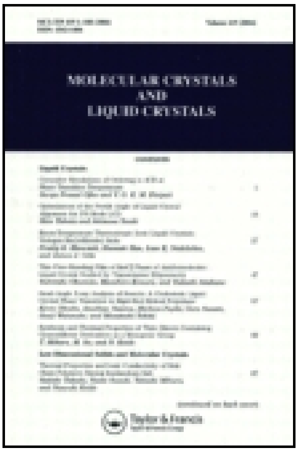

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PHOTOSTIMULATED FREE VALENCE MIGRATION IN THE SOLID ORGANIC MATRIX

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Abstract The main mechanisms, the general features, the length of reaction chain and the effectivity of the photochemical stage of the reaction of photostimulated radical migration in the organic solids and the photostimulated migration of isopropylbenzene radicals in glass isopropylbenzene are considered.

INTRODUCTION

It is known that the absorbtion spectra of different radicals are typically shifted to a longer wavelength light region compared to the spectra of the initial compounds. The shift value changing from tens to hundreds of nanometers.[1] The results of the absorbtion is high efficiency photochemical reactions of radicals that are widely occur and take an active part in nature.[2-4]

PHOTOMIGRATION OF FREE VALENCE

Main mechanisms of free valence photomigration

The reactions of excited radicals may be divided into two main types according to their chemical results.[1,3] (i) The excited radical R^* forms a stable molecule ρ and a thermal unstable, under the experimental conditions, radical r by the dissociation as it is shown by (a). The radical r can interact with an adjacent matrix molecule RH to regenerate the photochemical active radical R. (ii) The excited radical R^* interacts with the adjacent matrix molecule RH by an H-abstracting that results in the regeneration of the photochemical active radical R (see (b)).

$$\begin{tikzcd}[column sep=small] R + h\nu \arrow[r] & R^{*} \arrow[r] & r + p \\ r + RH \arrow[r] & rH + R \arrow[ull, bend left] & \end{tikzcd} \quad (a) \qquad \begin{tikzcd}[column sep=small] R + h\nu \arrow[r] & R^{*} \\ R^{*} + RH \arrow[r] & RH + R \arrow[ul, bend left] \end{tikzcd} \quad (b)$$

The result of these reactions is a photostimulated migration of free valence in the volume of a solid matrix that causes the change of the radical space distribution, the stable product (p and rH) formation and the radical recombination.

General features of the photomigration process

The main features of the considered processes are the possibility φ of one reaction cycle (where φ equals the quantum yield of the photochemical reactions for circle (a) or (b)) and the number of realized circles n (n equals the number of stable molecules p or rH for circle (a)). These two parameters are related to each other by the following equation

$$n = I_o \varphi t \int_o^t (1-\exp[-2,3\varepsilon N(t)l/v)dt / \int_o^t N(t)dt \qquad (1),$$

where I_o is the intensity of acted light, $N(t)l/v$ is the concentration dependence of the photoactive radicals on the photolysis time t (N is the number of radicals in the volume v of a solid matrix), ε is the extinction coefficient of radicals and l is the optical length. When the non-monochromatic light is used it is necessary to take into account the dependences of all parameters φ, ε and I_o on the wavelength and to use average values.

Length of reaction chain

Using a numerical integration assay we have shown that the value of the integral relation in (1) is constant within 15% of error when $\varepsilon N(t)l/v \leq 2$ and it is exactly $2,3\varepsilon l I_o$ when $\varepsilon N(t)l/v \leq 0.15$. Thus, the value of n should be proportional to the photolysis time t for the most of the possible investigated experimental situations. The data presented in Table 1 prove this dependence.

TABLE 1. The dependence of photoradical chain reaction length on the photolysis time for different chemical compounds at 77K.

