Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Photoredox Energetics of Transition Metal Complexes. A Critical Probing of the Proposed Redox and Nitrene Pathways in Azidopentaamminerhodium(III)

TOMOAKI INOUE, JOHN F. ENDICOTT,* and GUILLERMO J. FERRAUDI

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The charge-transfer photochemistry of $Rh(NH_3)_5N_3^{2+}$ has been examined very critically. No evidence for photoreactions producing rhodium(II) and azide radical could be found for irradiations of wavelengths longer than 214 nm; the previously reported nitrene pathway was the only significant photoreaction mode found for the longer wavelength ultraviolet irradiations of $Rh(NH_3)_5N_3^{2+}$. The $Rh(NH_3)_5NH_2Cl^{3+}$ product obtained from irradiations in acidic chloride solutions has been isolated and characterized, and aspects of its photosensitivity have been explored. The photochemistry of $Rh(NH_3)_5N_3^{2+}$ has been shown to be complicated by secondary photolysis of $Rh(NH_3)_5NH_2Cl^{3+}$. This secondary photoreaction and some accompanying thermal reactions are proposed to be the major source of $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_6^{3+}$ products found in photolyzed solutions. The photoredox energetics are discussed and previously proposed models of photoredox behavior are refined for application to acidopentaammine complexes of rhodium(III). In the application to $Rh(NH_3)_5N_3^{2+}$ it is found that several product configurations involving $Rh(NH_3)_5N^{2+}$ intermediates must be lower in energy than the rhodium(II)–azide radical product configuration. It is proposed that $\pi_d \rightarrow \pi_p$ back-bonding interactions in the excited state provide a mechanism for mixing of charge transfer to metal and ligand-centered excited states, leading to formation of nitrene products.

Introduction

The photochemistry of azido complexes of transition metals has continued to be a subject of much interest and many puzzles.[2–8] A substantial portion of the recent interest has derived from the discovery of an efficient photoinduced nitrene pathway in the heavy-metal complexes by Basolo and co-workers.[4] That the nitrene pathway (eq 1) has predominated

$$M(NH_3)_5N_3^{2+} + h\nu + H^+ \xrightarrow{\phi_B I_{a,A}} M(NH_3)_5NH^{3+} + N_2 \qquad (1)$$

for ultraviolet excitations of $Rh(NH_3)_5N_3^{2+}$ and $Ir(NH_3)_5N_3^{2+}$ has been a puzzling contrast to the observation of a redox (eq 2) rather than nitrene pathway for the cobalt

$$Co(NH_3)_5N_3^{2+} + h\nu \xrightarrow[H^+]{} Co^{2+} + 5NH_4^+ + N_3 \qquad (2)$$

analogue.[3,4] Basolo and co-workers[4c] did find evidence for some $Rh(NH_3)_5OH_2^{3+}$ product which they attributed to a conventional photoredox pathway, eq 3 and 4. This proposal

$$Rh(NH_3)_5N_3^{2+} + h\nu \rightarrow Rh(NH_3)_5^{2+} + \cdot N_3 \qquad (3)$$

$$Rh(NH_3)_5^{2+} + [Ox] \xrightarrow[H_2O]{} Rh(NH_3)_5OH_2^{3+} \qquad (4)$$

seemed surprising since flash photolysis studies had failed to provide direct evidence for free radicals[3b] and since rhodium(II) species, in which the metal is presumably low-spin d^7, appear to be labile in two (probably axial) coordination positions.[9,10]

These apparent contradictions and our more general concern with the energetics of photoredox processes[2b,3e,3f] have led us to reexamine the photochemistry of $Rh(NH_3)_5N_3^{2+}$. While this work was in progress, Zink[7] proposed, on the basis of a theoretical model, that (3) and (4) should be replaced by (5)–(7) to describe[11] the nonnitrene pathway reported by

$$Rh(NH_3)_5N_3^{2+} + h\nu \rightarrow Rh(NH_3)_5N_2^{3+} + N^- \qquad (5)$$

$$N^- + H_3O^+ \text{ (or HCl)} \rightarrow NH_2OH \text{ (or } NH_2Cl) \qquad (6)$$

$$Rh(NH_3)_5N_2^{3+} \xrightarrow[H_2O]{} Rh(NH_3)_5OH_2^{3+} + N_2 \qquad (7)$$

Basolo and co-workers. Consequently the present study was expanded to examine explicity this very interesting possibility. Thus, this report of our work brings new experimental evidence to bear on the contradictory mechanistic proposals for the photochemistry of $Rh(NH_3)_5N_3^{2+}$. In addition, a major goal of this report is to make a critical application to rhodium(III) systems of the quasi-thermodynamic analyses which we have been developing recently[3d–g] for the photoredox chemistry of transition metal complexes. In this regard, we have recently noted[3g] that since the primary product ground states are $^2(Rh(NH_3)_5^{2+})$ and $^4(Co(NH_3)_5^{2+})$, respectively, the photoredox behaviors of the acidopentaammines of rhodium(III) and cobalt(III) complexes may differ most in that only for the latter does a low-energy redox decomposition channel exist which does not correlate with the spectroscopic charge transfer to metal transitions (CTTM). On the basis of such a model one would not expect to find photoredox processes to follow from low-energy CTTM excitations of $Rh(NH_3)_5N_3^{2+}$ or of $Ir(NH_3)_5N_3^{2+}$; i.e., the lowest energy CTTM state ought to behave as a "bound state" so that redox decomposition should not be observed until the excitation energy exceeds the threshold for excited-state dissociation.

Experimental Section

A. Materials. The literature synthesis was used to prepare $[Rh(NH_3)_5N_3](ClO_4)_2$ from $[Rh(NH_3)_5OH_2](ClO_4)_3$.[12,13] The three times recrystallized product had somewhat larger absorption coefficients (ϵ(251 nm) 6569 M^{-1} cm^{-1}) than those reported by Schmitdtke (ϵ(251 nm) 5200 M^{-1} cm^{-1}); they were however in reasonable agreement with those reported by Davis and Lalor[13b] (ϵ(251 nm) 6760 M^{-1} cm^{-1}). These larger values of extinction coefficients, ϵ(251 nm) 6569 M^{-1} cm^{-1} and ϵ(335 nm) 690 M^{-1} cm^{-1}, were used in the analysis of the spectroscopic changes following irradiations of $Rh(NH_3)_5N_3^{2+}$. The $[Rh(NH_3)_5Cl]Cl_2$ starting material was obtained from Ventron, Beverly, Mass.

