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## THE KINETIC MODEL OF RADICAL REACTION IN PLASTIC CRYSTALS

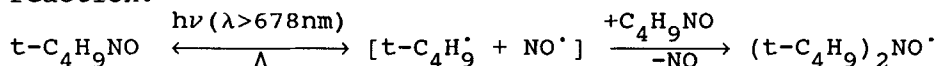
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**ABSTRACTS** The kinetic features of diffusion-depended model process of photoinduced nitroxide formation from 2-methyl-2-nitrosopropane in a number of plastic crystals (PC: cyclohexane, cyclohexanol, cyclohexanon, cyclopentanon, 1,1,1-trichlorethane, tert-butylchloride, tert-butylamine, tert-butanol, benzene have been studied by ESR.

The kinetic model that relates the nitroxide formation quantum yield with parameters of Lennard - Jones' potentials and thermodynamic properties of PC is proposed.

The plastic crystalline state is the state of matter which can be characterized by dynamic molecular orientational disordering in the solid phase.<sup>1</sup> The combination of fast rotational diffusion (the same as in fluids) and slow translational one (the same as in usual organic solids) provides the unique physico-chemical properties of plastic crystals (PC).<sup>1</sup>

The goal of this work is the experimental investigation and kinetic description of the PC ordering effect on diffusion-depended chemical processes. The radical generation under photolysis of monomer form of 2-methyl-2-nitrosopropane has been chosen as a model reaction:



The kinetics of the model process has been studied by ESR. Before the photolysis, the samples were degased. The ESR spectra obtained have been analyzed in order to estimate the di-tert-butyl-nitroxide radicals' reorientation frequency ( $\nu_r$ ). The construction of the phase diagram of

"monomer 2-methyl-2-nitrosopropane - PC", and the  $\Delta H$ -values of the phase transitions of PC have been obtained with high sensitive thermographic equipment manufactured in our laboratory. Such substances as  $c-C_6H_{12}$ ,  $c-C_6H_{10}O$ ,  $c-C_6H_{11}OH$ ,  $c-C_5H_{10}O$ ,  $C_6H_6$ ,  $t-C_4H_9Cl$ ,  $t-C_4H_9NH_2$ ,  $t-C_4H_9OH$ ,  $CCl_3CH_3$  have been used as the reaction matrix.

Some experimental results are given in Figures 1 - 6.

The quantitative kinetic description of the model process is based on some principal propositions:

- geminal radical pairs [ $t-C_4H_9\dot{H} + NO\cdot$ ] are forming during photolysis in direct diffusional contact and under such mutual orientation of particles which allows their reverse recombination. The probability of formation of such oriented radical pairs is approximately equal to 1;
- the nitrosocompound -  $t-C_4H_9NO$  can't be used as an external acceptor of primary tert-butyl radicals;
- the alteration of spin state of radical pairs during the process doesn't take place;
- cubic symmetry of high temperature solid crystalline phase of PC allows us to make the quantitative description of diffusion both in liquid phase and in plastic mesophase on the basis of Frenkel's model of quasicrystalline structure of fluids<sup>2</sup> and Noyes' model of jump-like diffusion,<sup>3</sup>
- in order to consider the anisotropy of the reactivity of radical pairs and its averaging by the way of mutual reorientation of particles the Salikhov's model has been used.<sup>4</sup>

Using these propositions the basic equation for the quantum yield of the process ( $\varphi$ ) is:

$$\varphi^{-1} = (1 + S/N) \left[ 1 + \frac{S f (N + 1)}{1 + N + S(1 - f)} \right], \quad (1)$$

here  $S = k \tau_c n$ ,  $N = n (\tau_c / \tau_r + 1)$ ,  $f$  - the part of mutual orientations of reagents which favor the radical pairs recombination,  $k$  - the recombination constant under the condition of favorable recombination mutual orientation of

