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SOLID-STATE PHOTOCHEMICAL REACTIONS OF TRANSITION-METAL COORDINATION COMPOUNDS

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CONTENTS

A. INTRODUCTION

During the past twenty years an increasingly large number of investigations involving the photochemical reactions of transition-metal coordination compounds in aqueous solutions has been reported. Much of this work has been summarized in the various reviews that have been published[1–5]. In contrast to the aqueous solution photochemical reactions, relatively few solid-state photochemical reactions of transition-metal complexes have been investigated. Undoubtedly the same energy levels are involved in the initial absorption processes regardless of the state of the sample. These processes, which have previously been discussed[1,4,6], are d–d transitions and charge transfer excitations. It has been pointed out that the former often result in ligand substitution reactions while the latter result in oxidation–reduction reactions[4]. Although the initial absorption processes are the same, the subsequent thermal or "dark" reactions are almost certainly different in the solid state than in aqueous solutions. For this reasons alone, the study of the solid-state photochemical reactions of transition-metal coordination compounds is important.

Probably the major reason that there have been fewer studies involving photochemical reactions of transition-metal complexes in the solid-state than in solution is the fact that the experimental difficulties are perhaps greater. It has only been recently that experimental techniques have been developed which make quantitative solid-state photochemical reactions convenient to study. In this review, these techniques will be briefly discussed along with some of the pertinent theoretical developments as well as the results of some of the more important investigations that have been reported. Studies dealing with the photolysis of simple salts (metal halides, azides, etc.) will be omitted as they have previously been reviewed[7–9].

B EXPERIMENTAL TECHNIQUES

(i) Radiation sources and intensity measurements

The radiation sources which have been used in solid-state photochemical investigations of transition-metal coordination compounds are, in general, the same as those used in many other photochemical studies[10]. Normally, any rather intense, visible or ultraviolet source is applicable. Wavelength control may be accomplished by the use of filters or a high-intensity monochromator. Intensity measurements are usually made with suitable actinometers such as the uranyl oxalate[11], the ferri oxalate[12,13] or the Reinecke's salt[14] systems. A radiometer involving the use of thermopiles has also proven convenient for radiation intensity measurements[15].

(ii) Methods of identification and analysis of photoproducts and reaction intermediates

Since solid-state photochemical reactions are essentially surface reactions, extremely small quantities of photoproduct may be formed. Most of the techniques which have been employed to identify or analyze the photoproducts were designed to circumvent this difficulty. In some investigations, alcoholic slurries of finely powdered reactant were photolyzed[16,17]. Reaction was carried out to completion and the photoproducts analyzed by wet chemical methods, magnetic susceptibility, or other conventional methods. Another method which has been employed in an attempt to force a solid-state photochemical reaction to completion involved the use of a rotating quartz reaction tube[18]. Finely powdered reactant, which was placed in the tube, was irradiated as the tube rotated. Using this method, evolved gases could also be analyzed by the use of mass spectrometry or gas chromatography. Other methods involving the coating of thin layers of the reactant

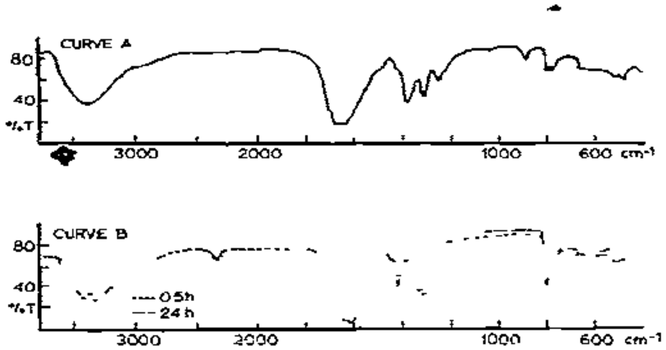


Fig. 1. (A) Infrared spectrum of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ in a KCl pellet. (B) Infrared spectrum of an irradiated KCl pellet containing $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, irradiation times indicated[20]. The peak at $2344\ cm^{-1}$ is due to CO_2 trapped in the pellet

on quartz plates have also been described[15,19].

A technique which has been proven to be especially convenient for the rapid identification of photoproducts involves the use of alkali halide pellets[20–24]. Using this method, a small amount of reactant was ground with dried alkali halide and pressed into the form of a transparent pellet which was then irradiated. In one investigation[20], the infrared spectra of the photoproducts were then obtained. An example of the spectra obtained for the products of the photochemical reaction of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ is given in Fig 1. As can be seen, not only were the solid photoproducts identified but also trapped gaseous photoproducts as well.

