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The Photoinduced Isomerization of *cis*-Dichlorobis(ethylenediamine)-cobalt(III) Chloride in Methanol

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The isomerization of *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride to its trans form is induced at 0°C in methanol by ultraviolet irradiation. The visible light in the wavelength region of the ligand field bands is not effective, but the ultraviolet light corresponding to the charge transfer band is essential. The effects of the dissolved oxygen, the initial concentration of the reactant, and the intensity of the incident light were examined, and the reaction was found to proceed further even after the cessation of irradiation. A chain mechanism is proposed which includes the Co(II) species, the photoreduction product of the Co(III) complex, as a chain carrier. The isomerization reaction was also conducted at 0°C in the dark in the presence of cobalt(II) chloride and ethylenediamine; the most effective catalyst was assumed to be a five-coordinated Co(II) species, $\mathrm{CoClen_2^+}$. The induction period which was observed in the photoreaction was explained as being due to the deactivation of the reactive Co(II) species throguh oxidation with the dissolved oxygen.

The isomerization of *cis*-dichlorobis(ethylenediamine)cobalt(III) to its trans form has been investigated in various solvents, such as methanol,[1,2] ethanol,[2] propanol,[2] 2-methoxyethanol,[3] dimethylformamide,[4] dimethylacetamide,[4] and dimethyl sulfoxide.[5] The equilibrium constant of the isomerization,

$$cis\text{-}\mathrm{CoCl_2en_2}^+ \overset{K}{\rightleftharpoons} trans\text{-}\mathrm{CoCl_2en_2}^+$$

was evaluated as 7 in dimethylformamide, 8 in dimethylacetamide, and 4.0 in dimethyl sulfoxide, all at 60°C. However, in alcohols there was no detectable amount of the cis isomer present at equilibrium, and the value of K was estimated to be larger than 40 in methanol at 25°C.[1]

Brasted and Hirayama[2] noticed that "the effect of sunlight on the rate was very marked." In recent years the photochemical reaction of metal complexes has attracted the attention of many investigators, but the photochemical isomerization of *cis*-dichlorobis(ethylenediamine)cobalt(III) has not yet been investigated in detail. We have now found that the isomerization reaction is really accelerated by the ultraviolet light; we will report here the experimental results obtained.

Experimental

Materials. *trans*-$[\mathrm{CoCl_2en_2}]\mathrm{Cl}$ and *cis*-$[\mathrm{CoCl_2en_2}]\mathrm{Cl\cdot H_2O}$ were synthesized according to standard methods.[6] Found: Co, 20.37; C, 17.50; H, 6.00; N, 19.12; Cl, 37.00%. Calcd for $\mathrm{CoC_4H_{16}N_4Cl_3}$ (trans form): Co, 20.79; C, 17.28; H, 5.68; N, 19.65; Cl, 37.40%. Found: Co, 19.50; C, 16.13; H, 5.94; N, 18.56; Cl, 34.30%. Calcd for $\mathrm{CoC_4H_{18}N_4OCl_3}$ (cis form): Co, 19.47; C, 15.87; H, 6.02; N, 18.50; Cl, 35.00%.

Commercial methyl alcohol was dehydrated by treatment with magnesium ribbon and iodine. Ethylenediamine was also dehydrated by distillation in the presence of sodium. Nitrogen was purified by passing it through a column of a saturated solution of ammonium carbonate containing copper tips, and then a washing bottle containing an alkaline solution of pyrogallol, and dried by passing it through concentrated sulfuric acid and then over solid potassium hydroxide.

Apparatus and Procedure. The whole arrangement of the experimental device is drawn schematically in Fig. 1. A super-high-pressure mercury lamp, SHL-100 UV, of the Toshiba Electric Co., Ltd., was used as the irradiation light source. To prevent thermal isomerization, the reaction was performed at 0°C in a vessel of the Dewar-bottle type, illustrated in Fig. 2. The reaction mixture was held in a cylindrical cell, C, the diameter of which was about 2 cm and the length, about 5 cm. Four quartz plates were used as windows to transmit the ultraviolet light. The reaction mixture was maintained at 0°C by ice and water in the part B. A is a vacuum jacket. The reaction vessel was fixed in a holder made of brass. A pocket to hold a suitable glass filter was placed in front of the light-entrance window, and another pocket to keep the photocell, behind the light-outlet window. A methanol solution of *cis*-$[\mathrm{CoCl_2en_2}]\mathrm{Cl}$ ($\sim 10^{-3}$ M) was prepared at

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[1] D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, **1953**, 2696; E. W. Davies, *J. Phys. Chem.*, **65**, 1328 (1961); B. Bosnich, C. K. Ingold and M. L. Tobe, *J. Chem. Soc.*, **1965**, 4074.

[2] R. C. Brasted and C. Hirayama, *J. Am. Chem. Soc.*, **80**, 788 (1958).

[3] R. F. Trimble, Jr., *ibid.*, **76**, 6321 (1954).

[4] M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, **1962**, 4614.

[5] M. L. Tobe and D. W. Watts, *ibid.*, **1964**, 2991.

[6] W. C. Fernelius (Ed.), "Inorganic Synthesis," Vol. II, McGraw-Hill Book Co., Inc., New York (1946), p. 222.

