so that reactions of different stereochemistry are being compared. It would appear that for Co(III) ammines expulsion of the labilized ligand occurs without being affected to any great degree by rigidity imposed by the ligands, to yield predominantly stereoretentive products, while the usual high quantum yields for Cr(III) ammines are found only if stereolability is geometrically feasible, which suggests a more concerted process.

The thermal reaction chemistry of a complex does not constitute a good guide to its photochemical behavior. The thermal chemistry does not predict antithermal reactions, of course. Further, $Co(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Cl^{2+}$ have much more similar thermal aquation rates, 1.7×10^{-6} and 7.3×10^{-6} sec^{-1}, at 25°, than photoaquation yields, even comparing only the ϕ_{Cl}^- values. Also, the 25° rate constants for chloride aquation are 3.2×10^{-5} and 2.4×10^{-5} M^{-1} sec^{-1} for trans-$Co(en)_2Cl_2^+$ and trans-$Cr(en)_2Cl_2^+$, respectively, or about the same, while the ϕ_{Cl}^- values differ by a factor of about 300. Finally, as seen in Table I, within the Co(III) acidoammine series there is no parallel between thermal aquation rate constants and quantum yields. By contrast, and curiously, such a parallel is present in the series trans-$CrLCl_2^+$, where L denotes $4NH_3$, 2 en, 2,3,2-tet, or cyclam,[33] even though the stereochemistries of the photo and thermal reactions are different in the first three cases.

It is our present feeling that while empirical photolysis rules are useful, ligand field theoretical rationalizations of such rules must be viewed with caution until radiationless deactivation rates, thexi state distortions, and detailed excited state mechanisms can be included. We

believe all of these factors to be important in Co(III) and Cr(III) photochemistry.

The effect of pH on the photolysis of $Co(NH_3)_5F^{2+}$ was studied with two possibilities in mind. Co(III) acidopentaammines are well known to undergo base-catalyzed aquation, probably through a counter-base mechanism.[29] One possibility was that the excited state responsible for aquation would have a sufficiently lower pK_a for hydroxide-catalyzed aquation to set in at lower pH's than for the thermal reaction. Alternatively, even a small degree of ground state deprotonation might produce a sufficiently photoactive species for a significant increase to occur in our low-aquation yields.

There is sufficient scatter in the values for ϕ_{NH_3} that no firm trend with pH can be claimed. The values for ϕ_F^-, however, do show a regular increase with pH, leveling off at pH 10 to about three times the value for acid solutions. Such leveling off would not occur if a ground state deprotonation were involved; pK_a of the ground state is large enough that no saturation effect is expected (or observed in the thermal base-catalyzed aquation reaction). We therefore assign the pH dependence of ϕ_F^- to an excited state acid–base equilibrium, the pK_a for which appears to be about 8 (the mid-point pH for the quantum yield change). The effective reactivity of the counter-base form of the excited state is evidently not much greater than that of the acid form, either because of little change in k_d and k_r or because of parallel changes in both rate constants.

(33) C. Kutal and A. W. Adamson, *Inorg. Chem.*, 12, 1990 (1973).

Photochemistry of Complex Ions. XIII. cis-[Co(en)$_2$Cl$_2$]$^+$ and cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$

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Abstract: The ligand field photolysis of cis-[Co(en)₂Cl₂]⁺ in acidic solution is shown to consist of chloride aquation ($\Phi = 0.0024$) to yield 70 to 75% trans-[Co(en)₂(H₂O)Cl]²⁺ and 25 to 30% cis-[Co(en)₂(H₂O)Cl]²⁺, after correction for secondary photolysis of the latter species. This species undergoes cis to trans isomerization with $\Phi = 0.0042$, while the trans isomer is photoinert. Quantum yields for other processes such as ethylenediamine aquation, second chloride aquation, or redox decomposition are entirely negligible. The photoinduced stereochemical rearrangements are antithermal in nature, and they are discussed in terms of the photolysis rules which have been used for Cr(III) complexes.

W e pursue in this paper the ligand field photochemistry of cis-[Co(en)₂Cl₂]⁺ and cis-[Co(en)₂(H₂O)Cl]²⁺ as part of a developing interest in the nonredox photochemistry of Co(III)–ammine complexes. The preceding paper[1] reports observations on the compounds [Co(NH₃)₅X]$^{n+}$ (X = NH₃, H₂O, F⁻, and Cl⁻), trans-[Co(en)₂Cl₂]⁺, and trans-[Co(cyclam)Cl₂]⁺. In general,

irradiation of the first or second ligand field (L₁ and L₂) bands caused ligand aquation, although at a low level of absolute quantum yield. Due to the choice of the nonammine ligands, and the irradiation wavelength (no charge-transfer absorption), complications due to photoinduced redox decomposition were minimal, and the photochemistry could be interpreted in terms of the photolysis rules used for Cr(III) complexes.[2]

(1) (a) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Amer. Chem. Soc.*, 96, 3027 (1974); (b) A. W. Adamson, *Proc. Int. Conf. Coord. Chem.*, *14th* (1972).

(2) A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

The kinetics and possible mechanisms of substitution reactions of Co(III) ammines have been the subject of very extensive investigations, including much emphasis on their stereochemistry.[3] Having established that Co(III) ammines do undergo characteristic excited state substitutions which may differ from the ground state (thermal) substitutions, it was natural to proceed to inquire into stereochemical aspects of the photochemistry.

