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PHOTOISOMERIZATION OF RHODIUM(III) AMINE COMPLEXES

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ABSTRACT

Ligand field excitation of hexacoordinated rhodium(III) amine complexes leads to ligand labilization and, in aqueous solution, to photoaquation with relatively high quantum yields. For *cis-* and *trans*-tetraammines, photoaquation or photochemical water exchange leads to both *cis-* and *trans* photoproducts in a ratio which is independent both of the leaving ligand and of the reactant stereochemistry, providing strong evidence for a photoisomerization mechanism with initial ligand dissociation followed by thermal equilibration between excited state intermediates of reduced coordination number. Observation of ammonia-scrambling as a result of chloride photoaquation in the chloropentaammine complex confirms that excited state rearrangement is fast compared to deactivation. Excited state ligand dissociation rates, obtained from a combination of photoaquation quantum yields and photoluminescence decay curves, indicate that *cis*-complexes are more reactive than their *trans*-counterparts, and that chelation accelerates halide dissociation, most significantly in the *cis*-series. The more substitution-labile excited state isomers have negative volumes of activation and are also those which show the greater degree of concomitant isomerization, suggesting some synchronous nature of the ligand dissociation- and the isomerization reactions.

INTRODUCTION

Rhodium(III) has the d^6 electronic configuration and forms very robust low-spin amine complexes, which have proved to be very valuable in elucidating the mechanism for photosubstitution reactions in solutions of octahedral d^6 configuration complexes in general (ref. 1-3). The marked robustness ensures that photochemical reactions can be studied under ambient conditions without interference from thermal reactions. Moreover, the charge transfer excited states are, at least for complexes with aliphatic amines, energetically well-separated from ligand field transition (d-d), and the study of photochemical ligand substitution reactions is normally not complicated by photoinduced redox reactions.

While some of the earliest studies (ref. 4) concluded that photosubstitution reactions proceeded with stereoretention, Muir and

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Huang (ref. 5) found evidence for *cis* to *trans* photoisomerization as a result of photoaquation of one chloride ligand in the ethylenediamine complex *cis*-$[Rh(en)_2Cl_2]^+$. Subsequent studies by different research groups showed that photochemical ligand substitution in rhodium(III) amine complexes is often accompanied by at least partial isomerization (ref. 6-13). The analogous thermal reactions are all stereoretentive, and this antithermal behaviour has stimulated theoretical modelling of the excited state rearrangements (ref. 14-16).

Photoisomerization has been studied in particular detail in the case of ammonia complexes (ref. 7,17-30), and for these rhodium(III) complexes, measurement of room temperature emission,assigned as ligand field phosphorescence from the lowest energy triplet, has allowed the estimation of excited state lifetimes and, in combination with reaction quantum yields, rate constants for the excited state substitution reactions (ref. 29-31). The following treatment attempts to summarize our present knowledge of the photostereochemistry of pentaammine- and tetraamminerhodium(III) complexes and to combine the photochemical- and photophysical results to obtain a description of the excited state rearrangement dynamics. Also, comparison will be made with a series of 1,3-propanediamine rhodium(III) complexes for which similar information is now available (ref. 32).

The study of the stereochemical consequences of ligand field photolysis of ammonia complexes of rhodium(III) was initiated by the observation by Strauss and Ford (ref. 7) of the photoisomerization

$$\underline{cis}\text{-}[Rh(NH_3)_4Cl_2]^+ + H_2O \xrightarrow[366\,nm]{h\nu} \underline{trans}\text{-}[Rh(NH_3)_4(H_2O)Cl]^{2+} + Cl^- \qquad (1)$$

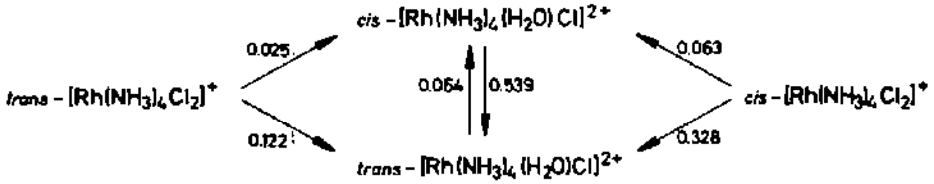
and the following account takes its starting point in this same reaction.

PHOTOISOMERIZATION

The quantum yields for the photoaquation- and photoisomerization reactions resulting from d-d excitation discussed in the following have been found to be independent of the wavelength of irradiation (*cf.* ref. 1-3). This discussion refers to results obtained in dilute aqueous solution at 25 °C and, where investigated, no ionic strength dependence on product distribution or on quantum yields was found (ref. 32).

