Charge-Transfer Photochemistry of Azido Complexes of Cobalt(III) and Rhodium(III). Observations on the Chemistry of Flash Photolytically Generated Nitrenes[1]

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Solutions of $Rh(NH_3)_5N_3{}^{2+}$ have been flash photolyzed and the reactions of intermediate species have been observed under a variety of conditions. Flash photolysis produces a transient bleaching of substrate absorptivity in the near-ultraviolet spectrum; regeneration of absorbance in this region is associated with reactions of the primary photoproducts, $Rh(NH_3)_5N^{2+}$ and $Rh(NH_3)_5NH^{3+}$, and their several successors. In solutions of low acidity $Rh(NH_3)_5N^{2+}$ and $Rh(NH_3)_5$-NH^{3+} dimerize to form two new transient species, related through a protonation reaction, which absorb strongly in the visible region of the spectrum. The dimerization reactions proceed in competition with reactions of the photoproducts with Cl^- or I^-. The reaction with I^- proceeds in three distinguishable steps, exhibited in the formation and decay of a transient intermediate followed by the formation of I_3^-. It is proposed that a number of features of the chemistry of complex nitrenes, *e.g.*, the dimerization reactions, are similar for several metals and that differences in overall reaction products can be accounted for in terms of a kinetic competition of different possible reaction pathways. Related cobalt(III) complexes, including $Co(CN)_5N_3{}^{3-}$, undergo photoredox reactions yielding predominantly azide radicals and cobalt(II).

Introduction

Basolo and coworkers have recently reported evidence that coordinated nitrene (nitrene = NH) intermediates are involved in chemical[2,3] and photochemical[4] decomposition of azido complexes of ruthenium,[2,3] iridium,[2-4] and rhodium.[4] For example, in the case of $Rh(NH_3)_5N_3{}^{2+}$ the nitrene, $Rh(NH_3)_5NH^{3+}$, has been postulated[4] as the reactive intermediate in the photochemical production of $Rh(NH_3)_5NH_2Cl^{3+}$

$$Rh(NH_3)_5N_3{}^{2+} + h\nu + 2H^+ + Cl^- \rightarrow Rh(NH_3)_5NH_2Cl^{3+} + N_2 \qquad (1)$$
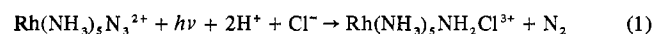
Mechanistic studies of metallonitrene complexes have been rare. There have been no previous applications of transient methods to the direct observation of the reactions of these proposed intermediates. For this reason we have undertaken a flash photolysis study of solutions of $Rh(NH_3)_5N_3{}^{2+}$. In this application the flash photolysis technique proves to be a useful tool for generating short-lived intermediate species. Aspects of the present study substantiate many features of the chemistry of $Rh(NH_3)_5NH^{3+}$ postulated by previous workers,[4] but we have also been able to explore the stepwise details of some of these reactions and to find reaction modes previously unsuspected in the rhodium complexes.

It has been argued[2-4] that nitrene intermediates should be far less important in the chemistry of first-row transition metal complexes than for complexes of the heavier metals. Since previous photochemical studies of cobalt(III) azide complexes had not considered the possible intermediacy of nitrene complexes,[5,6] we have attempted to use flash photolysis techniques as means of detecting such intermediates in these cases also.

The present report focuses largely on the chemical behavior of nitrene intermediates. Complementary to the present report we have made an extensive investigation of the photochemical behavior (*i.e.*, product yields obtained for different excitation energies) of azido complexes of cobalt(III) and rhodium(III). We have found several wavelength-dependent photochemical processes for each complex investigated; the photochemical details will be reported elsewhere.[7] Most pertinent to the present report is that the photochemical generation of nitrene (eq 2) is associated

$$M^{III}(L)_5\bar{N}_3 + h\nu \xrightarrow[H^+]{} M^{III}(L)_5NH + N_2 \qquad (2)$$
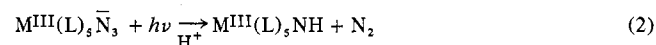
with excitations at 250 ± 30 nm in the case of $Rh(NH_3)_5N_3{}^{2+}$ and excitations at $\lambda \leqslant 254$ nm in the case of $Co(CN)_5N_3{}^{3-}$. In the latter case 254-nm excitations result predominantly in the formation of $Co(CN)_5{}^{3-} + \cdot N_3$

$$M^{III}(L)_5\bar{N}_3 + h\nu \rightarrow M^{III}(L)_5 + \cdot N_3 \qquad (3)$$
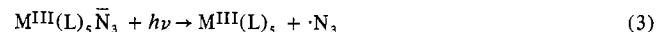
Experimental Section

The complexes $[Rh(NH_3)_5N_3](ClO_4)_2$, $[Rh(NH_3)_5OH_2](ClO_4)_3$, and $K_3[Co(CN)_5N_3]$ were prepared according to literature procedures.[8-10] Absorption spectra of these compounds were in good agreement with published spectra.[8-10] Other cobalt(III) complexes were available from previous studies.[11,12]

In order to prepare $[Rh(NH_3)_4(N_3)_2]ClO_4$ we first obtained solutions of *trans*-$Rh(NH_3)_4OH_2X^{2+}$ by means of the 254-nm irradiation of $Rh(NH_3)_5X^{2+}$ (X = I or Br) in 0.1 M $HClO_4$.[13] The haloaquotetraammine complexes were anated by adding[13] to the photolyte a threefold excess of NaN_3 and refluxing the resulting solution for 2 hr. The reaction mixture was concentrated and cooled, and the golden yellow crystals were collected. The product was recrystallized twice from warm water. *Anal.* Calcd for $RhN_{10}H_{12}O_4Cl$: N, 39.6; H, 3.4; Cl, 9.9. Found: N, 39.4; H, 3.4; Cl, 10.0. The absorption spectra of this compound (λ_{max} 379, 282, and 209

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nm with ϵ_{max} 755, 1.0 × 10^4, and 1.52 × 10^4 M^{-1} cm^{-1}, respectively) were very similar to those reported for [*trans*-Rh(en)$_2$-(N$_3$)$_2$]ClO$_4$.[14]

All other chemicals were reagent grade. Solutions were prepared with water redistilled from alkaline permanganate in a Pyrex apparatus.

The flash apparatus (Xenon Corp. Model 720) and procedures have been described previously.[11-13] For the present study the flash output was varied from 100 to 1600 J. Solutions were always discarded after a single flash.

