hydrogen isotope effect on photoisomerization of *cis*- and *trans*-[Rh(NH₃)₄(H₂O)₂]³⁺ (λ_{irr} = 366 nm) and *cis*- and *trans*-[Rh(NH₃)₄(H₂O)Cl]²⁺ (λ_{irr} = 366 and 405 nm) in acidic aqueous perchlorate solution at 25 °C.

	[Rh(NH ₃) ₄ (H ₂ O) ₂] ^{3+a}	[Rh(NH ₃) ₄ (D ₂ O) ₂] ³⁺	[Rh(ND ₃) ₄ (H ₂ O) ₂] ³⁺	[Rh(ND ₃) ₄ (D ₂ O) ₂] ³⁺
φ _{tc}	0.011(1)	0.016(2)	0.016(2)	0.018(3)
φ _{ct}	0.102(4)	0.22(1)	0.123(6)	0.23(1)
φ _{tc} /φ _{ct}	0.11(1)	0.07(1)	0.13(2)	0.08(1)
	[Rh(NH ₃) ₄ (H ₂ O)Cl] ^{2+b}	[Rh(NH ₃) ₄ (D ₂ O)Cl] ²⁺	[Rh(ND ₃) ₄ (H ₂ O)Cl] ²⁺	[Rh(ND ₃) ₄ (D ₂ O)Cl] ²⁺
φ _{tc}	0.064(3)	0.054(5)	0.057(5)	0.066(4)
φ _{ct}	0.52(1)	0.54(2)	0.60(2)	0.64(1)
φ _{tc} /φ _{ct}	0.12(1)	0.10(1)	0.10(1)	0.10(1)

^a From ref. 10. ^b From ref. 9.

and of $[\text{Rh}(\text{NH}_3)_4(\text{D}_2\text{O})_2]^{3+}$ by dissolution of $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ in 1 M- DClO_4 , D_2O for both the *cis*- and *trans*-series. Continuous wave photolyses^{9,10} (monitored spectrophotometrically, ferrioxalate actinometry) at 25 °C of each of these selectively deuteriated complex ions and of each of the isomers of $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ and $[\text{Rh}(\text{ND}_3)_4(\text{D}_2\text{O})_2]^{3+}$, the latter four complex ions being obtained by dissolution of the perprotio- and the perdeuterio-perchlorates in 1 M- HClO_4 , H_2O and 1 M- DClO_4 , D_2O , respectively, yielded the photoisomerization quantum yields (cf. equation 1) in Table 1.

The photoisomerization quantum yields for the four isomers of each of the two geometrical isomers of tetraammineaquachlororhodium(III) included in Table 1 were determined in a similar series of experiments, and it should be noted that the photoisomerization quantum yields are rather insensitive to deuteration. The significant exceptions are the *cis* to *trans* isomerization yields for $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ and $[\text{Rh}(\text{ND}_3)_4(\text{H}_2\text{O})_2]^{3+}$, which are both increased by a factor of ca. 2 by deuteration of water in either compound. This shows (i) that photoisomerization is relatively insensitive to deuteration of co-ordinated ammonia and (ii) that more than one water ligand is required in the co-ordination sphere before deuteration of co-ordinated water significantly affects the photoisomerization efficiencies. These findings, when considered together with the results from phosphorescence lifetime measurements, which have established that deuterium/hydrogen isotope effects on primary photochemical processes in rhodium(III) amines are unimolecular properties of the complex ions rather than properties of the solvent,^{12,13} show that deactivation of an excited-state intermediate of reduced co-ordination number created by water ligand dissociation is competing with excited-state rearrangement.

The reactive triplet states (3T_1 in octahedral symmetry) populated by internal conversion/intersystem crossing from initially populated singlet states are precursors for pentacoordinate apical (*trans*-geometries) and basal (*cis*-geometries) triplet excited-state intermediates which rearrange in competition with deactivation, cf. Figure 1.¹⁻⁵ The rate constant k_n for nonradiative deactivation is determined mostly by intramolecular processes (product of vibrational and electronic factors), and the most notable implication of the present results is the direct indication of a vibronic coupling between two electronic states dominated by high-frequency modes related to a co-ordinated water molecule. Only high-frequency vibrations can act as promoting modes when excited-state distortions are small (the so-called weak-coupling

limit^{7,12,14}), and it can be concluded that for ammineaquarhodium(III), the high-frequency oxygen-hydrogen $\nu(\text{OH}_2)$ modes, when available in the pentaco-ordinate intermediates, dominate the nonradiative deactivation of these excited-state molecules.

The quantum yield ratio ϕ_{ic}/ϕ_{ct} is a measure of the excited-state preference for either co-ordination geometry, and another important consequence of the result in Table 1 is that the ϕ_{ic}/ϕ_{ct} ratio is sensitive to aqua-ligand deuteration for the diaqua- but not for the aquachloro-complexes. Replacing the high-frequency O-H modes with lower frequency O-D modes is expected to lead to large decreases in nonradiative deactivation rate constants.¹² Clearly, the observed decrease in ϕ_{ic}/ϕ_{ct} for the diaqua-complexes can be explained by a higher sensitivity of the high-frequency vibrations to deuteration in the lower-symmetry basal isomer (*i.e.*, k_{nb} decreases more than k_{na}), suggesting a different balance between weak and strong coupling for the two isomers.

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