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Cage effects upon light irradiation on azo compounds: *cis*→*trans* isomerization in polymethyl methacrylate

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Abstract

Three azo compounds of different molecular sizes were used to study relation between the rates of *trans*→*cis* photoisomerization and inverse isomerization in the dark in a polymethyl methacrylate matrix. Molecule distribution over isomerization rates is observed for both direct and inverse isomerizations. It is shown that correlation between the rates of *trans*→*cis* photoisomerization and inverse dark isomerization takes place for compound of large molecular size: the molecules that are most quickly isomerized in the some direction are also quickly isomerized in the opposite direction. No correlation is recorded in case of small molecular size compound. These results are explained by a change in local matrix structure due to light energy dissipation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Azo compounds; Polymeric matrix; *Cis*→*trans* isomerization; Dissipation of energy

1. Introduction

It is known that the kinetics of chemical reactions in solid phase often does not obey a classical kinetic law. The reaction rate decreases anomalously with time [1,2]. For monomolecular reactions this is assigned to the different structures of cages which involve reacting molecules. Therefore, the reaction kinetics is described by the sum of exponents corresponding to different cage types. The present paper is devoted to the kinetic study of *cis*→*trans* isomerization of azo compounds in the amorphous polymethyl methacrylate (PMMA) matrix. It is known that in the solid matrix this reaction often disobeys the kinetic law of first order [3–5].

A standard enthalpy of azo compounds *cis* isomers is much larger than that of *trans* isomers. For instance, the difference in the standard enthalpies of azobenzene isomers is 11.7 kcal mol⁻¹ [6]. Thus, with thermodynamic equilibrium in the dark, azo compounds are mainly observed in the *trans* form. The *cis*→*trans* transformation can occur both under light and in the dark whereas *trans*→*cis* transformation occurs only under light.

It is shown [7] that the act of azobenzene *cis*→*trans* photoisomerization in liquid phase lasts about several hundreds of femtoseconds. For the next about 20 ps the energy is

transferred from an excited molecule to the environment through the vibrational degrees of freedom [7,8]. Studying azobenzene *cis*→*trans* photoisomerization in the liquid phase by the method of time-resolved optical spectroscopy, authors of [9] observe the spectrum of *trans* molecules in the excited state. 13–16 ps after photon absorption (the time depends on a solvent) the spectrum acquires a normal form. Obviously, during this time the molecule is deactivated. The time of azobenzene *trans*→*cis* isomerization upon excitation of *trans* molecule in the *n*-π* state was determined in [7] to be 0.32 ps. For the next 20 ps energy dissipation into the environment occurs.

The goal of the present paper is to elucidate whether photon energy dissipation in the matrix leads to rearrangement of its local structure. This problem is important for both radiation chemistry and solid state photochemistry and has been discussed in many papers, e.g., [10,11].

Trans→*cis* isomerization resulting in the formation of a *cis* molecule in the excited state is followed by excitation energy dissipation into the matrix. If this process causes no rearrangement in the local environment of the azo compound molecule then the direct and inverse conversion occur in the cages of the same structure. In this case a certain rate of inverse dark conversion corresponds to a certain photoisomerization rate. If energy dissipation in the matrix leads to rearrangement of its structure, the *trans*→*cis* isomerization and the inverse process occur in the cages of different

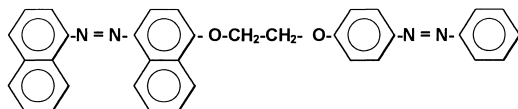
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configurations. In the case of random cage rearrangement there is no correspondence between the rates of direct and inverse processes.

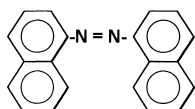
To reveal correlation between the rates of direct and inverse conversion we irradiated the *trans*-containing sample by a 405 nm light for different periods of time. Under short irradiation only the 'fast' (more reactive) *trans* molecules transform into the *cis* form. Under long irradiation both the 'fast' and 'slow' (less reactive) *trans* molecules transform into the *cis* form. If there is no correlation, a function of *cis* molecule distribution throughout the rate constants of dark isomerization is independent of the degree of preliminary *trans*→*cis* conversion. Otherwise, we observe the dependence of the kinetics of dark *cis*→*trans* isomerization on the initial content of a *cis* isomer.

2. Experimental details

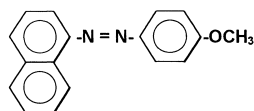
We used the following azo compounds. Compound I:



compound II (1,1'-azonaphthalene):



compound III (1-naphthyl-azomethoxybenzene):



All compounds were synthesized using commercial reagents as described in [12]. The absorption spectra of 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene are presented in [5].