Cobalt(II)[11,15] and chloramine[2-4] products were analyzed using literature procedures. Nitrogen yields have been determined chromatographically as described elsewhere.[5,7]

Results

A. Azido Complexes of Rhodium(III).
Flash photolysis of aqueous solutions containing Rh(NH$_3$)$_5$N$_3$$^{2+}$ or *trans*-Rh(NH$_3$)$_4$(N$_3$)$_2$$^+$ does produce absorbing transient species under various conditions; however these appear to be the products of the reaction of nitrene complexes with solution species rather than the nitrenes themselves. The results are conveniently organized in terms of the medium and photolysis conditions. Most of our studies are of Rh(NH$_3$)$_5$N$_3$$^{2+}$ substrates; *trans*-Rh(NH$_3$)$_4$(N$_3$)$_2$$^+$ behaves in a qualitatively similar manner.
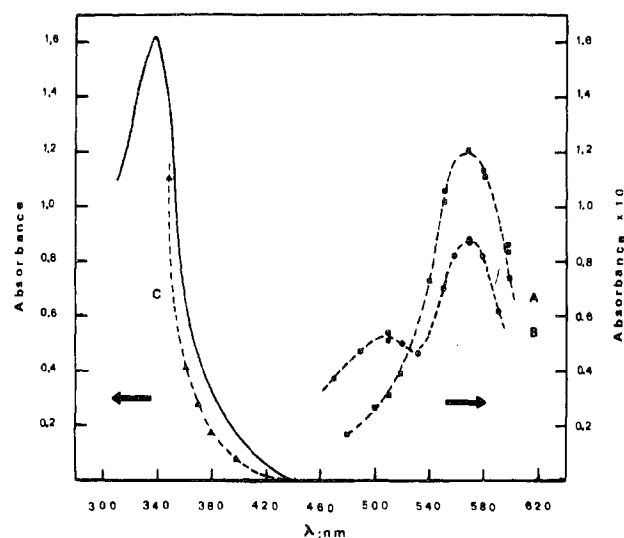
1. Transient Intermediates Produced in Perchlorate Solutions of Low Acidity.
Flash photolysis of solutions of pH >2 results in formation of transient species which absorb strongly between 500 and 600 nm; transient species which absorb more weakly than the substrates in the 370-nm spectral region (Figure 1) are also formed. The species which absorb strongly in the long-wavelength region are formed well after the decay of the flash pulse (Figure 2) and are not observed in solutions with [Cl$^-$] ≥ 0.1 M. The bleaching of substrate absorptivity at 370 nm occurs during the flash pulse and the amount of bleaching is independent of [Cl$^-$]. Our detailed investigations of the transient species involved are described in the sections below.

(a) Spectra of Transient Species. Solutions of Rh(NH$_3$)$_5$-N$_3$$^{2+}$ were flashed with a full-arc illumination and the response was monitored at different wavelengths from 600 to 350 nm. In attempting to detect any species absorbing in the region 370-430 nm we used 10^{-5} M ≤ [Rh(NH$_3$)$_5$-N$_3$$^{2+}$] ≤ 1.4 × 10^{-3} M. For these conditions of concentration only an absorbance bleaching was observed in the 350-420-nm region (Figure 1). The duration of this bleaching was around 300 μsec. The bleaching was observed for all solutions over the range 1 ≤ pH ≤ 6.

When the pH of the solution was greater than 3 but lower than 7, both the formation and decay of absorbing transient species were observed in the 460-600-nm spectral region. Two different transient absorbing species were observed, one with λ_{max} 510 nm and the other with λ_{max} 570 nm (Figure 1). The relative concentration of these two species was found to be pH dependent.

(b) Variation of the Transient Absorbance with pH. Solutions 2.0 × 10^{-3} M in Rh(NH$_3$)$_5$N$_3$$^{2+}$, containing different concentrations of HClO$_4$ ([HClO$_4$] + [NaClO$_4$] = 0.1 M) were flashed with full-arc illumination and the response was monitored at 510 nm or at 570 nm in different experiments. The transient with λ_{max} ≈510 nm reached its maximum concentration for 4.5 < pH < 5; the transient with λ_{max} 570 nm reached its maximum concentration for pH ≥5 (Figure 3).

(c) Dependence of Transient Generation on Type of Absorption Band Irradiated. By using a cutoff filter (naphthalene in ethanol[13,14]) we were able to demonstrate that all

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Figure 1. Absorption and bleaching spectra of transient species. Absorption values are for the 20-cm photolysis cell, 250-J flash: (A) pH 6.0, [Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 2.0 × 10^{-3} M; (B) pH 4.0, [Rh-(NH$_3$)$_5$N$_3$$^{2+}$] = 1.0 × 10^{-3} M; (C) pH 4.0, [Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 1.4 × 10^{-4} M. Solid line indicates absorbance due to substrate (1.4 × 10^{-4} M).
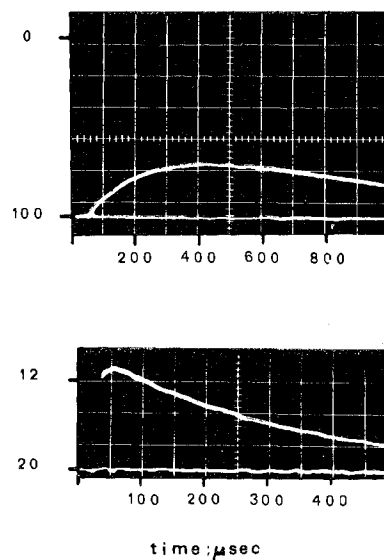
Figure 2. Transients generated in flash photolysis of Rh(NH$_3$)$_5$N$_3$$^{2+}$ and Co(CN)$_5$N$_3$$^-$ (with I$^-$): upper trace, transient species with λ_{max} at 570 nm, [Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 5.0 × 10^{-3} M, pH 6.0, 250-J flash; lower trace, I$_2$$^-$ transient generated from 250-J flash of 5 × 10^{-3} M Co(CN)$_5$N$_3$$^{3-}$ and 2.5 × 10^{-3} M I$^-$, pH 6.0, monitored at 380 nm, 2.5 × 10^{-2} M I$^-$ filter solution. Ordinate is % transmittance.

observed transient formation is associated exclusively with the irradiation at λ ≤320 nm. Although irradiation of the ligand field absorption bands of Rh(NH$_3$)$_5$N$_3$$^{2+}$ does not produce any of the transient absorbance changes described above, this type of irradiation does lead to azide aquation (ϕ = 0.02). Our studies of the ligand field photochemistry of Rh(NH$_3$)$_5$N$_3$$^{2+}$ will be reported elsewhere.

(d) Variations of Transient Kinetics and Yields with Flash Intensity. For these studies all solutions were initially 1.0 × 10^{-3} M in Rh(NH$_3$)$_5$N$_3$$^{2+}$, of pH 2, and 0.10 M in NaClO$_4$. Solutions were discarded after a single flash. The kinetics of transient formation and decay were monitored at 570 nm. The flash energy (full-arc illumination) was altered by changing the charging voltage and capacitance ($E = V^2C/2$).

Figure 3. Variation of transient yields with pH ([Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 2.0 × 10^{-3} M; 250-J flash): solid line, species observed at 570 nm; broken line, species observed at 510 nm.

The procedure we used for estimating initial reaction rates was as follows. Absorbance at 570 nm was plotted $vs.$ time and the slope of this curve was estimated graphically every 20 μsec, starting 20–50 μsec after flash initiation. These slopes were then plotted $vs.$ time and the limit was obtained as $t \rightarrow 0$. In our system the $1/e$ time for decay of scattered light with a 250-J flash was about 20 μsec; for this energy we have taken the flash "duration" to be 40 μsec, or approximately 3 half-lives for scattered light decay. The flash "duration" increases with flash energy, varying from 20 μsec at 40 J to 50 μsec at 500 J. In evaluation of kinetic data we have only used data points collected after the experimentally determined scattered light "duration" for the specified flash energy and wavelength.

