

- (2) K. L. Stevenson and D. D. Davis, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, No. INOR 15.
- (3) C. Kutal, D. P. Schwendiman, and P. Gratsch, private communication from C.K., 1976.
- (4) S. Sundarajan and E. J. Wehry, *J. Phys. Chem.*, **76**, 1528 (1972).
- (5) (a) R. L. Lintvedt, "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, Chapter 7, p 299; (b) H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, **92**, 1623 (1971).
- (6) (a) J. Y. Morimoto and B. A. DeGraaff, *J. Phys. Chem.*, **79**, 326 (1975); (b) *ibid.*, **76**, 1387 (1972).
- (7) D. R. McMillan and M. T. Backner, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, No. INOR 35.
- (8) Ligand abbreviation: [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; 8-en-2-oneN₄ = 14-amino-4,4,9,11,11-pentamethyl-5,8,12-triazatetradeca-8-en-2-one.
- (9) C. A. Parker and G. E. Hatchard, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
- (10) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966; (b) J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **95**, 630 (1973).
- (11) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975).
- (12) J. K. Kochi et al., *J. Am. Chem. Soc.*, **84**, 2121 (1962).
- (13) J. Fries, "Analysis of Traces", E. Merk, Darmstadt, 1971.
- (14) A. E. Vogel, "Elementary Practical Organic Chemistry", Longmans, London, 1958. For formaldehyde analysis: "Methods in Carbohydrate Chemistry", Vol. 1, Academic Press, London, 1962.
- (15) For descriptions of flash photolysis techniques see G. J. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).
- (16) N. Sadasivan and J. R. Endicott, *J. Am. Chem. Soc.*, **88**, 5468 (1966); N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966).
- (17) N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1358 (1972).
- (18) N. F. Curtis et al., *J. Chem. Soc. A*, 1075 (1966).
- (19) J. F. Endicott, J. M. Palmer, and E. Papaconstantinou, *Inorg. Chem.*, **8**, 1516 (1969).
- (20) The spectra of Cu([14]dieneN₄)⁺ were described previously by several authors; see ref 19, 21, and 27. The chemical stability of this species, generated in our experimental conditions, agreed with those reported in ref 19 and 21. Apparent discrepancies with the reactivity reported in ref 27 were probably caused by a different nature in the proton donor.
- (21) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **10**, 463 (1971).
- (22) R. D. Gillard, *Coord. Chem. Rev.*, **16**, 67 (1975).
- (23) G. Nord and O. Wernberg, *J. Chem. Soc., Dalton Trans.*, 845 (1975).
- (24) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci., U.S.A.*, **72**, 2858 (1975).
- (25) J. DelGaudio and G. N. LaMar, *J. Am. Chem. Soc.*, **98**, 3014 (1976).
- (26) R. H. Yamada, T. Kato, S. Shimizu, and S. Fukui, *Biochim. Biophys. Acta*, **117**, 13 (1966).
- (27) A. M. Tait, M. Z. Hoffman, and E. Hayon, *Inorg. Chem.*, **15**, 934 (1976). These authors report $k \approx 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the $\cdot\text{CH}_2\text{O}^-$ reduction of Cu([14]dieneN₄)²⁺ and that they were unable to detect the $\cdot\text{CH}_2\text{OH}$ reduction of the copper(II) complex. Their data seem to be consistent with $k_{11} \leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$; we have found a value of $2.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ which could correspond to reductions of Cu([14]dieneN₄)²⁺ by either $\cdot\text{CH}_2\text{OH}$ or CH_2O^- in neutral solution.

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Photoredox Energetics of Transition Metals. Redox and Nitrene Pathways in Azidopentaamminechromium(III)¹

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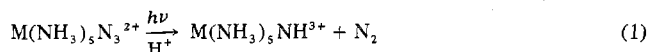
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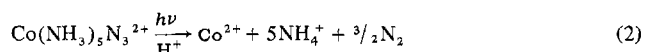
The charge-transfer photochemistry of Cr(NH₃)₅N₃²⁺ has been studied in detail under a variety of conditions. Both redox and nitrene pathways have been found. The redox and nitrene quantum yields have been obtained as a function of irradiation wavelength and they both show definite threshold energies which are in agreement with previous results and proposed models. The actual yields of products are diminished due to complicating secondary reactions of radical scavenging species. Scavenger concentration studies show that the $\phi_{\text{Cr(II)}}$ increases in deaerated solutions. Flash photolyses of acidic solutions of the complex imply the production of $\cdot\text{N}_3$ radical. A mechanistic scheme is proposed to explain the primary steps induced by photolysis and the secondary thermal reactions. The lowest charge-transfer excited state which is photoactive toward both the redox and nitrene reactive pathways is most likely a L → M state. The photochemistry of Cr(NH₃)₅N₃²⁺ is compared with that of the azido complexes of other transition metals.

Introduction

The photochemical behavior of transition-metal azide complexes has long been a subject of interest.² Renewed interest has followed the discovery by Basolo and co-workers³ of an efficient photoinduced coordinated nitrene pathway in iridium(III) and rhodium(III) azidopentaammine complexes, eq 1. This dominance of the nitrene pathway for the



heavy-metal complexes^{3,4} contrasts strikingly with the observation of photoredox modes, eq 2, for the analogous co-



balt(III) complexes.^{2,4,5} This contrast in photochemical behavior of the various azido complexes has been very puzzling. It has been variously proposed that the difference in photochemical behavior may be attributed to:⁶ (1) the involvement of metal-to-ligand charge-transfer states;⁷ (2) differences in the efficiencies of internal conversion processes populating

ligand centered states;³ or (3) differences in the metal-to-ligand back-bonding interactions in the charge transfer to metal excited state.^{3b,4} Miskowski et al.⁸ have recently found evidence that direct excitation of apparently ligand-centered bands of M(CN)₅N₃³⁻ (M = Ir, Rh) complexes does not lead to detectable nitrene formation, but rather only azide photoaquation was found for those complexes.⁹

It has previously been reported by Vogler¹¹ that the ligand-field excitations of Cr(NH₃)₅N₃²⁺ lead to efficient ammonia aquation while charge-transfer photolysis produces redox decomposition as the only reaction with a high quantum yield. We began investigating the photochemistry of Cr(NH₃)₅N₃²⁺ as a part of our systematic examination of the charge-transfer photochemistry of Cr(III) complexes¹⁰ and while these studies were in progress we learned of independent studies demonstrating a coordinated nitrene product following 313-nm irradiations.¹² These observations and our concern over the fact that the charge-transfer photochemistry of Cr(NH₃)₅N₃²⁺ is different in many regards from that of the other azidopentaamminechromium(III) complexes have led us to examine this system very critically. As a result of our

