Flash Photolytic, Isotope Tracer, and Chemical Scavenging Studies of the Ultraviolet Photochemistry of Pentaamminecobalt(III) Chloride. Evidence for Excited-State Intermediates[1,2]

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Abstract: Product analyses, flash photolysis, and chemical scavenging studies have shown that the oxidized radical resulting from the photoreduction of $Co(NH_3)_5Cl^{2+}$ is largely nitrogeneous. Of the detected final oxidized products all of the N_2O (a minor product) and some of the N_2 result from the oxidation of NH_3 in the coordination sphere of the complex at the time of photoreduction. The oxidized radicals initially formed can be stabilized by complexation with Cl^-. These primary radicals do not appear to react with bulk NH_4^+. Precursors to the formation of radicals can oxidize methanol. Methanol scavenging of these very short-lived, reactive photochemical intermediates has shown that only 50% of the $Co(NH_3)_5Cl^{2+}$ originally excited by absorption of 254-nm radiation can be scavenged. Since the scavenged species normally regenerates $Co(NH_3)_5Cl^{2+}$ (by means of a nonradiative decay process), it is concluded that the reactive intermediate is most likely a metastable charge-transfer excited state of the cobalt(III) complex.

Despite the many studies of the photochemistry of coordination complexes of cobalt(III), questions concerning the role of excited states in determining product distributions are still controversial.[4] A great deal of this discussion has focused on the photochemistry of simple acidoammine complexes of the type $Co(NH_3)_5X^{2+}$ ($X = Cl^-, Br^-, I^-$). Much of the mechanistic interest in complexes of this type is the result of the several possible photochemical reactions, photoreduction[5,6]

$$Co(NH_3)_5X^{2+} + h\nu \xrightarrow[{[H^+]}]{} Co^{2+} + 5NH_4^+ + X \tag{1}$$

or photolabilization[5-8]

$$Co(NH_3)_5X^{2+} + h\nu + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + X^- \tag{2}$$

$$\xrightarrow{H^+} Co(NH_3)_4OH_2X + NH_4^+ \tag{3}$$

For most of the acidoammine complexes which have been studied, reactions 1 and 2 have been reported to predominate. The variations in their relative importance with variation of X and with variation of the wavelength of the radiation used has led Adamson to argue strongly[4c,g,5] that the product distributions result from reactions characteristic of the solvent-trapped radical pairs, $(Co(NH_3)_5{}^{2+},X\cdot)$, generated following absorption of radiation. This radical-pair model does not ascribe any specific role to the initial or to metastable excited states which may be generated by the absorption of radiation.

Several authors have contended that the radical-pair mechanism cannot account for all the known photochemistry of cobalt(III) complexes.[4b,4d-f,6-8] The fairly general observations that the photochemically active region is the near- or middle-ultraviolet has led to the suspicion that the photochemically active species is a relatively low-energy, spectroscopically forbidden charge-transfer excited state. Some recent energy-transfer experiments have been interpreted as providing evidence for a low-energy ($<2.5 \times 10^{-3}$ cm^{-1}) charge-transfer excited state in $Co(NH_3)_6{}^{3+}$.[9]

It has also been pointed out[6] that since proton-transfer reactions are very rapid in aqueous solution, a photochemical reaction which results in the oxidation of an ammine ligand can in principle produce Co(II)–NH_2 species which, being stoichiometrically different from the original cobalt(III) substrate, would not be spectroscopically observable and could function as photochemical intermediates. The pH-dependent quantum yields for photoreduction of some cobalt(III) ammines have been cited as evidence for such species.[6,10,11] The most perplexing system has been

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[2] Preliminary reports of various aspects of this study have appeared in the following places: (a) R. G. Hughes, G. Caspari, J. F. Endicott, and M. Z. Hoffman, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, PHYS 134; (b) R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, Abstracts, 4th Mid-Atlantic Regional Meeting of the American Chemical Society, Washington, D. C., Feb 1969; (c) R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *Chem. Commun.*, 191 (1969).

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[4] For recent reviews, see (a) E. L. Wehry, *Quart. Rev., Chem. Soc.*, 21, 213 (1967); (b) V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, 1, 7 (1967); (c) A. W. Adamson, *Coord. Chem. Rev.*, 3, 169 (1968); (d) V. Balzani, L. Moggi, and V. Carassiti, *Ber. Bunsenges. Phys. Chem.*, 72, 288 (1968); (e) L. Moggi, V. Balzani, and V. Carassiti, *ibid.*, 72, 293 (1968); (f) D. Valentine, Jr., *Advan. Photochem.*, **6**, 123 (1968); (g) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Feischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968); (h) D. Valentine, Jr., *Annu. Surv. Photochem.*, 1, 459 (1969); (i) J. F. Endicott, *Israel J. Chem.*, **8**, 209 (1970).

[5] (a) A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960); (b) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

[6] J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

[7] L. Moggi, N. Sabbatini, and V. Balzani, *Gazz. Chim. Ital.*, **97**, 980 (1967).

[8] (a) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **90**, 4740 (1968); (b) J. F. Endicott, M. Z. Hoffman, and L. Beres, *J. Phys. Chem.*, **74**, 1021 (1970).

[9] (a) A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 5943 (1968); (b) A. Vogler and A. W. Adamson, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, INOR 169.

[10] Some recent more careful studies[11] have indicated that the pH dependence of photoreduction of $Co(en)_3{}^{3+}$ is within the limits of experimental error.

[11] M. F. Manfrin, G. Varani, L. Moggi, and V. Balzani, *Mol. Photochem.*, 1, 387 (1969).

$Co(NH_3)_5Cl^{2+}$. For this complex, (1) the quantum yield of cobalt(II), $\phi_{Co^{2+}}$, increased about threefold as the pH increased from 0 to 3; (2) the 254-nm photolysis is not greatly[12] complicated by photolabilization; (3) the quantum yields of Co^{2+} and Cl^- are reported[4b,6,7] to be stoichiometric and no oxidized species have been found;[13] (4) the absorption band irradiated at 254 nm has been assigned as $Cl^- \rightarrow Co(III)$ charge transfer.[14] These several considerations and the apparent[4g,5] relevance of the photochemistry of this complex to the radical-pair model have led us to reexamine the photochemistry of this complex from several different points of view. The results and interpretation of these studies are the subject of this report.

Experimental Section

Preparation of Reagents and Solutions. Standard literature methods[15,16] were used in the preparation of $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4OH_2Cl^{2+}$, $Co(NH_3)_6{}^{3+}$, $Co(NH_3)_5OH_2{}^{3+}$, and *trans*-Co(*trans*-[14]diene)$Cl_2{}^+$.[17] All complexes were obtained as the perchlorate salts. The method of preparation of Co(tetraen)Cl^{2+} [17] was substantially the same as reported by House and Garner[18] after the work on this complex reported in this paper had been largely completed.

The purity of complexes was determined by comparison of their absorption spectra with literature values and by the percentage cobalt found on complete photolysis.[19]

Solutions were prepared for photolysis using reagent grade chemicals and deionized distilled water. As a general practice solutions were deaerated by passing Cr^{2+}-scrubbed N_2 through them before and during photolysis. In the flash photolysis studies, solutions were deaerated by N_2 passed through the two-necked photolysis cell using syringe needles and serum caps.

Especial care was taken in the studies of $Co(NH_3)_5Cl^{2+}$ to use many independently prepared sample of the complex. In the flash photolysis studies we have used methanol and KCl from several different sources and in some cases spectral grade and ultra pure reagents.

Analysis for Oxidation Products. The possibility that oxidation products from the photoreduction of $Co(NH_3)_5Cl^{2+}$ remain in solution was explored using standard spot tests for $NO_2{}^-$, $NO_3{}^-$, NH_2OH, N_2H_4, and H_2O_2. Tests were performed on 5×10^{-3} *M* solutions of $Co(NH_3)_5Cl^{2+}$ which had been partially and fully photolyzed under each of the following conditions: (a) in 0.1 *M* $HClO_4$, no gas bubbling through photolyte; (b) in 0.1 *M* $HClO_4$, N_2 bubbling through photolyte; (c) in 0.1 *M* $HClO_4$, O_2 bubbling through photolyte; and (d) in 0.1 *M* $HClO_4$, photolyzed *in vacuo*. The distillate from (d) was also examined for the above species. The detection limits were determined experimentally and were found to be similar for a given test under all of the following conditions: (a) in the presence of 5×10^{-3} *M* $Co(NH_3)_5Cl^{2+}$; (b) in the presence of 5×10^{-3} *M* Co^{2+}, and (c) in the presence of a partially photolyzed solution of 5×10^{-3} *M* $Co(NH_3)_5Cl^{2+}$. Oxidizing and reducing properties of photolyzed solutions were determined with $KMnO_4$ and KI, respectively. Table I summarizes the analytical methods and the detection limits.