Probably the most rapid and convenient method which has been used for identifying products of photochemical reactions of powdered samples involves the use of reflectance spectroscopy. This was especially applicable to transition-metal complexes, most of which have unique visible spectra. The method was first employed in 1965[25] and has subsequently been used in a number of investigations[16–18,26,27]. The general procedure has been to obtain the visible reflectance spectrum of the sample after various irradiation times. The spectra of the photoproducts may then be identified. Examples of the spectra obtained during the photochemical reaction of powdered $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ are given in Fig 2. The spectrum after 90-minute irradiation was identified as that of $K_2[Co(C_2O_4)_2]$.

A promising new method of detecting minute quantities of short-lived free radical intermediates formed in solid-state photochemical reactions of transition-metal complexes by the use of ESR has recently been reported[28].

(iii) Quantum yield determinations

In only a few investigations have quantum yield values for solid-state photochemical reactions of transition-metal complexes been determined. Spencer[19] determined quantum yield values for the oxidation–reduction reactions of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ using various radiation intensities and wavelengths. Thin layers of the compounds on quartz plates were photolyzed and the transmittance and reflectance

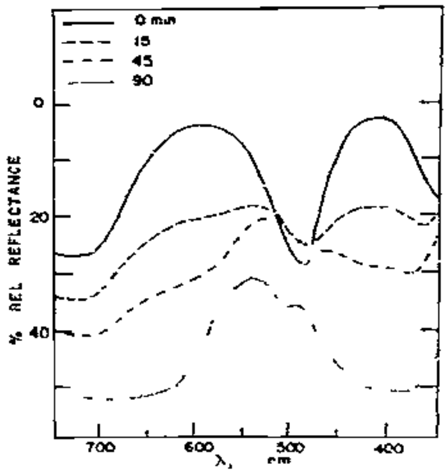


Fig 2 Reflectance spectra of the photoproducts of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$[26]. Original compound ———, after 15 min irradiation - - -; after 45 min irradiation — — — —; after 90 min irradiation . ..

values at the wavelength employed were measured at various time intervals during photolysis. The quantity reacted was determined by wet chemical analysis. This method had the disadvantage that absorption of radiation by the photoproduct was not taken into account. Using a similar method[15], in which quantum yield values of the oxidation–reduction reaction of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ at 400 nm and various radiation intensities were determined, the radiation absorbed by the photoproducts was also taken into account. The method made use of rate plots rather than chemical analysis and will be discussed in more detail in the next section Another method of determining the quantum yield of a solid-state photochemical reaction involves the use of alkali halide pellets[21,29].

C. RATE EQUATIONS

(i) Thin layers or plates

The development of equations describing the rate of the photochemical reaction of a sample in the form of a smooth layer or plate (such as a pressed alkali halide pellet) is particularly difficult since the radiation intensity is attenuated by absorption on passing through the sample. Thus, the concentration of reactant also varies with depth into the sample. A method for calculating the average radiation intensity for the case in which there is no concentration gradient in the sample was described in 1941[30]. Only recently, however, have attempts been made to treat cases in which there is a concentration gradient across the sample due to photochemical reaction theoretically. An attempt was made by Sliker[31] to determine the rate of the photochemical reaction of a solid for the case in which both the radiation intensity and reactant concentration vary with depth into the sample. He was unable to obtain a solution in closed form, although approximate solutions were obtained. Wilson[32] obtained rate equations for solid-state photochemical reactions in which the diffusion of gases through the sample was involved. By using Fick's first law for the diffusion process, he obtained expressions for the quantum yield for four different cases; these are listed in Table 1.

TABLE 1

Expressions for solid-state photochemical quantum yields

Equations for the quantum yield of solid-state photochemical reactions for four cases in which the diffusion of gases is important[32]; l is the depth into the sample, D the diffusion coefficient of the gases, I_a the rate of light absorption, θ_0 the initial product concentration function, θ_1 the product concentration function, ϕ the quantum yield, and k's are constants

Case I	Rate independent of gaseous product concentration	$\phi = \frac{k_1}{I_a}$
Case II	Rate proportional to gaseous product concentration	$\phi = \frac{8k_2\theta_0}{\pi^2 I_a} \sum_{n=1,3,5}^{\infty} \frac{1}{n^2} \left[\frac{1}{1-(k_2 l^2/Dn^2\pi^2)}\right]$
Case III	Rate independent of gaseous reactant concentration	$\phi = \frac{k_3 l - (k_3{}^2 l^2 - 8k_3 D\theta_1)^{1/2}}{I_a l}$
Case IV	Rate proportional to gaseous reactant concentration	$\phi = \frac{8k_4\theta_1}{\pi^2 I_a} \sum_{n=1,3,5}^{\infty} \frac{1}{n^2} \left[\frac{1}{1+(k_4 l^2/Dn^2\pi^2)}\right]$

One of the most applicable methods yet used to obtain an expression for the rate of the photochemical reaction of a solid layer is that given by Barker et al.[33]. A solid layer was divided into n smaller imaginary layers of thickness, δ (in mm) The radiation impinging on the i^{th} layer, $I_0(i, t)$ (in photons mm^{-2} . sec^{-1}), for the case in which photoproducts are transparent is given by eq. (1).

