# Evidence for a Common Excited State Intermediate in Ligand Field Photochemistry of *cis*- and *trans*-Tetraamminedichlororhodium(III) and Tetraammineaquachlororhodium(III) Ions

L. MØNSTED and L. H. SKIBSTED

Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark

Photolysis of *trans*-[Rh(NH$_3$)$_4$Cl$_2$]$^+$ gives a mixture of *cis*- and *trans*-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$ and the two products are photochemically interconvertible. The quantum yields are independent of the wavelength of irradiation and in aqueous acidic 1.0 M perchlorate solution at 25 °C the quantum yields (mol einstein^{-1}) are:
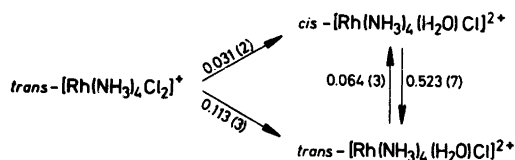
Irradiation of *trans*-[Rh(NH$_3$)$_4$Cl$_2$]$^+$ gives the same ratio between the quantum yields for stereomobile and stereoretentive chloride ligand photosubstitution as has previously been found for the water-exchange reactions in *trans*-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$ irradiated at 366 nm. For the corresponding reactions of the analogous *cis*-complexes the inverse ratio has been found, indicating one common excited state intermediate of reduced coordination number in the photochemical ligand substitutions of *cis*- and *trans*-[Rh(NH$_3$)$_4$Cl$_2$]$^+$ and of *cis*- and *trans*-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$.

It has recently been shown that the photoinduced chloride ligand substitution in *cis*-tetraamminedichlororhodium(III) and the photoinduced water exchange and isomerization of both *cis*- and *trans*-tetraammineaquachlororhodium(III) give the same relative amount of the latter two isomers.[1] This indicates that all these photoreactions proceed through a common excited state tetraamminechlororhodium(III) intermediate of reduced coordination number.

Litterature data for *trans*-tetraamminedichlororhodium(III)[2,3] are not in the agreement with the above interpretation: a chloride ligand is substituted, but only *trans*-tetraammineaquarhodium(III) is reported as a reaction product. Newly developed numerical methods,[4] which are particularly powerful for the identification of minor reaction products, and improved synthetic methods for rhodium(III) complexes of this type[5] have motivated this reinvestigation of the ligand field photochemistry of *trans*-tetraamminedichlororhodium(III) in aqueous solution in order to obtain a better understanding of the excited state rearrangement dynamics for these processes.

EXPERIMENTAL

Chemicals. *trans*-[Rh(NH$_3$)$_4$Cl$_2$]Cl·H$_2$O[5] and *cis*- and *trans*-[Rh(NH$_3$)$_4$(H$_2$O)Cl]S$_2$O$_6$[6] were prepared by published procedures. Other chemicals were of analytical grade.

Photolysis experiments were performed by continuous photolysis techniques as previously described[1] using 2 or 5 cm cylindrical cells thermostatted at 25.0 °C and monochromatic light selected from a high-pressure mercury lamp by the means of Spindler und Hoyer interference filters. Reactions were interrupted periodically for spectrophotometric measurements (Cary Varian 219 spectrophotometer) and they were con-
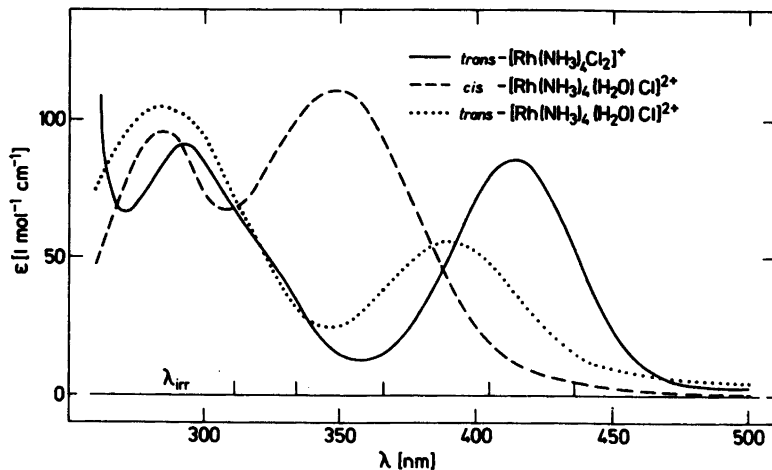
Fig. 1. Absorption spectra of tetraamminerhodium(III) complexes in aqueous 0.50 M HClO$_4$+0.50 M NaClO$_4$.

tinued until no further spectral changes were detectable. Dark reactions were run under identical conditions and were in all cases found to be insignificant.

Calculations. The reactant and product concentrations in the photolyzed solutions were calculated from the recorded absorption spectra using pure component spectra recorded under identical conditions. Readings at every 10 nm in the absorbing wavelength region (500−250 nm) were used in these calculations which were done within the framework of non-linear regression analysis using numerical procedures outlined previously.[7] Quantum yields were evaluated by

numerical integration[4] of the coupled photochemical differential equations using the calculated concentrations as a function of irradiation time in combination with the absorption coefficients at the wavelength of irradiation and the measured light intensities (standard ferrioxalate actinometry[8]).

