ing of the completed work[5,11] readily shows that the earlier relationship, based on limited data, was fortuitous. Our conclusion[5] with respect to such a relationship is, "As with the binding of a ligand L to CoP, no simple, general relationship exists between ΔG, ΔH, or ΔS of the oxygenation of LCoP and the basicity of the ligand L."[25]

GD have also intimated that there exist serious disagreements between Walker's[6-8] results, based on esr studies of tetraphenylporphyrin and its derivatives, and our results,[2-5] based on visible spectroscopic studies of protoporphyrin IX dimethyl ester. In fact, a careful reading of the papers in question will reveal that the

(25) The exact antithesis of this statement is presented by GD as one of our "essential conclusions."

only possible disagreement concerns the value of ΔH for MeIm relative to the other bases. While we differ on this point it is interesting that in terms of $-\Delta G$ the order found by Walker py $<$ pip $<$ 4-NMe$_2$py $<$ MeIm is identical with that found by us on a related but different system using a different technique.

Finally, while there are only small differences in the values of ΔH and ΔS for the various bases studied here, there are substantial differences between the results for these model systems and those for cobalt-substituted hemoglobin.[9] These differences have proved to be important in the assessment of the role of the globin in the oxygenation of heme groups.

Photochemical Reactions of the Azidopentaamminerhodium(III) Ion. Nitrene and Redox Reaction Paths

James L. Reed, Harry D. Gafney, and Fred Basolo*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received September 14, 1973

Abstract: Photolysis of aqueous solutions of Rh(NH$_3$)$_5$N$_3{}^{2+}$ in 1.00 M HCl results in the evolution of nitrogen and the formation of Rh(NH$_3$)$_5$NH$_2$Cl^{3+} and Rh(NH$_3$)$_5$H$_2$O^{3+}. The quantum yields are wavelength dependent, with the formation of Rh(NH$_3$)$_5$NH$_2$Cl^{3+} favored at the longer wavelengths. The data have been interpreted in terms of the formation of coordinated nitrene and rhodium(II) intermediates. An intermediate whose spectrum is unlike that reported for flash photolysis is observed when Rh(NH$_3$)$_5$N$_3{}^{2+}$ is irradiated in glasses at 77° K. A model for the nitrene path is proposed in which the reactive level is a low energy azido group excited state populated by internal conversion or intersystems crossing.

Nitrene intermediates have been reported in the reactions of azide ion,[1,2] hydrazoic acid,[3] and of a large number of organic azides.[4-6] However, reports of coordinated nitrene intermediates are conspicuously few.[7-9] The formation of coordinated nitrenes in the reactions of Ru(NH$_3$)$_5$N$_3{}^{2+}$ and of Ir(NH$_3$)$_5$N$_3{}^{2+}$ with aqueous acid was established in reports from these laboratories.[7,8] The chemistry of these intermediates was described as that of a strong electrophile, and they undergo a number of reactions which have analogs in both nitrene and organic nitrene chemistry.

In a recent communication from these laboratories, it was postulated that coordinated nitrene intermediates

are formed during the photolysis of Ir(NH$_3$)$_5$N$_3{}^{2+}$ and of Rh(NH$_3$)$_5$N$_3{}^{2+}$.[10] Prior to this report the photochemistry of azido complexes had been interpreted in terms of substitution and/or azide radical formation with reduction of the central metal.[11-14] This paper reports a detailed study of the mechanism for the photodecomposition of the Rh(NH$_3$)$_5$N$_3{}^{2+}$ ion and the formation of Rh(NH$_3$)$_5$NH$_2$Cl^{3+}.

In a recent paper the mechanism for the photocomposition of Ir(NH$_3$)$_5$N$_3{}^{2+}$ was reported.[15] In that report, a model for the photochemistry of coordinated azides was proposed. In that model it was proposed that a low energy excited state of the azido group was responsible for nitrene formation and that a charge transfer ligand to metal (CTTM) state of the azido complex was responsible for the photoreduction which has been observed for other azido complexes. The

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stoichiometric formation of coordinated nitrene on the photolysis of $Ir(NH_3)_5N_3^{2+}$ was attributed to $d\pi-p\pi$ stabilization of the nitrene, as well as the inaccessibility of CTTM state of the iridium complex. The study of the $Rh(NH_3)_5N_3^{2+}$ ion is of special interest because it lies, in the cobalt triad, between the two extremes proposed by the model. The results of this study show that rhodium displays both a cobalt-like and iridium-like photochemical behavior in the $M(NH_3)_5N_3^{2+}$ systems.

Experimental Section

Materials. $RhCl_3 \cdot 6H_2O$ was obtained on loan from the Matthey-Bishop Co. and was used without additional purification. $[Rh(NH_3)_5Cl]Cl_2$ and $[Rh(NH_3)_5H_2O](ClO_4)_3$ were prepared by standard literature methods.[16,17] $[Rh(NH_3)_5N_3](ClO_4)_2$ was prepared by a modification of the published method.[18] $[Rh(NH_3)_5H_2O](ClO_4)_3$, 0.5 g, and NaN_3, 0.5 g, were refluxed in 50 ml of water for 1 hr. The volume was then reduced to 5 ml, and the product precipitated immediately upon the addition of 10 ml of a solution of 5% $NaClO_4$ in methanol. The crude product was recrystallized by dissolving it in a minimum of hot water and adding a solution of 5% $NaClO_4$ in methanol until the solution had just become turbid. The solution was then cooled to 0° and the yellow crystalline product collected. The product was washed with methanol and ether, then dried under vacuum.

$[Rh(NH_3)_5N_3]Cl_2$ was prepared by passing an aqueous solution of the perchlorate salt over an ion-exchange column containing a fivefold excess of Amberlite IRA 4015 CP anion-exchange resin in the chloride ion form. The product was isolated by reducing the volume and precipitating it from the hot solution with methanol. The ultraviolet spectra of these products agreed with the published spectra.[18,19]

$[Rh(NH_3)_5N_3][B(C_6H_5)_4]_2$ was prepared by dissolving the perchlorate salt, 0.6 g, in a minimum amount of hot water, and adding dropwise a solution of $NaB(C_6H_5)_4$, 1.2 g, dissolved in a minimum amount of warm water. The resulting mixture was heated on a steam bath for 5 min, then cooled to room temperature. The bright yellow solid was collected on a frit, washed with cold water, and dried under vacuum.