In order to check the validity of our assumption that the flash intensity was proportional to flash energy, we flash photolyzed solutions 2.5 × 10^{-4} M in Co(NH$_3$)$_5$Br^{2+} and 1.0 × 10^{-3} M each in HClO$_4$ and NaBr. The 360-nm absorbance of Br$_2$$^-$ extrapolated to zero time was determined for flash energies in the range 30–300 J. This initial absorbance change (20-cm cell) was a linear function of energy

$$\Delta A_{t\rightarrow0} = (0.013 \pm 0.002)(V^2C/2)$$

For the solutions of Rh(NH$_3$)$_5$N$_3$$^{2+}$, the initial rates of absorbance change were found to be approximately second order in flash energy ($Nh\nu$) (Figure 4) and therefore approximately second order in flash intensity (assuming the spectral distribution does not vary strongly with variation of total flash energy). On the other hand the decay of the absorbing transients appears to be first order in the amount of transient formed (Table I).

The actual maximum amount of transient observed depends very strongly on the flash intensity. A plot of log A_{max} (A_{max} = maximum observed absorbance at 570 nm) $vs.$ the logarithm of charging voltage is very nearly linear with a slope of 3.7 (Figure 5). This implies a second-order dependence on flash intensity ($I \propto V^2$).

The transient with λ_{max} 510 nm exhibits similar kinetic features.

(e) **Kinetics of Recovery of Bleached Absorbance** (λ ~370 nm). The absorbance bleached in the 370-nm region is rapidly recovered (see Figure 2). The amount of bleaching (extrapolated to zero time) was found to be first order in flash intensity (Figure 6) and independent of pH in the
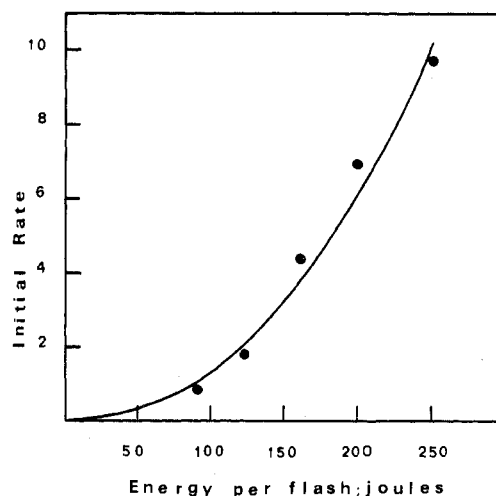

Figure 4. Variation of initial rate of formation of the 570-nm transient with flash energy ([Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 2.0 × 10^{-3} M, pH 6.0).

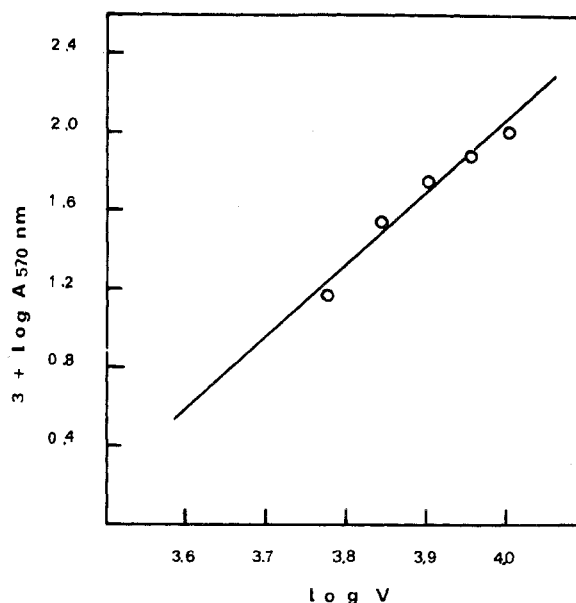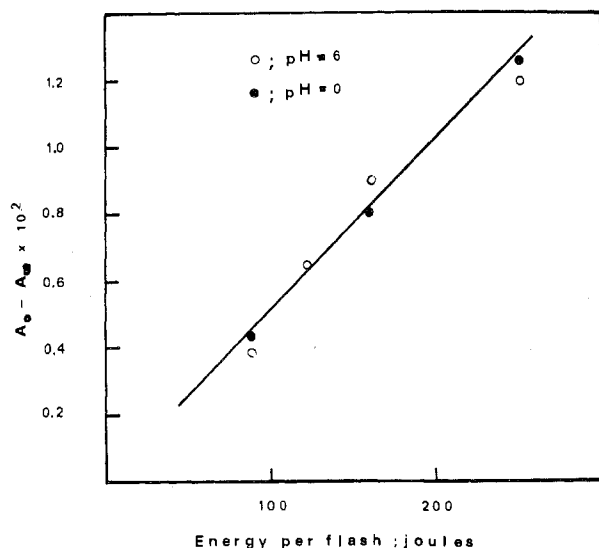**Figure 5.** Variation with charging voltage of the maximum amount of the 570-nm transient observed ([Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 2.0 × 10^{-3} M, pH 6.0). Slope of the line is 3.7. Note that energy per flash is given by $V^2C/2$; maximum energy 250 J.

Table I. Decay Kinetics of the Absorbing Transient Species

For transient with λ_{max} 570 nm			For transient with λ_{max} 510 nm		
Energy per flash, J	A_0^{a}	10^3k_d,^{b} sec^{-1}	Energy per flash, J	A_0^{a}	10^3k_d,^{b} sec^{-1}
360	0.20	2.0 ± 0.3^c	360	0.11	2.0 ± 0.3^d
250	0.11	1.8 ± 0.4^c	250	0.09	1.9 ± 0.3^d
202	0.09	1.9 ± 0.3^c			

^{a} A_0 obtained by extrapolating the decay rate to $t = 0$. ^{b} Mean and mean deviations for two or more determinations. ^{c} At pH 6. ^{d} At pH 4.

range 1 ≤ pH ≤ 6. The pseudo-first-order rate constant for the recovery of absorbance was (3.9 ± 1) × 10^3 sec^{-1} at pH 1 (or pH 6) and independent of flash intensity. The process leading to the recovery of absorbance was found to depend on the solution pH and anionic composition in a complex way (Table II). The pseudo-first-order rate constant for re-

Figure 6. Variation of yield of bleached absorbance ($A_0 - A_\infty$ at 370 nm) with flash energy ([Rh(NH$_3$)$_5$N$_3$$^{2+}$] = 2.0 × 10^{-3} M). A_0 was absorbance at 370 nm extrapolated to zero time; A_∞ was 370-nm absorbance at infinite time.

Table II. Recovery Kinetics at 370 nm[a]

| Anion, X$^-$	[X$^-$], M	pH	10^{-3}k,[b] sec^{-1}
ClO$_4$$^-$	0.1	6	4.0 ± 0.5
		4	6.6 ± 0.8
		3	12 ± 1
		1	4.0 ± 0.4
Cl$^-$	0.1	4	10 ± 1
		3	14 ± 2
		1	6.3 ± 0.8

a 250-J flash. *b* Mean and mean deviations for two or more determinations.

covery of absorbance at pH 1 varies linearly with the replacement of perchlorate by chloride and may be represented

$$k_{obsd} = \{(4.0 \pm 0.6) + (22 \pm 4)[Cl^-]\} \times 10^3 \text{ sec}^{-1}$$

Solutions flashed in the presence of 1 M Cl$^-$ eventually oxidized I$^-$ (10^{-3} M), as expected for Rh(NH$_3$)$_5$NH$_2$Cl^{3+} [3,4] (for this reaction $t_{1/2} > 10$ sec; $k < 70$ M^{-1} sec^{-1}).

