

SOLID PHASE PHOTOINITIATED LIGAND EXCHANGE REACTIONS IN CHROMIUM(III) COMPLEXES

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Summary

It is shown that the photolysis of glassy frozen solutions of $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ and $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ in 5 M and 10 M NaOH, 5 M and 10 M LiCl and 95% ethanol involves photochemical ligand exchange reactions. In the cases investigated, which included aqueous alkali and aqueous salt matrices, the substituting ligands were chloride and hydroxyl ions. No photoaquation was observed. The direction of the solid phase photochemical reactions was the same as that in the liquid solutions. The initial quantum yield is not dependent on temperature, increases with the concentration of the substituting ligand and is of the order of 10^{-2} . The quantum yield in the long wave d-d absorption band is generally higher than that in the short wave band. In the discussion of the results it is assumed that the photoinitiated ligand exchange reaction takes place in ion pairs or in more complex ion associates composed of the substituting ligand and the complex ion in the ground state. The reaction kinetics are controlled by the distribution of reactivities (quantum yields) of the complex molecules which is due to the different structures of their environments. The dissipation of absorbed photon energy in the matrix may result in restructuring of the immediate environment of the complex molecule and a change in its reactivity. A model based on these experimental observations is proposed to explain the reaction kinetics.

1. Introduction

Photochemical conversions of chromium(III) complexes in liquid solutions are attracting much attention at present [1, 2]. In solution these complexes are generally involved in photoinitiated ligand exchange reactions. Reduction-oxidation reactions are not characteristic of chromium(III) complexes. The photochemical behaviour of solid samples of chromium(III) has not been studied systematically [3]. None the less, such an investigation would be of interest as regards both the ligand exchange mechanism and the features specific to solid phase photochemical reactions.

At present all that is known about photoinitiated ligand exchange reactions in chromium(III) complexes is the general observation that they can take place in both the crystalline state and glassy solutions [3 - 8]. For example, pulsed irradiation of $[\text{Cr}(\text{en})_3]\text{X}_3$ crystals ($\text{X} \equiv \text{Cl}^-$, Br^- , NCS^- ; $\text{en} \equiv \text{CH}_2(\text{NH}_2)\text{CH}_2(\text{NH}_2)$) using a xenon lamp produces a photochemical reaction involving the formation of *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$, *cis*- $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ or *trans*- $[\text{Cr}(\text{en})_2(\text{NCS})_2](\text{NCS})$ [8]. The luminescence spectra obtained by irradiating $\text{Cr}(\text{NH}_3)_6\text{ZnCl}_4\text{X}$ ($\text{X} \equiv \text{NO}_3^-$, Cl^-) and $[\text{Cr}(\text{NH}_3)_6]\text{X}_3$ ($\text{X} \equiv \text{NO}_3^-$, Cl^- , Br^- , I^-) crystals showed that the reaction products were the pentaammines $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$ [7]. This reaction takes place at both room temperature (300 K) and low temperatures (80 K).

The temperature dependence of the quantum yield of ligand exchange reactions in $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ solutions was studied by Adamson [9] who measured the quantum yield of the release of free thiocyanate ions in glassy samples at low temperatures. The apparent activation energy of the reaction varied from 2.3 to 0.55 kcal mol⁻¹ as the solution changed from the liquid to the glassy state.

In this paper we report a more detailed and comprehensive study of the photoinitiated ligand exchange reaction in a solid glass-like matrix. The direction and effectiveness of the reaction, the effects of the photon energy, the temperature and the matrix composition, and the reaction kinetics were investigated.

2. Experimental details

Chromium(III) complexes were prepared by standard methods. The purity of the compounds was controlled using optical absorption spectra which agreed satisfactorily with published data.

The solvents used were aqueous solutions of LiCl and NaOH and 95% ethanol, all of which transformed to transparent glassy materials when they were cooled to liquid nitrogen temperature. The solutions of the complex compounds were prepared immediately prior to use. The concentration of the complex in solution was usually 0.01 - 0.05 mol l⁻¹. The solutions were contained in quartz ampoules of diameter 3 mm which were immersed in liquid nitrogen. The uniformity of the molecular distribution in the frozen solutions was checked by the absence of the dipole-dipole broadening effect in electron spin resonance (ESR) spectra.

