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# The Photochemistry of Coordination Compounds in Solution. I. Tris(ethylenediamine)cobalt(III) Chloride

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The irradiation of $[Co(en)_3]Cl_3$ in aqueous, buffered neutral, or acid solutions resulted in the formation of Co(II), formaldehyde, and ammonia; in addition, at least two-thirds of the ethylenediamine was recovered. The products can be explained in terms of a photochemical oxidation–reduction reaction between Co(III) and ethylenediamine accompanied by reaction with the solvent.

The two principal types of photolysis reactions reported for coordination compounds have been those in which either oxidation–reduction or substitution resulted. In one of the earliest studies Burger reported the photodecomposition of nitrosopentaamminecobalt(III) nitrate, and he concluded that Co(II) and NO were formed upon irradiation of the solution.[1] Most of the subsequent reports on the photolysis of cobalt coordination compounds for those cases which resulted in oxidation–reduction reactions dealt with compounds containing anion ligands, and the products indicated that the coordinated anion was oxidized as the Co(III) was reduced.[2–6] Berger noted that $[Co(en)_3]Cl_3$ was photosensitive, although much less so than the other compounds that he studied.[7] It was reported from these laboratories that when solid tris(ethylenediamine)cobalt(III) halides were irradiated in the solid state the formation of Co(II) and $NH_3$ resulted.[8]

Preliminary studies had shown that the photolysis products of $[Co(en)_3]^{+3}$ in solution were not the same as those observed in the solid state. Therefore, a more detailed examination of the solution reactions has been made in an attempt to learn more about the oxidation of the neutral ligands.

## Experimental

The preparations and physical measurements were similar to those reported earlier.[8]

**Preparation of $[Co(en)_3]Cl_3$.**—The method of Work was used.[9] In order to facilitate the removal of traces of Co(II), a Soxhlet extractor was utilized, permitting repeated washing of the product with fresh, hot solvent. The crystals were dried at 60° under vacuum.

*Anal.* Calcd. for $[Co(en)_3]Cl_3$: N, 24.3. Found: N, 24.4.

**Reagents.**—Nessler's reagent (Fisher Scientific Co.) was used in the qualitative detection of ammonia after dilution with an equal volume of 10% NaOH. The chloroplatinic acid used in the quantitative determination of amines and ammonia was a 10% solution of the acid obtained from Fisher Scientific Co. The 2,4-dinitrophenylhydrazine (DNPH) reagent was prepared by heating excess DNPH in 2 *M* HCl over a steam bath. The reagent was stored in the presence of undissolved DNPH which was removed by filtration prior to the use of the reagent in the qualitative and quantitative determination of carbonyl products.

**Physical Measurements.**—The ultraviolet and visible absorption spectra reported in this work were obtained with a Beckman Model DU spectrophotometer using 1-cm. cells. For the infrared absorption studies solid samples of the compounds were pressed into KBr disks; the dry KBr (200 mesh) was ground with the compound in an agate mortar. Generally 1% disks of 1-mm. thickness were used. The disks were formed in a 0.5-in. die at 10 tons/in.$^2$ pressure. A Perkin-Elmer Model 21 double beam recording spectrophotometer was used to record the absorption of the sample disks between 2 and 15 $\mu$.

The pH determinations of the solutions were made with a Beckman Model G pH meter.

A Gouy-type magnetic balance was used for the magnetic susceptibility measurements. It was calibrated with samples of $CuSO_4 \cdot 5H_2O$, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and water. The samples were suspended in a dry, nitrogen atmosphere during the measurements and in the cases of paramagnetic samples the measured susceptibilities were corrected for the underlying diamagnetism using the values published by Selwood.[10]