Anal. Calcd for $[Rh(NH_3)_5N_3][B(C_6H_5)_4]_2$: C, 66.29; H, 6.62; N, 12.71. Found: C, 67.15; H, 6.33; N, 12.89.

$[Rh(NH_3)_5NH_2OH]Cl_2$, was prepared by the photolysis of $[Rh(NH_3)_5N_3](ClO_4)_2$. $[Rh(NH_3)_5N_3](ClO_4)_2$, 0.3 g, was dissolved in 400 ml of 3.38×10^{-3} M $HClO_4$ and irradiated at 350 nm in a Rayonet reactor. After spectral analysis indicated that 78% of the starting material had decomposed, the volume of the photolyte was reduced to 25 ml. The photolyte was poured on an ion-exchange column $(1 \times 30$ cm) containing Dowex 50 $\times$ 2 (50–100 mesh) cation-exchange resin in the hydrogen ion form, and then eluted with 1.90 M HCl. The fraction with absorbance maxima at 250 and 299 nm was collected. The volume of the fraction was reduced to 5 ml and the product, $[Rh(NH_3)_5NH_2OH]Cl_2$, precipitated by the addition of 50 ml of ethanol and 20 ml of isopropyl alcohol. The off-white precipitate was collected on a frit, washed with ethanol and ether, and dried under vacuum. The yield was 0.115 g or 62% based on the amount of $Rh(NH_3)_5N_3^{2+}$ decomposed.

Anal. Calcd for $[Rh(NH_3)_5NH_2OH]Cl_2$: N, 25.66; H, 5.50. Found: N, 24.95; H, 5.47.

The electronic spectrum of $Rh(NH_3)_5NH_2OH^{3+}$ consists of two absorptions at 299 (150 M^{-1} cm^{-1}) and 250 nm (171 M^{-1} cm^{-1}). The ir spectrum shows two absorptions, typical of coordinated hydroxylamine, at 2850 and 960 cm^{-1}.[8] Titration with standardized 2.56×10^{-3} M NaOH indicates one acidic proton per mole of $Rh(NH_3)_5NH_2OH^{3+}$ with a pK_a of 8.8.

The results of the photolysis of solutions prepared with water redistilled in an all-Pyrex apparatus agreed with results obtained in distilled water. Therefore, the results reported in this paper were obtained with solutions prepared from distilled water. All other solvents were reagent grade.

Photolysis Procedures. Preliminary experiments for product isolation and gas evolution measurements were previously described.[10] Additional experiments were carried out in a quartz or Pyrex reaction vessel mounted in a Rayonet photochemical reactor. Wavelength isolation was achieved by making use of the 254-, 300-, and 350-nm light sources provided with the reactor.

The optical train used for the determination of quantum yields was previously described.[15] Light intensities $(I_0 \sim 10^{-6}$ einstein/ (l. sec)) were measured by ferrioxalate actinometry[20,21] before and after photolysis, and the average values for each run were used to calculate the quantum yields. The variation in measured light intensity was always less than 5%. The somewhat higher intensities $(1.1 \times 10^{-5}$ einstein/(l. sec)) required to detect any intensity dependence was obtained using the low-pressure lamps of a Rayonet photochemical reactor, and the lower intensities $(6.9 \times 10^{-8}$ einstein/(l. sec)) were obtained on the optical train by using narrower slit widths.

The oxygen dependence of the photochemical reactions was determined in a $10 \times 10 \times 40$ mm fused quartz spectrophotometer cell equipped with a 100-ml side arm. The solution to be photolyzed was pipetted into the side arm and degassed by three freeze-thaw cycles. Oxygen was added and allowed to come to equilibrium. The solution was then tipped into the cell and the quantum yield for the reaction was determined. Since no oxygen dependence was observed, all other measurements were made in air.

The quantum yield of nitrogen release from $Rh(NH_3)_5N_3^{2+}$ was measured in the same cell used to determine the oxygen dependence. The solutions were degassed by three freeze-thaw cycles, then irradiated. After irradiation, the gas produced was collected in a gas cell with a Toepler pump equipped with a liquid nitrogen trap to remove any condensable gases. The gas cell was then attached to a Hewlett-Packard 5700A gas chromatograph equipped with a 10-ft molecular sieve 5A (60–80 mesh) column and measured. This instrument was calibrated with known amounts of nitrogen using a procedure identical with the collection and measurement of the amount of nitrogen produced photochemically. The amount of nitrogen from air was always less than 5% of the amount of nitrogen measured.

A series of low temperature photolyses of $Rh(NH_3)_5N_3^{2+}$ were carried out using the apparatus and techniques previously described.[15] However, it was necessary to monitor both the ir and uv spectra of the glass to determine the extent of reaction. These experiments were carried out in a Beckman VLT-2 variable temperature cell equipped with CaF_2 windows, and thermostated to 77 °K with liquid nitrogen. Using 1:40:40 water-*sec*-butyl alcohol-ether uncracked glasses were obtained. This solvent was transparent throughout the uv and in the ir around 2030 cm^{-1}. For these photolyses, 350-nm light from the optical train described earlier was used.

Analytical Procedures. The amount of $Rh(NH_3)_5NH_2Cl^{3+}$ formed during photolysis was determined by the quantitative oxidation of iodide ion. The amount of I_3^- formed when an aliquot of a 10% KI solution was added to an aliquot of the photolyte was determined spectrally at 353 nm. The extinction coefficient of I_3^- at 353 nm, determined by the addition of known amounts of I_2 to equivalent aliquots of 10% KI solution, was found to be 2.46×10^4 $M^{-1}cm^{-1}$. The decrease in absorbance at 353 nm due to photolysis of $Rh(NH_3)_5N_3^{2+}$ was insignificant and disregarded. An equivalent aliquot of the unphotolyzed solution was treated in the same manner and the amount of I_3^- was determined from the difference in absorbance at 353 nm.