Compound I has two chromophore groups: azobenzene and azonaphthalene. The maximum of *trans* isomer absorption band of the former is observed for a wavelength of 348 nm (28750 cm^{-1}) and that of the latter is recorded at 413 nm (24200 cm^{-1}). The optical absorption spectrum and its evolution are represented in Fig. 1. In the present paper we have studied the kinetics of the dark *cis*→*trans* isomerization of azonaphthalene group.

The isomeric composition of the azobenzene fragment of compound I varies negligibly during the measurement of the dark isomerization kinetics of azonaphthalene fragment at 287 K due to a smaller value of the rate constant of its dark isomerization rather than of the azonaphthalene fragment. According to our measurements, the rate constant of the dark

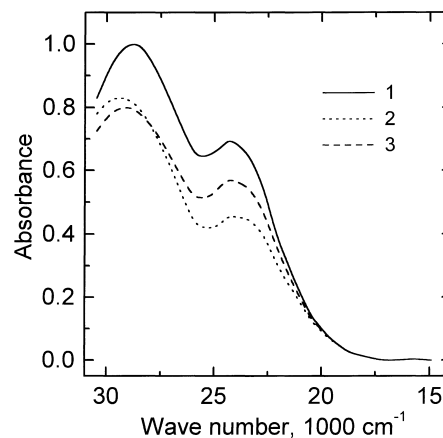


Fig. 1. UV VIS absorption spectrum of compound I before irradiation (1) and after 20 min of irradiation at 405 nm (2) at 287 K in PMMA. Spectrum 3 is a result of evolution of spectrum 2 during a 10 min in dark.

isomerization of azobenzene fragment at, e.g., 293 K does not exceed $5 \times 10^{-4}\text{ min}^{-1}$. It is assumed then that during the measurement of the kinetics of azonaphthalene fragment dark isomerization the isomer composition of azobenzene fragment remains constant. We have verified that the kinetics of azonaphthalene fragment isomerization is independent of the isomeric composition of the azobenzene fragment. In fact, the role of the latter is to increase the size of a molecule. Besides, as established experimentally, absorption at the wavelength of the record of azonaphthalene fragment isomerization (413 nm) does not vary with varying isomeric composition of azobenzene fragment.

The *trans*→*cis* conversion of azo compounds was carried out by means of 405 nm irradiation. A change in the content of isomers during reaction was recorded by measuring the optical density of samples at wavelength of the maximum of *trans* isomer $n-\pi^*$ absorption band. A value of this wavelength for 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene is equal to 403 and 382 nm, respectively. The values of *cis* isomer concentrations of compound I, 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene (photoequilibrium at 405 nm) in PMMA at 293 are estimated to be 35%, 45%, and 80%, respectively.

A 405 nm light is strongly absorbed by *trans* isomers of the azo compounds. To record photoisomerization kinetics, the samples were prepared in the form of a $10\text{ mm} \times 5\text{ mm} \times 1.7\text{ mm}$ parallelepiped. A probing spectrophotometer beam was directed onto the sample normally to a 10×1.7 face so that it passed through the middle of the face. A 405 nm light was directed across a 10×5 face. In this case, an increase in light intensity in the probed sample layer during the *trans*→*cis* isomerization did not exceed 13% for all compounds.

The 405 nm light intensity measured by azobenzene isomerization rate in isoctane using the data of [13] was $(12 \pm 0.3) \times 10^{16}\text{ s}^{-1}\text{ cm}^{-2}$. As a light source we used a mercury DRSh-500 lamp with a power of 500 W in concert with a glass filters. For more details see [5].

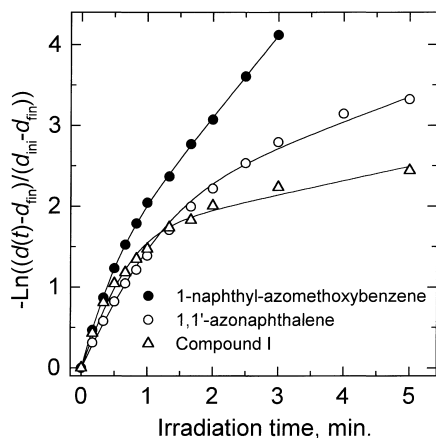


Fig. 2. First-order plots for 405 nm photoisomerization of azo compounds in PMMA at 287 K. Solid lines are approximation by biexponential law.