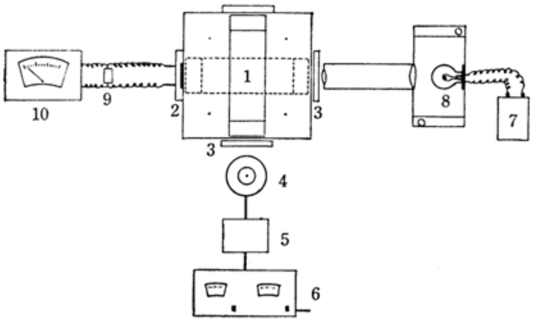

Fig. 1. Block diagram of the apparatus: (1) reaction cell, (2) silicon photo-cell, (3) light filter, (4) mercury lamp, (5) starter of mercury lamp, (6) voltage stabilizer, (7) battery, (8) tungsten lamp for spectrophotometric assay, (9) resistance (10 ohm), (10) microvoltmeter.

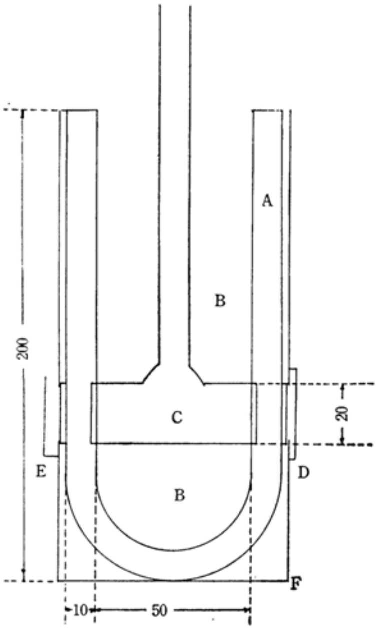

Fig. 2. Reaction vessel: (A) vacuum jacket, (B) ice room, (C) solution cell, (D) light filter, (E) photo-cell, (F) brass holder.

0°C and deaerated by bubbling purified nitrogen through it for about 30 min. During the reaction, nitrogen gas bubbling was continued through a narrow glass tube inserted at the upper part of the reaction mixture. At various time intervals the cell holder was turned at right angles and the concentration of the remaining reactant was spectrophotometrically determined. Light emitted from a tungsten lamp (6 V and 5A) was passed through the reaction cell *via* a Toshiba color glass filter VG-52, which shows the highest transmittance, of 20%, at 525 mμ. The intensity of the transmitted light was measured by means of a Sharp silicon photoelectric diode, SPD-111, and a microvoltmeter (Okura Electric AM 1001).

The absorption maximum of *cis*-[$CoCl_2en_2$]Cl at 537 mμ becomes lower as the isomerization to the trans form proceeds. In advance, the interrelation between the intensity of the transmitted light and the concentration of the cis or trans complex in methanol was studied and found to obey Beer's law.

$$\log(X_S/X) = \varepsilon c d \qquad (1)$$

In Eq. (1), X_S and X are readings of the microvoltmeter when the light was transmitted through the pure solvent and a solution with concentration c respectively. ε is an extinction coefficient, and d, the length of the light path in the reaction cell. From a linear plot of $\log(X_S/X)$ *vs.* c, the value of εd was obtained as 431 for the cis compound and as 80 for the trans compound. Utilizing these values, the concentration of the cis complex remaining in the reaction mixture was calculated from Eq. (2):

$$c_{cis} = \frac{\log(X_S/X) - \varepsilon_{trans} c_0 d}{(\varepsilon_{cis} - \varepsilon_{trans}) d} \qquad (2)$$

where c_{cis} and c_0 are the concentrations of the cis complex at time t and at zero respectively.

Determination of Photochemically-produced Cobalt(II). When an excess of ammonium thiocyanate is added to cobalt(II) chloride in methanol, $Co(NCS)_4^{2-}$ is formed which shows an absorption maximum at 620 mμ. The optical density of the solution at this wavelength increases linearly with the concentration of cobalt(II) ions in the range examined up to 1×10^{-3} M, and the molar extinction coefficient, ε, was calculated to be 1570 from the slope of this straight line. However, if ethylenediamine is added to the solution, the formation of the thiocyanate complex is retarded and the absorbance decreases with the amount of ethylenediamine added. In the present reaction system two molecules of ethylenediamine are present per cobalt atom. The conditions for determining cobalt(II) in the presence of twice as much ethylenediamine was investigated. Beer's law does not hold in this case. A plot of the absorbance against the Co(II) concentration deviates appreciably from a straight line as the concentration of Co(II) is increased, with the [Co(II)]/[ethylenediamine] ratio kept constant at 1/2. From the slope of the quasilinear part of the plot in the lower concentration region, the value of ε was assumed as 1290 for the cobalt(II) thiocyanate complex in the presence of twice as many moles of ethylenediamine.

Absorption Spectra. The absorption spectra were observed with a Hitachi Perkin-Elmer spectrophotometer, Model 139.

Results

A. General Pattern of the Photochemical Reaction. When a methanol solution of *cis*-[$CoCl_2en_2$]Cl was kept standing at room temperature, the color of the solution changed from violet to green in several days. The spectral change in the visible region is well-known.[1] The observed spectral change in the ultraviolet region is shown in Fig. 3(a). The final curve 5 coincides with the absorption curve of authentic *trans*-[$CoCl_2en_2$]Cl. Several distinct isosbestic points were observed, indicating that no reaction other than the *cis-trans* isomerization occurred. However, such a thermal isomerization was hardly detected at 0°C.