As a step in this direction we chose to study the photochemistry of cis-[Co(en)$_2$Cl$_2$]$^+$, for the thermal reactions of this complex, and of its aquation products, have been thoroughly studied. Our previous experience also suggested that with chloride as the non-amine ligand, little interference from redox decomposition would occur if irradiations were restricted to a ligand field, especially the L$_1$, band. In fact, an early study reported a quantum yield for chloride aquation of 0.0033 at about 600 nm, with negligible redox decomposition;[4] some work of others has shown that at 313 nm and shorter wavelengths, redox decomposition becomes the dominant photoreaction,[4] and we have therefore avoided this wavelength region in the present work.

Experimental Section

Preparation of Compounds. cis-[Co(en)$_2$Cl$_2$]$^+$. The method of Bailar[5] was used to prepare this compound, which was then twice recrystallized from dilute hydrochloric acid solution. Its visible absorption spectrum, and extinction coefficients, agreed closely with the published values.[6]

cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$. Solutions containing this complex were prepared by warming a solution of cis-[Co(en)$_2$Cl$_2$]$^+$ in hydrochloric acid (0.2 N) to 40° for 2 hr. The aquation is stereospecific[3] so that almost pure product was obtained, and minor amounts of dichloro and diaquo products were easily separated from the chloroaquo product by ion-exchange chromatography.

trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$. Dissolution of trans-[Co(en)$_2$(OH)-Cl]Cl in hydrochloric acid (0.2 N) resulted in the immediate formation of this complex. The trans-chlorohydroxo complex was prepared after the method of Baldwin, et al.[7]

Photolyses. Photolyses were performed in much the same manner as described earlier.[1] A jacketed 10-cm polarimeter cell of 5.0-ml volume was used, and the contents were kept near 0° by circulation of an ice–water slush. After irradiation, the cell could be transferred directly to a recording spectrophotometer (Cary Model 14R). The irradiation source was a continuous wave argon laser (Coherent Radiation Model 52B), with an output at 488 nm of about 0.4 W. Absorbed light intensities were measured as previously detailed,[1] that is, by the output meter reading as calibrated by reineckate actinometry. Due to the rapid thermal reactions of these complexes, it is doubtful whether this work could have been done without such a high intensity irradiation source.

Ion-Exchange Chromatography. All solutions were passed through a cationic exchange column (10 × 2 cm, Sephadex SP-C-25 resin) just before photolysis, to ensure their purity. The columns were jacketed and prechilled with ice in order to reduce the thermal isomerization of the cis complexes to an acceptable level. Ice-cold hydrochloric acid solutions were used as eluent.

After the photolysis of cis-[Co(en)$_2$Cl$_2$]$^+$ it was necessary to separate the photoproducts from the starting material, so the photolyzed solution was placed on a prechilled column and ice-cold hydro-

chloric acid (0.1 N) was used as eluent. With such a dilute eluent, cis-[Co(en)$_2$Cl$_2$]$^+$ moved down the column, while both the cis- and trans-chloroaquo ions, being dipositive, remained at the top. The top layer of resin was then physically removed and extracted with ice-cold 1.0 N hydrochloric acid. This quickly desorbed any dipositive ions present, and the visible spectrum of the resulting solution was then recorded with minimum delay.

Product Analysis. All analyses were made spectrophotometrically; the various complexes are sufficiently labile that any attempt to apply conventional analytical methods to the estimation of released ligand would have been subject to serious error. Cobalt(II) could be analyzed, however, by a method due to Kitson.[8]

Spectrophotometric analysis was easy in the case of irradiated cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ solutions, since trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ was the only detectable photoproduct. Irradiation of cis-[Co(en)$_2$Cl$_2$]$^+$ solutions, however, led to both chloroaquo isomers, so that in general we dealt with three component systems. Analysis was simplified algebraically by observing absorbance changes at one or another isosbestic point. Such restriction to a few selected wavelengths wastes the rest of the data, however, and we offer the following graphical procedure as both a convenient and informative one.

We consider the case of a mixture of species with a total concentration of C_0, so that for the three components, A, B, and C

$$F_C = 1 - F_A - F_B \qquad (1)$$

where F denotes concentration expressed as a fraction of C_0. Since

$$D_0 = F_A D_A + F_B D_B + F_C D_C \qquad (2)$$

where D_0 is the observed optical density, and the D's with letter subscripts represent the optical densities for the indicated component at concentration C_0. Combination of eq 1 and 2 gives

$$F_A = \frac{(D_0 - D_C)}{(D_A - D_C)} - F_B \frac{(D_B - D_C)}{(D_A - D_C)} \qquad (3)$$

Thus, at each wavelength chosen, insertion of the D values in eq 3 gives a particular linear relationship between F_A and F_B. A plot of F_A vs. F_B (on scales limited to range between 0 and 1) is thus the locus of all possible values consistent with the data at that wavelength. A set of plots for various wavelengths must show a common intersection at the actual solution composition if the data are accurate. Note that while it is necessary to know the spectrum of each of the components, this technique does not require the assumption that B and C (if products) be present in some constant ratio.

It is convenient to make the above plots on triangular graph paper (see Figure 5); each wavelength used still generates a straight line, and the common crossing point of the set of lines can be read to give all three F values directly. We find plots of this kind to be instructive in several ways. There is generally a zone rather than a point of crossing, the extent of which is indicative of experimental error. One immediately sees which wavelengths give lines with large angles of crossing and hence the best defined crossing points. Isosbestic wavelengths appear as lines of constant B/C ratio and hence passing through the A apex.