$$I_0(i, t) = I_0 \prod_{m=1}^{m=i-1} \exp\left[-\alpha C_A(m, t)\delta\right] \tag{1}$$

where I_0 is the radiation intensity at the sample surface, α the reactant absorption coefficient (in l.mole^{-1} . mm^{-1}), and $C_A(m, t)$ the reactant concentration of the m^{th} layer at time t (in mole.l^{-1}). The rate of reaction in the i^{th} layer is given by eq (2).

$$-\frac{dC_A(i, t)}{dt} = \frac{10^6 \phi I_0(i, t)}{N\delta} \{1 - \exp\left[-\alpha C_A(i, t)\delta\right]\} \tag{2}$$

where ϕ is the overall quantum yield and N is Avogrado's number Although an exact solution to eqs. (1) and (2) was not obtained, an approximate solution given by eq (3) was obtained by assuming that $\alpha C_A(i, t)\delta$ is small

$$C_A(k, t+\tau) = C_A(i, t) \exp\left(-\frac{10^6\alpha\phi t}{2N}\left[I_0(i, t+\tau) + I_0(i, t)\right]\right) \tag{3}$$

where $C_A(i, t+\tau)$ is the concentration of the i^{th} layer at time $t+\tau$ and $I_0(i, t+\tau)$ is the radiation intensity on the i^{th} layer at time $t+\tau$ A method was described by which eq. (3) could be used to determine the quantum yield by summing $C_A(i, t+\tau)$ over all imaginary layers by the use of a computer The case in which photoproducts absorb radiation was treated in an identical manner except that the term,

$$\sum_j n_j\beta_j\left[C_0 - C_A(m, t)\right]\delta$$

where n_j is the stoichiometry coefficient of the j^{th} product, β_j the absorption coefficient of the j^{th} product, and C_0 the initial reactant concentration, was added to the exponents in eqs. (1) and (2).

More recently, an exact solution to the problem for the case in which the photoproducts are transparent was obtained by a method making use of the following differential equations[34], the Beer–Lambert equation

$$\frac{\mathrm{d}I}{\mathrm{d}X} = -\alpha C_A I \tag{4}$$

and the local rate equation

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} = -\phi\alpha C_A I \tag{5}$$

where I is the radiation intensity and C_A the reactant concentration (both are functions of reaction time, t, and distance, X, across the sample). The solutions obtained for eqs. (4) and (5) for a solid layer are

$$C_A = C_0 \exp(-\phi I_0 \alpha t)\left\{\exp(-\phi\alpha I_0 t)\left[1-\exp(-\alpha C_0 X)\right] + \exp(-\alpha C_0 X)\right\}^{-1} \tag{6}$$

and

$$I = I_0 \exp(-C_0\alpha X)\left\{\exp(-\phi\alpha I_0 t)\left[1-\exp(-\alpha C_0 X)\right] + \exp(-\alpha C_0 X)\right\}^{-1} \tag{7}$$

Mauser[35] obtained the same equations by a different method for viscous samples

For the case in which photoproducts absorb radiation, a similar treatment yielded the following approximate equation which is valid for small t [34].

$$C_A = C_0\left\{1 + \left[\alpha/(\alpha-b)\right]\frac{\exp\left[-(\alpha-b)\phi I_0 t\right]\exp(-\alpha C_0 X) - \exp(-\alpha C_0 X)}{\exp\left[-(\alpha-b)\phi I_0 t\right](1-\exp(-\alpha C_0 X)] + \exp(-\alpha C_0 X)}\right\} \tag{8}$$

where b is a combination of stoichiometry coefficients and absorption coefficients of the photoproducts.

Using a different approach, Spencer and Schmidt[36] obtained a rate equation for the photochemical reaction of a solid layer by assuming that a defined boundary exists between the photoproduct layer and the reactant. The surface boundary was assumed to move downward as a function of time of irradiation.

(ii) Powdered samples

A rate equation has been obtained for the photochemical reaction of a thin layer of a powdered reactant coated onto a quartz plate[15]. The equations used are

$$\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = -\phi I \alpha_\mathrm{A} C_\mathrm{A} \tag{9}$$

and

$$1 - T - R = \alpha_\mathrm{A} C_\mathrm{A} + \alpha_\mathrm{P} C_\mathrm{P} \tag{10}$$

where R is the reflectance, T the transmittance, C the concentration in mole cm^{-2} (since the reactant is in the form of a very thin layer, it is convenient to measure the concentration in units of mole.cm^{-2}), α the absorption coefficient, and A and P refer to the reactant and product, respectively.