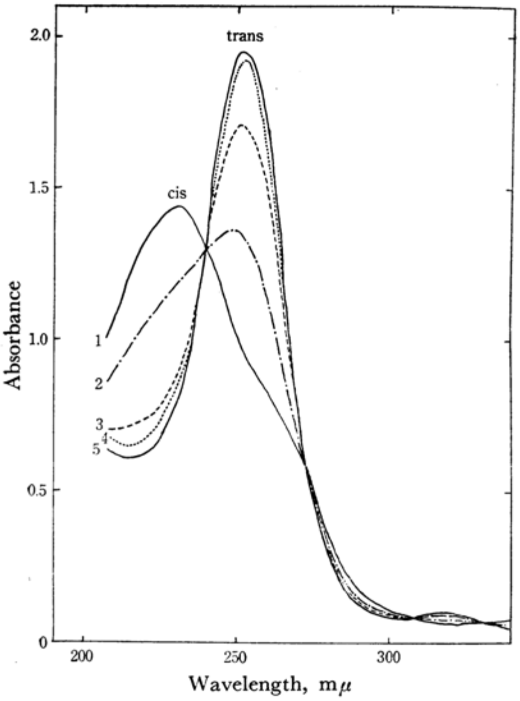

Fig. 3(a). The spectral change in the ultraviolet region during the thermochemical *cis-trans* isomerization of dichlorobis(ethylenediamine)cobalt(III) chloride in methanol at room temperature. Curves No. 1 through No. 5 were measured at arbitrary intervals among ten days.

When it was irradiated with ultraviolet light, the cis compound isomerized to the trans form in methanol, even at 0°C. The spectral change is quite similar as that in the thermal reaction. Figure 3(b) illustrates the change in the ultraviolet region. Three curves (1—3) show isosbestic points, and the trans peak becomes lower again upon prolonged illumination (curves 4 and 5). Thus, the main reaction occurring under ultraviolet irradiation is isomerization. The photo-decomposition of the complex seems to occur simultaneously, but it does not seriously disturb the kinetic study of the main reaction, as can be seen from the apperance of a clear isosbestic point at 241 mμ.

B. Dependency on the Wavelength of Illuminating Light. As is shown in Fig. 4, *cis*-$CoCl_2en_2{}^+$ has an intense charge transfer band in the ultraviolet region besides the ligand field bands in the visible region.⁷⁾ To determine the absorption band which is effective for the reaction, several cut-off filters were employed. The transmission coefficient of each Toshiba glass filter is depicted in Fig. 4. A UV-39 filter, for instance, transmits 50% of the incident light at 390 mμ.

The experimental results are shown in Fig. 5. At the initial stage of the photochemical reaction, the rate increases with time up to a stationary state, indicating the existence of an induction period; the length of this period was estimated by extrapolating the linear part of the reaction curve back to the initial value of the reactant concentration. The stationary rate of reaction is highest when no filter is employed; it becomes lower as

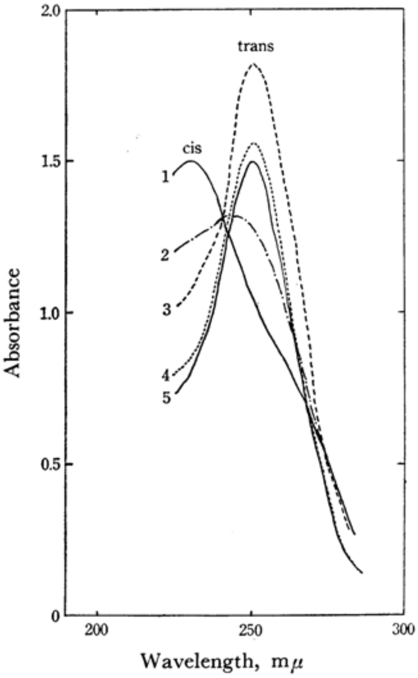

Fig. 3(b). The spectral change in the ultraviolet region during the photoinduced *cis-trans* isomerization of dichlorobis(ethylenediamine)cobalt(III) chloride in methanol at 0°C. Curves No. 1 through No. 5 were measured at arbitrary intervals during 150 min.

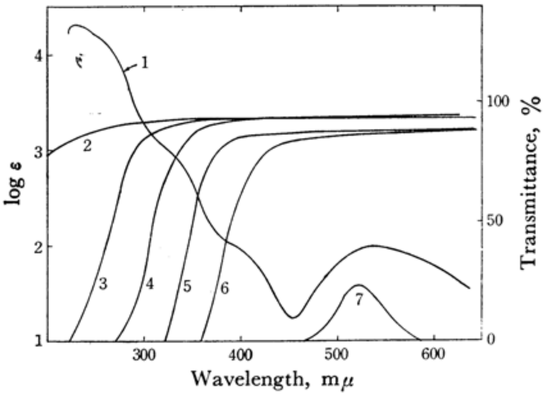

Fig. 4. The absorption spectrum of *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride in methanol (curve 1) and percentage transmittances of quartz glass (2), Toshiba glass filters UV-27 (3), UV-31 (4), UV-35 (5), UV-39 (6) and VG-52 (7).

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7) M. Linhard and M. Weigel, *Z. anorg. u. allgem. Chem.* **266**, 49 (1951); **271**, 101 (1952).