Tetraammine complexes

In acidic aqueous solution, cis-$[Rh(NH_3)_4Cl_2]^+$ undergoes photosubstitution/photoisomerization according to equation (1), and while it originally was thought that these pathways had equal quantum yields (ref. 7 and 17), a reexamination (ref. 25) has shown that a small percentage of the cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ ion is also produced, cf. Fig. 1. trans-$[Rh(NH_3)_4Cl_2]^+$ reacts in a similar fashion (Fig. 2), also producing a cis/trans-mixture of $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ (ref. 27). The isomeric aquachloro complexes, which are photochemically interconvertible, eventually form a cis/trans-photostationary state (λ_{irr} = 366 nm, quantum yields in mol/einstein):



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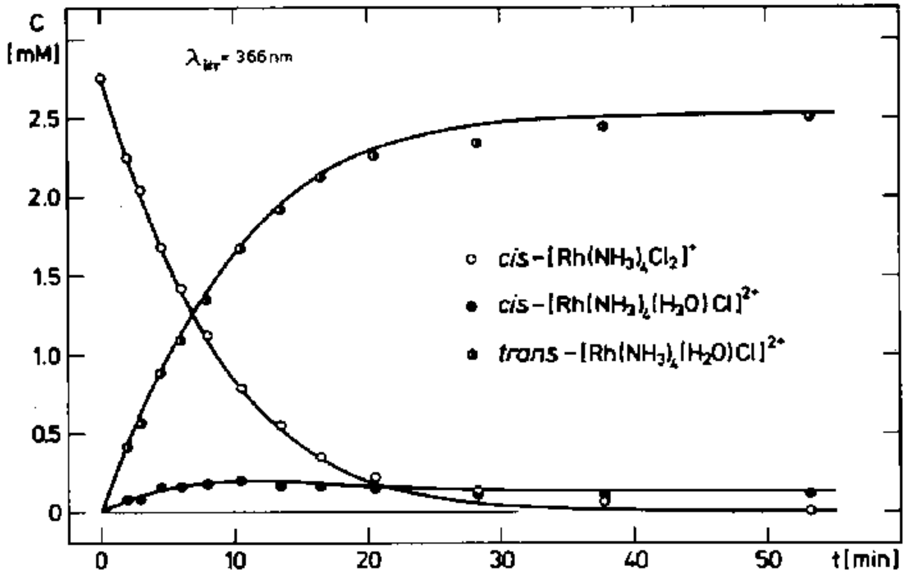
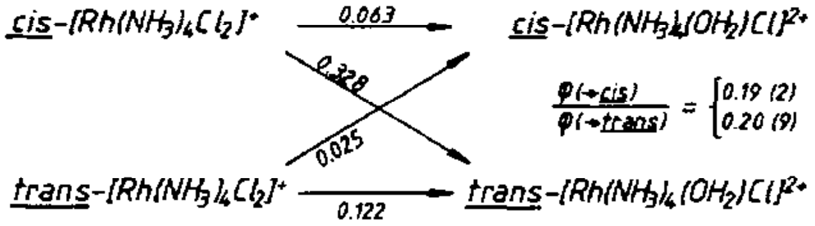


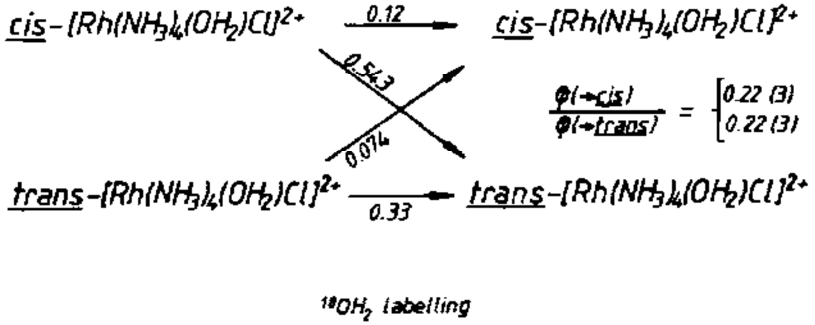
Fig. 1. Photolysis of a 2.75 mM cis-dichlorotetraamminerhodium(III) aqueous solution. The points are experimental values and the solid lines are calculated from the determined quantum yields, the molar absorptivities at 366 nm and the light intensity (ref. 25). This Fig. and Figs. 2 and 3 are reproduced with the permission of Acta Chem. Scand.