In writing eqs. (9) and (10) it was assumed that the sample layer is thin enough that the radiation intensity may be considered constant throughout the sample The rate equation from eqs. (9) and (10) is

$$\frac{\mathrm{d}\ln[T_\mathrm{P} + R_\mathrm{P} - R - T]}{\mathrm{d}t} = -\frac{[1 - T_\mathrm{A} - R_\mathrm{A}]}{C_0}\phi I \tag{11}$$

where C_0 is the initial reactant concentration. Equation (11) can be used to determine the quantum yield from the slope of a plot of ln $[T_\mathrm{P} + R_\mathrm{P} - R - T]$ vs t. Figure 3 illustrates such plots for the reaction of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$.

Powdered samples are more easily handled in bulk than in the form of thin layers on quartz plates. For this reason it would certainly be advantageous if reflectance measurements could be used to study photochemical reaction rates of bulk powdered samples, and this has, in fact, been attempted[16]. Unfortunately, however, the theory of reflectance spectroscopy has not yet been sufficiently developed to allow the calculation of trustworthy concentration values from reflectance measurements. The present status of the theory has been extensively reviewed[37–39]. In the past, two models representing a powdered sample have been widely used. In the first model, a powdered sample is treated as a continuous medium[40–42]. Unfortunately, equations obtained using such a model include optical parameters (such as the absorption coefficient) in some unknown fashion in two or more arbitrary constants. In the second widely used model, a powdered sample is treated as a collection of parallel plates[43–45]. Equations obtained using this model also fail to relate explicitly the reflectance to the optical parameters.

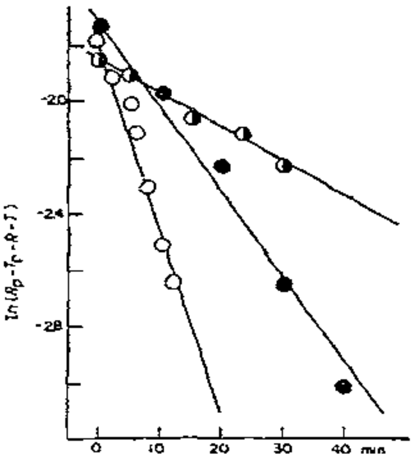


Fig. 3. Rate plots for $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ at a wavelength of 400 nm[15]. ○, $I = 1.47 \times 10^{-8}$ einsteins/cm² sec, ●, $I = 1.17 \times 10^{-8}$ einsteins/cm² sec, ◑, $I = 0.74 \times 10^{-8}$ einsteins/cm² sec

Probably the best model yet proposed is that due to Melamed[46]. He treated the randomly shaped and oriented particles of a powdered sample as a collection of uniformly sized rough-surfaced spheres The same model has recently been used to obtain a rather simple expression for the reflectance, R, of a weakly absorbing powdered sample[47].

$$R = \exp\left[-2n(kd/3)^{1/2}\right] \tag{12}$$

where n is the index of refraction, k the absorption coefficient (cm^{-1}) and d the particle diameter. Using eq. (12) along with the usual local rate equation (eq. (5)), the rate of the photochemical reaction of a powdered sample in terms of its reflectance was found to be given approximately by eq. (13)[48].

$$\frac{\mathrm{d}}{\mathrm{d}t}\ln\left[\frac{(\ln R)^2 - (\ln R_\mathrm{P})^2}{(\ln R_\mathrm{A})^2 - (\ln R_\mathrm{P})^2}\right] \cong \frac{(\ln R_\mathrm{A})^2}{2}\;\frac{\phi I_0}{C_0} \tag{13}$$

Thus, by measuring the change in the reflectance of a powdered sample with time of irradiation, the quantum yield may be determined if C_0 (in moles.cm^{-2}) is known. Many approximations, however, were made in the derivation of eq (13). For example, it was assumed that n and d remain constant throughout the reaction. Eq. (13) has not been rigorously tested experimentally, although preliminary results indicated that it may be applicable at least as a rough approximation[48]. Certainly more theoretical developments are needed in this area.

D. OXIDATION–REDUCTION REACTIONS

(i) Tris(oxalato) metal(III) complexes

The solid-state photochemical reactions of the compounds, $K_3[M(C_2O_4)_3]\cdot 3H_2O$ (M = Co, Mn, Fe), are among the most extensively investigated of the transition-metal coordination compounds[15–17,19,20,26,49,50]. The following color changes, which occur on exposure to ultraviolet radiation, are observed[51,52].