When the solutions were cooled to 77 K the optical absorption spectra of the complexes shifted towards shorter wavelengths and the extinction coefficients in the absorption band maxima decreased (Fig. 1). These effects were taken into account in the calculations of the quantum yields of the reactions.

The following light sources were used in this series of experiments: (1) a DRSh-500 high pressure mercury lamp in which the light of the required wavelength was isolated using standard glass filters (the intensity was about 5×10^{-7} einsteins s⁻¹); (2) a DKCSh-1000 xenon lamp with a grating mono-

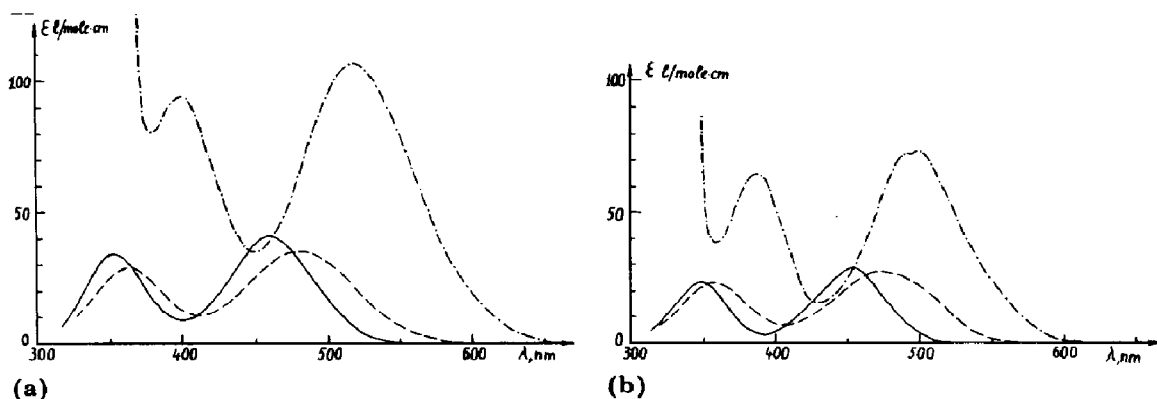


Fig. 1. Optical absorption spectra of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 10 M NaOH (—), $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ in 5 M LiCl (---) and $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ in 95% ethanol (-·-): (a) in liquid solutions (293 K); (b) in the solid phase (77 K).

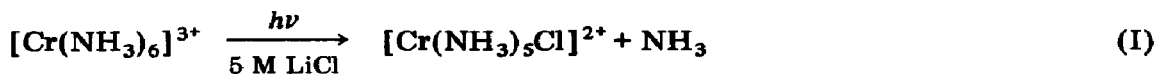
chromator (the monochromaticity of the light was about 4 nm). The photolysis at liquid nitrogen temperature (77 K) was carried out in a quartz Dewar vessel with a cylindrical beak or in a special-purpose cryostat where the sample was contained in a transparent quartz Dewar tube. Cold nitrogen vapour was blown through the tube to maintain the temperature at 77 K. The temperature was measured using a copper-constantan thermocouple with its working junction located adjacent to the sample. The sample temperature could be varied from 77 to 250 K with an accuracy to ± 2 K.

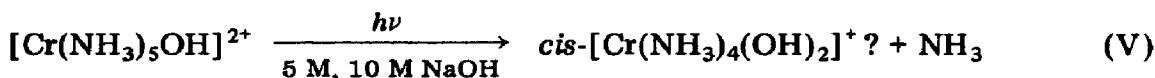
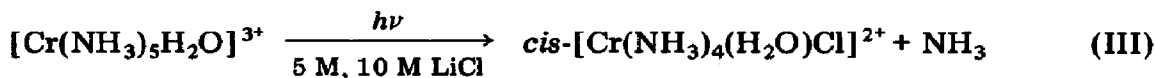
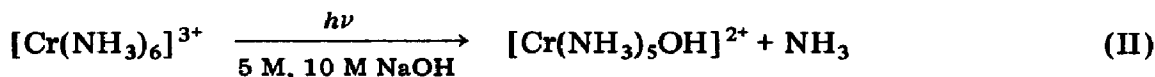
The intensity of the incident light was determined by ferrioxalate actinometry [10] (for light of wavelength about 365 nm) and by Reinckate salt actinometry [11] (for light of wavelengths 436 and 546 nm). The measurements at room temperature were carried out in the working ampoule with the Dewar vessel in the same position as during the photolysis. Preliminary experiments showed that light focusing by the liquid nitrogen was negligible.