The decomposition of $Rh(NH_3)_5N_3^{2+}$ was determined by measuring the decrease in absorbance at 251 nm. The amount of $Rh(NH_3)_5H_2O^{3+}$ was then determined from the difference in the amounts of $Rh(NH_3)_5N_3^{2+}$ decomposed and $Rh(NH_3)_5NH_2Cl^{3+}$ formed.

Azide ion determinations were made by the formation of an $Fe^{3+}-N_3^-$ complex which was measured spectrophotometrically at 455 nm, $\epsilon = 1.94 \times 10^3$ M^{-1} cm^{-1}.[22] Since chloride ion and hydrogen ion inhibit the formation of the $Fe^{3+}-N_3^-$ complex, azide ion determinations were made on solutions of $[Rh(NH_3)_5N_3](ClO_4)_2$ photolyzed in water.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer or a Beckman IR-5

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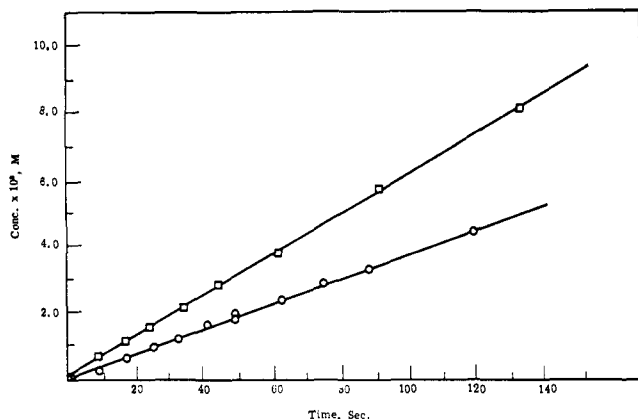(17) J. A. Osborn, K. Thomas, and G. Wilkinson, *Inorg. Syn.*, 13, 213 (1972).

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Figure 1. The concentration of Rh(NH₃)₅NH₂Cl³⁺, O, formed and of Rh(NH₃)₅N₃²⁺, □, decomposed vs. irradiation time for the 250-nm photolysis of a solution containing 6.39×10^{-4} M Rh-(NH₃)₅N₃](ClO₄)₂, 0.90 M NaCl, and 0.10 M HCl. Intensity $\sim 10^{-6}$ einstein/(l. sec).

spectrophotometer calibrated against polystyrene. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer and a Beckman DU-2 spectrophotometer. The titration of Rh(NH₃)₅-NH₂OH³⁺ was carried out with a Radiometer Titration 11 titrigraph equipped with glass and calomel electrodes. This instrument was standardized against a Harleco pH 5 buffer.

Results

Irradiation of aqueous solutions of Rh(NH₃)₅N₃²⁺ containing 1.00 M HCl with uv light results in the evolution of nitrogen and formation of Rh(NH₃)₅NH₂Cl³⁺ and Rh(NH₃)₅H₂O³⁺. The ratio of products yields is wavelength dependent.

At 350 nm of quantum yields of nitrogen formation and of substrate decomposition were found to be equal to the quantum yield of Rh(NH₃)₅NH₂Cl³⁺, 0.034. However at 275 nm the quantum yield of nitrogen, 0.18, was equal to the quantum yield of decomposition, but larger than the yield of Rh(NH₃)₅NH₂Cl³⁺, 0.096. The yield of nitrogen at this wavelength could be quenched by acrylamide.[23] Photolysis of a 4.7×10^{-2} M Rh(NH₃)₅N₃²⁺ solution containing 0.10 M acrylamide resulted in quenching 57% of the yield of nitrogen. It was not possible to carry out quenching experiments at lower wavelengths due to the strong absorption bands of acrylamide.

The products of the 254-nm photolysis of a 1.1×10^{-3} M Rh(NH₃)₅N₃²⁺ solution containing 0.88 M NaCl and 0.079 M HCl were separated by ion-exchange chromatography following reduction of the Rh(NH₃)₅-NH₂Cl³⁺ to Rh(NH₃)₆³⁺ by iodide ion. The isolated products, 59% Rh(NH₃)₆³⁺ and 41% Rh(NH₃)₅H₂O³⁺, were identified spectrophotometrically, and accounted for 93% of the amount of Rh(NH₃)₅N₃²⁺ decomposed as measured by the decrease in absorbance at 251 nm. Irradiation of an identical solution at 350 nm (half-width 30 nm) and isolation of the products by the same procedure indicated a substantial difference in product distribution. The Rh(NH₃)₆³⁺ accounted for 92% of the isolated product and for 96% of the amount of Rh(NH₃)₅N₃²⁺ decomposed. Also the yield of nitrogen at 350 nm was found to be equal to the yield of chloramine.

In order to detect possible secondary photolysis of the product, Rh(NH₃)₅NH₂Cl³⁺, at 250 nm, the depen-

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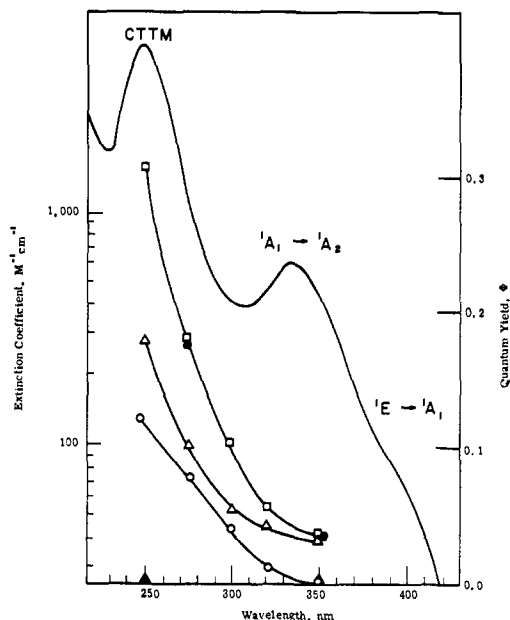
Figure 2. The uv spectrum of Rh(NH₃)₅N₃²⁺, —, and the quantum yields for its photochemical reactions at various wavelengths: ▲ = $\varphi_{N_3^-}$, ● = φ_{N_2}, □ = φ_{dec}, △ = φ_{NH_2Cl}, O = $\varphi_{dec} - \varphi_{NH_2Cl}$.