The ratios between the quantum yields for formation of cis-product and trans-product for the two dichlorotetraamminerhodium(III) complexes are identical within experimental uncertainties:



(3)

Moreover, the same cis/trans-product ratios were found for photochemical water exchange in the isomeric $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ (ref. 25), which also proceed with competition between isomerization and stereoretention:



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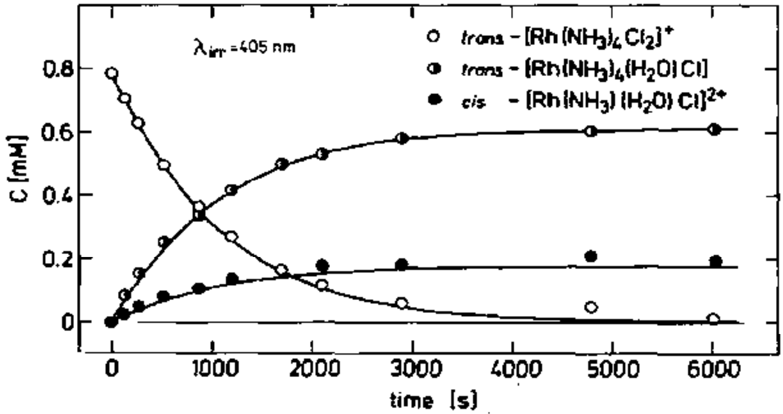


Fig. 2. Photolysis of a 0.79 mM trans-dichlorotetraamminerhodium(III) aqueous solution, cf. Fig. 1 (ref. 27).

The common *cis*/*trans*-ratio, independent of both the leaving ligand and of the reactant stereochemistry, provides strong evidence for a dissociative reaction mechanism with either a common excited state intermediate of reduced coordination number, or with thermal equilibration between excited state intermediates of reduced coordination number. The latter possibility is depicted in Fig. 3 and the ensuing discussion will explicitly refer to that mechanism.

The composition of the *cis*/*trans*-photostationary states for $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ depends both on the ratio between the quantum yields and on the ratio between the molar absorptivities at the wavelength of irradiation (ref. 19):

$$\frac{C^{\infty}_{cis}}{C^{\infty}_{trans}} = \frac{\phi_{t \to c}}{\phi_{c \to t}} \cdot \frac{\varepsilon_{trans}}{\varepsilon_{cis}} \tag{5}$$

The ratio between the quantum yields reflects the excited state preference for either stereochemistry and, as seen in Table 1, for $[Rh(NH_3)_4(H_2O)X]^{2+}$ this preference depends strongly on the nature of the ligand X. Thus, $[Rh(NH_3)_4(H_2O)I]^{2+}$ shows practically 100%

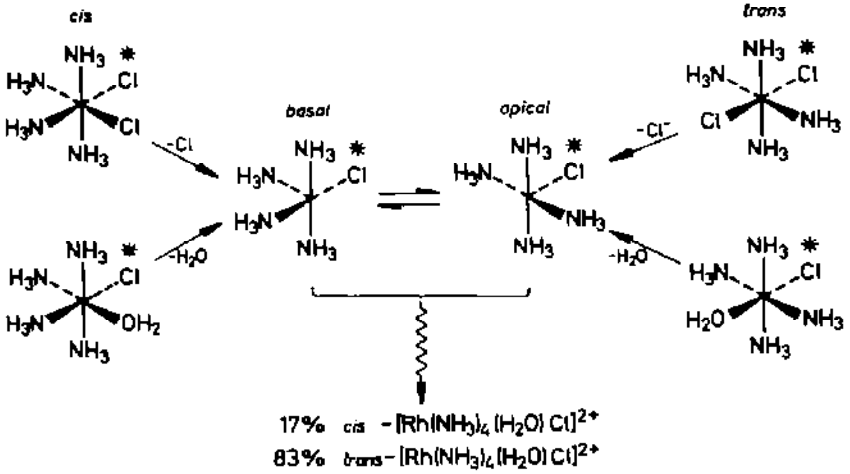


Fig. 3. Excited state reactions of *cis*- and *trans*-aquachlorotetraamminerhodium(III) and *cis*- and *trans*-dichlorotetraamminerhodium(III) within a limiting dissociative model. The *basal*- and *apical* excited state isomers can rearrange to each other in competition with deactivation to the ground state (ref. 27).

trans-preference (ref. 35), and the order of decreasing trans preference for different ligands X is I > Br > H_2O ~ Cl > OH ~ CN.

Photochemical water exchange in the two isomers of $[Rh(NH_3)_4(H_2O)_2]^{3+}$ was, in agreement with the mechanism of Fig. 3, also found to have higher quantum yields than the cis/trans photoisomerizations (ref.33), and the relative magnitudes of the quantum yields for the stereoretentive- and stereomobile water exchange reactions of each isomer strongly support the generality of the dissociative mechanism, cf. Fig. 4.

The conjugate bases of the trans-aquaacidotetraammine complexes of Table 1 are, with the notable exception of the cyanide complex, reactive toward photosubstitution and photoisomerization (ref. 18, 19, 22):

$$\text{trans-}[Rh(NH_3)_4(OH)X]^{+} + H_2O \xrightarrow{h\nu} \text{cis-}[Rh(NH_3)_4(OH)_2]^{+} + X^{-} + H^{+} \tag{6}$$

A similar reactivity has not been found for the cis-counterparts, including the cyanide complex.

