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# The Rotation Mobility of the Guest Molecules and its Reactivity in the Thermal Reaction in the Solid Matrix

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THE ROTATION MOBILITY OF THE GUEST MOLECULES AND ITS REACTIVITY IN THE THERMAL REACTION IN THE SOLID MATRIX

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Abstract Characteristic times thermal of the reaction and the molecular rotation for the molecules have been measured in polystyrene films. was Rotation mobility of molecules determined relaxation of the light induced optical anisotropy of the photoselected samples. of the activation agreement energies characteristic times of thermal reaction molecular rotation was observed. By the comparison of the induced optical anisotropy of the initial photoconverted molecules the angles of the of the molecular dipole transition moment instant of the elementary act of the photochemical conversion were determined.

#### INTRODUCTION

The molecular rotation mobility is known to correlate with molecules2.2. the reactivity of Commonly the molecular is measured by the spin label rotation mobility fluorescent methods. As a result the correlation molecular rotation and reaction of different molecules makes Photoselection it considered. possible investigate molecular rotation and reaction the of molecules simultaneously.

Photoselection means that under irradiation polarized light only preferably oriented molecules undergo photochemical reaction. As a result the macroscopic appears3,4. The optical anisotropy of the sample dark this anisotropy is determination of the rotation mobility of the molecules<sup>5</sup> . Comparison of the light induced optical anisotropy of initial and photoconverted molecules allows to measure the rotations movements of molecules at the moment of the elementary act of the chemical reaction.

## EXPERIMENTAL RESULTS AND DISCUSSION

Light induced optical anisotropy of samples were observed in the course of the following reactions carried out in polystyrene films under irradiation of polarized light:

R = 3 - pyrenil

photoisomerisation of 9-tert-butylanthracene (I) in its Dewar isomer (II) and photoisomerisation of pyrazolidone-(3)-azomethine imine (III) in aziridine (IV) (Figure 1).

The kinetics of the thermal relaxation of optical anisotropy of 9-tert-butylanthracene presented 2. The magnitudes of characteristic times for molecular were calculated due developed method earlier6,7 and presented in 1.

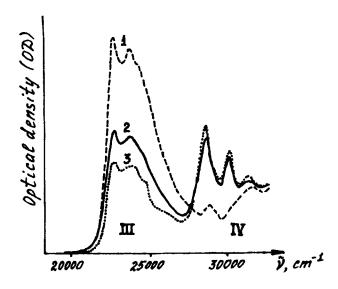


FIGURE 1 The spectra of III and IV in polystyrene film at room temperature: 1 - before irradiation, 2 and 3 - after irradiation with polarized light: polarizations of irradiating and probing light beams are mutually perpendicular (2) or parallel (3).

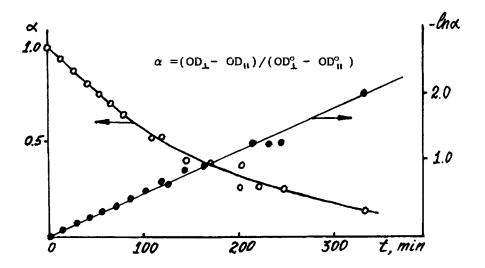


FIGURE 2 The dark relaxation of the light induced optical anisotropy of 9-tert-butylanthracene in polystyrene at 293 K.

The effective activation energies have been evaluated from the Arrhenius plots in the temperature range 293-323K (Table 1).

TABLE 1 Characteristic times and effective activation energies for thermal reaction and molecular rotations.

Compound	τ <sub>ROT</sub> 10 <sup>-4</sup> (sec)	τ <sub>REACT</sub> 10 <sup>-4</sup> (SeC)	E <sub>rot</sub> (kcal/M)	E <sub>REACT</sub> (kcal/M)
I <sup>7</sup>	(1.4÷2.0)	(2.0÷2.6)	25±3	22.1±0.3
IV	(2.1÷3.4)	(4.0÷7.1)	19±2	17±2

A good agreement of characteristic times for thermal reaction and molecular rotation was observed (Table 1). Presumably, the thermal reaction as well as the thermal rotation of the guest molecules in polystyrene are determined by the same properties of the surroundings.

Comparative analysis induced of light anisotropy of the initial and photoconverted molecules angles of the to measure the the molecular dipole transition moment  $(\theta)$  in the of the elementary act of the chemical conversion photoisomerisation of III and IV. For the experimental determination of  $\theta$  the equation was derived:

$$(OD_{II}-OD_{\perp})^{B} = R(OD_{\perp}-OD_{II})^{A}$$

were  $R=P_2(\cos\theta)[(\epsilon_z - \epsilon_x)\epsilon]^B/[(\epsilon_z - \epsilon_x )\epsilon]^A$ ,

 $P_z(\cos\theta)=(3\cos^2\theta-1)/2$ ,  $\epsilon_z$ ,  $\epsilon_x$  - the principle values of extinction coefficient tensor,  $\epsilon=(\epsilon_z+2\epsilon_x)/3$ .

The magnitudes of  $\boldsymbol{\theta}$ , calculated from the experimental data are presented in Table 2.

TABLE 2 Obtained magnitudes of  $\theta$ 

emperature	Proce	sses
Т, К	III—IV	IVIII
77	0÷8°	***
293	0÷8° 20±3°	30±2°

We associate the transition moments in this molecules with the pyrenil group. The fact, that the low temperature magnitude of  $\theta$  is smaller then the "high" temperature one, shows that the photochemical reaction at the temperature of boiling nitrogen occurs without restructuring of the immediate environment of pyrenil fragment. Ιt is with kinetic nonequivalency of molecules course of low temperature photochemical reaction. The 293 K reactions include the rotation of pyrenil group and associate with the rearrangement of polymer chains the molecular surrounding medium.

#### ACKNOWLEDGMENT

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