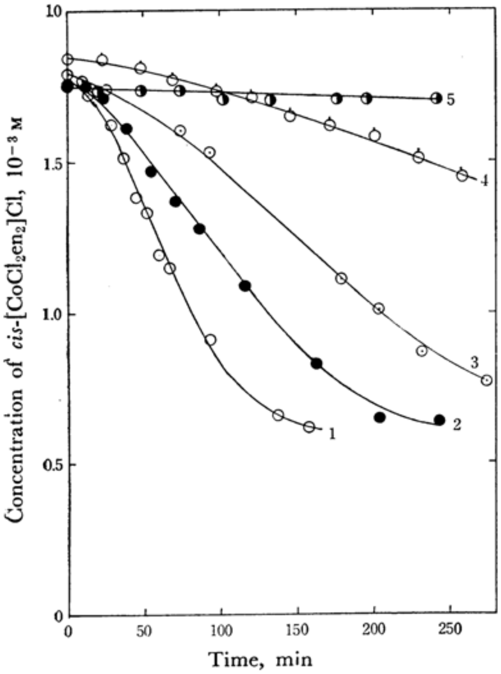

Fig. 5. The photoisomerization of *cis*-dichlorobis-(ethylenediamine)cobalt(III) chloride in methanol at 0°C in the presence of various light filters: (1) no filter, (2) UV-27, (3) UV-31, (4) UV-35, (5) UV-39.

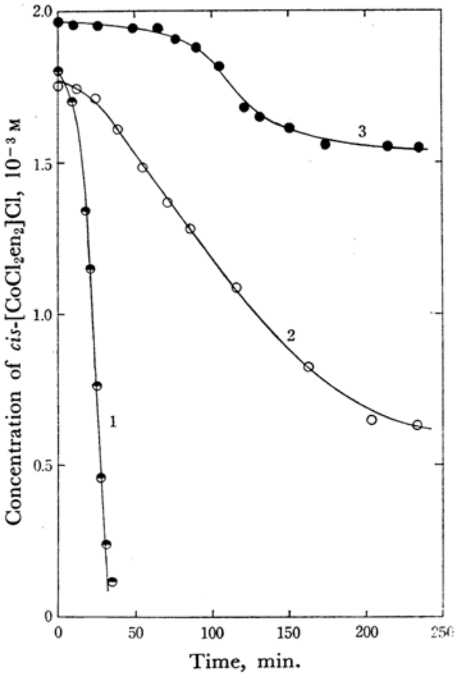

Fig. 6. The effect of gas bubbling upon the rate of photoisomerization of *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride in methanol at 0°C: (1) nitrogen, (2) no gas bubbling, (3) oxygen.

the shorter wavelength region of the illuminating light is cut off. If a UV-39 filter is used, the rate of reaction is immeasurably slow. Thus the light of ligand field bands is not effective, but the charge-transfer band in the ultraviolet region is useful for the isomerization of *cis*-[CoCl$_2$en$_2$]Cl. In the following experiments a UV-27 filter was used exclusively.

C. Effect of the Atmosphere. When oxygen was bubbled through the reaction mixture, the induction period became much longer than that under an open atmosphere, and the extent of reaction was very low. On the contrary, if nitrogen gas was bubbled through the reaction system, the induction period became much shorter and the reaction rate was very large (Fig. 6). These results indicate that dissolved oxygen has an inhibiting effect on the photochemical isomerization. Some kind of intermediate which is easily oxidized by molecular oxygen must be included in the over-all reaction pathway.

D. Effect of the Light Intensity. The effect of the incident light intensity (I_0) upon the length of the induction period (τ) and the stationary rate of the reaction (R) was examined. Two kinds of sooted metal net, with transmittances of 48.5 and 20.6% respectively, were inserted just in front of the glass filter to change the intensity of the illuminating light. The experimental results are shown in Fig. 7. As the light intensity is lowered,

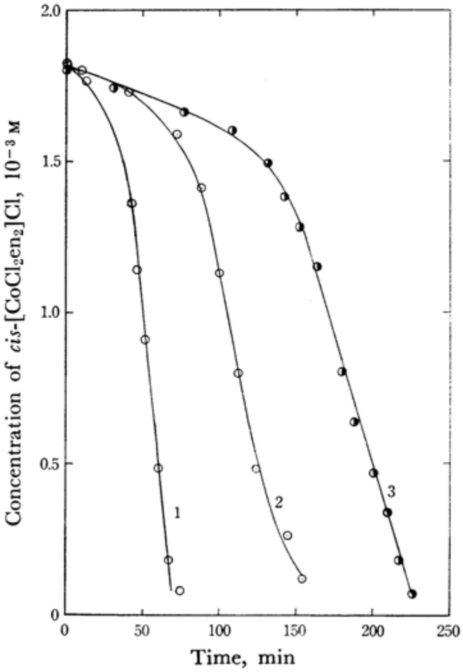

Fig. 7. The effect of incident light intensity upon the rate of photoisomerization of *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride in methanol at 0°C. Relative light intensity: (1) 100, (2) 48.5, (3) 20.6.

the induction period becomes longer and the stationary rate of reaction becomes slower. Linear plots of $\log \tau$ *vs.* $\log I_0$(relative) and $\log R$ *vs.* $\log I_0$(relative) indicate the following relations: $\tau \propto I_0^{-1}$, $R \propto I_0^{0.7}$. The length of the induction period is inversely proportional to the light intensity, and the stationary rate of reaction is proportional to a fractional power (nearly one) of the light intensity.