(f) Determination of ϵ_D (570 nm). The kinetic behaviors of the various transients which we have observed suggest (see Discussion) a mechanistic scheme of the type

Rh(NH$_3$)$_5$N$_3$$^{2+}$ + $h\nu$ → A

$$2A \xrightarrow{k_f} B \tag{4}$$

$$B \xrightarrow{k_d} products \tag{5}$$
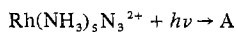
where "B" is the species with an absorption maximum at 570 nm. We have performed a few experiments which permit us to estimate the molar absorptivity, ϵ_D, of the dimer. The estimation procedures are described in detail in Appendix I. To determine the initial amount of monomer species, [A]$_0$, we performed a single flash of a solution 1 M in NaCl, 1.0 × 10^{-3} M in Rh(NH$_3$)$_5$N$_3$$^{2+}$, and of pH ≤3; we found [Rh(NH$_3$)$_5$NH$_2$Cl^{3+}] = 1.3 × 10^{-5} M. Under these conditions the intermediate species appears to be converted entirely to Rh(NH$_3$)$_5$NH$_2$Cl^{3+},[4,7] so [A]$_0$ ≈ 1.3 × 10^{-5} M. Various estimation procedures described in Appendix I give ϵ_D = 797 ± 15 M^{-1} cm^{-1}.

2. Reaction of Photochemical Intermediates with Iodide. Flash photolysis of Rh(NH$_3$)$_5$N$_3$$^{2+}$ in acidic solution (1 ≤

pH ≤ 6) and in the presence of small concentrations of I$^-$ resulted in the formation of I$_3$$^-$ and I$_2$ among the reaction products. In the quantitative experiments 2.0 × 10^{-3} M ≥ [I$^-$] ≥ 1.0 × 10^{-4} M and cutoff filters (usually 2.5 × 10^{-2} M iodide solutions) were used to prevent direct photolysis of I$^-$. The formation of I$_3$$^-$ and I$_2$ took place over a period of a few seconds and was monitored by observing absorbance changes at 404.7 nm; at this wavelength ϵ is 6200 and 245 M^{-1} cm^{-1}, respectively. The product distribution was obtained from $K = [I_3^-]/[I_2][I^-] = 7.6 \times 10^2$ M^{-1}. Since the triiodide equilibrium was not saturated at our [I$^-$], the total absorbance developed after a single flash was found to vary linearly with [I$^-$]: $A(404.7 \text{ nm}) = (44 \pm 6)[I^-]$. This absorbance was developed over a few seconds; the rate change of absorbance at 404.7 nm was pseudo first order in [I$^-$] and the total iodine at any time may be adequately represented

$$[I_2]_T = [I_2] + [I_3^-] = \left(\frac{7.6 \times 10^2 [I^-] + 1}{9.4 \times 10^7 [I^-] + 4.9 \times 10^3}\right)(44 \pm$$

$$6)[I^-](1 - e^{-k'[I^-]t})$$

where $k' = (2.6 \pm 0.5) \times 10^3$ M^{-1} sec^{-1} (see Appendix II).

The reactions producing iodine were preceded by transient changes of absorbance in the 450–370-nm spectral region during the first 10^{-3} sec after the flash pulse. Analysis of absorbance changes in this spectral region is complicated by the bleaching of absorbance ($\lambda \leq 400$ nm) which always occurs when Rh(NH$_3$)$_5$N$_3$$^{2+}$ solutions are flashed. The absorbance changes at $\lambda \leq 390$ nm are consistent with the usual initial bleaching followed by recovery of absorbance, while a new transient absorbance appeared at about 412 nm (Figure 7). The amount of the 412-nm transient observed varied linearly with [I$^-$] in the range 0 ≤ [I$^-$] ≤ 3 × 10^{-3} M: $A(412) = (17 \pm 2)[I^-]$. The 412-nm transient had a very short lifetime ($t_{1/2} \approx 180$ μsec; Figure 7) compared to iodine formation. On the other hand we observed an eventual absorbance decrease in the 380-nm region which occurred on about the same time scale ($t_{1/2} \approx 400$ μsec) as iodine formation. The yield of the 412-nm transient was also found to decrease as pH increased, but its lifetime was nearly independent of pH (1 ≤ pH ≤ 3).

We have also examined the reactivity of I$_2$$^-$ toward Rh(NH$_3$)$_5$N$_3$$^{2+}$. The diiodide radical anion was generated from I$^-$ containing solutions[16,17] in which I$_3$$^-$ or Co(NH$_3$)$_5$I^{2+} were the predominant absorbing species. The presence of [Rh(NH$_3$)$_5$N$_3$$^{2+}$] ≤ 6 × 10^{-6} M did not affect the I$_2$$^-$ lifetime. We found no evidence for reaction between I$_3$$^-$ and Rh(NH$_3$)$_5$N$_3$$^{2+}$.

3. Reaction of the Photochemical Intermediates with Chloride or Chloride and Iodide. The yields of the transients absorbing at 510 and 570 nm decreased in proportion to [Cl$^-$] in the solution during photolysis. With [Cl$^-$] ≥ 0.1 M, we were unable to detect these transients. We found that the half-life for transient formation (for the 510- and 570-nm transients) increased as [Cl$^-$] increased but that the transient decay rate was very nearly independent of [Cl$^-$].

We have also found that when experiments were carried out in solutions which were 2.5 × 10^{-3} M in I$^-$ and where 0 ≤ [Cl$^-$] ≤ 2 M, the yield of the 412-nm transient decreased as [Cl$^-$] increased and could not be detected for [Cl$^-$] ≥ 1.0 M. In these experiments the ultimate yield

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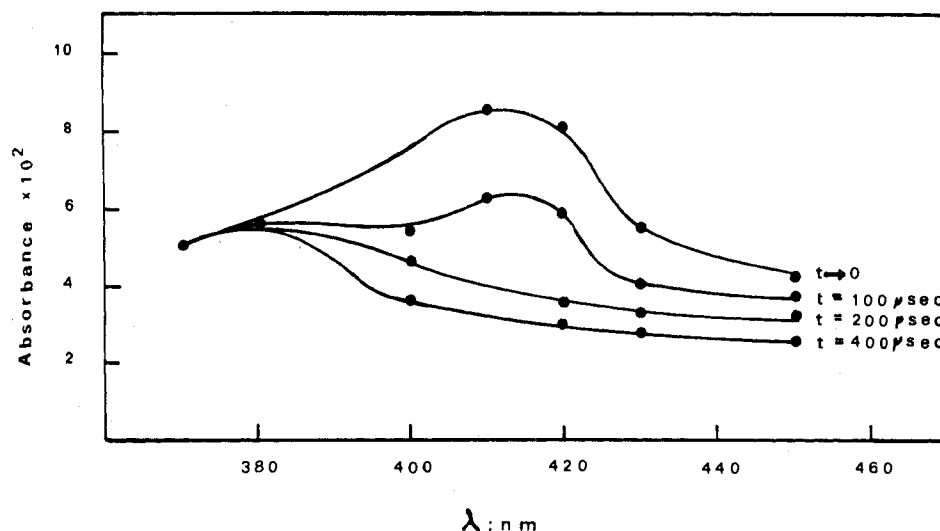
Figure 7. Absorbance spectrum of transient generated in the presence of I^-. Spectrum corrected for substrate absortivity and absorbance bleaching in the 370–390-nm region ($[Rh(NH_3)_5N_3{}^{2+}] = 2.0 \times 10^{-3} M$, pH 1.0).

