

where A_{\parallel} and A_{\perp} are the experimental values for absorbance when the electric vector of the light is parallel and perpendicular to the axis. The a_{\parallel} , b_{\parallel} , a_{\perp} , and b_{\perp} are, respectively, the actual values for absorbance for the A and B molecular axes when these axes are parallel and perpendicular to the electric vector of the light. Since A and B are optically equivalent molecules, $a_{\parallel} = b_{\parallel}$ and $a_{\perp} = b_{\perp}$. So the calculated spectra correspond to the equations

$$a_{\parallel} = 1.8252A_{\parallel} - 0.8252A_{\perp}$$

$$a_{\perp} = -0.8252A_{\parallel} + 1.8252A_{\perp}$$

where a_{\parallel} and a_{\perp} are the values for the total absorbance of the Fe-NO molecular groups, calculated as if they all were oriented unidirectionally parallel and perpendicular to the electric vector of the light. Both the uncorrected and corrected spectra are shown in Figure 5.

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Appendix

In the MO calculation of CN we have taken $1\sigma = 1s_N$ and $2\sigma = 1s_C$. The molecular orbitals $3\sigma, \dots, 6\sigma$ are constructed as linear combinations of $2s_C, 2s_N, 2p\sigma_C,$ and $2p\sigma_N$ atomic functions. Similarly π^b - and π^* -orbitals are linear combinations of $2p\pi_C$ and $2p\pi_N$ atomic functions. The atomic functions which we used to construct the MO's of CN are Clementi's double ζ -functions.³¹ The secular equations $(H_{ij} - S_{ij}E) = 0$ were solved, where the Coulomb integrals were taken as valence orbital ionization potentials of carbon and nitrogen and the resonance integrals were estimated as $H_{ij} = -2.00S_{ij}(H_{ii} \cdot H_{jj})^{1/2}$. The calculation was performed to obtain self-consistent charge and configuration on both atoms, using Mulliken's¹⁶ population analysis. Calculated one-electron energies are very close to the observed spectroscopic energies.

Table I summarizes the radial functions for Fe, CN, and NO used in the calculation. Tables II-V give orbital transformations, ligand-ligand corrections, group overlap integrals, coulomb integrals, and MO eigenvectors.

(31) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964); IBM Research Paper RJ256.

Photoreduction of Cobalt(III) Complexes at 2537 Å.¹

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Irradiation of ligand-metal charge-transfer bands of several Co(III) complexes at 2537 Å. has been found to lead only to photoreduction of the Co center. The quantum yield of Co(II) has been found to decrease markedly as the number of amine groups per ligand increases, to depend in a complicated way on pH, and to increase with [I⁻]. Species resulting from oxidation of the ligands have been identified in some cases. A few studies of the 2537-Å. irradiation of ion-pair charge-transfer bands have been performed. Much of the photochemistry seems best understood if photoreduction proceeds through a relatively long-lived ($\geq 10^{-8}$ sec.) metastable excited

state of the Co(III) complex. Mechanisms are proposed and discussed.

When aqueous solutions of Co(III) complexes are irradiated with visible light, both photoreduction and photoaquation take place.^{2a} The ratio of the quantum yields for these processes is dependent, to some extent, upon the wave length of the light and the temperature of the solution. In the near-ultraviolet, photoreduction is increasingly favored over photoaquation as the

(1) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) (a) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960); (b) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

ligands in the first coordination sphere become more reducing (e.g., $\text{Cl}^- < \text{Br}^- < \text{I}^-$); furthermore, the presence of free I^- in the solution catalyzes the photo-reduction process.² Of particular interest is the relative inertness of hexaamminecobalt(III) and tris(ethylenediamine)cobalt(III) to any photochemical process in the spectral regions previously studied.

A recent study³ of the γ -radiolytic reduction of aqueous solutions of aquopentaammine- and hexaamminecobalt(III) has shown that Co(II) is produced by the reaction of OH radicals, generated by the decomposition of the water, with the cobalt(III)-ammine substrate.

The work reported here was stimulated by our observation that the reduction of hexaamminecobalt(III) in aqueous solution proceeds very rapidly when 2537-Å. radiation is employed. There appear to have been few systematic investigations^{4,5} of the photochemistry of Co(III) complexes in the spectral regions where the Co(III) absorption bands are purely of the charge-transfer type. This study at 2537 Å. serves to extend the previous investigations of the dependence of the photochemistry of these complexes upon the wave length of the incident radiation. This particular wave length is chosen because of the convenience of its generation, the charge-transfer nature of the Co(III) absorption, and the lack of decomposition of the solvent, which might complicate the process.

The charge-transfer spectra of metal complexes are considered to fall, for convenience, into four classes⁶: (1) mononuclear complexes with the excited electron originally localized on the central metal ion and excited to be localized on the ligand (metal-to-ligand), (2) mononuclear complexes with the electron originally localized on one or several ligands and excited to be localized on the metal (ligand-to-metal), (3) mononuclear complexes with the excited electron localized on the ligands before and after excitation (ligand-ligand), (4) polynuclear complexes with different central ions (ion pair). The Co(III) complexes reported here have only aliphatic amines, ammonia, water, and/or halogens as ligands so the charge-transfer bands are of the ligand-metal type (2). In a few cases we have investigated the photochemistry of Co(III) complexes with ion-pair type (4) charge-transfer bands.

This paper represents the initial results of a systematic survey of the photochemistry at 2537 Å. of cationic complexes in which the rate of the reaction is determined as a function of the medium and of the ligands in the first coordination sphere of the metal ion.

Experimental

Preparation of Complexes.⁷ The literature preparations for $\text{Co}(\text{NH}_3)_6(\text{NO}_3)_3$, $\text{Co}(\text{en})_3(\text{NO}_3)_3$, $\text{Co}(\text{NH}_3)_5$ -

(3) D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68**, 1357 (1964).

(4) G. B. Porter, J. G. W. Doering, and S. Karanka, *J. Am. Chem. Soc.*, **84**, 4027 (1962).

(5) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 49 (1951).

(6) T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 229.

(7) The following abbreviations are employed in this paper for the amine ligands: en (ethylenediamine), tn (1,3-diaminopropane), den (diethylenetriamine), trien (triethylenetetramine), and cn (*trans*-1,2-diaminocyclohexane).

$\text{OH}_2(\text{NO}_3)_3$, $\text{Co}(\text{NH}_3)_5\text{Cl}_3$, $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{NO}_3$, and $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{NO}_3$ were used.⁸ $\text{Co}(\text{NH}_3)_5\text{Br}_3$ was prepared in small quantities by treating $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{NO}_3$ with concentrated HBr. $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2(\text{NO}_3)_3$ was prepared by treating $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{NO}_3$ with concentrated HClO_4 . Likewise, literature preparations for $\text{Co}(\text{den})_2\text{Cl}_3$ ⁹ and $\text{Co}(\text{trien})(\text{en})\text{Cl}_3$ ¹⁰ were used. Perchlorate salts of all the above complexes were prepared by adding concentrated HClO_4 to a saturated solution of the complex and collecting the crystals that formed (some formed only very slowly). All the perchlorate salts were recrystallized from distilled water.

$\text{Co}(\text{tn})_3(\text{ClO}_4)_3$ was prepared by use of a slight modification of the literature procedure¹¹ in which perchloric acid and perchlorate salts were used throughout. The salt was recrystallized from distilled water.