Other Analytical Procedures. The concentration of Cl^- in photolyzed solutions was determined potentiometrically by titration of solutions formed from the addition of a 5-ml aliquot of photolyte to 50 ml of acidic (100 ml of HNO_3 per gallon) acetone with 0.025 *M* $AgNO_3$ at 0°.[20]

Table I. Assay of Possible Oxidation Products in Solutions Following the Photoreduction of $Co(NH_3)_5Cl^{2+}$

Possible product	Detection limit, *M*	Max[a] electron, equiv %	Method	Ref
$NO_2{}^-$	5×10^{-7}	0.06	Sulfanilic acid with β-naphthylamine	*b*
$NO_3{}^-$	5×10^{-7}	0.08	Reduction with Zn–HO_2CCH_3 followed by $NO_2{}^-$ test[2]	*b*
NH_2OH	5×10^{-6}	0.2	NaO_2CCH_3; sulfanilic acid; I_2; $Na_2S_2O_3$ β-Naphthylamine	*c*
N_2H_4	5×10^{-6}	0.1	*p*-Dimethylamininobenzylamine	*d*
H_2O_2	3×10^{-5}	1.2	KI; ammonium molybdate	*e*
Oxidizing agents	1×10^{-5}	0.6[f]	KI	
Reducing agents	1×10^{-5}	0.6	$KMnO_4$	

[a] Equiv/mol of Co^{2+} produced × 100. [b] F. Feigl, "Spot Tests in Inorganic Analysis," 5th ed, Elsevier, Amsterdam, 1958, p 330. [c] Reference *b*, p 245. [d] Reference *b*, p 240. [e] C. L. Wilson and D. Wilson, "Comprehensive Analytical Chemistry," Vol. I, Elsevier, Amsterdam, 1962, p 278. [f] The amount of oxidant was greatest in solutions saturated with O_2.

The concentration of Co^{2+} was determined by the method of House[19,21] modified as below. A 4-ml aliquot of photolyte was mixed with 8 ml of 50% NH_4SCN (the NH_4SCN solution was extracted previous to use with methyl isobutyl ketone until the ketone extractant was colorless). Chilled (0°) acetone was added to bring the total volume to 25 ml. The absorbance at 625 nm of the resulting solutions was determined on a Beckman DU spectrophotometer ($\epsilon_{Co^{2+}}$ 1.75×10^3).

Gaseous products from solutions photolyzed *in vacuo* were determined using mass spectrometry (Nuclide Model RMS-60-6) and gas chromatography (F and M Model 810). Sample solutions were degassed prior to photolysis, isolated from the vacuum system, and photolyzed for a predetermined time; then the gaseous products were transferred through a cold trap to a gas cell by means of a Toepler pump.[8b] A 6-ft Linde molecular sieve 5A column heated to 250° was used for the determination of N_2O.[22] Calibrations of the chromatographic apparatus were performed by injection of known volumes of the pure gases. Iodine was spectrophotometrically determined as $I_3{}^-$ in 0.5 *M* KI (pH 1) as described previously[23] (ϵ_{353} 2.64×10^4).[24]

Bio-Rad AG 50 W-X4 cation-exchange resin (acidic form, 200–400 mesh) was used in the ion-exchange separation of reaction products.

Continuous-Photolysis Apparatus. The apparatus employed for continuous photolysis at 254 nm in this study provided approximately a 10^2-fold range of incident light intensities. A helical 250-W Hanovia low-pressure mercury lamp (air thermostated) was employed for the highest intensity range ($I_0 \simeq 6.6 \times 10^{-3}$ einstein $l.^{-1}$ min^{-1}).[6] Both of the lower intensity photolysis systems used Ultraviolet Products, Inc. low-pressure mercury immersion lamps. The simplest of these systems ($I_0 \simeq 5.5 \times 10^{-4}$ einstein $l.^{-1}$ min^{-1}) has been described in detail elsewhere.[9b] The lowest intensity lamp ($I_0 \simeq 6.0 \times 10^{-5}$ einstein $l.^{-1}$ min^{-1}) was fabricated with an additional quartz jacket around the lamp; this outer jacket was filled with a ($CoSO_4$–$NiSO_4$ and KI) filter solution.[25] The entire photolysis sytem was generally thermostated at 25°.

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(12) Although reaction 2 does not appear significant in the 254-nm photolysis of this complex some evidence for a small (<15%) contribution from reaction 3 has been cited.

(13) In a preliminary report of this work, we have pointed out that some oxidized nitrogeneous species are generated.[2c]

(14) (a) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962; (b) *Advan. Chem. Phys.*, **5**, 33 (1963).

(15) (a) A. Werner, *Justus Liebigs Ann. Chem.*, **386**, 165 (1912); (b) H. S. Booth, W. C. Fernelius, J. C. Bailar, Jr., T. Moeller, E. G. Rochow, *et al.*, *Inorg. Syn.*, **1–6** (1939–1960).

(16) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967).

(17) *trans*-[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; tetraen = tetraethylenepentamine.

(18) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).

(19) R. G. Hughes, J. F. Endicott, M. Z. Hoffman, and D. A. House, *J. Chem. Educ.*, **46**, 440 (1969).

(20) V. J. Shriner, Jr., and M. L. Smith, *Anal. Chem.*, 28, 1043 (1958).

(21) D. A. House, private communication to R. G. H.

(22) R. N. Dietz, *Anal. Chem.*, 40, 1576 (1968).

(23) J. F. Endicott and M. Z. Hoffman, *J. Phys. Chem.*, 70, 3389 (1966).

(24) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, 73, 1842 (1951).

(25) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, p 729.

For each of these photolysis systems, uranyl oxalate or ferrioxalate actinometry was performed at several different photolyte absorbancies. A calibration curve of absorbance *vs.* the actinometrically determined I_a was determined for each apparatus as described previously.[6]

Flash Photolysis. The flash apparatus (Xenon Corp., Medford, Mass.) could be operated in either a flash-spectrographic or kinetic-spectrophotometric mode. The main flash lamps dissipated 250 J at 10 kV with a rise time of 5 μsec, a half-peak duration of 20 μsec, and a total duration of less than 50 μsec. The spectra of transients produced were obtained when the spectroscopic flash lamp was fired after a calibrated time delay and were recorded photographically at the exit camera of a Hilger-Engis 0.6-m combination grating monochrometer–spectrometer. The kinetics of the decay of the transients so detected were monitered by replacing the spectroscopic flash lamp by a voltage-regulated 150-W continuous xenon arc, the light from which passed through the monochromator into an RCA 1P28 photomultiplier at the exit slit. The output of the photomultiplier was passed through compensating resistors into a Tektronix Model 564 storage oscilloscope.

The quartz vessels had a path length between the optically flat end windows of 22 cm. The arms of the vessel could be sealed with serum caps which provided a means of flushing the solutions with scrubbed nitrogen. The reaction vessel could be enclosed in Vycor or Pyrex tubing in order to restrict the flash radiation to wavelengths greater than 230 or 320 nm, respectively. In order to prevent unwanted photolysis, appropriate filters were placed in front of the analyzing lamp.

Experimental Procedures. Continuous Photolysis. Quantum yields of Co^{2+}, $\phi_{Co^{2+}}$, were determined from the slopes of a plot of $[Co^{2+}]$ *vs.* time. Aliquots of photolyte were taken for Co^{2+} analysis at convenient time intervals. For high values of absorptivity (*i.e.*, ~90% initially) plots of $[Co^{2+}]$ *vs.* time were linear for more than three half-lives for studies in any of the photolysis systems.[26] Thus values of $\phi_{Co^{2+}}$ generally represent six to ten determinations of $[Co^{2+}]$ at different exposure times. Initial quantum yields of Co^{2+} have been calculated in those experiments where plots of $[Co^{3+}]$ *vs.* time were not linear[27] for at least 50% of reaction. Such initial values of $\phi_{Co^{2+}}$ were estimated graphically. Gas yields were determined relative to the $[Co^{2+}]$ produced by irradiation of solutions.

Flash Photolysis. Rate constants for the transient decay were initially determined from the oscillographic traces by evaluating the slope of the best line drawn through the first- (log *A* *vs.* time) or second-order ($1/A$ *vs.* time) plots. The intensity of the main flash lamps could be varied by altering the voltage at which the lamps fired. A change in the flash energy resulted in a change in the absorbance of the transient.

The decay of the transient obtained from $Co(NH_3)_5Cl^{2+}$ could be represented adequately as either first- or second-order decay (see Results section B). In order to avoid forcing the data to fit an assumed rate law we have employed an alternative method of expressing the decay kinetics. The initial linear portion of the absorbance *vs.* time plot for each decay was extrapolated to the beginning of the flash pulse which was taken as $t = 0$. This initial linear portion generally extended across approximately one quarter-life of the decay. Extrapolation of the best first- or second-order line back to $t = 0$ yielded a value of A_0 that was within 20% of that obtained by *A* *vs.* *t* extrapolation. The half-life, $t_{1/2}$, was taken s the time for the absorbance to drop to one-half of the value of A_0.

Except where otherwise indicated, all solutions were discarded after the first flash.

Results

A. Continuous Photolysis. 1. Photoreduction Yields. Consistent with the previous reports[4b,6,7] the 254-nm irradiation of $Co(NH_3)_5Cl^{2+}$ gives, within the limits of experimental error, stoichiometric amounts of Co^{2+} and Cl^-, with yields independent of I_a (in the range 5×10^{-5}–6×10^{-3} einstein l.$^{-1}$ min^{-1}). These observations, together with the very similar observations for $Co(tetraen)Cl^{2+}$, are summarized in Table II.