To prepare $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$, 0.33 g of $[Rh(NH_3)_5N_3](ClO_4)_2$ and 3.07 g of NaCl were dissolved in 150 ml of 0.3 M HCl and the solution was irradiated at 254 nm. After the spectrum showed about 80% substrate decomposition, the solution was concentrated by vacuum evaporation near room temperature. The residue was dissolved in 15 ml of 0.3 M HCl, filtered, and then added to a column of Bio-Rad AG-50W-4 cation-exchange resin (30 ml, H-form). The charged resin was washed with 50 ml of 0.3 M HCl; then the cationic complexes were eluted with 2 M HCl in the order $Rh(NH_3)_5N_3^{2+}$, $Rh(NH_3)_5OH_2^{3+}$, and $Rh(NH_3)_5NH_2Cl^{3+}$. The effluent fraction with absorption maximum at 305 nm was collected and concentrated by vacuum evaporation at room temperature. During all of these operations samples were shielded from room light. The residue was combined with 5.5 ml of 0.3 M HCl and filtered; 0.4 ml of concentrated $HClO_4$ was added to the filtrate solution, which was cooled in an ice–water bath. The precipitate obtained by this means was filtered and then washed with 3 ml of ethyl alcohol. Recrystallization of the precipitate was accomplished from 3 ml of solution 0.3 M in HCl by the addition of 1 ml of concentrated $HClO_4$ as above.

Anal. Calcd for $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$: H, 3.19; N, 15.63; Cl, 26.36. Found: H, 3.36; N, 15.88; Cl, 26.37. The electronic

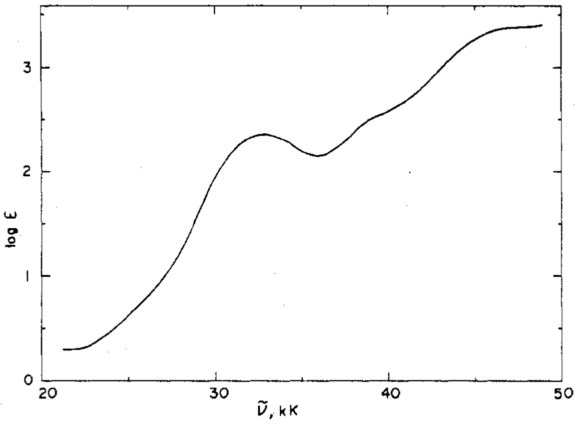


Figure 1. Absorption spectrum of $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$ in 0.3 M HCl.

spectrum of $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$ in 0.3 M HCl consists of an absorption maximum at 305 nm (225 M^{-1} cm^{-1}) and shoulders at 258 nm (304 M^{-1} cm^{-1}) and 210 nm (2416 M^{-1} cm^{-1}) (Figure 1).

Water was redistilled from alkaline permanganate in an all-glass apparatus. Nitrogen streams were purged of oxygen using scrubbing towers filled with chromous solution.

Literature preparations were used for $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$[14] and α-naphthylamine.[15]

The Bio-Rad 50W-X4 (100–200 mesh) resins were used in the acid form. The resin was washed in turn with solutions 6 M in HCl, 30% in NaCl, 2 M in NaOH, and 0.3 M in HCl. No absorbing species were detected in washings from the purified resins.

Other materials were reagent grade or spectroscopic grade and were used without further purification.

B. Photochemical Apparatus and Procedures. The photochemical apparatus used in this study has been described previously[3,16] and will be mentioned briefly here. Irradiations at 254 nm were performed using an Ultraviolet Products, Inc., low-pressure mercury loop lamp ($I_0 \simeq 6 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}), a collimating lens, and a filter solution. Irradiations at $\lambda > 254$ nm were performed using a Xenon Model 727 spectral irradiator. The irradiation wavelengths were selected with a Bausch and Lomb high-intensity monochromator; bandwidths at half-maximum intensity were ±5 nm. Philips spectral emission lamps were used for 214- and 229-nm irradiations. The Xenon Model 720 apparatus was used in the flash photolysis studies.

Actinometry was performed with $K_3[Fe(ox)_3]$ solution[14] before and after photolysis and the values always showed less than 3% variation.

In a typical photolysis experiment, 3 ml of the sample solution, containing $(1–26) \times 10^{-4}$ $M[Rh(NH_3)_5N_3](ClO_4)_2$, 0.7 M NaCl, and 0.30 M HCl was irradiated in a cuvette for predetermined times. The absorbance change was determined at 335 nm or at 251 nm using unphotolyzed sample solution as reference. The solution was then diluted to 10, 25, or 50 ml with 0.1 M NaI and the absorbance measured at 353 nm.

The amount of $Rh(NH_3)_5NH_2Cl^{3+}$ formed in photolyte solutions was determined from the quantity of I_3^- produced in solutions of 0.1 M NaI. The absorbance at 353 nm in 0.1 M NaI was corrected by subtracting that of the photolyzed solution; 26 400 M^{-1} cm^{-1} was used as the absorption coefficient of I_3^- at 353 nm.[18] The amount of $Rh(NH_3)_5N_3^{2+}$ decomposed was determined from the absorbance change at 335 or 251 nm, corrected for the absorbance of $Rh(NH_3)_5NH_2Cl^{3+}$.

C. Analytical Procedures. The initial effluents and washings from columns of cation-exchange resin charged with an aliquot of photolyte were analyzed for N_3^-, NH_2OH, and NH_2Cl. The colorimetric α-naphthylamine method of Feigl,[19] calibrated against known samples, was used for NH_2OH; the very similar method of Staples[20] was also calibrated and used for N_3^-. By use of these methods it was possible to detect as little as 2×10^{-6} M NH_2OH or N_3^-. Uncoordinated NH_2Cl was determined iodometrically.

Results

I. Photochemistry of $Rh(NH_3)_5N_3^{2+}$. A. The Search for Ligand Fragments. 1. NH_2OH. Two different photolyses were performed: solution a was photolyzed to 11% decomposition of $Rh(NH_3)_5N_3^{2+}$ and solution b to 49% decomposition. For solution a $R = 1.45$ (see section IC below) implying that $[Rh(NH_3)_5OH_2^{3+}] = 4.8 \times 10^{-5}$ M; for solution b $R = 1.93$ and the inferred $[Rh(NH_3)_5OH_2^{3+}] = 1.7 \times 10^{-4}$ M. Using the α-naphthylamine method we were unable to detect any NH_2OH in solutions from which the rhodium complexes had been removed; from our determination of the sensitivity of the method, we establish as an upper limit $[NH_2OH] < 3 \times 10^{-6}$ M in both experiments.

2. NH_2Cl (and Similar Oxidants). The initial effluents from cation-exchange resins separately charged with two different photolytes exhibited negligible oxidizing capacity toward I^-: $[\text{equivalents of oxidant}]/\{[Rh(NH_3)_5OH_2^{3+}] + [Rh(NH_3)_6^{3+}\} < 0.01$.