In the case of only two components, B and C, eq 1 and 2 reduce to

$$(D_0 - D_B)/(D_C - D_B) = F_C \qquad (4)$$

so that a graph of D_0 vs. F_C is a set of points which lie on a straight line, and a different line is generated for each wavelength chosen. After several such lines have been plotted, the ith point on each line should correspond to the same F_C value. (This method of spectral analysis is illustrated in Figure 2.)

Quantum Yields. Two different algebraic methods were used to determine the quantum yields. (a) In the case of cis-[Co(en)$_2$Cl$_2$]$^+$, photolyses were kept to less than 10% total reaction in order to reduce interference from secondary photolysis. Equation 5 was

$$\Phi = \frac{v}{I_0't} \left[(C_A^0 - C_A) + \frac{1}{2.3\epsilon_A l} \ln \frac{(1 - e^{-2.3\epsilon_A l C_A^0})}{(1 - e^{-2.3\epsilon_A l C_A})} \right] \qquad (5)$$

then used to calculate the absolute quantum yield[4] where v is the cell volume, I_0' the incident light intensity, ϵ_A the extinction coefficient at the irradiating wavelength, l the path length, and t the

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(4) See (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1971; (b) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, Chem. Rev., 68, 541 (1968).

(5) J. C. Bailar, Inorg. Syn., 2, 222 (1946).

(6) F. Basolo, C. J. Ballhausen, and J. Bjerrum, Acta Chem. Scand., 9, 810 (1955).

(7) M. E. Baldwin, S. C. Chan, and M. L. Tobe, J. Chem. Soc., 4637 (1961).
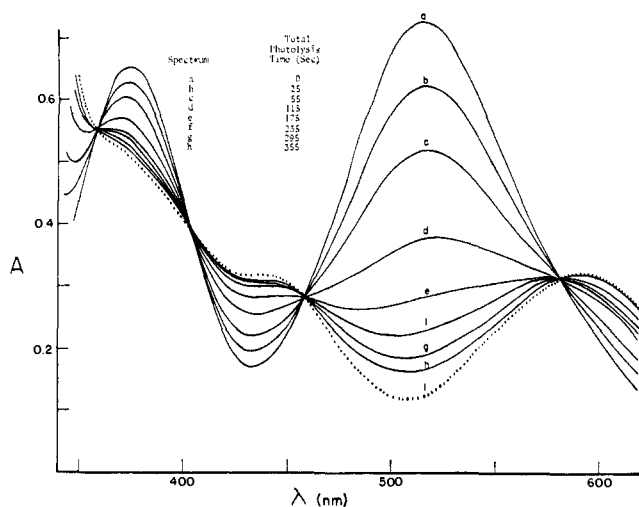
(8) R. E. Kitson, Anal. Chem., 22, 664 (1950).

Figure 1. Sequence of absorption spectra on 488-nm irradiation of cis-[Co(en)₂(H₂O)Cl]²⁺ in 0.2 N HCl at 0-1° (10-cm cell): (a) initial solution; (b-h) successive irradiations; (i) pure trans-[Co(en)₂(H₂O)Cl]²⁺.

photolysis time. This analysis assumed that cis-[Co(en)₂Cl₂]⁺ was the only absorbing species throughout the short photolysis period and that light absorption by photoproducts (and hence secondary photolysis) was negligible.

(b) The photolysis of cis-[Co(en)₂(H₂O)Cl]²⁺ (B) presented an unusual situation, for only one photoproduct formed (trans-[Co(en)₂(H₂O)Cl]²⁺ (C)) which is photoinert. In such a system, a more complete analysis of the spectra is possible, for the expression

$$-\frac{dC_B}{dt} = \Phi_B I_a \frac{\epsilon_B C_B}{\epsilon_B C_B + \epsilon_C C_C} \tag{6}$$

should hold throughout the photolysis. Since B and C are the only components ($C_0 = C_B + C_C$), then

$$-\frac{dC_B}{dt} = \Phi_B I_a \frac{\epsilon_B C_B}{C_B(\epsilon_B - \epsilon_C) + \epsilon_C C_0} \tag{7}$$

Integration of (7) leads to

$$(\epsilon_B - \epsilon_C)(C_B - C_0) + \epsilon_C C_0 \ln (C_B/C_0) = -\epsilon_B \Phi I_a t \tag{8}$$

The absorbed flux (I_a) is determined by the expression

$$I_a = I_0'(1 - 10^{-D_t})/V \tag{9}$$

where I_0' is the incident light intensity, and D_t is the total optical density at the irradiating wavelength. Substitution of (9) into (8) gives

$$(\epsilon_B - \epsilon_C)(C_B - C_0) + \epsilon_C C_0 \ln (C_B/C_0) =$$
$$\frac{(\epsilon_B \Phi_B I_0')}{V}(1 - 10^{-D_t})t \tag{10}$$

During a given photolysis period, the fraction of light absorbed ($1 - 10^{-D_t}$) varies in a nonlinear manner, but it was necessary to estimate an average value for this term. As a convenient, and reasonably accurate estimate, we took the arithmetic average between the initial and final value of $(1 - 10^{-D_t})$ during a photolysis period; no significant error is introduced if the per cent reaction is not large during this period.

Thus, after a photolysis period, C_B can be determined by graphical analysis (Figure 2), and the term on the left of eq 10 can be graphed as a function of $(1 - 10^{-D_t})(t)$. This generates a set of points, and if eq 6 is obeyed, these points will lie on a straight line which passes through the origin. The slope of this line is related to the absolute quantum yield by the expression

$$\text{slope} = -\epsilon_B \Phi_B I_0'/V \tag{11}$$

(The use of this more complete method is illustrated in Figure 3.)