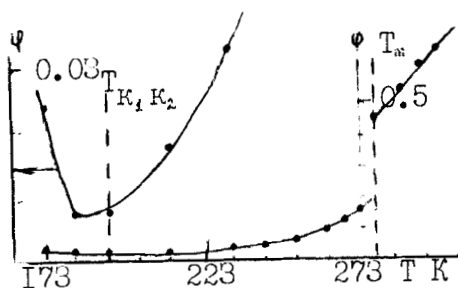


Fig. 1 The temperature dependence of  $\phi$  in the cyclohexane

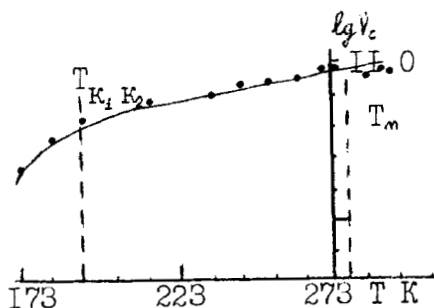


Fig. 2 The temperature dependence of  $\nu_r$  in the cyclohexane

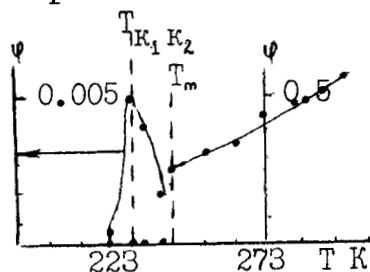


Fig. 4 The temperature dependence of  $\phi$  in the 1,1,1-trichloroethane

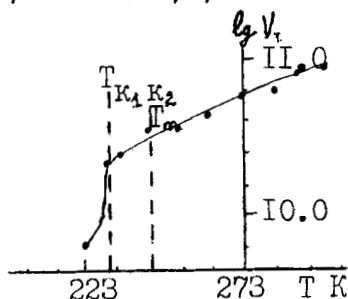
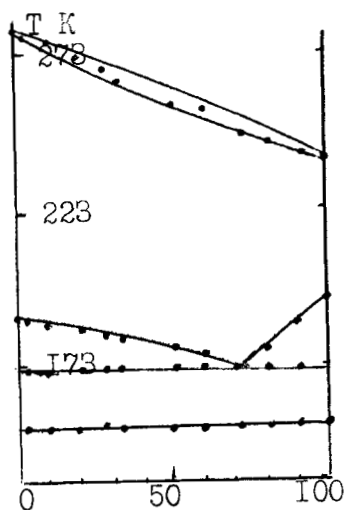
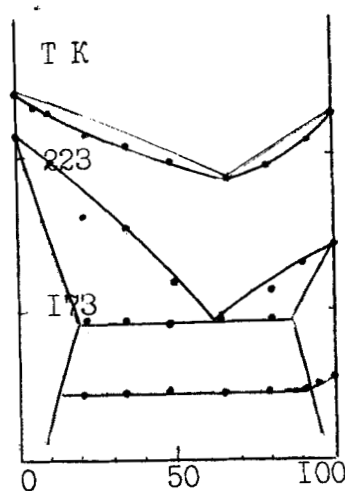


Fig. 5 The temperature dependence of  $\nu_r$  in the 1,1,1-trichloroethane



mol. %  $C_4H_9NO$

Fig. 3 The phase diagram of the system:  $l-C_4H_9NO - c-C_5H_{12}$



mol. %  $C_4H_9NO$

Fig. 6 The phase diagram of the system:  $l-C_4H_9NO - CCl_3CH_3$

reagents,  $n$  - the total number of the contacts of the particles in the solvent cage (for Frenkel's model  $n \approx 2$ ),  $\tau_c$  and  $\tau_r$  - specific times of translational and rotational diffusion. Under the conditions  $f \ll 1$ ,  $N \gg 1$  the equation (1) can be written as:

$$(\varphi)^{-1} - 1 = S (N^{-1} + f) = k \tau_c n \left[ \frac{1}{n (\tau_c/\tau_r + 1)} + f \right] \quad (2)$$

For liquid phase the ratio  $\tau_c/\tau_r$  may be estimated by the use of the Stocks - Einstein's equations:<sup>5</sup>

$$\tau_c = \lambda^2/6D_c = \pi\eta r \lambda^2/RT; \quad \tau_r = 1/6D_r = \pi\eta r^3/6RT, \text{ so:} \\ \tau_c/\tau_r = 6\lambda^2/r^2 \approx \text{const} \quad (3)$$