**Irradiation Studies.**—A Cenco quartz mercury arc light (Central Scientific Co., No. 87289) was used as the irradiation source throughout the course of the work. This lamp is a 140-watt, high-pressure, mercury type with 7.4% of the total radiation at 366 m$\mu$ and 2% at 254 m$\mu$. For the 366 m$\mu$ line a glass filter (Fisher Scientific Co., No. 11-989) was employed. This filter had a measured transmission of 60% at 366 m$\mu$, a half-width of 55 m$\mu$, and a transmission of less than 5% at 312 and 400 m$\mu$. In order to isolate the 254 m$\mu$ line, solution filters were prepared. These consisted of two 1-cm. quartz cells placed in series. One of these contained a band-pass filter solution prepared by dissolving 480 g. of $NiSO_4 \cdot 6H_2O$ and 90 g. of $CoSO_4 \cdot 7H_2O$ in 1 l. of water. This solution transmitted 58% at 254 m$\mu$ and had a half-width of 100 m$\mu$ with no transmission below 220 m$\mu$ or above 355 m$\mu$. The second cell contained a short-wave cut-off filter solution prepared by dissolving 108 mg. of $I_2$ and 155 mg. of KI in 1 l. of water. This solution transmitted 43% at 254 m$\mu$. Below 245 m$\mu$ there was no transmission. Together, the two filter solutions, when placed in series, yielded 25% transmission at the desired wave length.

For all determinations of the rates of reaction the distance between the cell and the lamp was maintained at 15 cm. For convenience, especially in cases where the absorption spectrum of a sample was to be studied after photolysis, a standard 1-cm. Beckman spectrophotometric silica cell equipped with a ground glass cap was generally employed. The volume contained within this

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[1] O. K. H. Burger, *Proc. Chem. Soc.*, **27**, 160 (1911).

[2] W. Vranek, *Z. Elektrochem.*, **23**, 336 (1917).

[3] G. Berger, *Rec. trav. chim.*, **44**, 47 (1925).

[4] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944), and many subsequent papers by Linhard and co-workers in *Z. Elektrochem.* and *Z. anorg. allgem. Chem.*

[5] A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

[6] S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).

[7] The abbreviation en is used for ethylenediamine.

[8] D. Klein, C. W. Moeller, and R. Ward, *J. Am. Chem. Soc.*, **80**, 265 (1958).

[9] J. B. Work, *Inorg. Syn.*, **2**, 221 (1946).

[10] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

type of cell is about 3.5 ml. For larger volumes of solution a flat fused-quartz cell of 1-cm. thickness and a capacity of approximately 25 ml. was used. These actinometer cells, 75 mm. in diameter, were obtained from Hanovia, No. 2681.

A uranyl oxalate actinometer was chosen for the determination of the quantum yields. A four-cell system, which was recommended by Noyes and Leighton for samples where absorption is not complete, was used.[11] The cells used were the 1-cm. silica cells. The actinometer solution employed consisted of a mixture of approximately 1 m$M$ uranyl oxalate and 5 m$M$ oxalic acid.

In order to employ monochromic radiation of 254 m$\mu$ for the quantum yield determination, the $I_2$–KI and $NiSO_4$–$CoSO_4$ filter solutions, described above, were used. Two sets of 1-cm. quartz cells were filled with these solutions and placed between the light source and the four actinometer cells.

The quantum yield was calculated from the equation given by Noyes and Leighton

$$\phi_u = \phi_a \frac{m_3}{m_1}\left(\frac{m_1 - m_2}{m_1 - m_4}\right)$$

where $\phi_u$ is the quantum yield for the unknown, $\phi_a$ is the quantum yield for the actinometer, and $m$ is the number of moles transformed; $m_3$ refers to the unknown.

## Results

**Basic and Neutral Solutions.**—The investigation of the photochemistry of $[Co(en)_3]Cl_3$ in solution was begun with the photolysis of aqueous solutions using the radiation from an unfiltered mercury lamp. Using dilute samples (about 5 m$M$), the solutions were found to change from the original orange color to red upon irradiation. After several hundred hours blue $Co(OH)_2$ began to accumulate along the bottom of the cell.

An increase in the absorption at 290 or 390 m$\mu$ was used to follow the rate of formation of the photolysis products. At these wave lengths the original complex had almost no absorption. It was found that the rate of formation was linear from about 20 to 100 min. of irradiation. Further investigation of the system disclosed that there was a slow dark reaction after irradiation. The dark reaction was found to be independent of the amount of prior irradiation and could be observed repeatedly on the same sample after each exposure to the ultraviolet source.