$\text{Co}(\text{cn})_3(\text{ClO}_4)_3$ was also prepared¹² from perchlorate salts. Commercial *trans*-1,2-diaminocyclohexane sulfate was converted to the perchlorate salt which was then dissolved in a NaOH solution. Slightly less than the stoichiometric amount of Co(II) perchlorate was added and the solution was air oxidized. Because both $\text{Co}(\text{cn})_3(\text{ClO}_4)_3$ and *trans*-1,2-diaminocyclohexane perchlorate are only slightly soluble in water, difficulty was experienced in the separation of the two. The amount of free amine contaminating the desired complex was reduced by treating the solid residue from the preparation with aqueous NaOH. A 50% water-acetone solution was saturated with the remaining residue and the slow evaporation of the acetone resulted in the formation of intensely yellow needles of $\text{Co}(\text{cn})_3(\text{ClO}_4)_3$.

The sample of $\text{Co}(\text{NH}_3)_5\text{I}(\text{ClO}_4)_2$ was generously provided by Professor Albert Haim.

The visible and ultraviolet spectra of the complexes used in this study were found to be in good agreement with the literature reports; cobalt analyses were likewise in good agreement with the calculated per cent compositions.

Apparatus. Photolysis was accomplished using a Hanovia SC-2537 low-pressure mercury lamp. About 85% of the output of this lamp is the 2537-Å. mercury resonance line. The intensity of the lamp could be adjusted by varying the power input to the lamp and maintained constant by the use of a constant-variable voltage transformer. Moderate temperature regulation was accomplished by the circulation of air from the room over the lamp and reaction cell.

The cylindrical reaction cell of approximately 80-ml. capacity was fabricated, with a tapered neck, of Type 7910 Vycor which is transparent only to wave lengths greater than 2100 Å. The homogeneity of the solutions was maintained during irradiation by the bubbling of a stream of purified N_2 . Prior to irradiation, solutions were thermostated at the desired temperature in a water bath.

The pH of solutions was determined with a Beckman

(8) H. S. Booth, W. C. Fernelius, J. C. Bailar, Jr., T. Moeller, E. G. Rochow, et al., Ed., "Inorganic Synthesis," Vol. 1, 2, 4, 5, and 6, McGraw-Hill Book Co., Inc., New York, N. Y., 1939-1960.

(9) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950); P. Job and J. Brigando, *Compt. rend.*, **210**, 438 (1940).

(10) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

(11) J. C. Bailar, Jr., and J. B. Work, *ibid.*, **68**, 2325 (1946).

(12) F. M. Jaeger and L. Bijkerk, *Z. anorg. allgem. Chem.*, **233**, 97 (1939).

expanded scale pH meter calibrated with the appropriate buffer solutions.

Gas samples were analyzed on an F and M Model 700 dual column gas chromatograph and a 6-ft. Linde Molecular Sieve 5A column.

Procedure. All solutions were prepared with triply distilled water from a Barnstead tin-lined still. Reagent grade salts and acid were used without further purification. A stock solution of NaClO_4 was prepared by the neutralization of a weighed amount of Na_2CO_3 by HClO_4 .

Solutions of $\text{Co}(\text{NH}_3)_5\text{I}^{+2}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$, and *cis*- and *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$ were prepared and handled in semidarkness as much as possible because of their sensitivity to visible light. Especial care was taken with $\text{Co}(\text{NH}_3)_5\text{I}^{+2}$ solutions to ensure photolysis and analysis with as little delay as possible. In some experiments when relatively long delays (60 min. or more) between the preparation of the solution and the completion of the analysis were unavoidable, a significant $[\text{Co}(\text{II})]_0$ (obtained by extrapolating the experimental data to zero exposure time) indicated that some thermal aquation had taken place followed by reduction of the complex by I^- .¹³

$[\text{Co}(\text{II})]$ was determined spectrophotometrically at 25° from the absorbance at 690 $m\mu$ of a 9 *M* HCl solution prepared by diluting an aliquot of sample solution with concentrated HCl. In all but the most concentrated solutions, these determinations were made using a 5-cm. cell.

The presence of an oxidant in the solution after photolysis was determined by the addition of I^- and the titration of any I_3^- formed with standard thio-sulfate. Reductants were likewise iodometrically determined by the back titration of excess I_3^- after the mixing of the aliquot of photolyzed solution with a standard solution of I_3^- .

The rates of the photochemical reactions were determined by removing aliquots (2 to 25 ml. depending upon the requirements of the determination) from the reaction cell at various intervals. For the slowest reactions, five to ten samples were taken over a period of approximately 1 hr. For some very rapid reactions, it was necessary to take samples at 10–15-sec. intervals. Titration analyses were performed immediately; for spectrophotometric determinations, the samples were stored in stoppered containers to await analysis.

In order to obtain samples of gas evolved during photolysis, narrow-bore capillary tubing was secured within the neck of the reaction cell just above the level of the solution. Any gas evolved was collected by displacement of water and transferred from the collection tube to the gas chromatograph through a serum cap by means of a gas syringe. In these experiments, no attempt was made to purge the system of air before photolysis; however, total air volume before photolysis was estimated to be less than 0.5 ml.

Treatment of Data. The values of $[\text{Co}(\text{II})]$ obtained from the analysis of aliquots of solution taken after various photolysis times were converted to $[\text{Co}(\text{III})]$. Rates of photolysis were obtained from zero-order plots of $[\text{Co}(\text{III})]$. Solutions having very high absorbance¹⁴

(13) R. G. Yalman, *Inorg. Chem.*, 1, 16 (1962).

(14) In this paper, all optical densities reported are with respect to 1-cm. path length.

(>15) produced excellent linear zero-order plots, while solutions with very low absorbance (<0.1) were well represented by first-order plots. Rates calculated from such first-order plots were always checked by comparison with the initial slopes of zero-order plots of the same data.

In a number of cases, both $[\text{Co}(\text{II})]$ and $[\text{Co}(\text{III})]$ were determined independently as a function of photolysis time. However, because the molar absorptivity, ϵ (550 $M^{-1} \text{ cm.}^{-1}$), of $\text{Co}(\text{II})$ in concentrated HCl at 690 $m\mu$ is much greater than ϵ ($\sim 50 M^{-1} \text{ cm.}^{-1}$) of the $\text{Co}(\text{III})$ complexes at the visible absorption maxima, the initial rate based upon the appearance of $\text{Co}(\text{II})$ is considered to be the more accurate and is, except where noted, the only value reported.¹⁵

Quantum yields, Φ , were calculated from the comparison of the initial rate of photolysis of the solution of $\text{Co}(\text{III})$ complex, R_i , with the initial rate of photolysis of a uranyl oxalate actinometer solution, R_u , at the same absorbance under identical conditions of lamp geometry, temperature, light intensity, cell, and N_2 bubbling. The value of Φ of the actinometer solution at 2537 Å. was taken to be 0.62.¹⁶

Actinometry. Uranyl oxalate actinometry was performed at each of the incident light intensities, I_0 , reported in this paper. Because the absorbances of the $\text{Co}(\text{III})$ solutions at 253.7 $m\mu$ ¹⁷ varied from less than 0.01 to greater than 30, R_u was determined over approximately the same range. At the higher absorbance, oxalate was determined by titration with permanganate¹⁸; in more dilute solutions, oxalate was determined spectrophotometrically by the ceric method.¹⁹ In all the actinometer solutions the initial $[\text{C}_2\text{O}_4^{-2}]$ and $[\text{UO}_2^{+2}]$ were in the ratio of 5:1.

The absorbance determined for the most dilute actinometer solutions gave $\epsilon_{253.7}$ as much as 10–15% lower than the values obtained at higher $[\text{UO}_2^{+2}]$. These systematic deviations from the Beer-Lambert law are probably due to the change of pH upon dilution of the solutions. Our measured value of $\epsilon_{253.7}$ of concentrated solutions, $3.5 \times 10^3 M^{-1} \text{ cm.}^{-1}$, differs from the literature value by about 20%, which is attributed to the inaccuracy of the estimated titer of our UO_2^{+2} stock solution. However, because R_u , and thus I_a , could be determined experimentally as a function of the measured absorbance of the solution without knowledge of the value of $[\text{UO}_2^{+2}]$, this latter quantity was not accurately determined. The experimental variation of I_a with optical density is shown in Figure 1; the error limits represent an uncertainty of 10% in the determination of the photolysis rates which we believe carries through all of the experiments.

