

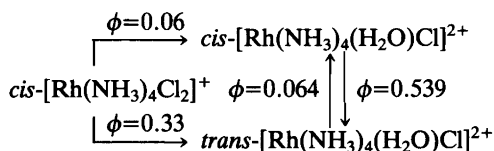
Photochemical Water Exchange of Rhodium(III) Complexes. I.

Photochemical Water Exchange in Relation to Photoisomerization of *cis*- and *trans*-Tetraammineaquachlororhodium(III) Ions in Aqueous Perchloric Acid

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The quantum yields for water exchange following ligand field excitation of *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ in aqueous acidic 1.0 M perchlorate solution at 25 °C are 0.66 ± 0.02 and $0.39 \pm 0.04 \text{ mol} \cdot \text{einstein}^{-1}$ and with the assumption that photoisomerization is accompanied by water exchange in these complexes, the quantum yields for stereoretentive water exchange are 0.12 ± 0.03 and $0.33 \pm 0.04 \text{ mol} \cdot \text{einstein}^{-1}$, respectively. Similar competition between stereoretentive and stereomobile photochemical ligand substitution processes was found in the formation of *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ from *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$, which proceeds according to:



Ligand field (LF) excitation of Rh(III) complexes of the tetraammine series leads to ligand labilization and, in aqueous solution, to photoaquation with relatively high, wavelength-independent quantum yields. Such photolysis reactions are reported typically to lead to only one major product, with other thermal or photochemical reaction paths being negligible at ambient temperature.¹⁻⁵

Observations on the stereochemical consequences of LF photolysis of these and related hexacoordinated low spin d^6 complexes, have been rationalized on the basis of different but closely related models,^{3,6-8} a key feature of which is that ligand dissociation from a hexacoordinated excited state precedes stereorearrangement.

A key experiment for testing these theoretical models is a determination of the relative extents of photochemical water exchange and photoisomerization of *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, in comparison with the stereochemical consequences of photoaquation of chloride in *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ under identical conditions. As the first part of our investigations of photochemical water exchange in Rh(III) complexes we report here the results of such experiments in aqueous acidic 1.0 M perchlorate solution.

EXPERIMENTAL

Chemicals. *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$,⁹ *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ¹⁰ and *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{S}_2\text{O}_6$ ³ were prepared by literature methods. Ag(tos), silver *p*-toluenesulfonate, was prepared as described previously.¹¹ H_2^{18}O (I.P. ~98 %) was obtained from 'Alfa products'. Other chemicals were of analytical grade.

Preparation of oxygen-18 enriched aquarhodium(III) complexes. 1.0 mmol portions of *cis*-

$[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ in 1 ml of ^{18}O -enriched water were treated with 1.9 mmol of $\text{Ag}(\text{tos})/\text{mmol}$ complex at 70°C for 17 h. The reaction mixture was then frozen and excess H_2^{18}O removed by sublimation in vacuum. The remaining solid, which is a mixture of rhodium(III) complexes, AgCl and unreacted $\text{Ag}(\text{tos})$, was treated with 0.01 M HClO_4 , and excess Ag^+ was precipitated by addition of an NaBr solution. AgCl and AgBr were filtered off and the filtrate was applied to a 10 cm \times 2 cm column of Sephadex SP-C-25. Elution with 0.25 M NaClO_4 , $\text{pH} \sim 2$, (~ 100 ml) until the major band containing $\text{cis}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ had moved $3/4$ of the column length, was found to separate the $\text{cis}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ well from $\text{cis}-[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ and $\text{cis}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$. The desired product, $\text{cis}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, was then eluted with 1.0 M NaClO_4 , $\text{pH} \sim 2$. The eluate was diluted with the appropriate amount of 1.0 M NaClO_4 and 1.0 M HClO_4 to give a final complex concentration between 1 and 4 mM in a 0.50 M HClO_4 + 0.50 M NaClO_4 reaction medium.