dence of the product yields on various irradiation times was determined. A 6.39×10^{-4} M solution of [Rh-(NH₃)₅N₃](ClO₄)₂ containing 0.1 M HCl and 0.90 M NaCl was irradiated for various times. The amounts of Rh(NH₃)₅N₃²⁺ decomposed and Rh(NH₃)₅NH₂Cl³⁺ formed were determined by measuring the decrease in absorbance at 251 nm and by oxidation of iodide ion, respectively. The results of these experiments are shown in Figure 1. The ratio of the rate of decomposition to the rate of chloramine formation of 0.60 is in excellent agreement with the stoichiometry obtained by product isolation. Furthermore, the linearity of the concentration vs. time plot, Figure 1, indicates secondary photolysis is not significant for short irradiation times. Furthermore, the ratio $\varphi_{NH_2Cl}/\varphi_{dec}$ was found to be independent of the intensity of the incident radiation over a range of 1.1×10^{-5} to 6.9×10^{-8} einstein/(l. sec), and independent of the concentration of Rh(NH₃)₅N₃²⁺ over a range of 3×10^{-3} to 3×10^{-5} M in complex. This would suggest that secondary photolysis of Rh-(NH₃)₅NH₂Cl³⁺, due to local concentration gradients, is not a problem.

At all wavelengths studied azide ion was not detected in the photolyte. To determine if azide ion formed during the photolysis could be detected, a solution containing 1.95×10^{-3} M Rh(NH₃)₅N₃²⁺ and 8×10^{-5} M NaN₃ was irradiated at 350 nm to 3.1% consumption of the reactant. Analysis with Fe-(NO₃)₃ indicated that 97% of the added azide ion could be recovered.

The quantum yields of the different reactions, determined at various wavelengths, are summarized in Table I and Figure 2. The reported values were calculated from plots of concentration vs. time similar to Figure 1. For concentrated solutions, optical densities greater than 2.8, the plots were linear up to 17% conversion, indicating secondary photolysis was not significant.

The quantum yields for decomposition at 250 nm reported in Table I were found to be independent of the
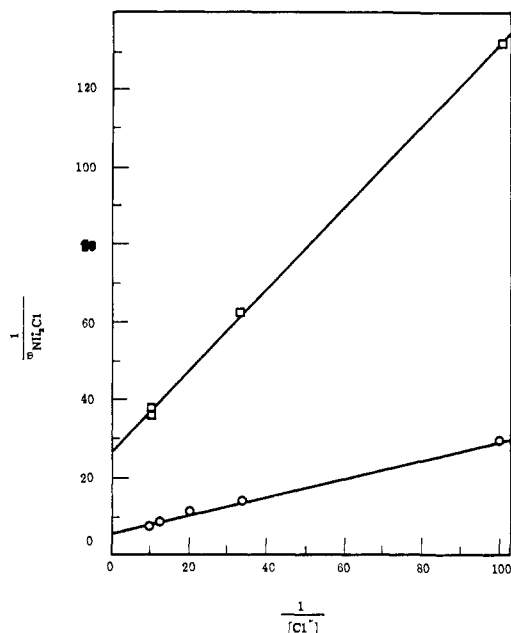
Figure 3. Dependendence of the quantum yield for Rh(NH₃)₅-NH₂Cl³⁺ formation on chloride ion concentration in 1.00 M H⁺ and irradiation at 250 (O) or 350 (□) nm.

Figure 4. Dependence of the quantum yield for $Rh(NH_3)_5NH_2Cl^{3+}$ formation, in 0.10 M HCl and irradiated at 250 nm, on perchlorate ion concentration.

Table I. Quantum Yields for the Photochemical Reactions of $Rh(NH_3)_5N_3^{2+}$

Wave-length, nm	φ_{dec},[a] mol einstein⁻¹	φ_{NH_2Cl},[a] mol einstein⁻¹	$\varphi_{N_3^-}$,[b] mol einstein⁻¹	φ_{N_2}, mol einstein⁻¹
250	0.31 ± 0.01	0.18 ± 0.01	<10⁻³	
275	0.178 ± 0.006	0.096 ± 0.005		0.18[c]
300	0.104 ± 0.004	0.053 ± 0.002		
320	0.054 ± 0.003	0.043 ± 0.002		
350	0.035 ± 0.002	0.034 ± 0.002	<2 × 10⁻⁴	0.035[d]

[a] Irradiated in 1.00 M HCl. [b] Irradiated in neutral solution.
[c] Irradiated in 0.020 M HCl. [d] Irradiated in 0.0020 M HCl.

concentration of oxygen. Varying the pressure of oxygen above the solution from less than 0.1 to 672 Torr did not change the quantum yield above experimental error. Nor was the quantum yield of Rh-$(NH_3)_5NH_2Cl^{3+}$ at 250 nm hydrogen ion dependent. The hydrogen ion concentration, at 2.00 M chloride ion concentration, was varied from 2.0 to 10⁻³ M without any change in the quantum yield.

However, the yield of $Rh(NH_3)_5NH_2Cl$ was found to be dependent on the concentration of chloride and perchlorate ions. The chloride ion dependence was determined by irradiating a 5 × 10⁻⁴ M $Rh(NH_3)_5N_3^{2+}$ solution. The chloride ion concentration was varied from 0.1 to 0.01 M. The results of these experiments, performed at 250 and 350 nm, are shown in Figure 3. Similarly, the dependence of the quantum yield on the concentration of perchlorate ion was also determined. The yield of $Rh(NH_3)_5NH_2Cl^{3+}$ was determined iodiometrically, since preliminary experiments indicated the product of the reaction of $Rh(NH_3)_5NH^{3+}$ and ClO_4^- did not oxidize iodide ion. Solutions containing 9.3 × 10⁻⁴ M $Rh(NH_3)_5N_3^{2+}$, 0.10 M HCl, and varying amounts of perchlorate ion were irradiated at 250 nm. The results of the experiments are shown in Figure 4.