Results

A. Determination of the Variables That Affect Quantum Yield. At the beginning of this study, it was by

(15) The initial rate of $\text{Co}(\text{II})$ appearance is hereafter designated as R_i .

(16) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941.

(17) In this paper we present all spectrophotometer wave lengths in units of $m\mu$. The resonance radiation of the mercury lamp is given as 2537 Å.

(18) H. A. Fales and F. Kenny, "Inorganic Quantitative Analysis," Appleton-Century-Crofts, Inc., New York, N. Y., 1939.

(19) J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor, and W. Brim, *J. Am. Chem. Soc.*, 77, 5499 (1955).

Table I. Variation of Φ with $[H^+]$ for Photoreduction of Co(III) Complexes ($37 \pm 2^\circ$; $I_0 = 6.8 \times 10^{-3}$ einstein $l^{-1} \text{ min}^{-1}$ except as indicated)

Complex	$[Co(III)]_i$ $\times 10^3 M$	$[HClO_4]$, M	$R_i \times 10^4 M$ min^{-1}	Φ
Co(NH ₃) ₆ ³⁺	1.45	0.186	0.58 ^a	0.62
	1.45	4.4×10^{-2}	0.59 ^a	0.70
	1.45	4.8×10^{-3}	0.59 ^a	0.78
	1.55	0.186	0.70 ^a	0.71
	1.31	0 ^b	0.66	0.89
	1.31	0 ^c	0.81	1.1
Co(en) ₃ ³⁺	1.33	0.186	3.9	0.12
	6.50	0.22	8.7	0.17
	3.32	0 ^b	3.1	0.07
	15.4	0.93	4.4	0.07
	15.4	0.022	8.4	0.14
	15.4	8.8×10^{-4}	5.3	0.09
	2.66	0 ^c	2.4	0.06
Co(tn) ₃ ³⁺	1.62	0.93	4.2	0.070
	2.11	0.558	4.6	0.075
	17.2	0.22	7.3 ^d	0.11
	2.11	0.186	5.0	0.08
	1.62	0.022	3.7	0.06
	0.81	1.1×10^{-4}	1.6	0.03
	1.05	0.186	5.9 ^e	0.11
Co(cn) ₃ ³⁺	0.437	0.24 ^e	2.5	0.059
	0.437	0.048 ^e	2.6	0.061
	0.437	4.8×10^{-3e}	2.6	0.061
	0.437	4.8×10^{-4e}	2.2	0.052
Co(trien)(en) ³⁺	2.67	1.86	4.5	0.13
	6.56	0.743	9.3	0.21
	3.05	0.372	5.3	0.15
	2.67	0.186	7.3	0.21
	6.56	0.088	10.8	0.24
	3.2	4.8×10^{-4}	6.5	0.18
Co(den) ₂ ³⁺	4.3	1.12	1.11	0.017
	0.92	0.22	1.5	0.029
	2.2	0.186	1.8	0.029
	2.34	0.001 ^f	1.2 ^g	0.019
	2.31	0 ^b	1.6 ^g	0.026
Co(NH ₃) ₅ OH ₂ ³⁺	5.96	1.86	6.0	0.20
	6.80	0.372	5.3	0.17
	0.60	0.372	1.3	0.18
	14.65	0.22	11.1	0.28
	7.22	0.24	8.1	0.23
	1.82	0.13	3.5	0.21
	6.80	0.044	7.5	0.25
	6.80	4.4×10^{-3}	7.8	0.26
Co(NH ₃) ₅ Cl ²⁺	3.00	0.93	6.9	0.13
	3.08	0.22	9.3	0.17
	3.08	0.044	11.1	0.21
	1.85	4.4×10^{-3}	15.9	0.34
	2.90	0.186	9.0 ⁱ	0.15
Co(NH ₃) ₅ Br ²⁺	0.934	0.93	10.5	0.19
	0.934	0.186	10.7	0.19
	0.934	0.044	10.6	0.19
<i>cis</i> -Co(en) ₂ Cl ₂ ⁺	2.4	1.0	6.4	0.10
	10.8	0.20	6.4 ^h	0.10
	2.5	0.12	4.3	0.07
	2.5	0.027	4.8	0.08
	1.2	0.0022	5.2	0.09
<i>trans</i> -Co(en) ₂ Cl ₂ ⁺	1.5	0.22	4.4	0.07
	1.5	0.046	4.5	0.07
	1.5	0.0059	4.0	0.06
	3.0	0.0030	5.2	0.08

^a $45 \pm 2^\circ$. ^b No electrolyte added; initial pH 6.5. ^c $[NaClO_4] = 0.2 M$; initial pH 11.0. ^d $-d[Co(III)]/dt = 7.8 \times 10^{-4} M \text{ min}^{-1}$. ^e As HCl. ^f $[NaClO_4] = 0.19 M$. ^g Rate calculated as $-d[Co(III)]/dt$. ^h $-d[Co(III)]/dt = 6.2 \times 10^{-4} M \text{ min}^{-1}$. ⁱ $60 \pm 2^\circ$.

no means clear which experimentally adjustable variables would significantly affect the quantum yield, Φ , at 2537 Å. We have systematically varied several parameters of the photolysis system to observe their effect on Φ , and we have qualitatively checked several others.

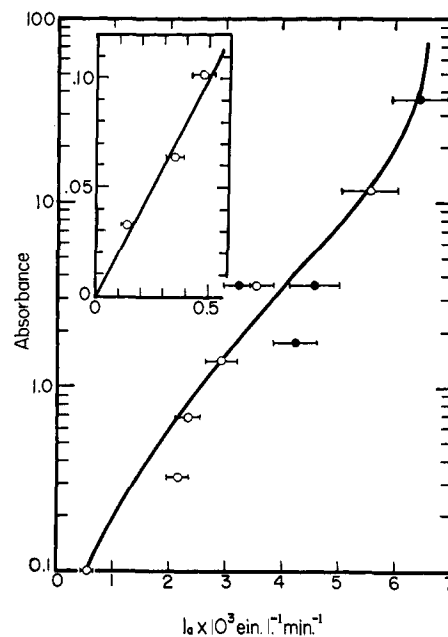


Figure 1. Variation of I_a with absorbance based on actinometry: O, oxalate determination by ceric method; ●, oxalate determination by permanganate titration.

1. Acidity of the Medium. Systematic studies were performed for the eleven complexes listed in Table I which includes some data for the photolyses of Co(NH₃)₆³⁺, Co(en)₃³⁺, and Co(den)₂³⁺ in neutral and basic solutions. When the pH is >7, strongly absorbing Co(II) species are rapidly formed with the eventual precipitation of Co(II) hydroxides. In addition, at high pH the association of Co(II) with the ligands is increased and the air oxidation of these resulting complexes to the corresponding Co(III) amines occurs in some cases while aliquots of the photolyzed solution are being taken. The result is that the measured rates of photoreduction of Co(III) complexes in basic solutions are not very reliable despite the use of initial rates which compensates somewhat for these difficulties.

It should be noted that the oxidation of the Co(II) amine product to form a Co(III) complex proved to be especially troublesome in the study of Co(den)₂³⁺. Here the affinity of Co(II) for diethylenetriamine appears to be high in all solutions except those of the highest acidity. The Co(III) product of the air oxidation of this Co(II) complex has a smaller ϵ at 465 m μ than does Co(den)₂³⁺, which exhibits an absorption maximum (ϵ 125 $M^{-1} \text{ cm}^{-1}$)²⁰ at that wave length. Both R_i and the initial rate of disappearance of Co(III) were measured for the photoreduction of Co(den)₂³⁺.

