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THE APPLICATION OF DIFFUSE REFLECTANCE SPECTROSCOPY TO THE CHEMISTRY OF TRANSITION METAL COORDINATION COMPOUNDS

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CONTENTS

A. INTRODUCTION

Accurate measurements of the diffuse reflectance spectra of materials were first made in the 1920's. Since that time, there has been considerable advancement in the instrumentation and the theory of diffuse reflectance spectroscopy. With these advances, there has been a broadening of the uses of the technique in a number of fields. Since most transition metal coordination compounds have unique visible and ultraviolet spectra, diffuse reflectance spectroscopy has proven an especially useful technique in the study of their solid-state chemical properties.

Diffuse reflectance spectroscopy has been used primarily to study four areas of the chemistry of solid transition metal coordination compounds. These are spectral properties, solid-state thermal reactions, solid-state photochemical reactions, and analytical applications. The use of diffuse reflectance spectroscopy to determine the spectral properties of solid transition metal coordination compounds is especially useful since many of the compounds are most conveniently obtained in the powdered form. Reflectance spectroscopy is also one of the most important tools available for studying solid-state thermal and photochemical reactions of coloured powders.

The purpose of this review is to summarize the work that has been done in the application of diffuse reflectance spectroscopy to the four previously mentioned areas of the chemistry of transition metal coordination compounds. Since the experimental techniques and the theories of diffuse reflectance spectroscopy have been reviewed in detail[1—3], these areas are only briefly summarized here.

B . EXPERIMENTAL METHODS

Probably the first instrument designed for reflectance studies was that described by Nutting[4,5] in 1912. Since that time, a large number of reflectance instruments have been described[1,2]. Today, highly sophisticated recording diffuse reflectance spectrometers which will cover any spectral range from the near-infrared to the ultraviolet are commercially available.

The only basic components necessary for a reflectance spectrometer are (*i*) a light source and means of obtaining monochromatic radiation, (*ii*) an integrating sphere, and (*iii*) a detection and recording system. The integrating sphere, the theory of which has been described[1], was introduced into the field of spectrophotometry[6] in 1900. It generally consists of a spherical enclosure, the interior surface of which is coated with a substance such as, for example, magnesium oxide, which diffusely reflects almost 100% of incident radiation. The reflectance of a sample is usually obtained in relation to a reference material which reflects almost 100% of incident radiation. Such reference materials are magnesium carbonate, magnesium oxide, and other white powders.

Instrumental modifications of reflectance spectrometers have been made to allow the reflectance of materials to be obtained at elevated temperatures[7—11]. Two types of high-temperature reflectance spectroscopy methods have been distinguished; these are a static-temperature method by which the spectrum of a sample can be obtained at a fixed elevated temperature, and a dynamic-temperature method (DRS) by which the change in the reflectance of a sample at a fixed wavelength can be observed as the temperature is linearly increased. The dynamic reflectance technique is especially important in detecting and following the progress of solid-state thermal reactions. High-temperature reflectance sample holders have been described for which the sample atmosphere can be controlled[12,13] and a combined high-temperature reflectance—gas evolution detection technique has been reported[14].

C. THEORETICAL CONSIDERATIONS

(i) Reflectance theories

There have been four major approaches to the theory of reflectance spectroscopy[1–3]. The approaches are (*i*) the integral equation method, (*ii*) the differential equation method, (*iii*) the statistical parallel plate method, and (*iv*) the statistical single particle method. These methods differ mainly in the model used to represent a powdered sample.

The integral equation method was first introduced by Schuster[15] and was further developed by Jackson[16] and King[17]. The method consists of a very general formulation of the scattering of light through a diffusing medium, which is a special case of the fundamental formulation of radiative transfer. Although a few authors have applied the equations obtained by the integral equation method[18,19] the method has met with very little success because of the complicated equations obtained and the simplifying assumptions necessary for their use.