Irradiation of glasses at 77°K containing $Rh(NH_3)_5$-N_3^{2+} with 254 or 350 nm uv light results in a disap-

pearance of the 335-nm absorption band of $Rh(NH_3)_5$-N_3^{2+} and the appearance of a new absorption band at 407 nm, which rapidly disappeared on warming the glass to room temperature. Monitoring the spectral changes occurring in the glass showed that isosbestic points at 307 and 355 nm were maintained for 20% reaction. Continued photolysis resulted in a loss of the isosbestic points, followed by a decrease in the absorption band at 407 nm. The spectral changes were independent of whether the anion of the complex was chloride, perchlorate, or tetraphenylborate or the solvent was 4:1 methanol–water, 1:100:20 water–methanol–ethanol, or 1:40:40 water–sec-butyl alcohol–ether. The same spectral changes were observed in acidic, 10⁻² M HCl, or neutral glasses.

To determine the extinction coefficient of the intermediate observed in a glass, a solution of [Rh(NH₃)₅-N₃][B(C₆H₅)₄]₂ in 1:40:40 water–sec-butyl alcohol–ether was cooled to 77°K in a Beckman VLT-z variable temperature cell and irradiated at 350 nm. The ir and uv spectra were recorded periodically during photolysis, and the amount of $Rh(NH_3)_5N_3^{2+}$ decomposed was determined from the decrease in absorbance of the azido group asymmetric stretch at 2030 cm⁻¹. Assuming a one to one stoichiometry between the intermediate and the amount of $Rh(NH_3)_5N_3^{2+}$ consumed, the spectrum reported in Figure 5 was calculated.

Discussion

Similar to $Ir(NH_3)_5N_3^{2+}$, irradiation of aqueous solutions of $Rh(NH_3)_5N_3^{2+}$ with uv light results in the evolution of nitrogen.[15] However, unlike the iridium(III) complex, the stoichiometry of the photochemical reaction of the rhodium(III) complex is wavelength dependent. At 350 nm 1 mol of nitrogen and 1 mol of Rh-$(NH_3)_5NH_2Cl^{3+}$ are formed per mole of complex decomposed. Azide ion is not detected in the photolyte, $\varphi_{N_3^-} < 2 \times 10^{-4}$. The photochemical reaction in hydrochloric acid is given in eq 1.
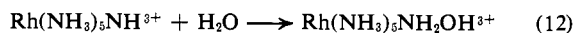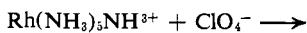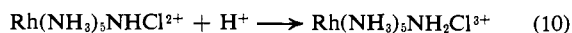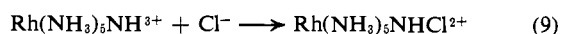
$$Rh(NH_3)_5N_3^{2+} + 2H^+ + Cl^- + h\nu(\lambda\ 350\ nm) \longrightarrow$$

$$Rh(NH_3)_5NH_2Cl^{3+} + N_2 \quad (1)$$
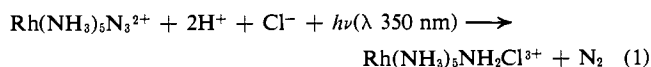
As the wavelength of exciting light increases, a second mode of reaction resulting in the formation of Rh-$(NH_3)_5H_2O^{3+}$ becomes increasingly important. Ion-exchange chromatography of solutions photolyzed at 254 nm indicated that the products of the photochemical reaction are $Rh(NH_3)_5NH_2Cl^{3+}$ and $Rh(NH_3)_5H_2O^{3+}$. The isolated yield of $Rh(NH_3)_5NH_2Cl^{3+}$, 0.59 mol per mole of $Rh(NH_3)_5N_3^{2+}$ decomposed, is in excellent

agreement with the value 0.60 obtained from the ratio of the rates of $Rh(NH_3)_5NH_2Cl^{3+}$ formation to that of $Rh(NH_3)_5N_3^{2+}$ decomposition (Figure 1). Azide ion was not detected in the photolyzed solution, $\varphi_{N_3^-} <$ 10^{-3}.

The formation of $Rh(NH_3)_5NH_2Cl^{3+}$ is readily explained by a coordinated nitrene intermediate, as the immediate product of the photochemical event. However, it seems unlikely that $Rh(NH_3)_5H_2O^{3+}$ is formed by a similar path. The linearity of the rates of formation of $Rh(NH_3)_5NH_2Cl^{3+}$ and decomposition of $Rh(NH_3)_5N_3^{2+}$ (Figure 1) rule out formation of $Rh(NH_3)_5$-H_2O^{3+} by secondary photolysis of the product $Rh(NH_3)_5NH_2Cl^{3+}$, nor is photoaquation an adequate explanation, since azide ion is not detected in the photolyte. Additional evidence that the aquo complex does not result from a secondary photolysis of the chloramine complex is provided by experiments done using different concentrations of the azido complex and at different light intensities. In all cases, the ratios of $\varphi_{NH_2Cl}/\varphi_{dec}$ were the same within experimental error. These ratios are expected to vary if secondary photolysis of $Rh(NH_3)_5NH_2Cl^{3+}$, due to local concentration gradients, were important.

