

KINETIC MODELS IN SOLID STATE PHOTOCHEMISTRY: THEIR VALIDITY AND INTERPRETATION IN THE CASE OF URANYL FORMATE MONOHYDRATE

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Summary

Three models interpreting the kinetics of solid state photodecomposition have been applied to the decomposition of uranyl formate monohydrate. The first two consider the absorption of light by the photoproduct layer. The better of the two allows the effective quantum yields of photodecomposition and fluorescence to be calculated from their respective apparent values. These two models, however, are valid only as long as the primary photoproduct (uranium V) has not been transformed into uranium IV. When longer irradiation times are used, the diffusion of the gaseous product CO_2 in the photoproduct layer has to be considered. This third model shows that CO_2 must be considered as a kinetic inhibitor of the photochemical step.

Introduction

There has been a renewal of interest in the photochemistry of inorganic solids owing to its numerous applications to non-conventional imaging techniques. Its study, however, comes up against many difficulties because of the heterogeneous character of the reaction. On the one hand, the solid products generally absorb light and therefore reduce the extent of reaction even for large exposure times. Therefore, their characterization by conventional analytical methods is not easy. They do not usually give any X-ray diffraction pattern, and techniques such as infrared spectroscopy [1], diffuse reflection spectroscopy [2] and Mössbauer spectroscopy [3] have been used for the identification of these solid products. On the other hand, when gaseous products are formed they have to diffuse out through the layer of solid photoproducts. Owing to the fact that the porosity of the starting material is only slightly modified by photodecomposition at room temperature, the diffusion coefficient of the gaseous products remains low as does the rate of their appearance in the reaction vessel [4].

For these reasons the true quantum yield of solid state photoreactions, *i.e.* the number of moles of photoproduct per absorbed einstein, has to be determined in the initial conditions. Though irreproachable in principle, this method is none the less awkward to apply since it is necessary to collect experimental data in the domain of maximum uncertainty.

This is why some models have been developed in recent years to determine the quantum yield from experiments of longer duration. Our purpose in the present work is to apply some of these models to the photodecomposition of uranyl formate monohydrate, the experimental study of which has already been reported [5, 6]. We shall discuss the validity of these models bearing in mind the well-known fact in chemical kinetics that checking an equation derived from a given model does not suffice to establish its general validity. Therefore the maximum of experimental information has to be gathered on the intermediate steps and species involved in the model [7]. Moreover, the greater its range of applicability, the greater is its likelihood.

We have not considered the model recently proposed by Simmons [8] in spite of its theoretical interest, since it assumes that the absorption coefficients of the reactant and of the photoproducts when the latter are absorbing are known. In the present case, these coefficients were not known. Moreover, this model relies on measurement of the transmittance of a solid layer, which is difficult and not easily reproducible.

The Spencer and Schmidt model

The Spencer and Schmidt model (SSM) [9] considers the limitations on the reaction because of the absorption of light by the photoproducts. These are assumed to build up a plane layer, the thickness of which at time t is l ($l = 0$ at $t = 0$). The light intensity reaching the unreacted material is then, according to Beer's law,

$$I = I_0 \exp(-kl)$$

where k is the linear absorption coefficient of the photoproducts at the wavelength used. (It should be noted that no light reflection is considered in this model.) If φ is the quantum yield, σ the number of species formed per unit surface and ρ the number of species formed per unit volume, the application of the SSM leads to

$$\sigma = \frac{\rho}{k} \ln \left(1 + \frac{k\varphi}{\rho} I_0 t \right) \quad (1)$$

The SSM has been applied to the photodecomposition of $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ [9] and $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ [10]. Its interest lies in the quantum yield determination. A computer curve fitting of the experimental data allows us to determine φ and k . The advantage of the method is a statistical one, its disadvantage is that it is insensitive to the intervention of secondary reactions.

Application to uranyl formate monohydrate

In multiplying both sides of eqn. (1) by the area S , we obtain

$$\sigma S = \frac{\rho S}{k} \ln \left(1 + \frac{k\varphi}{\rho S} I_0' t \right) \quad (2)$$

where $I_0' t$ is the number of incident photons which have reached the sample and σS is the number of species produced by irradiation, in our case uranium V ions. Hence

$$n(U^V) = \frac{\rho S}{k} \ln \left(1 + \frac{k\varphi}{\rho S} I_0' t \right) \quad (3)$$

We have determined the parameters of expression (3) so as to minimize $\Sigma \{n(U^V)_{\text{calc}} - n(U^V)_{\text{exp}}\}^2$. We limited this sum to the points corresponding to no detectable amount of uranium IV and found that

$$n(U^V)_{\text{calc}} = 1.412 \times 10^{18} \ln(1 + 5.442 \times 10^{-19} I_0' t) \quad (4)$$

which gives a quantum yield

$$\varphi = 0.77$$

The good agreement between the experimental and calculated values is shown in Fig. 1. The determination of k allows us to determine the molar extinction coefficient $\epsilon = 10.8 \times 10^5 \text{ mol}^{-1} \text{ cm}^2$ which will be compared with that obtained with the following model.