RESULTS

cis- and *trans-*Tetraammineaquachlororhodium(III) are photochemically interconvertible, and by varying the wavelength of irradiation, *cf.*
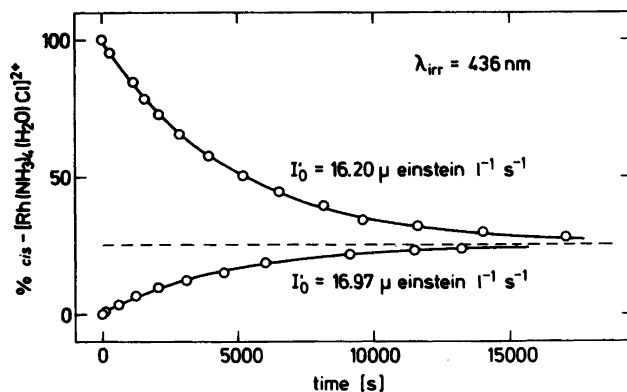

Fig. 2. Percentage of *cis-*[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$ during 436 nm photolysis at 25 °C of *ca.* 3 mM aqueous solutions of *cis-* and *trans-*[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$, respectively, (0.50 M HClO$_4$+0.50 M NaClO$_4$). The points are experimental values and the solid curves are calculated from the quantum yields (Table 1), the molar absorption coefficients at 436 nm, and the light intensities, I'_0.

Table 1. Photoisomerization quantum yields and photostationary states for *cis*- and *trans*-tetraammineaquachlororhodium(III) in aqueous 0.50 M $HClO_4$ plus 0.50 M $NaClO_4$ at 25 °C.
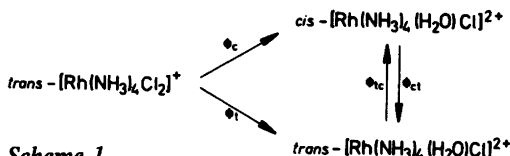
λ_{irr} nm	ϕ_{ct} mol einstein^{-1}	ϕ_{tc} mol einstein^{-1}	Photostationary state [a] % cis	% trans
312	0.522(12)	0.059(6)	11	89
334	0.533(15)	0.082(8)	5	95
366	0.543(14)	0.074(7)	5	95
405	0.498(15)	0.059(4)	22	78
436	0.47(5)	0.051(16)	25.5	74.5
Average	0.523(7)	0.064(3)		

[a] Calculated from: % $trans=100/(1+r)$, where $r=(\phi_{tc} \cdot \varepsilon_t^{irr})/(\phi_{ct} \cdot \varepsilon_c^{irr})$, cf. Ref. 9.

Fig. 1, photostationary states with different relative amounts of the two isomers can be attained. The system has previously been studied at 366 nm where the *trans*-isomer dominates the photostationary state and $\phi_{ct}=0.46(1)$ mol einstein^{-1} was found.[6] At higher wavelengths significantly more *cis*-isomer is present in the stationary state, as demonstrated by the experimental results shown in Fig. 2. Table 1 gives a summary of the results for several different wavelengths of irradiation, and it can be seen that the quantum yields are wavelength independent.

Irradiation of solutions of *trans*-tetraamminedichlororhodium(III) result in formation of *cis*- and *trans*-tetraammineaquachlororhodium(III). The *cis/trans*-ratio found in exhaustively photolyzed solutions at 405 or 366 nm is the same as that found after direct irradiation of either of the isomeric tetraammineaqua-chlororhodium(III) species. A numerical analysis of the absorption spectra recorded during the initial stages of the photolysis provides evidence, as demonstrated in Fig. 3, that *cis*-tetraammine-aquachlororhodium(III) is formed by direct photoaquation of the *trans*-tetraamminedichloro-rhodium(III) starting material. Quantum yields calculated in accordance with Scheme 1 incorpor-

cis - $[Rh(NH_3)_4(H_2O)Cl]^{2+}$

ϕ_c

$\phi_{tc} \Big| \phi_{ct}$

trans - $[Rh(NH_3)_4Cl_2]^+$

ϕ_t

Scheme 1.

trans - $[Rh(NH_3)_4(H_2O)Cl]^{2+}$

ating data for several experiments, including those started from the *cis*- and *trans*-tetra-ammineaquachlororhodium(III) isomers, are given in Table 2. The quantum yields are
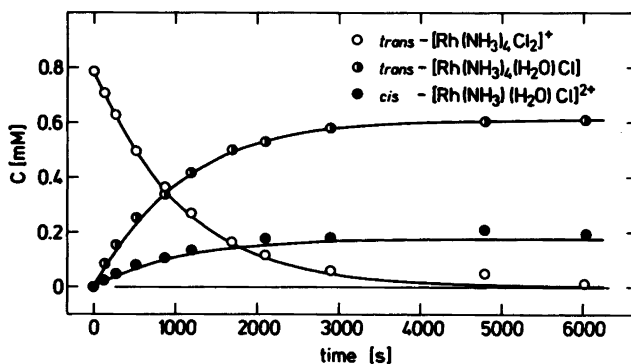

Fig. 3. 405 nm photolysis at 25 °C of a 0.79 mM *trans*-[Rh(NH₃)₄Cl₂]⁺ aqueous solution (0.50 M HClO₄+0.50 M NaClO₄). The points are experimental values and the solid lines are calculated from the quantum yields, (Tables 1 and 2), the molar absorption coefficients at 405 nm, and the light intensity, I_0. No ammonia release was detected during the photolysis.