E. Effect of the Initial Concentration of the cis Complex. When the initial concentration (c_0) of the cis complex is lowered, the induction period becomes longer and the stationary rate of the reaction (R) becomes slower. A plot of $\log R$ against $\log c_0$ was found to be linear, as is shown in Fig. 8. From the slope of this straight line, the following relation is obtained: $R \propto c_0^{1.14}$. Thus, the stationary rate of isomerization is nearly first-order with respect to the initial concentration of the reactant, though the reaction in each run apparently proceeds as a zeroth order.

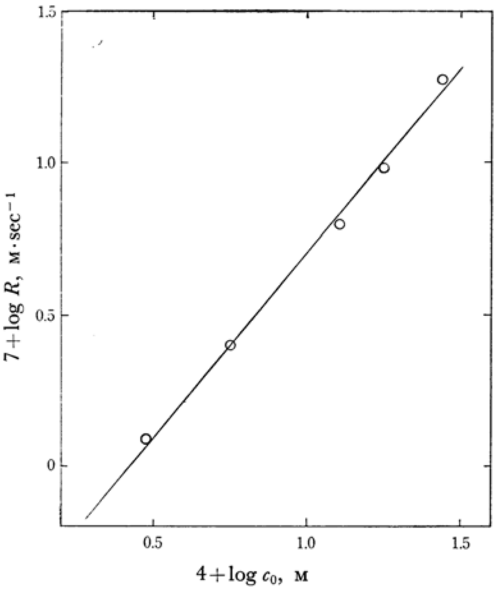

Fig. 8. The stationary rate of photoisomerization of *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride in methanol at 0°C as a function of the initial concentration.

F. Post-irradiation Reaction. Even when the incident light was turned off after illumination for a certain period, the reaction continued to proceed. The spectroscopic investigation of the product solution indicates that the product of this post-irradiation reaction is the same as that of the steady photoreaction. The rate of this reaction obeys the first-order-rate law with respect to the cis compound, and becomes faster as the illumination period becomes longer (Fig. 9). Thus, a pseudo-first-order rate constant of 2.8×10^{-5} sec^{-1} was obtained for run A in Fig. 9 after pre-illumination for 30 min, and 1.5×10^{-4} sec^{-1} for run B after pre-illumination for 40 min.

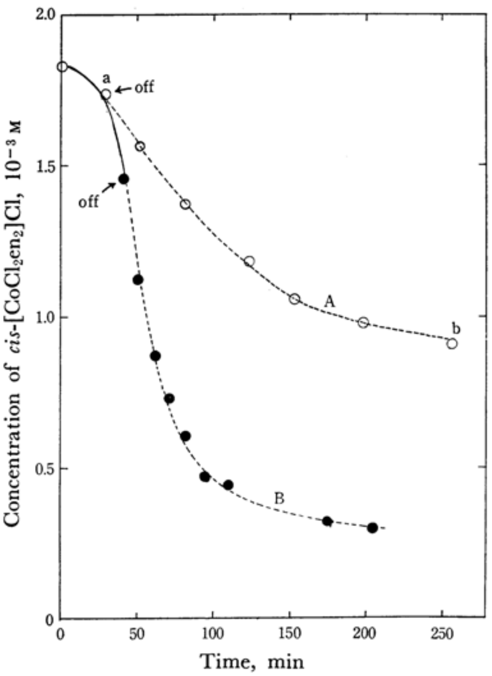

Fig. 9. Post-irradiation reaction. The illuminating light was turned off at points indicated by arrows. Co(II) content was determined at points a and b.

These experimental results strongly suggest that: (1) some chemical species is produced in the photoreaction which can promote the isomerization reaction in the dark; (2) this intermediate is accumulated during the irradiation, and (3) the concentration is maintained constant throughout the post-irradiation reaction in the dark. If a methanol solution of ammonium thiocyanate is added to an aliquot of the reaction mixture, the solution turns blue and shows an absorption maximum at 620 mμ which is characteristic of the cobalt(II) ion.

G. Photoproduction of Co(II). In the course of a steady photoreaction, aliquots of 5 m*l* each were taken at various time intervals and added to 5 m*l* of a 1 M NH_4SCN solution in methanol; the absorbance at 620 mμ was then determined. The concentration of Co(II) in the reaction system increased linearly with the time after a short induction period (Fig. 10). Similar experiments were also performed with *trans*-$[CoCl_2en_2]Cl$. The trans complex produces Co(II) a little more rapidly than the cis complex, as is illustrated in Fig. 10. The zeroth-order rate of Co(II) formation under the present conditions is 8.3×10^{-8} M·sec^{-1} for the cis and 9.0×10^{-8} M·sec^{-1} for the trans compound. Of course, these figures depend upon the intensity of light absorbed. In