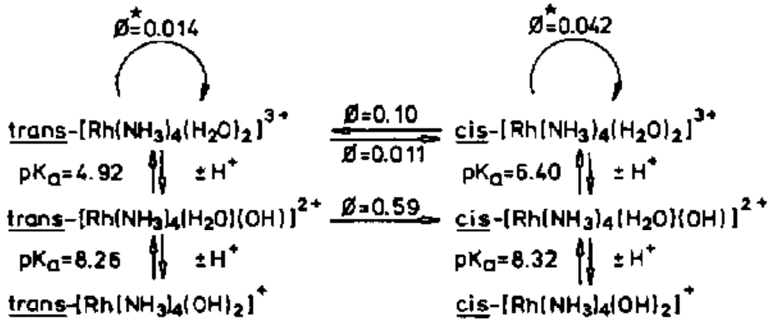


Fig. 4. Aqueous solution photochemistry of cis- and trans-diaquatetraamminerhodium(III) and conjugate bases. Φ* are quantum yields for stereoretentive water exchange (1 M perchlorate, ref. 19 and 33).

TABLE 1

Quantum yields for cis to trans and trans to cis photoisomerizations of the tetraammine-, bis(ethylenediamine)- and bis(1,3-propanediamine) complexes $[RhA_4(H_2O)X]^{2+}$. Aqueous solution, 25 °C.

	$(NH_3)_4$ [a]		$(en)_2$ [b]		$(tn)_2$ [c]	
X	$\Phi_{c\to t}$	$\Phi_{t\to c}$	$\Phi_{c\to t}$	$\Phi_{t\to c}$	$\Phi_{c\to t}$	$\Phi_{t\to c}$
Br	0.46	0.018	0.62	0.007	0.55	0.025
Cl	0.52	0.064	0.70	0.013	0.54	0.059
H_2O	0.10	0.011	0.27	d	0.29	0.10
OH	d	0.59	0.048	0.61	0.033	1.0
CN	d	0.52				

[a] From ref. 19, 22, 25, 27, 33 and 35.
[b] Ethylenediamine complexes, from ref. 24 and 34.
[c] 1,3-propanediamine, from ref. 26 and 32.
[d] Photoisomerization not detected.

Tetraamine complexes with chelating amines

The preference for either stereochemistry in the products resulting from ligand field photolyses of the bis(ethylenediamine)-- and bis(1,3-propanediamine)-complexes $[Rh(en)_2XY]^{z+}$ and $[Rh(tn)_2XY]^{z+}$, respectively, is qualitatively the same as for the analogous ammonia complexes (ref. 10, 12, 13, 32, 34). In particular, the dihalobis(1,3-propanediamine) complexes mimic their tetraammine counterparts,as can be seen from the quantum yields of Table 1. From the relative magnitude of these quantum yields it can also be concluded that for a given ligand X, the preference for trans stereochemistry for $[RhA_4(H_2O)X]^{z+}$ with respect to the amine A decreases in the order: A = $\frac{1}{2}$ ethylenediamine > $\frac{1}{2}$ 1,3-propanediamine ~ NH_3.

Photoisomerization of the diaquatetraaminerhodium(III) complexes and their conjugate bases results in photostationary states with cis/trans ratios which are strongly dependent on solution pH, as can be concluded from Figs. 4 to 6. The observed cis/trans ratios agree with those calculated from the isomerization quantum yields, the molar absorptivities at the wavelength of irradiation and, notably, the ground state pK_a-values (ref. 19, 24, 26).

Of the two triethylenetetraamine complexes cis-α- and cis-β--

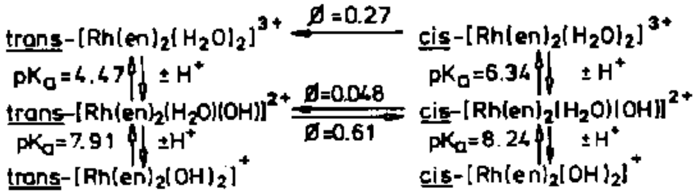


Fig. 5. Aqueous solution photochemistry of cis and trans-diaquabis(ethylenediamine)rhodium(III) and conjugate bases (1 M perchlorate, ref. 24).

[Rh(trien)Cl$_2$]$^+$, the α-isomer (having both secondary amines trans to chloride) is several orders of magnitude less reactive than the β-isomer with respect to chloride photoaquation. The reactive β-isomer yields cis-β-[Rh(trien)(H$_2$O)Cl]$^{2+}$ and trans-[Rh(trien)(H$_2$O)Cl]$^{2+}$ with a cis/trans product ratio of ca. 2 (ref. 9). On the other hand, the 1,4,8,11-tetraazaundecane complex cis-β-[Rh(2,3,2-tet)Cl$_2$]$^+$ forms cis-β- and trans-[Rh(2,3,2-tet)(H$_2$O)Cl]$^{2+}$ with a cis/trans product ratio of 0.3 (ref. 11), remarkably close to the cis/trans ratio observed for the tetraammine complexes, cf. eq. (3).