M = Co	dark green → violet
M = Mn	deep red → white
M = Fe	emerald green → yellow

By the use of reflectance spectroscopy and magnetic susceptibility as well as wet chemical analysis, the stoichiometries of the reactions have been established[16,17,26], these are

$$2\,K_3[M(C_2O_4)_3]\cdot 3H_2O \xrightarrow{h\nu} 2\,K_2[M(C_2O_4)_2] + K_2C_2O_4 + 2\,CO_2 + 6\,H_2O \qquad (14)$$

where M = Co, Mn and

$$2\,K_3[Fe(C_2O_4)_3]\cdot 3H_2O \xrightarrow{h\nu} 2\,FeC_2O_4 + 3\,K_2C_2O_4 + 2\,CO_2 + 6\,H_2O \qquad (15)$$

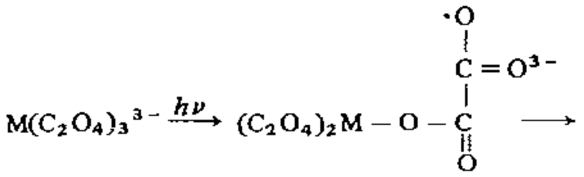
In each case the central metal ion is reduced from the trivalent to the divalent state and an oxalate ion is oxidized.

Spencer[19] has measured the quantum yield values for the reaction of the cobalt(III) and iron(III) compounds. For the iron compound, values between 0.07 – 0.20 mole/einstein were found. The quantum yield value increased with increasing intensity and with decreasing wavelength. For the cobalt compound, values between 0.1 and 0.6 mole/einstein were found. The quantum yield value passed through a maximum at 313 nm and was independent of intensity at this wavelength. The values found in all cases were less than those for the corresponding aqueous solution reactions[53–56]. However, as mentioned previously, absorption of radiation by the photoproducts was not taken into account, thus, the quantum yield values obtained are probably too low.

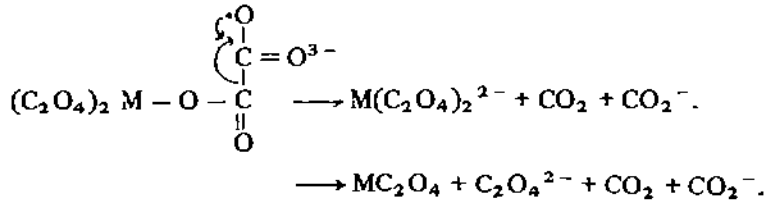
For the iron(III) complex, Pitts et al.[21], obtained a value of 1.3 for the quantum yield of the solid-state photochemical reaction using light of 334 nm wavelength. The value, which is considerably larger than the values obtained by Spencer[19], is also larger than those obtained by Ballardini et al.[29]. The latter obtained values of 0.9 at 245 nm, 0.75 at 313 nm, and 0.5 at 365 nm and found that the quantum yield increased with increasing pressure.

In another investigation[15], the quantum yield for the reaction of the analogous manganese(III) compound was measured at 400 nm. The value obtained (0.52 ± 0.09) was independent of the radiation intensity, and surprisingly, was about the same as that found for the corresponding aqueous solution reaction[56] at the same wavelength.

Mechanisms for reactions (14) and (15) have been proposed which involve oxalate ion radicals and bridged intermediates[16,17,26]. Recent ESR evidence[28], however, indicated the presence of the carbon dioxide ion radical during the solid-state photochemical reactions of these compounds. In view of this evidence, the most likely mechanism is as follows.



$$M(C_2O_4)_3{}^{3-} \xrightarrow{h\nu} (C_2O_4)_2M-O-\underset{\underset{\textstyle O}{\|}}{\overset{\overset{\overset{\textstyle \cdot O}{|}}{\textstyle C=O^{3-}}}{\underset{|}{C}}} \longrightarrow \tag{16}$$



$$(C_2O_4)_2\,M-O-\underset{\underset{\textstyle O}{\|}}{\overset{\overset{\overset{\textstyle \cdot O}{|}}{\textstyle C=O^{3-}}}{\underset{|}{C}}} \longrightarrow M(C_2O_4)_2{}^{2-} + CO_2 + CO_2{}^{-}. \quad (M = Co, Mn)$$
$$\longrightarrow MC_2O_4 + C_2O_4{}^{2-} + CO_2 + CO_2{}^{-}. \quad (M = Fe) \tag{17}$$

The ion radical most likely reacts with an adjacent molecule

$$\begin{aligned} M(C_2O_4)_3{}^{3-} + CO_2{}^{-}\cdot &\rightarrow M(C_2O_4)_2{}^{2-} + CO_2 + C_2O_4{}^{2-} \quad (M = Co, Mn)\\ &\rightarrow MC_2O_4 + 2\,C_2O_4{}^{2-} + CO_2 \quad (M = Fe)\end{aligned} \tag{18}$$

The initial absorption process is apparently a charge transfer excitation in all cases involving the transfer of an electron from a ligand orbital into a metal t_{2g} or e_g orbital. The similar compounds, $(NH_4)_3\ [Fe(C_2O_4)_3]\cdot 3H_2O$ and $Na_3[Fe(C_2O_4)_3]\cdot 3H_2O$, have also been studied in connection with photoconductivity investigations[57,58].