$\text{trans}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ was prepared and purified by a similar procedure starting with $\text{trans}-[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$. In this case, however, a reaction time of about 1 week at 70°C was allowed.

Electronic absorption spectra of eluted fractions were used to identify and check the purity of the complex ions.

Photolysis experiments. The optical train consisted of the light source, an Osram HBO 100/2 high pressure mercury lamp, a light condenser, a heat filter (a 5 cm water-filled cell), a 366 nm interference filter, a precision shutter connected to an electronic timer and lenses focusing the light into the thermostatted photolysis cell. All optical parts were of quartz (Spindler und Hoyer, Göttingen, GFR).

Solutions of ^{18}O -labelled complex ions were kept cold in the dark until a known volume (13 ml in a typical experiment) was transferred to a 5 cm cylindrical spectrophotometer cell. The solutions were allowed 8 min at 25°C for thermal equilibration in the photolysis cell in the thermostatted cell holder before exposure to light. During the thermal equilibration and irradiation the solutions were stirred magnetically with a teflon-coated magnetic bar. 10 ml aliquots of the photolyzed solution, for which electronic absorption spectra were recorded before and after exposure to light, were quickly frozen in liquid nitrogen and subsequently prepared for mass spectrometric analysis by sublimation in vacuum, as described previously.¹¹

The total time elapsed from the preparation of

the photolysis solution to freezing was monitored in order to make corrections for thermal exchange reactions.

Photolyses of $\text{cis}-[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ were carried out in 2 cm cylindrical cells thermostatted at 25.0°C . Reactions were interrupted periodically for spectrophotometric measurements and they were continued until no further spectral changes were detectable. Dark reactions were run under identical conditions.

Light intensities, I_0 , averaged $5 \cdot 10^{-6}$ einstein min^{-1} as determined by ferrioxalate actinometry¹² over a front window of 2.3 cm^2 .

Electronic absorption spectra were recorded on a Cary Varian 219 or on a Zeiss DMR 21 spectrophotometer and **mass spectrometric measurements** were performed as described previously.¹¹

Calculations. The results of mass spectrometric measurements, the $^{18}\text{O}/^{16}\text{O}$ ratios, were expressed as δ -values relative to Vienna Standard Mean Ocean Water and corrected for isotopic fractionation during the sublimation procedure by a previously deduced empirical formula¹¹ to give the reported values of δ_{corr} .

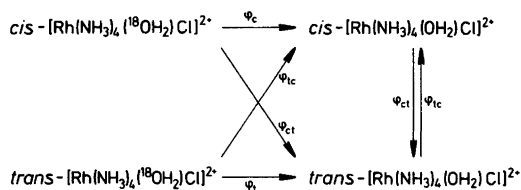
The reactant and product concentrations in the photolyzed solutions were calculated from the recorded absorption spectra using pure component spectra recorded on the same spectrophotometer under identical conditions. Readings at every 10 nm in the absorbing wavelength region down to ≈ 250 nm were used in these calculations which utilized numerical procedures outlined previously.¹³

The straight line in Fig. 1 of the form $y=ax$ was calculated by orthogonal regression analysis, *i.e.* by minimization of $\sum (y_{\text{obs}} - ax_{\text{obs}})^2 / [\sigma^2(y) + a^2\sigma^2(x)]$ where $\sigma^2(y)$ and $\sigma^2(x)$ are the variances upon y and x , respectively.

RESULTS

Two kinds of results were obtained in the present study. Firstly, from the experiments with oxygen-18 enriched complexes the relative extents of photochemical water exchange and photoisomerization of cis - and $\text{trans}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ were determined. Secondly, the product distribution during photolysis of $\text{cis}-[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ was evaluated from a spectral analysis.

$\text{cis}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$. Upon 366 nm irradiation of aqueous ≈ 2 mM solutions of oxygen-18 enriched $\text{cis}-[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ in 0.50 M HClO_4 plus 0.50 M NaClO_4 the absorption spectrum changed and the δ -values increased.



Scheme 1.

