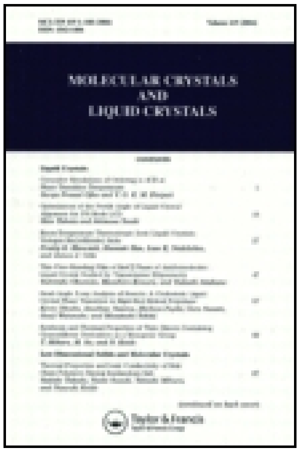

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Migration of triplet excitations generated by ionizing radiation in organic materials

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The problem of triplet excitations migration for the case both of the diffusion - controlled triplet-triplet annihilation and of the concentration - controlled one has been considered.

Keywords radioluminescence, organic crystals, ionizing radiation

INTRODUCTION

Losses of ionizing radiation energy E in an organic material result in generation of secondary electrons both of high (δ-electrons) and of low energies[1]. The electrons of low energies create high activation density regions, i.e., the regions which contain ionized, exited and chemically activated centers as well as products of their interaction. For the ionizing radiation with high specific energy losses ($dE/dx \geq 10^1$ MeV/cm). Such regions are cylindrically symmetrical (tracks), and for the radiation with low specific energy losses ($dE/dx \leq 10^{-1}$ MeV/cm) they are spherically symmetrical (spurs). The ratio of the generation probabilities of the singlet- and triplet-excited molecules within these regions is 1:3 and outside of them is $1{:}10^{-6}$. Such a difference in the concentration of T-states results in a situation when T-T annihilation (see Eq.(1)) which causes the radioluminescence (RL) pulse slow component formation takes place in the tracks or spurs. The slow component of the RL pulse arises when the probability of the singlet channel of the T-T annihilation Eq.(1) is high

$$T_1 + T_2 \Rightarrow \begin{cases} S_1 + S_0 \Rightarrow h\nu + 2S_0 \\ T_1 + S_0 \\ \ldots\ldots \end{cases} \tag{1}$$

In such a case, the energy hν of a delayed RL photon is the same as for the prompt RL, but the moments of a photon emission are delayed for the time needed for the transport of the lowest T-excited states (T_1) to each other. In Eq.(1) S_1 is the lowest excited singlet state, and S_0 is the ground state.

The first attempts to describe this process in the terms of the diffusion of T-excitations were made in 60-ies. These results did not agree with the photoluminescence experimental data[1,2]. This problem was solved much later when the limits of the "diffusion approach" were taken into consideration and the r_0-values (3) were determined. For the case when there is no strong single molecular decay of T-excitations, the RL pulse slow component is described as follows[3]:

$$i(t) \approx M(t)(1 + t / t_D)^{-k} \tag{2}$$

$$t_D = r_0^{\,2} / 4D_T \tag{3}$$

In Eq.(2) k=m/2, where m=3, 2 and 1 for three-, two- and one-dimensional diffusion of T-states, respectively. The m values is determined by the symmetry of the high activation density regions as well as by anisotropy of diffusion coefficients D_T of T-excitation. In Eq.(2) for time after excitation $t \geq 50$ ns M(t) is constant, t_D is the time constant. In Eq.(3), r_0 is either an initial radius of track or the spur cross-section.

EXPERIMENT

The radionuclide sources of alpha- (^{241}Am), neutron- (^{252}Cf) and gamma-excitation (^{60}Co) were used for study of the RL slow component. For these cases $dE/dx \approx 10^3$, $10^2 \ldots 10^1$ and 10^{-2} MeV/cm, it allows to create high activation density regions with r_0=50, 65 and 100 nm, respectively. The study of the RL of single crystals with different structure perfection has shown than the slow component intensity of RL pulse was several times higher for the perfect structure organic crystals.

Structural imperfections of an organic crystal which cause the kinetics of a RL pulse slow component form the traps with the depth of ≥1,0 eV and ≥0,2 eV for charge carriers and excitation respectively.