Compounds	Time, min					
	5	10	15	20	30	
isobutyraldehyde	1,4	3,2	5	-	-	
acetaldehyde	-	18	-	24	30	
polyvinylacetate	1,8	3,4	4,6	5,7	7,5	
	60	120	180	240	300	360
ethanol	9	15	-	23	-	30
methylamine	8	17	-	33	-	48
acetanhydride	6,5	11	-	16,5	-	21
polyacrylic acid	8	17	26	35	44	-
polyacrylamide	15	30	45	60	76	-

Efficiency of photochemical reactions

To evaluate the efficiency of the production of radicals *r* (a) we have analyzed quantum yields of a radical formation for a photodissociation of different stable molecules or stabilized radicals in organic solids at 77K.[5] We have also made the attempt to connect the efficiency of cage escape for the radical *r* with the Van der Waals volume v of this radical (Figure 1). The regression analysis has been made and the linear dependence of $\log\varphi$ on v : $-\log\varphi \simeq 0{,}1v$ or $-\log\varphi \simeq 1 + 0{,}7v$ which allows to evaluate the value of $\log\varphi$ within 25% of error has been suggested.

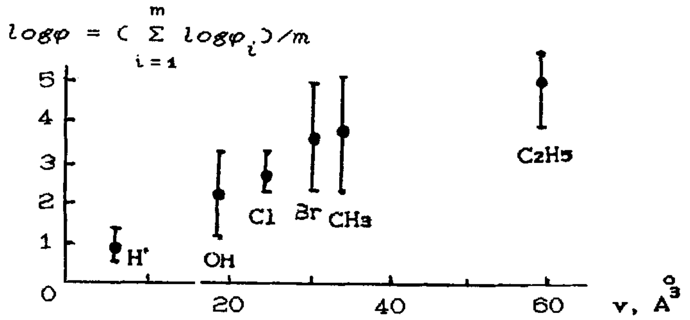

FIGURE 1. The dependence of the quantum yields for homolytic photodissociation of different stable molecules and the stabilized radicals on the volume of radical escaping cage of the solid matrix (m is the number of the investigated systems and m = 9 (for H), 3 (OH), 9 (Cl), 2 (Br), 36 (CH_3), 6 (C_2H_5); the vertical lines denote variation intervals for the experimental values of the quantum yields).

The free valence photomigration conseqence

It was shown earlier that the concentration reduction of the paramagnetic particles in glasses is well described by the isotropic model of radical photomigration.[3,6-8] The space distribution of the produced molecules (stable molecules ρ and rH for (a)) may be described by this hypothesis but it is necessary to take into account the initial space distribution of photoactive radicals. The average size of the migration region can be determined by a sphere with radius ρ which is approximated by the following relation $\rho \simeq \lambda\sqrt{n}$ for the condition of $n \geq 4$, where λ is the average distance of the free valence transfer for a circle. This parameter depending on the nature, the size and the activity of a radical r. The value of λ changes from $\simeq$0.3 nm (R = $(CH_3)_2\dot{C}OH$, r = H, low-molecular glass)[8] to $\simeq$2.2 nm (R = $\sim CH_2\dot{C}(COOH)\sim$, r = OH, high-molecular glass)[3] for all our experiments. The average product density in the photomigration region in frames of such condition should be given by the relation $\beta \simeq 1/(4\lambda^3\cdot\sqrt{n})$.

Photostimulated migration of isopropylbenzene radicals

We investigated the photostimulated migration of $(CH_3)_2CPh$ radicals which underwent an action of the light beam with wavelength of 313 nm in the isopropylbenzene glasses that takes place according to mechanism (b).[9] This migration was revealed by decreasing of an EPR-spectrum line broadening that results from the increasing distance in the radical pairs. (The initial distance distribution in radical pairs is the result of the way of their formation by photolysis of chlorine molecules in the isopropylbenzene glass.) The distance between radicals in any radical pair during the experiment was such that the photomigration does not result a change of the number of radical pairs under the experimental conditions. We have found the dependence of the charge for an EPR-spectrum parameter on the distance between radicals in a radical pair. Based on the previous results obtained[10], where kinetics of radical recombination in separated radical pairs was simulated by Monte- Carlo method. The dependence of the distance in a radical pairs on the doze of light absorbed by the radicals has been calculated. Being in frames of the hypothesis of isotropic photostimulated migration in glasses and assuming that the distance of free valence transfer for one circle equal the molecular size, we have evaluated the possibility of the realization of one circle for the photomigration of isopropylbenzene radicals $\varphi \simeq (4 \div 6) \cdot 10^{-4}$.

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