(20) R. C. Whealy and S. O. Colgate, *Anal. Chem.*, 28, 1897 (1956).

In all the experiments with this complex, except those at high pH, the two rates were essentially in agreement, and we have reported only R_i . In very basic solution R_i was as much as 50% less than the initial rate of Co(III) disappearance and we have reported the latter. In general, the kinetic data for this particular system are rather badly scattered with an average deviation from the zero-order plot of about 20%.

For most of the complexes reported in Table I we have found R_i to be nearly the same as the initial rate based on the direct measurement of $[\text{Co(III)}]$; a few specific determinations are noted in the table.

The visible absorption spectra of solutions resulting from partial photolyses of $\text{Co(NH}_3)_6^{+3}$, Co(en)_3^{+3} , and $\text{Co(NH}_3)_5\text{Cl}^{+2}$ solutions have been examined for evidence of partially aquated Co(III) species, and no evidence for such species has been found. This observation is consistent with the generally observed equality of R_i and the rate of Co(III) disappearance.

2. *Variation of the Ligands.* As is evident from Table I, the variation of Φ with acidity of the solution depends markedly on the ligands coordinated to Co(III). Except for the case of $\text{Co(NH}_3)_5\text{Cl}^{+2}$, the differences in Φ for different complexes are smallest at a pH of 0.7.

3. *Intensity of the Absorbed Radiation.* Experiments were performed on eight complexes at two intensities of incident radiation, I_0 , which differed by a factor of 6.0: 6.8×10^{-3} and 1.1×10^{-3} einstein $\text{l}^{-1} \text{min}^{-1}$. In all cases the intensity of the absorbed radiation, I_a , was calculated from the absorbance of the solution and the actinometry calibration curve (Figure 1). The data are summarized in Table II.

We have included in Table II the net results of our study of $\text{Co(NH}_3)_5\text{I}^{+2}$. The exact reason for the extraordinary scatter of these data is not known. In some determinations the zero-order plots exhibited considerable curvature in the first half-life which undoubtedly led to inaccurate determination of R_i . These data represent approximately a 20-fold variation in concentration of the substrate. Thus some of the scatter may be due to variation of I_a ; however, the values of Φ show similar scatter. If there is any variation of Φ with concentration of substrate, it is less than the scatter of the data.

4. *Temperature.* We have found that the rates of photoreduction of the complexes are fairly insensitive to small ($\pm 5^\circ$) fluctuations of temperature. In the case of $\text{Co(NH}_3)_6^{+3}$ in a ClO_4^- medium, it is known²¹ that the molar absorbance at 253.7 $\text{m}\mu$ depends significantly on temperature, and so it is to be expected that R_i for this complex would show variation with temperature. The data obtained for this complex at 45° are reported in this study and were obtained with some care after a large number of earlier studies at 37° were found to be badly scattered (mean deviation of about 20%). Values of R_i obtained at 45 and 37° are approximately the same to within the reproducibility of the determinations. We conclude that the temperature of the solution is not a major factor affecting Φ in the 2537- \AA . irradiation of Co(III) complexes.

5. *Concentration and Nature of the Supporting Electrolyte.* A systematic study of the effect of the

substitution of Cl^- for ClO_4^- in the supporting electrolyte upon Φ has been made for several selected compounds (Table III). We have found ϵ to be 0.0012 and 0.0037 $\text{M}^{-1} \text{cm}^{-1}$ at 253.7 $\text{m}\mu$ for HCl and HClO_4 , respectively, thereby ensuring the absence of any

Table II. Variation of Φ with I_a ($37 \pm 2^\circ$; $[\text{HClO}_4] = 0.2 \text{ M}$ except as indicated)

Complex	$I_a \times$ [Co- 10^4 ein- (III)] _i steins $\times 10^3$		$R_i \times 10^4$ min. ⁻¹ M	Φ	n^a
	M	min. ⁻¹ M			
$\text{Co(NH}_3)_6^{+3}$	1.55	0.98	0.70 ^b	0.71 ^b	0.94
	1.05	0.089	0.074 ^b	0.83 ^b	
Co(tn)_3^{+3}	2.11	61.5	5.0	0.08	1.01
	1.05	9.4	0.75	0.08	
$\text{Co(trien)(en)}^{+3}$	3.05	36	5.3	0.15	0.99
	4.35	6.7	1.0	0.15	
$\text{Co(NH}_3)_5\text{OH}_2^{+3}$	7.22	36	8.1 ^c	0.22	1.07
	7.22	6.01	1.2 ^c	0.20	
$\text{Co(NH}_3)_5\text{Cl}^{+2}$	2.90	53	8.0	0.15	1.07
	2.81	8.9	1.18	0.13	
$\text{Co(NH}_3)_5\text{Br}^{+2}$	0.93	56	10.7	0.19	0.69
	0.87	9.3	3.1	0.33 ^d	
$\text{Co(NH}_3)_5\text{I}^{+2}$...	46 ^e	23 ± 5	0.50 ± 0.13	0.61 ^e
	...	7.7 ^f	7.7 ± 1.5	1.0 ± 0.2	
<i>cis</i> - $\text{Co(en)}_2\text{Cl}_2^+$	10.8	67	6.4	0.10	1.02
	3.75	1.09	1.01	0.093	

^a Order calculated as n in $R_i = \Phi I_a^n$. ^b $45 \pm 2^\circ$. ^c $[\text{HClO}_4] = 0.37 \text{ M}$. ^d Two additional determinations involving only 10% reduction of $\text{Co(NH}_3)_5\text{Br}^{+2}$ gave $\Phi = 0.33$ and $\Phi = 0.23$ for $[\text{Co(NH}_3)_5\text{Br}^{+2}]_i = 0.934 \times 10^{-3}$ and $2.79 \times 10^{-3} \text{ M}$, respectively. ^e Average of three determinations in which $[\text{Co(NH}_3)_5\text{I}^{+2}]_i = 1.1 \times 10^{-3}$, 1.7×10^{-3} , and $3.4 \times 10^{-3} \text{ M}$. An average value of I_a is cited. ^f Average of seven determinations; $[\text{Co(NH}_3)_5\text{I}^{+2}]_i$ varied from 0.25×10^{-3} to $3.4 \times 10^{-3} \text{ M}$. An average value of I_a is cited. ^g Order calculated as $n = [\log(\Phi I_a)_2 - \log(\Phi I_a)] / [\log(I_a)_2 - \log(I_a)]$

interference due to the absorption of radiation by the medium. A few studies indicate that substitution of Na^+ for H^+ in the supporting electrolyte has little effect on Φ . It should also be noted that over the range of $[\text{HClO}_4]$ used in these studies, the mean ionic activity coefficient of HClO_4 varies by only about 20%.²²

When I^- is present in the solution, a large fraction of the incident radiation is absorbed by the medium ($\epsilon_{253.7} = 251 \text{ M}^{-1} \text{cm}^{-1}$). This is particularly important in the case of weakly absorbing complexes such as $\text{Co(NH}_3)_6^{+3}$ and $\text{Co(NH}_3)_5\text{OH}_2^{+3}$. In two experi-

(22) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958.

(21) F. Posey and H. Taube, *J. Am. Chem. Soc.*, 78, 15 (1956).