3. N_3^-. We have tried many procedures for the quantitative determination of N_3^-. Each of these procedures has had its unique deficiencies; most of the methods tried were not sufficiently sensitive to determine very small quantities of N_3^-. The results we have included here are based on the very sensitive colorimetric method of Staples;[20] this method, using α-naphthylamine, proved to be somewhat indiscriminate. Thus, the first washings from a charged resin always gave a positive response equivalent to 3×10^{-5} M N_3^- in the solution added to the resin, whether or not the sample had been irradiated. On the basis of this response $[N_3^-]$ was less than 40% of the apparent yield (based on spectroscopic changes) of $Rh(NH_3)_5OH_2^{3+}$ in two experiments photolyzed at 254 nm to about 20% decomposition of $Rh(NH_3)_5N_3^{2+}$. Experiments in which there was 4.3% photodecomposition (254-nm irradiations) of $Rh(NH_3)_5N_3^{2+}$ and in which a sample of substrate was not exposed to radiation gave the same apparent $[N_3^-] = 3.1 \times 10^{-5}$ M. Correction for this "background" response would give $[N_3^-]$ less than 7% of the apparent $[Rh(NH_3)_5OH_2^{3+}]$ for 254-nm irradiations.

We did find evidence for some N_3^- resulting from the longer wavelength irradiations. Because the total quantum yield becomes quite small and the substrate absorbance becomes small for $\lambda > 350$ nm, we do not wish to report a quantitative estimate of the quantum yield of N_3^-. We can set an upper limit: $\phi(N_3^-) \leq 0.01$ for $\lambda \geq 350$ nm.

4. $\cdot N_3$. When $Rh(NH_3)_5N_3^{2+}$ was flash photolyzed in the presence of $[I^-] \leq 9 \times 10^{-4}$ M (2.5×10^{-2} M KI filter solution), there was no evidence of I_2^- on the first flash. Since the $(\cdot N_3 + I^-)$ reaction is very rapid,[2b,3b] we can rule out formation of $\cdot N_3$ as a major photoprocess. Flash photolysis of $Rh(NH_3)_5NH_2Cl^{3+}$ in chloride solutions did produce the Cl_2^- transient.

B. The Rhodium Products. In our hands ion-exchange chromatography nicely separated $Rh(NH_3)_5NH_2Cl^{3+}$ from $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5N_3^{2+}$. The chloramine fraction yielded some $[Rh(NH_3)_6](ClO_4)_3$ upon concentration and recrystallization. Thus we would infer that both $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_6^{3+}$ should be considered as possible photolysis products. Since the aquopentaammine and hexaammine are found in smaller yield and since both absorb less strongly than $Rh(NH_3)_5NH_2Cl^{3+}$, quantitative discrimination between these species has not been possible in our hands. No additional rhodium(III) products were found for excitations with $\lambda \geq 254$ nm.

Two distinct photochemical processes appeared to result from 214-nm excitations: (1) a temperature-independent process yielding the nitrene species and (2) a temperature-dependent process. When samples of photolyte from the 214-nm irradiations of solutions thermostated at 70 °C were heated in 0.1 M NaI, *trans*-$Rh(NH_3)_4I_2^+$ formed in an amount corresponding to a quantum yield of ~0.04. Similar treatment of samples of photolyte from 214-nm (at 25 °C) or 254-nm (at 25 or 70 °C) irradiations of $Rh(NH_3)_5N_3^{2+}$

Table I. Quantum Yields from Irradiations of $Rh^{III}(NH_3)_5X$ (in 0.7 M NaCl, 0.3 M HCl)

X	Excitation Wavelength, nm	$10^5 I_0$, einsteins $l.^{-1}$ min^{-1}	$\phi(\Delta[Rh^{III}(NH_3)_5X])$	$\phi(Rh(NH_3)_5NH_2Cl^{3+})$
N_3^-	214	4.5	0.040 ± 0.02 (2)	0.006 ± 0.002 (2)
	229	1.0	0.120 ± 0.05 (3)	0.120 ± 0.05 (3)
	254	31	0.184 ± 0.003 (2)	0.121 ± 0.002 (2)
		6.0	0.190 ± 0.006 (3)	0.14 ± 0.01 (3)
		2.6	0.21 (1)	0.15 (1)
	300	6.3	0.094	0.068 (1)
	350	9.0	0.045 (1)	0.037 (1)
		7.1	0.047 (1)	0.038 (1)
	394	9.1	0.039 (1)	0.031 (1)
		8.4	0.039 (1)	0.034 (1)
NH_2Cl	254	31	0.07 ± 0.001 (2)	
	350	9	$\leqslant 0.18$	

did not result in the formation of detectable $Rh(NH_3)_4I_2^+$.

C. Quantum and Product Yields. The determination of accurate quantum yields in this system has been a very difficult and frustrating problem. One aspect of the difficulty has been the variability of the quantum yields of $Rh(NH_3)_5NH_2Cl^{3+}$, which we have now shown to depend on the conditions of the photolysis. At times during our studies these yields seemed more a function of the investigator, perhaps the laboratory, than of systematic physical or chemical parameters. The results reported here have proved reasonably reproducible. In order to obtain them, we have had to be scrupulously careful of each of the following.

(1) Substrate Purity. $[Rh(NH_3)_5N_3](ClO_4)_2$ was recrystallized until the complex absorptivity agreed well with the data of Davis and Lalor.[13b]

(2) Product Absorptivity. Since $Rh(NH_3)_5NH_2Cl^{3+}$ absorbs significantly, this absorbance had to be taken into account in spectroscopic determinations of the amount of $Rh(NH_3)_5N_3^{2+}$ decomposed. The absorbancies of $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_6^{3+}$ are not large enough to make a significant contribution at 335 nm.

(3) Analytical Manipulations. We worked under conditions which minimized the number of transfers or dilutions of photolyte solutions (e.g., substrate absorbance changes were determined on undiluted photolyte solutions whenever possible).

(4) Substrate Concentration. This had to be large enough to give reasonable absorbance changes for small percentages of substrate decomposition.

Even with the greatest precautions, our data were generally scattered for small percentages of substrate decomposition (<5%). The major source of error for our determinations are obvious: for ~1% substrate decomposition and a total absorbance of about 2, one must determine an absorbance change of 0.02 and the optimum spectrophotometer response (>0.003 absorbance unit) results in approximately a 30% error in the determination. This error can be reduced somewhat by a differential absorbance measurement; however the concomitant loss of sensitivity in such determinations can lead to systematic errors in the determination of very small absorbance changes (e. g., see Figure 7[21]). Any dilution of the photolyte, even with calibrated apparatus, would necessarily double the error in determination of such small absorbance changes. Further, the more dilute the solution, the smaller the absorbance change corresponding to 1% decomposition and the larger the percentage error in the absorbance determination. At the highest concentrations, $(3–6) \times 10^{-3}$ M, the differences between duplicate determinations imply that our errors average about ±20% for less than 5% substrate decomposition.

