Photochemistry of the Isocyanatopentaammineruthenium(III) Ion*. Observations on the Corresponding Iridium(III) and Rhodium(III) Complexes

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Photochemical studies of azido metal complexes of the type $[M(NH_3)_5N_3]^{2+}$, where M = Ir(III) and Rh(III) suggest the decomposition of the azido group via a coordinated nitrene intermediate [1–3]. The Ir(III) complex [4] and the corresponding Ru(III) complex [5] also react thermally with acid by a similar process. Since azido complexes (M-N₃) are isoelectronic with isocyanato complexes (M-NCO), it was decided to examine the photolysis of the latter in order to determine if a nitrene intermediate also forms. We wish to report here, however, that the photochemical reaction of $[M(NH_3)_5NCO](ClO_4)_2$ for Ir (III) and Rh(III) do not involve a nitrene path, and in neutral aqueous solutions photolysis of the Ru(III) complex proceeds by ammonia aquation.

Experimental

Syntheses

The compounds $[Ir(NH_3)_5NCO](ClO_4)_2$, $[Rh(NH_3)_5NCO](ClO_4)_2$, $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5OH_2](ClO_4)_3$, $[Ru(NH_3)_5OH](ClO_4)_2$ and $[Ru(NH_3)_5NCO](ClO_4)_2$ were prepared by published methods [6–8], and characterized by ultraviolet, visible and infrared spectra and by elemental analyses. $[Ru(NH_3)_6]Cl_3$ was obtained from Johnson-Matthey and Co. Ltd. (London), as a pale-yellow powder and characterized as stated for the compounds which were prepared. All other chemicals and compounds used were analytical reagent grade.

Chromatographic Procedures

Chromatographic separation of aquopentaammine and hexaammine-ruthenium(III) ions was done using Bio-Rad AG 50W-X2 (100-200 mesh) cation exchange resin in the H⁺ form. The absorbed mixture was eluted with 2.0 M HClO₄ solution. Separation of the two compounds was not sharp and an overlap region was always observed. The method was thus not accurate enough to quantitatively analyze the photolyte. Nevertheless it was very useful in providing an estimate of the relative amounts of the different metal complexes in the acidified photolyte.

Chromatographic separation of the constituents of the photolyte in neutral aqueous solutions was done on Bio-Rad AG 50W-X2 (100 - 200 mesh) cation exchange resin in the Mg^{2+} form. The adsorbed mixture was eluted with 1.5 M Mg(ClO₄)₂. In this case the separation was sharp and a quantitative estimate of the composition of the mixture was possible. All anion exchange chromatography was done using Bio-Rad AG 1-X8 (100 - 200 mesh) in the ClO_4^- form.

Analytical Methods

Spot tests for the presence of free cyanate ion were done using the hydroxylamine–hydrochloride ferric chloride reagent [9]. The test was done on effluents from cation exchange resins (Mg^{2+} form), eluted with water.

Analyses for ammonia were done by the Nessler's reagent [10], and by the hypobromite [11] methods. Standard concentration calibration curves were first prepared for these methods.

Analyses for ruthenium were done colorimetrically, using the thiourea [12] and 8-quinolinol [13] methods.