The intensity of RL pulse slow component for routine type plastics was negligible. The same result has been obtained for cross-linked copolymers for the case of gamma-excitation. For the cases of alpha- and neutron-excitation the intensity of RL pulse slow component for such plastics was just the same as for crystals, i.e. t_D=45 ns, and 10 ns, respectively. The intensity of RL pulse slow component increased with decrease of mean distance between linking chains.

DISCUSSION

To consider processes responsible for low yield of RL of organic molecular systems, it is also necessary to know $\xi_{i,j}$ -values (4) characterizing the integral quenching effect, i.e. total losses for both fast and slow RL components:

$$\xi_{i,j} = \{N_i / E_i\}\{N_j / E_j\}^{-1} \qquad (4)$$

where N is the number of photons emitted by a sample under the i- or j- type of irradiation with energy E, i.e. the ratio of intensities of light signals normalized on the exciting radiation energy. Using the slow component intensity I, we can discriminate the effect of quenching in high activation density regions. Results of I measurement for single crystals are presented in Table 1. The directions of the irradiation which is given in Table 1 are following: parallel to the crystallographic axis a, b, normal to the ab plane (c').

TABLE 1. Results of I measurement for single crystals of anthracene (A), stilbene (S) and *p*-terphenyl (T) doped by 0,1% of diphenylbutadiene

Excitation		I, arb. Units		
Type	Direction	A	S	T
α	a	0,15	0,23	0,20
	b	0,13	0,21	0,19
	c'	0,16	0,24	0,2
γ	a, b, c'	0,03	0,02	0,03

For these crystals $\xi_{\alpha,\gamma}$ -values are 0,04; 0,05 and 0,07, respectively. The $\xi_{\alpha,\gamma}$ -values obtained at various irradiation orientations were averaged. For a plasmon energy E~20 eV, the length of alpha-particle track L~30μm[4]. We obtain that a track having the volume $V \approx 2{,}4 \cdot 10^{-13}$ cm^3 can contain to $n \approx 2{,}7 \cdot 10^5$ plasmons. Thus, the concentration C of states which are formed in the track is about 10^8 cm^{-3}.

The RL light-pulse arising in anthracene under the action of alpha particle source (^{241}Am) contains $(4\text{-}5) \cdot 10^3$ photons within the range up to 2 μs [5]. Let us calculate the mean photons number μ in the RL-pulse in the absence of losses using these data and the $\xi_{\alpha,\gamma}$ -values. In the case of gamma excitation when no track is formed and therefore losses within it is absent, the μ-value can be considered as the calculated number of photons in the pulse. Then reducing to the particle energy of 1 MeV (what corresponds not n, but to

η=5·10^4 plasmons/MeV) one can calculate photons number in the RL pulse under the gamma excitation i.e. $N_\gamma=\mu/E_\alpha$, where E_α is the alpha particle energy. The number of photons calculated for 1 MeV of energy in the fast component N_F and in the slow one N_S can be obtained from the Table 1. In order to obtain the number of photons in alpha-scintillation N_α for another sample one can use the light signal ratio of alpha-scintillation for this and that sample. The Table 2 shows the results of calculation , in which the number of photons are reduced to 1 MeV of the particle energy in the RL pulse (N_i), its fast (N_{iF}) and slow (N_{iS}) components and are given for i-th excitation type (i=α,γ).

TABLE 2. Results of calculation of the number of photons reduced to 1 MeV of the particle energy in RL pulse (N_i), its fast (N_{iF}) and slow (N_{iS}) components for i (i.e. α,γ)-excitation.

