KINETICS OF PHOTOCHEMICAL DECOMPOSITION OF SOLIDS (I)

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A model which describes the kinetics of photochemical decomposition: $aA_{(S)} \rightarrow bB_{(S)} + cC_{(g)}$

(the reaction area being located near the reactant surface) is presented.
The general rate equation is discussed for various ratios between the radiation absorption coefficients of the solids A and B. The curves (reaction rate, degree of conversion) have been calculated using a program written in BASIC language.

Introduction

The interest generated by the investigation of photochemical decomposition of solids are determined mainly by its applications in the photographic technique [1,2].

Reaction mechanisms for photochemical decomposition of alkaline halides, azides, perchlorates have been worked out [3].

This paper aims a general kinetic model, which takes into account the mass absorption coefficients of X-Ray of the reactant and product. The results are valid too-with some modification – for other radiations either in static or in kinematic conditions.

The Rate Equation

In order to describe a reaction which occurs according the equation:

$$aA_S \xrightarrow{\ h\nu\ } bB_{(S)} + cC_{(g)}$$
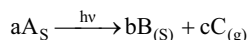
the degree of conversion α defined by the relationship (1) is going to be used:

$$\alpha = \frac{N_A^0 - N_A}{N_A^0} = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

where N_A^0 and N_A are the number of particles of the reactant A at the initial moment t_0 and respectively at the moment t; m_0, m and m_f are the sample mass for $\alpha = 0$ at the initial moment t_0, for the moment t and respectively for the total decomposition of $A_{(S)}$.

In the following we shall express the reaction rate through $d\alpha/dt$. Taking into account the relation (1) it follows that:

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$$\frac{d\alpha}{dt} = -\frac{1}{N_A^0} \cdot \frac{dN_A}{dt} \tag{2}$$

The photophysical primary processes, generate active intermediate species like excitons, positive holes which migrate and near irradiated surface of solid reactant $A_{(S)}$ are trapped by lattice defects (vacancies, dislocations, F centers etc.). The groups of such associated and captured active intermediates decompose generating the reaction products.

The gaseous product $C_{(g)}$ is evolved and $B_{(S)}$ forms a surface layer.

The further considerations are based on the following hypotheses:

1. The limiting step of the decomposition is the simultaneous capture of a number of i ($i = 1, 2, 3$) actives particles at a defect level located near the reactant surface and thus generating one active group.

2. During the irradiation a steady state is reached, thus the number N_g of the active groups is constant and their decomposition rate equals their generation rate. In such conditions the decomposition rate can be expressed as:

$$\frac{dN_A}{dt} = i \cdot \frac{dN_g}{dt} \tag{3}$$

taking into account that an active group consist of i reactant particles.

3. The capture process can be characterized by a constant K, which is the capture probability W of an active intermediate by a trap in the surface vicinity for a radiation intensity I_a (watt/m^2 or einstein*s^{-1}*m^{-2}) absorbed by the reactant Thus, according to the definition:

$$K = \frac{W}{I_a} \tag{4}$$

4. The rate of active group generation equals the product between the simultaneous probability of i particles captured and the number of defects. Thus:

$$\frac{dN_g}{dt} = (W)^i n_d S \tag{5}$$

where n_d and S are the surface defects concentration and respectively the irradiated surface area.

The capture of the I particles is a compound event whose probability is expressed by the product of the probabilities of individual events.

Combining relationships (2)÷(5) we get:

$$\frac{d\alpha}{dt} = \frac{i(KI_a)^i n_d S}{N_A^0} \tag{6}$$

In order to evaluate the intensity I_a one has to notice that the energy of the incident radiation is partly absorbed by the product B. According to the hypothesis no. 1 the

decomposition is located at the reactant surface where the volatile component is evolved. As a consequence the product $B_{(S)}$ appears as a layer with growing thickness in time.