Table III. Effect of Ionic Medium on Φ ($37 \pm 2^\circ$, $I_0 = 6.8 \times 10^3$ einstein l. $^{-1}$ min. $^{-1}$ except as indicated)

Complex	[Co(III)] _i $\times 10^3 M$	[H ⁺], M	[Cl ⁻], ^a M	Absorbance (253.7 m μ)	$I_a \times 10^3$ einstein l. $^{-1}$ min. $^{-1}$	$R_i \times 10^4$ M min. $^{-1}$	Φ
Co(NH ₃) ₆ ³⁺	1.55	0.96	0.96	0.400 ^b	1.65	10 ^b	0.61
	1.55	0.12	0.12	0.182 ^b	0.97	5.4 ^b	0.56
	1.55	0.234	0.0048	0.075 ^b	0.36	2.5 ^b	0.69
	1.55	0.191	0.00048	0.029 ^b	0.14	1.0 ^b	0.75
Co(en) ₃ ³⁺	1.33	0.120	0.120	2.06	3.4	3.9	0.12
	1.33	0.193	0.0072	1.860	3.4	3.9	0.12
Co(NH ₃) ₅ OH ₂ ³⁺	6.80	0.48	0.48	3.57 ^c	4.0	14.2	0.36
	6.80	0.468	0.096	2.05	3.4	11	0.32
	6.80	0.382	0.0096	1.602	3.1	8.3	0.25
Co(tn) ₃ ³⁺	1.05	0.022	0.196 ^d	12.3 ^e	5.6	3.7	0.067
	1.05	~0.01 ^f	0	12.3 ^e	5.6	3.7	0.067
<i>trans</i> -Co(en) ₂ Cl ₂ ⁺	2.3	0.002 ^g	0	45.5 ^e	6.5	3.9	0.060

^a Except when [Cl⁻] is specified, all anions are ClO₄⁻. ^b $45 \pm 2^\circ$. ^c Extrapolated from measured optical densities at 290, 280, 270, and 260 m μ . ^d As NaCl. ^e Calculated from Φ from extinction coefficient. ^f [NaClO₄] = 0.25 M . ^g [NaClO₄] = 0.01 M .

ments at 45° , both with $[\text{Co}(\text{NH}_3)_6^{3+}] = 1.45 \times 10^{-3} M$ and $[\text{HClO}_4] = 0.186 M$, R_i was $0.66 \times 10^{-4} M$ min. $^{-1}$ when $[\text{NaI}] = 2.5 \times 10^{-3} M$ and was $1.37 \times 10^{-4} M$ min. $^{-1}$ when $[\text{NaI}] = 5.0 \times 10^{-2} M$. In a single experiment at 35° with $[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}] = 2.3 \times 10^{-3} M$, $[\text{HClO}_4] = 0.372 M$, and $[\text{NaI}] = 5.0 \times 10^{-2} M$, R_i was found to be $1.9 \times 10^{-4} M$ min. $^{-1}$. The absorbance of the latter solution was found to be 1.95 at 253.7 m μ .

6. *Presence of Nonabsorbing Transition Metal Ions.* It has been suggested³ that Co(II) catalyzes the reduction of Co(III) by γ -rays. In order to test this in the photolysis, $\text{Co}(\text{ClO}_4)_2$ ($\epsilon_{253.7} 0.2 M^{-1} \text{ cm.}^{-1}$) was added to solutions $1.45 \times 10^{-3} M$ in $\text{Co}(\text{NH}_3)_6^{3+}$ and 0.186 M in HClO_4 . For photolysis at 45° of solutions initially 0.67×10^{-3} and $4.1 \times 10^{-3} M$ in Co(II), we found $R_i = 0.55 \times 10^{-4}$ and $0.78 \times 10^{-4} M$ min. $^{-1}$, respectively. In addition to this insensitivity to [Co(II)] in the case of $\text{Co}(\text{NH}_3)_6^{3+}$, we have not observed deviations of the experimental data for any systems reported here from zero-order (high absorbance) or first-order (low absorbance) behavior which could be attributed to the increase in [Co(II)] as the photolysis proceeds even though in many cases the reaction was followed to about 90% of completion.

We have also observed that the presence of from 1.5×10^{-3} to $3.2 \times 10^{-2} M$ $\text{Cu}(\text{ClO}_4)_2$ does not significantly affect R_i for the photoreduction of $\text{Co}(\text{NH}_3)_6^{3+}$ or $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$.

7. *Presence of H₂O₂.* In an experiment at 45° with $[\text{Co}(\text{NH}_3)_6^{3+}] = 1.45 \times 10^{-3}$ and $[\text{HClO}_4] = 0.186 M$, we found that the presence of approximately 1 M H_2O_2 (absorbance at 253.7 m μ = 6.85) significantly inhibited the production of Co(II) (less than 0.1% reaction in 5 min.). In a preliminary study with $\text{Co}(\text{den})_2^{3+}$ at 0.186 M HClO_4 , we seem to have evidence that the presence of 0.1 M H_2O_2 decreased R_i while at the same time catalyzing the initial rate of disappearance of $\text{Co}(\text{den})_2^{3+}$.

B. *Determination of the Oxidized Species.* In experiments involving $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ or $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, sufficient I_2 and Br_2 were formed that solutions became distinctly brown or yellow after about 1-min.

irradiation. Irradiation of any solutions containing I^- yielded I_3^- or I_2 depending on the duration of irradiation and concentration. For the other compounds reported in this paper, the oxidized product has been much more elusive. We have found that of all the compounds tested in acidic solution, only the irradiated solutions of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ oxidized acidic KI. We have not been able to find any evidence for gaseous or dissolved Cl_2 as a product of irradiation of solutions of either $\text{Co}(\text{NH}_3)_6^{3+}$ or $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ in 0.2 M HCl or of the irradiation of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. In the case of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ we have found that 98.8% of the Cl^- originally coordinated to Co(III) remains in the irradiated solution as Cl^- (determined as AgCl).

Since neither Cl^- (as AgCl) nor H_2O_2 ²³ was detected after 30-min. irradiation of $1.55 \times 10^{-3} M$ $\text{Co}(\text{NH}_3)_6^{3+}$ in 0.186 M HClO_4 , we have concluded that neither the solvent water nor ClO_4^- can be the source of the electron which is transferred to the Co(III) center in the photo-reduction process. The only species which remains is the coordinated NH_3 . The determination of oxidized nitrogen species has been somewhat limited by the low solubility of $\text{Co}(\text{NH}_3)_6^{3+}$ in HClO_4 . We have been able to detect neither N_2H_4 nor NH_2OH ²⁴ in these solutions although the presence of Co(II) made the NH_2OH test using Cu(II) acetate solutions somewhat ambiguous. Analysis of this irradiated $\text{Co}(\text{NH}_3)_6^{3+}$ solution for N_2H_4 by the I^- and IO_3^- methods²⁵ showed that the concentration of this species after photolysis could not exceed $0.02 \times 10^{-3} M$.

On the other hand, irradiation of a neutral solution initially $1.55 \times 10^{-3} M$ in $\text{Co}(\text{NH}_3)_6^{3+}$ produced a solution which oxidized acidic (but not neutral or basic) I^- . The oxidant detected corresponded to 0.5×10^{-4} and 3.0×10^{-4} equiv. of iodine for solutions with no added electrolyte and 0.128 M NaCl , respectively. The formation of precipitates of Co(II) hydroxides under these conditions makes the sampling of irradiated solutions inaccurate and may account for some of the dif-

(23) Determined by the molybdate-iodide method of C. J. Hoch and adel, *J. Phys. Chem.*, **56**, 587 (1952).

(24) F. Feigl, "Chemistry of Specific, Selective, and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949.

(25) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957.

ferences in oxidizing titer of these two solutions. However, the presence of Cl^- may change the mechanism for the decomposition of the NH_2 radical produced by the one-electron oxidation of NH_3 .