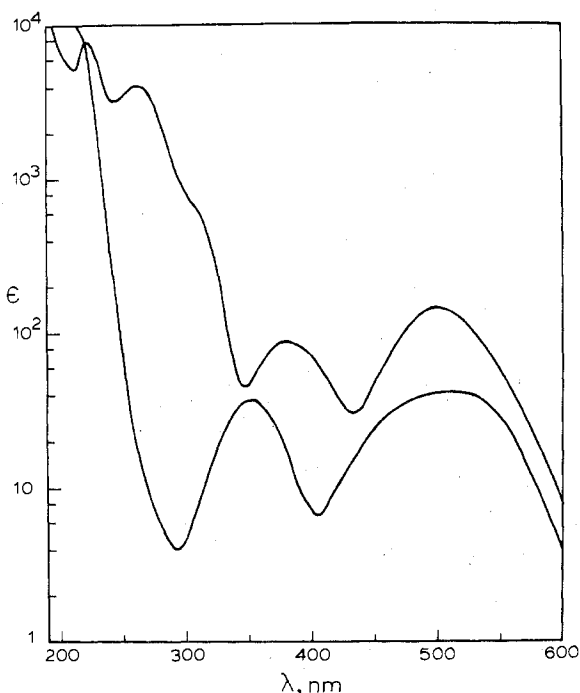


Figure 1. Absorption spectra of $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ (upper curve) and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ (lower curve).

study we have found that the mechanistic pathways induced by photolysis are complicated and that the thermal reactions of radical species produced by photolysis further complicate the quantitative photochemical analysis.

A major goal of the present investigation is to correlate our data with the quasi-thermodynamic analysis for the photoredox chemistry of transition-metal complexes.^{6,13} In this regard the lowest energy product ground state for this system would be $\{\text{Cr}^{\text{V}}(\text{NH}_3)_5^{2+}\cdot\text{X}\}$, while the product species correlated with the lowest energy charge-transfer absorption would be $\{\text{Cr}^{\text{III}}(\text{NH}_3)_5^{2+}\cdot\text{X}\}$.⁵⁶ We would expect this configurational difference to give rise to a relatively low threshold energy for the onset of redox processes.

Experimental Section

Materials and Reagents. Azidopentaamminechromium(III) perchlorate was prepared by the method of Linhard and Berthold.¹⁴ The starting material, $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_3\cdot\text{NH}_4\text{NO}_3$, was synthesized by the method of Mori¹⁵ and then converted to the perchlorate salt by adding saturated aqueous NaClO_4 to an aqueous solution of the complex at room temperature. *Warning!* Transition-metal ammine perchlorates have been known to detonate easily. While we encountered no problems in our study, this material should be handled with extreme caution. The $[\text{Cr}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ was recrystallized twice and its absorption spectrum agreed well with that reported in the literature ($\lambda_{\text{max}}/\epsilon_{\text{max}} = 498/145, 382/90$), Figure 1. Chromium was analyzed spectrophotometrically after oxidation to CrO_4^{2-} with alkaline H_2O_2 . The absorbance was measured at 373 nm ($\epsilon_{\text{CrO}_4} = 5.10 \times 10^3 \text{ cm}^{-1}$).¹⁶ Other elements were analyzed commercially by Midwest Microlab, Inc.

Anal. Calcd for $[\text{Cr}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$: Cr, 13.75; N, 29.64; H, 3.99; O, 33.85; Cl, 18.75. Found: Cr, 13.29; N, 28.96; H, 3.92; O, 31.82; Cl, 18.82.

Fluoropentaamminecobalt(III) perchlorate was synthesized by the literature method¹⁷ and its purity was checked by its absorption spectrum. $[\text{Rh}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ and $[\text{Rh}(\text{NH}_3)_5\text{NH}_2\text{Cl}](\text{ClO}_4)_3$ were available to us from previous workers⁴ from this laboratory. All other reagents were commercially obtained without any further purification and were of analytical or spectral quality.

Water was redistilled from alkaline permanganate in an all-glass apparatus. For the deaeration experiments, tank nitrogen was purged of oxygen using scrubbing towers filled with chromous solution and was again saturated with water vapor by passing through distilled water. Literature preparation¹⁸ was used for $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$

which was recrystallized three times.

For ion-exchange separations, Bio-Rad 50W-X8 (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 finally 0.3 M in HCl. The final washings from the purified resin were free of any absorbing species.

Photolysis Setup and Procedures. Different setups were used for the photolysis at various wavelengths. Irradiations at 254 nm were performed in a Ultraviolet Products Inc. low-pressure mercury loop lamp equipped with a quartz collimating lens and filter solution¹⁹ to isolate the 2537 Å mercury line. For other wavelengths we used either a Xenon Model 727 spectral irradiator or an Eimac-Varian high-pressure xenon lamp which was prefocused by means of an aluminum reflector and had a sapphire window for maximum UV transmittance. The latter had a nearly flat intensity distribution in the range 200–2000 nm. The irradiation wavelengths were isolated with a Bausch and Lomb high-intensity monochromator together with cutoff filters which helped to exclude longer wavelengths of the second-order dispersion of the grating especially when the monochromator was used in the extremes of its wavelength scales. Bandwidths at half-maximum intensity of wavelengths obtained by the above means were ± 5 nm. Rectangular quartz cells (1 cm path length) were exclusively used for 254-nm excitations whereas a 2-cm path length cylindrical quartz cell (volume = 10 mL) was used for photolysis at other wavelengths. Ditic Optics Inc., or Ealing narrow band pass (bandwidth = 10 nm) interference filters, were sometimes used in the photolysis path. Ealing neutral density filters were employed to attenuate incident light intensity.

A Xenon Corporation flash photolysis setup described previously⁴ was used for the flash experiments. A 20-cm path length quartz cell equipped with an outer jacket to contain the filter solutions was used. A filter to cut off wavelengths below 350 nm was placed in the monitoring beam. After several trials, the monitoring beam was allowed to pass through the sample solution only for a few seconds before the flash. Such precautions were necessary since ϕ_{NH} is high below 350 nm. In the presence of excess I^- , appreciable quantities of I_3^- would be formed within a few minutes if the solution were photolyzed by unfiltered monitoring light.

All absorbance measurements were made on a Cary-14 recording spectrophotometer. For the photolysis in the absence of air, oxygen-free nitrogen was bubbled through the photolyte for 30–45 min prior to photolysis and bubbling was continued throughout the irradiation.

Ferrioxalate actinometry was performed before and after each photolysis and variations in incident light intensity were usually within 3%.