Table 2. Quantum yields for stereoretentive and stereomobile photoaquation of chloride in *trans*-tetraamminedichlororhodium(III) in aqueous 0.50 M $HClO_4$ plus 0.50 M $NaClO_4$ at 25 °C.

Product	λ_{irr}, nm	ϕ, mol · einstein^{-1}	
trans-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	366	0.122(9)	0.113(3)
	405	0.112(3)	
cis-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	366	0,025(9)	0.031(2)
	405	0.031(2)	

wavelength independent and the total quantum yield for photoaquation of one chloride ligand in *trans*-[Rh(NH$_3$)$_4$Cl$_2$]$^+$, 0.144(3) mol einstein^{-1}, is in good agreement with literature values of 0.14(1) mol einstein^{-1} at 407 nm[2] and 0.152(2) mol einstein^{-1} at 410 nm.[3]

DISCUSSION

cis- and *trans*-Tetraamminedichloro- and *cis*- and *trans*-tetraammineaquachlororhodium(III) all react photochemically to give a mixture of the latter two complexes, as shown in Fig. 4.

Table 3 shows the measured quantum yields and it is seen that all four reactant complexes produce the same relative amounts of the two reaction products. This result strongly indicates that both the photochemical loss of coordinated chloride and the photochemical exchange of water in the two sets of tetraamminerhodium(III) isomers proceed *via* the *same* excited state intermediate of *reduced* coordination number.[1,10]

Much speculation has been devoted to rationalizing the results of photochemical experiments in terms of the stereochemistry and reactivity of the excited state intermediates.[6,11–14] Current semi-theoretical rationalizations seem to prefer five coordinate intermediates having a square pyramidal geometry, and the present results may well be in keeping with this hypothesis, provided that the rearrangement between different square pyramids, *cf.* Fig. 4, is sufficiently fast. More experiments are definitely required before a detailed understanding of these processes can be achieved, and in order to test the possible generality of our present findings we are currently studying the photochemical water-exchange and isomerization of tetraamminediaquarhodium(III) complexes.
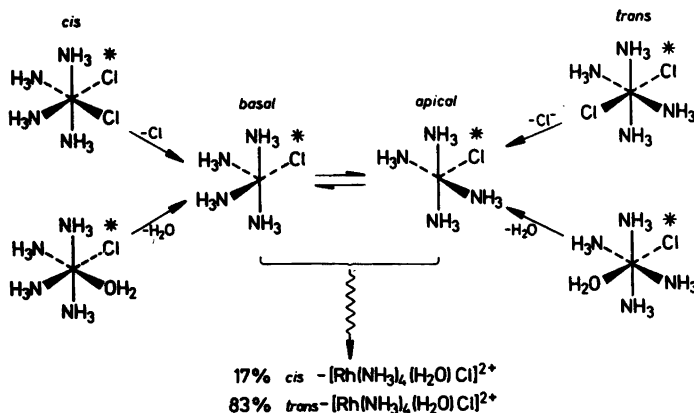
Fig. 4. Excited state reactions of *cis*- and *trans* [Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$ and *cis*- and *trans*-[Rh(NH$_3$)$_4$Cl$_2$]$^+$ within a limiting dissociative model. The *basal*- and *apical* excited state isomers, which are formed by ligand dissociation of the *cis*- and *trans*-complexes, respectively, can rearrange to each other in competition with deactivation to the ground state.

Table 3. Ligand photosubstitution quantum yields for tetraamminerhodium(III) complexes resulting from 366 nm excitation in aqueous 0.50 M HClO$_4$ plus 0.50 M NaClO$_4$ at 25 °C.

Complex	Products	ϕ[mol·einstein^{-1}]	x^a	Ref.
Water exchange				
trans-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	trans-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.33(4)		1
	cis-Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.074(2)	0.22(3)	Present work
cis-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	cis-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.12(3)		1
	trans-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.543(14)	0.22(3)	Present work
Chloride hydrolysis				
trans-[Rh(NH$_3$)$_4$Cl$_2$]$^+$	trans-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.122(9)		
	cis-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.025(9)	0.20(9)	Present work
cis-[Rh(NH$_3$)$_4$Cl$_2$]$^+$	cis-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.063(7)		
	trans-[Rh(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$	0.328(9)	0.19(2)	1

^{a} x denotes the ratio between the quantum yield for formation of cis-product and that for the formation of trans-product, i.e. $x=\phi_{tc}/\phi_t$ for trans-complexes and ϕ_c/ϕ_{tc} for cis-complexes.

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