Employing the 25-ml. quartz cell, a large volume of nearly saturated $[Co(en)_3]Cl_3$ solution was irradiated for over 2 weeks time. Periodically 0.1-ml. samples were withdrawn for the spectrophotometric determinations of Co(II) and 1-ml. samples for the measurement of magnetic susceptibilities. During this time no precaution was taken to prevent the entrance of air into the cell. At first the quantity of Co(II) determined spectrophotometrically and magnetically was found to increase with the time of irradiation. However, after about 10 days of irradiation the rate of Co(II) formation was noticeably lower than the initial rate. At this point 12% of the total cobalt content was Co(II). The change in magnetic susceptibility of the samples in the dark suggested the reoxidation of the Co(II) initially formed by irradiation. The magnetic results coupled with the changes in the absorption spectrum indicated the formation of a Co(III) complex which was different from the starting material.

The measurement of the pH of solutions of $[Co(en)_3]Cl_3$ undergoing photolysis showed that the pH increased with time of irradiation. This increase could have been due to ammonia liberated by the decomposition of the ethylenediamine, as well as due to free ethylenediamine. Therefore, the detection of ammonia was attempted with Nessler's reagent. The presence of both ammonia and an organic amine in the photolyzed solutions was indicated by the observed reaction with this reagent.

Chloroplatinic acid was used for the identification of the organic amine. The chloroplatinate salts of ammonium ions and organic aminium ions are insoluble in water. When $H_2PtCl_6$ was added to a photolyzed solution of $[Co(en)_3]Cl_3$ a finely crystalline, yellow chloroplatinate precipitate was obtained. By comparing the infrared absorption spectrum of this precipitate with those of ammonium and ethylenediaminium chloroplatinates it was established that the precipitate contained only these two compounds.

An experiment was performed in order to determine whether the ammonia originated from the decomposition of the ethylenediamine while it was coordinated within the tris(ethylenediamine)cobalt(III) molecule or after it had been stripped from the cobalt. It was necessary to employ purified solutions of ethylenediamine because commercially available solutions were found to be contaminated with ammonia. A 10% solution of ethylenediamine was prepared by the addition of NaOH to recrystallized ethylenediamine hydrochloride. After 20 hr. of irradiation of this solution no ammonia was detected either by Nessler's reagent or in the chloroplatinate precipitate.

The 2,4-dinitrophenylhydrazone reagent was employed to aid in the isolation and identification of the carbonyl compound or compounds that could be expected to accompany the formation of ammonia from ethylenediamine. Treatment of photolyzed $[Co(en)_3]Cl_3$ solution with DNPH reagent produced a yellow precipitate. Its melting point of 166–167° suggested that it might be the hydrazone of formaldehyde or acetaldehyde. Melting point mixtures prepared with known hydrazone samples indicated that the carbonyl in question was formaldehyde. A check of a 10% solution of ethylenediamine after 20 hr. of irradiation failed to produce any hydrazone precipitate upon addition of DNPH reagent.

Neither peroxides nor chlorine were found to be present among the photolysis products. Their presence was sought using the spectrophotometric titanium method for peroxide[12] and *o*-tolidine reagent for chlorine.[13]

In summary, it was observed that the photolysis of $[Co(en)_3]Cl_3$ in aqueous solution produced a photo-

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[11] W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 83, 84.

[12] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," The Macmillan Co., New York, N. Y., 1949, p. 742.

[13] N. S. Chamberlain and R. J. Glass, *J. Am. Water Works Assoc.*, **35**, 1665 (1943).

sensitive Co(III)–ethylenediamine intermediate complex, ammonia, formaldehyde, and Co(II). The quantitative analyses were not sufficiently precise to exclude the possibility of other photolysis products.

**Hydrochloric Acid Solutions.**—When solutions of $[Co(en)_3]Cl_3$ in concentrated HCl were irradiated, the yellow-orange of the original solution ultimately was converted to a bright blue. The absorption spectra of these blue solutions were found to exhibit the characteristic absorption peaks of the chlorocobalt(II) anion. Furthermore, the concentration of the Co(II) was calculated from the spectral data, and it was found that the cobalt of the original complex had been quantitatively reduced to the lower oxidation state. When the concentration of HCl was on the order of 6 *M* or less the photolyzed solutions appeared pink in color due to the inability to form the chlorocobalt(II) anion. By placing aliquots of such solutions in 12 *M* HCl the blue color of the chlorocobalt(II) anion was formed. This allowed the determination of the Co(II) content to be made spectrophotometrically, and it was found that Co(II) was formed quantitatively, also, in dilute HCl solutions.