The processes in the glassy samples were monitored by low temperature spectrophotometry and ESR spectroscopy. The optical absorption spectra were recorded at 77 K using a Unicam SP-8000 spectrophotometer. The samples were contained in the same ampoules as were used for the photolysis and were enclosed in a special cryostat [12] in which the sample temperature was maintained to within 2 K of liquid nitrogen temperature. The relative and absolute accuracies of measurement of the optical densities of samples at 77 K were 2% and 5% respectively. The ESR spectra were recorded using a Varian E-3 spectrometer.

3. Results

The following reactions were initiated by photolysis of chromium(III) complexes in glassy matrices at low temperatures:

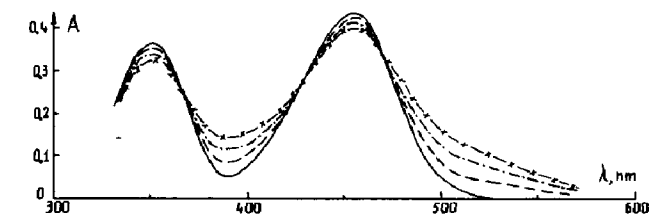




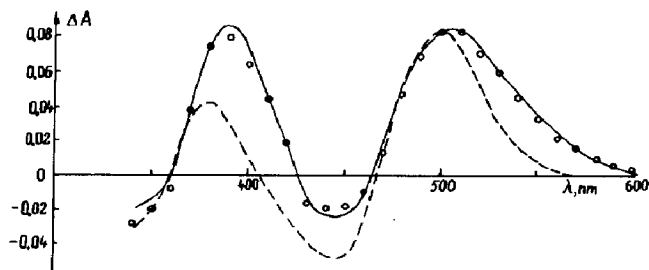
The photolysis was carried out in the d-d absorption bands of the complex compounds.

The product of reaction (I) was insoluble in aqueous 5 M LiCl and precipitated when the samples were melted. The reaction product was identified by the optical absorption spectrum of its aqueous solution after separation from the reaction mixture.

The products of reactions (II) and (III) were identified by simulating the differential optical absorption spectra from the optical absorption spectra of the starting compounds and of the predicted products and comparing them with the experimental data. Such simulated spectra for reaction (II) are shown in Fig. 2. The model and experimental spectra are in satisfactory



(a)



(b)

Fig. 2. Optical absorption spectra of $[\text{Cr}(\text{NH}_3)_5]^{3+}$ in 10 M NaOH photolysed at 436 nm ($T = 77 \text{ K}$): (a) measured during the photolysis (—, 0 min; ---, 15 min; -·-, 45 min; -x-, 90 min); (b) the differential spectra (○, 45 min after photolysis; —, simulated from the spectra of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$; ---, simulated from the spectra of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$).

agreement provided that the reaction product is hydroxopentamminechromium. The simulated differential optical absorption spectra calculated for reaction (III) are in satisfactory agreement with the experimental spectra only for small degrees of conversion by the secondary photochemical reaction.

We did not identify the products of reactions (IV) and (V). The amount of thiocyanate ion formed in reaction (IV) was determined as described in ref. 11 by adding a reagent containing Fe^{3+} ions to the sample after melting. The solid phase reaction (V) is characterized by a very small quantum yield (less than 10^{-3}). We therefore identified the products of the photochemical reaction in a liquid solution of the same composition.

The direction of reactions (I) - (IV) did not change in the transition from liquid solutions at room temperature to glassy frozen solutions and did not depend on the wavelength of the d-d absorption bands.

The quantum yields of the solid phase photochemical reactions are presented and compared with those obtained in liquid solutions in Table 1. The quantum yields were determined from the initial regions of the curves of optical density *versus* photolysis time. Reaction (I) could also be monitored using the ESR signal which decreased during the reaction since the ESR spectra of the starting complex and the reaction product were very different.