(ii) Manganese(III) malonato complexes

The solid-state photochemical oxidation–reduction reactions of the complexes, $M[Mn(mal)_2(H_2O)_2]\cdot 2H_2O$, $M[Mn(mal)_2(H_2O)_2]$, and $M[Mn(mal)_2]$ ($M = NH_4$, Na, and K), have been investigated by the use of reflectance spectroscopy, magnetic susceptibility, as well as by wet chemical analysis[18]. No difference in the reactions of $M[Mn(mal)_2(H_2O)_2]\cdot 2H_2O$ and $M[Mn(mal)_2(H_2O)_2]$ was observed except that the hydrated compound lost the water of hydration. In the reaction of $M[Mn(mal)_2(H_2O)_2]$, the first step appeared to be a dehydration

$$M[Mn(mal)_2(H_2O)_2] \xrightarrow{h\nu} M[Mn(mal)_2] + 2\,H_2O \tag{19}$$

On further irradiation, this complex reacted according to the reaction

$$2\,M[Mn(mal)_2] \xrightarrow{h\nu} M_2mal + 2\,Mnmal + H_2O + 3\,CO \tag{20}$$

Further irradiation in an air atmosphere decomposed the manganese malonate, or

$$2\,MnC_3H_2O_4 + 2\,O_2 \xrightarrow{h\nu} 2\,MnCO_3 + CH_3COOH + 2\,CO_2 \qquad (21)$$

Some manganese(II) acetate was found in the photolysis product which was thought to be due to the reaction between $MnCO_3$ and acetic acid.

The amount of the complex, $K[Mn(mal)_2(H_2O)_2]\cdot 2H_2O$, reacted after 30 min of irradiation was determined at several wavelengths These data are given in Fig 4. As can be seen, there is a maximum in the curve at about 325 nm, which most likely corresponds to the charge transfer band maximum.

(iii) Mercury(II) di-alkyl mercaptides

The solid-state photochemical oxidation–reduction reactions of six different mercury (II) di-alkyl mercaptides at 253.7 nm have been investigated[59]. Among the products were mercury, mercuric sulfide, and alkyl disulfides. The order of the susceptibility toward reaction was alkyl = benzyl > *n*-propyl > isopropyl ~ cyclopentyl > *t*-butyl > phenyl The susceptibility order was thought to be controlled by the relative stability of the thio-free radical which was thought to be a reaction intermediate

(iv) Cobalt(III) ammine complexes

The solid-state photochemical reactions of the complexes, $[Co(en)_3]X_3$ (X = F, Cl, Br, I), have been investigated[60] Polarographic analyses, infrared spectroscopy, magnetic susceptibility, and mass spectrometry were used to analyze the reaction products Cobalt(II) as well as cobalt(III) ion was found in the products and the two were present in a 1 1 ratio. Halide oxidation was not observed, but two moles of ammonia were evolved for each cobalt(II) ion produced. The cobalt(II) was apparently present in the

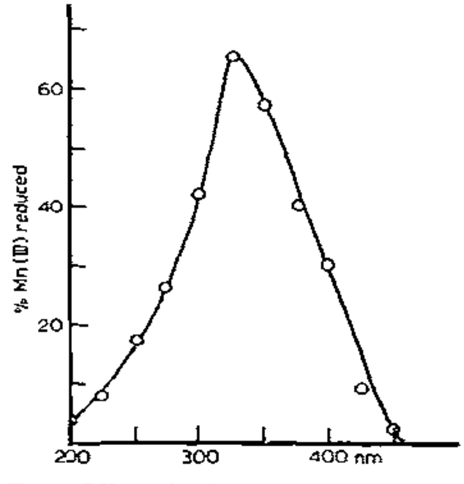


Fig. 4. Effect of radiation wavelength on the photolysis of $K[Mn(mal)_2(H_2O)_2]\cdot 2H_2O$. Irradiation period at each wavelength was 30 min[18].

products as a tetracoordinate ion and the cobalt(III) was present as some unidentified yellow complex ion. Both the cobalt(II) and the cobalt(III) were thought to be part of a polymer structure involving amine condensation products The reactivity order of the complexes increased in the order F > Cl > Br > I, which is the reverse of the order expected on the basis of the ease of electron transfer from the halide. The reactivity order was explained on the basis of the anion mobility in the crystalline lattice

The photochemical reactions of the solid compounds, $[Co(pn)_3]Cl_3$ and $[Co(NH_3)_6]Cl_3$, were studied in the same investigation[60] The reactivity order of the three chloride compounds increased in the order $[Co(NH_3)_6]Cl_3 > [Co(en)_3]Cl_3 > [Co(pn)_3]Cl_3$. The kinetics of the solid-state photochemical reactions of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ have been studied[61], but the reaction mechanism was found to be extremely complex.