of $I_3{}^-$ was independent of Cl^- for $[Cl^-] \leqslant 0.03 M$, but the $I_3{}^-$ yield increased with increasing $[Cl^-]$ at higher concentrations. In $1 M Cl^-$ the $I_3{}^-$ yield was approximately double its value for $[Cl^-] = 0$.

B. $Co(CN)_5N_3{}^{3-}$. Solutions of $Co(CN)_5N_3{}^{3-}$ were flash photolyzed in various media in attempts to produce transients corresponding to nitrene-based intermediates of the types reported in section A above. In these studies we varied $[Co(CN)_5N_3{}^{3-}]$ from 1.0×10^{-6} to $1.0 \times 10^{-3} M$ and $[H^+]$ over the range $1 \leqslant pH \leqslant 8$; in the studies with pH $\leqslant 3$ it was necessary to prepare sample solutions by placing suitable quantities of solid $K_3[Co(CN)_5N_3]$ in previously deareated $HClO_4$ and to flash the resulting solutions immediately, in order to avoid significant hydrolysis of the substrate. For each set of solution conditions, successive sample solutions were flashed and spectral changes were observed approximately every 200 nm for the range 800 nm $\geqslant \lambda \geqslant 380$ nm. The only process observed in these studies was the photochemical destruction of substrate absorbance during the photolysis flash.

In contrast, when solutions containing $Co(CN)_5N_3{}^-$ (5×10^{-5} to $1.0 \times 10^{-4} M$) and a low concentration of I^- ($\sim 10^{-3} M$) were flash photolyzed, a transient species with an absorption maximum at 380 nm was formed in much less than 30 μsec; in these studies we used solutions of $2.5 \times 10^{-2} M$ NaI as a cutoff filter for the photolysis flash (wavelengths $\geqslant 251$ nm transmitted). The spectra and decay characteristic (Figure 2) of the transient species were similar to those reported for $I_2{}^-$.[13,16,17] In continuous photolyses under these conditions we found that the evolution of N_2 was nearly quenched;[7] the nitrogen produced from irradiation of $Rh(NH_3)_5N_3{}^{2+}$ under similar conditions cannot be quenched by $10^{-3} M I^-$. Furthermore we found that flash photolysis of $Co(NH_3)_5N_3{}^{2+}$ in $10^{-3} M I^-$ produced the $I_2{}^-$ transient in times less than 30 μsec, indicating that $k_6 > 4 \times 10^7 M^{-1}$ sec^{-1} for the oxidation[5,17] of I^- by the azide radical (eq 6).

$$\cdot N_3 + I^- \rightarrow N_3{}^- + \cdot I \qquad (6)$$

No such transient was observed when similar solutions of $Co(CN)_5N_3{}^{3-}$ (5×10^{-5} to $5 \times 10^{-4} M$) and iodide were flashed using a 320-nm cutoff filter (naphthalene in ethanol). The decay of $I_2{}^-$ was observed in alternate experiments at 404.7 nm ($\epsilon_{I_3{}^-} \ll \epsilon_{I_2{}^-}$)[16] and at 380 nm ($\epsilon_{I_3{}^-} \simeq \epsilon_{I_2{}^-}$)[16] in attempts to observe net formation of $I_3{}^-$. Very little net

Table III. Product Yields in Flash Photolysis of $Co(CN)_5N_3{}^{3-}$ [a]

Wavelength region irradiated, nm	Product yields × 10^6, M		Yield ratio (Aq/redox)
	aquation	Redox	
$\geqslant 320$	5.8 ± 0.6[b]	<3.8	$>1.7 \times 10^2$
251–320[c]	2.0 ± 0.2[b,d]	1.1 ± 0.2	2.0

[a] 250-J flash of solutions $5 \times 10^{-5} M$ in $Co(CN)_5N_3{}^-$, 1.0×10^{-4} M in $HClO_4$, and 0.01 M in $NaClO_4$. [b] Values determined as aquation yield = $[Co(CN)_5OH_2{}^{2-}]$ in the absence of I^- and aquation yield = $[Co(CN)_5OH_2{}^{2-}] + [Co(CN)_5I^{3-}]$ in $10^{-3} M$ NaI. [c] Obtained from differences in yields obtained using different cutoff filters. [d] Values corrected for bulk solution reoxidation of $Co(CN)_5{}^{3-}$ by $I_2{}^-$ or $I_3{}^-$; *i.e.*, aquation yield = $[Co(CN)_5OH_2{}^{2-}] - [I_2{}^-]_{t \rightarrow 0}$.

formation of $I_3{}^-$ was observed (less than $10^{-7} M$ per flash; compare Table III) in solutions with pH >3 which had been carefully deareated before flashing. For solutions with pH $\leqslant 3$, $I_3{}^-$ was found to be an important reaction product. In solutions of high pH, the absorbance decay at 404.7 and 380 nm was not the usual second-order function of $[I_2{}^-]$, with deviations consistent with competitive reactions. Under these conditions $Co(CN)_5I^{3-}$ was found to be a significant reaction product and the initial, apparent second-order rate constant for $I_2{}^-$ decay (solutions initially at pH 4) was found to be $5.2 \times 10^9 M^{-1} sec^{-1}$ for a solution $5.0 \times 10^{-5} M$ in $Co(CN)_5N_3{}^{3-}$ and $2.5 \times 10^{-3} M$ in I^- compared to 3.6×10^9 $M^{-1} sec^{-1}$ for a solution $5.0 \times 10^{-5} M$ in $Co(NH_3)_6{}^{3+}$ and $2.5 \times 10^{-3} M$ in I^- (counterions for complexes were potassium and perchlorate, respectively; see also Figure 8). The faster decay rate of $I_2{}^-$ in the presence of $Co(CN)_5{}^{3-}$ is consistent with a recombination reaction of these photochemical fragments (eq 7) and is similar to the previously investi-

$$Co(CN)_5{}^{3-} + I_2{}^- \rightarrow Co(CN)_5I^{3-} + I^- \qquad (7)$$

gated case of $Rh(NH_3)_5I^{2+}$.[13a] The generation of $I_2{}^-$ from solutions containing $Co(NH_3)_6{}^{3+}$ and I^- has been discussed in detail by Malone and Endicott.[17]