Table II. Yields of Co^{2+} and Cl^- in the 254-nm Irradiation of $Co(NH_3)_5Cl^{2+}$ and $Co(tetraen)Cl^{2+}$ (25°, 0.1 *M* $HClO_4$)

$[Co(III)] \times 10^3$ M^a	I_a, einstein l.$^{-1}$ min^{-1} $\times 10^{-4}$	$\phi_{Co^{2+}}$	ϕ_{Cl^-}
	$Co(NH_3)_5Cl^{2+}$		
2.9	53	0.15[b]	0.15[b,c]
2.8	8.9	0.13[b]	
5.3	5.5	0.17	0.16
2.61 ± 0.05	5.5	0.17 ± 0.01[d]	
2.0	0.54	0.18	
	$Co(tetraen)Cl^{2+}$		
1.0 ± 0.1	52	0.030 ± 0.001[e]	0.030
1.0 ± 0.1	9.6	0.035 ± 0.001[f]	

[a] Initial concentration. Single determination except as noted. [b] Reference 6. [c] Determined relative to $\phi_{Co^{2+}}$. [d] Average and average deviation of five determinations. [e] Average and average deviation of three determinations ($0.1 \leq pH \leq 2$). For pH ≥ 3, $d[Co^{2+}]/dt$ was not constant owing to the changes in I_a which occur as Co(II) hydroxides precipitate. Initial values of $\phi_{Co^{2+}}$ estimated were 0.02 at pH 3 and 0.014 at pH 4. [f] Average and average deviation of two determinations.

2. The Search for Oxidized Products. The tests for oxidized species in photolyzed solutions of $Co(NH_3)_5Cl^{2+}$ were generally negative so that the experimental limits of detectability in Table I can be taken to represent the maximum concentration of the respective species present. Photolyzed solutions of $Co(NH_3)_5Cl^{2+}$ are always slightly (about 1 equiv %) oxidizing toward acidic I^+.

As related in our preliminary report,[2c] there are gaseous nitrogenous products resulting from the 254-nm irradiation of $Co(NH_3)_5Cl^{2+}$. The products identified are N_2 and N_2O, and their yields clearly depend on the composition of the medium in a complex manner (Table III).

Table III. Gas Yields in the 254-nm Photolysis of $Co(NH_3)_5Cl^{2+}$ (~25°; $I_a \sim 6 \times 10^{-3}$ einstein l.$^{-1}$ min^{-1})

Medium	No. of determinations	Equiv % product[a] N_2	N_2O
0.01 *M* $HClO_4$	1	7	9
0.1 *M* $HClO_4$	3	17 ± 1	4.5 ± 1
0.5 *M* $HClO_4$	1	18	*b*
0.1 *M* $HClO_4$; 0.1 *M* NH_4ClO_4	2	19 ± 1	*b*
0.1 *M* $HClO_4$; 0.1 *M* KCl	3	41 ± 1	5 ± 1
0.1 *M* $HClO_4$; 0.1 *M* NH_4Cl	4	72 ± 3	4 ± 1
0.1 *M* $HClO_4$	1[c]	18	*b*
0.1 *M* $HClO_4$	2[d]	19 ± 2	*b*
0.1 *M* $HClO_4$	1[e]	15	*b*
0.1 *M* $HClO_4$; 5×10^{-3} *M* I^-	1	0[f]	0[f]
0.1 *M* $HClO_4$; 1×10^{-3} *M* I^-	1	10	2
0.1 *M* $HClO_4$; 0.1 *M* CH_3OH	1	0[g]	0[g]

[a] (Oxidation equiv of gas/$[Co^{2+}]$) × 100. Mean values and averages deviations are cited for duplicate determinations. Gas yields determined chromatographically. Exposure time = 10 min except as indicated. Initial $[Co(NH_3)_5Cl^{2+}] = 5 \times 10^{-3}$ *M*. [b] Not determined. [c] Irradiated 0.50 min. [d] Irradiated 1.0 min. [e] Irradiated 5.0 min. [f] No gases detected. [g] About 2% H_2 detected; no other gases were detected.

3. Mass Spectral Identificationt of Gaseous Products. The predominant gaseous products from the photolysis of $Co(NH_3)_5Cl^{2+}$ were identified by comparison of the

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(26) It is to be noted that the photolysis lamps must be warmed up for several minutes before photolysis if reliable results are to be obtained. See further discussion of procedural details in ref 8b.

(27) Such nonlinearity results when the substrate absorptivity is initially low (less than 50%) or when absorbing products (*e.g.*, I_3^-) are generated during the photolysis.

Table IV. Irradiation (254 nm) of $Co(NH_3)_5Cl^{2+}$. ^{15}N Tracer Studies

Composition of solution[a]	Ratio of coord to bulk NH_3	Obsd atom% ^{15}N in products N_2O	N_2	Estimated atom% ^{15}N in N_2[b] A[c]	B
$Co(NH_3)_5Cl^{2+}$ + 0.1 *M* $^{15}NH_4Cl$[d]	25/1	2.1 ± 0.3[e]	26.0 ± 0.5[e]	27	21
$Co(NH_3)_5Cl^{2+}$ + 0.01 *M* $^{15}NH_4Cl$[f]	2.5/1	1.5	5	13	2
$Co(^{15}NH_3)_5Cl^{2+}$ + 0.1 *M* NH_4Cl	0.25/1	4.2 ± 0.3[e]	1.6 ± 0.2[e]	1.0	1.8
$Co(^{15}NH_3)_5Cl^{2+}$		4.4	4.5		

[a] All solutions 0.1 *M* in $HClO_4$, 5×10^{-3} *M* in $Co(NH_3)_5Cl^{2+}$; $I_a \simeq 6 \times 10^{-3}$ einstein l.$^{-1}$ min^{-1}; exposure time = 10 min. [b] Assuming isotope effects can be neglected. Column A, if all is from bulk; column B, if yield from coordinated NH_3 is invarient. [c] Using $N_C/(N_B + N_C) \simeq 0.0125/([NH_4^+]_0 + 0.0125)$ to find the fraction of N_2 which had its source in NH_4^+ released to solution by reduction of $Co(NH_3)_5Cl^{2+}$. N_C and N_B are the concentrations of NH_4^+ which had their source in the coordination sphere of $Co(NH_3)_5Cl^{2+}$ or in the bulk solution, respectively. [d] Initial enrichment of NH_4Cl = 30 atom %; after photolysis enrichment = 25 atom %. [e] Duplicate determinations. [f] Initial enrichment of NH_4Cl = 30 atom %; after photolysis enrichment = 8 atom %.

mass spectra of a reaction sample with those of pure N_2 and N_2O. Mass spectra of the evolved gases show that chlorine-containing species cannot exceed 1% of the amount of N_2 produced.

4. **Tracer Studies.** Table IV summarizes the results of several studies of the 254-nm photoreduction of $Co(NH_3)_5Cl^{2+}$ in which $^{15}NH_3$ was used as a tracer to elucidate the source of gaseous photolysis products. In order to estimate the expected enrichment in the N_2 which results from bulk reaction of NH_4^+, it is necessary to account for changes in the bulk enrichment of $^{15}NH_4^+$ due to changes in $[NH_4^+]$. Since the $Co(NH_3)_5Cl^{2+}$ is sufficiently high that the photochemical reactions are zero order to about 90% of reaction and that the rate of release of coordinated $*NH_3$ into bulk solution is very nearly equal to five times the zero-order rate of production of Co^{2+}, $d[NH_4^-]/dt \simeq 5\phi I_a$. Thus at any time t after onset of irradiation the total concentration of NH_4^+ in bulk is given by $[NH_4^+]_B \simeq [NH_4^+]_0 + 5\phi I_a t$. If the rate of bulk production of N_2 is taken as $k[NH_4^+]_B$ and if the photolysis is performed for $t_f = 5 \times 10^{-3}/\phi I_a$ min (*i.e.*, nearly to complete decomposition), then the fraction of N_2 resulting from the reaction of $*NH_4^+$ (which at $t = 0$ was coordinated to cobalt(III)) is given approximately by

$$f \simeq \frac{\left(\dfrac{5I_a t_f}{2}\right)}{\left([NH_4^+]_0 + \dfrac{5\phi I_a}{5}\right)}$$

or setting $t_f = 5 \times 10^{-3}/\phi I_a$ and $\phi = 0.17$, $f = 0.0125/([NH_4^-]_0 + 0.0125)$. This expression has been used with the initial isotopic compositions of coordinated and bulk NH_3 (assuming a normal abundance of $^{15}N^{14}N$, compared to $^{14}N_2$, of 0.4 atom% ^{15}N and ignoring isotope effects) to estimate the expected statistical isotope distributions in Table IV.

5. **Chemical Scavenging Studies.** Some of the changes which occur in the distribution of photolysis produts in the presence of various potential chemical scavengers are reported in Tables III and IV. It has been our experience that it is relatively simple to find scavengers which can alter the yields of gaseous products (*e.g.*, see Table III), but it is relatively difficult to find nonabsorbing substances that can alter the yield of cobalt(II). We have found that $\phi_{Co^{2+}}$ is independent of NaCl, NH_4Cl, NaBr, and methanol up to 0.1 *M* and of $[HCl] \leq 1$ *M*. In the case of NaI, the absorptivity of I^+ limited our studies to concentrations ≤ 0.01 *M*; within this limit $\phi_{Co^{2+}}$ was independent of the added salt.