Several experiments were performed to collect and analyze gaseous products of the photolysis in acidic solutions. In our system approximately 0.5 ml. of gaseous material was collected from the irradiation of pure water. Presumably this gas resulted from the thermal expansion of the water and the air in the space above it as well as from the decreased solubility of gases in water as the temperature is increased owing to the exposure. Irradiation of approximately 82 ml. of a solution containing $2.5 \times 10^{-2} M \text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ and $0.186 M \text{HClO}_4$ for a period of 2.5 hr. yielded approximately 4.5 ml. of gaseous products. It was quite evident at the end of the experiment that not all the gaseous material had been collected. A 2-ml. sample of this gas was analyzed chromatographically. The N_2 and O_2 peak heights in this sample were in the ratio of 3.37:1. By the same technique and using the same sample size the $\text{N}_2:\text{O}_2$ peak height of air was $1.40 \pm 0.04:1$. Thus, the sample of gas collected from this experiment had a composition of approximately 91% N_2 and 9% O_2 . The residual O_2 is nearly the amount soluble in 82 ml. of water at 25° and was probably swept out by the evolved N_2 . This experiment is consistent with the view that with regard to $\text{Co}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$, irradiation at 2537 \AA . results in the oxidation of NH_3 ; we are not in a position at this time to explain the details of the subsequent degradation of the NH_2 or NH_3^+ radicals to form N_2 .

It is of interest to note that irradiation of $2.6 \times 10^{-2} M \text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ in $0.24 M \text{HCl}$ gave a result similar to that of this compound in HClO_4 ; approximately 4.5 ml. of gases was collected in 2 hr. by the displacement of a $0.2 M \text{NaI}$ solution with no evidence of the formation of I_3^- in the displaced solution. This is in striking contrast to the irradiation of $2.5 \times 10^{-2} M \text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$ in $0.186 M \text{HClO}_4$ which yielded about 2 ml. of gases only after 18.5 hr. of irradiation. In this latter case, the ratio of the $\text{N}_2:\text{O}_2$ chromatographic peak heights was found to be 2.25:1 for a 0.8-ml. sample of the collected gases compared to 1.54:1 for $\text{N}_2:\text{O}_2$ in a 0.8-ml. sample of air. Thus, the collected gases were about 85% N_2 and 15% O_2 with the larger O_2 contamination arising from the smaller volume of collected gas. The gases evolved in this case also contained no Cl_2 (checked by displacement of a $0.2 M \text{NaI}$ solution) and analysis of the irradiated solution for NO_3^- , NO_2^- , N_2H_4 , and H_2O_2 revealed that none of these materials could be present in excess of $10^{-4} M$. The test for NH_2OH was essentially negative although somewhat ambiguous as noted above. The evolution of gases was very slow throughout this experiment and was observed to decrease significantly as the irradiation time increased.

We have found that irradiation of solutions of $\text{Co}(\text{en})_3^{+3}$ does not produce N_2 . This observation is consistent with a recent report that the $254\text{-m}\mu$ irradiation of solutions of several tris-diamine complexes of $\text{Co}(\text{III})$ produces nearly stoichiometric amounts of an aldehyde, ammonia, and a monoamine as the predominant products resulting from oxidation of the ligands.²⁶

Discussion

The identification of $\text{Co}(\text{II})$ and the various oxidized species is qualitative evidence that the absorption of 2537-\AA . radiation by these complex ions results in a transfer of charge from a ligand to the $\text{Co}(\text{III})$ center. The formation of an aquated $\text{Co}(\text{III})$ species to any significant extent is ruled out on the basis of the equality of the rates of appearance and disappearance of $\text{Co}(\text{II})$ and $\text{Co}(\text{III})$, respectively, and the dependence of R_i on no greater than the first power of I_a . Additional evidence that photoaquation and photo-oxidation-reduction processes do not compete at 2537 \AA . is provided by the observation that the presence of Cl^- in the first coordination sphere of $\text{Co}(\text{III})$ effectively quenches the rapid evolution of N_2 which is characteristic of the photoreduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$.

In this study we observe no obvious correlation between the oxidation potentials of the ligands and Φ of the photoreduction process. Irradiation at the ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$ bands of these same complexes has been shown to lead to competitive oxidation-reduction and aquation processes with Φ for photoreduction being related to the "ease of oxidation of the ligand involved"^{2a}; irradiation at the ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ bands leads only to photoaquation.^{2a} However, at 2537 \AA . the only effect is photoreduction. The differences in the effects of the ligands at the various wave lengths can be attributed to the differences in the chemistry of the excited states generated by irradiation.

In addition, the values of Φ obtained correlate with neither the energy nor ϵ of the maximum of the charge-transfer bands. This is illustrated in Table IV.

Table IV. Comparison of Φ with Charge-Transfer Maxima ($37 \pm 2^\circ$; $[\text{HClO}_4] = 0.2 M$, $I_0 = 6.8 \times 10^{-3}$ einstein $\text{l.}^{-1} \text{min.}^{-1}$ except as indicated)

Complex	$\nu \times 10^4$ cm.^{-1a}	Φ	$\epsilon \times 10^{-4}$ M^{-1} cm.^{-1a}
$\text{Co}(\text{NH}_3)_6^{+3}$	~ 5	0.71 ^b	2
$\text{Co}(\text{en})_3^{+3}$	~ 5	0.12	...
$\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$	5.22	0.28	2.5
$\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$	4.39	0.17	2
$\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$	3.95	0.16	1.85
$\text{Co}(\text{NH}_3)_5\text{I}^{+2}$	3.49	0.50	1.65
<i>cis</i> - $\text{Co}(\text{en})_2\text{Cl}_2^+$	~ 4.2	0.10	1.9
<i>trans</i> - $\text{Co}(\text{en})_2\text{Cl}_2^+$	4.03	0.07	2.7

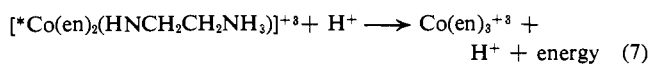
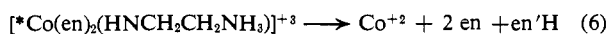
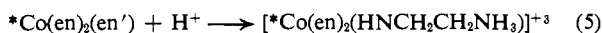
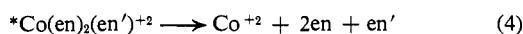
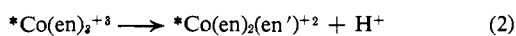
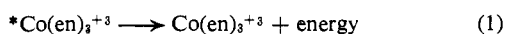
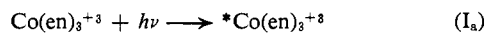
^a C. K. Jørgensen in "Advances in Chemical Physics," Vol. 5, I. Prigogine, Ed., Interscience Publishers, New York, N. Y., 1963, p. 33. ^b 45° .

It is seen in Table I that Φ of $\text{Co}(\text{II})$ formation (at pH 0.7) decreases markedly as the number of coordinating positions per ligand increases. This could be explained in terms of a dissociative mechanism such as has been assumed to be operative in the photochemistry of metallic complexes^{2a,4} whereby the dissociation of the oxidized ligand from the coordination sphere is an important factor in determining the relative probability of reduction of the metal center or re-formation

(26) D. Klein and C. W. Moeller, *Inorg. Chem.*, **4**, 394 (1965); W. C. Taylor, Jr., and C. W. Moeller, *ibid.*, **4**, 398 (1965).

of the original ion. However, in the specific case of Co(III) complexes this assumption must be very carefully considered. The spin-allowed charge-transfer transitions correspond to the transfer of an electron from a σ -orbital centered on a nitrogen atom to an e_g antibonding orbital of the Co center. This electron transfer leaves the Co ion in a formal oxidation state of +2; however, this Co(II) center has necessarily remained spin-paired. Since Co(II) is normally spin-free, it is important to assess the role played by the change in electronic configuration $t_{2g}^6e_g^1 \rightarrow t_{2g}^5e_g^2$ in the determination of the efficiency of photolysis.