The second major problem has been identification of the source of $Rh(NH_3)_5OH_2^{3+}$ and/or $Rh(NH_3)_6^{3+}$ and the determination of the yields of these species. This problem is to a significant extent a corollary of the first. In order to examine this problem critically we have examined product yields under a variety of conditions. For limited substrate decomposition, plots of concentration (substrate or product) vs. irradiation time were nearly linear, more or less consistent with the report of Reed et al.;[4c,22] however, such plots were definitely curved for high percentages of substrate decomposition. Quantum yield data in Table I are based on the initial slopes of such plots. For a more critical analysis of the photochemical behavior of the system it is useful to represent the experimental product yields in a somewhat different manner.

Since the total concentration of rhodium, $[Rh_T]$, in a given photolysis solution is constant and since there is evidence for only three possible rhodium products, we have defined a yield ratio, R, such that

$$R = ([Rh_T] - [Rh(NH_3)_5N_3^{2+}])/[Rh(NH_3)_5NH_2Cl^{3+}]$$

The numerator of this expression is equal to the sum of the concentrations of weakly absorbing as well as chloramine product species, i.e., we may assume $[Rh_T] - [Rh(NH_3)_5N_3^{2+}] = [Rh(NH_3)_5OH_2^{3+}] + [Rh(NH_3)_6^{3+}] + [Rh(NH_3)_5NH_2Cl^{3+}]$. If all of the photoproducts are produced from decompositions of excited states of $Rh(NH_3)_5N_3^{2+}$, then a plot of R vs. the percentage of substrate decomposition, $100 \cdot ([Rh_T] - [Rh(NH_3)_5N_3^{2+}])/[Rh_T]$, should have a slope of zero and $R = (1 + \phi_X/\phi_N)$ where ϕ_X is the quantum yield of weakly absorbing rhodium species ($Rh(NH_3)_6^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$) and ϕ_N is the quantum yield of $Rh(NH_3)_5NH_2Cl^{3+}$.

We find that R is a function of the extent of substrate decomposition (Figures 2 and 3; Table II[21]), the excitation wavelength (Figure 2), and the concentration of substrate (Figure 3). If the data for small extents of photolysis (<10%) in Figure 2A are averaged, there appears to be some curvature with R possibly approaching a value of unity. A linear extrapolation of the points for greater than 5% $Rh(NH_3)_5N_3^{2+}$ decomposition would give $R = 1.39$ for the data in Figure 2A ($[Rh_T] = 2.6 \times 10^{-3}$ M and $I_0 = 3 \times 10^{-4}$ einstein $l.^{-1}$ min^{-1} at 254 nm). Similar extrapolations of data in Figure 3 for smaller $[Rh_T]$ would give $R = 1.0$; the analytical errors are of course magnified at these concentrations.

II. Photochemistry of $Rh(NH_3)_5NH_2Cl^{3+}$. Irradiations of $Rh(NH_3)_5NH_2Cl^{3+}$ result in reasonably systematic changes of near-ultraviolet absorbance and some not so straightforward absorbance changes in the deeper ultraviolet (see Figure 4). Since we were only able to prepare a few tenths of 1 g of the purified complex, we were unable to make extensive separations and characterizations of the photoproducts. Nevertheless, the absorbance changes at the longer wavelengths are consistent with formation of $Rh(NH_3)_5OH_2^{3+}$, *trans*-Rh-

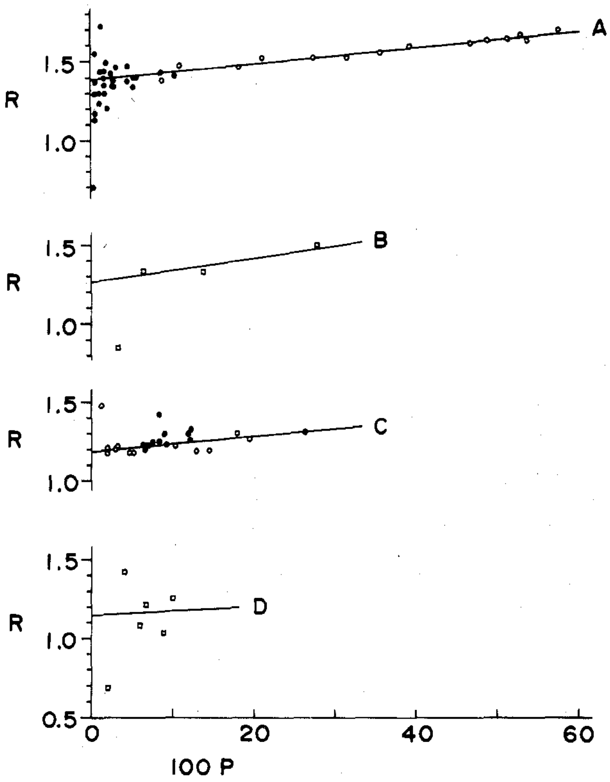


Figure 2. Relationship between the product ratio R and the percent conversion ($100P$) for various excitation wavelengths: A, 254 nm (●, $I_0 = 7.3 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}; ○, $I_0 = 3.1 \times 10^{-4}$ einstein $l.^{-1}$ min^{-1}); B, 300 nm ($I_0 = 6.3 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}); C, 350 nm (●, $I_0 = 7.2 \times 10^{-6}$ einstein $l.^{-1}$ min^{-1}; ○, $I_0 = (8 \pm 1) \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}); D, 394 nm ($I_0 = 8.5 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}). Initial $[Rh(NH_3)_5N_3^{2+}] \simeq 2 \times 10^{-3}$ M; 0.3 M HCl, 0.7 M NaCl. Points plotted are for single determinations. The scatter of points for replicate determinations is indicative of the error statistics (see text). Note that the error in determination of R becomes very large as the absorbance change measured approaches zero (e.g., as $P \to 0$).