Pentaammine complexes

Ligand field excitation of [Rh(NH$_3$)$_5$X]$^{z+}$ leads to photoaquation of either X or NH$_3$ ligands in a ratio which for a given solvent

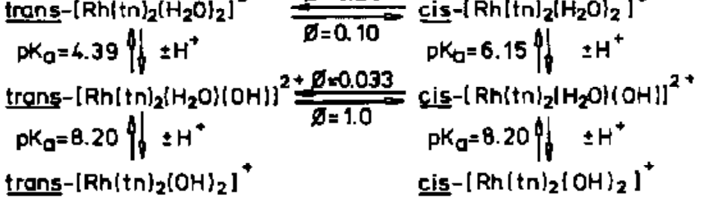
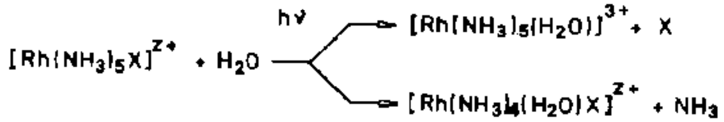


Fig. 6. Aqueous solution photochemistry of cis- and trans-diaquabis(1,3-propanediamine)rhodium(III) and conjugate bases (1 M perchlorate, ref. 26).

depends on the nature of the ligand X:



$$[Rh(NH_3)_5X]^{z+} + H_2O \xrightarrow{h\nu} \begin{cases} [Rh(NH_3)_5(H_2O)]^{3+} + X \\ [Rh(NH_3)_4(H_2O)X]^{z+} + NH_3 \end{cases} \qquad (7)$$

Ammonia photoaquation occurs almost exclusively for X = I and CN, and decreases in importance with other ligands X in the order Br > Cl > H_2O (ref. 22, 30, 36, 37). According to the model of Fig. 3 the $[Rh(NH_3)_4(H_2O)X]^{z+}$ products should be formed in the same *cis*/*trans*-ratio as that resulting from photoaquation of *cis*-- and *trans*-$[Rh(NH_3)_4X_2]^{z+}$, and they eventually form *cis*/*trans*-photostationary states, the composition of which can be calculated for a given ligand X from the quantum yields of Table 1.

In octahedral complexes belonging to the pentaammine series, two different ammonia ligands can be distinguished, and the ammonia which becomes substituted by water according to eq. (7) can originate from either the axial position on the unique tetragonal axis or from an equatorial position, *cf*. Fig. 7. The product stereochemistry found for such reactions is, however, not necessarily indicative of whether axial or equatorial ammonia is substituted, since such excited state reactions show a high degree of stereomobility, *cf*. Fig. 3.

A direct indication of the stereochemical origin of the photoaquated ammonia has, however, been obtained by 15-N labelling (ref. 23, 35). The fraction of equatorial ammonia photoaquated increases on going from the weaker field ligands, *i.e.*, iodide and brom-

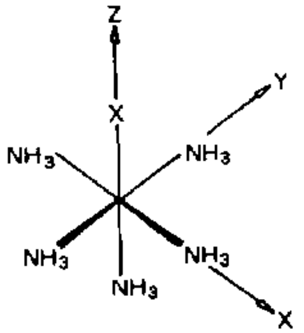


Fig. 7. Two different ammonia ligands can be distinguished in pentaammine complexes.

TABLE 2
Stereochemical origin of photoaquated ammonia in pentaammine-rhodium(III) complexes as determined by 15-N labelling.[a]

Substrate	Equatorial NH_3 [b]	Lowest energy triplet state
trans-$[Rh(NH_3)_4(^{15}NH_3)I]^{2+}$	*ca.* 0.20	^3E
trans-$[Rh(NH_3)_4(^{15}NH_3)Br]^{2+}$	*ca.* 0.10	^3E
cis-$[Rh(NH_3)_4(^{15}NH_3)Cl]^{2+}$	0.49	^3E
trans-$[Rh(NH_3)_4(^{15}NH_3)Cl]^{2+}$	0.48	
trans-$[Rh(NH_3)_4(^{15}NH_3)CN]^{2+}$	> 0.95	^3A

[a] From ref. 23 and 35.
[b] Equatorial NH_3 released as a fraction of total released NH_3.

ide, to the strong field ligand cyanide, as can be seen from the experimental results in Table 2. Chloride is intermediate, and equal fractions of axial and equatorial ammonia are photoaquated. With the introduction of a simple statistical correction, the experimental result for $[Rh(NH_3)_5Cl]^{2+}$ implies that the axial ammonia in this latter complex is labilized four times as efficiently as the equatorial ammonia ligands.