Effect of Secondary Photolysis. It became apparent that sec-

ondary photolysis was a likely complication in the case of cis-[Co(en)₂Cl₂]⁺. Our somewhat special case is that of a reactant A going to some mixture of absorbing species B and C, with B also photoreactive to give C; while C absorbs, it is photoinert. Under

$$A \xrightarrow{h\nu} (x)B + (y)C$$

$$B \xrightarrow{h\nu} C$$
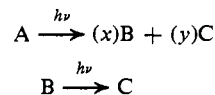
such conditions a straightforward interval calculation was sufficient to estimate the degree of secondary photolysis. Let ϕ_A be the quantum yield whereby A reacts, with ϕ_{AB} and ϕ_{AC} being the partial yields to give B and C, respectively. We can then write

$$-\frac{dC_A}{dt} = \Phi_A I_a \frac{\epsilon_A C_A}{D_t} \tag{12}$$

where the symbols have their usual meanings. For the formation of B and C we can write

$$\frac{dC_B}{dt} = \phi_{AB} I_a \frac{\epsilon_A C_A}{D_t} \tag{13}$$

and

$$\frac{dC_C}{dt} = \Phi_{AC} I_a \frac{\epsilon_A C_A}{D_t} \tag{14}$$

In the case of cis-[Co(en)₂Cl₂]⁺ (A), secondary photolysis of photoproduct cis-[Co(en)₂(H₂O)Cl]²⁺ (B) produced trans-[Co(en)₂(H₂O)Cl]²⁺ (C). For a given assumed ratio ϕ_{AC}/ϕ_{AB} it was sufficient to take intervals of about 1/12th of the total irradiation time, or of about 5 sec, and to first calculate the change in C_A over the first interval by means of eq 12. For this first step, secondary photolysis is ignored.

To account for secondary photolysis, an average value of C_B throughout the initial photolysis period must be estimated; the arithmetic average between the initial and final values (as determined by eq 13) was used and is a good approximation during a short photolysis period. The change in concentration of B and C due to secondary photolysis can then be calculated by eq 15

$$\frac{dC_C}{dt} = -\frac{dC_B}{dt} = \phi_B I_a \frac{\epsilon_B C_B}{D_t} \tag{15}$$

These values were then added to (or subtracted from) the values of C_B and C_C calculated during the primary photolysis (eq 13 and 14).

By successive iterations of this procedure (eq 12-14 followed by eq 15), the concentrations of A, B, and C can then be estimated after any given amount of photolysis. The entire procedure was repeated for several values of ϕ_{AC}/ϕ_{AB}, and the ratio for which the results best agreed with experiment was taken to be the true one for the primary photolysis step. We were fortunate, for we not only knew the necessary extinction coefficients for the irradiation wavelength of 488 nm, but we also knew ϕ_B from separate experiments. The assumption that C is photoinert is retained throughout this analysis.

Results

cis-[Co(en)₂(H₂O)Cl]²⁺. Figure 1 shows a typical sequence of the changes that occur upon 488-nm irradiation of a 1 × 10⁻³ M solution of cis-[Co(en)₂(H₂O)Cl]²⁺ in 0.2 N hydrochloric acid and at 0-1°. The clean isosbestic points at 460 and 585 nm are those expected for trans-[Co(en)₂(H₂O)Cl]²⁺ being the only product. Further, as shown in Figure 2, eq 4 was obeyed for wavelengths ranging from 380 to 610 nm; the calculated cis-trans composition varied little with the choice of wavelength used in the analysis for irradiations producing up to 90% conversion to the trans isomer.

The photolysis kinetics obeyed eq 6 with $\phi_B = 0.0042$ (Figure 3). The quantum yield for trans to cis isomerization could not have been more than $0.2\phi_B$, nor could any appreciable photoaquation of chloride
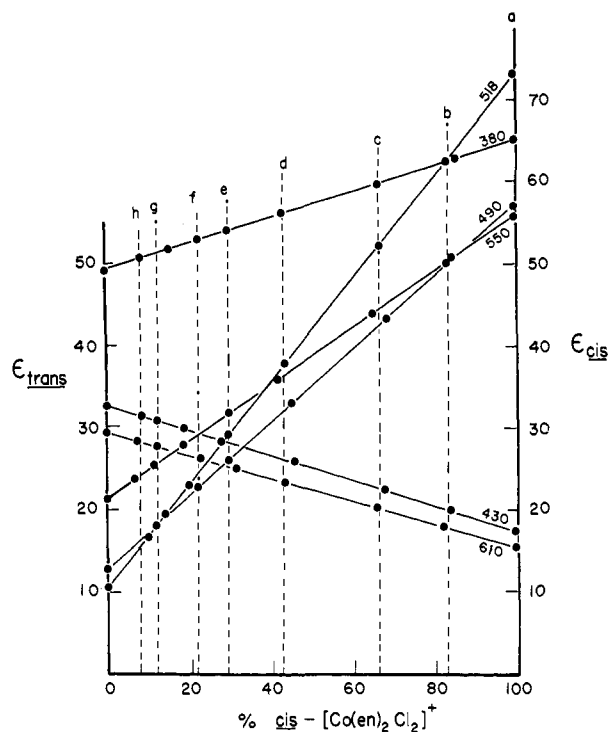
Figure 2. Analysis of the spectra in Figure 1. The solid diagonal lines connect the extinction coefficients of pure cis-[Co(en)$_2$Cl$_2$]$^+$ (on the right) with the extinction coefficients of pure $trans$-[Co(en)$_2$-(H$_2$O)Cl]$^{2+}$ (on the left); the wavelength (in nm) for each line is given near the right axis. After each photolysis period, the observed optical density (apparent extinction coefficient) at these wavelengths is plotted along the appropriate line. The dotted vertical lines then give the isomer composition after each photolysis period.
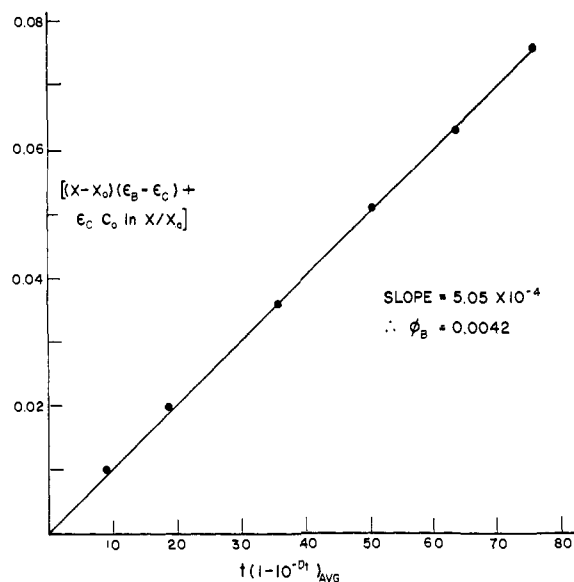