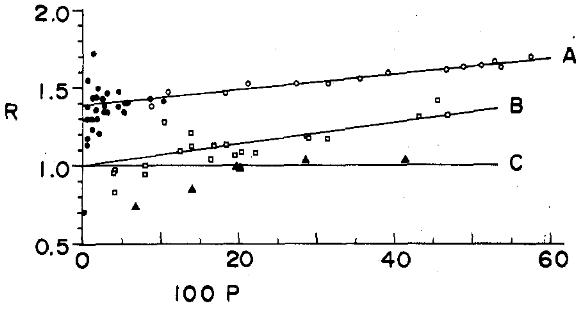


Figure 3. Relationship between the product ratio R and the percent conversion ($100P$) for 254-nm irradiations of different substrate concentrations in 0.3 M HCl and 0.7 M NaCl: A, $[Rh_T] = 2.6 \times 10^{-3}$ M (●, $I_0 = 7.3 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}; ○, $I_0 = 3.1 \times 10^{-4}$ einstein $l.^{-1}$ min^{-1}); B, $[Rh_T] = 2 \times 10^{-4}$ M ($I_0 = 6.0 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}); C, $[Rh_T] = 0.97 \times 10^{-4}$ M ($I_0 = 6 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}).

$(NH_3)_4(OH_2)_2^{3+}$, and $Rh(NH_3)_5NH_2OH^{3+}$ or with mixtures of the aquo–, chloramine–, and hydroxylamine–pentaammine or –tetraammine complexes. The relatively small changes of absorbance at shorter wavelengths are not consistent with contributions of only aquo and ammine complexes of rhodium(III). We found $Rh(NH_3)_5NH_2Cl^{3+}$ to be stable in the dark for more than 16 h in solutions such as those photolyzed.

We have used changes in the iodometrically determined $[Rh(NH_3)_5NH_2Cl^{3+}]$ to determine the photodecomposition quantum yield of this complex. The zero-order plots of

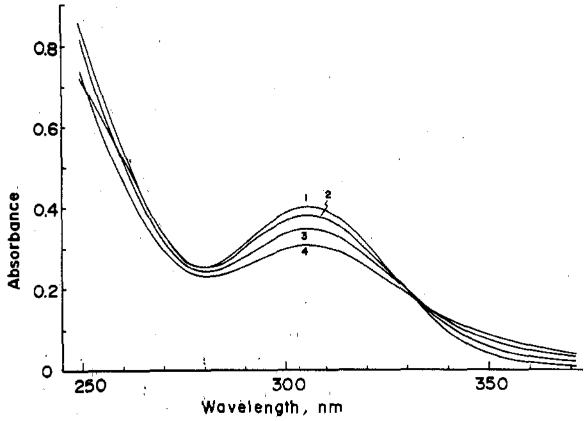


Figure 4. Changes of absorption spectra for 254-nm photolyses of $Rh(NH_3)_5NH_2Cl^{3+}$ in 0.3 M HCl and 0.7 M NaCl. Duration of exposure: 1, 0 min; 2, 7 min; 3, 17 min; 4, 30 min.

$[Rh(NH_3)_5NH_2Cl^{3+}]$ vs. irradiation time were nearly linear to about 50% decomposition for 254-nm irradiation. Appreciable negative curvature of the zero-order plots was found for 350-nm irradiations; such curvature is suggestive of a secondary photolysis effect. The quantum yields are 0.07 ± 0.01 for 254-nm irradiations ($I_0 = 7.3 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}) and ≤0.18 for 350-nm irradiations ($I_0 = 7.0 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}), from the initial slopes of the zero-order plots.

Discussion

A. Photochemistry of $Rh(NH_3)_5N_3^{2+}$. A major matter of concern has been the source of the weakly absorbing rhodium(III) products ($Rh(NH_3)_5OH_2^{3+} + Rh(NH_3)_6^{3+} + \ldots$). That the yield of hydroxylamine or chloramine was found to be less than about 2% of ($[Rh_T] - [Rh(NH_3)_5N_3^{2+}] - [Rh(NH_3)_5NH_2Cl^{3+}] = [Rh_A]$) rules out Zink's mechanism,[23-26] eq 5–7, as a major source of such species. The undetectably small yields of either free radicals or *trans*-$Rh(NH_3)_4(OH_2)_2^{3+}$ products makes the Reed–Gafney–Basolo mechanism, eq 3 and 4, implausible. Although the results are more ambiguous, we do not believe there is appreciable photoaquation of azide (ϕ ≤0.01).

On the other hand, the observed variation of the product ratio R with the extent of photodecomposition of $Rh(NH_3)_5N_3^{2+}$ demonstrates unambiguously that secondary photolysis does contribute to the yield of weakly absorbing rhodium species. The photoproducts from irradiation of $Rh(NH_3)_5NH_2Cl^{3+}$ are weakly absorbing species and there is some evidence for free-radical intermediates. A free-radical decomposition mode for $Rh(NH_3)_5NH_2Cl^{3+}$ in the presence of $Rh(NH_3)_5N_3^{2+}$ could tend to magnify the rate of production of weakly absorbing species; e.g., reactions such as indicated in (8)–(11) produce 3 mol of weakly absorbing

$$Rh(NH_3)_5NH_2Cl^{3+} + h\nu \xrightarrow{\phi_c I_{a,B}} Rh(NH_3)_5NH_2^{3+} + \cdot Cl \tag{8}$$

$$H_2O + \cdot Cl + Rh(NH_3)_5N_3^{2+} \to Rh(NH_3)_5OH_2^{3+} + Cl^- + \cdot N_3 \tag{9}$$

$$H_3O^+ + Rh(NH_3)_5NH_2^{3+} + Rh(NH_3)_5N_3^{2+} \to Rh(NH_3)_6^{3+} + Rh(NH_3)_5OH_2^{3+} + \cdot N_3 \tag{10}$$

$$2(\cdot N_3) \to 3N_2 \tag{11}$$

products per mole of $Rh(NH_3)_5NH_2Cl^{3+}$ decomposed. Our attempts to develop a kinetic treatment which would analyze the data in Figures 2 and 3 in terms of the essential mechanistic features embodied in reactions 1 and 8–11 have not resulted in useful analytical expressions since (1) photolyses were performed under highly absorbing conditions where Beer's law cannot be linearized, (2) as a consequence of (1) the region of the photolysis cell between the light source and the bulk of the photolyte must contain a relatively high concentration of product (i.e., concentration gradients are generated), and (3) inner filter effects cannot be neglected.[27] Some sense of the magnitude of these complications can be obtained from a simplied analysis of the manifestations of secondary photolysis in this system. Thus we estimate from Figure 2A that $\mathrm{d}R/\mathrm{d}P \simeq 0.4$ at 10% substrate decomposition ($P = 0.1$). Since

$$R = P[\mathrm{Rh(III)}]_{\mathrm{total}}/\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}]$$

