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Complexes with asymmetric tetraamine ligands VI*. Photoaquation of rhodium(III) complexes

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Abstract

Ligand field photolyses of the dichloro complexes $[Rh(Me_n trien)Cl_2]X$ ($X = Cl^-$ or ClO_4^-; $n = 0$, 2 or 3) were carried out and the quantum yields for Cl^- release were determined. The stereochemistry of each of the chloroaquo photoproducts was characterized. The *cis-α* and *trans* isomers gave complete retention of configuration, but the *cis-β* isomers rearranged to give the *trans* chloroaquo products. The methyl substituents on the ligands had no effect on the stereochemical course of the reactions but did affect the quantum yields.

Introduction

Stereochemical studies of photochemical reactions of complexes of Rh(III) are of interest for comparison with other widely studied systems such as Co(III) and with theoretical predictions of photochemical reactivity [3–7]. The kinetics of hydrolysis reactions of complexes of Rh(III) and of Co(III) with optically active tetraamine ligands have been reported previously [1, 8]. It was of interest to compare the photoaquation reactions of these complexes with the thermal hydrolysis reactions.

The general formula of the complexes studied is $[Rh(Me_n trien)Cl_2]X$, where $n = 0$, 2 or 3; $X = Cl^-$ or ClO_4^- and Me_ntrien is a tetradentate ligand of general formula $H_2N–CHR–CH_2–NH–CHR'–CH_2–NH–CH_2–CHR–NH_2$. The optically active tetraamines used in the study were the methyl-substituted triethylenetetramine (trien) derivatives: 2*S*, 9*S*-dimethyltrien ($R = CH_3$, $R' = H$), 2*S*, 5*R*, 9*S*-trimethyltrien and 2*S*, 5*S*, 9*S*-trimethyltrien ($R = R' = CH_3$)[†]. The syntheses and characterization of the ligands [9] and of the complexes [10, 11] have already been reported. The reactions studied were:

$$Rh(Me_n trien)Cl_2{}^+ \xrightarrow[H_2O]{h\nu} Rh(Me_n trien)(OH_2)Cl^{2+} + Cl^- \quad (1)$$

Experimental

Materials

Ligands and complexes were prepared and characterized as reported previously [9–11]. All gave satisfactory elemental analyses. Water was distilled in an all-glass still. All other substances were reagent grade materials.

Photolyses

A Bausch and Lomb mercury source and a UV–Vis high intensity monochromator were used. The exit slit of the monochromator was set at 3.00 mm and the bandwidth of excitation was 10 nm. The intensity of the incident light was measured by the Reineckate actinometer [12] for those photolysis wavelengths in the visible region and with the potassium ferrioxalate actinometer [13] in the UV region (below 370 nm).

A volume of 2.5 ml of sample solution was placed in a 1.00 cm quartz spectrophotometer cell. The concentration of the aqueous solution varied from 1.71×10^{-3} M to 2.51×10^{-3} M. The temperature of the sample was maintained at 25.0 °C. For the determination of quantum yields, the duration of photolysis was adjusted so that the maximum extent of reaction

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*For Part V, see ref. 1; presented in part previously, see ref. 2a; taken in part from ref. 2b.

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[†] *R* and *S* refer to the configurations at the asymmetric carbons, assigned by CIP priorities. For the IUPAC nomenclature of the ligands, see ref. 9.

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was 20%. However, some experiments with much longer photolysis times were carried out in order to obtain spectra of the photolysis products. The wavelength for photolysis was set at the absorption maximum of the longest wavelength.

Changes in the spectrum were followed by stopping the photolysis and recording the UV–Vis spectrum. The concentration of chloride released during the course of the photolysis was measured with a Markson ultrasensitive chloride electrode and a double-junction reference electrode. A calibration curve for $[Cl^-]$ was prepared using standard KCl solutions with KNO_3 added to adjust the ionic strength to $\mu = 0.1$ M. No dependence of the quantum yields on ionic strength was found for $\mu = 0.005$ M to 0.1 M. Both the spectral measurements and the determination of chloride concentrations were also carried out for solutions kept in the dark. Corrections for thermal reaction were negligible for solutions at acid or neutral pH. Little variation in quantum yield was found with duration of photolysis in the early stages of photolysis, so no extrapolation to zero time was necessary.