Table 1 shows that the quantum yields of the solid phase ligand exchange reactions are normally about 10^{-2} . The only exception was reaction (V) (hydroxopentamminechromium(III) in an aqueous alkali matrix) where the quantum yield was much smaller (less than 10^{-3}). The probable reason for this low quantum yield is electrostatic repulsion of the substituting hydroxyl ion by the hydroxyl group in the original complex molecule. The values of the quantum yields depend weakly on the matrix composition and the wavelength of the irradiating light. An increase in the concentration of the substituting ligand (Cl^- or OH^-) in the frozen matrix produces an increase in the quantum yield of the reaction. The wavelength of the d-d absorption bands has the following effects on the quantum yield.

(1) The quantum yields of both the liquid and the solid phase ligand exchange reactions are generally greater for irradiation in the long wavelength absorption band than for irradiation in the short wavelength absorption band.

(2) The quantum yield of the solid phase photoinitiated reaction of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 5 M LiCl increases with decreasing wavelength in the long wavelength absorption band but remains constant within the short wavelength band.

The different quantum yields observed in the different absorption bands are probably due to the photophysical occupation and deactivation of the various excited states of the complex molecules. It is usually assumed that the photoinitiated reaction occurs from the lowest quartet excited state. When excitation occurs in the short wavelength absorption band, *i.e.* excitation to a higher quartet state, the probability of population of a reactive excited state becomes lower, perhaps as the result of deactivation via a system of doublet excited states.

TABLE 1
Quantum yields of ligand exchange reactions

Reaction	Matrix	T (K)	λ (nm)	ϕ	
$[\text{Cr}(\text{NH}_3)_6]^{3+} \rightarrow [\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$	5 M LiCl	293	436	0.29	
		293	365	0.22	
		77	480	0.009 ^a	
		77	455	0.012 ^a	
		77	436	0.016	
		77	365	0.009	
		77	345	0.08 ^a	
		77	325	0.010 ^a	
$[\text{Cr}(\text{NH}_3)_6]^{3+} \rightarrow [\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$	5 M NaOH	293	436	0.15 ₄	
		293	365	0.07 ₀	
	10 M NaOH	293	436	0.09 ₁	
		293	365	0.04 ₆	
	5 M NaOH	77	436	0.015	
		77	365	0.010	
	10 M NaOH	77 - 168	436	0.021	
		77 - 183	365	0.011	
$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} \rightarrow \text{cis-}[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$	5 M LiCl	293	546	0.30	
		293	436	0.29	
		293	365	0.27	
		77	436	0.010	
		77	365	0.007	
		128	436	0.011	
		128	365	0.007	
		10 M LiCl	77	436	0.020
			77	365	0.010
		$\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$	95% ethanol	77	546
77	436			0.012	
77	365			0.015	
$[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+} \rightarrow \text{cis-}[\text{Cr}(\text{NH}_3)_4(\text{OH})_2]^+$?	10 M NaOH	293	436	0.08 ₀	
		293	365	0.02 ₇	
		77		$< 10^{-3}$	

The quantum yields are given with relative errors of not more than 10% at the 95% confidence level.

^aRelative errors of 15% at the 95% confidence level.

It should be noted that the initial quantum yields of the solid phase ligand exchange reactions did not depend on the temperature of the glassy sample. This experimental observation will be discussed further below.

The ligand exchange reactions in solid matrices exhibit interesting kinetics. Wherever possible we plotted kinetic curves in terms of the degree α of conversion given by $\alpha = P/C_0$ where P is the concentration of the reaction product and C_0 is the initial concentration of the original complex *versus* the