Analytical Procedures. Co(II) was analyzed by a slightly modified^{4,5} procedure of Kitson.²⁰ Even analytical grade commercial NH_4NCS contained considerable quantity of iron. Hence it was removed as follows. A saturated aqueous solution of NH_4NCS was extracted repeatedly with 4-pentanone (in which all the Fe–NCS complex was most soluble) until the organic layer was colorless. The aqueous layer was separated and filtered and finally air was bubbled through the solution until no smell of 4-pentanone could be detected.

In a typical experiment 3 mL of the sample solution containing 3.5×10^{-3} M $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$, 3.0×10^{-3} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, and 0.1 M HClO_4 was irradiated in the cuvette for predetermined times. The photolyzed solution was then transferred to a 25-mL volumetric flask and the cuvette was rinsed three times with distilled water and the washings were added to the solution in the flask. Then 0.5 mL of concentrated HCl and 2 mL of NH_4NCS solution were added to the above solution and mixed. Finally the volume was adjusted to 25 mL with acetone. The absorbance of this solution was measured at 625 nm ($\epsilon = 1.71 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) using 5-cm path length cells immediately after mixing the reagents. These absorbance values were compared with those of the blank solution prepared in an identical manner using 3 mL of sample solution stored in the dark. All analyses were done immediately after photolysis in order to minimize possible dark reactions.

The chromium–chloramine complex 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 (measured against 0.1 M NaI) was corrected by subtracting that of the photolyzed solution. For example, 3 mL of a solution 3.5×10^{-3} M in $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$, 1 M in Cl^- , and 0.1 M in H^+ was photolyzed for a few minutes and transferred to a 10-mL volumetric flask by means of a syringe. The cell was washed three times with 1.5 mL of 0.1 M NaI and the rinsings were added to the

Table I. Photolysis of $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ in Aqueous Solutions at 25 °C^a

λ , nm	$\phi_{\text{Co(II)}}$ in 0.01 M HClO_4 , mol einstein ⁻¹	$\phi_{\text{Co(II)}}$ in 0.1 M HClO_4 + 0.9 M Cl^- , mol einstein ⁻¹	ϕ_{nitrene} in 0.1 M HClO_4 + 0.9 M Cl^- , mol einstein ⁻¹
230	0.05 (4) ^b		0.15 ± 0.01 (3)
254	0.01 ± 0.001 (4)	0.048 ± 0.003 (5)	0.10 ± 0.01 (7)
260	(6.5 ± 0.1) × 10 ⁻³ (2)		
270	4.6 × 10 ⁻³ (2)		
280	(4.0 ± 0.1) × 10 ⁻³ (2)	(8.9 ± 6) × 10 ⁻³ (2)	0.12 ± 0.01 (3)
300	(2.5 ± 0.1) × 10 ⁻³ (2)	(5.3 ± 4) × 10 ⁻³ (2)	0.16 ± 0.02 (4)
320	2.6 × 10 ⁻³ (2)	(3.7 ± 0.3) × 10 ⁻³ (2)	0.18 ± 0.01 (2)
330			0.20 ± 0.01 (2)
340	(2.1 ± 0.1) × 10 ⁻³ (2)	(1.7 ± 0.2) × 10 ⁻³ (2)	0.14 ± 0.01 (2)
350			0.06 ± 0.01 (2)
360	3 × 10 ⁻⁴ (2)		
380			<2. × 10 ⁻⁴ (2)

^a All determinations were done in air-saturated solutions. Number of determinations in parentheses. Co(II) determinations were done in solutions containing 7.0×10^{-3} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$. $[\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}] = 3.5 \times 10^{-3}$ M. ^b Quantum yield increases with time of irradiation. Hence reported value was extrapolated to zero time.

solution. Finally the volume was adjusted to 10 mL using 0.1 M I^- . Absorbance at 353 nm was determined immediately after mixing the solution, using 1-cm quartz cells. The value of ϵ for I_3^- used was $2.64 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.²¹ Ammonia analyses were performed using an Orion Model 801A ionalyzer with the Orion ammonia electrode. The electrode was calibrated using NH_4Cl solutions of known concentrations.

Results

(A) **General Observations.** Our spectroscopic and qualitative observations were in decent agreement with those of Vogler.¹¹ Thus ligand-field irradiation of $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ in 0.1 M HClO_4 resulted in well-defined isosbestic points in the absorption spectra and ammonia aqutation seemed to be the only major product, at least during the initial stages. The charge-transfer excitation, however, was quite different: Evolution of gas bubbles was observed. After extensive irradiations absorption spectra showed uniform drop in intensity at all wavelengths, except at the minimum (435 nm) where a slight increase was noticed. Also two isosbestic points were noticed as reported by Vogler.¹¹ The quantum yield calculated from the disappearance of the complex was around 0.4.

(B) **Redox Products. (1) Azide Radical.** We were able to confirm the formation of $\cdot\text{N}_3$ radical through flash photolysis of the complex ion in the presence of added I^- .^{4,5} Solutions 1.1×10^{-4} M in $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$, 5×10^{-3} M in NaI , and 0.1 M in HClO_4 were flash photolyzed in the 20 cm path length cell using a filter solution of 5% benzene in MeOH to cut off wavelengths shorter than 275 nm. The monitoring wavelength was set at 404.7 nm.²² We observed a moderately strong transient during the first flash. We identified the transient as I_2^- by its decay kinetics and spectral properties.²² This experiment was repeated several times using fresh solutions. Each solution was discarded after the first flash since the I_3^- formed during photolysis by itself can produce the transient I_2^- on further flash photolysis.

That the transient I_2^- is produced by the reactions of the $\cdot\text{N}_3$ ^{4,5} radical with I^- and not by direct absorption of light by the I^- present in solution was further confirmed by repeating the experiments in the absence of the chromium complex; similarly filtered flash photolysis of a solution of 5×10^{-3} M I^- in 0.1 M HClO_4 did not produce any species absorbing at 380 nm. From the I_2^- transient decay analysis, we calculated the initial concentration of I_2^- to be about 4.6×10^{-7} M and the $t_{1/2}$ to be 2.6×10^{-4} s; the second order rate constant for the decay of I_2^- was about $5 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$. These values are in reasonable agreement with literature values reported for similar systems.^{2a,4,5,23}

(2) **The Search for Cr(II).** We used $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ as the scavenger for Cr(II). Of the several Co(III) complexes the