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{[\mathrm{Rh_T}]}{[\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}]}\left(\frac{\mathrm{d}P}{\mathrm{d}t}\right) - \frac{[\mathrm{Rh_T}]P}{[\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}]^2}\left(\frac{\mathrm{d}[\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}]}{\mathrm{d}t}\right)$$

and

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{Rh(NH_3)_5N_3{}^{2+}}]}{\mathrm{d}t}\left(\frac{1}{[\mathrm{Rh_T}]}\right)$$

substitution from eq 1 and 8, using stationary-state values for [·Cl] and [$\mathrm{Rh(NH_3)_5NH_2{}^{3+}}$], and division by $\mathrm{d}P/\mathrm{d}t$ gave the slope as

$$\frac{\mathrm{d}R}{\mathrm{d}P} = \frac{[\mathrm{Rh_T}]}{[\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}]} \Bigg/ \left(1 - \frac{[\mathrm{Rh_T}]P}{[\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}]}\left(\frac{\phi_\mathrm{B}I_{\mathrm{a,A}} - \phi_\mathrm{c}I_{\mathrm{a,B}}}{\phi_\mathrm{B}I_{\mathrm{a,A}} - 2\phi_\mathrm{c}I_{\mathrm{a,B}}}\right)\right)$$

Since [$\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}$]/[$\mathrm{Rh_T}$] $\simeq 0.07$ for $P = 0.1$ in Figure 2A, substitution of experimental values into this expression for $\mathrm{d}R/\mathrm{d}P$ indicates that $\phi_\mathrm{c}I_{\mathrm{a,B}}/\phi_\mathrm{B}I_{\mathrm{a,A}} \approx 0.14$ and $I_{\mathrm{a,B}}/I_{\mathrm{a,A}} \approx 0.34$. This is much greater than the ratio of $I_{\mathrm{a,B}}/I_{\mathrm{a,A}}$ based on the relative absorptivities of a homogeneous solution in which [$\mathrm{Rh(NH_3)_5NH_2Cl^{3+}}$] ≈ 0.08[$\mathrm{Rh(NH_3)_5N_3{}^{2+}}$]. However, we note that in the experiments represented in Figure 2A, the absorbance at 254 nm (the photolysis wavelength) is about 18 and about 90% of the incident radiation is absorbed in the first 0.6 mm of exposed solution. At our light intensities 10–20% of the substrate in this volume would be decomposed in 2 s of irradiation (i.e., for about $^1/_{20}$th of the irradiation period required to achieve 10% substrate decomposition) so most of the products are generated near the surface of the photolysis cell, not homogeneously through the solution, and under these circumstances photolysis of the products becomes disproportionately important. Consistent with this qualitative argument, Figures 2 and 3 demonstrate that values of R become smaller as the substrate absorbance at the excitation wavelength is decreased (i.e., as λ increases or as [$\mathrm{Rh(NH_3)_5N_3{}^{2+}}$] decreases); thus we infer that secondary photolysis becomes less important as the volume of photolyte traversed by the photolysis beam becomes greater. Furthermore, R is found to approach a value of unity for conditions of decreasing absorbance at the photolysis wavelength.

We conclude that eq 1 adequately describes the predominant mode of photodecomposition of $\mathrm{Rh(NH_3)_5N_3{}^{2+}}$ for excitations at λ >254 nm in acidic solutions. We find strong evidence for contribution of secondary photochemical processes such as described in eq 8–11, and we find no evidence for any source of $\mathrm{Rh(NH_3)_5OH_2{}^{3+}}$ other than secondary photolysis. Thus we conclude that the $\mathrm{N_3{}^-} \rightarrow$ Rh(III) charge-transfer photochemistry of $\mathrm{Rh(NH_3)_5N_3{}^{2+}}$ is different in kind from the $\mathrm{N_3{}^-} \rightarrow$ Co(III) charge-transfer photochemistry of $\mathrm{Co(NH_3)_5N_3{}^{2+}}$. In fact the recently evolved[2b,3d–f] models for the photoredox behavior of transition metal complexes would strongly argue that such a qualitative contrast in behavior should exist since the excited cobalt system may decompose through a relatively low-energy reaction channel which leads to formation of a high-spin cobalt(II) species and since such a low-energy reaction channel is not available to an excited rhodium system.

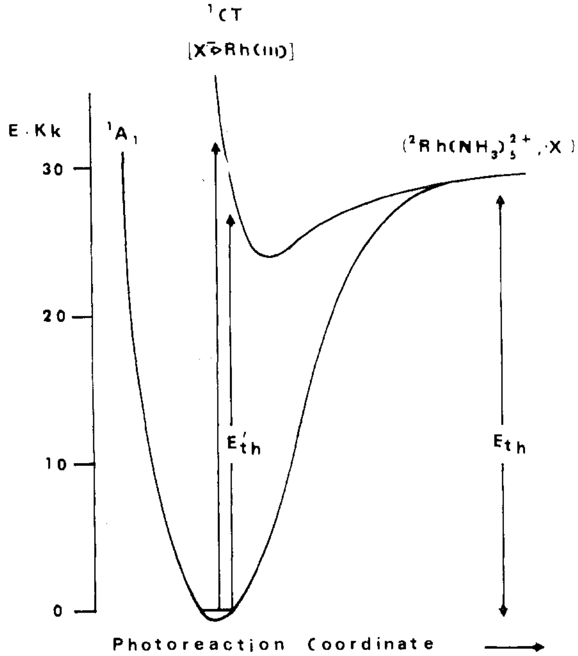


Figure 5. Qualitative representation of potential energy manifolds for the ground state and lowest CTTM state of $\mathrm{Rh^{III}(NH_3)_5X}$ complexes. Numerical values of parameters are based on $\mathrm{Rh(NH_3)_5I^{2+}}$.

B. Some Considerations of the Energetics of Redox Decompositions of Rhodium(III) Complexes. The work of Kelly and Endicott[8] demonstrated a photoredox decomposition mode in $\mathrm{Rh(NH_3)_5I^{2+}}$. The threshold energy for redox decomposition of this complex may be estimated very approximately as $E_{\mathrm{th}} \simeq 3.0\ \mu\mathrm{m}^{-1}$ from the data in ref 8. This may be compared to an estimated threshold energy of $E_{\mathrm{th}} \simeq 1.7\ \mu\mathrm{m}^{-1}$ for $\mathrm{Co(NH_3)_5I^{2+}}$.[2d,3e] From these quantities and the appropriate spectroscopic parameters we estimate that the lowest energy CTTM state has about 0.4 $\mu\mathrm{m}^{-1}$ mol^{-1} "binding energy" with respect to dissociation into a "radical" pair species {$\mathrm{Rh(NH_3)_5{}^{2+}}$,·I} as indicated in Figure 5. Further we may estimate $\Delta H° \approx 1.8\ \mu\mathrm{m}^{-1}\ \mathrm{mol}^{-1}$ for the $\mathrm{Rh(NH_3)_5OH_2{}^{3+}}|\mathrm{Rh(NH_3)_5{}^{2+}}$ couple.[28] These quantities lead to $E_{\mathrm{th}} \approx 3.5\ \mu\mathrm{m}^{-1}$ for the onset of photoredox behavior in $\mathrm{Rh(NH_3)_5N_3{}^{2+}}$.[2b,3e] Our experimental observations seem to indicate that $E_{\mathrm{th}} \gtrsim 3.9\ \mu\mathrm{m}^{-1}$, which is reasonably consistent with the estimate in view of the current uncertainties of the energetics of rhodium systems and the experimental difficulties in detecting very small redox yields[29] in the presence of a predominant nitrene pathway.