For $[Rh(NH_3)_5Cl]^{2+}$ ammonia photoaquation is the minor reaction path ($\Phi_{NH_3} = 0.02$, $\Phi_{Cl^-} = 0.18$, ref. 30), but in a chloride solution, the $^3[Rh(NH_3)_5(H_2O)]^{3+}$ formed in the principal photoreaction will subsequently photoanate (ref. 36), and the isomers of $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ thus constitutes the final photoproducts, *cf.* Fig. 8. The result of the 15-N labelling experiment outlined in this latter figure can only reasonably be explained quantitatively assuming scrambling between the five ammonia ligands remaining in the pentaammine fragment generated by chloride- or water dissociation, confirming that excited state rearrangements are fast compared to deactivation.

LIGAND DISSOCIATION

The reactive state

Investigations using wavelength-dependence and sensitization techniques (ref. 37, *cf*. ref. 1-3) have concluded that haloamine-rhodium(III) complexes form the lowest energy triplet state with quantum yields of approximately unity as the result of excitation of the multiplicity-allowed ligand field transitions. These states, from which weak phosphorescence has been observed, are held responsible for the majority of the observed photoreactivity.

When symmetry is lowered from O_h to C_{4v}, the reactive ^3T triplet splits into ^3E and ^3A levels. For $[Rh(NH_3)_5CN]^{2+}$ in which the heteroligand is of stronger field than ammonia, the ^3A level has the lower energy, and the σ-antibonding e_g orbital is concentrated in the x-y plane, *cf*. Fig. 7. However, for the iodo- and bromopentaammine complexes, the ^3E is the lower energy triplet with preferentially axial labilization. The results in Table 2 show that ammonia photoaquation is as anticipated on the basis of these arguments. Moreover, the result for $[Rh(NH_3)_5Cl]^{2+}$ seems to imply that for this intermediate ligand, the two triplet levels are very close in energy. An ascertainment of an increase in the equatorial/axial photoaquation ratio with temperature would indicate that the higher energy ^3A- is in thermal equilibrium with the ^3E triplet.

Kinetics of ligand dissociation

The establishment of a single reactive state or of reacting states of same multiplicity in thermal equilibrium has allowed rate constants for the individual deactivation processes to be calculated from phosphorescence lifetimes together with reaction quantum yields (ref. 20, 29, 30, 32, 38), *cf*. Fig. 9.

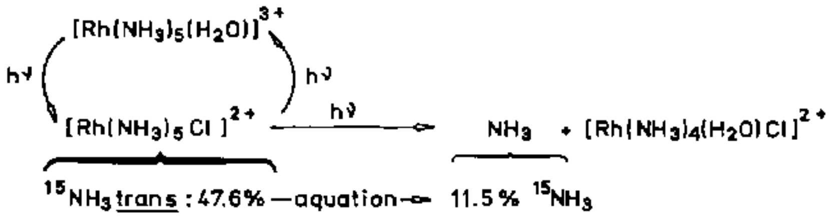


Fig. 8. Photolysis of chloropentaamminerhodium(III) in 0.5 M Cl^- gives eventually *cis*/*trans*-aquachlorotetraamminerhodium(III) plus *cis*/*trans*-dichlorotetraamminerhodium(III).

The lifetimes for the tetraammine complexes at 25 °C are in the ns range, indicating that the dissociation rates are increased by more than eleven orders of magnitude relative to the thermal reactions (ref. 29). The cis-complexes react faster than their trans-counterparts, and as can be seen in Table 3, the volumes of activation for the ligand dissociation reactions which lead to isomerization range from -9 to 0 ml/mol, while for retentive photosubstitution, $+3 < \Delta V_p^{\ddagger} < +9$ ml/mol. Notably, the more substitution--labile excited state isomers have in all cases been found to be those which show the greater degree of concomitant isomerization (ref. 29), cf. Table 3. The cis-dihalobis(1,3-propanediamine)rhodium(III) complexes have likewise been found to be more reactive than the trans, as can be seen from the halide dissociation rate constants of Table 4. More significantly, a comparison of the tetraammine- with the chelate 1,3-propanediamine complexes reveals that chelation accelerates only dissociation from the stereolabile cis-isomer (ref. 32). A similar parallelism between ligand dissociation and stereochemical photolability was reported by Martins and Sheridan (ref. 9) for trien rhodium(III) complexes. These observations seem to imply that the photosubstitution- and isomerization processes are linked.