Figure 3. Determination of the absolute quantum yield for photolysis of cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ by a graphical method (eq 10 and 11).
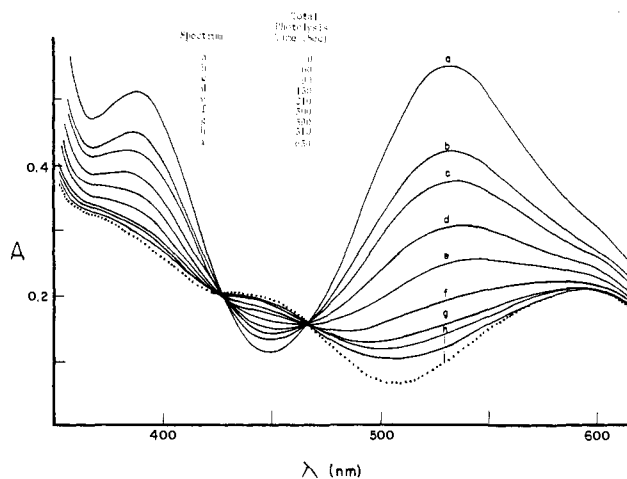

Figure 4. Sequence of absorption spectra on 488-mn irradiation of cis-[Co(en)$_2$Cl$_2$]$^+$ in 0.2 N HCl at 0–1° (10-cm cell): (a) initial solution; (b–i) successive irradiations; (j) pure $trans$-[Co(en)$_2$-(H$_2$O)Cl]$^{2+}$.

or of ethylenediamine have occurred for either isomer. Any of these last processes would have led to spectral changes not obeying eq 4 and 6. Based on the known spectrum of cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$, for example, the quantum yield for chloride aquation was less than 5 × 10^{-4}. About the same upper limit can similarly be assigned to ethylenediamine aquation.

It is known from thermal studies that the equilibrium isomer composition (at 25°) for the chloroaquo complex is 73% cis and that the isomerization equilibrium is rapid compared to chloride aquation (no ethylenediamine aquation is known to occur).[6] We observed that a solution of cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$, photolyzed to 90% conversion to the trans form, returned on standing in the dark (at room temperature) to a mixture whose absorption spectrum was undistinguishable from that of an unphotolyzed solution allowed to equilibrate for the same period of time (<0.5% difference in optical density over the visible region). This observation confirms that negligible ethylenediamine photoaquation occurred; such a process would have been irreversible in our acidic media, and an accumulation of the corresponding photoproducts would have been apparent. Finally, no detectable Co(II) was photoproduced. From the limits of the detection method the quantum yield for photoredox decomposition is less than 1 × 10^{-6}.

In summary, we find the photochemistry of cis-[Co-(en)$_2$(H$_2$O)Cl]$^{2+}$ to be clearly one of isomerization only and that $trans$-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ is quite photoinert. Much longer irradiations than those described above

do lead eventually to further special changes; their source was not investigated.