The spectral changes agreed with those expected for the photoisomerization reaction,^{3,21} and the magnitude of the changes in δ indicated qualitatively a simultaneous water exchange reaction. The rates of these two reactions of enriched $cis\text{-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ can both be described by Scheme 1 in which isomerization is the result of a water exchange reaction and by the following rate equations for isomerization and water exchange, respectively,

$$-dc_c/dt = (I_0/VA)(1-10^{-A})(\phi_{ct}\epsilon_c c_c - \phi_{tc}\epsilon_t c_t) + k_{ct}c_c - k_{tc}c_t$$

$$-dc_c^*/dt = (I_0/VA)(1-10^{-A})(\phi_c + \phi_{ct})\epsilon_c c_c^* + (k_c + k_{ct})c_c^*$$

in which c_c and c_t denote the concentration of $cis\text{-}$ and $trans\text{-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, respectively, and k 's are the thermal first-order rate constants.

I_0 is the intensity of the incident light, V is the volume of the solution under irradiation in a cell with a light path l , and A and ϵ are the absorbance of the solution and the molar absorption coefficients of the complexes, respectively, at the wavelength of irradiation. Thermal isomerization has not been detected³ and thermal water exchange has a first-order rate constant $k_c = (1.43 \pm 0.02) \times 10^{-3} \text{ min}^{-1}$ at 25 °C in 1.0 M aqueous perchlorate solution.¹⁴ Thermal reactions are therefore negligible under the present experimental conditions (*cf.* Table 1), and the coupled first-order differential equations for Scheme 1 can therefore be integrated to give:

$$\ln(c_c^*/c_0^*) = \ln(\delta_\infty - \delta)/(\delta_\infty - \delta_0) = [(1 + \phi_c/\phi_{ct})/(1 + \rho)] \ln[(c_c/c_0)(1 + \rho) - \rho] \quad (1)$$

with $\rho \equiv \phi_{tc}\epsilon_t/\phi_{ct}\epsilon_c$. The experimental results from two series of experiments are presented in Table 1 as the concentrations of $cis\text{-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ evaluated from spectral analysis and as δ_{corr} -values. The quantum yield ratio was calculated by linear regression analysis, *cf.* Fig. 1. From the calculated ratio $(1 + \phi_c/\phi_{ct})/(1 + \rho) = 1.17 \pm 0.03$, $\phi_{ct} = 0.539 \pm 0.011 \text{ mol einstein}^{-1}$ ²¹ and $\rho = 0.049 \pm 0.002$ the stereoretentive photochemical water exchange quantum yield ϕ_c is calculated to be $0.12 \pm 0.03 \text{ mol einstein}^{-1}$.¹ $trans\text{-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$. 366 nm irradiation.

Table 1. Two series of simultaneous determinations of the degree of photochemical water exchange and of the degree of photoisomerization of $cis\text{-}[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ at 25 °C after irradiation at 366 nm.

t_{irr} min	$[cis\text{-Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ mM	δ_{corr} ‰	$\delta_{\text{corr},\infty}$ ‰
Series 1			
0	1.956(18)	-11.36(19)	
1.00	1.853(15)	-10.78(19)	
3.00	1.708(18)	-9.45(15)	2.18(6)
5.00	1.521(17)	-7.50(16)	
7.00	1.383(17)	-6.27(23)	
Series 2			
0	3.23(7)	-11.48(6)	
1.667	2.98(13)	-9.39(11)	
2.00	2.79(10)	-8.26(16)	
2.00	2.90(10)	-8.99(10)	10.91(6)
2.00	2.88(13)	-9.13(19)	
2.00	2.94(10)	-8.89(11)	
2.00	2.86(9)	-8.77(10)	

