Identification of the Products of Photolysis Reactions of cis- and trans-Amminechloro- and Ammineaquabis(1,2-ethanediame)-rhodium(III) Complexes by $^{13}$C NMR Spectroscopy

P. Moore and L. Mønsted

*Chemistry Department, University of Warwick, Coventry CV4 7AL, U.K., and †Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg, Denmark


The cis- and trans-amminechlorobis(1,2-ethanediame)rhodium(III) ions have been irradiated at 366 nm and 25 °C, and the photolysis products identified by $^{13}$C NMR spectroscopy. Both complexes lose the chloride ligand on irradiation, and both form the cis-ammineaquabis(1,2-ethanediame) complex as the primary product. The trans-amminechloro complex also loses ammonia during irradiation and forms the trans-aquachlorobis(1,2-ethanediame)rhodium(III) ion. This complex is only a minor product on irradiation of the cis-amminechloro complex. The cis- and trans-ammineaquabis(1,2-ethanediame)rhodium(III) ions isomerize to a photostationary state containing comparable concentrations of the two complexes when irradiated at 366 nm.

The photochemical reactivity of the isomeric ammineaquabis(1,2-ethanediame)rhodium(III) ions was first investigated by a combination of $^{13}$C NMR spectroscopy for product identification and UV–VIS spectrophotometry for quantum yield determination. The results of this work can be summarized as a stereo- and temperature-dependent ligand photoaquation, followed by a strongly temperature-dependent photoisomerization between the generated ammineaquabis(1,2-ethanediame)rhodium(III) isomers.

A recent reinvestigation of this system supplemented with photochemical water ligand exchange studies and photoracemization studies was not in agreement with these previous results. Instead cis-ammineaquabis(1,2-ethanediame)rhodium(III) was found to be the dominant product of photolysis of both amminechlorobis(1,2-ethanediame)rhodium(III) isomers. Significant photochemical ammine ligand aquation was also found to occur, particularly in the trans complex, and at 25 °C photoisomerization of the ammineaquabis(1,2-ethanediame)rhodium(III) isomers was found to take place with fairly large quantum yields. In this study the reactions were followed spectrophotometrically, and the products and quantum yields were determined by a multiwavelength analysis of the spectrophotometric data.

The significant discrepancy between these studies is

Scheme 1. Summary of the results published for the photochemical reactions of cis- and trans-[Rh(en)$_2$(NH$_3$)$_2$Cl]$_2$ irradiated at 366 nm and 25 °C; (A) Refs. 1 and 2; (B) Ref. 3.

* To whom correspondence should be addressed.

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Fig. 1. Proton decoupled $^{13}$C NMR spectra of cis- and trans-
[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{1+}$ before irradiation and after 16 h
irradiation, respectively. The chemical shifts are given in Table
1. The splitting always seen for the resonance at 47.79 ppm of
the cis complex is caused by slow exchange of hydrogen atoms
by deuterium on the amine nitrogens. When the solutions are
aged all resonances will split analogously for all the complexes.
The nitrogen atom of the cis complex which exchanges
hydrogen substantially faster than the other nitrogen atoms is
probably the nitrogen in a trans position to water.

shown in Scheme 1. The differences can hardly be the
result of a change of reaction medium from 0.014 M
HClO$_4$ to 0.5 M HClO$_4$ + 0.5 M NaClO$_4$ and it was
therefore decided to reinvestigate the system by $^{13}$C NMR
spectroscopy.

**Results and discussion**

Solutions of cis- and trans-ammineaquaa- and amminecloro-
robis(1,2-ethanediamine)rhodium(III) complexes were ir-
radiated at 366 nm in acidic aqueous solutions, and the
photochemical reactions followed by $^{13}$C NMR as a func-
tion of time. The reactions of these four individual
complexes will be treated separately, as described below:

cis- and trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{1+}$. In Fig. 1 are shown
the proton decoupled $^{13}$C NMR spectra of cis-and trans-[Rh
(en)$_2$(NH$_3$)(OH$_2$)]$^{1+}$ ions before and after irradiation for 16 h
at 366 nm and 25°C. The spectra of the non-irradiated
solutions show one resonance for the trans compound
and four resonances for the cis compound, as expected, and
within the detection limits of the NMR spectrometer the
compounds are seen to be pure. Solutions of the two iso-
mers after irradiation for 16 h are seen to have identical
spectra, indicating that a photostationary mixture has been
formed. The ratio between the concentrations of the trans
and the cis isomers is about 0.6 judged from the integrals.
This is in excellent agreement with predictions based on the
results given in Ref. 3 and presented in Scheme 1B.