The estimation of the ratio  $\tau_c/\tau_r$  from equation (3) gives us the value of 30. It means that  $N \approx 60$  and for the liquid phase the condition  $N \gg 1$  is correct. In order to evaluate the specific time of translational diffusion of reagents in the liquid phase the following equations have been used:

$$\tau_c = \lambda^2/6D, \quad D = D_1 + D_2 = \frac{RT}{6\pi\eta r_1 F_1} + \frac{RT}{6\pi\eta r_2 F_2}.$$

Here  $\eta$  - viscosity of the solution,  $r_1$ ,  $r_2$  - radii of tert-butyl radical and NO molecule,  $\lambda$  - the value of the elementary diffusional translation ( $\lambda \approx 2 r_0$ ),  $r_0$  - radius of the solvent molecules,  $F_1$  and  $F_2$  - the correction factors which have been estimated using the equation:<sup>6</sup>  $F = 0,16 + 0,40 r/r_0$ . For liquid phase  $N^{-1} \gg f$ , so:

$$\varphi^{-1} - 1 \approx k \tau_c (\tau_c/\tau_r + 1)^{-1} \quad (4)$$

The correlation between  $(\varphi^{-1} - 1)$  and  $T/\eta$  - values is experimentally observed for all the cases except  $t\text{-C}_4\text{H}_9\text{NH}_2$ . Probably it is due to the existence of specific intermolecular interactions in the later system and the complex formation by NO and  $\text{NH}_2$  groups.

The  $k$  - values for different solvents obtained from equation (4) are equal to  $1.2 - 6.4 \cdot 10^{-12} \text{ c}^{-1}$ . It is the value of preexponential factor for elementary monomolecular reactions.

In the plastic mesophase the condition  $\tau_c/\tau_r \approx \text{const}$  is not correct. For this phase  $\tau_c/\tau_r \rightarrow \infty$  under  $T \rightarrow 0$ .

It means that for temperatures, insignificantly lower (10 - 12 K) than the melting point,  $N \gg f^{-1}$ . In this case the equation (3) can be written as:

$$(\varphi)^{-1} - 1 = k \tau_c n f \quad (5)$$

In the case of the incorporation of molecules of 2-methyl-2-nitrosopropane into crystalline matrix of PC (the nitroso compound and plastic mesogen form solid solution) the jump-like decrease of  $\varphi$ -value is obtained as a result of the crystallization. Such collapse of  $\varphi$  is due to sharp increase of  $\tau_c$ . The specific feature of solids in contrast to fluids is the strong dependence of diffusional parameters vs the sizes of incorporated and host particles. Thus far, as the tert-butyl radicals have the same dimensions as the matrix molecules, their translational displacement are provided by matrix self-diffusion mechanism. The small size of NO molecules allows it to incorporate into octahedral holes of PC face-centered cubic lattice without remarkable distortions; thus NO diffusion may occur between interstices. At low temperatures the NO diffusion makes the main contribution to mechanism of the geminal radical pairs  $[t-C_4H_9^\cdot + NO^\cdot]$  separation and followed nitroxide formation.

In order to calculate the  $\tau_c$ -values for high-temperature crystalline phases of PC Frenkel's equation has been applied:<sup>2</sup>

$$\tau_c = \tau_c^0 \exp((\Delta E_c)_m / RT) \exp(-\gamma), \quad (6)$$

here  $(\Delta E_c)_m$  - the activation energy of translational diffusion of NO,  $\gamma$  - the coefficient that reflects the thermal expansion of crystalline lattice:

$\gamma = 1/3 (\Delta E_c)_m \propto R^{-1}$ , where  $\alpha = (dV/dT)_p V^{-1}$  - the volume coefficient of thermal expansion.

For the  $\Delta E_c$ -value estimation the following equation has been proposed:

$$\Delta E_c = 12 * 4 * \varepsilon * [(\frac{\sigma}{\sigma - \Delta R})^{12} - (\frac{\sigma}{\sigma - \Delta R})^6] \quad (7)$$

there are  $\varepsilon$ ,  $\sigma$  - the parameters of Lennard-Jones potential,

$\Delta R$  - empiric parameter.