The differential equation method is by far the most commonly used approach to the theory of reflectance spectroscopy. Although a large number of authors have derived equations using the method[1], the general theory is generally referred to as the Kubelka—Munk theory[20]. In the theory, a powdered sample is treated as a continuous medium and two arbitrary constants are introduced to account for the absorption and the scattering of radiation by the medium. The two differential equations obtained to describe the change in the radiation intensity in a sample with respect to depth, x, into the sample are

$$dI/dx = -(k+s)I + sJ \tag{1}$$

and

$$dJ/dx = (k+s)J - sI \tag{2}$$

where I is the radiation intensity in the downward direction, J the radiation intensity in the upward direction, and k and s are the arbitrary constants absorption coefficient and scattering coefficient, respectively. These constants are not related to the fundamental optical parameters in the Kubelka—Munk theory although k is sometimes equated with the true absorption coefficient as defined through the Beer—Lambert law. Solutions to eqs. (1) and (2) for a large number of boundary conditions have been obtained and tabulated by Kubelka[21]. The solution mainly of interest is that for an infinitely thick powdered sample, which is applicable to most samples encountered in practice. For this case, the reflectance, R, is given by

$$R = \frac{1 - (k/(k+2s))^{\frac{1}{2}}}{1 + (k/(k+2s))^{\frac{1}{2}}} \tag{3}$$

which may be rearranged to give the widely used remission function, f(R),

$$f(R) = k/s = (1 - R)^2/2R \tag{4}$$

Hence, if k is identified with the true absorption coefficient, then f(R) is proportional to it[22].

In the statistical parallel plate approach to the theory of reflectance spectroscopy, a powdered sample is considered to be a collection of parallel plates with a thickness equal to the average particle diameter. This model has been employed by a number of authors[1,23—26]. Although the equations obtained using the statistical parallel plate approach are cumbersome, they are apparently applicable although they are not nearly so widely used as the Kubelka—Munk equations.

Probably the most satisfactory approach to the theory of reflectance spectroscopy is the statistical single particle theory. In this theory, a powdered sample is considered to be a collection of uniformly sized rough-surfaced spherical particles. The theory is based upon two fundamental equations (the Beer—Lambert equation and the Fresnel equation) and the phenomenological, but widely accepted, Lambert cosine law. The equations obtained by Melamed[27] for the reflectance of a powdered sample based on the particle model are apparently successful in relating the reflectance to two fundamental optical parameters, namely the absorption coefficient and the relative index of refraction, and the average particle diameter. The equations are, however, cumbersome and require lengthy calculations or the use of a computer for the calculation of reflectance values. Using the same model, an extremely simple approximate equation for the reflectance of a weakly absorbing powdered sample was obtained[28]. This equation is

$$R = \exp\left(-2\eta(kd/3)^{\frac{1}{2}}\right) \tag{5}$$

where η is the relative index of refraction, k the true absorption coefficient, and d the average particle diameter. Although several assumptions and approximations were made in the derivation of eqn. (5), it appears to be in agreement with experiment for the reflectance values of powdered didymium glass[28] and has subsequently been applied to other reflectance problems[29,30].

(ii) Spectra

The two most important types of absorption bands of transition metal coordination compounds in the visible and ultraviolet spectral regions are those due to charge transfer between the metal ion and ligands and those due to d—d (or f—f) transitions. Reflectance spectroscopy is especially important in identifying absorption bands since the spectra of some compounds differ in the solid state and in solution because of solvent interactions[31]. Therefore any reaction of the solvent with a solute can usually be detected by comparing the diffuse reflectance spectrum of the pure solid with the spectrum of the solid dissolved in the solvent.

From the positions of absorption bands arising from d—d transitions, the ligand field splitting parameter, Dq, and the Racah parameter, B, can be calculated[32,33]. From these values, the value of the nephelauxetic ratio, $\beta = B$ (complex)/B(free ion), can be calculated. The parameter β is of considerable interest in the chemistry of coordination compounds because it gives information concerning the degree of covalency in a metal—ligand bond. According to Jørgensen[34], for the spectrochemical series

$$Dq = f(\text{ligands}) \cdot g(\text{ion}) \tag{6}$$

and for the nephelauxetic series,

$$1 - \beta = h(\text{ligands}) \cdot k(\text{ion}) \tag{7}$$

where f and h depend only upon the ligands and g and k depend only on the central metal ion.

Absorption coefficients values for absorption bands can be calculated from reflectance values by the use of equations obtained by the Kubelka—Munk theory[1,2] or by the particle model theory[35]. From absorption coefficients obtained at different wavelengths, the integrated absorption coefficient can be determined.

(iii) Photochemical reaction rates

Reflectance spectroscopy is a particularly useful tool for following the extent of photochemical reactions of powdered coordination compounds[36]. Qualitatively, the technique may be used to identify photoproducts. Also, for more quantitative applications, the technique may be used to determine quantum yield values by obtaining the reflectance spectrum of a sample undergoing a photochemical reaction at various reaction times[36].

Spencer and Schmidt[37] derived an equation describing the rate of the photochemical reaction of an opaque powdered layer by assuming that a definite boundary exists between the photoproduct layer and the reactant. The equations obtained do not relate the reaction rate to the sample reflectance but reflectance measurements were used to determine the amount of radiation absorbed by the sample.