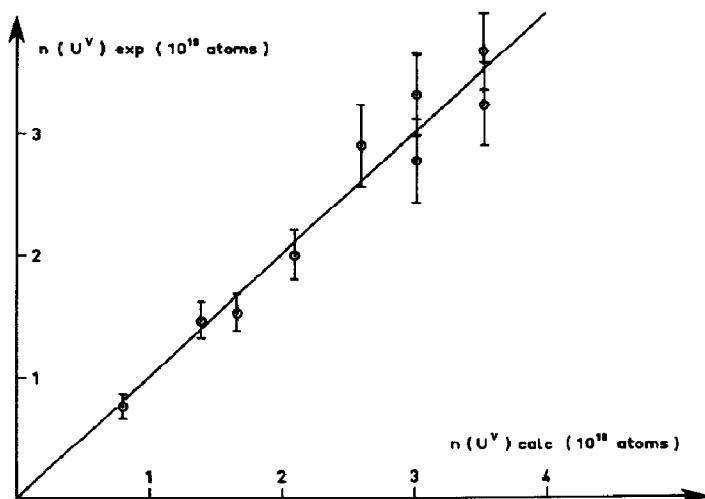


Fig. 1. Experimental and calculated (after the SSM) values of $n(U^V)$.

The improved photoproduct absorption model

In the improved photoproduct absorption model (IPAM) we keep the fundamental feature of the SSM, *i.e.* the fact that the build-up of the layer of photoproduct causes the reaction to slow down.

The improvement lies in the continuous monitoring firstly of the surface reflection [6], which allows the number N_a of photons actually absorbed by the sample to be determined, and secondly of the intensity of the photoluminescence characteristic of the disappearance of the initial reactant. At the beginning of the reaction only uranium V is formed, and this photoproduct constitutes a planar layer of mean thickness l (Fig. 2). The total number of absorbed photons is

$$N_a = N_a(U^V) + N_a(U^{VI}) \quad (5)$$

For uranium V formation the apparent quantum yield is defined by

$$\varphi_{app} = \frac{n(U^V)}{N_a} \quad (6)$$

$$\varphi_{app} = \frac{n(U^V)}{N_a(U^V) + N_a(U^{VI})}$$

whereas the effective quantum yield is [6]

$$\varphi_{eff} = \varphi_{app}^0 = \frac{n(U^V)}{N_a(U^{VI})} \quad (7)$$

Therefore

$$\frac{1}{\varphi_{app}} = \frac{1}{\varphi_{eff}} \left\{ 1 + \frac{N_a(U^V)}{N_a(U^{VI})} \right\} \quad (8)$$

If we suppose that Beer's law holds,

$$\begin{aligned} N_a(U^{VI}) &= N_a \exp \{-\epsilon_1 l \rho(U^V)\} \\ &= N_a \exp \left\{ -\frac{\epsilon_1}{S} n(U^V) \right\} \end{aligned} \quad (9)$$

Hence

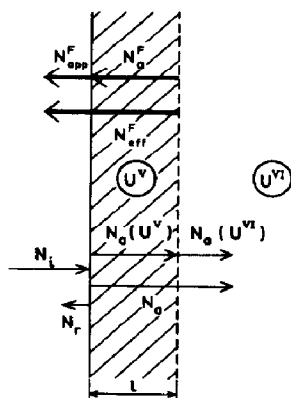


Fig. 2. Absorption and reflection of light due to the photoproduct layer.

$$\varphi_{\text{app}} = \varphi_{\text{eff}} \exp \left\{ -\frac{\epsilon_1}{S} n(\text{U}^{\text{V}}) \right\} \quad (10)$$