The yields of $Co(CN)_5OH_2{}^{2-}$ (a product of d–d excitation) and $Co(CN)_5I^{3-}$ produced by flash photolysis of $Co(CN)_5N_3{}^{3-}$ solutions, in the presence or the absence of I^-, with $\lambda \geqslant 320$ nm (Table III) were determined from changes in absorption spectra of solutions before and after flashing.
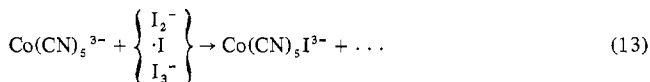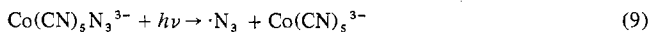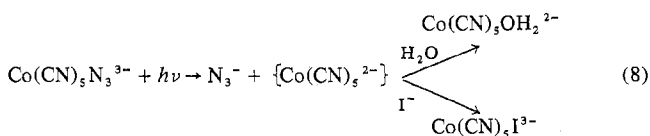
In order to obtain yields for irradiation of the 251–320-
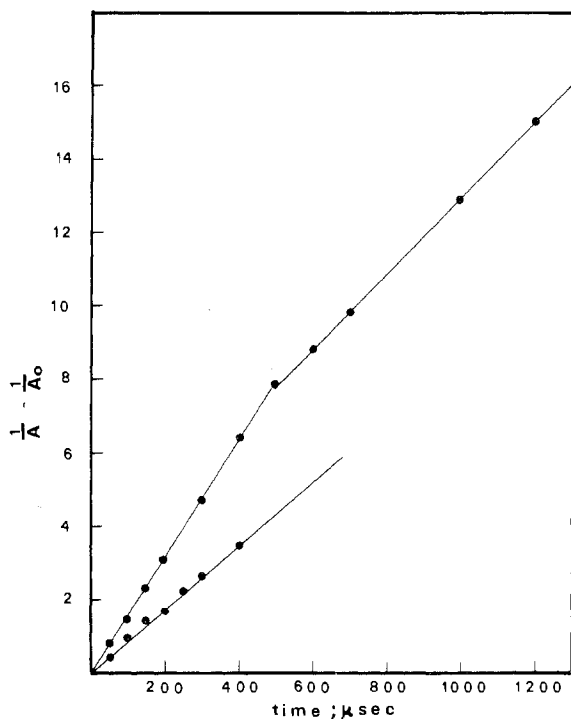
Figure 8. Diiodide radical anion decay kinetics: upper curve, decay of I_2^- generated in the photoreduction of $Co(CN)_5N_3^{3-}$ in 10^{-3} M I^-; lower curve, decay of I_2^- generated from 10^{-3} M $Co(NH_3)_6^{3+}$ and 10^{-3} M I^-.

nm spectral region, two identical solutions were flashed, the first with the 320-nm cutoff filter and the second with the 251-nm cutoff filter. The desired yields were then obtained from the differences in observed yields. Redox yields were estimated from $[I_2^-]$ extrapolated to zero irradiation time. Since two kinds of reactions producing $Co(CN)_5I^{3-}$ were observed for irradiations at $\lambda \geqslant 251$ nm, *i.e.*, reactions 8[18] and 9–13, the sum of the yields of $Co(CN)_5OH_2^{2-}$ and

$$Co(CN)_5N_3^{3-} + h\nu \rightarrow N_3^- + \{Co(CN)_5^{2-}\} \begin{array}{c} \xrightarrow{H_2O} Co(CN)_5OH_2^{2-} \\ \xrightarrow{I^-} Co(CN)_5I^{3-} \end{array} \quad (8)$$

$$Co(CN)_5N_3^{3-} + h\nu \rightarrow \cdot N_3 + Co(CN)_5^{3-} \quad (9)$$

$$\cdot N_3 + I^- \rightarrow N_3^- + \cdot I \quad (10)$$

$$\cdot I + I^- \rightleftarrows I_2^- \quad (11)$$

$$2I_2^- \rightarrow I_3^- + I^- \quad (12)$$

$$Co(CN)_5^{3-} + \left\{ \begin{array}{c} I_2^- \\ \cdot I \\ I_3^- \end{array} \right\} \rightarrow Co(CN)_5I^{3-} + \cdots \quad (13)$$

$Co(CN)_5I^{3-}$ had to be corrected for (13) in order to estimate aquation yields; this correction was accomplished by subtracting from the above sum the yield of I_2^- at zero irradiation time. No transients were observed in the near-infrared spectrum, indicating that photoelectron production was not a problem. It is also to be noted that the near-infrared absorptivity of $Co(CN)_5^{3-}$ is too weak to permit us to detect this species in this region in flash photolysis experiments.

C. Other Cobalt(III) Complexes. We have also flash photolyzed solutions containing $Co(NH_3)_5N_3^{2+}$ and *trans*-$Co(N_4)(N_3)_2^+$ ($N_4 = 5,7,7,12,14,14$-hexamethyl-1,4,8,11-

(18) A. W. Adamson, A. Chiang, and E. Zinato, *J. Amer. Chem. Soc.*, **91**, 5467 (1969).
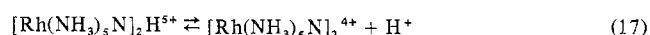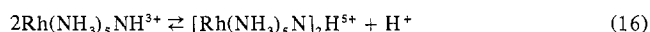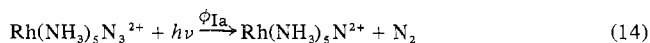
tetraazacyclotetradeca-4,11-diene). These systems did not exhibit the transient intermediates which were found to be characteristic of the rhodium(III)–nitrene species.

Discussion

A. Aqueous Chemistry of Rhodium Nitrenes. Our observations of the behavior of intermediates in the photochemistry of $Rh(NH_3)_5N_3^{2+}$ largely substantiate the previously postulated[4] generation of coordinated nitrene intermediates. The detailed chemical behavior of these intermediates is more complex than previously[2-4] supposed although the general properties and types of reactions are quite consistent with the previous mechanistic inferences. The nitrene complexes of rhodium(III) have sufficiently long lifetimes that much of their chemistry can be observed directly or indirectly using flash photolysis techniques.

The bleaching of absorbance at about 370 nm which we have observed when $Rh(NH_3)_5N_3^{2+}$ is flash photolyzed can be associated with the formation of nitrene intermediates or their conjugate bases. The regeneration of absorbance in this spectral region appears to be associated with the formation of the final reaction products, *i.e.*, with those complexes in which coordinated –NH has been replaced by coordinated –NH₂OH, –NH₂Cl, or –NH₃. We have not observed new absorption bands which can be associated with the primary nitrene products of photolysis.

We have observed new absorbances in weakly acidic solution. These absorbances appear to be associated with the formation of dimeric species from the primary photolysis products. This dimerization does not occur to a detectable extent for pH <2, so we would infer that the nitrene species themselves do not form very stable dimers. Thus the processes we have observed may be summarized in eq 14–17, where we associate $[Rh(NH_3)_5N]_2H^{5+}$ with the transient

$$Rh(NH_3)_5N_3^{2+} + h\nu \xrightarrow{\phi Ia} Rh(NH_3)_5N^{2+} + N_2 \quad (14)$$

$$Rh(NH_3)_5N^{2+} + H^+ \rightleftarrows Rh(NH_3)_5NH^{3+} \quad (15)$$

$$2Rh(NH_3)_5NH^{3+} \rightleftarrows [Rh(NH_3)_5N]_2H^{5+} + H^+ \quad (16)$$

$$[Rh(NH_3)_5N]_2H^{5+} \rightleftarrows [Rh(NH_3)_5N]_2^{4+} + H^+ \quad (17)$$

with λ_{max} 510 nm and $[Rh(NH_3)_5N]_2^{4+}$ with the transient with λ_{max} 570 nm. From Figure 3 and for $\{[Rh(NH_3)_5-NH] + [Rh(NH_3)_5N]\} \approx 1.3 \times 10^{-5}$ M, we estimate $K_{14} \approx 1$ and $pK_{15} \approx 4$.