Results

Each complex was photolyzed in aqueous solution at the wavelength corresponding to its absorption maximum of longest wavelength. The photolysis products were characterized by the changes in the UV–Vis spectra, as shown in Figs. 1–3. Changes in the ORD curves were also used to help characterize the products [1]. For all the *cis-α* and *trans* isomers, retention of configuration was obtained for the chloroaquo products. However, the *cis-β* isomers rearranged to give the *trans* chloroaquo product. The ORD curves were used to assign the configurations of the products and to show that optical activity was not lost upon aquation. The *trans* chloroaquo products all have the *trans-SS* configuration, whether the starting isomer was the *trans-SS* dichloro or *cis-β-SS* dichloro complex. The *cis-α-RR* dichloro complexes gave *cis-α-RR* chloroaquo products. The products are summarized in Table 1.

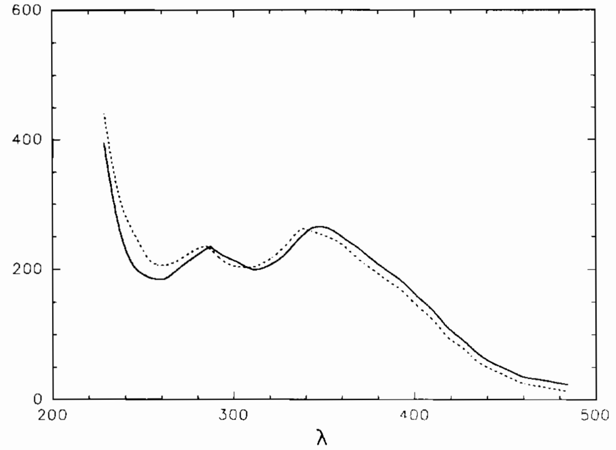


Fig. 1. Molar absorptivity ϵ ($l\ mol^{-1}\ cm^{-1}$) from $\lambda = 200$–500 nm for aqueous solutions of *Λ-cis-α-RR*-[Rh(2*S*, 5*R*, 9*S*-Me_3trien)XY]$^+$: —— before photolysis, X = Y = Cl; – – – after ligand field photolysis, X = Cl, Y = H_2O.

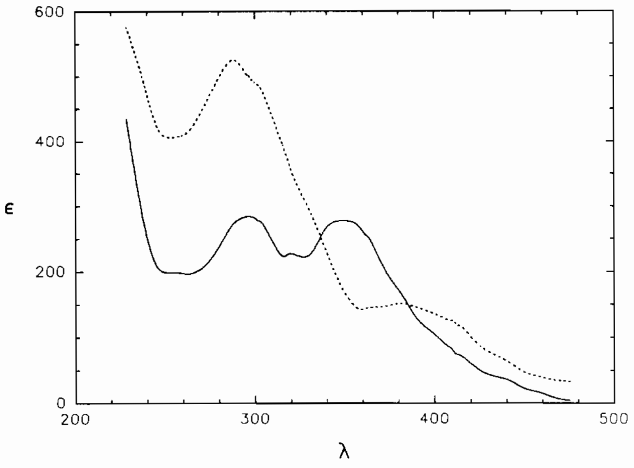


Fig. 2. Molar absorptivity ϵ ($l\ mol^{-1}\ cm^{-1}$) from $\lambda = 200$–500 nm for aqueous solutions of *Λ-cis-β-SS*-[Rh(2*S*, 5*R*, 9*S*-Me_3trien)XY]$^+$: —— before photolysis, X = Y = Cl; – – – after ligand field photolysis, X = Cl, Y = H_2O.

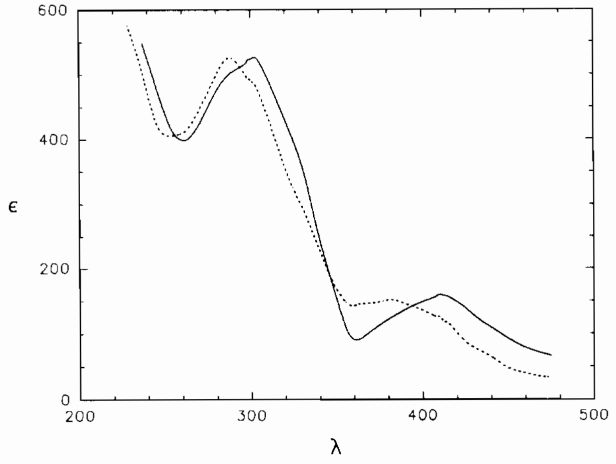


Fig. 3. Molar absorptivity ϵ ($l\ mol^{-1}\ cm^{-1}$) from $\lambda = 200$–500 nm for aqueous solutions of *trans-SS*-[Rh(2*S*, 5*R*, 9*S*-Me_3trien)XY]$^+$: —— before photolysis, X = Y = Cl; – – – after ligand field photolysis, X = Cl, Y = H_2O.