It is contrary, however, to the results in Ref. 2, where it
has been reported that only irradiation of these isomers at
50°C leads to significant photoisomerization, and that ir-
radiation at 25°C is accompanied by only minor photoreact-
vity. This was explained by an energy barrier between an
apical and a basal five-coordinated intermediate large
enough to prevent isomerization at the lower temperature.

However, attempts to reproduce this temperature de-
pendence were not successful, and irradiation of the trans-
[Rh(en)$_2$(NH$_3$)(OH)$_2$]$^{1+}$ complex at 50°C gave exactly
the same results as the experiment at 25°C, except for a split-
ting of all the $^{13}$C resonances caused by thermal exchange of hydrogen for deuterium on the amine nitrogens (see the legend to Fig. 1).

cis- and trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$. The molar absorption coefficients of the cis- and trans-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$ complexes are rather small compared to the molar absorption coefficients of the cis- and trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ complexes at 366 nm. Therefore, this wavelength provides the best possibility for detection of the primary photoproducts which at lower wavelengths readily photoisomerize.

In Fig. 2 is shown the proton decoupled $^{13}$C NMR spectra of cis-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ as a function of the irradiation time. The spectrum of the non-irradiated solution shows four resonances as expected, and there are no signs of impurities. The spectra after irradiation for 1 and 2 h, respectively, show that both cis- and trans-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$ are formed during the reaction. After irradiation for 1 h the trans/cis concentration ratio is about 0.15, whereas the ratio after 2 h of irradiation is about 0.25. This indicates that the cis-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$ complex is the dominant primary photoproduct, which then isomerizes to give the trans isomer. In agreement with this, the spectrum after 16 h of irradiation is identical with the spectrum of the exhaustively photolyzed aqua complexes (Fig. 1) except for the small resonance at 45.59 ppm. This is attributed to the formation of trans-$[\text{Rh(en)}_2(\text{OH})_2\text{Cl}]^{2+}$ as predicted from the quantum yields of Scheme 1.

In Fig. 3 is shown the proton decoupled $^{13}$C NMR spectra of irradiated trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ as a function of irradiation time. The spectrum of the non-irradiated solution confirms the purity of the compound, but after irradiation for 20 min an additional resonance from the trans-$[\text{Rh(en)}_2(\text{OH})_2\text{Cl}]^{2+}$ complex is clearly seen, and it is also just possible to detect the 4 resonances from cis-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$. After 1 and 3 h of irradiation, respectively, these resonances are more pronounced. It is not possible, with the spectrometer used, to resolve adequately the resonances from trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ and trans-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$. The $^{13}$C NMR spectrum of a solution containing equal amounts of trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ and trans-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$ shows two closely overlapping resonances with an overall linewidth for the two resonances of ca. 2.5 Hz, and with the resonances only just resolved when a line broadening of 1 Hz is added to improve signal-to-noise ratio to a satisfactory level. Therefore, for mixtures containing only small amounts of one of these complexes, it is not possible to determine the amounts of the minor species from our $^{13}$C NMR spectra. Nevertheless, we observe that the chemical shift of one of the resonances changes from 45.59 to 45.62 ppm (Table 1) as a function of irradiation time. This indicates that the trans-chloroamine complex disappears and that the trans-ammineaquaa complex is formed. The merged resonances for these two complexes have a chemical shift of 45.59 ppm after 1 h of irradiation, which is identical to that of the pure trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ complex. The concentration of the trans-ammineaquaa complex is therefore much smaller than the concentration of the parent trans-amminechloro complex, and since a considerable amount of the cis-ammineaquaa complex has been formed at this stage of the photolysis, this is independent evidence that the dominant primary photoproduct in the photochemical loss of a chloride ligand from the trans-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ complex is cis-$[\text{Rh(en)}_2(\text{NH}_3)(\text{OH})_2]^{2+}$. After irradiation for 16 h the spectrum shows a relatively large resonance from trans-$[\text{Rh(en)}_2(\text{OH})_2\text{Cl}]^{2+}$, in addition to the spectral characteristics.
Table 1. $^{13}$C chemical shifts for the non-irradiated solutions and for cis- and trans-[Rh(en)$_2$(NH$_3$)Cl]$_2$$^{2+}$ after irradiation for 1 and 16 h, respectively.