Figure 3 shows that this law is well obeyed. A least squares computation gives $\varphi_{\text{eff}} = 0.96 \pm 0.09$, which fits the value of 0.83 ± 0.13 [6] previously given but is higher than the value of 0.77 derived from the SSM. This is quite normal, since the preceding model takes into account the incident and not the absorbed photons. The slope of the straight line of Fig. 3 gives

$$\epsilon_1 = (6.28 \pm 0.38) \times 10^5 \text{ mol}^{-1} \text{ cm}^2$$

This model is no longer valid for values of $n(\text{U}^{\text{V}})$ greater than 0.65×10^{-5} . This is obviously due to the formation of U^{IV} , which has been neglected in eqn. (5). The same model can be applied to the decay of the apparent quantum yield Φ_{app} of fluorescence. According to the scheme of Fig. 2

$$\Phi_{\text{app}} = \frac{N_{\text{app}}^{\text{F}}}{N_{\text{a}}} = \frac{N_{\text{app}}^{\text{F}}}{N_{\text{a}}(\text{U}^{\text{V}}) + N_{\text{a}}(\text{U}^{\text{VI}})} \quad (11)$$

and

$$\Phi_{\text{eff}} = \Phi_{\text{app}}^{\text{O}} = \frac{N_{\text{eff}}^{\text{F}}}{N_{\text{a}}(\text{U}^{\text{VI}})} \quad (12)$$

If we admit that the fluorescence emitted by the uranyl ions at the interface is not reflected but is partially absorbed by the layer of photo-products, we can write

$$N_{\text{app}}^{\text{F}} = N_{\text{eff}}^{\text{F}} \exp \{ -\epsilon_2 l \rho(\text{U}^{\text{V}}) \} \quad (13)$$

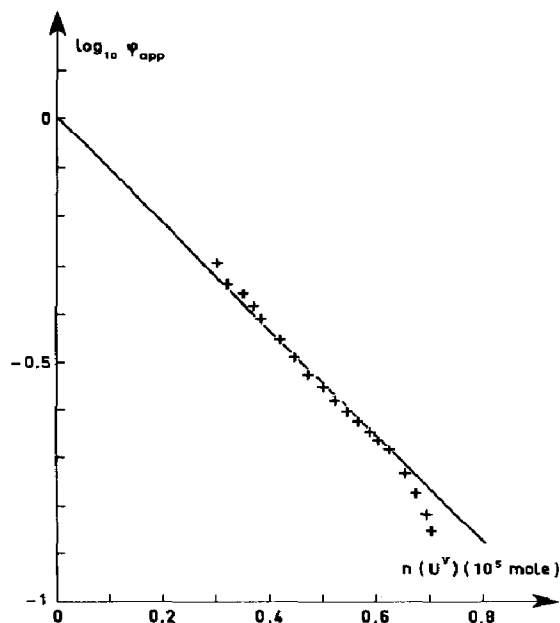


Fig. 3. $\log_{10} \varphi_{\text{app}}$ as a function of $n(\text{U}^{\text{V}})$ according to the IPAM (eqn. (10)).

ϵ_2 being the mean molal extinction coefficient of the photoproducts for the fluorescence bands peaking at 512 nm [11]. Putting eqns. (13) and (12) into

$$\frac{1}{\Phi_{\text{app}}} = \frac{N_a(U^{VI})}{N_{\text{app}}^F} + \frac{N_a(U^V)}{N_{\text{app}}^F} \quad (14)$$

we obtain

$$\frac{1}{\Phi_{\text{app}}} = \frac{1}{\Phi_{\text{eff}}} \left\{ 1 + \frac{N_a(U^V)}{N_a(U^{VI})} \right\} \exp \left\{ \frac{\epsilon_2}{S} n(U^V) \right\} \quad (15)$$

and taking into account eqn. (9), we have

$$\Phi_{\text{app}} = \Phi_{\text{eff}} \exp \left\{ - \frac{\epsilon_1 + \epsilon_2}{S} n(U^V) \right\} \quad (16)$$

The straight line obtained in Fig. 4 checks the validity of eqn. (16) and allows us to determine $\epsilon_2 \leq 0.55 \times 10^5 \text{ mol}^{-1} \text{ cm}^2$ if the experimental error is taken into account. This value compared with that of ϵ_1 shows that the apparent decay of fluorescence is due mainly to the absorption of the incident light and only secondarily to that of the fluorescent light.

As a conclusion, the IPAM explains the apparent quantum yields both of the photoreaction and of fluorescence, as long as the primary photoproduct U^V does not evolve to U^{IV} . For irradiation times longer than about 30 min, we must have recourse to other models.