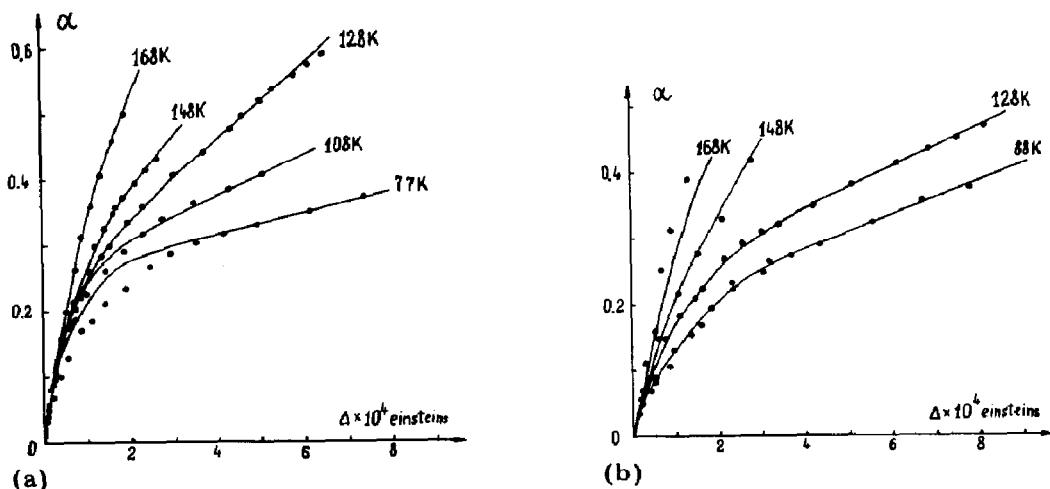


Fig. 3. Degree of conversion *vs.* absorbed light dose for the photolysis of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 10 M NaOH at various temperatures (\bullet , experimental data; —, calculated from eqns. (5)): (a) photolysis at 436 nm; (b) photolysis at 365 nm.

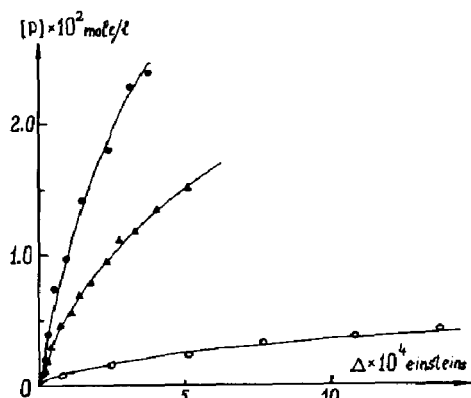


Fig. 4. Reaction product concentration *vs.* absorbed light dose for the photolysis of $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ in 95% ethanol at 77 K using light of wavelengths 365 nm (\bullet), 436 nm (\blacktriangle) and 546 nm (\circ).

light dose $\Delta(t)$ absorbed by the original complex. $\Delta(t)$ was calculated numerically from

$$\Delta(t) = I_0 \int_0^t \frac{A_1}{A_1 + A_2} \{1 - 10^{-(A_1 + A_2)}\} dt$$

where I_0 is the intensity of the incident light and A_1 and A_2 are the optical densities of the original complex and the reaction product respectively at the wavelength of the irradiating light. Figures 3 and 4 show such curves for two of the systems investigated. These experimental curves are substantially non-linear, *i.e.* the quantum yield of the reaction varies during the photolysis, in

contrast with the results obtained in the liquid phase. The non-linearity of the experimental curves may be due to "kinetic non-equivalence", *i.e.* to the fact that the probability of a complex molecule being involved in a photolytic reaction depends on the structure of its environment. Therefore the complex molecules will have widely varying reactivities (or quantum yields). In photolysis the concentration of the most reactive molecules rapidly decreases because they are consumed by the chemical reaction, and the restoration of the original reactivity distribution is strongly hindered in a frozen solution. Thus the quantum yields will decrease during photolysis. A similar effect has been reported [13] for some photoinitiated reactions in polymer matrices.

The kinetic non-equivalence effect in the systems investigated in the present work was demonstrated by the following experiments. A sample was subjected to long-term photolysis at 77 K until the reaction rate was substantially less than the initial rate. The sample was then held at the devitrification temperature T_g of the solvent for several minutes to restore the original reactivity distribution (the devitrification temperatures of the solvents used in this study are given in Table 2). The sample was then photolysed again at 77 K. Figure 5 shows the results of this experiment for a glassy solution of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 10 M NaOH where it can be seen that after holding the sample at T_g the reactivity of the complex molecules in the ligand exchange reaction was fully restored. If such an operation were used to restore the original reactivity distribution after shorter photolysis periods, the experimental curves would become linear. Experiments of this type were used to demonstrate the kinetic non-equivalence phenomenon in the following systems: $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 5 M and 10 M NaOH; $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NSC})_4]$ in 95% ethanol; $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ in 5 M LiCl.

Figures 3 and 4 also show that the shape of the experimental curves varies with the irradiation wavelength and the temperature. These effects are discussed below.