C. The Nitrene Pathway. Consideration of the enthalpies (or free energies) of formation of product species indicates that the failure to observe nitrene decomposition pathways may be more surprising than their observation.[24,30,31] For example the minimum energy required to form nitrene (and $\mathrm{N_2}$) from $\mathrm{HN_3}$ is only 0.33 $\mu\mathrm{m}^{-1}$ mol^{-1} [31] which may be compared with the excitation range of 2.0–4.0 $\mu\mathrm{m}^{-1}$ used in this and other studies of transition metal azides. While the M–N bonds may be somewhat weaker than the H–N bond, this difference in bond energy cannot be more than a small fraction[32] of the noted discrepancy between excitation energy and the threshold energy for product formation. Thus it appears that the

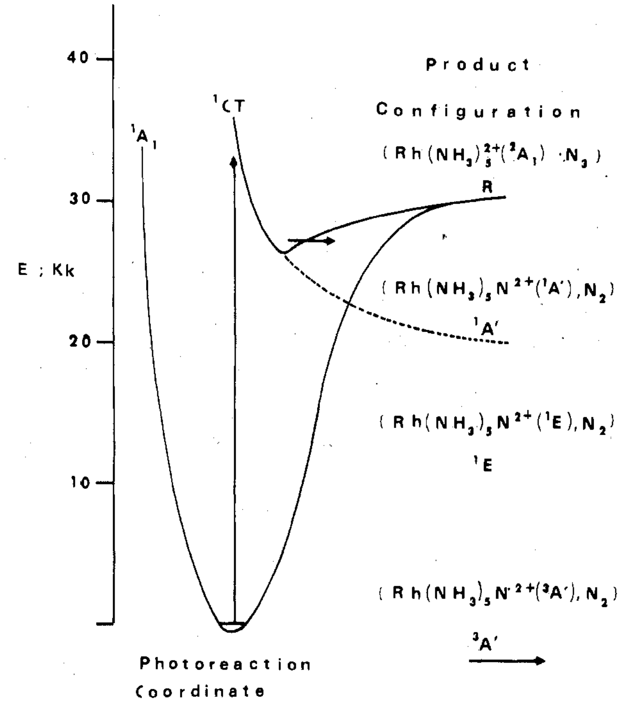
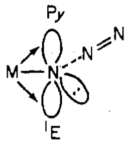


Figure 6. Qualitative representation of potential energy manifolds for the ground state and the lowest excited state and the relative energy of various possible product configurations for $Rh(NH_3)_5N_3^{2+}$. Dinitrogen, the azide radical, and $Rh(NH_3)_5^{2+}$ are taken to be in their electronic ground states. The energies of the different electronic configurations of the nitrene fragment are based on the energies of the corresponding states in NH.[31]

thermodynamically most feasible excited-state decomposition mode for azidocobalt(III) complexes does not occur. The prohibition against this decomposition mode must be quantum mechanical in origin, and the quantum mechanical constraints must be somehow relaxed for the heavy-metal analogues containing no other π-acceptor ligands (Miskowski et al.[8] have found contrasting behavior for the heavy-metal–cyano complexes).

The three lowest energy decomposition pathways of HN_3 yield N_2 in its ground electronic state and NH in its ground ($^3\Sigma^-$) and first two excited ($^1\Delta$ and $^1\Sigma^+$, respectively) electronic states. The energetics of the decomposition of metalloazides should differ from those of HN_3 only by the amount of the differences between M–N_3, H–N_3, M–N, and H–N bond energies. If one assumes the principal bonding interactions are σ in character, thus similar in H–X and M–X (S = N_3 or N), then the hierarchy of primary product "states" will be qualitatively as indicated in Figure 6 where the $^3A'$ state is derived from ($^3\Sigma^-$)NH, ^1E from ($^1\Delta$)NH, and $^1A'$ from ($^1\Sigma^+$)NH. The $Rh(NH_3)_5N^{2+}$ product species are all energetically more accessible from excited states populated by the photochemical excitations than are the redox products. For $Co(NH_3)_5N_3^{2+}$, the $^1A'$ products have energies equal to or higher than the energies of the redox products containing quartet $Co(NH_3)_5^{2+}$, but the ^1E and $^3A'$ products remain energetically more favorable. Of these lower energy product configurations, formation of ^1E is orbitally forbidden while formation of $^3A'$ is spin forbidden. Obviously the exact energies of these product configurations are unknown at this time. We have made only the simplest assumptions in constructing Figure 6.

The difference between the d^6 metalloazides seem most naturally described in terms of the ^1E product configuration. For example, approximate sp^2 hybridization of the innermost nitrogen would allow for stabilization of this configuration by metal-to-ligand ($d_{yz} \rightarrow$ vacant p_y) back-bonding as indicated in I for ^1E. On the other hand, electronic repulsions should



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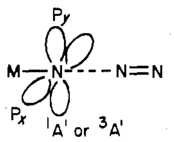

II

lead to smaller back-bonding interactions with the singly occupied p_x and p_y orbitals of the inntermost nitrogen in the $^1A'$ and $^3A'$ configurations (see II). Back-bonding to azide in the ground state has been claimed to be insignificant for cobalt(III)[32] but undoubtedly increases in significance for the heavier metals. The greater the back-bonding interactions, the more readily one would expect the excited complex to decompose through a reaction channel leading to nitrene products.

The possible correlation of the ^1E product configuration to variations in photochemical reactivity raises some interesting points with regard to the thermal production of nitrenes. Thus appreciable back-bonding plus protonation of the nonbonding electron pair could lower the ground state – ^1E energy difference from 193 kJ/mol in HN_3 to only a few kilojoules per mole in $(NH_3)_5IrN_3^{2+}$, thus providing a convenient metal-dependent and acid-dependent pathway for thermal generation of intermediate nitrene complexes.[17]

The thermochemical considerations outlined above also make it evident that the mechanism proposed by Zink,[7,11] eq 5–7, fails because the proposed product configuration, $\{Rh(NH_3)_5N_2^{3+},N^-\}$, can only be formed at an energy greater by at least 0.7 μm^{-1} [33] than the energy required to form $\{Rh(NH_3)_5N^{2+},N_2\}$.