The enhanced yield of nitrogen as compared to the yield of $Rh(NH_3)_5NH_2Cl^{3+}$ and the fact that the additional yield of nitrogen formed, $\varphi_{dec} - \varphi_{NH_2Cl}$, can be quenched by acrylamide[23] strongly suggest that $Rh(NH_3)_5H_2O^{3+}$ is formed by a redox process which results in the formation of an azide radical. Consistent with these observations, the mechanism, eq 2-13, is proposed.

$$Rh(NH_3)_5N_3^{2+} + h\nu \longrightarrow [Rh(NH_3)_5N_3^{2+}]^* \quad (2)$$

$$[Rh(NH_3)_5N_3^{2+}]^* \longrightarrow Rh(NH_3)_5N_3^{2+} + \Delta \quad (3)$$

$$[Rh(NH_3)_5N_3^{2+}]^* \longrightarrow Rh(NH_3)_5N^{2+} + N_2 \quad (4)$$

$$[Rh(NH_3)_5N_3^{2+}]^* \longrightarrow Rh(NH_3)_5^{2+} + N_3 \cdot \quad (5)$$

$$Rh(NH_3)_5^{2+} + H_2O + oxidant \longrightarrow$$

$$Rh(NH_3)_5H_2O^{3+} + reduced\ product \quad (6)$$

$$N_3 \cdot \longrightarrow 1.5N_2 \quad (7)$$

$$Rh(NH_3)_5N^{2+} + H^+ \longrightarrow Rh(NH_3)_5NH^{3+} \quad (8)$$

$$Rh(NH_3)_5NH^{3+} + Cl^- \longrightarrow Rh(NH_3)_5NHCl^{2+} \quad (9)$$

$$Rh(NH_3)_5NHCl^{2+} + H^+ \longrightarrow Rh(NH_3)_5NH_2Cl^{3+} \quad (10)$$

$$Rh(NH_3)_5NH^{3+} + ClO_4^- \longrightarrow$$

$$Rh(NH_3)_5NHOClO_3^{2+} \longrightarrow P \quad (11)$$

$$Rh(NH_3)_5NH^{3+} + H_2O \longrightarrow Rh(NH_3)_5NH_2OH^{3+} \quad (12)$$

$$2Rh(NH_3)_5NH^{3+} \longrightarrow [Rh(NH_3)_5N]_2H^{5+} + H^+ \quad (13)$$
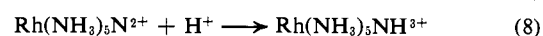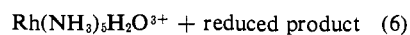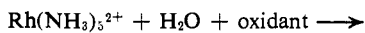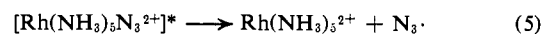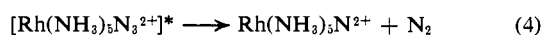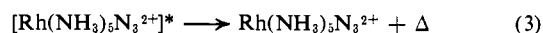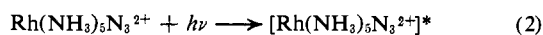
Equation 13 represents a dimerization reaction, recently reported[24] in a study of the flash photolytic behavior of $Rh(NH_3)_5N_3^{2+}$. Since the steady-state experiments described in this paper were carried out with solutions containing sufficient concentrations of chloride ion and/or hydrogen ion to quench the dimerization reaction, it was not observed and is neglected in the kinetic analysis. Neither the previously reported flash photolysis data[24] nor the results of these experiments allow a distinction between chloride ion scavenging the coordinated nitrene, $Rh(NH_3)_5NH^{3+}$, followed by a rapid protonation reaction to form the chloramine or protonation of the nitrene prior to addition of chloride

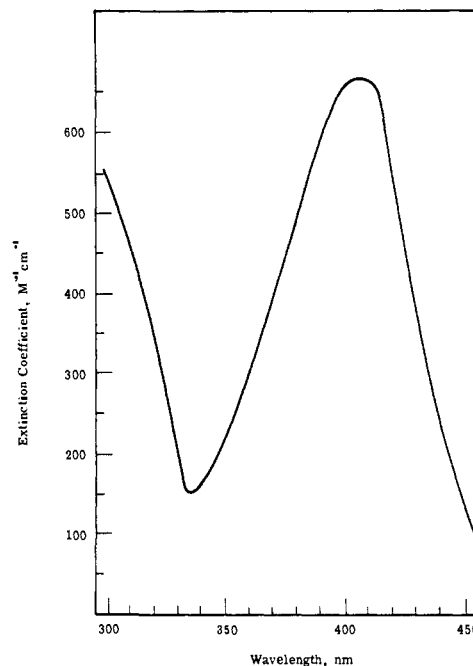(24) J. F. Endicott and G. Ferraudi, *J. Amer. Chem. Soc.*, **95**, 2371 (1973).

Figure 5. Spectrum of the rhodium intermediate formed by the photolysis at 350 nm of $Rh(NH_3)_5N_3^{2+}$ in 1:100:20 water-methanol-ethanol glass at 77°K.

ion. This does not affect the kinetic analysis, however, since the quantum yields were found to be independent of pH.

Steady-state analysis of the proposed mechanism leads to the expression

$$1/\varphi_{NH_2Cl} = 1/\Phi_N + \frac{k_{11}[ClO_4^-] + k_{12}[H_2O]}{\Phi_N k_9 [Cl^-]} \quad (14)$$

where φ_{NH_2Cl} and Φ_N represent the observed yield of $Rh(NH_3)_5NH_2Cl^{3+}$ and $Rh(NH_3)_5N^{2+}$, respectively. Although a slight error, $\leq 4\%$, is introduced into the intercept of Figure 3 by the variation of the concentration of perchlorate ion to maintain a constant ionic strength, it is within experimental error and is neglected to simplify the kinetic analysis given below. The values obtained by either a complete or simplified analysis were identical. The intercepts of Figure 3 yield values of Φ_N of 0.19 ± 0.01 and 0.039 ± 0.002 for excitation at 250 and 350 nm, respectively. The values are within experimental error of those observed for φ_{NH_2Cl}, on direct photolysis of solutions containing 1.0 M HCl at these wavelengths. This indicates that all the nitrene intermediate, $Rh(NH_3)_5NH^{3+}$, is scavenged by chloride ion to yield $Rh(NH_3)_5NH_2Cl^{3+}$ in solutions containing 1.0 M or greater chloride ion. The ratio of intercept to slope yields values of 21.7 and 23.2 M^{-1} for $k_9/(k_{11}[ClO_4^-] + k_{12}[H_2O])$, for excitation at 250 and 350 nm, respectively. At constant ClO_4^- concentration, the value of $k_9/(k_{11}[ClO_4^-] + k_{12}[H_2O])$ is wavelength independent. This is in accord with the ratio of rates representing the reactions of coordinated nitrene, the photolysis product, with various nucleophiles.