The quantum yields Φ_{Cl} for photoaquation of chloride were determined by measuring the amounts of chloride released per absorbed photon and are listed in Table 1. No amine release could be detected by monitoring the pH of the reaction mixture, which is the expected result for a chelating tetraamine. The reaction (1) was

TABLE 1. Products obtained in the photoaquation reactions and in the base hydrolysis reactions

Reactant complex $[Rh(L)Cl_2]^+$	Base hydrolysis product isomer[a] $[Rh(L)(OH)_2]^+$	Photoaquation product isomer $[Rh(L)(H_2O)Cl]^+$	λ_{phot} (nm)	$10^2\Phi_{Cl}$ (mol/einstein)
trien				
cis-α	*cis-α*	*cis-α*[b]	350	0.96[c] (<0.05[d])
cis-β	*cis-β*	*trans*	360	12[c] (20[d])
trans	*cis-β*	*trans*	408	3.1
SS-Me$_2$trien				
Λ-cis-α-RR	*Λ-cis-α*-RR	*Λ-cis-α*-RR	350	1.7
Λ-cis-β-SS	*Λ-cis-β*-SS	*trans*-SS	360	6.9
trans-SS	*Λ-cis-β*-SS	*trans*-SS	408	5.1
SRS-Me$_3$trien				
Λ-cis-α-RR	*Λ-cis-α-RR*	*Λ-cis-α-RR*	340	14
Λ-cis-β-SS	*Λ-cis-β-SS*	*trans-SS*	340	22
trans-SS	*Λ-cis-β-SS*	*trans-SS*	408	0.45
SSS-Me$_3$trien				
Λ-cis-β-SS	*Λ-cisβ-SS*	*trans-SS*	340	25
trans-SS	*Λ-cis-β-SS*	*trans-SS*	408	0.26

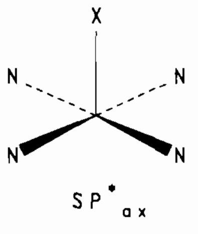
[a] Information from ref. 1. [b] This complex was reported to give *trans* in ref. 14. [c] This work. Values are averages of two or more determinations with deviations of 10% or less. [d] Result taken from ref. 14.

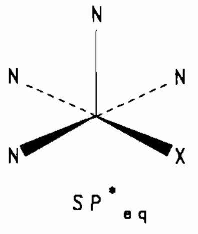
also followed spectrophotometrically by taking UV–Vis spectra at given intervals during the photolysis. The pH was approximately five, so as to avoid the possibility of base hydrolysis [1]. The intensity of the incident light was determined at the wavelength at which each complex was photolyzed. The light intensity measurements were repeated periodically before and after photolysis, and the source was found to be stable within 2%.

Discussion

The photochemical behavior of these Rh(III) systems shows interesting variations both in the quantum yields of chloride release and in the stereochemistries of the photoaquation reactions. The absorption bands at lowest energy have been identified as ligand-field bands, so all the photolyses reported here are ligand-field photolyses [14].

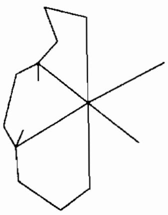
The Vanquickenborne model based on AOM [15–18], which has proved useful for understanding the photoaquation of other complexes of Rh(III), is consistent with the stereochemical results observed. According to the model, the lowest energy singlet excited state undergoes efficient intersystem crossing to give a triplet excited state from which a ligand dissociates to give a five-coordinate square pyramidal (SP) triplet excited state (SP*). The resultant SP* can undergo deactivation and acquisition of a water molecule with complete retention of geometry or it can undergo rearrangement to give a different SP* via a triplet trigonal bipyramid (TBP*). With a chelating amine such as trien, no loss of amine is observed, so only two SP* excited species, designated as SP_{ax}* and SP_{eq}* according to the position of the Cl in the intermediate, need to be considered. For aliphatic amine and chloride ligands, the SP_{ax}* triplet state should be about 35% more stable than the SP_{eq}* triplet state [7, 18]. This difference should be relatively independent of the starting isomer, since it involves only loss of a chloride with little change in the ring conformations. However, the stability of the TBP*, through which interconversion of the two SP* states might occur, should depend greatly on the isomer, since significant changes in the chelate ring conformations would be necessary for formation of the TBP*.