When very concentrated (nearly saturated) solutions of $[Co(en)_3]Cl_3$ in 12 *M* HCl were photolyzed, blue crystals were deposited along the bottom of the photolysis cell. Elemental analysis showed that this product was $(NH_3CH_2CH_2NH_3)_2CoCl_6$.[14] The almost quantitative yield suggested that at least two of the original three molecules of ethylenediamine contained in $[Co(en)_3]Cl_3$ remained unaffected by the photolytic reaction.

The addition of chloroplatinic acid, after photolysis, to dilute solutions of the complex (dilute to avoid deposition of $(enH_2)_2CoCl_6$) yielded a precipitate, which was found to contain only ammonium and ethylenediaminium chloroplatinates when examined by infrared analysis. A specific quantitative determination of ammonia in the presence of ethylenediamine was accomplished by the precipitation of $Na(NH_4)_2Co(NO_2)_6$.[15] This established that 1 mole of ammonia was produced for each mole of Co(II) formed. Quantitative recovery of the mixed chloroplatinate precipitates of ammonia and ethylenediamine indicated that there was more than 2 moles of ethylenediamine per mole of ammonia.

Addition of hydroquinone to a solution of $[Co(en)_3]Cl_3$ in 6 *M* HCl, prior to irradiation, was made so that it might act as a scavenger for free radicals, thereby, perhaps, altering the photolytic products. After photolysis the infrared spectrum of the precipitated chloroplatinates showed that only ammonia and ethylenediamine were present in the precipitate.

A yellow precipitate was obtained upon the addition of 2,4-dinitrophenylhydrazone (DNPH) reagent to a photolyzed solution of $[Co(en)_3]Cl_3$. Elemental analysis of the derivative after sublimation showed that it had the same composition as the hydrazone of formaldehyde. The sublimate was also found to have the same melting point as the formaldehyde derivative, and a mixture melting point showed no depression (166–166.5°).

The DNPH derivative was also used for the quantitative determination of the formaldehyde. This reagent is particularly well suited for the precipitation of aldehyde under the conditions prevailing in the photolyzed solutions. Unlike many derivative-forming carbonyl reagents, DNPH was found to work well in the presence of moderate concentrations of HCl, making it unnecessary to pretreat the solution prior to precipitation. The determination showed about 1 mole of formaldehyde for each mole of Co(II) formed.

Photolysis of the complex in the presence of Ti(IV) failed to reveal the presence of peroxide. A check for chlorine in the 12 *M* HCl solutions, however, showed it to be present. A photolysis cell equipped with a gas inlet and outlet tube was filled with a nearly saturated solution of $[Co(en)_3]Cl_3$ in concentrated HCl. After photolysis, for a time sufficient to impart a deep blue color to the solution, the cell was swept by a stream of nitrogen which was then bubbled through a solution of *o*-tolidine. The average of two runs indicated that $0.337 \pm 0.015$ equivalent of chlorine was present for each mole of Co(II) produced. However, a check of hydrochloric acid itself, under the same experimental conditions, showed that HCl is photolytically decomposed to form chlorine. Photolysis of $[Co(en)_3]Cl_3$ in saturated LiCl (about 9 *M*) failed to produce any detectable chlorine. From these results it may be concluded that chlorine formation was not involved in the reduction of the complex to Co(II). In the photolysis reactions with lower HCl concentration the chloride ion concentration was not decreased in the course of the reaction.

The rate of Co(II) formation in 12 *M* HCl was measured spectrophotometrically. The maximum absorption of the chlorocobalt(II) anion at 687.5 m$\mu$ (molar extinction coefficient 565) is in a region where the original complex has no absorption. Over a concentration range of $[Co(en)_3]Cl_3$ from 0.51 to 2.4 m*M* the rate of Co(II) formation was found to be linear up to about 40% decomposition and averaged $5.3 \pm 0.3\ \mu M$/min.

The quantum yield for a 1.01 m*M* solution of $[Co(en)_3]Cl_3$ in 12 *M* HCl was found to be 0.070 at 254 m$\mu$, using a uranyl oxalate actinometer. An estimate of the quantum yield at 366 m$\mu$ showed a quantum yield of 0.0005 for a 17 m*M* solution of the complex. This calculation involved a comparison of the change in optical density at 687.5 m$\mu$ after irradiation with 366 m$\mu$ light compared to 254 m$\mu$ irradiation; corrections were made for the differences in light intensity and absorption at the two wave lengths.