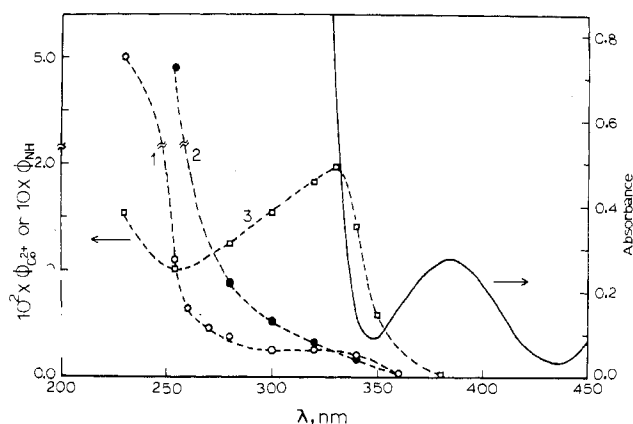


Figure 2. Product quantum yields as a function of excitation wavelength. Curve (1) redox yield in aerated HClO_4 ; curve (2) redox yield in aerated 0.1 M HCl , 0.9 M NaCl ; curve (3) yield of nitrene products in 0.1 M HCl , 0.9 M NaCl . A portion of the absorption spectrum of $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ is shown at the right.

fluoropentaammine complex is one of the more efficient scavengers of Cr^{2+} ,²⁴ and its absorption spectrum permits the use of relatively high concentrations since it has only weak absorptions in the range 254–320 nm.

Aerated solutions of 3.5×10^{-3} M $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ and 7.0×10^{-3} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ in 0.1 M HClO_4 were photolyzed at 254 nm and the amount of Co^{2+} produced was analyzed. Such experiments gave $\phi_{\text{Co(II)}} = 0.01$ (Table I and Figure 2). Photolyses of $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ in 0.1 M HClO_4 , 1 M NaClO_4 , and 7×10^{-3} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ produced very similar yields of Co^{2+} . This is in contrast to many other Cr(III) ammine complexes under similar conditions which have higher photoredox yields for similar charge-transfer excitations.¹⁰

When $\phi_{\text{Co(II)}}$ was obtained at different wavelengths, the yields were low for excitations with $\lambda > 254$ nm even though the threshold for redox was around 360 nm (Figure 2). Since these yields were so small, we investigated the possibility that one of the products of photolysis could act as an internal scavenger for Cr^{2+} in competition with $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and O_2 . When a solution of 3.5×10^{-3} M $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ in 0.1 M HCl , 0.9 M NaCl , and 7.0×10^{-3} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ was photolyzed at 254 nm, the Co(II) analysis showed that there was roughly a fivefold increase in $[\text{Co}^{2+}]$. That is, conditions favorable to formation of a chloramine complex increased the apparent yield of Cr(II). Hence the determinations were repeated at other wavelengths. The data, Table I and Figure 2, show that though there is an increase at most wavelengths this is not so dramatic for $\lambda > 254$ nm. Furthermore, $\phi_{\text{NH}_2\text{Cl}}$

Table II. ϕ_{nitrene} in the Presence of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$

$[\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}]$, 10^{-3} M	$[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$, 10^{-3} M	ϕ
(a) At 254 nm $[\text{H}^+] = 0.1$ M, $[\text{Cl}^-] = 1.0$ M		
6.2	7.5	0.110
6.2	7.5	0.109
		$\phi_{\text{av}} 0.110$
(b) At 300 nm $[\text{H}^+] = 0.1$ M, $[\text{Cl}^-] = 1.0$ M		
3.61	7.07	0.198
3.61	7.07	0.177
3.61	7.07	0.188
3.61	7.07	0.188
3.61	7.07	0.197
		$\phi_{\text{av}} 0.192$

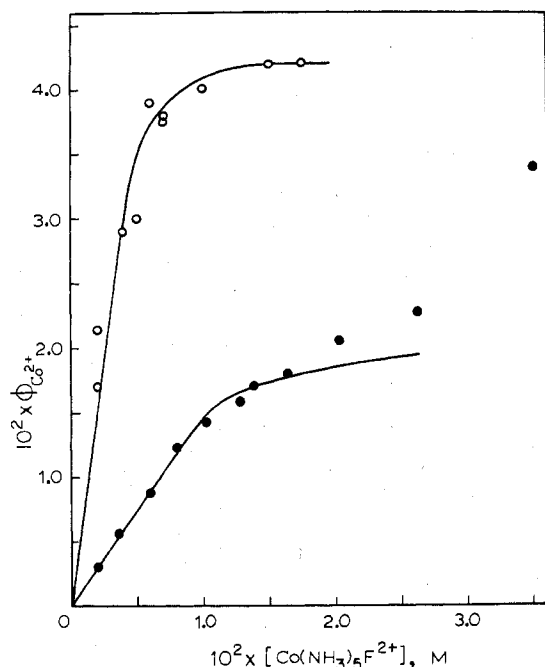


Figure 3. Redox quantum yields as a function of $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ in aerated (lower curve) and deaerated (upper curve) perchloric acid (0.1 M) solution.

was not changed by the presence of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ (Table II).

The maximum experimental yield of Cr(II) was determined from the quantum yields for Co(II) at different concentrations of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$. A plot of $\phi_{\text{Co}^{2+}}$ vs. $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$, Figure 3, Table S1,²⁵ was linear up to 1.2×10^{-2} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ after which there was a plateau. At much higher concentrations of scavenger, there was again a steady increase in [Co(III)]. This latter observation is attributable to the fact that direct photolysis of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ at these concentrations becomes important owing to the fractional absorbance of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$. For these larger $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$, the actual yield of Co^{2+} should increase with increasing $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ until the cobalt complex absorbs all the light. Since the direct photolysis of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ must be zero order in substrate the later section of the plot of $\phi_{\text{Co}^{2+}}$ vs. $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ in Figure 3 should approximately extrapolate to the origin, as observed.