Co(III) Complexes with Only Amines, Ammonia, and Water as Ligands. Because the ground states of the $\text{Co}(\text{NH}_3)_6^{+3}$ and the Co(III)-amine complexes all have pK_a values greater than 11, it is necessary to attribute the observed effects of pH to the acidities of the excited states of the respective ions. The acid-dependent mechanism must be consistent with the probable lifetimes of excited states produced in the photolysis and must involve protolysis of the ligands in the excited state. We feel the mechanism of photoreduction is best described in terms of the following steps (taking $\text{Co}(\text{en})_3^{+3}$ as the example, where $\text{en}' = \text{HNCH}_2\text{CH}_2\text{NH}_2$)



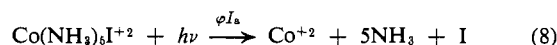
The primary absorption step is assumed to form an excited singlet state, ${}^*\text{Co}(\text{en})_3^{+3}$, with a Co d-electron configuration $t_{2g}^6e_g^1$. This excited state may decay to the ground state either by fluorescence or *via* a degradative internal conversion process. It may also undergo internal conversion to a second excited state (reaction 2) possibly through loss of a proton which amounts to chemical stabilization of this second state. Reactions 3 and 4 or reactions 1 and 4 account for what appears to be the low limiting value of Φ (~ 0.07) for this complex in basic solution. Reactions 5–7 describe the pH dependence of Φ that is observed in acid media. This mechanism is visualized as involving addition of a proton to an electron pair of a nitrogen atom. The electron pair of a coordinated amine nitrogen can be available for protolysis only if the ligand is sufficiently flexible so that the nitrogen can be at least partly dissociated from coordination to the Co center. Thus the insensitivity of Φ to acidity in the case of photoreduction of $\text{Co}(\text{en})_3^{+3}$ provides qualitative

support of this mechanism, since neither amine group of the inflexible *trans*-1,2-diaminocyclohexane ligand can be easily protonated prior to complete dissociation of the ligand from the coordination sphere.

It has been suggested that values of Φ less than unity may be the result of the primary recombination of the oxidized radical and the reduced ion trapped in a solvent cage.^{2a,4} Since an explanation of the complex pH effect apparently requires two protolyses with the one at high acidity decreasing Φ , we find it difficult to believe that simple recombination in the solvent cage is the operative process.

Since the protolyses of free amines proceed at specific rates $< 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$,²⁷ any pH-dependent mechanism which does not involve a metastable, excited state of Co(III) is compatible only with the decay of the photoproduced excited states *via* fluorescence. In the absence of knowledge about the fluorescence of these complexes when excited with 2537-Å. radiation, a metastable excited state cannot be unequivocally implicated. However, it has been reported that solutions of these and similar complexes show no fluorescence when excitation is with visible light or radiation in the near-ultraviolet.^{2b,4}

Co(III) Complexes with Halogens as Ligands. Because of the dependence of R_i on I_a and the identification of halogens as products, it is probable that the photoreduction of $\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$ and $\text{Co}(\text{NH}_3)_5\text{I}^{+2}$ proceeds *via* a mechanism different from that of the amine and ammonia complexes already discussed. It has been proposed²⁸ that the photolysis of $\text{Co}(\text{NH}_3)_5\text{I}^{+2}$ may be understood in terms of the reactions



where reaction 9 is rapid compared to the recombination of I atoms. However, the specific rate of recombination of I atoms in water is about $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$,²⁹ so that under the conditions of our experiments, where $I_a \sim 10^{-3} \text{ einstein l.}^{-1} \text{ min.}^{-1}$ and $[\text{Co}(\text{III})] \sim 10^{-3} \text{ M}$, the recombination of I atoms is significant compared to reaction 9 if $k_9 \leq 4.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$.

The steady-state treatment of this mechanism when the recombination of I atoms is significant leads to an expression containing a small term proportional to $[\text{Co}(\text{NH}_3)_5\text{I}^{+2}]$. We have not observed any effect of concentration changes upon Φ outside of the scatter of the data. Furthermore, the mechanism holds that Φ can vary only over a factor of two dependent upon the competition of reaction 9 with the recombination of I atoms. We have found that a sixfold decrease in I_0 changed Φ from 0.5 to 1.2, indicating the possible increase in prominence of the I atom recombination reaction at higher light intensities. However, Haim and Taube,²⁸ working at light intensities lower than ours, obtained $\Phi = 1.95$. If this mechanism is oper-

(27) M. Eigen, W. Kruse, G. Maas, and L. DeMayer, *Progr. Reaction Kinetics*, 2, 287 (1964).

(28) A. Haim and H. Taube, *J. Am. Chem. Soc.*, 85, 499 (1963).

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

ative, it cannot explain a variation of Φ over a factor of 3–4. The consistency between their data and ours must be pointed out, however, since our observation that $R_i \propto I_a^{0.7 \pm 0.1}$ is shown in Figure 2 to correlate very well with their data.

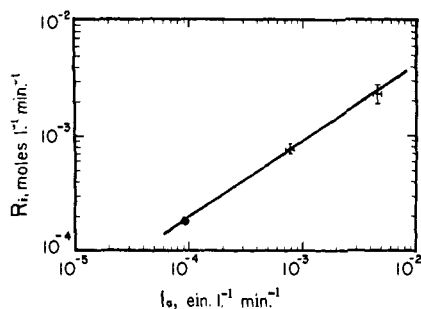


Figure 2. Dependence of R_i on I_a for $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$: \blacktriangle , this study; \bullet , data of Haim and Taube.²⁸

The similarities between the photoreduction of $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ with regard to I_a dependence and the halogen products of the reactions might lead one to suggest similar mechanisms for the two compounds. However, I atoms do not seem to be very effective in reducing $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$,²⁸ and Br atoms should be even less effective. Unfortunately, the establishment of the over-all stoichiometry does not necessarily establish which ligand contributed the electron to the Co(III) center in the primary photochemical act. It is noted that NH_3 is a reasonable reducing agent compared to I^- or Br^- , whereas NH_4^+ is not.³⁰ The lack of a pH effect for $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ may only be a reflection of the lifetimes of the excited states rather than the acidity of the oxidized ligand.

The small pH effect in the photoreduction of *cis*- $\text{Co}(\text{en})_2\text{Cl}_2^+$ seems to be significant outside of the experimental error: $\Phi = 0.107 \pm 0.013$ for $[\text{H}^+] \geq 0.186 M$ and $\Phi = 0.080 \pm 0.013$ for $[\text{H}^+] \leq 0.12 M$ (where the error limits are standard deviations of the three determinations made in each case). For *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$, $\Phi = 0.069 \pm 0.006$ (standard deviation) independent of $[\text{H}^+] (\leq 0.186 M)$. Thus, both Φ and the chemistry of the excited state may be somewhat influenced by the geometry of the molecule as well as by the kind of ligands in the coordination sphere.

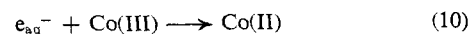
In the case of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, the larger pH effect must be attributed to the protolysis of the excited states of the ions, and it is by no means clear that the ligand oxidized in the primary photochemical step is Cl^- rather than NH_3 . Even if Cl atoms were produced, it should be noted that the oxidation of NH_3 by Cl_2 is thermodynamically favorable in acidic solution³⁰ and certainly even more so in the coordination sphere of Co(II) following the reduction. On the other hand, the pH effect is most easily understood if the electron is transferred from NH_3 to Co(III).