4. Discussion

At first glance a photoinitiated ligand exchange reaction appears to be unlikely in the solid phase since it would require the motion of particles of considerable size in the frozen matrix. However, the experimentally measured quantum yields are higher than is expected in the solid phase. This observation can be explained if we assume that chromium complexes in the ground state form ion pairs or more complex ion associates with the substituting ligands in the same way as has been proposed for ligand exchange reactions in liquid solutions of chromium complexes [14 - 16]. The following observations appear to corroborate the fact that the solid phase ligand exchange reaction occurs as the result of the photoexcitation of ion pairs or associates.

TABLE 2

Devitrification temperatures of the matrix solutions

Matrix	T_g (K)
5 M LiCl	142 - 152
5 M NaOH	164 - 171
10 M NaOH	189 - 195
95% ethanol	103 - 107

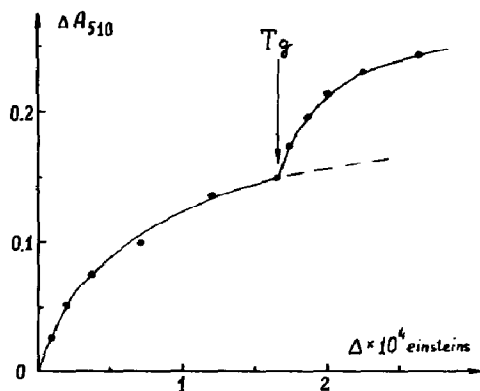


Fig. 5. The optical density of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ at 510 nm vs. the light dose absorbed by hexaamminechromium in the photolysis of an alkaline solution of $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_3)_3$ at 77 K using light of wavelength 436 nm. The arrow shows the point at which the sample was kept in the dark at the matrix devitrification temperature.

(1) Complexes of ammonia with chromium form ion pairs with various anions in dilute aqueous solutions (the value of $\log K_{\text{equil}}$ for aqueous solutions of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and Cl^- is 1.37 - 1.5 [17]).

(2) IR spectroscopy investigations [18] have revealed that in crystalline chromium(III) complexes hydrogen bonds exist between the NH_3 groups in the complex molecules and Cl^- anions.

(3) In the solutions investigated in this work there were usually two ligands capable of taking part in the photoinitiated ligand exchange reaction (Cl^- and H_2O or OH^- and H_2O) and the concentration of the water molecules was always the greater (5 M LiCl contains 49.9 mol $\text{H}_2\text{O l}^{-1}$). The fact that the reactions involve only one ligand indicates that they occur within ion associations.

It can thus be concluded that ligand exchange reactions of chromium(III) complexes in the solid phase take place within ion pairs or ion associations composed of the substituting ligand and the complex ion in the ground state.

Ion associations probably have different compositions and structures in a frozen solution. This may be responsible for the different reactivities of the complex molecules which manifest themselves through the unusual reaction kinetics. Since the efficiency of the reaction is determined to a large extent by the composition and structure of the ion associations, the variation

of the initial quantum yield with the matrix composition and its independence of the temperature of the glassy solution is not unexpected. (The structure of the frozen solutions was unchanged regardless of the experimental temperature because all the samples were initially frozen to liquid nitrogen temperature in the same manner.)

In apparent contradiction with these conclusions, Adamson [9] has reported that the quantum yield of the release of free thiocyanate ions in the photolysis of a glassy solution of $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ varies with temperature and has an activation energy of $0.55 \text{ kcal mol}^{-1}$. The probable reason for this contradiction is that, as we have shown, the quantum yield of the ligand exchange reaction varies with time during the photolysis. In our experiments we measured the initial quantum yields of the reaction for small degrees of conversion of the initial complex. These values were independent of temperature, whereas the quantum yields measured for large degrees of conversion were not.

A closer examination of the experimental relationships between the degree of conversion and the light dose absorbed by the initial hexaamminechromium at different temperatures shows the following (Fig. 3).

(1) The reaction quantum yield ϕ_0 calculated for the initial portions of the curves is independent of temperature (see Table 3).

(2) During photolysis the quantum yield of the photochemical reaction shows a temperature-dependent decrease.

(3) After a long period of photolysis, linear portions appear in the experimental curves.

(4) The higher the temperature is, the higher is the position of the kinetic curve; the quantum yield in the linear portion increases with temperature.

Analysis of the above features allows the following conclusions to be drawn.

(1) The initial reactivity distribution of the complex molecules is temperature independent.

(2) During photolysis the original reactivity distribution is both perturbed and restored. Therefore a steady state reactivity distribution is established after a specific time and a linear portion appears in the experimental curves. The quantum yield in the linear portion is the weighted average of the steady state distribution.