The perchlorate ion dependence on the yield of $Rh(NH_3)_5NH_2Cl^{3+}$, Figure 4, can be described by eq 14. The slope of Figure 4, $k_{11}/\Phi_N k_9 [Cl^-]$, is evaluated to be 3.98. Since the experiments were carried out at a constant chloride ion concentration, 0.1 M, and Φ_N was evaluated from the intercept of Figure 3, the ratio of

rate constants k_{11}/k_9 is calculated to be 0.071. By substituting the value of k_{11}/k_9 into eq 14, the ratio k_{12}/k_9 is calculated to be 7.9×10^{-4}.

Like nitrene and coordinated nitrenes, $Rh(NH_3)_5$-NH^{3+} is a strong electrophile. Electrophilicity is characteristic of singlet nitrenes with one vacant valence orbital, suggesting that $Rh(NH_3)_5NH^{3+}$ is a singlet.[1,3] The absence of an effect due to oxygen, an efficient quencher of triplet arylnitrenes,[25] further suggests the singlet character of $Rh(NH_3)_5NH^{3+}$. Previous investigations[3] have also indicated that nitrene and coordinated nitrene are soft Lewis acids which have a preference for soft Lewis bases. The relative rate constants for scavenging of $Rh(NH_3)_5NH^{3+}$ by H_2O, ClO_4^-, and Cl^- are calculated from the values of k_{11}/k_9 and k_{12}/k_9 to be 1, 90, and 1270, respectively, indicating $Rh(NH_3)_5NH^{3+}$ is also a soft Lewis acid.

There is a substantial difference in the ratio of the rate of reaction with chloride ion relative to solvent observed for rhodium nitrene, 22 M^{-1}, as compared to that previously observed[15] with iridium nitrene, 1740 M^{-1}. The substantial difference in the ratios of rates suggests that the iridium coordinated nitrene complex is more stable[15] and thus more discriminating in its reactions with various nucleophiles than is the corresponding rhodium complex.

As already discussed, the photochemical formation of $Rh(NH_3)_5H_2O^{3+}$ cannot be readily explained in terms of a coordinated nitrene intermediate, secondary photolysis of $Rh(NH_3)_5NH_2Cl^{3+}$, or photoaquation. According to the proposed mechanism, the larger quantum yield of nitrogen, $\varphi_{N_2} = 0.18 \pm 0.01$, relative to the quantum yield of $Rh(NH_3)_5NH_2Cl^{3+}$, $\varphi_{NH_2Cl} = 0.096 \pm 0.005$, at 275 nm is attributed to a combination of azide radicals (eq 7). As previous investigations of the photoredox behavior of azido metal complexes have shown, the yield of nitrogen resulting from a combination of azide radicals is quenched by radical scavengers such as iodide ion or acrylamide.[23] Similarly photolysis of a 4.8×10^{-2} M $Rh(NH_3)_5N_3^{2+}$ solution containing 0.1 M acrylamide at 275 nm resulted in a quantum yield of nitrogen, φ_{N_2}, of 0.083 ± 0.01, a value within experimental error of that required by the proposed mechanism, 0.096. These observations strongly support the contention that $Rh(NH_3)_5H_2O^{3+}$ is the final product of a photoreduction reaction (eq 5). The initially formed $Rh(NH_3)_5^{2+}$, a strong reductant, undergoes additional reactions producing $Rh(NH_3)_5$-H_2O^{3+}. It should be noted, however, that the proposed mechanism requires the quantum yield of nitrogen to be 0.22 as compared to an observed yield of 0.18. The apparent stoichiometric defect suggests that only 66% of the azide radicals combine to form molecular nitrogen, and this is attributed to alternative reaction paths for the reactive azide radical which are in kinetic competition with the bimolecular radical–radical reaction (eq 7).

The proposed mechanism requires $Rh(NH_3)_5H_2O^{3+}$ to be formed by a redox process, and as indicated by Figure 2 this is most efficient in the charge-transfer region of the spectrum of $Rh(NH_3)_5N_3^{2+}$. Such behavior is characteristic of azide ion and azido metal complexes. Irradiation of azide ion in the charge-transfer absorption, <230 nm, results in azide radical

formation, whereas irradiation of internal azide transitions, 254 nm, leads to nitrene formation.[26] Similarly, irradiation of azido complexes in the charge-transfer region results in photoreduction of the metal ion and the formation of azide radicals.[11–14] Photoreduction has recently been demonstrated to be important following excitation of the charge-transfer absorption of $Rh(NH_3)_5I^{2+}$. Although the isolated products,[27,28] Rh-$(NH_3)_4I_2^+$ and $Rh(NH_3)_4(H_2O)I^{2+}$, suggest the intermediate rhodium(II) species is a tetraammine, a similar intermediate in the formation of $Rh(NH_3)_5H_2O^{3+}$ seems unlikely. Rather the differences in the products may be due to differences in the physical properties of the charge-transfer state populated and/or differences in the rates of secondary cage or bulk solution reaction leading to the final products.

The uv spectra of several arylnitrenes isolated in organic glasses have been reported by Reiser, et al.[6a] Furthermore the spectra observed in a glass agreed with the spectra of transients observed in the flash photolysis of the arylazide precursors.[6b] Thomas and Crosby[29] have reported the appearance of a brown coloration when 4:1 methanol–water glasses containing $Rh(NH_3)_5N_3^{2+}$ were irradiated with uv light. Irradiation of 4:1 methanol–water or 1:40:40 water–sec-butyl alcohol–ether glasses at 77°K containing Rh-$(NH_3)_5N_3^{2+}$ resulted in the appearance of an intermediate (Figure 5) which was indefinitely stable at 77°K but rapidly disappeared on warming to room temperature. Monitoring the uv spectrum and the asymmetric azide ion stretch at 2030 cm^{-1} established that the formation of the intermediate was concomitant with decomposition of the azide ligand. The spectral changes observed in the glasses, where dimerization should not occur, differed substantially from the reported[24] spectra of the dimers, $[Rh(NH_3)_5N]_2H^{5+}$ and $[Rh(NH_3)_5N]_2^{4+}$, observed on flash photolysis of $Rh(NH_3)_5N_3^{2+}$. Furthermore, the maintenance of isosbestic points suggest that the conversion of the azido complex to this new species is quantitative. Spectral evidence also indicated that the intermediate observed in a glass was not the result of a reaction with the anion, since spectral changes were independent of whether the anion present was Cl^-, ClO_4^-, or $B(C_6H_5)_4^-$. The intermediate was indefinitely stable in neutral glasses, as well as in glasses made 0.01 M in HCl. When glasses containing added HCl were allowed to thaw, the solutions oxidize iodide ion to iodine suggesting the formation of $Rh(NH_3)_5$-NH_2Cl^{3+}. However, glasses which do not contain HCl thaw to produce nonoxidizing solutions characteristic of the hydroxylamine product. In addition, the same spectral changes were observed whether the photolyses were performed at 254 or at 350 nm. Although positive identification of this species is not possible, these results suggest that the species is the rhodium nitrene, $Rh(NH_3)_5NH^{3+}$. However, it should be noted that the spectral changes are similar to those observed for the photolysis of $Ir(NH_3)_5N_3^{2+}$, and the iridium intermediate was assumed to be the product of the nitrene reaction with the solvent.[15]