Table V. Yields of Oxidized Product Resulting from Irradiation of $Co(NH_3)_5Cl^{2+}$ in the Presence of I^- and Br^- [a]

$[X^-]$, $M \times 10^2$	$\phi_{I_3^-} \times 10^2$ [b]
0	0.56
$X = I^-$	
0.016	1.7 ± 0.5[c]
0.020	3.5 ± 0.8[c]
0.060	3.9
0.080	4.4
0.100	4.7 ± 0.6[c]
0.200	5.2 ± 1.1[c]
0.40	5.5 ± 1.0[c]
0.040	0.096[d]
0.100	0.12[e]
$X = Br^-$	
0.3	0.56
1.0	2.2
2.0	2.2
2.5	2.3
3.0	2.7 ± 0.3[c]
5.0	2.8 ± 0.3[c]
10.0	3.2 ± 0.4[c]

[a] At $T = 25^\circ$; $[HClO_4] = 0.1$ *M*; 1×10^{-3} $M \leq [Co(NH_3)_5Cl^{2+}] \leq 5 \times 10^{-3}$ *M*; $I_a = 5.0 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1}, except as indicated. [b] $[I_3^-]$ determined spectrophotometrically in 0.5 *M* I. 0.1 *M* H^+; ref 20. $\phi_{I_3^-}$ is the initial yield of I_3^-. [c] Mean value and mean deviation from the mean for three determinations. [d] $I_a = 1.9 \times 10^{-5}$ einstein l.$^{-1}$ min^{-1}. [e] $I_a = 1.7 \times 10^{-5}$ einstein l.$^{-1}$ min^{-1}.

When NaI was added to irradiated solutions of $Co(NH_3)_5Cl^{2+}$, only a trace of I_3^- was formed (see Table I), but when $Co(NH_3)_5Cl^{2+}$ was photolyzed in the presence of I^-, appreciable quantities of I_3^- were formed.[28] Irradiation of $Co(NH_3)_5Cl^{2+}$ in the presence of Br^- produced smaller amounts of an oxidant, eventually determined as I_3^-. The results of these studies are summarized in Table V. That the halogen product derives from species formed subsequent to the irradiation of $Co(NH_3)_5Cl^{2+}$ rather than from direct photolysis of X^- is illustrated dramatically in Figure 1. In this experiment the rate of production of I_3^- decreased unusually rapidly (90% of the $Co(NH_3)_5Cl^{2+}$ was photoreduced) for *two* reasons: (1) toward the end of the experiments the absorbance of the $Co(NH_3)_5Cl^{2+}$ substrate was low enough that $I_a \propto [Co(NH_3)_5Cl^{2+}]$ and (2) $\phi_{I_3^-}$ decreases approximately in proportion to I_a (see Table V). In this and in the experiments reported in Table V, $\phi_{Co^{2+}}$ was found to be independent of $[I^-]$. In the

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(28) Note that these photolyses were performed using $[Co(NH_3)_5Cl^{2+}]$ and $[I^-]$ such that $Co(NH_3)_5Cl^{2+}$ absorbed over 90% of the incident 254-nm radiation.

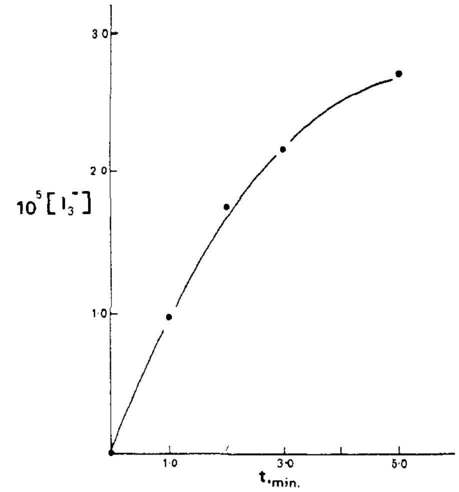

Figure 1. Variation of $[I_3^-]$ with decomposition of $Co(NH_3)_5Cl^{2+}$ substrate: initial concentrations, $Co(NH_3)_5Cl^{2+}$, 1.96 × 10^{-4} *M;* NaI, 4.0 × $l.^{-3}$ *M;* $HClO_4$, 0.10 *M;* initial I_a = 2.2 × 10^{-4} einstein $l.^{-1}$ min^{-1}; $\phi_{Co^{2+}}$ = 0.17. Note that $[I_3^-]$ at the end of the experiment is 25% of the initial [Co(III)].

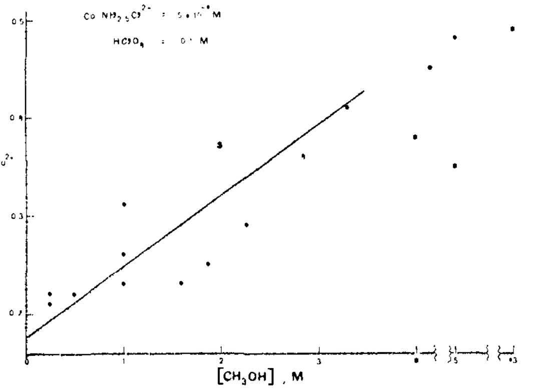

Figure 2. Variation of $\phi_{Co^{2+}}$ with $[CH_3OH]$: initial concentrations, $Co(NH_3)_5Cl^{2+}$, 5 × 10^{-4}; $HClO_4$, 0.10 *M;* initial I_a = 4.7 × 10^{-4} einstein $l.^{-1}$ min^{-1}.

studies reported in Table V, $[Co(NH_3)_5Cl^{2+}]$ was in the range (1–5) × 10^{-3} *M* so that I_a did not vary significantly during the first 25% of reaction.

In contrast to these observations, $\phi_{Co^{2+}}$ was found to increase in relatively concentrated (0.1 $M \leq [CH_3OH] \leq 13$ *M*) methanolic solutions (Figure 2). A limiting value of $\phi_{Co^{2+}} \simeq 0.5$ appears to be reached for $[CH_3OH] \geq 6$ *M*. For each of the experiments represented by a point in Figure 2, the rate of photolysis of $Co(NH_3)_5Cl^{2+}$ in 0.10 *M* $HClO_4$ was determined before the photolysis of the methanolic solution in order to ensure the correctness of the value of I_a used to calculate $\phi_{Co^{2+}}$.

6. Cation-Exchange Separation of Products. A solution 5.0 × 10^{-3} *M* in $Co(NH_3)_5Cl^{2+}$ and 0.1 *M* in $HClO_4$ was photolyzed for 2 min ($I_a \simeq 6 \times 10^{-3}$ einstein $l.^{-1}$ min^{-1}). A 50-ml aliquot of this photolyte was diluted to 200 ml and added to the top of a 200 × 10 mm column of resin (Bio-Rad AG 50W-X4, 200–400 mesh) which had been washed successively with 100 ml of 0.01 *M* $HClO_4$ and 100 ml of 0.01 *M* $HClO_4$. In a slow elution with 0.75 *M* in $HClO_4$, Co^{2+} separated first, followed by the unreacted complex. The Co^{2+} was completely removed with about 200 ml of eluent. The passage of an additional 200 ml of eluent slowly (total time ~ 1 hr) through the resin seemed to result in some separation of the remaining band. Spectral analysis of the aliquots eluted showed that the first part of this band was $Co(NH_3)_5Cl^{2+}$. The minor component (if any) would not be definitely distinguished from this, although the wavelength of the low-energy absorption maximum of the trailing material appeared to be shifted 3–5 nm toward higher energy (bands were broad and weak, however). All material was eluted from the resin. Blank determinations with equal concentrations of $Co(NH_3)_5Cl^{2+}$ and *cis*-$Co(NH_3)_4OH_2Cl^{2+}$ showed that these complexes can be separated by means of this technique and that $Co(NH_3)_4OH_2Cl^{2-}$ is the first species eluted. However, any $Co(NH_3)_5OH_2^{3+}$ formed due to adsorption on the resin would elute after $Co(NH_3)_5Cl^{2+}$.[29] Clearly any photolabilization is a minor process.

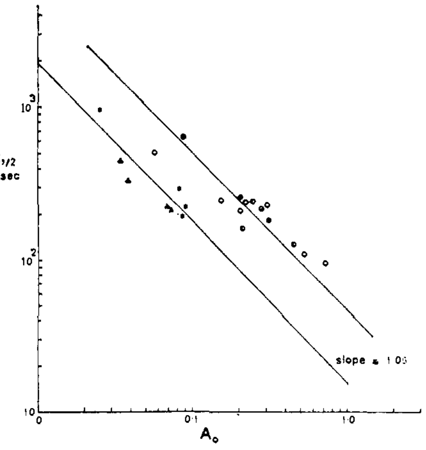

Figure 3. Order of transient decay rate in concentrated chloride solutions: for KCl only, [KCl] = 1.0 × 10^{-2} *M*, pH 6, ▲; for $[Co(NH_3)_5Cl^{2+}]$ = 10^{-4} *M* at pH 1, [KCl] = 0.10 *M*, ●; [KCl] = 1.0 × 10^{-2} *M*, ○. Transients observed at 340 nm. The flash intensity was changed in order to obtain variations in A_0.