Photolysis Experiments

Quantum yield experiments were carried out using an optical train. The source of exciting radiation was an Oriel Optics 1000 Watt high pressure mercury–xenon lamp, housed in an Oriel Optics Model C-60-53 universal lamp housing. A Bausch and Lomb Model 33-86-08 U.V.–Visible high intensity monochromator was employed to obtain a monochromatic beam. Irradiations were done in a 1 cm optical cell placed in a constant temperature cell block, thermostatted by circulating water. A 0.5 mm magnetic bar was used to agitate the solution. All other photolysis experiments were made either in a Rayonet Photochemical Reactor or in an Ace Glass photochemical apparatus (cat. no. 6532) containing a water jacketed quartz reaction vessel thermostatted at 25 °C and irradiated with a Hanovia 100 watt high pressure quartz mercury arc together with quartz vycor or pyrex filters. In the Rayonet experiments solutions were irradiated with four of the photochemical reactor lamps of appropriate wavelength (2537, 3000, or 3500 Å, which is the wavelength of an absorption band (ϵ = 230 M^{-1} cm^{-1}) of the complex. Three separate experiments were performed with solutions
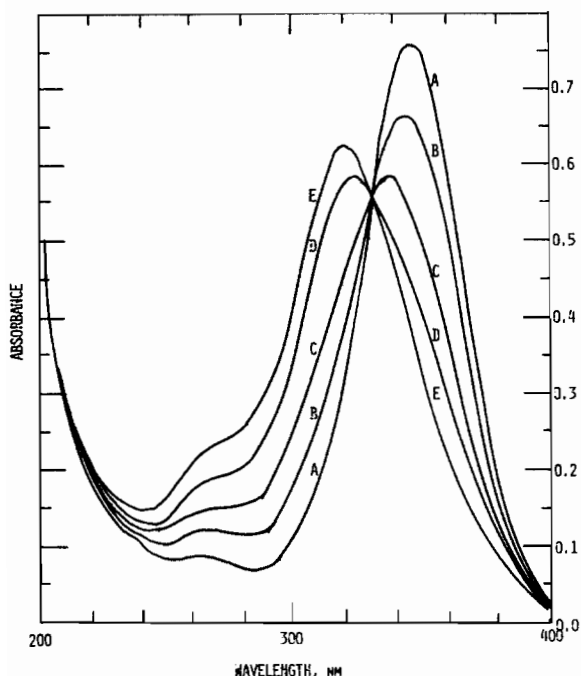
Figure 1. Spectrophotometric traces during the photolysis of 2.0×10^{-4} M [Ru(NH$_3$)$_5$NCO](ClO$_4$)$_2$ in neutral aqueous solutions at times; A) 0.0 min; B) 30 min; C) 60 min; D) 100 min and E) 160 min.

Figure 2. Absorption spectra for A) [Ru(NH$_3$)$_5$NCO]$^{2+}$ in water, and B) the photolysis produced [Ru(NH$_3$)$_4$(H$_2$O)-NCO]$^{2+}$ in 1.5 M Mg(ClO$_4$)$_2$.

of initial concentrations of 2.5×10^{-3} M complex, 1.0×10^{-4} M H$^+$, and 0.1 M Cl$^-$. In two cases the experiments were performed in air, but in one case the solution was purged with argon. At various times aliquots of the photolytes were removed and tested [2] for the presence of coordinated chloramine by the addition of a solution of KI. Even after 45 min of irradiation, the iodide test was negative. However, small changes in the optical spectra of the solutions did occur. The same experiments with Rh(NH$_3$)$_5$-NCO^{2+} gave similar results.

Freeze Drying Experiments

Isolation of compounds from aqueous solutions of the reaction mixture was done using the freeze drying technique. For this purpose, a Virtronics freeze drying unit was used. Samples (20 ml) of the photolyte were placed in the appropriate bottles and frozen in liquid nitrogen. The water in the sample is then sublimed under low pressure. It was possible to freeze dry a total of six bottles of solution at the same time.