(3) The rate of restoration of the original reactivity distribution is temperature dependent: the higher the temperature is, the faster is the rate.

As we have already noted, the original distribution of reactivities among the complex molecules can be thermally restored if the sample is exposed to the matrix devitrification temperature T_g . However, this can only occur in the temperature range from T_g to $T_g - 20 \text{ K}$. Therefore in order to account for the experimental curves it must be assumed that the original reactivity distribution can be restored by the action of light. A reorganization of the molecular environment as a result of the effects of light can be explained as follows. In cases where the absorbed photon is not photochemically active its energy dissipates in the matrix. This enhances the molecular mobility in

the local environment of the complex molecule. As the temperature is increased, the probability of matrix reorganization due to the dissipation of the energy of absorbed photons must also increase.

5. Kinetic model of the solid phase ligand exchange reaction

The following model can be used to describe solid phase ligand exchange kinetics.

In a frozen solution there is a characteristic initial distribution of reactivity (*i.e.* quantum yield) among the complex molecules. Photolysis affects this distribution, *i.e.* the distribution function is that of the absorbed light dose:

$$\frac{\partial N}{\partial \phi} = f(\phi, \Delta)$$

where N is the number of molecules and ϕ is the quantum yield. As a molecule absorbs a photon it can either react with a probability ϕ or reorganize its environment with a probability $\beta = \beta(T)$ which is a function of temperature. Further, the reorganization of the environment results in the restoration of the initial distribution. With these assumptions, the following equation is valid:

$$\frac{\partial f(\phi, \Delta)}{\partial \Delta} = -\frac{f(\phi, \Delta)}{N(\Delta)} \phi - \frac{f(\phi, \Delta)}{N(\Delta)} \beta \left\{ 1 - \frac{f_0(\phi)}{N_0} \right\} + \left\{ 1 - \frac{f(\phi, \Delta)}{N(\Delta)} \right\} \beta \frac{f_0(\phi)}{N_0} \quad (1)$$

where N_0 and

$$N(\Delta) = \int_0^1 f(\phi, \Delta) d\phi$$

are respectively the initial and final numbers of molecules of the original compound in the sample.

This equation describes a change in the distribution function which depends on the absorbed light dose. The physical meaning of the equation becomes clear if it is assumed that it is valid for a molecular group with quantum yields within the range ϕ to $\phi + d\phi$. The number of photons absorbed by molecules with their quantum yields in this range is proportional to the ratio of the optical density of the molecular group with quantum yield ϕ to the integral optical density of the sample at the wavelength of the photolyzing light:

$$I_\phi = I_0 \frac{A_\phi}{A_\Sigma} (1 - 10^{-A_\Sigma})$$

If it is assumed that all molecules, regardless of their reactivity, have the same extinction coefficient, the light dose absorbed by molecules with a given quantum yield will be

$$\frac{A_\phi}{A_\Sigma} = \frac{f(\phi, \Delta) d\phi}{N(\Delta)}$$

Thus

$$1 - \frac{f(\phi, \Delta) d\phi}{N(\Delta)}$$

will give the light dose absorbed by the rest of the molecules. The first term in eqn. (1) accounts for the reduction in the number of molecules with a given quantum yield ϕ as a result of the photochemical reaction. The second term in eqn. (1) represents the molecules of a given group which, on absorption of light, reorganize their environment with a probability β and thus fall into molecular groups with a quantum yield other than ϕ . The third term accounts for fresh molecules arriving in the group as a result of the reorganization of the environments of molecules with a quantum yield other than ϕ .

Equation (1) transforms to

$$\frac{\partial f(\phi, \Delta)}{\partial \Delta} = - \frac{f(\phi, \Delta)}{N(\Delta)} (\phi + \beta) + \beta \frac{f_0(\phi)}{N_0} \quad (2)$$

This equation and the initial distribution function are sufficient to describe the evolution of the distribution function during photolysis and can be used to obtain a numerical description of the experimental curves.