The rate of formation of dimer, eq 16 and 17, is second order in the primary $Rh(NH_3)_5N^{2+}$ or $Rh(NH_3)_5NH^{3+}$ product, while the decay of dimer is first order in dimer formed; therefore, the maximum concentration of dimer is achieved

$$\frac{d[dimer]}{dt} = 2k_f\{[Rh(NH_3)_5N^{2+}] + [Rh(NH_3)_5NH^{3+}]\}^2 - k_d[dimer]$$

when $d[dimer]/dt = 0$ or when

$$2k_f\{[Rh(NH_3)_5N^{2+}]_m + [Rh(NH_3)_5NH^{3+}]_m\}^2 = k_d[dimer]_m$$

In one experiment we determined that

$$[Rh(NH_3)_5N^{2+}]_m + [Rh(NH_3)_5NH^{3+}]_m + 2[dimer]_m = 1.3 \times 10^{-5} M$$

and that the absorbance due to dimer under these conditions was 0.088 in a 20-cm cell. Substitution of these values, with $k_d = 2.0 \times 10^3$ sec^{-1}, leads to $k_f = 1.2 \times 10^9$ M^{-1} sec^{-1}, indicating a very nearly diffusion-controlled dimerization.
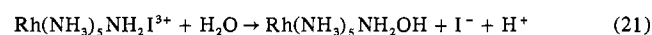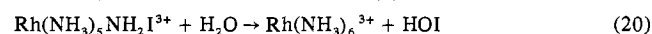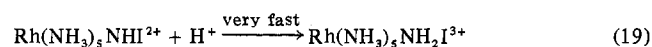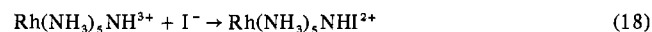
The value of k_f which we have estimated is a composite value in the sense that we have no way of estimating K_{13} and thus do not know the distribution of acidic and basic nitrene intermediates at pH 6.

It is of interest that although the products obtained in the thermal[3] and photochemical[4] decomposition of rhodium(III) azide complexes have not required the postulation of a dimeric intermediate, thermal decomposition of ruthenium(III) azide complexes did lead Kane-Maguire, *et al.*,[2] to infer the intermediacy of a dimeric species. A major chemical difference between ruthenium(III) and rhodium(III) complexes is that the former are far more facile oxidants so that the intramolecular redox reaction postulated in the case of nitrene dimers of ruthenium(III) would be expected to occur more slowly during the lifetime of the corresponding rhodium(III) species. This difference in the net chemical behavior of ruthenium(III) and rhodium(III) "nitrenes" is thus not necessarily a difference in the tendencies of nitrene complexes to dimerize, in the sense of (16) and (17). We presume that the dimer species contain a Rh–N–N–Rh bond (analogous to diimine, N_2H_4). The low-energy absorbance of this species, which appears to be red shifted from that of $Rh(NH_3)_5$-NH^{3+},[19] might be a metal-centered transition, the intensity borrowed from mixing with π or charge-transfer transitions, or a weakly forbidden charge-transfer to ligand transition.

B. Reactions of Photochemical Intermediates with Iodide. We have found evidence for at least three intermediate species and four steps in photochemical decomposition of $Rh(NH_3)_5N_3^{2+}$ in the presence of I^-: (1) primary photochemical generation of a nitrene intermediate, as above, followed by (2) a very rapid ($t_{1/2} < 40~\mu sec$) reaction of the nitrene with I^- to form a species absorbing at 412 nm; (3) the decay of the 412-nm transient; (4) the eventual formation of iodine. No I_2^- transients were observed in these studies. Thus the reaction with I^- does help distinguish azide radical formations from nitrene formation in the primary step.

These observations are adequately represented by reactions 18–22. The nature of the 412-nm intermediate is

$$Rh(NH_3)_5NH^{3+} + I^- \rightarrow Rh(NH_3)_5NHI^{2+} \tag{18}$$

$$Rh(NH_3)_5NHI^{2+} + H^+ \xrightarrow{\text{very fast}} Rh(NH_3)_5NH_2I^{3+} \tag{19}$$

$$Rh(NH_3)_5NH_2I^{3+} + H_2O \rightarrow Rh(NH_3)_6^{3+} + HOI \tag{20}$$

$$Rh(NH_3)_5NH_2I^{3+} + H_2O \rightarrow Rh(NH_3)_5NH_2OH + I^- + H^+ \tag{21}$$

$$HOI + I^- + H^+ \rightarrow H_2O + I_2 \tag{22}$$

quite ambiguous; however reactions 18–22 are consistent with the behavior observed in halide-containing media, where $k_{18} \geqslant 10^7~M^{-1}~sec^{-1}$, and the 412-nm transient is associated with $Rh(NH_3)_5NH_2I^{3+}$. The increased I_2 yield in $1~M~Cl^-$ suggests the competitive decay modes, (20) and (21), since $Rh(NH_3)_5NH_2OH^{3+}$ is relatively unreactive toward I^-; the former reaction finds precedent in the hydrolysis of NX_3;[20] the latter in hydrolysis of metallochloramine complexes.[2,3] In our studies in $1~M~Cl^-$ and $2.5 \times 10^{-3}~M~I^-$ we would find that the reaction of I^- with $Rh(NH_3)_5NH_2Cl^{3+}$ was too slow for kinetic determinations to be made in the flash photolysis experiments.

C. Contrasting Behavior of Azido Complexes of Cobalt(III). Flash photolysis has not proved to be an effective means of detecting nitrene intermediates in the photochemistry of azido complexes of cobalt(III). There is evidence[7] for photochemical generation of nitrene as a minor process in the case of $Co(CN)_5N_3^{3-}$; the only transient species detected in flash photolysis of this and other cobalt complexes appeared to result from the reactions of the azide radical.

The photochemical behavior of the azido complexes of cobalt(III) and rhodium(III) is extraordinarily varied and complex. The very narrow range of excitations over which $Rh(NH_3)_5NH^{3+}$ may be photochemically generated make the discovery of this process by Basolo and coworkers[4] very remarkable.

Appendix I. Estimates of Dimer Absorptivity

We have used two different kinds of approaches in estimating ϵ_D: absorbance extrapolation and an algebraic estimate based on a series solution to the differential equation for reaction scheme of eq 4 and 5.