<table>
<thead>
<tr>
<th>Complex irradiated</th>
<th>Chemical shifts (ppm)</th>
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<tr>
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<td></td>
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<tr>
<td>0 h</td>
<td></td>
</tr>
<tr>
<td>trans-[Rh(en)$_2$(OH$_2$)Cl]$^{2+}$</td>
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</tr>
<tr>
<td>trans-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$</td>
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<tr>
<td>trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$</td>
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</tr>
<tr>
<td>cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$</td>
<td>47.79</td>
</tr>
<tr>
<td>cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$</td>
<td>47.79</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td></td>
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<tr>
<td>trans-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$</td>
<td>47.77</td>
</tr>
<tr>
<td>cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$</td>
<td>47.78</td>
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<tr>
<td>cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$</td>
<td>47.78</td>
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<td></td>
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<tr>
<td>16 h</td>
<td></td>
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<tr>
<td>trans-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$</td>
<td>47.78</td>
</tr>
<tr>
<td>cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$</td>
<td>47.78</td>
</tr>
<tr>
<td>cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$</td>
<td>47.78</td>
</tr>
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</table>

*The values are in agreement with the values given in Refs. 1 and 4. Chemical shifts are reported vs. Me$_4$Si with dioxane (67.4 ppm) as an internal reference.

The $^{13}$C NMR spectra have so far substantiated the photostationary mixture of cis- and trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$. The $^{13}$C NMR spectra have so far substantiated the photosensitization reported in Ref. 3, and as shown in Fig. 4 there is also a good agreement between the concentrations of cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$ found from integration of the $^{13}$C NMR spectra and the concentrations calculated from the quantum yields, molar absorption coefficients and the reaction scheme given in Ref. 3 (Scheme 1B).

Conclusions

This work has shown that the photochemical reaction scheme and quantum yields outlined in Scheme 1B (Ref. 3) are correct within the given error limits, and that monitoring photochemical transformations by UV–VIS spectrophotometry is a reliable method, particularly when the data are treated rigorously by the multivariate calculations described earlier. In the present case UV–VIS spectrophotometry is even more informative than $^{13}$C NMR spectroscopy because, using the present spectrometer, it is impossible to separate adequately resonances as close as 0.03 ppm from the trans-[Rh(en)$_2$(OH$_2$)Cl]$^{2+}$ and trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$ ions.

![Fig. 4. Concentrations of cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{2+}$ as a function of irradiation time for the photochemical reactions of cis- and trans-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$, respectively. The points are experimental values found from integration of the $^{13}$C NMR spectra drawn with a vertical extent corresponding to ± the estimated uncertainty, and the curves are calculated from the quantum yields, molar absorption coefficients and the reaction scheme published in Ref. 3 (Scheme 1B).](image)

Experimental

Chemicals. cis-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$, trans-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)$_2$], cis[Rh(en)$_2$(NH$_3$)(NO$_3$)](ClO$_4$)$_2$ and trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)](ClO$_4$)$_2$ were prepared by literature methods. Most of the compounds used were the same as were used for the investigation in Ref. 3. D$_2$O was from the Cambridge Isotope Laboratories. HClO$_4$ was of analytical grade.

NMR measurements. The proton decoupled $^{13}$C NMR spectra were recorded at 62.896 MHz with a Bruker AC 250 MHz Fourier-transform spectrometer. Data [typically (4–5) x 10$^4$ transients] were recorded at 297 K using a pulse width of 2 μs (45°), sweep width 2000 Hz, and 8K data points (zero-filled to 32K data before Fourier transformation; digitiser resolution 0.122 Hz/point in the final spectrum). Under these conditions the acquisition time is 1.024 s per free induction decay, and a relaxation delay between pulses was not found to be necessary. Chemical shifts are reported on the δ scale with reference to internal 1,4-dioxane at δ=67.4 ppm.

Photolysis procedures. All photolyses were carried out at 25°C in 1 cm cylindrical quartz cells, and the solutions were irradiated at 366 nm. The equipment used was that de-
scribed earlier. The intensity of the lamp was $4.15 \times 10^{-6}$ einstein min$^{-1}$.

Preparation of solutions for photolysis experiments. Most solutions were prepared by directly dissolving the solid compounds in aqueous 0.01 M HClO$_4$, containing 20% in D$_2$O (lock solvent), to give about 13 mM solutions. The $\text{cis-}[\text{Rh(en)}_2(\text{NH}_3)(\text{OH}_2)]^+$ solution was made by heating the nitrato complex in the reaction medium at 80°C for 1 h prior to irradiation and $^{13}$C NMR measurements.

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References


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