Results and Discussion

Typical spectrophotometric traces of a photolysis experiment for [Ru(NH$_3$)$_5$NCO]$^{2+}$ are shown in Figure 1. All reactions were done in neutral aqueous
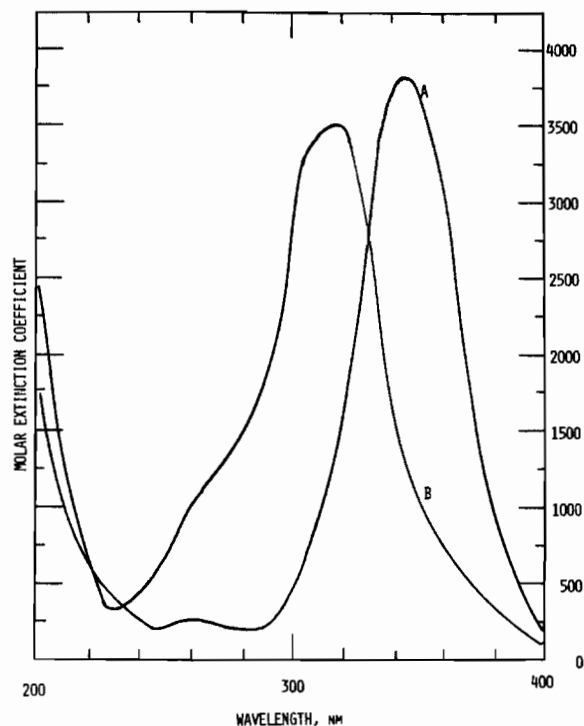
solutions, since the acid and base catalyzed reactions are faster than the photochemical reaction. Similar spectral changes were observed for the photolysis of the isocyanato complex at irradiations of 234, 254, 300, and 350 nm. An isosbestic point was always maintained up to 90% reaction. The position of the isosbestic point, however, shifted towards higher wavelength, the higher the wavelength of irradiating light. The isosbestic points were observed at 318, 325, 326 and 329 nm for irradiation light of wavelength 234, 254, 300 and 350 nm, respectively. We were not able to determine the reasons for these isosbestic shifts, but one possible reason is that different amounts of *cis–trans*-aquo isomers are produced at different wavelengths of irradiation. No significant changes in the spectrophotometric traces were observed for reactions done in a) water, b) 0.5 M Cl$^-$ (as NaCl), c) 0.5 M Br$^-$ (as NaBr), d) buffer solution, pH = 6.8 (0.025 M Na$_2$HPO$_4$ and 0.025 M KH$_2$PO$_4$), and e) 0.5 M NaNCO. Furthermore, no changes were observed for reactions carried out in air or under an argon atmosphere. The spectrum of a 90% photolyzed dilute aqueous solution of the iso-cyanato complex (3.0×10^{-4} M) was different from that of the known spectra of [Ru(NH$_3$)$_5$H$_2$O]$^{3+}$, [Ru(NH$_3$)$_5$OH]$^{2+}$ and [Ru(NH$_3$)$_6$]$^{3+}$. However, the addition of perchloric acid to a 90% photolyzed reaction mixture gave a solution with a spectrum similar to that of the aquopentaammine complex (see eq. 2).

TABLE I. Chromatography of Photolyte Solutions.

Experiment	Photolysis Time, min	% NH_3 Found	% $[Ru(NH_3)_5OH_2]^{3+}$	% $[Ru(NH_3)_6]^{3+}$
1	150	62	70 ± 10	13 ± 10
2	180	77	85 ± 10	27 ± 10
3	240	91	95 ± 05	0.0

Quantitative separation of the photolysis products was done on Bio-Rad AG 50W-X2 (100 - 200 mesh), cation exchange resin in Mg^{2+} form. Elution of the column with 1.50 M $Mg(ClO_4)_2$ gave two fractions: a) a fraction with an absorption maximum at 325 ± 3 nm which upon acidification with perchloric acid gave a solution with the same spectrum as that of $[Ru(NH_3)_5H_2O]^{3+}$ and b) a fraction with a spectrum identical to the starting material. Addition of perchloric acid to the latter fraction gave the expected spectrum of the complex $[Ru(NH_3)_6]^{3+}$ (see eq. 1). No other species were eluted off the column, using up to 3.0 M $Mg(ClO_4)_2$ solution as eluent.

The optical spectrum of the photolysis product and of the starting material are shown in Figure 2. Adsorption of a photolysis mixture on a cation exchange resin in the H^+ form, before or after addition of $HClO_4$, gave upon elution with 2.0 M perchloric acid, the $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5H_2O]^{3+}$ cations only. The hexaammine comes from the known [8] rapid acid hydrolysis of coordinated isocyanate in the starting material (eq. 1),

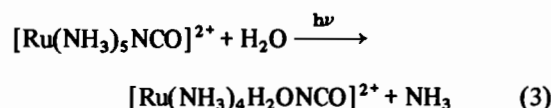$$[Ru(NH_3)_5NCO]^{2+} + H^+ + H_2O \rightarrow$$

$$[Ru(NH_3)_6]^{3+} + CO_2 \qquad (1)$$
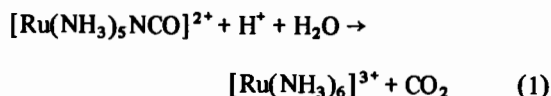
and the pentaammine is formed by the hydrolysis reaction of the presumed photolysis product (eq. 2):

$$[Ru(NH_3)_4H_2ONCO]^{2+} + H^+ + H_2O \rightarrow$$

$$[Ru(NH_3)_5H_2O]^{3+} + CO_2 \qquad (2)$$
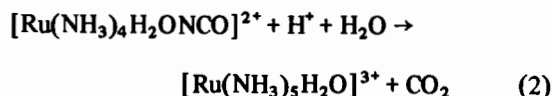
Elution of the photolysis mixture adsorbed on Dowex 50W-X2 H^+-form with 0.01 M perchloric acid also gave an eluent containing NH_4^+ ions, tested by Nessler's reagent and hypobromite tests. Spot tests, however, for NCO^- and NH_3 on solutions eluted by H_2O off a Mg^{2+} cation exchange resin gave negative results.