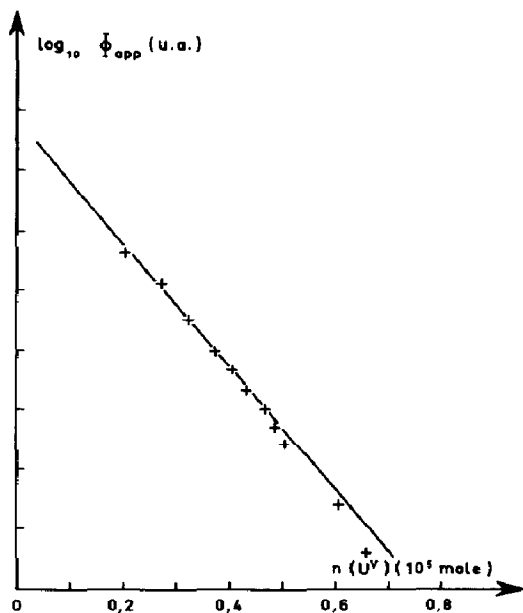


Fig. 4. $\log_{10} \Phi_{\text{app}}$ as a function of $n(U^V)$ according to the IPAM (eqn. (16)).

The Morantz, Scott and Shortland model

Morantz *et al.* [12] have applied to the photodecomposition of lead bromide a model (MSSM) which assumes that the diffusion of bromine through the layer of solid photoproducts is the rate determining step. A basic hypothesis is that the continuation of the photolytic action depends on the evolution of bromine. It can thus be shown that the thickness of the photoproduct layer can be put into the form

$$l = kt^{1/2} \quad (17)$$

where t is the duration of illumination. In order to check relation (17), we irradiated uranyl formate monohydrate in air and titrated by spectrophotometry [13]. The total quantity $n(U^V) + n(U^{IV})$ appeared after definite time intervals up to a total duration of 148 h. Figure 5 shows that this quantity is effectively proportional to $t^{1/2}$. This by itself does not suffice to establish the validity of the MSSM in our case. It is desirable to show that the diffusing product CO_2 influences the photoreaction rate. Identical experiments performed (i) *in vacuo* and (ii) at 1 atm CO_2 indicated that in the latter case a decrease of U^V production occurred, reaching a maximum of about 20%. Moreover, this decrease is due to a kinetic inhibition and not to a dark reaction of CO_2 on the photoproducts. As a matter of fact there is no difference between the results of two experiments consisting of a 1 h irradiation followed by a 1.5 h dark period, the first *in vacuo* and the second in CO_2 .

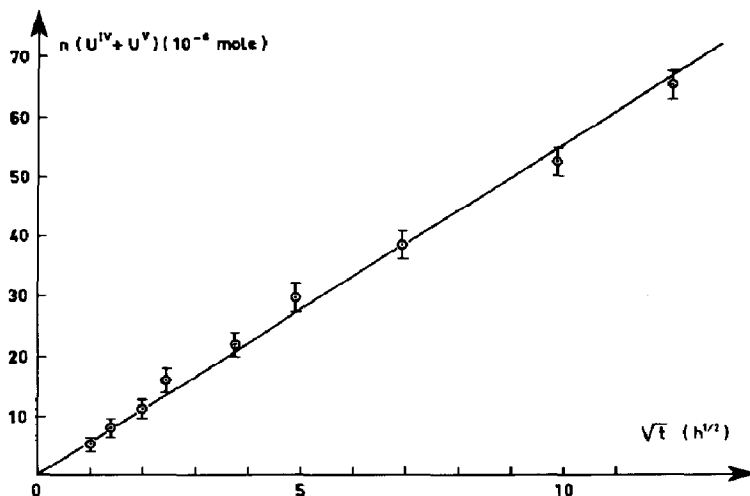
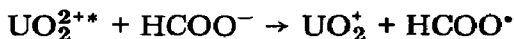


Fig. 5. $n(U^V) + n(U^{IV})$ as a function of $t^{1/2}$ according to the MSSM.

Conclusion

The proposed IPAM fits the experimental observations well for short irradiation times (less than 30 min in our case) when the sole primary photo-

product U^V is formed. For longer irradiations the diffusion of the gaseous product CO_2 limits the reaction rate. It can be assumed that CO_2 acts as an inhibitor of the electronic transfer (step 4 of ref. 6)



Nomenclature

<i>I</i>	light intensity
<i>k</i>	light absorption coefficient
<i>l</i>	thickness of the layer of solid photoproducts
<i>n</i>	number of moles
<i>N</i>	number of photons
<i>S</i>	illuminated area
<i>t</i>	time

Greek symbols

<i>ε</i>	molar extinction coefficient
<i>ρ</i>	number of moles of photoproducts formed per unit volume
<i>σ</i>	number of moles of photoproducts formed per unit surface
<i>φ</i>	quantum yield of U^V formation
<i>Φ</i>	quantum yield of fluorescence

Subscripts

<i>a</i>	absorbed
<i>app</i>	apparent
<i>eff</i>	effective
<i>0</i>	incident

Superscripts

<i>F</i>	fluorescence
<i>0</i>	initial value

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