	I	N_i	N_{iS}	N_{iF}
A	α	(7-9)·10^2	(1-1,5)·10^2	(5,5-7,3)·10^2
	γ	(1,8-2,3)·10^4	(5-7)·10^2	(1,8-2,2)·10^4
S	α	(5,3-6,8)·10^2	(1,3-1,6)·10^2	(4-7)·10^2
	γ	(1-1,4)·10^2	(1,7-2,2)·10^2	(1-1,4)·10^2
P	α	(8,4-10,8)·10^2	(1,7-2,2)·10^2	(6,7-8,6)·10^2
	γ	(1,2-1,5)·10^4	(3,6-4,5)·10^2	(1,2-1,4)·10^4

In the Table 2 N_γ -values is given for the case of gamma excitation and describe a certain theoretical case of RL without any losses in the track. If it is the case of alpha excitation, than e.g. for anthracene, instead of $N_{\alpha S}$ the value of $N_{\alpha S}^* \approx N_\gamma - N_{\alpha S} \approx (1{,}7\text{-}2{,}2)\cdot 10^4$ photons/MeV would be obtained (see Table 3). It means that the alpha particle losses 94-98% of its energy, E_α, within a track. The $N_{\alpha S}$-values are calculated according to Table 2, and the values $N_{\alpha S}^* \sim N_\gamma - N_{\alpha F}$ are calculated for the case of no losses.

TABLE 3. Results of calculation of the number of photons reduced to 1 MeV of the particle energy in slow component of RL pulse for organic single crystals of anthracene (A), stilbene (S) and *p*-terphenyl (T) doped by 0,1% of diphenylbutadiene.

	$N_{\alpha s}^{*}$	$N_{\alpha s}$
A	$(1{,}7\text{-}2{,}2)\cdot 10^4$	$(1\text{-}1{,}5)\cdot 10^2$
S	$(1\text{-}1{,}4)\cdot 10^4$	$(1{,}3\text{-}1{,}6)\cdot 10^2$
T	$(1{,}1\text{-}1{,}4)\cdot 10^4$	$(1{,}7\text{-}2{,}2)\cdot 10^2$

In the situation under discussion $N=10^{-2}N^{*}$. Using founded diffusion coefficients D_T -values[3] we obtain that the mean time necessary for two T-state to encounter is 10^{-11}s and 10^{-8}s when T-state concentrations, C_T, are 10^{18} and 10^{16}cm^{-3}, respectively. Quantities η and N are of the same order of magnitude. In the case of alpha excitation, $\eta \sim N_{\alpha S}^{*}$ and $N_{aS}^{*} \sim (N_{\alpha S})^2$. It must be note that a square relationship is typical for bimolecular interaction while linear one for monomolecular, as it follows directly from the form of kinetic equations for described processes[6].

From the fact that the quenching in a track is of the bimolecular character follows that the only description (5) of such a process not contradicts to the requirement of high initial T-excitations concentration

$$T^{*} + T^{*} + (J) \Rightarrow \begin{cases} S_1 + S_0 + T \Rightarrow 2S_0 + J \\ T_1 + S_0 \\ ? \end{cases} \qquad (5)$$

In contrast to the T-T annihilation process (1) where a low T-states concentration is assumed in «cooled» high excitation density regions, it is necessary to account that for «hot» states annihilation the process described by (5) is not diffusion-controlled one. The T^{*}-T^{*} annihilation process (5) is defined by concentration of triplet state T^{*} that should drop steeply with time as is usually for the case of concentration quenching processes. It could be shown for Eq.(1) that formation of quintet states is unfavorable[1]. For Eq.(5) that statement may be not valid since it not proved for «hot» states interaction. Therefore, the question mark is positioned in Eq.(5) in place of similar transitions.

CONCLUSIONS

Since the probability of bimolecular reactions is defined by the initial concentration of interacting states (see Eq.(5)), then, at a given primary particle energy E the quenching intensity is defined by size of high activation density regions and the energy fraction being loosed therein. That circumstance does explain the well-know experimental fact that the RL quenching intensity grows when dE/dx increases. The revealed dependence of r_0 on dE/dx evidences a strong nonlinearity of the quenching intensity increases with growing dE/dx, since, when a cylinder length diminishes, its volume decreases linearly while with the r_0 decrease, it drops quadratically.

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