In summary, the photolysis of $[Co(en)_3]Cl_3$ in the presence of HCl was found to lead to the formation of approximately 1 mole of formaldehyde, 1 mole of ammonia, 1 mole of Co(II), and more than 2 moles of ethylenediamine for each mole of complex irradiated.

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(14) J. Meyer and K. Hoehne, *Z. anorg. allgem. Chem.*, **222**, 161 (1935).

(15) J. L. Gove, H. Baum, and E. L. Stanley, *Anal. Chem.*, **23**, 721 (1951).

## Discussion

These results led to the proposing of an over-all reaction

$$[\mathrm{Co(NH_2CH_2CH_2NH_2)_3}]^{+3} + 5\mathrm{H}^+ + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{Co}^{+2} + \mathrm{CH_2O} + \mathrm{NH_4}^+ + 2.5(\mathrm{NH_3CH_2CH_2NH_3})^{+2}$$

The steps proposed for the reaction are (* = excited state, Δ = thermally liberated energy): (1) absorption of energy

$$[\mathrm{Co(en)_3}]^{+3} + h\nu \longrightarrow [\mathrm{Co(en)_3}]^{+3*}$$

(1a) dissipation of energy

$$[\mathrm{Co(en_3)}]^{+*3} \longrightarrow [\mathrm{Co(en)_3}]^{+3} + \Delta$$

(2) electron transfer

$$[\mathrm{Co(en)_3}]^{+3*} \longrightarrow [\mathrm{Co(en)_2(en\cdot)}]^{+3}$$

(2a) electron return

$$[\mathrm{Co(en)_2(en\cdot)}]^{+3} \longrightarrow [\mathrm{Co(en)_3}]^{+3}$$

(3) β-elimination and hydrolysis of the organic radical

$$[\mathrm{Co(en)_2(en\cdot)}]^{+3} + \mathrm{H_2O} \longrightarrow [\mathrm{Co(en)_2(NH_2CH_2\cdot)}]^{+2} + \mathrm{NH_4}^+ + \mathrm{CH_2O}$$

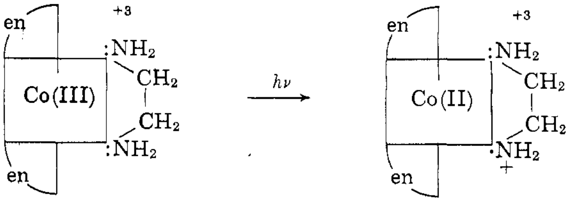
(4) subsequent reaction of the aminomethyl radical. The bases for the proposed reaction mechanism are as follows.

(1).—For the $[\mathrm{Co(en)_3}]^{+3}$ ion there were found to be three absorption peaks, occurring at 465 mμ, 21,500 cm.$^{-1}$ ($E_{\mathrm{M}}$ 86.5); 340 mμ, 29,400 cm.$^{-1}$ ($E_{\mathrm{M}}$ 79.7); and 211 mμ, 47,400 cm.$^{-1}$ ($E_{\mathrm{M}}$ 21,200). It would appear that the first two absorptions are of the ligand field type and that the 211 mμ peak is an electron-transfer band. It was observed that the quantum yield at 254 mμ, within the electron-transfer band, was 0.070. Radiation within a ligand band, at 366 mμ, was estimated to have a quantum yield of only 0.0005. At both wave lengths the photolysis was found to result in the reduction of the Co(III) to Co(II). It is suggested that decomposition of $[\mathrm{Co(en)_3}]^{+3}$ occurs at 366 mμ not because this is within a ligand field band but rather that the trailing edge of the electron-transfer band extends to this wave length.

The energy determined for the Co–N bond of $[\mathrm{Co(NH_3)_6}]^{+3}$ is reported to be 134 kcal./mole.[16] The energy of the Co–N bond of $[\mathrm{Co(en)_3}]^{+3}$ would not be expected to be markedly different. In support of this it is noted that an einstein of light of 211 mμ corresponds to an energy of 133 kcal./mole. The 211 mμ peak must arise from electronic transitions in the Co–N bond of the complexes. Based on the products, it is felt that it is this bond which is involved in the photolytic decomposition of $[\mathrm{Co(en)_3}]^{+3}$.