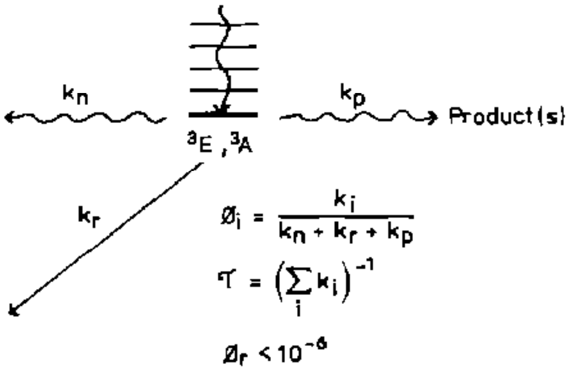


Fig. 9. Deactivation of triplet excited states formed by intersystem crossing of unity efficiency occurs by three pathways: ligand dissociation, non-radiative- and radiative deactivation, the latter of which is the minor. Individual rate constants can be estimated from phosphorescence lifetimes, τ, and reaction quantum yields, Φ_p.

TABLE 3

Excited state ligand dissociation of tetraamminerhodium(III) complexes: Quantum yields, volumes of activation,[a] phosphorescence lifetimes and calculated ligand dissociation rate constants in aqueous solution at ambient pressure and 25 °C (ref. 21, 29). $M = Rh(NH_3)_4$.

Complex	Principal product	Φ_p mol/einstein	$\Delta V^{\ddagger}_p$ ml/mol	τ ns	k_p 10^7 s^{-1}
t-$M(OH)Cl^+$	*c*-$M(OH)_2^+$	0.21	−9	2.7	8
c-$M(H_2O)Cl^{2+}$	*t*-$M(H_2O)Cl^{2+}$	0.66	0	2.4	28
c-$M(H_2O)Br^{2+}$	*t*-$M(H_2O)Br^{2+}$	>0.50	−1	1.6	>31
c-MCl_2^+	*t*-$M(H_2O)Cl^{2+}$	0.39	−4	1.3	30
c-MBr_2^+ [b]	*t*-$M(H_2O)Br^{2+}$	0.24	−2	1.0	24
	$Rh(NH_3)_3(H_2O)Br_2^+$	0.06	+9	1.0	6
t-MCl_2^+	*t*-$M(H_2O)Cl^{2+}$	0.14	+3	1.8	8
t-MBr_2^+	*t*-$M(H_2O)Br^{2+}$	0.10	+3	1.5	7

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[a] From pressure dependence on reaction quantum yields. Pressure effects on k_n and k_r (Fig. 9) are small (ref. 39), and $\Delta V^{\ddagger}_p$ approximates the volume of activation for ligand dissociation.

[b] The stereochemistry of the photoproduct $[Rh(NH_3)_3(H_2O)Br_2]^+$ is as yet unknown, but the unsymm *mer* isomer is expected as a result of *trans*-NH_3 photoaquation (ref. 35).

EXCITED STATE REARRANGEMENT

Energetics

Two closely related spectroscopic models based on angular overlap calculations (Vanquickenborne and Ceulemans, ref. 14-15; and Purcell, Clark and Petersen, ref. 16) have been successful in rationalizing the stereochemistry of the products formed on photolysis of rhodium(III) amine complexes. These models explicitly assume a dissociative reaction mode and invoke rearrangement of the excited state *basal*- and *apical* isomers via a trigonal bipyramidal intermediate. The preference for *trans*-configuration of the photoproduct, $[RhA_4(H_2O)X]^{z+}$, decreases for a given amine in the order: X = I > Br > Cl ~ H_2O > OH ~ CN, whereas for a given ligand X the

TABLE 4

Calculated rate constants (10^7 s^{-1}) for halide dissociation and non-radiative deactivation from the lowest energy ligand field excited state for dihalobis(1,3-propanediamine)rhodium(III)- and dihalotetraamminerhodium(III) complexes in aqueous solution at 25 °C (ref. 29, 32).

	bis(1,3-propanediamine)		tetraammine	
	k_p	k_n	k_p	k_n
trans-$[RhA_4Cl_2]^+$	6	70	8	50
cis-$[RhA_4Cl_2]^+$	62	49	30	50
trans-$[RhA_4Br_2]^+$	8	140	7	60
cis-$[RhA_4Br_2]^+$	210	120	24	70

order with respect to the amine is: A = ½ ethylenediamine > ½ 1,3-propanediamine ~ NH_3. Given the tentative σ-donor strength series CN > OH > en > NH_3 ~ tn > H_2O > Cl > Br > I, these observations are fully accounted for on the basis of an energetic preference for the stronger σ-donor in the apical position of the square pyramidal pentacoordinate intermediate, cf. Fig. 10 (ref. 14-17).

The cis/trans-photoproduct ratio can, however, only be regarded as an experimental determination of the basal/apical excited state equilibrium constant if one assumes equal deactivation efficiencies for the basal- and apical isomers (ref. 40), an assumption which draws at least some support from the fact that the magnitudes of the non-radiative deactivation rate constants (labelled (4) and (5) in Fig. 10) depend on the nature of the ligands rather than on the stereochemistry (cf. Table 4 and ref. 29).