An equation has been derived which describes the rate of the photochemical reaction of a thin, weakly absorbing powdered layer in terms of the reflectance and transmittance of the layer[38]. The equations used are

$$\mathrm{d}C_\mathrm{A}/\mathrm{d}t = -\phi I \alpha_\mathrm{A} C_\mathrm{A} \tag{8}$$

and

$$1 - T - R = \alpha_\mathrm{A} C_\mathrm{A} + \alpha_\mathrm{P} C_\mathrm{P} \tag{9}$$

where R is the layer reflectance, T the layer transmittance, C the concentration in mole.cm^{-2}, α the phenomenological absorption coefficient, and A and P refer to the reactant and the product respectively. The assumption was made that the layer is sufficiently thin for the radiation intensity to be considered as uniform throughout the sample. Equations (8) and (9) can be combined to give

$$\mathrm{d}\ln(T_\mathrm{P}+R_\mathrm{P}-R-T)/\mathrm{d}t = -(1-T_\mathrm{A}-R_\mathrm{A})\,\phi I/C_0' \tag{10}$$

where C_0 is the initial reactant concentration. Equation (10) can therefore be used to determine the value of the quantum yield from the slope of a plot of $\ln(T_\mathrm{P}+R_\mathrm{P}-R-T)$ vs. t. The phenomenological absorption coefficient, α, has been related to the fundamental optical parameters by the use of the rough-surfaced spherical particle model and is given by[39]

$$\alpha = \eta^2\,\epsilon \tag{11}$$

where ϵ is the absorption coefficient defined through Beer's law and η the index of refraction.

An equation describing the rate of the photochemical reaction of a bulk powdered sample has also been derived on the basis of the rough-surfaced spherical particle model and, for weakly absorbing powders with transparent photoproducts, is[40]

$$\mathrm{d}\,f(R)/\mathrm{d}t = \phi\epsilon\eta^2 I_0 \tag{12}$$

where I_0 is the radiation intensity at the sample surface and

$$\mathrm{f}(R) = R/(1+R^2) + \tan^{-1}R \tag{13}$$

Equations (12) and (13) can be used to determine ϕ from reflectance measurements of a powder during photochemical reaction.

D. SPECTRAL PROPERTIES

(i) Absorption bands

A large number of studies of the diffuse reflectance spectra of transition metal coordination compounds have been made in terms of the ligand field theory[31,32,35,41—58]. Some examples of these numerous studies are briefly discussed here.

The diffuse reflectance of a number of transition metal halides with electronic configurations, d^0—d^6, have been obtained[32] and were analyzed by first-order perturbation theory. For VCl_2, the values of $Dq = 900\ \mathrm{cm}^{-1}$ and $B = 606\ \mathrm{cm}^{-1}$ were obtained. A value of $\beta = 0.8$ was calculated. Comparing this value with that for $V(H_2O)_6{}^{2+}$ obtained from solution spectra illustrates that the ligand field strength of Cl^- is about 73% of that of water[32] and that the degree of covalency of the metal—chlorine bond is greater than that of the metal—oxygen bond.

The observation that the diffuse reflectance spectrum of $CrCl_3$ is almost identical to the solution spectrum of $CrCl_6{}^{3-}$ indicates that the ligand field strength of a terminal chlorine ion must be similar to that of a bridging chlorine ion[32]. Also, the values of Dq for various halide ions parallel those for water for a number of electronic configurations[32].

The reflectance spectra of a number of Cr^{5+} compounds have been analyzed and the ligand field parameters calculated[55,56]. From these values, the expressions $Dq = 1740\ f\ \text{cm}^{-1}$ and $B = 918-193\ h\ \text{cm}^{-1}$ were determined.

The reflectance spectra of two forms of manganese(II)sulphide have been studied[59]. The octahedrally coordinated form is green and the tetrahedrally coordinated form is red. Perturbation calculations give the ratio of the ligand field parameters as $Dq/Dq_0 = -4/9$. This indicates that Mn^{2+} exhibits a greater energy difference for the splitting terms ${}^4A$, ${}^4E$, ${}^4T_1$ and ${}^4T_2$ derived from the ${}^4G$ term of the free Mn^{2+} ion for the octahedral structure than for the tetrahedral form.

One of the problems encountered in obtaining absorption band positions from diffuse reflectance spectra is that often the resolution is low. This problem has been overcome in a number of studies by obtaining the reflectance spectra at very low temperatures. Decreasing the temperature increases the spectral resolution considerably[32,45,46,53].