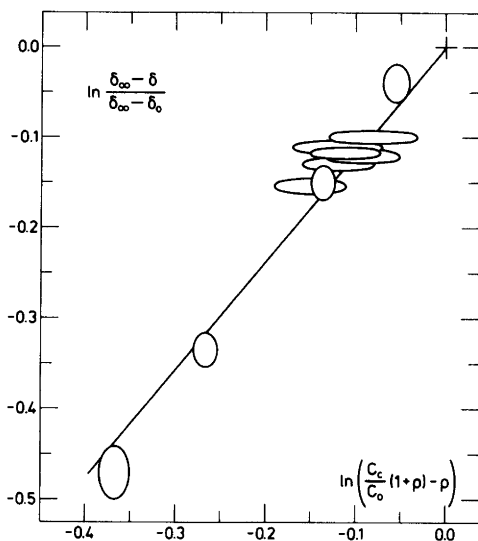


Fig. 1. Determination of the ratio between the water exchange quantum yield and the isomerization quantum yield for *cis*-[Rh(NH₃)₄(H₂O)Cl]²⁺ at 25 °C. $\lambda_{\text{irr}}=366$ nm. The experimental points are indicated with a range corresponding to $\pm\sigma$ and the full line is calculated by linear regression analysis, cf. eqn. (1).

tion of ≈ 1 mM *trans*-[Rh(NH₃)₄(H₂O)Cl]²⁺ solutions in 0.50 M NaClO₄ plus 0.50 M HClO₄ at 25 °C results in only small spectral changes. At this irradiation wavelength the absorbance is almost constant during the experiment, and therefore water exchange occurs at a constant rate proportional to the light intensity. The oxygen-18 enriched complex disappears (and δ_{corr} increases) according to a pseudo first-order rate law:

$$d\delta_{\text{corr}}/dt \propto -dc_t^*/dt =$$

$$[(\phi_t + \phi_{\text{tc}})(I_0/V)(1-10^{-A})(I \cdot \epsilon_t/A) + k_t]c_t^* = k_{\text{obs}}c_t^*$$

Experimental values of δ_{corr} as a function of irradiation time, t , were approximated by a curve calculated from

$$\delta = \delta_0 + \delta' [\exp(-k_{\text{obs}}t) - 1]$$

by non-linear regression analysis involving minimization of

$$\Sigma\{\delta_{\text{corr}} - \delta\}^2/\sigma^2(\delta_{\text{corr}})$$

$\sigma^2(\delta_{\text{corr}})$ is the variance of δ_{corr} . Fig. 2 shows the experimental points and the calculated curve. As the thermal reaction time is ≈ 1 min longer than the time of irradiation, the rate equation is not exact. However, the error introduced hereby is negligible, since k_{obs} has the value of $(3.7 \pm 0.4) \times 10^{-2} \text{ min}^{-1}$ and k_t has been determined to be $(0.203 \pm 0.005) \times 10^{-2} \text{ min}^{-1}$ under identical conditions.¹⁴ From these data, the photochemical quantum yield was calculated to be $(\phi_t + \phi_{\text{tc}}) = 0.39 \pm 0.04 \text{ mol einstein}^{-1}$, which in combination with the quantum yield for *trans* to *cis* isomerization $\phi_{\text{tc}} = 0.064 \pm 0.002$,²¹ gives $\phi_t = 0.33 \pm 0.04 \text{ mol einstein}^{-1}$.

cis-[Rh(NH₃)₄Cl₂]⁺. Irradiation of an aqueous ~ 3 mM *cis*-[Rh(NH₃)₄Cl₂]⁺ solution at 366 nm results in formation of a mixture containing mainly *cis*- and *trans*-[Rh(NH₃)₄(H₂O)Cl]²⁺. Spectra recorded during the photolysis showed isosbestic points at 291 and 268 nm throughout the photolysis, but a numerical analysis revealed

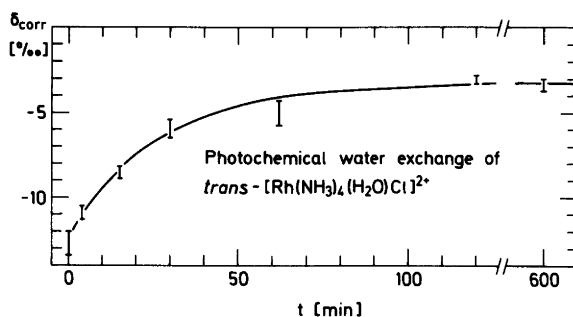


Fig. 2. Photochemical water exchange in *trans*-[Rh(NH₃)₄(H₂O)Cl]²⁺ at 25 °C. $\lambda_{\text{irr}}=366$ nm. The experimental points are indicated with a range corresponding to $\pm 3\sigma$. The solid curve is calculated from the determined parameters.