(25) R. A. Abramovitch, J. Chem. Soc., Chem. Commun., 964 (1972).

(26) A. Treinin and E. Hayon, J. Chem. Phys., 50, 538 (1969); I. Burak and A. Treinin, J. Amer. Chem. Soc., 87, 4031 (1965).
(27) T. Kelly and J. F. Endicott, J. Amer. Chem. Soc., 92, 5733 (1970).
(28) T. M. Kelly and J. F. Endicott, J. Amer. Chem. Soc., 94, 1797 (1972).
(29) T. R. Thomas and G. A. Crosby, J. Mol. Spectrosc., 38, 118 (1971).

Isosbestic points are observed when $Rh(NH_3)_5N_3^{2+}$ is irradiated in a glass at 350 or 254 nm. This is expected at 350 nm, since only one product, $Rh(NH_3)_5$-NH_2Cl^{3+}, is formed. However, photolysis of Rh-$(NH_3)_5N_3^{2+}$ at 254 nm in fluid solution yields two products, $Rh(NH_3)_5NH_2Cl^{3+}$ and $Rh(NH_3)_5H_2O^{3+}$. The aquo product is proposed to be formed by homolytic fission of the rhodium–azide bond, followed by oxidation and aquation of $Rh(NH_3)_5^{2+}$. In a glass the recombination reaction would be more favorable than escape of the azide radical from the solvent cage. Thus in a glass the azide radical may return to the complex and only formation of the nitrene intermediate occurs to give the observed isosbestic points which are identical with those observed on photolysis at 350 nm.

The assignment of the absorption and emission spectra, summarized in Table II, has recently been made

Table II. Excited-State Energies (kK) of $Rh(NH_3)_5N_3^{2+}$

Transition	Energy, kK
$^3(E, A_2) \longrightarrow {}^1A_1$	15.41[a]
$^1A_1 \longrightarrow {}^3(E, A_2)$	22.4[a]
$^1A_1 \longrightarrow {}^1E$	25.4[a]
$^1A_1 \longrightarrow {}^1A_2$	29.9[a]
CTTM	39.9[b]

[a] Reference 29. [b] H. H. Schmidtke, private communication.

by Thomas and Crosby.[29] Comparison of these spectral assignments with the quantum yields determined at various wavelengths, Table I, shows that excitation of the ligand-field transitions leads to chloramine formation, whereas excitation in the charge-transfer transition leads to photoreduction and chloramine formation. It is difficult to associate fission of the nitrogen–nitrogen bond, necessary for formation of a nitrene intermediate, with reaction from either the singlet or triplet metal centered ligand-field excited states. Rather it is proposed, as was previously suggested[15] for the formation of $Ir(NH_3)_5NH_2Cl^{3+}$ from $Ir(NH_3)_5N_3^{2+}$, that the reaction resulting in the formation of the chloramine takes place from an internal azide ligand excited state which is lower in energy than the singlet ligand-field excited states. Deb[30] has reported an emission from alkali metal azides centered at 480 nm, thus suggesting that

(30) S. K. Deb, J. Chem. Phys., 35, 2122 (1961).

a thermally equilibrated azido ligand excited state may be very low in energy. In terms of this model, the wavelength dependence of the quantum yield reflects differences in the efficiency of internal conversion or intersystems crossing to the reactive state. The enhanced yield of $Rh(NH_3)_5NH_2Cl^{3+}$ at 250 nm could be attributed to a more efficient conversion to the reactive azide excited state or appreciable direct excitation of the azide ligand occurs at these wavelengths, since azide ion and alkylazides absorb strongly in this region.

Although the quantum yield of $Rh(NH_3)_5H_2O^{3+}$ is a maximum for excitation in the charge-transfer transition, the data recorded in this study do not distinguish whether photoredox occurs from the singlet or a lower energy triplet charge-transfer state.

Conclusion

There appears to be a very definite trend in the photochemistry of the cobalt(III), rhodium(III), and iridium (III) azidopentaammine complexes. In the case of cobalt, the photochemistry is predominantly redox. For rhodium both redox and nitrene formation occur, whereas for iridium only nitrene formation occurs. The plus two oxidation state becomes less favorable with increasing atomic number, shifting the CTTM excited state to higher energy. According to the proposed model the CTTM excited state of $Co(NH_3)_5N_3^{2+}$ lies below the reactive azide state and only redox photochemistry occurs. With $Rh(NH_3)_5N_3^{2+}$ the states are of similar energy, and both redox and nitrene formation occurs. With $Ir(NH_3)_5N_3^{2+}$, however, the CTTM excited state lies above the reactive azide excited state and only nitrene formation occurs.

This trend in the photochemistry is also consistent with the increasing stability of the coordinate nitrene intermediate. As the size of the outer d orbitals increases with increasing atomic number, the $d\pi$–$p\pi$ interaction increases thus stabilizing the coordinated nitrene intermediate. This further suggests that nitrene formation is most important in the photochemical reactions of the second- and third-row transition metal azidopentaammine complexes.