Fig. 1 shows the succession of solid phases A and B in the reaction system, as well as the change of the radiation intensity with the space coordinate.
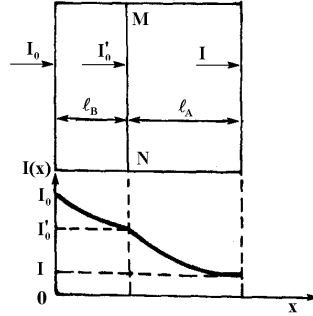

Fig. 1: *The succession of solid phases A and B in the reaction system:*
M-N phases interface (upper part). Curve I(x) (intensity vs. position
coordinate; downside of the figure).

The intensity of the radiation (transmission flux density) which penetrates a layer from a material with the linear absorption coefficient μ (m^{-1}) decreases with the thickness x according to the exponential law:

$$I(x) = I_0 \, e^{-\mu x} \tag{7}$$

where I_0 is the intensity of the incident radiation.

The rate of absorption R_a (watt·m^{-3}) is defined by:

$$R_a = -\frac{dI}{dx} = \mu I_0 \, e^{-\mu x} \tag{8}$$

Because the solid phases $A_{(s)}$ and $B_{(s)}$ are homogeneous, μ is a constant. For the layer of reactant $A_{(s)}$ (figure 1), with thickness l_A and absorption coefficient μ_A, the absorbed power density I_a is obtained by integration.

$$I_a = \mu_A I_0' \int_0^{l_A} e^{-\mu_A x} \, dx$$

$$I_a = I_0' \left(1 - e^{-\mu_A l_A} \right) \tag{9}$$

On the other hand I_0' is the intensity of the beam transmitted through the layer of the product B with the thickness l_B and the absorption coefficient μ_B. Thus I_0' could be expressed through the intensity I_0 of the incident radiation at the external surface of the system by the relationship:

$$I_0^{'} = I_0 \, e^{-\mu_B l_B} \tag{10}$$

Taking into account this result the relationship (9) can be transcribed as:

$$I_a = I_0 \, e^{-\mu_B l_B} \left(l - e^{-\mu_A l_A} \right) \tag{11}$$

In order to reduce the number of variables, which describe the kinetic behaviour of the system we must express l_A and l_B through the degree of conversion:

$$l_A = \frac{m_A^0 (1-\alpha)}{\rho_A S} \tag{12}$$

$$l_B = \frac{m_A^0 \alpha b M_B}{M_A a \rho_B S} \tag{13}$$

where m_A^0 is the initial mass of the reactant and ρ_x – the density of phase x. The molecular weight M_A and M_B as well as the coefficients a and b enter in relation (13) because the mass of the product B was expressed through the mass $m_A^0 \alpha$ of the transformed reactant.

From relations (6), (11)÷(12) the following rate equation is obtained:

$$\frac{d\alpha}{dt} = \frac{i(KI_0)^i n_d S}{N_A^0} \cdot e^{-i\left(\frac{\mu}{\rho}\right)_B \cdot \frac{m_A^0}{S} \cdot \frac{b}{a} \cdot \frac{M_B}{M_A} \alpha} \cdot \left[1 - e^{-\left(\frac{\mu_A}{\rho}\right)_A \cdot \frac{m_A^0}{S} \cdot (1-\alpha)} \right]^i \tag{14}$$

The ratio μ/ρ (m^2/kg) is the mass absorption coefficient of the radiation in the phases A and B and can evaluated using the literature data.

If phases A and B are well separated, the reaction occurrence can be followed either measuring the B product layer thickness or measuring the A reactant layer thickness. In such conditions:

$$\alpha = \frac{l_B}{l_B^f} = 1 - \frac{l_A}{l_A^0} \tag{15}$$

where superscripts 0 and f mean initial and final thickness of the reactant and product.

For a poor separation of the phases A and B, the reaction is followed by recording the mass change of the system time. In such conditions the degree of conversion is calculated by the relation (1).

Obviously if the system does not exhibit a phase stratification and reaction product is disseminated in the reactant mass, equation (14) cannot be applied and hypothesis 1) should be modified.