Table I gives the analytical results of three experiments on the chromatographically separated eluents of photolysis mixtures. Note that the calculated percentages are based on the initial concentration of the isocyanato complex, *e.g.* 77% for NH_3 means that we obtained 77% of what would be expected if the

reaction went to completion and released one ammonia molecule per $[Ru(NH_3)_5NCO]^{2+}$ ion. The NH_3 concentration was determined by Nessler's reagent and hypobromite methods, and the ruthenium concentration by the thiourea and 8-quinolinol methods. The quantum yield for the reaction (eq. 3) at irradiation of 254 nm was found to be 0.10:

$$[Ru(NH_3)_5NCO]^{2+} + H_2O \xrightarrow{h\nu}$$

$$[Ru(NH_3)_4H_2ONCO]^{2+} + NH_3 \qquad (3)$$

Attempts to precipitate the photochemical product from the photolyte solution were unsuccessful. Although the starting material, $[Ru(NH_3)_5NCO]^{2+}$, at concentrations similar to those used in the photolysis experiments ($10^{-4}-10^{-3}$ M) precipitates as greenish yellow needles upon the addition of sodium tetraphenylborate and as yellowish crystals when either sodium hexafluorophosphate or lithium tetrachlorozincate are added, no crystals separate when these salts are added to the photolyte after photolysis. Furthermore photolyte solutions, separated by cation exchange chromatography with $Mg(ClO_4)_2$, decomposed when allowed to stand in light for two hours and in the dark for over twelve hours. It was therefore decided to remove the solvent (H_2O) from the photolyzed solution under mild conditions. This was done by freeze drying the photolyte solutions. This gave yellow fluffy solid residues which had ir spectra identical to that of the starting material except for a band at 1400 cm^{-1} (this same treatment of a solution of the starting material gave a solid with an ir spectrum of the starting material, without the 1400 cm^{-1} band). This band is characteristic of NH_4^+ ion [14]. Elemental analyses of the resulting solids were inconsistent from one experiment to the other. In general they all gave N content lower than expected, but the carbon content was always within 0.5% of the theoretical value for $[Ru(NH_3)_4H_2ONCO](ClO_4)_2$. This presence of carbon, plus the ir spectra showing the presence of coordinated NCO^- and NH_4^+ are in accord with a photoaquation reaction (eq. 3) involving the loss of NH_3. There is ample precedence [15] for the photoaquation of complexes of the type $[M(NH_3)_5X]^{2+}$ to yield $[M(NH_3)_4H_2OX]^{2+}$.

The very low concentration of the photolyzed solution, coupled with the unstable nature of the product, made it impossible to completely characterize the photolysis product. However, all indications are that ammonia photoaquation is the primary photochemical process. In addition the presence of a good isosbestic point for up to 90% reaction indicates that only two absorbing species were present at any time during the reaction, and that no intermediate of widely varying chemical nature accumulated. We were unable to ascertain whether the ammonia photoaquation takes place *cis* and/or *trans* to the isocyanato group, and it should be noted that both isomers when treated with acid would yield $[Ru(NH_3)_5H_2O]^{3+}$. Despite all our efforts to do so, no evidence was found for any photochemical reaction involving the isocyanato group itself. This surprized us, because we were expecting NCO^- to behave similar to its isoelectronic N_3^- in these systems, and thus to undergo a photochemical loss of CO (in place of N_2) with the formation of a nitrene intermediate [2]. Our observations on the corresponding iridium(III) and rhodium(III) complexes also suggest that they do not photochemically react by a nitrene path. We do not know why the isocyanato complexes behave different from what we had expected, and we wish only to report the experimental facts. Furthermore, although a great deal of work has been done on the photochemistry of ruthenium(II) complexes [16], very little has been reported [17] on corresponding ruthenium(III) systems. It is of interest that the photolysis of $[Ru(NH_3)_5Cl]^{2+}$ yields predominantly *cis*-$[Ru(NH_3)_4H_2OCl]^{2+}$ similar to our observation of ammonia aquation for $[Ru(NH_3)_5NCO]^{2+}$.

Acknowledgments

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