cis-[Co(en)$_2$Cl$_2$]$^+$. Figure 4 shows a typical sequence of the changes that occur on 488-nm irradiation of a 1 × 10^{-3} M solution of cis-[Co(en)$_2$Cl$_2$]$^+$ in 0.2 N hydrochloric acid at 0–1°. This sequence, including the positions of the isosbestic points, indicates that the principal product is $trans$-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$. Small deviations from eq 4 (written for species A and C) are present, however, and the triangular graphical method of analysis, shown in Figure 5, confirmed that up to about 10% cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ was present in the photoproducts and that about 75% $trans$- and 25% cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ were produced. There was no detectable Co(II) formation, the quantum yield for redox decomposition being less than 1 × 10^{-6}. Again, a solution photolyzed to 85% reaction and then allowed to equilibrate at 25° in the dark gave an absorption spectrum indistinguishable from that of a similarly
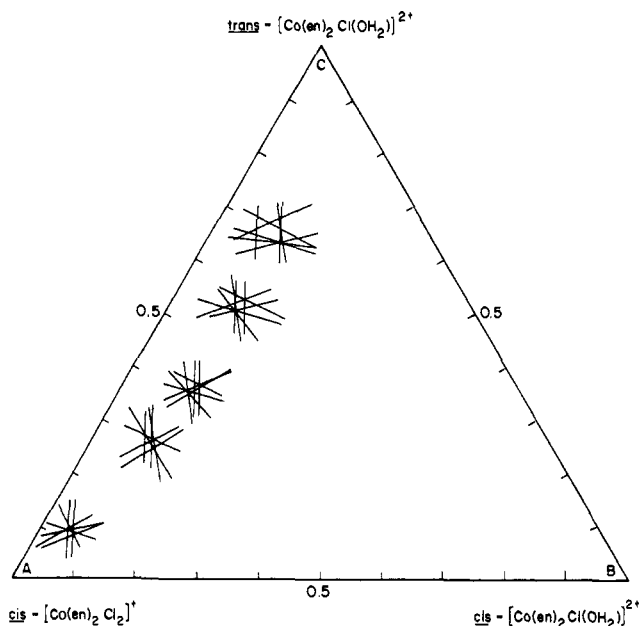
Figure 5. Composition analyses for the sequence of Figure 4.

equilibrated unphotolyzed solution. In both cases the final mixture was the equilibrium one of 73% cis- and 27% trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$. Thus, negligible photoaquation of ethylenediamine occurs ($\phi < 5 \times 10^{-4}$).

No appreciable photoisomerization to trans-[Co(en)$_2$Cl$_2$]$^+$ occurred, as another possibility. The presence of this species would not have been evident from the absorption spectra of photolyzed solutions because of the similarity to the absorption spectrum of trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$. However, trans-[Co(en)$_2$Cl$_2$]$^+$ is thermally stable at 0°[3] and is much less photosensitive than the cis isomer,[1] so that, if formed, it would constitute an essentially stable photoproduct. Experiments were accordingly made in which photolyzed solutions were treated chromatographically to separate di- from monocharged species. As little as 1% of the trans isomer could be detected spectrally in the fraction containing 2+ charged species; separate experiments also established that no trans to cis isomerization or chloride aquation of the trans form was catalyzed by the ion exchanger. No trans-[Co(en)$_2$Cl$_2$]$^+$ could be detected in solutions of cis-[Co(en)$_2$Cl$_2$]$^+$ irradiated to 80% reaction and we place the yield for cis to trans photoisomerization of the dichloro complex as less than 5×10^{-5}.

The above experiments established that the principal photoreaction of cis-[Co(en)$_2$Cl$_2$]$^+$ is one of chloride aquation and that the produced isomer is largely the trans-chloroaquo ion. We wished, of course, to establish the actual isomer composition as closely as possible. First, cis- and trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ have the same extinction coefficients as 580 nm, so that the optical density at this wavelength of irradiated solutions gives the total amount of chloroaquo species produced. Such analyses on solutions photolyzed to about 5% reaction gave $\phi_A = 0.0024$. Further, cis-[Co(en)$_2$Cl$_2$]$^+$ and cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ have the same extinction coefficient at 500 nm, so that the optical density at this wavelength of irradiated solutions gives the amount of trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ present. The corresponding quantum yield, ϕ_{AC} was thus found to be 0.0016. The

analysis therefore indicates that photoaquation of cis-[Co(en)$_2$Cl$_2$]$^+$ gives 67% trans- and 33% cis-chloroaquo species.

The above procedures are relatively inaccurate because of the large background absorption due to unphotolyzed starting material. We wished, of course, to minimize the importance of secondary photolysis (of cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ to trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$) and were therefore restricted to small degrees of photolysis. As an alternative approach, several irradiations were made to about 10% reaction, and the chloroaquo products were separated by chromatography so as to obtain a more accurate analysis of their isomer composition than possible from spectral analyses of the unseparated mixture. The results of three such experiments gave 73, 70, and 69% trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ (the rest being the cis isomer). These are minimum values since it was found that even at 0° the ion exchanger catalyzed aquation of cis-[Co(en)$_2$Cl$_2$]$^+$ (to the cis-chloroaquo complex); the degree of such catalysis amounted to a per cent or two of reaction and varied somewhat from one test run to another. We conclude that for small degrees of photolysis the chloroaquo product is 70 to 75% trans.

The above results indicated that secondary photolysis was not highly important (the fraction of cis-chloroaquo complex formed did not rise noticeably with short photolysis times). A direct calculation of the effect was made, however, using the experimental ϕ_A and ϕ_B values and the known extinction coefficients, as outlined under the Experimental Section. For the case of about 10% total photolysis, if ϕ_{AC}/ϕ_A were zero, secondary photolysis would have given 15% trans isomer in the chloroaquo product. If ϕ_{AC}/ϕ_A were 0.5, the observed per cent of trans-chloroaquo isomer would have been 57%; and if ϕ_{AC}/ϕ_A were 0.65, 71% trans isomer would be expected. Secondary photolysis thus increased the per cent of trans isomer by about 5%. On applying this correction, we estimate the primary photolysis reaction to give 65-70% trans- and 35-30% cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$.