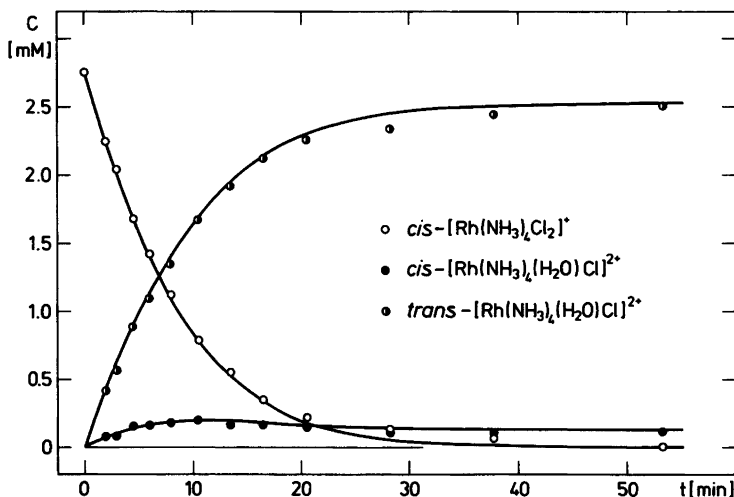


Fig. 3. 366 nm photolysis at 25 °C of 5.52 ml of a 2.75 mM *cis*-[Rh(NH₃)₄Cl₂]⁺ aqueous solution (0.50 M HClO₄+0.50 M NaClO₄). The experimental points are calculated from the absorption spectra of the pure components of the reaction mixtures as described in Ref. 13. The solid curves are calculated by numerical integration of the coupled photochemical differential equations using the light intensities, the molar absorption coefficients at the wavelength of irradiation (366 nm), and quantum yields determined by linear regression analysis using data for this experiment as well as for similar experiments²¹ starting from the isomeric tetraammineaquachlororhodium(III) species, as described in Ref. 14. The determined quantum yields are given in Table 2. The curve for formation of the triammine species is omitted for the sake of clarity.

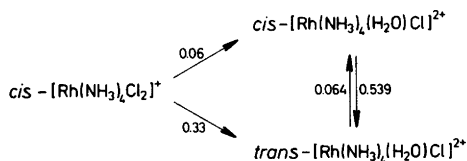
that the reaction mixture, in addition to the parent *cis*-[Rh(NH₃)₄Cl₂]⁺ and the products *cis*- and *trans*-[Rh(NH₃)₄(H₂O)Cl]²⁺, contained

small amounts of at least one other component. Fig. 3 shows the result of a spectral analysis using the pure component spectra of *cis*-

Table 2. Ligand photosubstitution quantum yields for some Rh(III) complexes in aqueous solution.^a

Complex	Products	ϕ [mol einstein ⁻¹]	κ^b	Ref.
Water exchange				
[Rh(NH ₃) ₅ (H ₂ O)] ³⁺	[Rh(NH ₃) ₅ (H ₂ O)] ³⁺	0.43(3)		15
<i>trans</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	<i>trans</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.33(4)	0.19(2)	Present work
	<i>cis</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.064(2)		
<i>cis</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	<i>cis</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.12(3)	0.22(3)	Present work
	<i>trans</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.539(11)		
Chloride hydrolysis				
[Rh(NH ₃) ₅ Cl] ²⁺	[Rh(NH ₃) ₅ (H ₂ O)] ³⁺	0.18(1)		16
<i>trans</i> -[Rh(NH ₃) ₄ Cl ₂] ⁺	<i>trans</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.14(1)		1
	<i>cis</i> -[Rh(NH ₃) ₄ Cl ₂] ⁺	<i>cis</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.063(7)	0.19(2)
	<i>trans</i> -[Rh(NH ₃) ₄ (H ₂ O)Cl] ²⁺	0.328(9)		
	triamminerhodium(III) species	0.013(3)		