B. Flash Photolysis.[30] **1. $Co(NH_3)_5Cl^{2+}$.** The flash photolysis of $[Co(NH_3)_5Cl](ClO_3)_2$ does not produce a transient on the first flash unless some free halide ion is present. When $Co(NH_3)_5Cl^{2+}$ is flashed in the presence of free Cl^- a transient is produced which absorbs strongly in the 320–360-nm region, similar to the Cl_2^- radical generated from Cl^- in the absence of the complex. All kinetic determinations were made at λ 340 nm. The transient decay rate appears to be nearly second order for $[Cl^-] \geq 10^{-3}$ *M* (Figure 3). The second-order decay rate of the transient (expressed as $1/A_0t_{1/2}$ since there is considerable uncertainty in the molar absorptivities of the transients) was dependent on $[Cl^-]$ (Figure 4 and Table VI) and pH (Figure 5). It is important to note that at low pH and high $[Cl^-]$ the transient obtained from $Co(NH_3)_5Cl^{2+}$ (Vycor filter) can have a longer decay lifetime than the Cl_2^- transient obtained by flashing $[Co(NH_3)_6]Cl_3$ or KCl or NH_4Cl (no filter).

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[29] M. D. Archer and M. Spiro, *J. Chem. Soc. A*, 68 (1969).

[30] Detailed transient decay parameters have been deposited as Document No. NAPS-01071 with the ASIS Auxiliary Publications Service, % CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

Table VI. Comparison of Transients from Several Cobalt(III) Complexes

[KCl]	$t_{1/2}$, μsec[a]	$A_0t_{1/2}$[a,b]	Species irradiated[c]
1.0×10^{-5}	70		$Co(NH_3)_5Cl^{2+}$
1.0×10^{-4}	80–220[d]	40 ± 5 (5)	
1.0×10^{-3}	110–270[d]	65 ± 6 (3)	
1.0×10^{-2}	95–240[d]	57 ± 10 (8)	
1.0×10^{-1}	85–200[d]	56 ± 3 (4)	
1.0×10^{-4}	380–500[e]	18 ± 4 (2)	$Co(tetraen)Cl^{2+}$
1.0×10^{-2}	400[e]	18 (1)	
$1.0 \times 2 \times 10^{-4}$ [f]	95	79 (1)	*cis*-$Co(NH_3)_4OH_2Cl^{2+}$
1.0×10^{-2}	100	90 (1)	
1.0×10^{-1} [g]	120	8.4 (1)	*trans*-Co(*trans*-[14]diene)Cl^{2+}
1.0[g]	120	11 (1)	
3×10^{-4} [f]	300[e]	6 (1)	$Co(NH_3)_6^{3+}$ [h]
1.0×10^{-3}	260	9 (1)	
1.0×10^{-2}	60–250	19 ± 3 (3)	
1.0×10^{-4}	40	4.8 (1)	$Co(NH_3)_5OH_2^{3+}$ [h]
1.0×10^{-2}	50	15 (1)	

[a] A_0 and $t_{1/2}$ were determined by extrapolation as described in the Experimental Section. [b] Average value and average deviations listed for duplicate determinations. Number of determinations in parentheses. [c] pH 1; [complex] = 10^{-4} *M* except as indicated. Data quoted for transients appearing on first flash. Perchlorate salt except as indicated. [d] Decay appears to be second order. [e] Weak ($A_0 \sim 0.045$) transient. [f] Chloride salt of complex was used. [g] NaCl; pH 3. [h] Transients due to irradiation of outer-sphere (or ion-pair) complex.

It has been reported[31,32] that the X_2^- radical anions (or their precursors) react with methanol. We have attempted to use these reactions with methanol to help characterize the radicals obtained from $Co(NH_3)_5Cl^{2+}$. The variation of transient decay parameters with methanol is illustrated in Figure 6, and kinetic parameters for those studies are presented in Table VII.[30]

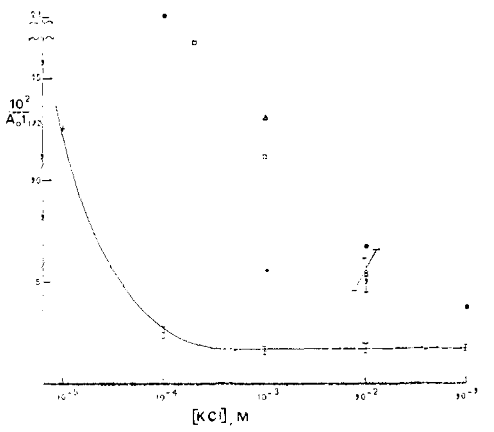

Figure 4. The [Cl^-] dependence of the second-order decay constant of the transient obtained from $Co(NH_3)_5Cl^{2+}$. Since the molar absorptivity of the transients at 340 nm is unknown, $k\epsilon = 10^2/A_0t_{1/2}$ ($t_{1/2}$ in μsec, 21-cm optical path) is plotted. Error flags indicate mean deviations of two to eight experiments; for [$Co(NH_3)_5Cl^{2+}$] = 1.0×10^{-4} *M*, pH 1, +. Similar constants for the Cl_2^- transient are included for comparison; for pure KCl, pH 6, Δ; for pure KCl, pH 1, ▲; for 1.0×10^{-4} *M* $Co(NH_3)_6^{3+}$ in KCl, pH 1, □; for 1.0×10^{-4} *M* $Co(NH_3)_5OH_2^{3+}$ in KCl, pH 1, ■.

2. Other Cobalt(III) Chloride Complexes. For comparison we have flashed $Co(tetraen)Cl^{2+}$, *cis*-$Co(NH_3)_4OH_2Cl^{2+}$, *trans*-Co(*trans*-[14]diene)Cl_2^+, and chloride-containing solutions of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5OH_2^{3+}$, the results of which are reported in Table VI. To facilitate direct comparison, some representative entries for $Co(NH_3)_5Cl^{2+}$ are also included. Note that the transient from $Co(NH_3)_6^{3+}$–Cl^- and $Co(NH_3)_5OH_2^{3+}$–Cl^- was indistinguishable from Cl_2^- as shown in Figure 4.

3. Determination of the Absorptivity of the Transient from $Co(NH_3)_5Cl^{2+}$. A 1.0×10^{-3} *M* solution of $Co(NH_3)_5Cl^{2+}$ in 0.1 *M* KCl and 0.1 *M* $HClO_4$ was flashed ten times. The transient absorbance, extrapolated to a time corresponding to 20 μsec after the flash initiation, averaged 0.046 (per centimeter path length). From these ten flashes, 6.3×10^{-5} *M* Co^{2+} was formed. If the transient yield was initially equivalent to the Co^{2+} yield, then ϵ_{340} 7×10^3 M^{-1} cm^{-1} for the transient (extrapolation to $t = 0$ would raise the value to about 9×10^3). This can be compared to ϵ_{340} 1.2×10^4 for Cl_2^-.[33]

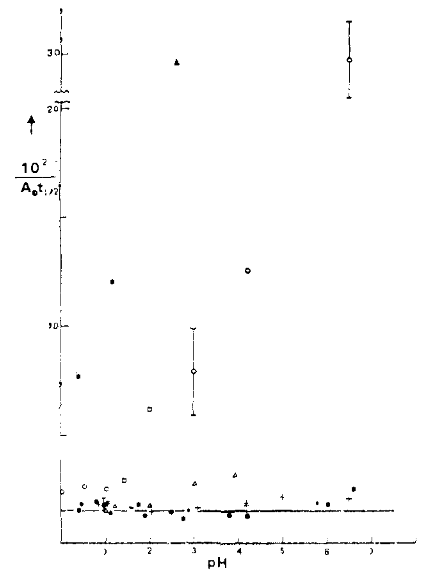

Figure 5. The pH dependence of the second-order decay constant of the transient obtained from $Co(NH_3)_5Cl^{2+}$. The ordinate is $kt = 10^2/A_0t_{1/2}$ ($t_{1/2}$ in μsec; 21-cm optical path); see caption to Figure 4. In each experiment [$Co(NH_3)_5Cl^{2+}$] = 1.0×10^{-4} *M*: [KCl] = 0.10 M, +; [KCl] = 1.0×10^{-2} *M*, ●; [KCl] = 1.0×10^{-3} *M*, Δ; [KCl] = 1.0×10^{-4} *M*, ○; [KCl] = 1.0×10^{-5} *M*, ▲.

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(31) M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, 67, 2613 (1963).

(32) M. E. Langmuir and E. Hayon, *ibid.*, 71, 3808 (1967).

(33) M. Anbar and J. K. Thomas, *ibid.*, 68, 3829 (1964).