A remaining possibility is that photolytically produced traces of Co(II) were catalyzing the aquation. Such catalysis of [Co(en)$_3$]$^{3+}$ racemization has been reported,[9] presumably through a charge-transfer mechanism involving Co(II)-ethylenediamine complexes. We rule out such a mechanism in our system because of the very low levels of Co(II) and of free ethylenediamine present and because reaction stopped immediately on stopping an irradiation (except for slower, normal thermal reactions). Nor, of course, could catalysis produce the nonequilibrium mixtures observed.

Discussion

The results may be examined from several points of view. First, Figure 6 summarizes the pattern of thermal and photochemical reactions present. The latter are clearly stereospecific in different ways than are the former. Thus, cis-[Co(en)$_2$Cl$_2$]$^+$ gives only cis-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ on thermal aquation but mainly trans-[Co(en)$_2$(H$_2$O)Cl]$^{2+}$ on photolysis. The efficiency, that is, the quantum yield, for the cis to trans conversion of [Co(en)$_2$(H$_2$O)Cl]$^{2+}$ is at least five times that

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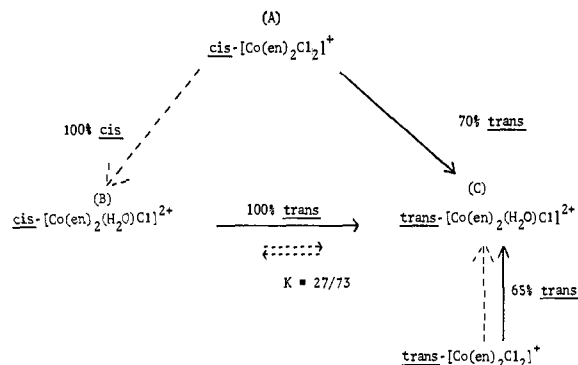
Figure 6. Reactions of $[Co(en)_2Cl_2]^+$ and $[Co(en)_2(H_2O)Cl]^{2+}$: (- - -) thermal, (—) photochemical.

Figure 7. A simple application of photolysis rules to $[Co(en)_2Cl_2]^+$ and $[Co(en)_2(H_2O)Cl]^{2+}$.

for the reverse process, while for the thermal isomerization the forward rate constant is only one third of the reverse one ($K = 27/73$). The general picture is one of specific excited state chemistries rather than one of photocatalyses of the usual thermal reactions.

Our quantum yield for chloride aquation of cis-$[Co(en)_2Cl_2]^+$, 0.0024, may be compared with an early value of 0.0033 at about 600 nm[10] and at a pH of ca. 5 (that of the complex in water). A more detailed study would be needed to determine if, indeed, there is a wavelength or pH dependence of this yield.

The photochemistry may be compared to that of other Co(III) complexes. The quantum yields for our systems are somewhat higher than those found for the Co(III) ammines of ref 1. Unlike the case with the $[Co(NH_3)_5X]^{n+}$ series, no ammine aquation occurs, although detachment, in our systems, of one end of an ethylenediamine would not have been detected if recoordination were even moderately rapid. The photochemistry of cis-$[Co(en)_2Cl_2]^+$ is similar to that of the trans isomer; both photolyze mainly to trans-$[Co(en)_2-(H_2O)Cl]^{2+}$. In fact, the ratio of the quantum yields, 0.0024:0.0005 = 4.8, is not very different from the ratio of the thermal aquation constants, 7.5 (from ref 3). Of course, the stereochemistries of the photoinduced and thermally induced aquation of cis-$[Co(en)_2Cl_2]^+$ differ, so the meaning of such a comparison is more than normally obscure. Our maximum quantum yield for redox decomposition, 1×10^{-6}, is smaller than that reported for trans-$[Co(en)_2Cl_2]^+$, 2×10^{-4}, although Co(II) was not a significant photoproduct in either system.

As another approach, it was noted[1] that the photolysis rules for Cr(III) ammines were obeyed for various Co(III) ammines, although less stringently. These rules predict, for the present systems, labilization of that end of an ethylenediamine lying on the weakest ligand field axis and are predictive of our results if it is assumed that recoordination to an adjacent octahedral position occurs rather than complete dissociation. The sequences shown in Figure 7 are based on the assumption[1] that the thermally equilibrated excited (or thexi) state of Co(III) ammines react by means of a stereoretentive expulsion of the labilized ligand (or point of attachment of a chelate ligand), followed by aquation at the vacated position. In determining which axis is involved, we note that chloride is of lower ligand field strength than water.[11]
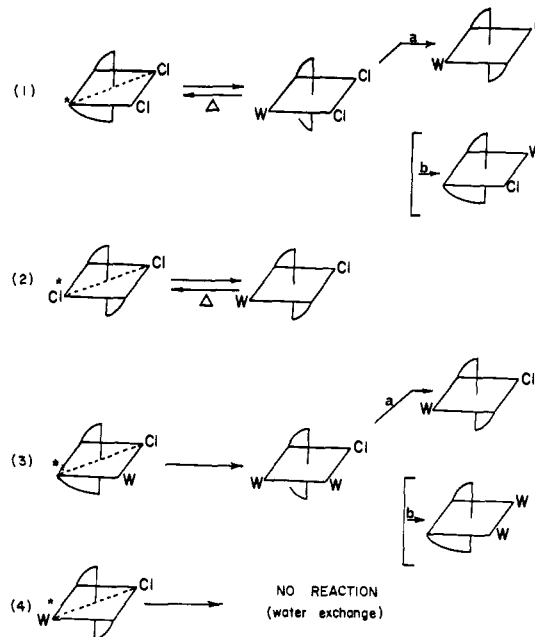
In the sequences, the labilized axis is shown as a dashed line and the labilized position is starred. Thus, in reaction sequence 1 a nitrogen trans to chloride is detached, the position is then either subsequently or in a concerted fashion occupied by water. Recoordination of the ethylenediamine to the position cis to its original one gives trans-$[Co(en)_2(H_2O)Cl]^{2+}$ (reaction 1a). The minor yield of cis product is assigned as either due to recoordination at the position trans to the original one or due to incomplete discrimination on the weak field axis (direct chloride aquation). This latter explanation is necessary to account for the 3:1 ratio of ammonia to chloride aquation in $[Co(NH_3)_5Cl]^{2+}$.[1] Reaction 2 correctly predicts that trans-$[Co(en)_2(H_2O)Cl]^{2+}$ is the major product upon photolysis of trans-$[Co(en)_2Cl_2]^+$, and reaction 4 correctly predicts photoinertness for trans-$[Co(en)_2(H_2O)Cl]^{2+}$, except for water exchange. Reaction 3 accounts for the observed isomerization of cis-$[Co(en)_2(H_2O)Cl]^{2+}$ (reaction 3a); the lack of an observed diaquo product indicates that direct chloride release (reaction 3b) is not a significant photoprocess.