Dynamics

The rearrangement reaction labelled (1) in Fig. 10 has been shown to attain equilibrium, at least for triplet-$[Rh(NH_3)_4Cl]^{2+}$, cf. Fig. 3. The fact that equatorial/axial photolabilization ratios in $[Rh(NH_3)_5X]^{z+}$ are generally different from the cis/trans photoproduct ratios, and the observation of ammonia scrambling in triplet-$[Rh(NH_3)_5]^{3+}$ provides further support for the existence of a thermal equilibrium between excited state isomers. Thus, it is notable that photoaquation of chloride in cis- and trans-$[Rh(en)_2(NH_3)Cl]^{2+}$ has been reported to result in only little photoisomerization (ref. 10). The interpretation offered was that the average ligand field of triplet-$[Rh(en)_2(NH_3)]^{3+}$ increased the kinetic barrier for rearrangement to a level where deactivation is faster. The observation of isomerization as a result of photochemical water exchange in either isomer of $[Rh(en)_2(NH_3)(H_2O)]^{3+}$ at 25 °C (ref. 33) is not in agreement with these latter results, and it should also be noted that the triplet-$[Rh(NH_3)_4(H_2O)]^{3+}$ isomers, having a ligand field of almost the same average strength, appear to attain thermal equilibrium, cf. Fig. 4. The present results suggest the generality of thermal equilibrium in the triplet excited states of rhodium(III) amine complexes at ambient temperature.

In the model of Fig. 10, the ligand dissociation and the rearrangement are considered as separate reactions. For the dissociation step, rate constants are available for several complexes, cf. Tables 3 and 4, but the failure to detect emission from the pentacoordinate intermediates leaves us without any direct information about the lifetimes of these key intermediates. It is at least certain that none of the aqua- or hydroxo intermediates are sufficiently long-lived to attain acid/base equilibrium with the solvent (relaxation times of ca. 200 µs, ref. 19), since the compositions of the pH-dependent cis/trans-photostationary states are consistent

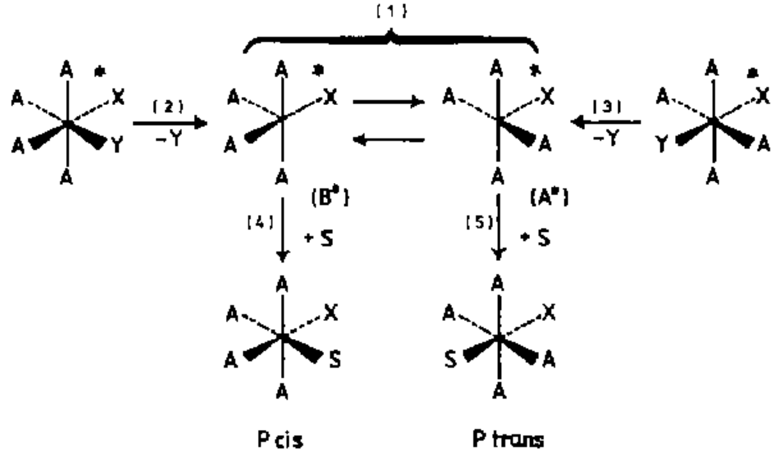
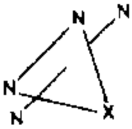


Fig. 10. Excited state rearrangement for tetraaminerhodium(III) complexes. A = nitrogen donor, S = solvent molecule.

with the ground-state pK_a-values, cf. Fig. 4-6.

A growing body of evidence seems to indicate synchronism between the dissociation- and rearrangement reactions, and in that respect the model of Fig. 10 is an oversimplification. However, the results obtained for the tetraammine complexes favour a description which invokes the existence of an excited state equilibrium rather than the formation of one single intermediate by concerted dissociation and rearrangement. In such common intermediates with assumedly trigonal bipyramidal structures the trajectory of attacking water would control the product stereochemistry (ref. 9):



Water attacking adjacent to the ligand X would give cis-product, while rearside attack would lead to trans-product. Steric effects would clearly be important and the observed photoproduct stereochemistry is better rationalized on the basis of ligand donor properties rather than on ligand sizes. Stokes' shifts have been observed to be significantly larger for cis- than for trans-isomers (ref. 28, 29), indicating a greater excited state distortion for the former isomer. This might imply a stronger interaction with the solvent for the cis isomer, as the smaller partial molar volume of the cis-isomers also indicates (trans-cis difference > 16 ml/mol; ref. 21). The cis isomers notably have negative volumes of activation for excited state ligand dissociation (Table 3), whereas the larger trans isomers have positive volumes of activation. Ligand dissociation from the two isomers evidently results in different products which subsequently undergo equilibration.

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