Relation (14) shows that the photochemical decomposition rate of solids depends on the radiation intensity, on the wavelength (through the coefficient μ), on the temperature which changes the concentration n_d according to an exponential law, on the irradiation surface

area and obviously on the degree of conversion and on the nature of the reactant and the solid product.

The mechanical, thermal and chemical treatments, which modify the defects concentration, could influence the kinetics of the photodecomposition.

In order to express equation (14) in a more compact form, the following notation is introduced:

$$k = \frac{i(KI_0)^i n_d S}{N_A^0} \tag{16}$$

$$k_A = \left(\frac{\mu}{\rho}\right)_A \cdot \frac{m_A^0}{S} \tag{17}$$

$$k_B = \left(\frac{\mu}{\rho}\right)_B \cdot \frac{m_A^0}{S} \cdot \frac{b}{a} \cdot \frac{M_B}{M_A} \tag{18}$$

$$v = \frac{d\alpha}{dt} \tag{19}$$

where k is the overall rate constant and the ratios k_A and k_B will be called dimensionless absorption coefficients of the radiation. These are not material constants as they depend not only on the intrinsic properties of phases A and B on the surface density (m_A/S) too, thus on the sample thickness, which can be changed from an experiment to the other.

Taking into account this notations the reaction rate can be expressed by the equation:

$$v = kI_0^i \cdot e^{-ik_B\alpha} \cdot \left[1 - e^{-k_A(1-\alpha)}\right]^i \tag{20}$$

for $I_0 = 0$ or $\alpha = 1$ $v = 0$.

Introducing in equation (20) the condition $\alpha = 0$ the initial rate v_0 results:

$$v_0 = kI_0^i\left(1 - e^{-k_A}\right)^i \tag{21}$$

According to the presented model the reaction begins to occur with its maximum value ($v_0 = v_{max}$). The reaction rate can be evaluated from the experimental curves $\alpha = f(t)$ and the radiation intensity by help of the definition relationship.

$$I_0 = P/S \ (\text{watt/m}^2) \tag{22}$$

where P is the beam power. If the steady state settles up after an induction period, the initial rate can be evaluated through extrapolation.

The logarithmic form of the equation (21):

$$\lg v_0 = \lg\left[k\left(1 - e^{-k_A}\right)^i\right] + i\lg I_0 \tag{23}$$

shows that the plot $\lg v_0 = f(I_0)$ is linear with the slope i.

If the photochemical decomposition is a single reaction and the described model can be applied one should obtain $i = 1$ or $i = 2$. Higher values of i mean simultaneous capture of three active particles by the same lattice defect, which is a rare event.

The coefficient k_A can be evaluated by help of the relation (17) and the constant k from the intercept.

The shape of the rate curves

The shape of the rate curves depends on the ratio of the absorption coefficients of the reactant and product. To plot the rate curves is useful to define a relative rate v_r according to the relation:

$$v_r = \frac{v}{v_0} \tag{24}$$

Introducing relation (20) and (21) in (24), one obtains:

$$v_r = \left(1 - e^{-k_A}\right)^{-i} \cdot e^{-ik_B\alpha} \cdot \left[1 - e^{-k_A(1-\alpha)}\right]^i \tag{25}$$

The advantage of using v_r consists on its dimensionless character.

Fig. 2 shows the rate curves $v_r = f(\alpha)$ for the following values of the ratio k_A / k_B'' a) 0.5; b) 1; c) 2 and for $i = 1$.
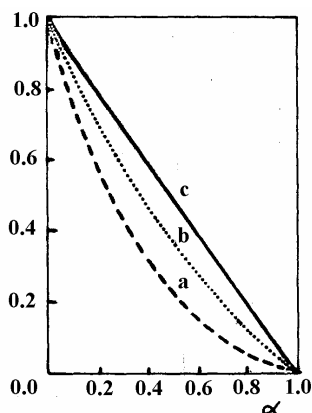

Fig. 2: *The curve* $\bar{v}_r(\alpha)$ *for three values of the ratio k_A/k_B:*
a) 0,5; b) 1; c) 2.

For simplicity sake for all three curves k_A was kept at a constant values $(k_A = 1)$.