To find β we use the fact that the distribution function is stationary on the linear portion of the kinetic curve. In a stationary distribution the form of the distribution function does not change, *i.e.* the relative number of molecules with a given quantum yield is constant:

$$\frac{f_{st}(\phi, \Delta)}{N(\Delta)} = \text{constant}$$

$$\frac{d}{d\Delta} \left\{ \frac{f_{st}(\phi, \Delta)}{N(\Delta)} \right\} = 0$$

If we differentiate this equation, remembering that $dN(\Delta)/d\Delta = \phi_{st}$ is the experimental quantum yield on the linear portion of the curve and use eqn. (2), we obtain the following equation:

$$\frac{\beta}{N_0} \int_0^1 \frac{f_0(\phi)}{\phi + \beta - \phi_{st}} d\phi = 1 \quad (3)$$

Since we know the initial distribution function and the reaction quantum yield over the linear portion, we can determine β from this equation.

Therefore to solve eqn. (2) the distribution function of the quantum yield for complex molecules must be known. However, it is impossible to determine the form of the distribution function experimentally. In practice an appropriate distribution function is assumed and its agreement with the true distribution function is assessed by comparing the calculated and experimental kinetic curves.

Two conditions are imposed on the initial distribution function:

$$\int_0^1 f_0(\phi) d\phi = N_0$$

$$\frac{1}{N_0} \int_0^1 f(\phi)\phi d\phi = \phi_0$$
(4)

These conditions are used to determine the parameters of the initial distribution function.

We carried out calculations for frozen solutions of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in 10 M NaOH. In this system the photochemical reaction is almost free from secondary photoinitiated processes. Therefore correct experimental curves were obtained for even high degrees of conversion. In the calculations the simplest form of initial distribution function was used. This function is based on the assumption that the system contains a molecules that react with a quantum yield ϕ and b non-reactive molecules. Then the initial distribution parameter is given by

$$\gamma = \frac{a_0}{a_0 + b_0}$$

It is assumed that a molecule that has absorbed a quantum of light can reorganize its environment with a temperature-dependent probability $\beta = \beta(T)$. The probability that the molecule becomes reactive on reorganization of the environment is equal to the initial distribution parameter γ . Then, allowing for light absorption by molecules of both types, the following set of differential equations can be derived from eqn. (2).

$$\frac{da}{d\Delta} = \beta\gamma - \frac{a}{a+b} (\phi + \beta)$$

$$\frac{db}{d\Delta} = \frac{a}{a+b} \beta - \beta\gamma$$
(5)

Using conditions (3) and (4) we obtain

$$\phi_0 = \phi\gamma$$

$$\phi_{st}(\phi + \beta - \phi_{st}) = \beta\gamma\phi$$
(6)

After applying eqns. (6) the only unknown parameter in eqns. (5) is γ . It was found that the results of calculations with $\gamma = 0.29 \pm 0.03$ agreed well with the experimental curves obtained for photolysis at two wavelengths (365 and 436 nm) throughout the temperature range investigated (Fig. 3). The β values obtained by making the above assumptions are given in Table 3.

6. Conclusion

Photoinitiated ligand exchange reactions of chromium(III) complexes in solid frozen solutions can have substantial quantum yields. The reaction

TABLE 3

Kinetic parameters used for describing the photoinitiated ligand exchange reaction of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in aqueous 10 M NaOH (eqns. (5) and (6))

T (K)	$\lambda = 365 \text{ nm}$			$\lambda = 436 \text{ nm}$		
	ϕ_0	ϕ_{st}	β	ϕ_0	ϕ_{st}	β
77	0.0108	0.0012	0.005	0.021	—	—
88	0.0090	—	—	0.021	0.00095	0.004
108	0.010	—	—	0.020	0.00125	0.005
128	0.010	0.0017	0.006	0.022	0.0028	0.011
148	0.0115	0.0055	0.033	0.033	0.0052	0.022
168	0.012	—	—	0.023	0.012	0.073
183	0.011	—	—	—	—	—

takes place via the excitation of ion pairs or more complex ion associations composed of the complex molecule in the ground state and the substituting ligand. The direction of the solid phase exchange reaction is the same as that in liquid solutions of the same composition, whereas the quantum yield drops by a factor of 5 - 30 on going from room temperature to liquid nitrogen temperature.

Reactions of this kind are affected by the kinetic non-equivalence of the reacting particles owing to the rather wide range of reactivities of the complex molecules. It was possible to describe the experimental curves in terms of two concurrent processes, a perturbation of the original reactivity distribution among the complex molecules as a result of the chemical reaction and its restoration due to the absorption of photon energy dissipated in the matrix.

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