Each of the following compounds have been found to undergo solid-state photochemical oxidation–reduction reactions, although the reaction stoichiometries have not been determined. $[Co(NH_3)_5Cl]Cl_2$ [61], $[Co(NH_3)_5(NCS)](SCN)_2$ [61], $[Co(phen)_2C_2O_4]\text{-}I\cdot H_2O$ [62], $[Co(NH_3)_5Br]Cl_2$ [61], $K[Co(en)(C_2O_4)_2]$ [63], and $[Co(NH_3)_5H_2O]X_3$ ($X = Cl, Br, I$) [28]. Photo-induced isotopic exchange between Co(III) complexes and cobalt(II) has also been investigated recently[64].

(v) Miscellaneous

Beacom[52] observed color changes on irradiation of a large number of solid transition metal coordination compounds with ultraviolet light. Many of these were undoubtedly oxidation–reduction reactions; unfortunately, however, the stoichiometries of most of the reactions were not determined. The compounds, $K_3[Co(mal)_3]\cdot 3H_2O$, has been observed to change from a green to a brown color on irradiation with ultraviolet light[65]. It has been established that at least some of the cobalt(III) is reduced during the reaction. The reaction stoichiometry, however, has not been established.

The iron(III) complexes, $H[Fe(H_2O)(EDTA)]$ [23,24], $H_2[Fe(DTPA)]$ [23,24], ferric ammonium citrate[66], and several others[67] have been observed to undergo solid-state photochemical reactions which probably involve oxidation–reduction. The tungsten and molybdenum complexes $K_3[Mo(CN)_8]$ [68], $K_4[W(CN)_8]$ [68], $K_3[Mo(CN)_8]$ [69], $K_3[W(CN)_8]\cdot 2H_2O$ [70,71] and $H_3[W(CN)_8]\cdot 6H_2O$ [70,71], were also found to be photosensitive in the solid state. Of the silver and gold coordination compounds, the following have been observed to undergo photochemical oxidation–reduction reactions. $Co[Ag_4(S_2O_3)_5]\cdot nH_2O$ [72], $[Ag(2\text{-phenylisophosphinol})_2]NO_3$ [73], $[(AgX)_2en]$ ($X = Cl, Br, I$) [74], $[Au(CNCH_3)_2]ClO_4$ [75], $AuP(C_6H_5)_3N_3$ [76], and $[As(C_6H_5)_4][Au(N_3)_4]$[77].

In studies connected with the phototropism of solids, certain polymolybdates and tungstates doped with titanium oxide have been found to undergo photochemical oxidation–reduction reactions[78]. However, since phototropism has previously been reviewed[79], this area will not be covered here.

E. LIGAND SUBSTITUTION REACTIONS

(i) Chromium(III) ammine complexes

The decoloration of the complexes, $[Cr(en)_3]X_3$ ($X = Cl, Br, SCN$), on exposure to visible light has been observed[52,80]. More recently, the reaction stoichiometries have been determined by the use of reflectance measurements[25] and found to follow the equations

$$[Cr(en)_3]X_3 \xrightarrow{h\nu} cis\text{-}[Cr(en)_2X_2]X + en (X = Cl, Br) \tag{22}$$

and

$$[Cr(en)_3](SCN)_3 \xrightarrow{h\nu} trans\text{-}[Cr(en)_2(SCN)_2]SCN + en \tag{23}$$

The corresponding iodine compound did not undergo a photochemical ligand substitution reaction under visible light. The susceptibility toward reaction was found to be $SCN \gg Cl > Br$, which is the same as the order of these ligands in the spectrochemical series. Probably, in the case of the SCN complex, steric hindrance prevents the formation of the *cis*-compounds; the more stable *trans*-compound is therefore formed. The complexes, $[Cr(NH_3)_5H_2O]Br_3$ [81], $[Cr(NH_3)_5H_2O]_2(SO_4)_3 \cdot 3H_2O$ [81], $[Cr(NH_3)_6]X_3$ [82,83], and $[Cr(pn)_3]Cl_3$ [83] have been observed to undergo solid-state photochemical reactions which probably involve ligand substitution

(ii) Nitro–nitrito isomerization

On irradiation of the solid complexes, $[Co(NH_3)_5NO_2]X_2$ ($X = Cl, Br, NO_3$) Beacom[52] observed a change in color. By the use of reflectance measurements, Wendlandt and Woodlock[27] found that this color change was due to the isomerization reaction

$$[Co(NH_3)_5NO_2]X_2 \xrightarrow{h\nu} [Co(NH_3)_5ONO]X_2 \tag{24}$$

The compounds, $[Co(NH_3)_3(NO_2)_3]$, *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$ and *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ did not undergo photochemical isomerization reactions[27].