Table VII. Kinetic Parameters for Transient Reactions with Methanol

[KCl], M	pH	k', M^{-1} sec$^{-1\,a}$	k'[Cl$^-$], sec$^{-1\,a}$
A. For [Co(NH$_3$)$_5$Cl^{2+}] = 10^{-4} M			
0.10	1.1	7×10^4	7×10^3
	4.2	3.5×10^4	4×10^3
1.0×10^{-2}	1.1	6.4×10^5	6×10^3
	4.2	3.5×10^5	4×10^3
1.0×10^{-4}	1.1	4.4×10^7	4×10^3
	3.0	5.8×10^7	5×10^3
Mean value of k'[Cl$^-$] = $(5 \pm 1) \times 10^3$ sec^{-1}			
B. For KCl Only			
1.0×10^{-2}	1.1	1.2×10^6	1.2×10^4
1.0×10^{-3}	1.1	1.4×10^7	1.4×10^4

[a] For Co(NH$_3$)$_5$Cl^{2+}, $k' = k_{16}'$; for KCl only, $k' = k_{15}'$.

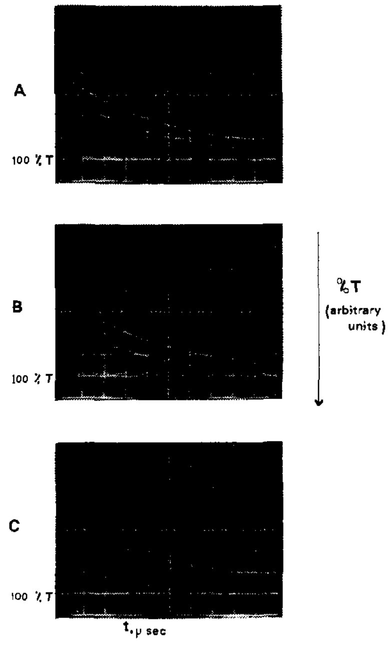

Figure 6. Variation of the decay characteristics of the Cl$_2^-$ transient in 0.1 M KCl as a function of [CH$_3$OH]. Upper curve in each case is the decay of the transient in pure KCl. The transmittance scale is in arbitrary units, the sweep time is 100 µsec per division, and 100% transmittance appears at about one division in each figure. In each case the upper curve has been displaced (0.8 division in A and C and 0.5 division in B) upward from the recorded base (*i.e.*, 100% transmittance) line. In A, [CH$_3$OH] = 0.050 M; in B, [CH$_3$OH] = 0.10 M; in C, [CH$_3$OH] = 0.25 M.

Discussion

A. The Final Oxidized Products. It is clear that the chloride ligand appears in the final solution as Cl$^-$, stoichiometric with Co^{2+}, following photoreduction of Co(NH$_3$)$_5$Cl^{2+}. That the yields of I$_2$ and Br$_2$ (for photoreductions carried out in the presence of I$^-$ and Br$^-$, respectively) are less than stoichiometric with Co^{2+} suggests that these oxidants are not formed by bulk solution reaction with Cl atoms. In fact, the decrease of ϕ_{I_3} with decreasing I_a implies that I$_2$ is formed by reaction with a species other than an initial oxidized radical (see discussion below).

The search for oxidized products has been frustrating. Although the oxidized radicals escaping the coordination sphere of Co(NH$_3$)$_5$Cl^{2+} seem to be extremely reactive, they can apparently be stabilized by complex formation with Cl$^-$. The complex radical anion, XCl$^-$, undergoes a second-order decomposition reaction which is independent of [NH$_4^+$], to form some species which reacts with NH$_4^+$ to form (eventually) N$_2$. By means of NH$_4^+$ scavenging for the successor to XCl$^-$, the equivalents of oxidized material can be accounted for. The fate of the oxidized material in ClO$_4^-$ solutions remains unclear; at present it seems most likely to us that trace amounts of impurity (always difficult to remove completely; see ref 23) in solution or on the walls of the reaction vessel must scavenge for the reactive intermediate radicals.

The ^{15}N tracer studies (Table IV) and the [NH$_4^+$] independence of ϕ_{N_2O} show that the N$_2$O observed has its source in coordinated NH$_3$. Clearly some N$_2$ is formed by means of a bulk reaction between NH$_4^+$ and oxidized species resulting from the photolysis (Table III). In each of the three different systems examined the observed isotopic distribution and that expected if a constant fraction (17 equiv % compared to Co^{2+}) of N$_2$ were obtained from coordinated NH$_3$ are compared in Table IV. Evidently not all the observed N$_2$ arises from the reaction of a nonnitrogenous radical and bulk NH$_4^+$. This conclusion is consistent with the observations (Table III) that the equivalent yield of N$_2$ is independent of the photolysis time and is more strongly a function of [Cl$^-$] in bulk than of [NH$_4^+$] in bulk.

The above considerations, based on final product yields, show that at least some nitrogenous radicals must escape the coordination sphere of photoreduced Co(NH$_3$)$_5$Cl^{2+}.

B. The Immediate Products of Photolysis. The use of final product yields to infer the nature of the intermediate (generally radical) fragments which result from a photoreduction process is often ambiguous. In cases where some of these fragments are extremely reactive radicals (*e.g.*, Cl or NH$_2$), the difficulties are compounded due to possible reactions with solvent, substrate, or scavenging impurities. However, if a product yield can be profoundly altered by performing the photolysis in the presence of nonabsorbing radical scavengers, then one may obtain a great deal of insight into the nature of the reactive radicals initially produced. Some radical scavengers (*e.g.*, alcohols less than 0.1 M in concentration) only repress the formation of easily detected products (*e.g.*, N$_2$). More useful to the present discussion are scavengers (*e.g.*, I$^-$ or Br$^-$) which produce new easily detected products.

Somewhat different information may be obtained by reducing the time duration between the primary photochemical event and the detection of products. Since the transient species observed in flash photolysis are very closely related in time to the species formed in the primary process, an examination of the flash results leads to information about the immediate reaction products.

1. Radical Scavenging with I$^-$ and Br$^-$. With both I$^-$ and Br$^-$ the final yield of oxidized halogen as a function of the bulk [X$^-$] appears to approach a limit. (Note, however, that the range of [I$^-$] was limited by the 254-nm absorptivity of I$^-$.[28]) The data in Table V show that I$^-$ and Br$^-$ within our limits of concentration are no more than 75% efficient in scavenging for the oxidized radicals resulting from photoreduction of Cl(NH$_3$)$_5$Cl^{2+}. Furthermore, the efficiency of I$^-$ as a radical scavenger drops markedly as I_a decreases (Table V; Figure 1). A simple mechanism for the formation if I_2 (or Br_2) which is consistent with these facts and with the flash data can be written[34]

$$Co(NH_3)_5Cl^{2+} + h\nu \xrightarrow{H^+} Co^{2+} + X + nNH_4^+ + (5 - n)Cl^- \quad (I_a)$$

$$X + I^- \rightleftarrows IX^- \quad (4)$$

$$2IX^- \longrightarrow I_2 + 2X^- \quad (5)$$

$$X + S \longrightarrow \text{products} \quad (6)$$

Where X^- could be NH_3 or Cl^-, step 4 is a labile equilibrium and (5) and (6) are competitive (S is some radical scavenger). The competition of (5) and (6) would account for the observation that $2\phi_{I_3^-} < \phi_{Co^{2+}}$; of course, this inequality of yields can also arise from the formation of more than one radical species X of different reactivities.

2. The Nature of Intermediates Observed in the Flash Photolysis. When $[Co(NH_3)_5Cl](ClO_4)_2$ is flashed (Vycor filter) in $HClO_4$ solution there is no transient observed on the first flash.[35] On subsequent flashes a transient with an absorption maximum in the 340-nm region appears. These observations *could* be consistent with the photolytic generation of Cl, and a necessity that free Cl^- be present for a transient to be observed. As little as 10^{-5} *M* free Cl^- resulted in the formation of a transient on the first flash. Both the transient absorbance and lifetime are a function of $[Cl^-]$. At $[Cl^-] \geq 10^{-3}$ *M* the transient lifetime is inversely proportional to the initial concentration, indicating that the decay is second order in the concentration of transient. Since many of these features are also exhibited by Cl_2^- we flashed KCl solutions (with no filter) under conditions identical with those used for $Co(NH_3)_5Cl^{2+}$ (Vycor filter). From Figure 3 it is clear that the specific decay rate of Cl_2^- is faster than that for the transient, XCl^-, obtained from $Co(NH_3)_5Cl^{2-}$ in Cl^+ (assuming the transients have similar molar absorptivities).[36] When $[Cl^-]$ is sufficiently small the decays of both Cl_2^- and XCl^- become first order ($t_{1/2}$ becomes approximately independent of A_0; see also Figure 4) similar to the behavior observed for I_2^-.[37] This and the other evidence discussed in this paper suggest that in each case the observed species, a dihalide radical, is in labile equilibrium with a much more reactive radical precursor

$$Cl + Cl^- \rightleftarrows Cl_2^- \quad (7)$$

$$X + Cl^- \rightleftarrows XCl^- \quad (8)$$

However, neither Cl_2^- nor XCl^- appears to be as stable as I_2^- and K_7 is about one order of magnitude less than K_8 (Figure 4). In fact much of the scatter in the data for the Cl_2^- transient at low $[Cl^-]$ (Figures 3 and 5) is undoubtedly due to the contribution of a large first-order component to the decay. These differences in behavior indicate that XCl^- and Cl_2^- are different species.