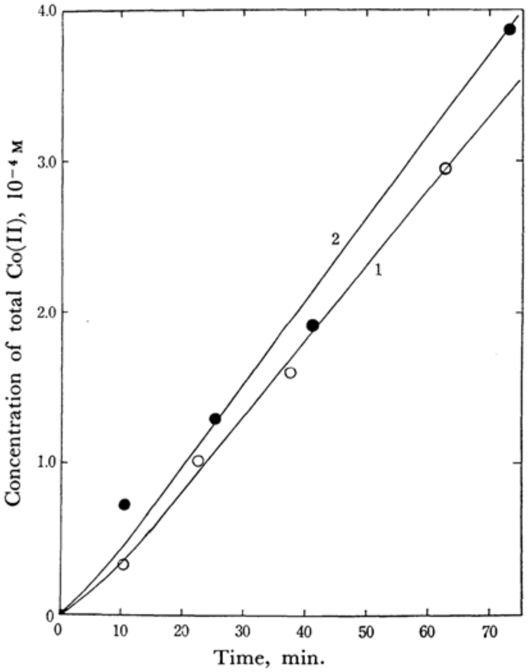

Fig. 10. The photoreduction of Co(III) in methanol at 0°C: (1), *cis*-$[CoCl_2en_2]Cl$, (2), *trans*-$[CoCl_2en_2]Cl$.

a post-irradiation reaction, run A in Fig. 9, the Co(II) concentration was determined for aliquots taken at points a and b; the same value of 5×10^{-5} M was obtained for both.

H. Search for the Reactive Intermediate. As has been described in the foregoing sections, a certain reactive intermediate is produced photochemically which can catalyze the isomerization reaction. This catalyst seems to be some kind of Co(II) compound. The trans compound produced through the reaction also decomposes photochemically, as Figs. 3(b) and 10 show, and the total concentration of Co(II) continues to increase even after the end of the isomerization reaction.

Even if anhydrous cobalt(II) chloride was added to a methanol solution of *cis*-$CoCl_2en_2^+$, no reaction occurred, but when both cobalt(II) chloride and ethylenediamine were added, isomerization was observed at 0°C in the dark. Preliminary experiments showed that the addition of ethylenediamine made the solution basic and caused solvolysis. To prevent disturbance, ammonium chloride of nearly the same concentration as ethylenediamine was added. For instance, a reaction mixture of the 1.8×10^{-3} M cis complex, 5×10^{-3} M ethylenediamine, and 7×10^{-3} M NH_4Cl shows a pH value of 6.4—6.5, without any sign of solvolysis.

A methanol solution of cobalt(II) chloride, ethylenediamine, and ammonium chloride was prepared at 0°C and added to a solution of the cis compound which had been kept in a nitrogen atmosphere at 0°C. The concentration of $CoCl_2$ was kept constant at 6×10^{-5} M in each run. The initial concentration of *cis*-$[CoCl_2en_2]Cl$ was about 1.6×10^{-4} M, and the mole ratio of $CoCl_2$ to ethylenediamine was changed in the range from 1 : 1 to 1 : 50. Ammonium chloride, equimolar as ethylenediamine, was employed in each experiment. The course of reaction can be reproduced by a first-order rate equation:

$$-\mathrm{d}[cis]/\mathrm{d}t = k_{\mathrm{obs}}[cis] \tag{3}$$

The observed values of the pseudo-first-order rate constant are listed in Table 1.

Table 1. The rate of isomerization of *cis*-$[CoCl_2en_2]Cl$ catalyzed by a mixture of cobalt(II) chloride and ethylenediamine at 0°C in the dark
$[CoCl_2]=6\times10^{-5}$ M, $[cis\text{-}CoCl_2en_2^+]_0=1.6—1.7\times10^{-4}$ M, $[NH_4Cl]=$[ethylenediamine]

$[CoCl_2]$: [en] mole ratio	Pseudo 1st order rate const. $k_{\mathrm{obs}}\times10^4$, sec^{-1}	$k_{\mathrm{obs}}/[CoCl_2]$ $\mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$
1 : 0	0	0
1 : 1	2.2	3.7
1 : 2	6.5	$10._8$
1 : 3	5.2	8.5
1 : 5	3.5	5.9
1 : 10	3.0	5.0
1 : 50	0.79	1.3

The product in solution was identified as *trans*-$CoCl_2en_2^+$ by means of ultraviolet spectroscopy. The fact that the isomerization proceeds as a first-order reaction with respect to the cis compound nearly up to completion, in spite of the very low concentration of Co(II), clearly indicates that some effective catalyst composed of Co(II) and ethylenediamine survives throughout the reaction. Cobalt(II) chloride is not effective by itself, but becomes active in the presence of ethylenediamine. Since formation constants of the cobalt(II) ethylenediamine complexes in methanol are not available, the concentration of each complex species contained in the reaction system can not be estimated, but the rate data in Table 1 suggest that a one-to-two complex of $CoCl_2$ with ethylenediamine is most effective. Thus the pseudo first-order rate constant in Eq. (3) can be represented by Eq. (4):

$$k_{\mathrm{obs}} = \sum_{i=1}^{3} k_i[\mathrm{CoCl_2(en)}_i] \tag{4}$$

Here, $\sum_{i=0}^{3}[\mathrm{CoCl_2(en)}_i] = [\mathrm{CoCl_2}]_{\mathrm{total}}$, and the lower limit of the second-order rate constant due to the most active catalyst species, say $CoCl_2en_2$, can be estimated to be $10._8$ $\mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$, as in the last column of Table 1.