The complex, *trans*-$[Co(en)_2(SCN)(NO_2)]ClO_4$, was observed to undergo a photochemical reaction in the solid state which was assumed to be a nitro–nitrito isomerization reaction[84]. Similarly, the complexes, $[Co(NH_3)_5(NO_2)](C_2O_4)_2$ [84,85] and $[Ir(NH_3)_5(NO_2)]Cl_2$ [86] undergo linkage isomerization reactions on irradiation with ultraviolet light. The thermal nitrito–nitro isomerization reaction of $[Pt(NH_3)_5ONO]Cl_3$ was found to be accelerated by irradiation with 254 and 313 nm radiation[87]

F. COMPARISON WITH SOLID-STATE THERMAL AND PHOTOCHEMICAL REACTIONS

Several transition-metal coordination compounds have been observed to undergo similar thermal and photochemical reactions. For example, the compounds, $K_3[M(C_2O_4)_3] \cdot 3H_2O$ ($M = Co, Mn, Fe$), all undergo thermal oxidation–reduction reactions which, except for the cobalt compound, have stoichiometries identical to the corresponding photochemical reactions[16,19,26]. For the cobalt(III) compound, water enters the thermal reaction but not the photochemical reaction Probably, since water is evolved concurrently with the thermal reaction, unbound water is available for reaction. It has been observed that the rate of the photochemical reactions of the three compounds under continuous ultraviolet light could be correlated with the thermal reaction temperatures[88]. This is shown in Table 2. The relative order of the rates of the photochemical reactions is the same as the order of the instability of the trivalent oxidation state of the central metal ion. The corresponding chromium(III) compound undergoes neither a thermal nor a photochemical oxidation–reduction reaction involving the formation of Cr(II).

TABLE 2

Comparison of the susceptibility of some metal complexes toward photochemical reactions with the thermal reaction temperatures

Oxidation–reduction reactions of some tris(oxalato) metal complexes[88]

Relative rates of the photochemical reactions	$K_3[Mn(C_2O_4)_3]\cdot 3H_2O >$	$K_3[Co(C_2O_4)_3]\cdot 3H_2O >$	$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$
Thermal reaction temperature (°C)	85	120	~ 300

Ligand substitution reactions of some tris(ethylenediamine) chromium(III) complexes[25]

Complex	*Number of discharges beyond which no change could be noticed*	*Reaction temperature (°C)*
$[Cr(en)_3](SCN)_3$	50	130
$[Cr(en)_3]Cl_3$	430	210
$[Cr(en)_3]Br_3$	850	

Similar correlations were observed between the thermal and the photochemical reactions of the complexes, $[Cr(en)_3]X_3$ (X = Cl, Br, SCN), in the solid state[25]. Table 2 gives the number of flashes of a high-intensity flash lamp beyond which no noticeable color change was observed. The thermal reaction temperatures are also given. The compound, $[Cr(en)_2Br_2]Br$, was not observed as a product of the thermal reaction of the bromide compound, a competing oxidation–reduction reaction was thought to be the cause of this anomaly.

It is reasonable to assume that, in most cases, the mechanisms of the thermal and photochemical reactions are the same, except for the method of excitation. An exception is the nitro–nitrito isomerization reactions of $[Co(NH_3)_5NO_2]X_2$ (X = Cl, Br, NO_3) which undergo the reverse of eq. (24) when heated[27].

$$[Co(NH_3)_5NO_2]X_2 \underset{\text{heat}}{\overset{h\nu}{\rightleftharpoons}} [Co(NH_3)_5ONO]X_2 \qquad (25)$$

Most likely, the nitrito isomer is statistically favored (there are two oxygen ligands and one nitrogen ligand on an NO_2^- ion) while the nitro isomer is thermodynamically favored. Thus, when a cobalt—nitro bond is photochemically dissociated at room temperature, the reformation of a cobalt—nitrito bond is statistically favored. At higher temperatures, however, when the cobalt—nitrito bond is thermally dissociated, the reformation of the thermodynamically more stable bond is favored.

G CONCLUDING REMARKS

It is encouraging to note that there has been a sharp increase in the number of quantitative investigations dealing with the solid-state photochemistry of transition-metal coordination compounds during the past several years. This increase has been accompanied by an increase in the attention paid to theoretical problems connected with solid-state photochemical reactions. As yet, however, there is insufficient information to suggest important generalizations concerning the solid-state photochemistry of transition-metal complexes. Only a few reaction mechanisms have been reasonably well determined However, it is safe to say that the solid-state photochemistry of transition-metal coordination compounds certainly differs from the aqueous solution photochemistry as far as reaction mechanisms are concerned in three major aspects These are (1) water molecules are usually not available to enter the coordination sphere or to stabilize certain reaction intermediates, (2) ions and molecules are closer together, and (3) translational and rotational motions are restricted. These differences must be taken into account in the postulation of reaction mechanisms

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