Finally it should be noted that the photochemistry of oxalato–amine complexes of cobalt(III) is similar in a number of features to the systems discussed above in that (a) the heterolytic cleavage of a coordinated ligand ($C_2O_4^{2-} \rightarrow CO_2^{2-} + CO_2$) has been found to result from CTTM excitations,[34] (b) one of the products of this reaction is an exceptionally stable molecular species (CO_2), and (c) the energy of the primary product species ($M{-}CO_2^- + CO_2$) is relatively small compared to the energy of the photochemical excitations used. It is likely in this case also that the correlated ligand-centered excited state probably involves the generation of an electron-deficient atom (C) in near proximity to an electron-rich metal (by means of a n → π^* transition) so that back-bonding effects may again play a crucial role in determining the pathway for excited state decomposition.

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Registry No. $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$, 60479-90-5; $Rh(NH_3)_5N_3^{2+}$, 21393-76-0.

Supplementary Material Available: Table II listing photochemical data and Figure 7 showing systematic variations of *R* for low percent conversion (5 pages). Ordering information is given on any current masthead page.

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(1) (a) Partial support of this research by the National Science Foundation and the National Institutes of Health is gratefully acknowledged. (b) Presented in part at the 168th National Meeting of the American Chemical Society, Chicago, Ill., 1973; see Abstracts, No. INOR 143.

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(11) Actually in ref 7, Zink proposed formation of $Rh(NH_3)_5N_2^{2+} + \cdot N$. Naturally the production of nitrogen atoms is highly unlikely for low-energy excitations and the evidence of the present report and of ref 3b rules out such a pathway. Apparently this representation of the results of Zink's calculations was a misprint: J. I. Zink, private communication to J.F.E., 1975. Zink has also pointed out to us that "reactions 5 and 7 could occur from the *high* energy MTLCT state according to the calculations and will occur only *if* there is a wavelength dependence and *if* the reaction originates from the high energy MTLCT state" (J. I. Zink, private communication, June 22, 1976). While there is a wavelength dependence, we have been unable to identify the "high energy MTLCT state".

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(21) Supplementary material.

(22) We have been unable to quantitatively or consistently reproduce the linearity of $\Delta[Rh(NH_3)_5N_3^{2+}]$ with exposure time which Reed et al.[4c] reported in their Figure 1. We believe the discrepancy lies in the measurement limits discussed in section C2. Reed et al.[4c] used a 6.4 $\times 10^{-4}$ M solution of $Rh(NH_3)_5N_3^{2+}$ and reported changes of concentration of substrate ranging from 9×10^{-6} to 8×10^{-5} M. Assuming a single calibrated dilution and optimal spectrophotometric precision, we would estimate the errors in these determinations to vary from ~60% to ~7%, respectively.

(23) Since one would expect generation of NH in solution to result in formation of NH_2Cl, $NHCl_2$, and/or NCl_3 under the photolysis conditions,[24-26] the observation that $\Delta[Rh(NH_3)_5N_3^{2+}] \geq$ equivalents of oxidant is qualitatively inconsistent with Zink's mechanism.

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(27) We, together with Professor R. R. Schroeder, have attempted to devise a computer model to simulate photolyses of optically dense solutions. In developing this model we noted that photolysis of an optically dense substrate followed by photolysis of a primary product is similar in many regards to the electrolysis of a substrate to generate an electrochemically active intermediate. In each instance one can distinguish a localized, chemically important region (the electrochemical double layer and a "photolysis" layer) from the bulk solution; in both cases a concentration gradient is established with a diffusional replacement of substrate in the chemically active region. The secondary photolysis effect described in this paper is similar to effects following the depletion of substrate in an electrochemical double layer. Owing to the expense of the computer program developed we were only able to simulate situations where the photolysis rate was large compared to the diffusion rate. In this limit values of dR/dP were profoundly dependent on the choice of boundary conditions.

(28) For detailed discussions of such estimates see ref 2b, 3e, and 3f.

(29) One would expect smaller net redox quantum yields for rhodium(III) complexes than for cobalt(III) complexes on the basis that rhodium(II) is likely to be a better reducing agent than cobalt(II), making cage recombination more likely (see ref 2, 3e). Furthermore, if the relative redox yields of $Co^{III}(NH_3)_5X$ complexes are roughly the same as those for $Rh^{III}(NH_3)_5X$ complexes (i.e., $\phi(X = I)/\phi(X = N_3) \approx 3$) one might expect a maximum value of $\phi_{redox} \approx 0.08$ for $Rh(NH_3)_5N_3^{2+}$. This value should decline to zero at the threshold, and one might expect $\phi_{redox} < 0.02$ at 3.9 μm^{-1} even with a 3.5-μm^{-1} threshold energy. On the basis of our observations we would set $\phi_{redox} \leq 0.01$ at 3.9 μm^{-1}.

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Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2E1

Solvent Effects on Dissociation of the Monocomplex of Nickel(II) with Isoquinoline

P. K. CHATTOPADHYAY and B. KRATOCHVIL*

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Dissociation rate constants and associated activation parameters for the monocomplex of nickel(II) with isoquinoline in acetonitrile and propylene carbonate as solvents were obtained from measurements by stopped-flow spectrophotometry. Overall equilibrium constants for formation of the complex in water, methanol, dimethyl sulfoxide, and *N*,*N*-dimethylformamide were obtained from spectrophotometric measurements. Dissociation rate constants and associated activation parameters in water, methanol, dimethyl sulfoxide, and *N*,*N*-dimethylformamide are calculated. Neither dissociation rate constants nor equilibrium constants for complex formation correlate with Gutmann's donicity scale for solvents, but the enthalpy of activation for dissociation of the complex ($\Delta H_b^{\ddagger}$) shows a linear relationship with solvent donicity.

Introduction

Although an improved understanding of solvent properties is emerging from recent studies on the formation of labile metal–ligand complexes in various solvents, few kinetic studies on the dissociation of labile complexes in solution, especially in nonaqueous solvents, have been made. Results of kinetic studies of substitution reactions in water,[1] methanol,[2] ethanol,[3] acetonitrile,[4] and *N*,*N*-dimethylformamide[5] indicate that formation of labile complexes of nickel(II) with many ligands proceeds by a dissociative type of interchange mechanism[6] (I_d), and the rate of solvent exchange between NiS_6^{2+} (where S is a solvent molecule) and bulk solvent is the rate-controlling step. The exact mechanism of substitution at nickel(II), however, even with "simple" monodentate ligands, has not been ascertained as yet in dimethyl sulfoxide.[5a] With nickel(II) and a monodentate ligand L, the pathways of an I_d type