(ii) Effects of dilution and particle size

Two other methods are often used for increasing the resolution of diffuse reflectance spectra; these are to decrease the particle size or to dilute a strongly absorbing material with a non-absorbing diluent. It has been found[50], for example, that decreasing the particle size of powdered $K_3(Fe(CN)_6)$ dramatically increased the resolution of the spectral peaks. It was suggested that the very low resolution for large particle samples was due to a large component of surface (specular) reflection and to strong damping of electronic vibrations assumed by the dispersion theory. Spectra of samples with extremely small particle sizes (less than one μm) were, however, more poorly resolved than those for samples with particle sizes of 1 to 2 μm. This was thought to be due to effects caused by the particle sizes being comparable to the wavelength of light[60].

It has been found that for samples consisting of a 0.17 mole% potassium permanganate in potassium perchlorate (a solid solution), as the particle size was decreased the reflectance increased[45]. This was thought to be due to a decrease in the depth of penetration into the sample by the light for decreasing particle size. These results were compared with those for pure potassium permanganate and some remarkable differences were observed. The apparent absorbances of pure potassium permanganate samples were not much greater than those for the solid solutions despite the 500-fold difference in concentration. This indicates that the depth of penetration of light into the solid solution sample is much greater than for pure potassium permanganate samples. Also, for pure potassium permanganate samples, there was a decrease in reflectance with a decrease in particle size.

E. SOLID-STATE THERMAL REACTIONS

(i) Ammines

The thermal decomposition of a large number of transition metal ammine compounds has been studied by the techniques of high temperature reflectance spectroscopy and dynamic reflectance spectroscopy. Among these are $(Co(NH_3)_5H_2O)X_3$ (X = Cl,Br) (refs. 8, 14), $Cu(en)(H_2O)_2SO_4$ (ref. 9), $(Co(NH_3)_4(H_2O)_2)Br_3$ (ref. 61), $Co(py)_2Cl_2$ (refs. 62, 63), $Ni(py)_4Cl_2$ (ref. 11), $(Co(NH_3)_6)Cl_3$ (ref. 64), $(Co(NH_3)_6)Br_3$ (ref. 65), and $(Cr(en)_3)X_3$ (X = a large number of anions) (ref. 66). By the use of the reflectance techniques, the reaction products were identified and the reaction temperatures were determined.

The reactions of all of the aquo ammine compounds involved an initial reaction in which an outer-sphere anion replaced the water molecule(s) in the inner coordination sphere. The reactions of the $(Cr(en)_3)X_3$ compounds involved the replacement of an en group by two outer-sphere anions. The compound, $Co(py)_2Cl_2$, undergoes a transformation from an α form to a β form, the former being a violet compound consisting of polymeric chains with the cobalt ion octahedrally coordinated and the latter a blue compound consisting of tetrahedrally coordinated cobalt ions. If the α form is heated over 110°C, it is converted to the β form. Figure 1 illustrates a dynamic reflectance spectroscopy curve at 625 nm. As can be seen, the $\alpha \rightarrow \beta$ transition began at over 100°C and was completed at about 135°C. The compound, $Ni(py)_4Cl_2$, was found from high-temperature reflectance spectra to undergo the reactions

$$Ni(py)_4Cl_2 \rightarrow Ni(py)_2Cl_2 \rightarrow Ni(py)Cl_2 \rightarrow NiCl_2 \qquad (14)$$

The use of high-temperature reflectance spectroscopy allowed the identification of reaction intermediates in the solid-state thermal reactions of

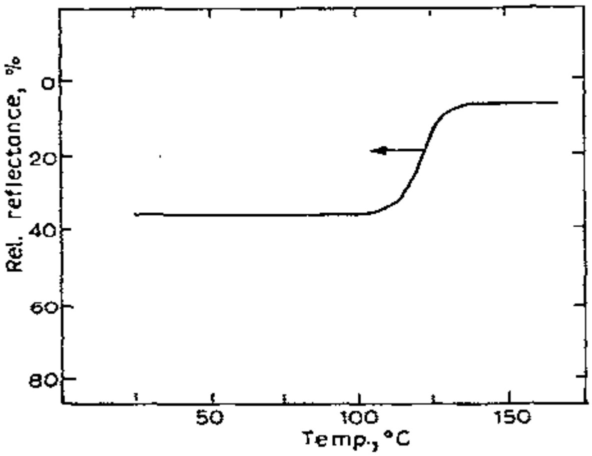
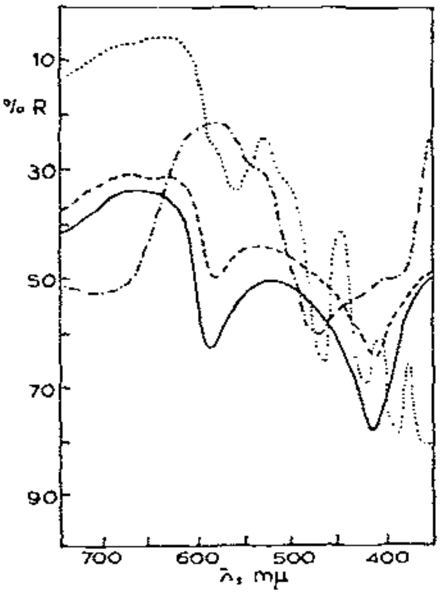