^a Wavelength of irradiation 366 nm except for [Rh(NH₃)₅(H₂O)]³⁺ (313 nm) and *trans*-[Rh(NH₃)₄Cl₂]⁺ (407 nm). Temperature 25 °C except for [Rh(NH₃)₅(H₂O)]³⁺ (20 °C). ^b κ denotes the ratio of the quantum yield for formation of *cis*-product and that for formation of *trans*-product, i.e. $\kappa = \phi_c/\phi_t$ for *trans*-complexes and ϕ_c/ϕ_{ct} for *cis*-complexes, respectively.



Scheme 2.

$[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$, *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ and a spectrum of the unknown additional component calculated assuming that the end photolyzed solution contained 4 % of the species. The quantum yields calculated from this analysis according to Scheme 2 are given in Table 2. The formation of aquation products by thermal processes could be excluded, since a solution left in the dark during the photolysis showed no spectral changes.

DISCUSSION

LF irradiation of *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$, *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ and *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ in acidic aqueous solution is known to result in formation of the common principal photoproduct *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, which has been considered photoinert since only minor spectral changes have been observed after the completion of the primary photoreactions.¹⁻³ This apparent insensitivity to light does not, however, preclude photoinduced exchange of coordinated water with solvent water molecules, and the present study clearly demonstrates that *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ is photoactive with a ligand substitution quantum yield comparable to those for other related rhodium(III) complexes. The photochemical water exchange does, however, result in partial photoisomerization to *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, and the water exchange quantum yield is thus the sum of the quantum yield for the stereoretentive and for the stereomobile exchange processes, of which the former is by far the predominant. The sum of the quantum yields for the stereoretentive and the stereomobile water exchange ($\phi_t + \phi_{tc}$) in *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ is comparable with the quantum yield for the water exchange in $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ determined previously by Ford and Petersen,¹⁵ as seen from Table 2. In contrast, the total quantum yield ($\phi_c + \phi_{ct}$) for

water exchange in *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ is significantly higher. The relative magnitude of the water exchange quantum yields for these three aqua-complexes parallel the relative magnitudes of the chloride hydrolysis quantum yields in the corresponding series of chloro-complexes (see Table 2). However, as was recently demonstrated¹⁷ for a series of amminebromorhodium(III) complexes, the reaction quantum yields do not simply reflect the excited state reactivities for this type of compound, since a reaction quantum yield is the ratio between the rate constant for the chemical reaction of the excited state and the sum of the rate constants for all processes which drain the excited state. A combination of the water exchange quantum yields in Table 2 with excited state lifetime and luminescence quantum yield data permits an evaluation of the factors which control the excited state reactivities for the ammineaqua-rhodium(III) complexes in question.^{21,22}

The observation of both stereoretentive and stereomobile photochemical water exchange in the isomeric $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ species is important from a mechanistic point of view. Theories dealing with the photoisomerization reactions of d^6 complexes assume that ligand dissociation from a hexacoordinate triplet excited state precedes stereorearrangement,^{3,6-8} and according to these theories, the product stereochemistries are controlled by the relative energies of the *basal* and the *apical* isomers of the square-pyramidal five-coordinate intermediate, both of which are in a triplet excited state and can isomerize *via* a trigonal bipyramidal intermediate prior to deactivation and trapping by a solvent molecule. According to AOM-calculations⁶⁻⁸ the stronger σ -donor ligand prefers a *basal* position in the square pyramidal intermediate, which, when the proposed^{6,18} series $\sigma_{\text{OH}^-} > \sigma_{\text{NH}_3} > \sigma_{\text{Cl}^-}$ is taken into account, explains the experimental observations of photoisomerization between *cis* and *trans* complexes.³⁻⁵

This model also provides an explanation for the observed photoisomerization of *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ in postulating that photoisomerization is initiated by dissociation of the water ligand. In contrast to this, both empirical and semitheoretical rules^{19,20} predict that an equatorial ammonia ligand should be labilized, suggesting that photoisomerization in this type of compound is a purely intramolecular process.