Photochemistry Involving Charge-Transfer Bands of the "Ion-Pair" Type. Consistent with the observations of

(30) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

previous workers,^{21,31} we find that the presence of certain anions very greatly increases the observed values of $\epsilon_{253.7}$ for $\text{Co}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{en})_3^{+3}$. When Cl^- is the anion, $\epsilon_{253.7}$ is increased by approximately $200 M^{-1} \text{ cm}^{-1}$. However, the effect of the presence of Cl^- on the observed value of Φ is striking only in the case of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ for which an increase of $[\text{Cl}^-]$ from 0.0 to 0.4 M approximately doubles Φ . For $\text{Co}(\text{NH}_3)_6^{+3}$, Φ varies from 0.75 to 0.56 when $[\text{Cl}^-]$ is varied from 0.0 to 0.9 M , which is not sufficiently outside the range of our experimental error to be significant. In 0.2 M Cl^- solution, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ is about 90% associated to form the outer-sphere complex $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} \cdot \text{Cl}^-$, and although Φ is increased, the qualitative aspects of the photochemistry (*i.e.*, the rapid evolution of N_2) do not seem to differ from those observed in the absence of Cl^- . However, association to form the inner-sphere complex $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ effectively quenches the evolution of N_2 . Although in the latter case this could be taken as evidence that the primary photochemical process is transfer of an electron from Cl^- to Co(III), we find no chemical evidence for a similar mechanism operating in the case of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} \cdot \text{Cl}^-$. It is possible that the observed increase in ϵ associated with ion-pair formation in these systems can be better attributed to a polarization of ligand electrons or to hydrogen bonding of Cl^- to NH_3 than to a change in the nature of the charge-transfer absorption.

In the experiments involving the irradiation of $\text{Co}(\text{NH}_3)_6^{+3}$ in solutions containing 2.5×10^{-3} and $5.0 \times 10^{-2} M$ NaI, over 90% of I_a is absorbed by I^- . A maximum value $\Phi = 0.29$ has been reported for the production of e_{aq}^- from the 2537-Å. photolysis of NaI solutions at 25°. ³² The reaction of e_{aq}^- with $\text{Co}(\text{NH}_3)_6^{+3}$



has been reported to have a specific rate $k_{10} = 9.1 \times 10^{10} M^{-1} \text{ sec}^{-1}$.³³ Under the conditions of our experiments, the competition between reaction 10 and



which has a specific rate $k_{11} = 2.3 \times 10^{10} M^{-1} \text{ sec}^{-1}$,³⁴ should lead to a significant rate of production of Co(II). Using the value $K \approx 22 M^{-1}$ as the formation constant and $\epsilon_{253.7} \approx 6 \times 10^2 M^{-1} \text{ cm}^{-1}$ for the $\text{Co}(\text{NH}_3)_6^{+3} \cdot \text{I}^-$ ion pair at 45°, ³¹ we estimate that 75–85% of the observed value of R_i in these two experiments is due to reaction 10. If $\phi'I_a'$ is the rate of production of e_{aq}^- from the photolysis of I^- , then using the steady-state approximation for $[e_{\text{aq}}^-]$

$$\frac{d[\text{Co(II)}]}{dt} = \frac{\phi'I_a'}{1 + \frac{k_{11}[\text{H}^+]}{k_{10}[\text{Co(III)}]}} + \phi I_a + \phi''I_a''$$

(31) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1949).

(32) J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **68**, 247 (1964).

(33) J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Chem. Soc.*, 242 (1963).

(34) L. M. Dorfman and I. A. Taub, *J. Am. Chem. Soc.*, **85**, 2370 (1963); S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

where ϕI_a and $\phi'' I_a''$ are the rates of production of Co(II) from the direct irradiation of $\text{Co}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{NH}_3)_6^{+3} \cdot \text{I}^-$, respectively. After making the necessary correction for absorption of radiation by the several species present, we estimate that $k_{10}/k_{11} = 5$ in both experiments. Considering the approximations and differences in conditions, we feel that this compares very well with the ratio calculated from the literature values of k_{10} and k_{11} (~ 4).⁸⁵

Conclusions

(1) The quantum yields for photoreduction of Co(III) complexes at 2537 Å. are high even for complexes that are relatively inert to visible light. The relative values of the quantum yields at 2537 Å. often show the

(35) NOTE ADDED IN PROOF. Since writing this paper we have more exhaustively investigated photolysis of I⁻-Co(III) systems. This recent work has qualitatively confirmed the most important features of the discussion presented here; however, the very approximate treatment of the data and the limited number of experiments cited in this paper led to inaccurate values of k_{10}/k_{11} . The more correct result seems to be $k_{10}/k_{11} \approx 1.8$ for both $\text{Co}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$.

reverse order of that reported for longer wave length irradiation. For example, we find the quantum yields decrease in the series: $\text{Co}(\text{NH}_3)_6^{+3} > \text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} > \text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$.

(2) The over-all quantum yields for Co(II) production are, for many of the complexes, found to vary with the acidity of the solutions. The sensitivity to pH and the type of variation observed depends on the kind of ligands in the first coordination sphere of the Co(III) center. For flexible bidentate ligands (en and tn) there is a maximum quantum yield at $[\text{H}^+] = 0.2 M$.

(3) The observed pH effects are best understood if the photoreduction of Co(III) complexes proceeds through a metastable excited state (which may be chemically stabilized) of sufficiently long life so that it can participate in the simple protolysis of the ligands.

(4) The photoreduction of the ion pair $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} \cdot \text{Cl}^-$ resembles more the photoreduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ than that of $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$.

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Preparation and Properties of Monoalkali Xenates

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Monosodium, -potassium, -cesium, and -rubidium xenates have been prepared by lyophilization of 0.1 M xenon trioxide and alkali hydroxides in 1:1 ratio. The existence of alkali xenates has been confirmed by infrared spectroscopy, X-ray powder diffraction patterns, and the determination of the oxidation equivalent by the "hi-lo" titration method. Sodium xenate has an apparent formula weight of 247 ± 4 . Sodium xenate is more stable than xenon trioxide and less stable than sodium perxenate. At room temperature, sodium xenate does not react readily with anhydrous methyl alcohol. The salt of sodium xenate is stable under anhydrous conditions, otherwise it disproportionates to xenon(0) and xenon(VIII).

In a recent publication, Appelman and Malm¹ questioned the preparation of barium xenate as reported by Kirshenbaum and Grosse.² Appelman and Malm observed that freshly precipitated barium xenate is readily converted to barium perxenate and that the transitory compound, barium xenate, is unstable under the preparative conditions. It has been observed and confirmed by Koch and Williamson³ that xenon(VI)

(1) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(2) A. D. Kirshenbaum and A. V. Grosse, *Science*, **142**, 3592 (1963).

(3) C. W. Koch and S. M. Williamson, *J. Am. Chem. Soc.*, **86**, 5439 (1964).

disproportionates and that the rate increases with the concentration of hydroxyl ion. In addition, it has been suggested by Appelman and Malm¹ that species such as HXeO_4^- and H_5XeO_6^- are possibilities at the first equivalence point when xenon trioxide is titrated with sodium hydroxide.

In the hope of shedding some light on the nature of the xenate ion, a project to prepare the mono- and dialkali xenate salts has been initiated.

Experimental

Chemicals and Apparatus. Solutions of xenon trioxide were obtained from the Argonne National Laboratory. Approximately 0.1 M xenon trioxide solutions were employed for the preparation of alkali salts. Sodium and potassium hydroxide solutions were prepared by routine methods. Rubidium and cesium hydroxides were prepared by the reaction of high purity chlorides (99.9%), supplied by Fisher Scientific Co., with freshly precipitated silver oxide. All preparations of xenate salts were done on a vacuum line. The normal operating pressure was about 10^{-5} mm.

Infrared spectra of these salts as well as of xenon trioxide, perxenates, and related iodine and tellurium compounds were run in a silver chloride matrix using the Perkin-Elmer 21 and KBr Infracord recording