We emphasize that the yields of Co^{2+} only provide lower limits for the actual yields of Cr^{2+} since there were other efficient scavengers for the chromium(II) ions in our photolysis solutions. One such scavenger was O_2 . Deaerated perchlorate solutions were photolyzed at 254 nm and the $\phi_{\text{Co}^{2+}}$ yield was roughly four times higher than for air-saturated solutions for

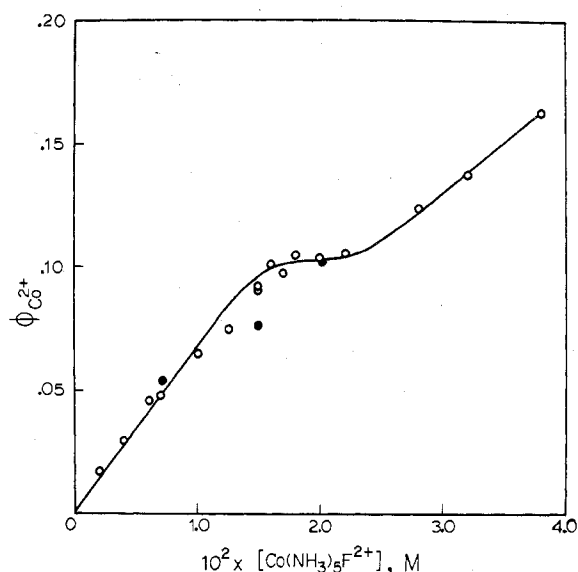


Figure 4. Redox quantum yields as a function of $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ in aerated (O) and deaerated (●) 0.1 M HCl and 0.9 M NaCl.

the same concentrations of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$. This observation clearly indicates that O_2 is one of the important scavengers for Cr(II). Again $\phi_{\text{Co}^{2+}}$ was determined for various $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ and a plot of $\phi_{\text{Co}^{2+}}$ vs. $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ was linear up to about 1.2×10^{-2} M $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ after which it reached a clear plateau, Figure 4 and Table S1.²⁵ However, this plateau was less than one-half the apparent limiting value of $\phi \sim 0.11$ found in 1 M Cl^- solutions (Figure 3). Furthermore, deaeration of the chloride solutions did not increase the yield of reduced species. The observation that $\phi_{\text{Co}^{2+}}$ increased with $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ even in deaerated chloride solutions suggests that yet another scavenging reaction may be important in this system.

(C) The Search for Products Derived from Nitrene Intermediates. Since $\phi_{\text{Co(II)}}$ was only 0.01 for 254-nm irradiations of aerated solutions, whereas the quantum yield for disappearance of complex ion was 0.4, another reaction must be important. In order to detect reaction products of nitrene intermediates, solutions 3.5×10^{-3} M in $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$, 0.9 M in NaCl, and 0.1 M in HCl were photolyzed. Photolyte solutions were immediately treated with 0.1 M NaI and analyzed for the formation of I_3^- . The quantum yield for the chromium chloramine complex thus determined, ϕ_{NH} , was only 0.1 at 254 nm. Still there was yet another reaction since we had to account for the difference in quantum yield at this wavelength. This discrepancy will be discussed in a later section.

In order to determine the extent of secondary photolysis, ϕ_{NH} was determined for different periods of irradiation at 254 nm. These values, listed in Table III, indicate that at least up to 20 min of photolysis the values were constant, Figure S1.²⁵ However, most of our results were obtained for 5 min or less irradiation time. It was also necessary to optimize such conditions of the photolyte as $[\text{Cl}^-]$ and $[\text{H}^+]$ in order to get reliable quantum-yield values. Thus ϕ_{NH} vs. $[\text{H}^+]$, Table III and Figure S2,²⁵ showed an increase with increasing $[\text{H}^+]$.

It was important to confirm that the $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ was in fact reduced by Cr(II) producing Co(II), and not by any of the species already present in solution or formed during photolysis. This was done by an indirect method. When $\text{Rh}(\text{NH}_3)_5\text{N}_3^{2+}$ was photolyzed in the presence of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ (7.0×10^{-3} M in 1 M HCl) under similar conditions we could not find any significant yield of Co(II). Under the above conditions Rh(III) is known to produce the $\text{Rh}(\text{NH}_3)_5\text{NH}_2\text{Cl}^{3+}$,³ complex with a high quantum yield. Similar

Table III. Quantum Yields for Nitrene Products

(a) As a Function of Time of Irradiation at 254 nm ^a			
<i>t</i> , min	ϕ_{nitrene}	<i>t</i> , min	ϕ_{nitrene}
1	0.090	10	0.103
4	0.100	15	0.102
6	0.101	20	0.103
8	0.100		
(b) Variations of ϕ_{nitrene} with [H ⁺] at 254 nm			
[Cr(NH ₃) ₅ N ₃ ²⁺], 10 ⁻³ M	[H ⁺], M	[Cl ⁻], M	ϕ_{nitrene}
3.5	0.01	1.0	0.09 ± 0.01 (3)
3.5	0.1	1.0	0.11 ± 0.01 (3)
3.5	0.3	1.0	0.12 ± 0.01 (3)
3.4	1.0	1.0	0.13 ± 0.01 (3)
3.5	2.0	2.0	0.13 ± 0.01 (3)
(c) Variations of ϕ_{nitrene} with <i>I</i> _a at 300 nm ^b			
<i>I</i> _a , 10 ⁻⁵ einstein L ⁻¹ min	ϕ_{nitrene} , mol einstein ⁻¹	<i>I</i> _a , 10 ⁻⁵ einstein L ⁻¹ min	ϕ_{nitrene} , mol einstein ⁻¹
1.67	0.188 ± 0.003 (2)	2.49	0.167 ± 0.001 (2)
1.74	0.181 ± 0.003 (2)	3.29	0.197 ± 0.002 (2)
1.80	0.174 ± 0.003 (2)	3.35	0.193 ± 0.002 (2)
1.88	0.157 ± 0.014 (2)	3.42	0.190 ± 0.002 (2)
2.37	0.176 ± 0.001 (2)	3.51	0.151 ± 0.005 (2)

^a [Cr(NH₃)₅N₃²⁺] = 3.5 × 10⁻³ M, [H⁺] = 0.1 M, [Cl⁻] = 1.0 M, *I*_a = 5.5 × 10⁻⁵ einstein L⁻¹ min. ^b [Cr(NH₃)₅N₃²⁺] = 3.5 × 10⁻³ M, [H⁺] = 0.1 M, [Cl⁻] = 1.0 M.

experiments employing Rh(NH₃)₅NH₂Cl³⁺ also failed to generate reducing species. In addition, a solution of Cr(NH₃)₅N₃²⁺, Cl⁻, and H⁺ was photolyzed in a cell with a serum cap, and following photolysis, Co(NH₃)₅F²⁺ was introduced by means of a syringe immediately after shutting off the incident light beam. This experiment did produce small amounts of Co²⁺ ($\phi \sim 10^{-3}$).

Finally, a plot of ϕ_{NH} vs. λ showed a steady increase up to 330 nm after which it showed a steep decline and we take the threshold energy for nitrene formation to be about 2.7 μm^{-1} (Figure 2).

We investigated the possibility of an effect of intensity on the quantum yield. This was possible since the xenon arc lamp we used has a steady increase in output as λ increases in the near-ultraviolet. Hence quantum yields were calculated for different values of *I*_a at 300 nm. The data are somewhat scattered, Table III, Figure S3,²⁵ but there was no systematic effect of incident light intensity on ϕ_{NH} . Our observations are in agreement with Volger's report¹¹ that the overall quantum yield for the disappearance of the complex at 313 nm is higher than at 263 nm.