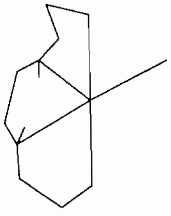
cis-α Isomers

The photolysis of *cis-α*-$[Rh(trien)Cl_2]^+$ has been reported previously [14]. The quantum yield upper limit was reported to be 5×10^{-4} mol/Einstein, and the reaction was reported to give isomerization to the *trans* chloroaquo isomer. Those results could not be duplicated in this laboratory. The *cis*-α trien complex **1** gave a quantum yield of 0.0096 mol/Einstein, which is consistent with results from biacetyl-sensitized photolysis of the complex [19]. The other *cis*-α complexes gave values of Φ_{Cl} which were even larger.



1

cis-α



2

$SP^*_{eq}(\alpha)$

As shown in Table 1, the *cis*-α trien complex gave retention of geometry, as did both the other *cis*-α complexes. No rearrangement upon photolysis of either the *cis*-α dichloro complex or the resulting *cis*-α chloroaquo product could be detected, even after photolysis periods which were long enough to give 90 to 95% reaction, based on the initial concentration of the dichloro complex. The ORD curves of *cis*-α, *cis*-β and *trans* isomers differ to a much greater extent than do the UV–Vis spectra [1], so that any isomerization reactions should be more readily detected for the optically active complexes. Since the lack of rearrangement was observed for the *cis*-α optically active complexes as well as for the *cis*-α isomer of the trien complex, we are confident that this is the correct result for that geometry. For the *cis*-α *SRS*-Me_3trien complex, the two chlorides in the dichloro complex are not equivalent, so that two SP_{eq}^* *cis*-α intermediates **2** and then two chloroaquo complexes could result. In one, the remaining Cl^- is *trans* to the *sec*-N which is adjacent to the asymmetric C of the central chelate ring, while in the other isomer it is the H_2O which is *trans* to that *sec*-N. Any difference in spectra between these isomers would be much too small to be able to detect any preference for formation of one or the other, and no effort was made to separate or detect these isomers.

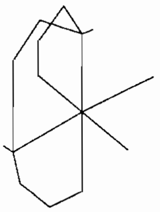
The total retention of configuration by the *cis*-α systems is consistent with the steric constraint of the *cis*-α isomer **1** which would impede the formation of a TBP* intermediate from the original SP_{eq}^* intermediate **2** formed. In order to form the TBP* intermediate, one chelate ring would have to span about 120°. This resistance to rearrangement by *cis*-α was also observed for the base hydrolysis reactions [1]. Apparently, not even the larger energy provided by electronic excitation is large enough to promote rearrangement in the *cis*-α complexes. The results obtained in this laboratory, in which retention of configuration was observed for all the *cis*-α isomers, are more in agreement with the behavior predicted from stereochemical considerations than those previously reported for the trien complex [14].

trans-Isomers

The *trans*-*SS*-$[Rh(Me_n trien)Cl_2]^+$ complexes also gave photoaquation of chloride with retention of configuration. The photochemistry of the *trans* complex with trien had not been reported previously, probably due to the very small yields of *trans* isomer obtained with the earlier synthetic methods [20, 21], so no comparison of quantum yields can be made.

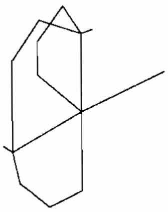
cis-β Isomers

All of the *cis*-β isomers gave rearrangement to the corresponding *trans*-*SS*-$[Rh(Me_n trien)(H_2O)Cl]^{2+}$ isomers, with higher quantum yields than were observed for the *cis*-α isomers. Other studies have shown *cis* to *trans* isomerization upon ligand-field photolysis. [5, 14, 22–26]. Martins and Sheridan [14] showed that for *cis*-β-$[Rh(trien)Cl_2]^+$ two processes occurred: photoaquation of the *cis*-β dichloro complex to yield the *cis*-β chloroaquo complex, followed by rearrangement of that species to the *trans*-$[Rh(trien)(H_2O)Cl]^{2+}$. All of the *cis*-β complexes **3** studied in this work showed the same behavior. The spectrum of the reaction mixture corresponded to a mixture of three species, the *cis*-β dichloro, *cis*-β chloroaquo and *trans* chloroaquo complexes. If photolysis is continued sufficiently long, however, only the *trans* chloroaquo could be detected. Since the two Cl^- in the *cis*-β complexes are not equivalent, two different $SP_{eq}^*(\beta)$ isomers can be formed: species **4** with the remaining Cl *trans* to a *sec* N, and another species with the Cl *trans* to a terminal NH_2, so there may actually be four species in solution during the reaction. It was not possible, given the rather small samples used and the number of species in solution, to determine the relative amounts of the two *cis*-β chloroaquo isomers. Both would give TBP* **5** and then the *trans* isomer.