A. Absorbance Extrapolations. The rate of change in [B] is given by (IA). For very short times, the second term will

$$d[B]/dt = 2k_f[A]^2 - k_d[B] \tag{IA}$$

not contribute significantly and

$$\frac{1}{[A]_0 - [B]} - \frac{1}{[A]_0} \cong k_f t$$

For A_t (absorbance of B at time t) $= l\epsilon_D[B]$ and $2A_\infty = l\epsilon_D[A]_0$

$$\frac{1}{2A_\infty - A_t} - \frac{1}{2A_\infty} = k_a t = \frac{k_f}{l\epsilon_D}t$$

Rearranging

$$\frac{1}{A_t} = \frac{1}{2A_\infty} + \frac{1}{4A_\infty^2 k_a t}$$

Thus the intercept of a plot of $1/A_t$ *vs.* $1/t$ gives an approximate measure of A_∞; from such a procedure we obtained $A_\infty \simeq 0.106$ (20-cm path length) and $\epsilon_D = 817~cm^{-1}~M^{-1}$.

In an alternative extrapolation procedure, (IA) was considered at times long compared to the first reaction stage. Under these conditions $[B] = [B]_0 e^{-k_a t}$. Thus extrapolation to "zero time" of a first-order plot of the final stages of decay of the 570-nm absorbance yielded a "maximum" absorbance value of 0.103 (20-cm path length); for this extrapolation procedure $\epsilon_D = 791~cm^{-1}~M^{-1}$.

B. Estimation of ϵ_D from the Maximum Absorbance Observed at 570 nm. Solutions to (IA) are known;[21] thus, the concentration of B at any time t is given by

$$[B] = \frac{[A]_0 e^{-a}}{e^{a(w-1)}}\left\{e^a - \frac{e^{aw}}{w} + a\left[\log w + a(w-1) + \frac{a^2}{4}(w^2 - 1) + \dots\right]\right\} \tag{IB}$$

In the experiments described in the text we observed the maximum absorbance at $t_m \simeq 200~\mu sec$. We may use values of $[A]_0 = 1.3 \times 10^{-5}~M$, $k_f \simeq 1.2 \times 10^9~M^{-1}~sec^{-1}$, and

(19) Basolo and coworkers (F. Basolo, private communication, 1973) have evidence that $Rh(NH_3)_5NH^{3+}$ has an absorbance maximum at 407 nm ($\epsilon_{max} \simeq 680$) at $77°$K in a CH_3OH-H_2O glass. We could not detect so small an absorbance in a spectral region exhibiting appreciable substrate absorptivity.

(20) E. S. Gould, "Inorganic Reactions and Structure," Holt, Rinehart and Winston, New York, N. Y., 1963, pp 218-220.

(21) L. Capellos and B. H. J. Bielski, "Kinetic Systems," Wiley-Interscience, New York, N. Y., 1972, pp 96-100.

$k_d \simeq 2.0 \times 10^3$ sec^{-1}, to obtain $a = k_d/[A]_0 k_f = 0.128$ and $w = (1 + 2k_f[A]_0 t) = 1 + (3.1 \times 10^4)t$. Using these parameters we estimate $[B] = 5.3 \times 10^{-6}$ M at 200 μsec; the measured absorbance (20 cm) was 0.083 so $\epsilon_D = 783$ cm^{-1} M^{-1}.

Appendix II. Final Stages of the Reaction of Rh(NH$_3$)$_5$NH^{3+} with I$^-$

For the absorbance of iodine species at 404.7 nm at any time in a 20-cm cell, $A = 12.4 \times 10^4 [I_3^-] + 4.9 \times 10^3 [I_2]$. Thus $[I_2] = A/\{1.24 \times 10^5 [I^-]K + 4.9 \times 10^3\}$ and $[I_3^-] = KA[I^-]/\{1.24 \times 10^5 [I^-]/K + 4.9 \times 10^3\}$, so

$$[I_2]_T = [I_2] + [I_3^-] = \left\{ \frac{1 + K[I^-]}{1.24 \times 10^5 [I^-]K + 4.9 \times 10^3} \right\} A$$

where A has been found to be equal to $(44 \pm 6)[I^-]$. This final reaction stage is pseudo first order in $[I^-]$

$$d[I_2]_T/dt = k'[I^-][Rh(NH_3)_5NH^{3+}]$$

The value of $[I_2]_T$ at any time t may thus be represented by the equation in the text.

Reactions of π-Cyclopentadienyldicarbonylrhodium and π-Cyclopentadienyldicarbonyliridium with Disubstituted Acetylenes[1]

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The reactions of π-cyclopentadienyldicarbonylrhodium (1) and diphenylacetylene (2) in refluxing xylene or toluene produce hexaphenylbenzene, in addition to several novel di- and trinuclear organorhodium complexes, many of which are analogous to those isolated from reactions of iron carbonyls with acetylenes. The catalytic behavior of 1 in the cyclotrimerization of 2 to hexaphenylbenzene has been demonstrated. Reactions of π-cyclopentadienyldicarbonyliridium with bis(pentafluorophenyl)acetylene have been observed to produce low yields of the trimerization product, hexakis(pentafluorophenyl)benzene, as well as several organoiridium compounds analogous to the newly isolated rhodium complexes.

Introduction

While reactions of π-cyclopentadienyldicarbonylcobalt with disubstituted acetylenes have been described extensively in the literature,[2-10] the analogous reactions of π-cyclopentadienyldicarbonylrhodium (1) have received little attention. Dickson[11] has reported the formation of several organorhodium complexes from the reaction of 1 with hexafluoro-2-butyne, including a dirhodium species containing a bridging acetylene.[12] Another product from this reaction, π-cyclopentadienyl[hexakis(trifluoromethyl)benzene]rhodium, was shown to represent the first example of an arene acting as a four-electron donor.[13]

We have recently reported that a reaction between 1 and bis(pentafluorophenyl)acetylene[14] produces a good yield of trimerized acetylene, hexakis(pentafluorophenyl)benzene, in addition to several new di- and trinuclear rhodium complexes. In light of the extensive trimerization of the acetylene, the catalytic behavior of 1 with acetylenes is currently under investigation.

The differences in rhodium *vs.* cobalt modes of interaction with acetylenes observed in compounds resulting from the above reactions prompted further investigations of reactions of 1 with other disubstituted acetylenes. Certain similiarities to iron carbonyl reactions with acetylenes were noted in our previous work[14] [Fe(CO)$_3$ and (π-C$_5$H$_5$)Rh are isoelectronic], and Dahl[15] had formally compared the solution and solid-state structures of Fe$_3$CO$_{12}$ to those of the known tris(π-cyclopentadienylcarbonylrhodium) isomers.[16-18] Thus, considering the increased strength of metal–metal bonds[19] as one descends a column of the periodic table, the formation of a number of other compounds analogous to the well-known acetylene–carbonyl–iron series[20] was recognized as a possibility. This bonding effect has already been demonstrated by a comparison of the chemistry of iron and ruthenium triangular derivatives of the type M$_3$(CO)$_{12}$.[19] However, more systematic work on studies of the second-row transition metals was needed to support these observations in the cobalt triad.

(1) (a) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13-17, 1971; see Abstracts, No. INOR 163. (b) Presented in part at the Vth International Conference on Organometallic Chemistry, Moscow, U.S.S.R., Aug 16-21, 1971; *Pure Appl. Chem.*, **30**, 523 (1972).

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