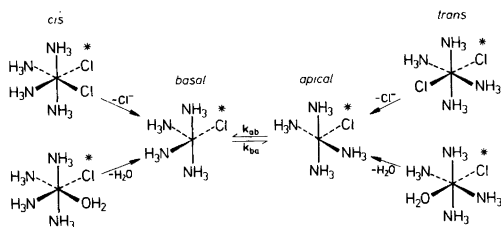


Fig. 4. Excited-state reactions of *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ and *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ within a limiting dissociative model. Excitation and deactivation processes are not shown. *basal*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}]^{2+*}$ is the common intermediate initially formed from *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+*}$ and *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ by ligand dissociation, and, similarly, *apical*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}]^{2+*}$ is the common intermediate formed from *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+*}$ and *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$.

The results reported here are very conclusive since water is the labilized ligand and water exchange is thus associated with the photoisomerization process.

A key feature of the dissociative model is that both the isomeric tetraamminedichloro- and tetraammineaquachlororhodium(III) species react *via* a common penta-coordinated excited-state intermediate, $[\text{Rh}(\text{NH}_3)_4\text{Cl}]^{2+*}$, capable of undergoing *basal/apical* rearrangement as depicted in Fig. 4. Fig. 3 shows additional experimental data in support of this hypothesis, since the photolysis of *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ is seen to result in both stereomobile and stereoretentive chloride substitution. However, the photoreactions of *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ outlined in Scheme 2 are complicated by significant loss of coordinated ammonia for which a quantum yield of 0.007 mol einstein⁻¹ has been reported.³ This is in contrast to the behaviour of the isomeric tetraammineaquachlororhodium(III) species, for which photochemical ammonia ligand aquation has not been detected.^{3,21} The small amounts of uncharacterized reaction products formed in the photolysis of *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ can thus be accounted for as a mixture of isomeric triammineaquadichloro- and mainly triamminediaquachlororhodium(III) species. From the absorption spectrum of the exhaustively photolyzed solution a triammine isomer mixture can constitute $\approx 4\%$ if reasonable molar absorption coeffi-

cients for the rhodium(III) species are assumed. The presence of a triammine mixture content leads to a quantum yield for the ammonia loss of 0.013 ± 0.003 mol einstein⁻¹ in good agreement with the previously published value.³

The dissociation of chloride from *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$ and of water from *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ generates the same intermediate, *basal*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}]^{2+*}$, and the ratio ϕ_c/ϕ_{ct} is consequently expected to be identical for the photoreactions of the two *cis*-tetraammine complexes. The limiting dissociative model for excited-state ligand substitution reactions of aminorhodium(III) complexes has now been tested by a variety of different experiments.^{3,17,23,24} The data presented in Table 2, which show that the ϕ_c/ϕ_{ct} ratios are identical within experimental error, provide strong evidence for a common five-coordinated excited-state intermediate in the photoreactions of *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ and *cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$. This observation provides circumstantial evidence in support of the limiting dissociative model.

The observation that ϕ_{tc}/ϕ_t for the water exchange in *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ is identical to ϕ_c/ϕ_{ct} for the two *cis*-tetraammine complexes, could indicate that *basal/apical* excited-state equilibrium is attained prior to deactivation. A distinction between thermodynamic and kinetic control^{3,24} of the product stereochemistry cannot, however, be made solely on the basis of the results presented in Table 2, but requires excited-state lifetime data. A more detailed discussion has, therefore, to await such data²² and the results of a reinvestigation of the photochemistry of *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]^+$, which is now in progress.²¹

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