(D) Ion-Exchange Studies. Our attempts to separate cationic species from the photolyte solutions using acidic forms of cation exchange resins were frustrated by decomposition of the complex during separation. Our main aim was to isolate and characterize the Cr(NH₃)₅NH₂Cl³⁺ species. Solutions of Cr(NH₃)₅N₃²⁺ in 0.1 M HClO₄ and 0.9 M NaCl were irradiated at 320 nm for up to 30% decomposition of the complex. The photolyte was poured onto a column of Dowex 50W-X8 resin in the acid form. We were unable to identify Cr(NH₃)₅NH₂Cl³⁺ in any of the effluents obtained by washing the charged column with up to 3 M HCl. More importantly, we failed to elute any of the unreacted Cr(NH₃)₅N₃²⁺. Instead, large quantities of Cr(NH₃)₅OH₂³⁺ were obtained, apparently formed in an acid-catalyzed hydrolysis of the substrate at high concentrations of acid (3–5 M).²⁶ This latter

observation was further confirmed by conducting a control experiment. When an equimolar mixture of Cr(NH₃)₅OH₂³⁺ and Cr(NH₃)₅N₃²⁺ was poured onto the same ion-exchange column and eluted with HCl, we could not isolate Cr(NH₃)₅N₃²⁺ and large quantities of Cr(NH₃)₅OH₂³⁺ were obtained. Also we found that in very highly acidic solutions (3–5 M), the substrate Cr(NH₃)₅N₃²⁺ underwent relatively fast aquation and some decomposition.

The ion-exchange studies did provide some useful information. Small ($\phi \sim 0.01$ compared to $\phi_{\text{NH}} \sim 0.18$) amounts of free NH₂Cl were identified in early effluents from columns charged with the photolyte. These were most likely due to decomposition of the complex ion on the resins. More importantly small quantities of Cr(H₂O)₆³⁺ were also obtained. When 2 M HCl was passed through the column and the effluent concentrated under vacuum, we obtained products which appeared to be predominantly Cr(H₂O)₅Cl²⁺. These latter observations qualitatively confirm the redox decomposition of Cr(NH₃)₅N₃²⁺.

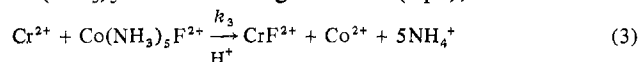
(E) Ligand-Field Photochemistry. For irradiations at wavelengths larger than 360 nm, around the middle of the second quartet band, we could not detect any Co²⁺ or chloramine. The spectral analysis and also NH₃ analysis indicate aquation of ammonia as the only major reaction. This is also true at 500 nm where the spectral changes strongly implicate ammonia aquation. It is somewhat surprising that the yield at 380 nm is less than that at 500 nm.

Discussion

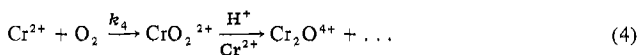
The photochemistry of Cr(NH₃)₅N₃²⁺ is quite remarkable and provides some new insights into the nitrene pathway. We note the following features unique to this system: (1) redox and nitrene modes occur in competition, and (2) there is a reasonably well-defined threshold energy for the nitrene as well as for the redox mode. These points will be considered below after a brief discussion of some of the thermal reactions of transient species generated in photolyses of Cr(NH₃)₅N₃²⁺.

Before we enter into a detailed discussion of the photochemical behavior of Cr(NH₃)₅N₃²⁺, a few comments about the near-ultraviolet spectrum of this complex are in order. The Cr^{III}(NH₃)₅X complexes have much more complex charge-transfer absorption spectra than their cobalt analogues.²⁷ This is presumably because either π_{M} or σ_{M}^* orbitals in chromium may act as acceptors in CTTM transitions so that the number of transitions possible is about twice as many for Cr(III) as for Co(III). Most azido complexes have a low-intensity transition near 320 nm which is often assigned as an internal ligand transition (e.g., see ref 8). The specific assignment of the near-ultraviolet transitions in Cr(NH₃)₅N₃²⁺ must consequently be ambiguous. However, the quasi-thermodynamic comparison with Co(NH₃)₅N₃^{5,6,13} indicates that the CTTM absorption threshold should occur at about 2.9 μm^{-1} in Cr(NH₃)₅N₃²⁺.

(A) Thermal Reactions of Transient Species. Our use of Co(NH₃)₅F²⁺ as a scavenger of Cr²⁺ (eq 3), and therefore as



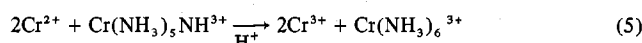
a means of determining the redox yield, has been complicated by what appears to be competition with other Cr²⁺ scavengers. The easiest way to identify of these competing reactions is the reaction with dioxygen (eq 4). Since *k*₄ is quite large (~ 1.6



× 10⁸ M⁻¹ s⁻¹)²⁸ compared to *k*₃ (2 × 10⁵ M⁻¹ s⁻¹),²⁴ (4) is important even when [Co(NH₃)₅F²⁺] > [O₂]. It is significant that deaeration increases both the limiting yields of Co²⁺ and the rate of approach to this limit (Figure 4). That the apparent redox yield increases with [Co(NH₃)₅F²⁺] for small scavenger

concentrations implies that even in deaerated solutions (2) must compete with another reaction (or reactions) which consumes Cr^{2+} species.

The apparent redox yields were much larger in chloride-containing solutions. Evidently Cl^- scavenges for some transient oxidant or its precursor. Since these same medium conditions result in formation of $\text{Cr}(\text{NH}_3)_5\text{NH}_2\text{Cl}^{3+}$, it seems natural to ascribe most of the remaining Cr^{2+} scavenging to reactions, such as (5), with coordinated nitrene intermediates,

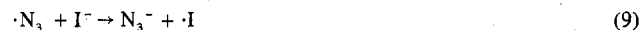
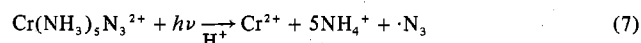


where these reactions, (5), occur in competition with other reactions of coordinated nitrene, such as (6).



The use of cobalt(III) complexes as scavengers for Cr^{2+} photoproducts is ultimately limited by the photolysis of cobalt(III) competitively with the chromium(III) substrate. For example, for the data in Figure 3, direct photoreduction of cobalt(III) becomes important for $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}] > 0.022 \text{ M}$. As a consequence even the largest useful $[\text{Co}(\text{NH}_3)_5\text{F}^{2+}]$ may not be sufficient to scavenge all the Cr^{2+} produced photochemically. Additional scavenging reactions are possible in this system.