Fig. 1. The dynamic reflectance spectrum of $Co(py)_2Cl_2$ (ref. 62). Heating rate, 2°C/min.



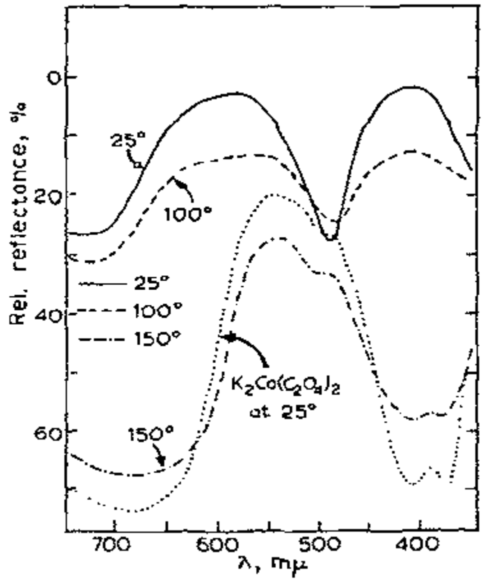


Fig. 2. High-temperature reflectance spectra of $(Co(NH_3)_6)Cl_3$ and reflectance spectra of intermediate compounds[59]. (------) $CoCl_2$; (· · · ·) $(NH_4)_2(CoCl_4)$; (· - ·) 1 : 1 mixture $CoCl_2$ — $(NH_4)_2(CoCl_4)$; (——) decomposition products of $(Co(NH_3)_6)Cl_3$ at 225°C.

Fig. 3. High-temperature reflectance spectra of $K_3(Co(C_2O_4)_3).3H_2O$ and the reflectance spectrum of $K_2(Co(C_2O_4)_2)$[67].

$(Co(NH_3)_6)Cl_3$ (ref. 59) and $(Co(NH_3)_6)Br_3$ (ref. 60). The reactions were found to proceed by the equations

$$6\,(Co(NH_3)_6)X_3 \rightarrow 3\,CoX_2 + 3\,(NH_4)_2(CoX_4) + N_2 + 28\,NH_3 \tag{15}$$

where X = Cl, Br, followed at higher temperatures by

$$3\,(NH_4)_2\,(CoX_4) \rightarrow 6\,NH_4X + 3\,CoX_2 \tag{16}$$

Figure 2 illustrates how the intermediates, $(NH_4)_2(CoX_4) + CoCl_2$, were identified from the high-temperature reflectance spectra.

(ii) Oxalates

High-temperature reflectance spectroscopy has been used to determine the stoichiometries of the solid-state thermal oxidation—reduction reactions of $K_3(Co(C_2O_4)_3).\,3H_2O$ (ref. 67) and $K_3(Mn(C_2O_4)_3).\,3H_2O$ (ref. 68). Figure 3 illustrates the high-temperature reflectance spectra of the cobalt compound along with the spectrum of $K_2(Co(C_2O_4)_2)$, which was identified as a reactant. Figure 4 illustrates similar curves for $K_3(Mn(C_2O_4)_3).\,3H_2O$. From the reflectance data along with chemical analytical data, the reaction stoichiometries