Discussion

The isomerization of *cis*-$[CoCl_2en_2]Cl$ to the trans form in methanol is induced not by the visible light but by the ultraviolet light. The photoreduction of Co(III) in an aqueous solution has been amply demonstrated by several authors.[8,9] Although the diamine molecule is oxidized by cobalt(III) in the excited state of $Co(diamine)_3{}^{3+}$ compounds,[10] the acido group is oxidized in the case of $CoX(NH_3)_5{}^{2+}$ salts ($X=I$, Br, N_3).[11] In a similar manner, a Co(II) species was produced photochemically; its concentration increased linearly with the irradiation time, as is shown in Fig. 10. The rate of photoreduction is represented by:

$$d[Co(II)]_{total}/dt = \phi I_{abs} = \phi I_0(1 - e^{-\varepsilon cd}) \quad (5)$$

since Beer's law holds for methanol solutions of *cis*- and *trans*-$[CoCl_2en_2]Cl$. Here ϕ is the quantum yield for the photoreduction, and ε, c, and d are the molar extinction coefficient of a complex, the molar concentration, and the width of the light path respectively. The value of ε of *cis*-$CoCl_2en_2{}^+$ in the ultraviolet region is 10^3—10^4 in the order of magnitude; the initial concentration of the complex employed is usually about 1.7×10^{-3} M, and d is about 5 cm. Therefore, εcd seems to be larger than 5, and so Eq. (5) may be safely approximated by Eq. (6);

$$d[Co(II)]_{total}/dt = \phi I_0 \quad (6)$$

That is, the effective light may be absorbed almost completely. This assumption is consistent with the experimental fact that the photoproduction of the Co(II) species proceeds following the zeroth-order kinetics after a short induction period.

According to Endicott and Hoffman[12] the quantum yield of the photoreduction of *cis*-$CoCl_2en_2{}^+$ with an ultraviolet light of 2537 Å, $\phi=0.080\pm0.013$ at $[H^+]\leq0.12$ M, is a little larger than that for the trans complex, $\phi=0.069\pm0.006$ at $[H^+]\leq0.186$ M. The reason why the rate of Co(II) production is larger for the trans than for the cis compound (Fig. 10) may be due to the fact that I_{abs} is larger for the trans than for the cis compound in the present case since the absorption maximum of the former lies at a longer wavelength region with a higher ε value (Fig. 3).

The role of ultraviolet light in the present reaction is to produce the effective Co(II) species. After some quantity of the effective Co(II) species has been produced, the isomerization proceeds even if the illuminating light is turned off, as is shown in Fig. 9. Furthermore, if both cobalt(II) chloride and ethylenediamine are added to a solution of the cis complex, the isomerization occurs in the dark. The nature of the Co(II) species which promotes the reaction is not quite clear, but it is certain that the effective species contains ethylenediamine. If we assume the following reaction scheme, all the experimental results obtained so far may be explained well:

light absorption:

$$cis\text{-}CoCl_2en_2{}^+ + h\nu \xrightarrow{I_{abs}} [cis\text{-}CoCl_2en_2{}^+]^* \quad (7)$$

deactivation:

$$[cis\text{-}CoCl_2en_2{}^+]^* \longrightarrow cis\text{-}CoCl_2en_2{}^+ + \text{heat} \quad (8)$$

redox process:

$$[cis\text{-}CoCl_2en_2{}^+]^* \xrightarrow{\phi} CoClen_2{}^+ + Cl \quad (9)$$

isomerization *via* electron transfer:

$$\begin{aligned} CoClen_2{}^+ + cis\text{-}CoCl_2en_2{}^+ &\xrightarrow{k_p} \\ trans\text{-}CoCl_2en_2{}^+ &+ CoClen_2{}^+ \end{aligned} \quad (10)$$

decomposition of catalyst:

$$\begin{aligned} CoClen_2{}^+ &\rightleftarrows CoClen^+ + en \\ &\rightleftarrows CoCl^+ + 2en \end{aligned} \quad (11)$$

This is a kind of chain reaction. Steps (9), (10) and (11) are chain initiation, propagation and termination respectively. In the photodecomposition of bromo- and iodo-pentaamminecobalt(III) complexes, bromine and iodine molecules were identified respectively,[12] suggesting that an electron was transferred from the bromine or the iodine atom to cobalt(III) in the coordination sphere. In the case of chloropentamminecobalt(III), chlorine was not identified, but an electron transfer from a chloride ligand to the central cobalt(III) may be assumed here by analogy to other halide ligands. The resulting five-coordinated intermediate $CoClen_2{}^+$ might decompose according to Eq. (11). However, the experimental facts that the concentration of the effective intermediate was maintained constant throughout the post-irradiation reaction, and that cobalt(II) chloride alone could not promote the reaction in the dark, indicate that the equilibrium represented by Eq. (11) is favorable to the left-hand side. In methanol the stabilization of a metal ion by solvation is not as effective as in water, and so the formation equilibrium of the Co(II) ethylenediamine complex will be more favored than in water.

In the dark, the reaction must involve the following equilibria in the presence of cobalt(II) chloride and ethylenediamine:

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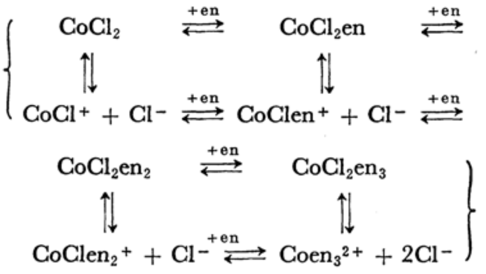
[8] A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960); A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958), and other papers cited therein.