Reaction 1 represents the absorption of a photon with the production of an excited state. As with all excited states this energy can be dissipated in several different modes. Fluorescence, one of the modes, was sought in a qualitative way and was not observed. The return to the ground state (reaction 1a) through loss of kinetic and vibrational energy as a result of collisions is proposed as a more important process.

(2) **Electron Transfer.**—The ultraviolet absorption energy is centered in the electrons of the Co–N bond of $[\mathrm{Co(en)_3}]^{+3}$. The homolytic fission of a Co–N bond of $[\mathrm{Co(en)_3}]^{+3}$ would produce an unpaired electron in the previously occupied bond site and would result in the formation of a monodentate ethylenediaminium radical. The positive charge of the ethylenediaminium radical, centered on one nitrogen, would be expected to repel the uncoordinated mobile end of the molecule away from the positively charged coordination sphere. Recoordination would be possible if the mobile end of the radical, in its oscillation about the coordinated end, were brought close to the cobalt octahedral position which is not occupied (reaction 2a).



(3) **β-Elimination and Hydrolysis of the Organic Radical.**—The formation of ammonia and formaldehyde observed upon photolysis of $[\mathrm{Co(en)_3}]^{+3}$ suggested that the unpaired electron on the ethylenediaminium radical was shifted. This shift would explain the C–C bond fission through the production of the aminomethyl radical ($\mathrm{NH_2CH_2\cdot}$) and methyliminium ion. The methyliminium ion would be expected to be unstable in the presence of water and to decompose to yield ammonia and formaldehyde.

$$\mathrm{Co{-}NH_2{-}CH_2{:}CH_2{-}}\underset{\cdot}{\overset{+}{\mathrm{N}}}\mathrm{H_2} \longrightarrow \mathrm{Co{-}NH_2{-}}\underset{\cdot}{\mathrm{C}}\mathrm{H_2} + \mathrm{CH_2{=}}\overset{+}{\mathrm{N}}\mathrm{H_2}$$

$$\mathrm{CH_2{=}}\overset{+}{\mathrm{N}}\mathrm{H_2} + \mathrm{H_2O} \longrightarrow \mathrm{CH_2O} + \mathrm{NH_4}^+$$

The results of the study of the reaction in the solid state, in the absence of water, indicate that the reaction which is outlined above in two steps is probably a concerted attack of water accompanied by the β-elimination. Under the anhydrous conditions the ethylenediaminium radical undergoes condensation rather than β-elimination.[8]

(4) **Subsequent Reaction of the Aminomethyl Radical.**—During the course of hydrolysis, described above, one end of the radical was considered still to be coordinated to the cobalt and thereby stabilized sufficiently to undergo subsequent dimerization. This is suggested by the fact that no methylamine was initially detected among the photolysis products. Even after photolysis in the presence of hydroquinone none was detected. Hydroquinone, as a ready source of hydrogen, might have been expected to react with aminomethyl radicals to form methylamine. Also, it has been reported that aminomethyl radicals, both in the gas phase and in solution, will recombine to form ethylenediamine.[17,18] There is the possibility that methylamine was not detectable under the reaction

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(16) K. B. Yatsimirskii, *Dokl. Akad. Nauk SSSR*, **72**, 307 (1950); *Chem. Abstr.*, **44**, 7701*a* (1950).

(17) B. W. Weeks, U. S. Atomic Energy Commission Report UCRl-3071.

(18) C. I. Johnson and H. A. Taylor, *J. Chem. Phys.*, **19**, 613 (1951).

conditions due to a rapid polymerization reaction with $CH_2O$.[19]

(5) **Dissociation and Aquation.**—After completion of the free radical reaction, the pH of the solvent influences the further course of the reaction. Cobalt(II)-amine complexes are unstable and are readily dissociated.[20] In acidic solutions the Co(II) complexes would dissociate rapidly and the ethylenediamine would be protonated and prevented from entering into further reaction.