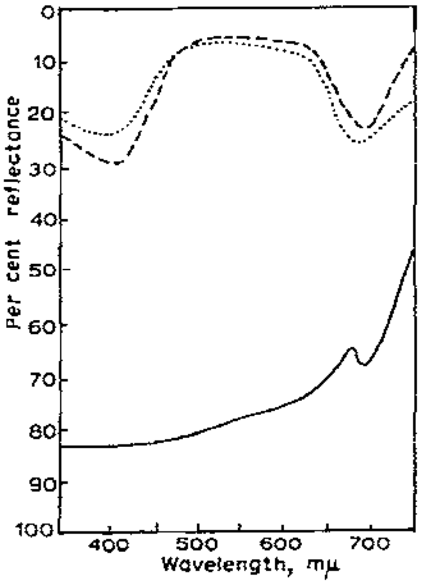


Fig. 4. High-temperature reflectance spectra of $K_3(Mn(C_2O_3)_3).3H_2O$. (- - -) 25°C, (· · · ·) 75°C, (——) 100°C.

$$2\,K_3(Co(C_2O_4)_3).3H_2O \rightarrow 2\,K_2(Co(C_2O_4)_2) + KHCO_3 + KHC_2O_4 + CO_2 + 5\,H_2O \quad (17)$$

and

$$2\,K_3\,(Mn(C_2O_4)_3)\,.\,3H_2O \rightarrow 2\,K_2(Mn(C_2O_4)_2) + K_2C_2O_4 + 2\,CO_2 + 6\,H_2O \quad (18)$$

were found.

(iii) Halides and hydrates

Solid-state thermal reactions of several halide and hydrate transition metal coordination compounds have been studied by the use of high-temperature and dynamic reflectance spectroscopy. Among these are $CoBr_2.6H_2O$ (ref. 9), $CoCl_2.6H_2O$ (ref. 69), $Cu\,SO_4.5H_2O$ (ref. 16), and the series of compounds which undergo thermochromic transformations (ref. 70), $Cu_2(HgI_4)$, $Ag_2(HgI_4)$ $Tl(HgI_4)$, $Pb(HgI_4)$, and $Hg(HgI_4)$. The high-temperature and dynamic reflectance techniques proved especially useful for studying the thermochromic behaviour of the latter compounds since they undergo dramatic colour changes at elevated temperatures. The reactions appear to be reversible if the compounds are cooled and allowed to stand at room temperature.

The cobalt halide hydrates undergo thermal dehydration reaction at elevated temperatures which involve a number of intermediates. For $Co(H_2O)_6Cl_2$, the reaction scheme[69]

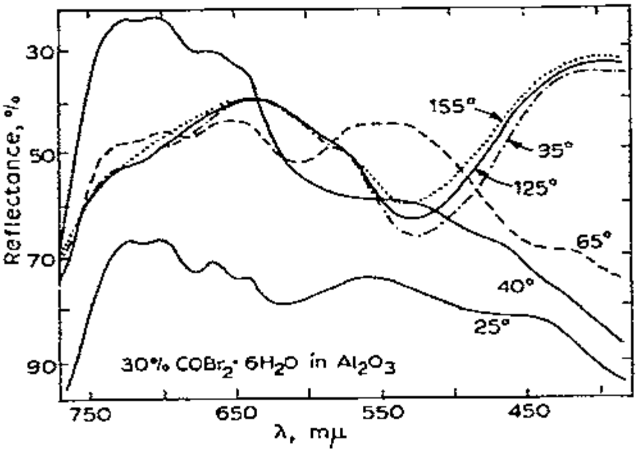


Fig. 5. Reflectance spectra of the intermediates found during the deaquation of $CoBr.6H_2O$ (ref. 9).

$$CoCl_2.6H_2O \text{ (octahedral)} \rightarrow CoCl_4^{2-} \text{ (tetrahedral)} \rightarrow$$

$$CoCl_2.2H_2O \text{ (octahedral)} \rightarrow CoCl_4^{2-} \text{ (tetrahedral)} \qquad (19)$$

was determined. The reflectance spectra in Figure 5 illustrate the formation and dissociation of a number of intermediates formed during the thermal deaquation of $CoBr_2.6H_2O$ (ref. 9).