[9] V. Balzani, V. Carassiti, L. Moggi and N. Sabbatini, *Inorg. Chem.*, **4**, 1247 (1965).

[10] D. Klein and C. W. Moeller, *ibid.*, **4**, 394 (1965); W. C. Taylor and C. W. Moeller, *ibid.*, **4**, 398 (1965).

[11] S. A. Penkett and A. W. Adamson, *J. Am. Chem. Soc.*, **87**, 2514 (1965).

[12] J. F. Endicott and M. Z. Hoffman, *ibid.*, **87**, 3348 (1965).

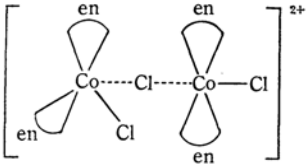


(12)

The experimental results in Table 1 suggest that the bis(ethylenediamine)cobalt(II) species is most effective.

For the electron transfer reaction two distinct types of mechanisms have been proposed, types containing the outer-sphere activated complex and the inner-sphere(bridged) activated complex respectively.[13] In the present system the electron transfer process is essential, but its mechanism is not at all clear. The *cis*-$CoCl_2en_2^+$ reactant in the ground state might receive an electron without any change in the coordination sphere, and might then isomerize to the trans form *via* the intermolecular mechanism, since the Co(II) complex is substitution-labile. Unfortunately, no rate data on electron transfer reaction between $CoCl_2en_2$ and $CoCl_2en_2^+$ are available; however, such a reaction between the high-spin d^7 complex and the low-spin d^6 complex seems to be very slow. In fact, the second-order rate constants of electron transfer in the $Co(NH_3)_6^{2+}$-$Co(NH_3)_6^{3+}$ and $Co(en)_3^{2+}$-$Co(en)_3^{3+}$ systems are reported to be $<10^{-9}$ (64.5°C)[14] and 5.6×10^{-3} (98°C)[15] $\text{M}^{-1}\cdot\text{sec}^{-1}$ respectively. The present data in Table 1 seem too large to fit this outer-sphere mechanism.

While the electron transfer between Cr^{2+}(aq.) and $Co(NH_3)_6^{3+}$ proceeds as an outer-sphere reaction with $k=9.0\times10^{-5}\ \text{M}^{-1}\cdot\text{sec}^{-1}$ at 25°C,[16] the reaction between Cr^{2+}(aq.) and $Co(NH_3)_5Cl^{2+}$ proceeds *via* the inner-sphere path and $k>10^3\ \text{M}^{-1}\cdot\text{sec}^{-1}$ at 20°C.[17] The present data in Table 1 are near the latter example, and reaction (10) could be presumed to proceed *via* the following transition state:



According to the above reaction scheme, the overall rate of the photoinduced reaction is represented by Eq. (14):

$$-\mathrm{d}[cis]/\mathrm{d}t = \phi I_{\text{abs}} + k_p[\text{CoClen}_2{}^+][cis] \quad (13)$$

$$= k_p[\text{CoClen}_2{}^+][cis] \quad (14)$$

since the first term on the right-hand side in Eq. (13) is much smaller than the second term. If the rates of various runs are compared at the same concentration of $CoClen_2^+$, after the induction period, the rate must be proportional to the concentration of the cis compound. This is nearly consistent with the experimental data illustrated in Fig. 8. In the course of the reaction the concentration of the reactant cis compound decreases with the extent of reaction. On the other hand, the total Co(II) concentration increases linearly with the time, as was represented by Eq. (6); therefore, the concentration of $CoClen_2^+$ must also increase with the time, compensating for the decrease in the cis compound. The observed behavior that the stationary reaction proceeds according to the zeroth-order kinetics might be due to such a situation.

If oxygen is included in the reaction system, the effective Co(II) species will be deactivated by oxidation. This may be the cause of the induction period. Figure 6 clearly demonstrates the retarding effect of dissolved oxygen. As long as an appreciable concentration of oxygen exists, the effective Co(II) species will be reoxidized at once and the rate of oxygen consumption will be equal to the rate of Co(II) production.

$$-\mathrm{d}[O_2]/\mathrm{d}t = \phi I_{\text{abs}} \quad (15)$$

If we assume that dissolved oxygen will not react practically with Co(II) when its concentration decreases from the initial value $[O_2]_{\text{I}}$ to $[O_2]_{\text{II}}$, the length of the induction period, τ, that is, the time required to diminish the oxygen concentration down to the value $[O_2]_{\text{II}}$, may be represented by Eq. (16):

$$\tau = \frac{[O_2]_{\text{I}} - [O_2]_{\text{II}}}{\phi I_{\text{abs}}} \quad (16)$$

Thus, τ is inversely proportional to the light intensity if it is compared at the same initial concentration of dissolved oxygen.

The *cis-trans* isomerization of $CoCl_2en_2^+$ in methanol will be initiated by other suitable trigger reductants, too. In fact, chromium(II) chloride together with ethylenediamine can initiate the reaction. The quality required for a reductant is the ability to abstract an electron from $CoCl_2en_2^+$.

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17) R. K. Murmann, H. Taube and F. A. Posey, *ibid.*, **79**, 262 (1957).