The photoredox mode has been qualitatively demonstrated in the flash photolysis experiments which may be represented in eq 7–12.^{3,4}



(B) The Nitrene Pathway. A unique and important feature of our investigations is the observation of a definite threshold energy for the nitrene pathway in $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$. This is the first complex for which a threshold for nitrene formation has been found. In $\text{Rh}(\text{NH}_3)_5\text{N}_3^{2+}$, for example, photochemical production of nitrene species is induced even by relatively long wavelength (ligand field) irradiations.^{3b,4c} Such small energy requirements are probably a reflection of product stability but give no insight into the mechanism of formation or the kind of product states involved.^{4c}

The nitrene pathway is observed over a limited wavelength range and could be associated with an absorption feature at $\sim 330 \text{ nm}$ ($\epsilon \sim 400$). However, the work of Miskowski et al.⁸ demonstrates that excitation of ligand-centered absorptions at about this energy does not necessarily lead to nitrene pathways. It has been argued that the nitrene pathway is mediated by metal-to-ligand back-bonding interactions and that a state correlated with the $(^1\Delta)\text{NH}$ configuration should provide the best opportunity for such back-bonding.^{4c} Back-bonding from Cr^{III} seems unlikely, *except* for those excited electronic states with doublet spin configurations corresponding to double occupancy of a d_{xz} or d_{yz} orbital. The threshold energy for the nitrene pathway ($2.6 \mu\text{m}^{-1}$) is slightly less than the sum of the energies of the $(^1\Delta)\text{NH}$ ($1.6 \mu\text{m}^{-1}$)²⁹ and the $(^2\text{E})\text{Cr}^{\text{III}}$ ($1.3 \mu\text{m}^{-1}$) electronic states and is therefore in very good agreement with the back-bonding argument. While the $\sim 0.3\text{-}\mu\text{m}^{-1}$ difference between the threshold for nitrene products and the sum of $(^1\Delta)\text{NH}$ and $(^2\text{E})\text{Cr}^{\text{III}}$ energies is not distinctly greater than the experimental uncertainties, a $0.2\text{--}0.5 \mu\text{m}^{-1}$ stabilization of the $(^1\Delta)\text{NH}$ configuration through back-bonding is reasonable. These energy relationships are summarized schematically in Figure 5. The

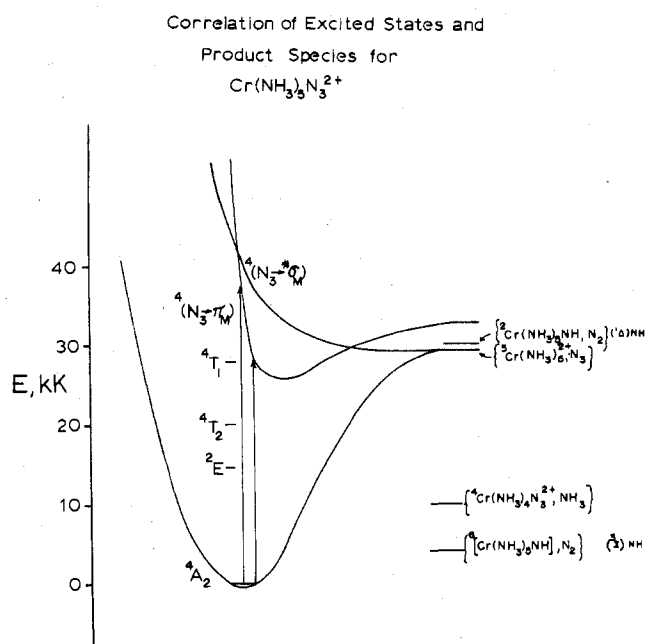


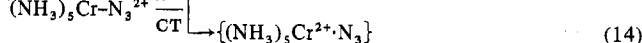
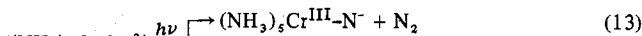
Figure 5. Correlation of excited states and product species for $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$. The lowest energy CTTM states are indicated, but the ligand field states are omitted for simplicity. See text for description of product states.

product configurations considered in Figure 5 are those based on the $(^3\Sigma)\text{NH}$ configuration²⁹ with the $(^4\text{A}_2)\text{Cr}^{\text{III}}$ configuration, the $(^1\Delta)\text{NH}$ configuration²⁹ with the $(^2\text{E})\text{Cr}^{\text{III}}$ configuration, the transition state for substitution of NH_3 in the ground state,³⁰ and the redox radical pair.^{5c,6,31}

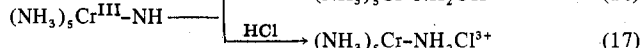
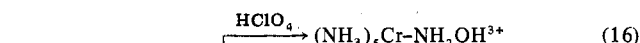
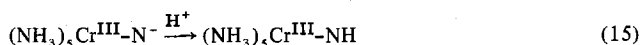
Clearly CTTM excitation provides sufficient energy for formation of all types of products.

Conclusions

We have found that CT excitation of $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ leads to two primary products according to eq 13 and 14. The first



reaction creates the nitrene radical while the second forms the radical pair primary products ($\text{Cr}(\text{II})$ species and the azide radical). The final products of the nitrene pathway are undoubtedly $\text{Cr}(\text{NH}_3)_5\text{NH}_2\text{Cl}^{3+}$ and $\text{Cr}(\text{NH}_3)_5\text{NH}_2\text{OH}^{3+}$, depending on medium conditions³ (eq 15–17). The redox



pathway, however, is complicated since the partners of the radical pair when they diffuse away from the solvent cage have several modes of decay owing to the many scavengers that are reactive toward the chromous ion. That $(\phi_{\text{NH}} + \phi_{\text{Co}^{2+}}) < \phi_{\Delta\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}}$ suggests that even the chloramine and/or hydroxylamine products may be reactive toward Cr^{2+} . Photoprocesses resulting in ammonia or azide hydrolysis may also contribute to some extent.

The threshold energy for photoredox in $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ is greater than that of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ by very nearly the amount predicted^{5c} from the differences in potential for cobalt(III)/cobalt(II) and chromium(III)/chromium(II) redox couples ($\sim 0.8 \text{ V}$).

A threshold has been found for the nitrene pathway in $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$ which is consistent with this pathway origi-

nating from an excited state correlated with the ($^1\Delta$)NH and (2E)Cr^{III} electronic configurations and mediated by metal-to-ligand back-bonding.

Registry No. Cr(NH₃)₅N₃²⁺, 22317-10-8; Co(NH₃)₅F²⁺, 15392-06-0.