F. SOLID-STATE PHOTOCHEMICAL REACTIONS

(i) Oxalates and malonates

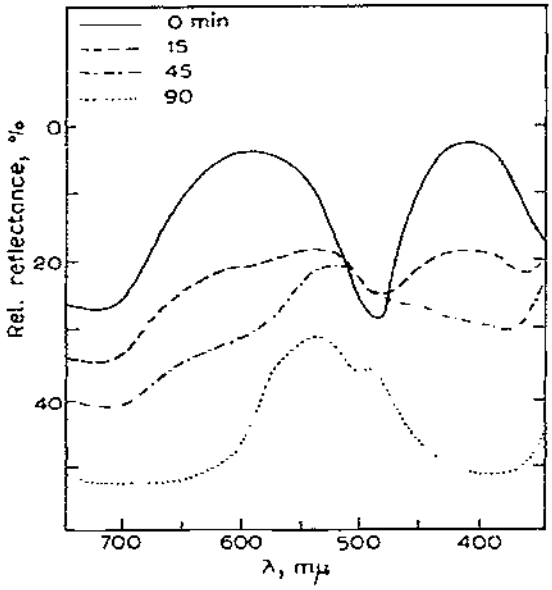
The solid-state photochemical reactions of the compounds, $K_3(M(C_2O_4)_3).3H_2O$ (M = Mn, Fe, Co) have been thoroughly investigated by the use of the technique of diffuse reflectance spectroscopy[36—40,67,68]. By the use of this and other techniques, the reaction stoichiometries of the reactions have been found to be[67,68,71]

$$2\,K_3(M(C_2O_4)_3).3H_2O \xrightarrow{h\nu} 2\,K_2(M(C_2O_4)_2) + K_2C_2O_4 + 2\,CO_2 + 6\,H_2O \qquad (20)$$

where M = Co, Mn and

$$2\,K_3(Fe(C_2O_4)_3).3H_2O \xrightarrow{h\nu} 2\,FeC_2O_4 + 3\,K_2C_2O_4 + 2\,CO_2 + 6\,H_2O \qquad (21)$$

The rate of the photochemical reactions of the compounds increased in the order Fe < Co < Mn, which is the same as the order of decreasing temperature of the thermal reactions of the compounds. Figure 6 illustrates the reflectance spectra of the cobalt compound after various lengths of time of



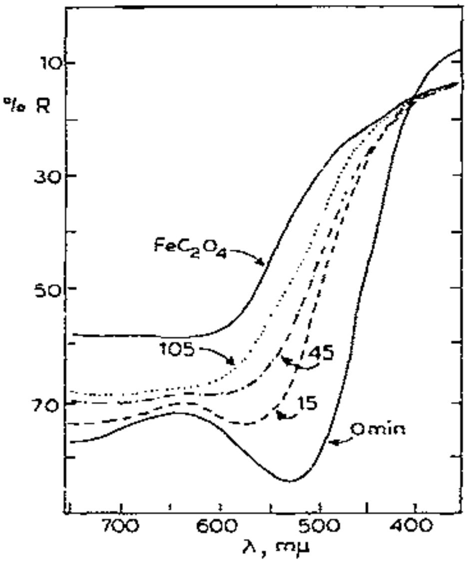


Fig. 6. Reflectance spectrum of $K_3(Co(C_2O_4)_3).3H_2O$ after various lengths of time of exposure to ultraviolet radiation[67].

Fig. 7. Reflectance spectrum of $K_3(Fe(C_2O_4)_3).3H_2O$ after various lengths of time of exposure to ultraviolet radiation[71]:

exposure to ultraviolet radiation. Figure 7 illustrates the corresponding spectra for the iron compound. From each spectrum, some of the reaction products were identified.

The quantum yields for the solid-state reactions of the iron, cobalt, and manganese oxalate compounds have been measured by the use of reflectance measurements of thin powdered layers during photochemical reactions. The values obtained were: $K_3(Fe(C_2O_4)_3).3H_2O$, $\phi = 0.07-0.20$ mole/einstein (ref. 37); $K_3(Co(C_2O_4)_3).3H_2O$, $\phi = 0.1-0.6$ mole/einstein (ref. 37); and $K_3(Mn(C_2O_4)_3).3H_2O$, $\phi = 0.4-0.6$ mole/einstein (ref. 38). These values were obtained over a range of radiation wavelengths for the first two compounds and at 350 nm and 400 nm for the latter compound.

The solid-state photochemical reactions of the complexes, $M(Mn(mal)_2(H_2O)_2).2H_2O$, $M(Mn(mal)_2(H_2O)_2)$ and $M(Mn(mal)_2)$ ($M = NH_4$, Na, K) have been investigated by the use of reflectance spectroscopy[72]. The reaction scheme observed was

$$M(Mn(mal)_2(H_2O)_2).2H_2O \xrightarrow{h\nu} M(Mn(mal)_2(H_2O)_2) \tag{22}$$

$$M(Mn(mal)_2(H_2O)_2) \xrightarrow{h\nu} M(Mn(mal)_2) \tag{23}$$

$$2\,M(Mn(mal)_2) \xrightarrow{h\nu} M\,mal + 2\,Mn\,mal + H_2O + 3\,CO \tag{24}$$

$$2\ MnC_3H_2O_4 + 2\ O_2 \xrightarrow{h\nu} 2\ MnCO_3 + CH_3COOH + 2\ CO_2 \qquad (25)$$

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.