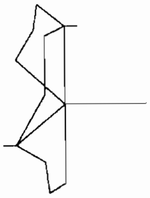
3

cis-β



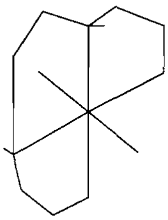
4

$SP^*_{eq}(\beta)$



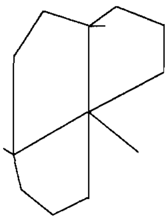
5

TBP*



6

trans



7

SP^{*}_{ax}(trans)

If the barrier to conversion between the two SP* species is not too high, photolysis of either *cis-β* 3 or *trans* 6 should lead to the *trans* product, since it would arise from the more stable SP_{ax}* 7 state. Neither the SP_{eq}*(β) 4 from a *cis-β* complex nor the SP_{ax}* 7 from a *trans* complex needs to undergo large changes in the ring conformations to form the TBP* species 5, so the observed rearrangement of the *cis-β* to *trans* is consistent with the predictions of the model. The observation of some *cis-β* product during the reaction is reasonable, since addition of water and deactivation of the SP_{eq}*(β) 4 intermediate would give the *cis-β* chloroaquo complex. Chloroaquo complexes have been shown to undergo water exchange upon photolysis [5, 27], so further conversion to *trans* could easily occur. Further support for the proposed mechanism of rearrangement comes from the observation that there is no change in the stereochemistry at the secondary nitrogen atoms and no tendency for racemization. No dissociation of these nitrogens is required by the model to explain the observed products.

Although the same electronic effects might also be used to predict rearrangement of the *cis-α* isomers, the interconversion of the SP_{eq}*(α) 2 and the TBP* would have a very large barrier due to the need for one chelate ring to span 120° in the TBP* intermediate. Thus, the stereoretention of the *cis-α* isomers is reasonable.

The use of the optically active Me_ntrien ligands was intended to clarify the nature of the geometrical isomers obtained for each complex photolyzed, since the ORD curves show much greater differences than do the absorption spectra. This expectation was clearly fulfilled. However, much more work would be needed to determine the more detailed stereochemical questions, as discussed for the *cis-α* and *cis-β* systems.

It is interesting to compare the results of the photolyses with the stereochemistry and rates of base hydrolysis of the same complexes [1]. The dihydroxo products of base hydrolysis are included in Table 1. Both photoaquation and base hydrolysis of *cis-α* occur with retention of configuration. However, the results for *cis-β* and *trans* complexes differ. Both these isomers give *cis-β* products upon base hydrolysis, but both give *trans* products upon photolysis. While the major steric effects for a given complex might be similar for both types of reaction, there is undoubtedly a significant difference in the reactive species: a deprotonated, amido five-coordinate species for hydrolyses and a triplet excited state amino five-coordinate species for photolyses. The photolysis results correspond to the more stable product if the TBP* barrier is not too high. It is not possible to decide whether the hydrolysis products result from kinetic control or from altered stabilities of the possible transition states.

Conclusions

The results of this work are in agreement with currently accepted mechanisms for photoaquation of octahedral complexes. Although the proposed mechanisms for both base hydrolysis [1] and photoaquation involve five-coordinate intermediates, the species are very different, so the tendency to rearrange is different. For the photoaquation reactions, the five-coordinate species are proposed to be excited state triplets, which are sufficiently long-lived to undergo rearrangements before reacting with water and returning to the ground state. The five-coordinate species in the base hydrolysis reactions are in the electronic ground state and can have quite different relative stabilities than the excited state intermediates. The ground state intermediates, which have an amido group, can be stabilized by π-bonding. The differences observed between the photoreactions and the ground state reactions lend support to the idea that the photochemical rearrangement is occurring in the excited state rather than in a vibrationally excited, electronic ground state.

Acknowledgements

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