The used program written in BASIC language [4] allows to display the numerical values of the reaction rate, the plot of the curves as well as the placing of experimental points on this curves in order to compare the experimental results with the theoretical ones [5].

As shown in Fig. 1 for the same value of the degree of conversion ($\alpha = 0{,}5$ for instance), the reaction rate increases with the ratio $k_A = k_B$. Thus, the photochemical decomposition is favoured for high values of the absorption of the reactant and low values of the absorption coefficient of the product.

Particular cases

a) Low values of the absorption coefficients.

The fact that k_A and k_B depend on the layer thickness is an advantage since using samples of low mass and high exposition surfaces the conditions:

$$k_B\alpha << k_A(1-\alpha) << 1, k_A << 1$$

are fulfilled. As a consequence the exponentials can be expanded in series. Keeping only the first two terms, relations (20)-(23) and (25) take the appropriate forms:

$$v = kk_A^i I_0^i (1 - ik_B\alpha)(1-\alpha)^i \tag{26}$$

$$v_0 = kk_A^i I_0^i \tag{27}$$

$$\lg v_0 = \lg kk_A^i - i \lg I_0 \tag{28}$$

$$v_r = k_A^{-i}(1 - ik_B\alpha)[k_A(1-\alpha)]^i \tag{29}$$

more suitable for processing the data as these equations can be integrated.

b) The reaction product is transparent.

If the reaction product does not absorb the radiation, its accumulation does not inhibit the decomposition.

From (25) for $k_B \to 0$ one obtains:

$$v_r = \left(1 - e^{-k_A}\right)^{-i} \cdot \left[1 - e^{-k_A(1-\alpha)}\right]^i \tag{30}$$

c) The reaction product is opaque $(k_A \to \infty)$

If the solid product is photo protective the reaction is stopped $(v_r \to 0)$ as soon as the surface is covered by a thin layer of it.

d) The reactant is transparent $k_A \to 0$.

Obviously in such conditions $(v_r \to 0)$ and the reaction does not occurs as being conditioned by the generation of active intermediate by the observed radiation.

e) The reactant is opaque $(k_A \to \infty)$.

In such conditions, the reaction rate:

$$v_r = e^{-ik_B\alpha} \quad 0 \le \alpha \le 1 \tag{31}$$

does not depend on the amount of the undecomposed reactant.

Irradiation with moving sample

When using high power beams (UV, X ray, γ or laser radiation) the sample is placed in a moving carrier with the constant speed [6, 7]. The speed (v_l) (fig. 3) is oriented normally with respect to the beam (F) with the width (L) and thickness (d).
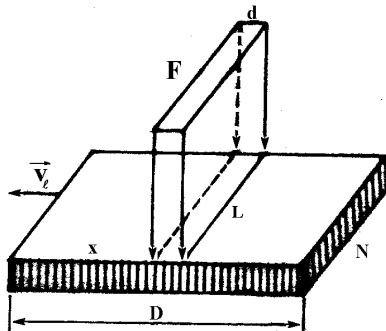

Fig. 3: *Irradiation with moving samples:*
F – the irradiation beam, N – the sample carrier, x – position coordinate.

Relation (22) should be modified through the substitution of the samples area S by the section area $S = Ld$.

The crossing time t_1 of a sample surface point with the beam can be expressed as $t_1 = d / v_l$.

In order to reach a given degree of conversion, a number of n passing through the beam are necessary. Thus, total irradiation time can be calculated according to the relation:

$$t = \frac{nd}{v_l} \tag{32}$$

With these changes the derived kinetic equations can be used for moving samples.

Conclusions

1. A general model of the photochemical decomposition of solids was worked out.

2. The model allows plotting the curves of the reaction rate against the degree of conversion.

3. The theoretical model indicates that the photochemical decomposition of solids is favoured by high values of the absorption coefficient of the reactant and low values of the product absorption coefficient.

4. Five particular cases are represented in the framework of the general model with respect to the absorption coefficient of reactant and product.

5. The changes of the obtained equations for moving samples are equally considered.

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