The combination of equations 2, 4, 6 and 7 allows us to deduce the expression for the quantitative description of degree of jump-like collapse of  $\varphi$ -value at the phase transition from the liquid phase (L) to the plastic mesophase (M). It is convenient to introduce  $\beta$ -parameter:

$$\beta = ((\varphi)_M^{-1} - 1) ((\varphi)_L^{-1} - 1)^{-1}.$$

So far as  $(\tau_r)_L \approx (\tau_r)_M$ ,  $N_M \gg 1$ ,  $n_L \approx n_M$ ,  $(\tau_0)_L \approx (\tau_0)_M$ ,

$$\beta \approx \frac{N_L}{N_L - n} [(\frac{N_L - n}{N_L})^{-1} + f - (\tau_c)_M / (\tau_c)_L]. \quad (8)$$

The ratios  $(\tau_c)_M / (\tau_c)_L$  have been estimated from the equation (6),

$$(\tau_c)_M / (\tau_c)_L = \exp((\Delta E_c)_M - (\Delta E_c)_L) / RT \cdot \exp(-(\gamma_M - \gamma_L)), \quad (9)$$

$$\gamma_M - \gamma_L = 1/3 R^{-1} [(\Delta E_c)_M (\alpha_M - \alpha_S) + ((\Delta E_c)_M - (\Delta E_c)_L) \alpha_L]. \quad (10)$$

Here  $(\Delta E_c)_L = \Delta E_\eta + R T_m$ , where  $\Delta E_\eta$  - the activation energy corresponding to the temperature dependence of the viscosity of the solution. In order to calculate  $(\alpha_L - \alpha_M)$  - value, the thermodynamic correlation has been used:

$$\alpha_L - \alpha_M = \Delta C_p (\Delta V_m / V) (\Delta H_m)^{-1}, \quad (11)$$

here  $\Delta C_p$ ,  $\Delta V_m$ ,  $\Delta H_m$  are the alterations of the isobaric thermal heat capacity, molar volume and enthalpy of the melting process of the system.

The  $f$ -value, estimated from experimental data for cyclohexane is  $2.0 \cdot 10^{-4}$ . It means that the assumptions made for equations (3) and (5) are correct. The  $f$ -value has been used for  $\beta$ -parameter evaluation for other PC. Experimentally obtained and theoretically estimated values of  $\beta$  ( $\beta^{\text{exp}}$  and  $\beta^{\text{th}}$ ) are given in Table 1. Comparison of  $\beta^{\text{exp}}$  and  $\beta^{\text{th}}$ -values indicates a good applicability of the proposed kinetic model for the quantitative description of diffusion-depended chemical processes in PC.

The disagreement of  $\beta^{\text{exp}}$  and  $\beta^{\text{th}}$ -values in the case of  $C_4H_9NH_2$  is probably due to the specific intermolecular interactions in the system "nitrosocompound - amine". In these conditions the principal propositions of kinetic model are incorrect.

The unusual temperature dependence of  $\varphi$ -value in the case of  $\text{CCl}_3\text{CH}_3$  is due to the self-ordering of 2-methyl-2-nitrosopropane in the crystalline host matrix. The tendency to self-organization and the difference between the geometrical sizes of nitroso compound and host molecules are the largest for this system. The processes of self-organization can be described by introducing the temperature dependence of the parameters  $\epsilon$  and  $\sigma$  (see the equation 7).

Thus the present investigation demonstrates the applicability of PC as a media for realizing the chemical process with diffusion-depended stages at low temperatures. It shows the possibility of regulation of the diffusional parameters of the PC by varying the temperature and plastic mesogen nature.

Table 1

PC	a, nm	$T_m$ , K	$\Delta H_m$ , kJ/mol	$\Delta V_m/V$	$\beta^{\text{exp}}$	$\beta^{\text{th}}$
c-C <sub>6</sub> H <sub>12</sub>	0.876	280	2.68	0.052	4.0	-
c-C <sub>6</sub> H <sub>10</sub>	0.861	230	1.78	0.025	1.3	1.5
c-C <sub>6</sub> H <sub>11</sub> OH	0.883	295	1.00	0.024	1.0	1.6
t-C <sub>6</sub> H <sub>9</sub> Cl	0.862	245.5	2.09	0.075	19.8	12.3
$\text{CCl}_3\text{CH}_3$	0.839	242.5	2.09	0.048	174	35.3
t-C <sub>6</sub> H <sub>9</sub> NH <sub>2</sub>	0.880	208	0.87	-	37	~ 2
t-C <sub>6</sub> H <sub>9</sub> NO	0.880	237	1.26	-	1.0	~ 2

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