(6) **Reoxidation.**—In neutral solutions the liberated ethylenediamine as a moderately strong base causes an increase in the pH of the solution. In the presence of air, reoxidation of the Co(II) occurs with the formation of all possible Co(III)–ethylenediamine–water–hydroxide species. The red material, which formed as a consequence of the photolysis of $[Co(en)_3]^{+3}$ in aqueous solution, was found to contain cobalt(III). The spectrum of this material had no specific absorption peaks. This is the type of optical absorption pattern expected for a mixture of a large number of components with overlapping absorption peaks. The subsequent decomposition of the red material after long irradiation demonstrated that it was a photosensitive intermediate in the over-all photodecomposition of $[Co(en)_3]^{+3}$ in aqueous solution. Continued irradiation of such solutions might lead to the complete decomposition of the ethylenediamine. However, complete decomposition could only be approached slowly since, as the concentration of ammonium ions increased, the $Co(OH)_2$ began to precipitate. As the cobalt ion was removed from solution, the number of coordination sites available was depleted, and in the absence of coordination the ethylenediamine solutions were found to be photochemically stable under the conditions used.

**Acknowledgment.**—This work was supported in part by a grant from the National Science Foundation.

(19) J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1953.

(20) J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p. 428.

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# The Photochemistry of Coordination Compounds in Solution. II. Tris(propylenediamine)cobalt(III) Chloride and Tris(butylenediamine)cobalt(III) Chloride

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The irradiation with ultraviolet light of coordination compounds of Co(III) which contain the diamine ligands ethylenediamine, 1,2-diaminopropane, or 2,3-diaminobutane leads to photodecomposition. The major products are Co(II), $NH_3$, the diamine, an aldehyde, a monoamine, and an aminocarbonyl. The specific nature of the aldehyde and the monoamine obtained with the different ligands points to a $\beta$-elimination reaction; thus the photolysis of $[Co(pn)_3]Cl_3$ results in $CH_2O$ and $CH_3CH_2NH_2$, while from $[Co(bn)_3]Cl_3$ there are obtained $CH_3CHO$ and $CH_3CH_2NH_2$.

A number of studies have been made on the use of ultraviolet irradiation to induce the reduction of Co(III) to Co(II) in coordination compounds that are quite stable under ordinary conditions.[2–5] However, there have been very few detailed product analyses, especially for complexes with neutral ligands.

Due to their observation that $[Co(NH_3)_6]I_3$ was reduced by ultraviolet light of 370 mμ only if an excess of $I^-$ ions was present, Adamson and Sporer felt that electron transfer resulted from ion pairing.[6] On the other hand, it was found[7] that reduction of Co(III) occurred upon irradiation of the solid ethylenediamine (en) complex, $[Co(en)_3]Cl_3$, with no evidence of a corresponding oxidation of the chloride ion; ammonia was the only gaseous product detected. Studies made on the decomposition of the complex ion in aqueous solutions led to the proposing of a mechanism involving the transfer of an electron from one of the nitrogen atoms to the Co(III), followed by the fission of the C–C bond in the diamine.[8] The nature of the products indicated that the use of unsymmetrical diamine ligands would be interesting since subsequent reactions of the radicals formed should produce new amines which could help in the determination of the mechanism. This article describes such a study using 1,2-diaminopropane (pn) as the unsymmetrical diamine and 2,3-diaminobutane (bn) to test further the course of the reaction.

## Experimental

**Preparations.**—$[Co(en)_3]Cl_3$ and $[Co(pn)_3]Cl_3$ were prepared by direct oxidation as described by Work, using Eastman diamines and Baker and Adamson reagent grade $CoCl_2 \cdot 6H_2O$.[9]

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(1) Abstracted in part from the Ph.D. dissertation of William C. Taylor, Jr., The University of Connecticut, 1963.

(2) R. Schwartz and H. Weiss, *Ber.*, **58B**, 746 (1925).

(3) R. Schwartz and K. Tede, *ibid.*, **60B**, 63 (1927).

(4) S. T. Spees, Jr., and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).

(5) S. E. Beacom, Ph.D. Dissertation, The University of Connecticut, 1954.

(6) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

(7) D. Klein, C. W. Moeller, and R. Ward, *ibid.*, **80**, 265 (1958).

(8) D. Klein and C. W. Moeller, *Inorg. Chem.*, **4**, 394 (1965).

(9) J. B. Work, *Inorg. Syn.*, **2**, 221 (1946).