(ii) Ammines

The reaction stoichiometries of the photochemical ligand substitution reactions of the solid complexes, $(Cr(en)_3)X_3$ (X = Cl, Br, SCN) have been determined with the help of reflectance spectroscopy[73] and were found to follow the equations

$$(Cr(en)_3)X_3 \xrightarrow{h\nu} cis\text{-}(Cr(en)_2X_2)X + en\ (X = Cl, Br) \qquad (26)$$

and

$$(Cr(en)_3)(SCN)_3 \xrightarrow{h\nu} trans\text{-}(Cr(en)_2(SCN)_2)SCN \qquad (27)$$

The corresponding iodine compound did not undergo a photochemical ligand substitution reaction. The order of the susceptibility toward reaction was found to be SCN $\gg$ Cl $>$ Br. In the case of the SCN compound, steric hindrance was thought to prevent the formation of the *cis*-complex.

On the ultraviolet irradiation of the solid complexes $(Co(NH_3)_5NO_2)X_2$ ($X = Cl, Br, NO_3$), colour changes occur which, by the use of reflectance spectroscopy, were found to be due to the following isomerization reactions[74].

$$(Co(NH_3)_5NO_2)X_2 \xrightarrow{h\nu} (Co(NH_3)_5ONO)X_2\ (X = Cl, Br, NO_3) \qquad (28)$$

When the nitrite isomer is heated it undergoes the reverse reaction to form the nitro isomer[74]. The compounds $(Co(NH_3)_3(NO_2)_3)$, *cis*-$(Co(NH_3)_4(NO_2)_2)$-NO_3, and *cis*- and *trans*-$(Co(en)_2(NO_2)_2)NO_3$ were found to undergo no photochemical isomerization reactions[74].

G. ANALYTICAL APPLICATIONS

Diffuse reflectance techniques have been reported by which concentrations of some transition metals in certain substances can be measured or their presence determined. A method has been described by which the concentrations of small amounts of copper as well as mercury and lead can be determined by precipitating the metals as their sulphides along with excess zinc and measuring the reflectance of the mixtures[75]. In another study[76], a method has been developed by which 0.01-μg quantities of nickel and manganese can be detected by the use of diffuse reflectance spectroscopy. The metal ions were concentrated by the use of cation-exchange paper and then the reflectance of the paper, which was treated with various reagents, was obtained.

A reflectance method for the determination of microgram quantities of copper, iron, and nickel has been reported[77]. The method involves obtaining the reflectance of the metal sulphides on filter paper. Plots of concentration vs. reflectance were linear curves provided great care was taken to maintain standard conditions. Reasons have been pointed out, however, for doubting the utility of this reflectance method of analysis[78,79]; it is very difficult to obtain a homogeneous distribution of material on paper fibre.

In another study[80], reflectance values of copper(II) oxide and iron(II) oxide in barium sulphate powdered mixtures were obtained. It was found that plots of log $(R-R_m)$, where R is the reflectance of the mixture and R_m the reflectance of the pure metal oxide, vs. the inverse of the concentrations of the oxides were linear for both metals. Hence, the method was applicable for analyses of the metal oxides.

A comprehensive investigation of the use of reflectance spectroscopy in the analyses of coloured substances on filter paper has been made[81]. Calibration curves for copper and iron were prepared and straight-line plots were obtained in the low concentration range (12—100 g/l).

H. DISCUSSION

It is clear that the applications of diffuse reflectance spectroscopy in the study of the chemistry of transition metal coordination compounds have increased rapidly, especially in recent years. This increase is undoubtedly mainly due to instrumental developments for the technique. The main drawback at present in the field of reflectance spectroscopy is that many of the applications of the technique are necessarily of a qualitative nature. Because of the extremely complicated nature of the interaction of light with a powdered sample, the development of the theory of diffuse reflectance spectroscopy has lagged behind the development of its applications. What is needed for the applications of diffuse reflectance spectroscopy to become more quantitative is the development of a rigorously proven theory which will allow the diffuse reflectance to be related to the fundamental optical parameters. Such a theory would allow the calculation of reliable absorption coefficient and integrated band intensity values from reflectance measurements.

In conclusion, the technique of diffuse reflectance spectroscopy is especially important to the study of transition metal compounds because the chemistry of the solid state is not nearly as well understood for the compounds as their aqueous solution chemistry, and reflectance techniques are among the most important of the methods available for studying solid-state chemical reactions.

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