Finally it is significant that the lifetime of XCl^- is pH dependent for sufficiently low $[Cl^-]$ (Figure 5). This again differs from the behavior of Cl_2^- and suggests a labile protolytic equilibrium involving X or XCl^-. An additional point is that the transient obtained from NH_4Cl (pH 1–7) cannot be distinguished from Cl_2^- obtained by flashing KCl under identical conditions. The observation that the presence of NH_4^+ does not affect the characteristics of the transient decay is consistent with poor scavenging of the initial radical products by NH_4^+ (see Table III).

It is clear that at least some of the primary oxidized radicals resulting from the photoreduction of $Co(NH_3)_5Cl^{2+}$ are nitrogeneous and must result from a 1-equiv oxidation of coordinated NH_3. The simplest hypothesis is that all the primary radicals X result from the one-electron oxidation of coordinated NH_3. Thus if X is taken to be the NH_2 radical, which is isoelectronic with Cl, then this radical can react in a number of ways with bulk solvent species (reactions 9–11). Within

$$NH_2 + H^+ \rightleftarrows NH_3^+ \quad (9)$$

$$NH_2 + Cl^- \rightleftarrows NH_2Cl^- \quad (10)$$

$$NH_3^+ + Cl^- \rightleftarrows NH_3Cl \quad (11)$$

the context of this model, the slower decay rate at low pH (Figure 5) implies that NH_3Cl is more stable than NH_2Cl^-. Although the predominant species X, formed in the primary photochemical act, cannot be Cl, the formation of Cl as a relatively minor primary product cannot be excluded.

The flash photolyses of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_4OH_2Cl^{2+}$ seem to produce relatively long-lived and probably similar[38] transients. That the flash photolysis of *trans*-Co(*trans*-[14]diene)Cl_2^+ and Co(tetraen)Cl^{2+} should produce only small amounts of relatively unstable transients is particularly interesting. For these complexes a 1-equiv oxidation of a coordinated amine nitrogen does not produce a species which can be easily removed from coordination to the metal. Thus the observed transients undoubtedly correspond to relatively small yields of Cl_2^- (note that $\phi_{Co^{2+}}$ for the photoreduction of Co(tetraen)Cl^{2+} is very small). The exceptionally rapid decay of the transient obtained from *trans*-Co(*trans*-[14]diene)Cl_2^+ is an anticipated result, since the cyclic *trans*-[14]diene ligand is known to be inert to substitution when coordinated to cobalt(II) and the Co(*trans*-[14]diene)$^{2+}$ complex is easily oxidized.[39]

The data reported in Table VI for the flash photolysis of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5OH_2^{3+}$ in Cl^- solutions are of very great importance. The case of $Co(NH_3)_6^{3+}$ is the most easily interpreted, so we will confine our specific remarks to that system; the $Co(NH_3)_5OH_2^{3+}$ system is clearly similar. In the presence of Cl^- the ultraviolet absorptivity of $Co(NH_3)_6^{3+}$ increases strikingly and this increase in absorptivity is clearly attribu-

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(34) As discussed below, the primary photochemical event seems to produce mostly oxidized NH_3 (either NH_3^+ or NH_2) with perhaps some Cl. Thus X may be identified with NH_3^- (in which case $n = 4$) or with Cl (in which case $n = 5$).

(35) It is to be noted that the halogen *atoms* all have their high-intensity transitions in the far-ultraviolet.

(36) As noted in the Results section, the reported molar absorptivities of Cl_2^- and XCl^- stand in a ratio of approximately 1:1.7. The apparent second-order rate constant, assuming similar absorptivities of Cl_2^- and XCl^-, stand in the ratio of about 1:2.8. Thus the kinetic data show that *either* the lifetime of XCl^- is greater than the lifetime of Cl_2^- under identical conditions or that the molar absorptivity of XCl^- is greater than the molar absorptivity of Cl_2^-. In either case they must be different species.

(37) L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, 61, 1089 (1957).

(38) The apparently longer lifetimes reported for the transient form $Co(NH_3)_4OH_2Cl^{2+}$ are within the range of values for $Co(NH_3)_5Cl^{2+}$ under identical conditions.

(39) M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, 91, 3892 (1969); M. P. Liteplo and J. F. Endicott, unpublished observations.

table to the formation of outer-sphere ion-pair complexes, $Co(NH_3)_6{}^{3+},Cl^-$.[40] The absorption of radiation in this region can be attributed to a $Cl^- \rightarrow Co(III)$ charge-transfer transition. The formation of these labile outer-sphere $Co(NH_3)_6{}^{3+},Cl^-$ complexes is diffusion controlled and the $Co(NH_3)_6{}^{2+},Cl$ species which result from the absorption of radiation almost certainly must be as labile as the ground state and should be regarded as a solvent-trapped radical pair. It is significant that in this situation the transient produced appears to be Cl_2^-. Apparently the lifetime of the $Co(NH_3)_6{}^{2+},Cl$ radical pair is too short to permit oxidation of NH_3 released from coordination to cobalt. It is further to be kept in mind that in the case of neutral atom–cation radical pairs, lifetimes are largely a function of solvent viscosity. The $Co(NH_3)_5{}^{2+},Cl$ and $Co(NH_3)_6{}^{2+},Cl$ radical pairs should be similar in lifetime.

The radicals Cl and X, precursors to the observed transients, are very reactive. Since methanol has been reported[32] to react at a measurable rate with Cl_2^-, we had hoped to be able to use the reaction with methanol to help us distinguish between Cl_2^- and XCl^-. Unfortunately, we have found that Cl_2^- does not react rapidly with methanol. For example, at $[Cl^-]$ sufficiently large that the dissociation of Cl_2^- (7) is negligible, $[CH_3OH]$ must be greater than 0.1 M in order to noticeably affect the transient decay lifetime (Figure 6). Furthermore, it appears that values of A_0 change more rapidly with change in $[CH_3OH]$ than do the decay lifetimes. This behavior, similar for Cl_2^- and XCl^-, suggests that methanol scavenges very efficiently for the precursor species Cl and X, respectively.

Taking Cl_2^- as an example, the transient decay rate in excess methanol is expected to follow a rate law of the form.[41]

$$\text{observed rate of decay} = k_{15}'[Cl_2^-] + k_{13}[Cl_2^-]^2 \quad (12)$$

The second-order term in (12) corresponds to the normal decay mode (13) at high $[Cl^-]$ in the absence of

$$2Cl_2^- \longrightarrow \text{products} \quad (13)$$

methanol, and the pseudo-first-order term results from the reaction of Cl_2^- with CH_3OH. As Figure 4 shows, the k_{13} term should become first order in Cl_2^- at low $[Cl^-]$. To an adequate approximation we may substitute the appropriate half-lives for the terms of (12), obtaining[42]

$$\frac{1}{(t_{1/2})_{\text{obsd}}} \simeq \frac{0.69}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2} \quad (14)$$

This may be rearranged to permit the calculation of $0.69/(t_{1/2})_1$ from the difference between the experimentally determined decay half-lives, at constant $[Cl^-]$, with and without methanol. From such calculations we find that k_{15}' varies with $[CH_3OH]$ in the manner expected for a pseudo-first-order rate constant within the limits of error (the k_{15}' and k_{13} terms of (12) make comparable contributions in the measurable range of $[CH_3OH]$). Values of the second-order specific rate constants $k_{15}' = [0.69/(t_{1/2})_1](1/[CH_3OH])$ are tabulated as a function of $[Cl^-]$ in Table VII. The estimated values of k_{15}' are inversely proportional to $[Cl^-]$. This implies that even the apparent Cl_2^-/CH_3OH reaction proceeds by means of the dissociation [*i.e.*, the reverse of (7)] of Cl_2^- followed by reaction of Cl with CH_3OH

$$Cl + CH_3OH \longrightarrow \text{products} \quad (15)$$

so that $k_{15}/K_7 = k_{15}'[Cl^-]$. The radical X produced in the photoreduction of $Co(NH_3)_5Cl^{2+}$ is similarly scavenged by CH_3OH and values of $k_{16}'[Cl^-]$ are entered in Table VII.

$$X + CH_3OH \longrightarrow \text{products} \quad (16)$$

It appears that k_{16}/K_8 is independent of pH. This is somewhat surprising in the case of $[Cl^-] = 10^{-4}\ M$, since the decay lifetime of XCl^- is pH dependent (Figure 5) under these conditions. This pH independence of k_{16}/K_8 implies that k_{16} and K_8 vary with pH in the same way.

It appears that $k_{15}'[Cl^-]$ is about twice $k_{16}'[Cl^-]$. Thus the observed transients do seem distinguishable by means of their reactions with methanol.[43]

Although the primary radicals Cl and X are extremely reactive, there is no evidence that either these radicals or the observed transients which are their successors react with NH_4^+. Values of A_0 and $A_0t_{1/2}$ are independent (within reasonable error limits) of whether the source of $[Cl^-]$ is NH_4Cl or KCl. This behavior and the observation that the N_2 yield from irradiation of $Co(NH_3)_5Cl^{2+}$ does not increase with $[NH_4^+]$ unless free Cl^- is present show that NH_4^+ does not react with X or XCl^- (or with Cl or Cl_2^-) but with some decomposition product of XCl^-.