While the above scheme is reasonably predictive, there is question as to its chemical plausibility. Specifically, if detachment of one end of an ethylenediamine occurs, should not protonation in our acid media stabilize the product so that species such as $[Co(en)-(enH)(H_2O)_2Cl]^{3+}$ should have been present as final products? We find this point difficult to assess. Two groups of investigators[12,13] have invoked a monodentate ethylenediamine intermediate in the base-catalyzed aquation of bis(ethylenediamine) complexes of Co(III). In their cases, it was postulated that the position trans to an hydroxyo group was labilized; in ours, of course, we taken the labilization to be an attribute of the excited state. The same type of mechanism, treated as concerted, was used to explain the stereospecific

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aquation of trans-[Co(trien)Cl₂]⁺.[14] On the other hand, in a rather complex study, the reaction of trans-[Co(en)₂Cl₂]⁺ with ethylenediamine in methanol has been deduced to give the species cis-[Co(en)₂(enH)Cl]³⁺, and it was concluded that this species was stable in aqueous solution.[15] We feel, however, that the chemical question is not yet fully resolved.

It is, of course, a possibility that ligand detachment at the point of labilization is followed by rearrangement to an intermediate of trigonal bipyramidal geometry rather than by prompt, stereoretentive coordination of solvent. Subsequent reactions of this intermediate would then give the observed products. We are not able at present to distinguish between these two types of possibilities but prefer the scheme of Figure 6 as being simpler and, so far, adequately predictive. Further, the five-coordinated intermediate seems to be preferred by kineticists,[3] and, if the same were involved for the photochemical reactions, it becomes awkward to explain their different stereochemistries.

Finally, some attempts have been made recently to rationalize the photochemistry of Cr(III) and Co(III) ammines in terms of σ and π bonding changes predicted by simple ligand field theory.[16,17] Zink would, for example, predict (correctly) that chloride aquation would occur on photolysis of cis-[Co(en)₂Cl₂]⁺, due to the breaking of the weakest Co-ligand bond, although the contrast to the predominant photoinduced ammonia aquation in [Co(NH₃)₅Cl]²⁺ requires some additional explanation. Also, his treatment does not make stereochemical predictions. The ligand field analysis of bonding differences between the ground and the excited states of [Co(en)₂(H₂O)Cl]²⁺ becomes yet more complicated since the three pseudooctahedral axes are all different. It would now be necessary to decide that the Co-water bond is the weakest, but it is not clear now to proceed to predict that the cis isomer would be much more photosensitive toward isomerization than the trans one.

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Laser-Excited Raman Spectroscopy of Biomolecules. V. Conformational Changes Associated with the Chemical Denaturation of Lysozyme

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Abstract: When lysozyme is chemically denatured by reductive cleavage of the S-S bonds with subsequent cyanoethylation of the sulfhydryl groups, its Raman spectrum is drastically changed. The amide III frequency decreases to 1243 cm⁻¹ from 1260 in aqueous solution of the native enzyme and intensifies considerably, while the amide I increases to 1672 cm⁻¹ from 1660 with sharpening. These changes are to be expected if the protein assumes a random-coil conformation. Similar changes are found when the native enzyme is denatured by 6 M LiBr or precipitated from a mixture of 1% SDS-7% lysozyme, but the S-S bonds remain intact though distorted. However, at SDS concentrations of 7% or higher, lysozyme is soluble with little apparent conformational change.

The denaturation of aqueous lysozyme by thermal means has been studied in several investigations by optical rotatory dispersion,[1] pmr spectroscopy,[2,3] and the Raman effect.[4,5] It is of interest to examine the effects of other denaturing agents on this enzyme, both to determine their structural effects as compared with thermal denaturation and also try to learn something about the changes in the spectra of various important constituents of the molecule when their intramolecular environments alter. Since chemical denaturation can be carried out with a variety of agents, some measure of control over the conformational changes can be exerted and the spectroscopic changes produced thereby can be interpreted more precisely.

In this paper the effects on the Raman spectrum of aqueous lysozyme produced by lithium bromide (LiBr), by sodium dodecyl sulfate (SDS), and by S-S bond reduction and subsequent blocking of the resultant sulfhydryl groups by S-cyanoethylation are reported. Some of the these results have been published in preliminary form.[6,7]

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