Supplementary Material Available: Quantum yield data for 254-nm irradiations of Cr(NH₃)₅N₃²⁺ in the presence of Co(NH₃)₅F²⁺ (Table SI) and Figures S1–S3, showing variations of ϕ_{nitrene} with irradiation time, [H⁺], and I_a (5 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Partial support of this research by the National Science Foundation (CHE 76-00429) is gratefully acknowledged.
- (2) For reviews see: (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970; (b) A. W. Adamson and P. D. Fleischauer, Ed., "Concepts in Inorganic Photochemistry", Wiley, New York, N.Y., 1975.
- (3) (a) J. L. Reed, F. Wang, and F. Basolo, *J. Am. Chem. Soc.*, **94**, 7173 (1972); (b) J. L. Reed, H. D. Gafney, and F. Basolo, *ibid.*, **96**, 1363 (1974); (c) H. D. Gafney, J. Reed, and F. Basolo, *ibid.*, **95**, 7998 (1973).
- (4) (a) G. J. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973); (b) *J. Am. Chem. Soc.*, **95**, 2371 (1973); (c) T. Inoue, J. F. Endicott, and G. J. Ferraudi, *Inorg. Chem.*, **15**, 3098 (1976).
- (5) (a) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970); (b) G. J. Ferraudi, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **97**, 6406 (1975); (c) J. F. Endicott and G. J. Ferraudi, *Inorg. Chem.*, **14**, 3133 (1975).
- (6) See, J. F. Endicott, in ref 2b, p 81.
- (7) J. I. Zink, *Inorg. Chem.*, **14**, 446 (1975).
- (8) V. M. Miskowski, G. L. Nobinger, and G. S. Hammond, *Inorg. Chem.*, **15**, 2904 (1976).
- (9) The azide aquation mode has also been found to be an important, but not the exclusive, photodecomposition mode of Co(CN)₅N₃³⁻.^{5c}
- (10) (a) R. Sriram and J. F. Endicott, *J. Chem. Soc., Chem. Commun.*, 683 (1976); (b) in preparation.
- (11) A. Vogler, *J. Am. Chem. Soc.*, **93**, 5212 (1971).
- (12) (a) H. D. Gafney, private communication to J.F.E., April 1976; (b) M. Katz and H. D. Gafney, *J. Am. Chem. Soc.*, **98**, 7458 (1976).
- (13) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975).
- (14) M. Linhard and W. Berthold, *Z. Anorg. Allg. Chem.*, **279**, 173 (1955).
- (15) M. Mori, *Inorg. Synth.*, **5**, 131 (1957).
- (16) G. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 414 (1952).
- (17) F. Basolo and R. K. Murman, *Inorg. Synth.*, **4**, 171 (1953).
- (18) (a) C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220**, 104 (1933); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **205**, 518 (1956).
- (19) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966.
- (20) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1959).
- (21) A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).
- (22) L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).
- (23) (a) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972); (b) S. D. Malone and J. F. Endicott, *J. Phys. Chem.*, **76**, 2223 (1972).
- (24) J. P. Caldin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).
- (25) Supplementary material.
- (26) P. J. Staples, *J. Chem. Soc. A*, 2731 (1968).
- (27) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **266**, (1951).
- (28) R. M. Sellers and M. G. Simic, *J. Am. Chem. Soc.*, **98**, 6145 (1976).
- (29) H. Okabe, *J. Chem. Phys.*, **49**, 2726 (1968).
- (30) J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem.*, **80**, 949 (1976).
- (31) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975).

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Trans Effects in Octahedral Complexes: Substitution of Chloromethyl- and Dichloromethylpentaquochromium(III) Ions by Thiocyanate Ion¹

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Equilibrium and kinetic data were evaluated for formation of the 1:1 complexes of NCS⁻ with (H₂O)₅CrCH₂Cl²⁺ and (H₂O)₅CrCHCl₂²⁺. Equilibrium is established within <100 s, which is unusually rapid for Cr(III) substitution. This corresponds to replacement of only a single H₂O molecule for both NCS⁻ and CH₃OH as entering groups, verified for NCS⁻ by species tests and equilibrium constant determinations and for CH₃OH by chemical analysis. The formation constants for NCS⁻ are 10.4 and 12.8 M⁻¹ for CrCH₂Cl²⁺ and CrCHCl₂²⁺, respectively. The kinetic data for anation follow the expression $k_{\text{an}} = A[\text{NCS}^-]/(1 + C[\text{NCS}^-])$ and are consistent with both a limiting S_N1 and an ion-pairing mechanism.

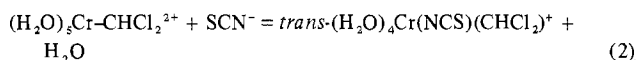
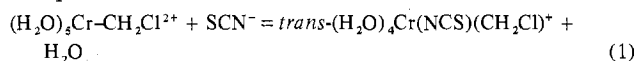
Introduction

Recent publications²⁻⁵ have cited the large trans labilizing effect of an alkyl group in cobalt complexes, particularly in vitamin B₁₂ and related model complexes containing a planar tetradentate macrocycle.

In the present work we report equilibrium and kinetic studies on anation reactions of two complexes which are members of the family (H₂O)₅CrR²⁺. The particular R groups studied, CH₂Cl and CHCl₂, are complexes in which decomposition of the Cr–C bond via protonolysis occurs very slowly⁶ in contrast to more rapid protonolysis of simple alkyls.⁷

Demonstration of an appreciable kinetic trans effect in pentaquochromium complexes has been accomplished only rarely, although other workers have noted some substantial effects particularly for coordinated iodide and sulfite ions^{8a-d} and also for the trifluoromethyl complex (H₂O)₅CrCF₃²⁺.^{8e} In the present paper we report (1) proof that only a single water molecule, and therefore most likely that in the trans position, undergoes rapid substitution, based on competition between H₂O and CH₃OH, (2) equilibrium constants for the

two anation reactions, and (3) kinetic data for the reactions in eq 1 and 2.



After completion of this work there appeared in the recent literature⁹ an independent determination of the equilibrium constant and kinetics of reaction 2. The published results, as discussed later, are in substantial agreement with ours as regards the equilibrium formulation but in considerable disagreement concerning kinetics; our data show rates only ~10⁻³ of theirs and with a different dependence upon [SCN⁻].

Results

Induced Solvolysis. Reaction of CrCH₂Cl²⁺ with Hg²⁺ results in alkyl transfer (eq 3),⁶ a reaction which has a rate



constant of 0.59 dm³ mol⁻¹ s⁻¹ (25.0 °C, in water, μ = 1.0 M).⁹