Some indirect inference may be made concerning the nature and chemistry of the metal ion fragment which results from the photoreduction of $Co(NH_3)_6Cl^{2+}$. The independence of $\phi_{Co^{2+}}$ of I_a over about a 100-fold range shows that bulk solution back-reactions between $Co(NH_3)_n{}^{2+}$ and X or XCl^- are negligible even at the relatively high values of I_a employed in this study. This conclusion is not too surprising, since the lifetime of $Co(NH_3)_n{}^{2+}$ ($n \geq 3$) in aqueous solution is $\leq 10^{-5}$ sec,[44] and the formation of the very stable Co^{2+} ion would be expected to compete very effectively with bulk back-reactions. However, the case of $Co(\textit{trans}\text{-}[14]\text{diene})Cl_2^+$ is very different. The cobalt(II) complex ion in this case is stable to loss of the cyclic ligand.[39] As noted above, it appears from the flash photolysis data that the transient, Cl_2^- in this case, has an unusually short half-life, implying that (17)[45] competes effectively with (13). By means of an equation analagous to (14) with the $[Co(\textit{trans}[14]\text{diene}^{2+}] \simeq 3 \times 10^{-7}\ M$ (estimated

$$YCo(\textit{trans}\text{-}[14]\text{diene})^{2+} + Cl_2^- \longrightarrow YCo(\textit{trans}\text{-}[14]\text{diene})Cl^{2+} + Cl^- \quad (17)$$

from A_0 using $\epsilon_{Cl_2^-} \sim 10^4$), we find $k_{17} \simeq 1.5 \times 10^{10}\ M^{-1}$

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(40) (a) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953); (b) M. T. Beck, *Coord. Chem. Rev.*, 3, 91 (1968).

(41) In this case the subscripts used with the rate constants refer to reactions 13 and 15 which follow in the text. Note that $k_{15}'[Cl^-] = k_{15}/K_7$.

(42) Where $k_{\text{obsd}} \simeq 1/(t_{1/2})_{\text{obsd}}$, $k_{15}' \simeq 0.69/(t_{1/2})_1$, and $k_{13}[Cl_2^-] \simeq 1/(t_{1/2})_2$.

(43) It should be recalled that the apparent rate constants k_{15}' and k_{16}' will also reflect any differences in the molar absorptivities of Cl_2^- and XCl^-. If the reported absorptivities are approximately correct, then $k_{15}'/\epsilon(Cl_2^-) \simeq k_{16}'/\epsilon(XCl^-)$.

(44) (a) T. J. Swift and R. Connick, *J. Chem. Phys.*, 37, 307 (1962); (b) R. G. Wilkins and M. Eigen, *Advan. Chem. Ser.*, No. **49**, 55 (1965).

(45) Although the cobalt(II) complexes of *trans*-[14]diene are usually labile in the axial positions, it is possible that complete equilibration does not occur in the time scale of the present reaction. Hence the unspecified ligand Y in (17).

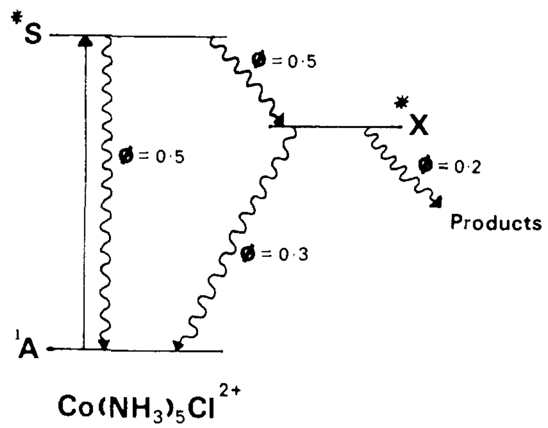

Figure 7. Proposed scheme of excited states resulting from the 254-nm irradiation of $Co(NH_3)_5Cl^{2+}$. The initial singlet excited state, *S, can be identified with a $Cl^- \rightarrow Co(III)$ transition and is presumed to be too short-lived to be scavengeable with methanol. By means of an intersystem crossing process, *S may be converted (with about 50% efficiency) to a metastable state *X, which is sufficiently long-lived to be scavengeable with methanol. The metastable intermediate *X normally returns to the original ground-state $Co(NH_3)_5Cl^{2+}$ about 60% of the time.

sec^{-1}. The back-reaction in this case appears to be diffusion controlled.

C. Precursors to Bulk Radicals in the Photoreduction of $Co(NH_3)_5Cl^{2+}$. The evidence cited above indicates that (18) represents a substantial fraction of the

$$Co(NH_3)_5Cl^{2+} + h\nu \longrightarrow Co(II) + Cl^- + NH_2 \quad (18)$$

primary process in the photoreduction of $Co(NH_3)_5Cl^{2+}$, where the nature of the immediate cobalt(II) species is as yet unknown. It appears that the nitrogeneous radical arises from a reaction in the coordination sphere of the intermediate species which is produced when $Co(NH_3)_5Cl^{2+}$ absorbs ultraviolet radiation. There have been attempts to ascribe all the photochemistry of $Co^{III}(NH_3)_5X$ complexes to the production of solvent-trapped radical pairs, $Co(NH_3)_5{}^{2+},X$.[4g,5] Since the irradiated band of $Co(NH_3)_5Cl^{2+}$ is undoubtedly largely $Cl^- \rightarrow Co(III)$ charge-transfer in character, the radical-pair model would require a very efficient Cl· oxidation of coordinated NH_3 during the very short ($\leq 10^{-10}$ sec) pair lifetime in order to account for (18). Such an oxidation does not occur if Cl is generated in the second coordination shell. It is possible to attribute such chemical complexity to radical pairs despite the lack of reactivity of $NH_4{}^+$ and Cl in bulk solution. But such assumptions are not necessary and in fact the radical-pair mechanism is not compatible with all our observations on the continuous photolysis of $Co(NH_3)_5Cl^{2+}$.

The increase of $\phi_{Co^{2+}}$ with $[CH_3OH]$ to a limiting value of 0.5 (Figure 2) shows that a metastable cobalt(III) oxidant is generated by the absorption of 254-nm radiation. In order for just detectable scavenging of a radical pair with a lifetime $\leq 10^{-10}$ sec to occur with $[CH_3OH] \sim 0.1$ *M*, the rate of reaction of CH_3OH with the radical pair would have to exceed 10^{10} M^{-1} sec^{-1}. This seems unreasonable. Furthermore, a limiting yield of $\phi_{Co^{2+}} \simeq 0.5$ at $[CH_3OH] \geq 5$ *M* shows that there are at least two intermediate species, one scavengeable and one not scavengeable with methanol. The simplest interpretation of these observations is that the excited state initially populated, *S, is too short-lived to react with simple scavengers, but by means of an intersystem crossing process a scavengeable, metastable state, *X, can be formed from *S. At pH 1, *X normally decays into products 40% of the time and returns to the ground state[46] 60% of the time (Figure 7). In the presence of sufficient reducing scavenger, *X is completely converted into the final products.

The $Co(NH_3)_5Cl^{2+}$ system also has the features that $\phi_{Co^{2+}}$ increases with pH and that a predominant oxidized product is nitrogeneous. These features could be accommodated within the scheme represented in Figure 7 if the *S → *X transition included an acid-base reaction

$$*[(NH_3)_5Co^{II}*Cl)]^{2+} \longrightarrow *[(NH_3)_4Co^{II}(NH_2)(Cl^-)]^+ + H^+ \quad (19)$$

The species *X′ as formally represented on the right-hand side of (19) corresponds to the charge-transfer excited state of the cobalt(III) complex, $(NH_3)_4Co(NH_2)Cl^+$. Thus, there is a very good possibility that the transitions *S → *X′ and *X′ → A cannot be spectroscopically allowed under any conditions since *X′ may be stoichiometrically different from both *S and the ground state. The intermediacy of such an excited state must depend on the basicity of the solvent and on the possibility of very rapid proton transfer reactions.

Since electronic and nuclear motions rarely occur simultaneously, (19) probably should not be regarded as a simple one-step process. Since the $NH_3 \rightarrow Co(III)$ transition is higher in energy than the $Cl^- \rightarrow Co(III)$ transitions, it can be argued that loss of a proton must "precede" this electronic rearrangement if all the species *X are to be identified with the right-hand side of (19). A simpler hypothesis is that there are several species *X (Figure 7) which are scavengeable by methanol. It seems quite probable that the feature which permits the chemical distinction between the initially excited singlet state *S and the reactive species *X is that in the latter some of the excitation energy is stored in a triplet state (or states).

Although an unequivocal description of the excited state intermediate *X is not possible at present, it is clear that the radical-pair mechanism cannot be general for photochemical reactions of cobalt(III). Despite the short lieftimes of such intermediates and the great reactivity of the immediate reaction products, techniques are available for the characterization of these species. In the systems to which these techniques have so far been applied, there is no evidence that radical-pair intermediates play any significant chemical role. The prevailing prejudice that the photochemistry of cobalt(III) is simple and that the mechanistic principles were established long ago has apparently inhibited the critical examination of these systems.

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(46) It is important to keep in mind that there is no Cl^- and little ammonia aquation during these processes.