3. Results and discussion

Fig. 2 shows the kinetic curves for *trans*→*cis* photoisomerization of the azo compounds at 405 nm in PMMA. The curves do not follow the exponential law. The distribution of reacting particles over quantum yields of photoisomerization takes place for the given azo compounds. Strictly speaking, there is a distribution over sums of the quantum yields of direct and inverse processes. A values of the quantum yields of *trans*→*cis* and *cis*→*trans* conversions depends on the geometry of the cage.

Fig. 3 shows the kinetic curves for the dark *cis*→*trans* isomerization of the azo compounds in PMMA for various

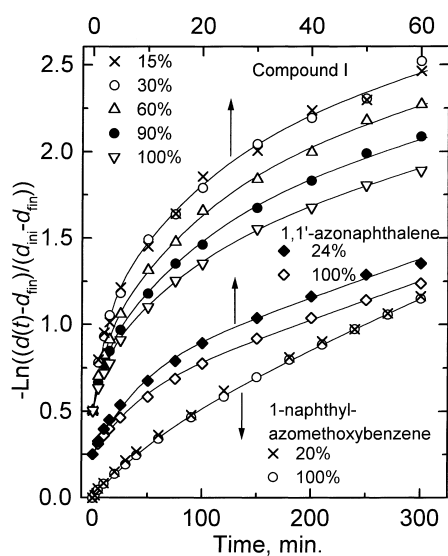


Fig. 3. Dependence of dark *cis*→*trans* isomerization kinetics from initial *cis* isomer content. First-order plots for dark isomerization of compound I and 1,1'-azonaphthalene at 287 K and 1-naphthyl-azomethoxybenzene at 293 K in PMMA. 100% corresponds to 405 nm photoequilibrium content of *cis* isomer. Solid lines are approximation by law (1) (compound I) or biexponential law (1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene). Curves for isomerization of compound I and 1,1'-azonaphthalene shifted vertically upward.

initial contents of a *cis* isomer. Firstly, let us consider the dark isomerization kinetics of compound I. As follows from the Fig. 3, the kinetic curves corresponding to the initial *cis* isomer content of 15% and 30% of the maximum content coincide. A further increase in the initial *cis* isomer content leads to retardation of dark isomerization. It is concluded then that correlation between the rates of *trans*→*cis* photoisomerization and inverse dark *cis*→*trans* isomerization takes place. If a particle converts quickly from *trans* form to *cis* one under light then it isomerizes rapidly back. Thus, the steric obstacles exert the same effect on the direct and inverse conversions of compound I.

Coincidence of the curves, corresponding to the 15% and 30% initial contents of *cis* isomer, can be explained as follows. At small *trans*→*cis* conversion degrees the exponential laws, describing changes in the concentrations of isomers in various ensembles can be substituted by linear laws to within fair accuracy. In this case, the accumulation of *cis* molecules in each ensemble is in direct proportion to time. The number of *cis* molecules increases and their relative distribution in various ensembles remains the same.

To describe quantitatively the experimental kinetic curves we have used the next approximation. We assumed the molecules are distributed over three nonmixing ensembles. Each ensemble is characterized by both its value of dark isomerization rate constant and the number of particles involved. We have chosen three ensembles because this is the minimum number at which we could describe the experimental kinetic curves well. Some contents of isomers are established in each ensemble under irradiation of certain duration.

The isomerization rate constants of particles from different ensembles were determined from the kinetic curve of dark isomerization with the initial content of isomers equal to the 405 nm photoequilibrium one. This curve was approximated by the function

$$\frac{(d(t) - d_{\text{fin}})}{(d_{\text{ini}} - d_{\text{fin}})} = p_1 \exp(-k_1 t) + p_2 \exp(-k_2 t) + p_3 \exp(-k_3 t) \quad (1)$$

where t is the time, $d(t)$, d_{ini} , d_{fin} are the current, initial, and final values of the sample optical density at wavelength of the maximum of *trans* isomer absorption, k_1 , k_2 , k_3 are the dark isomerization rate constants and $p_1 + p_2 + p_3 = 1$. When the equilibrium fractions of isomers in each ensemble are the same, the p_1 , p_2 , p_3 coefficients are equal to the fractions of azo compound particles belonging to different ensembles. We assumed the fulfilment of this condition.

If irradiation was performed for shorter time than it was necessary to the establishment of photoequilibrium, the time dependence $d(t)$ was also described by Eq. (1). The p_1 , p_2 , p_3 values in this case are the initial fractions of *cis* particles from different ensembles. Their values were determined by approximating the kinetic curves of dark isomerization in terms of expression (1). In this case we used previously determined values k_1 , k_2 , k_3 . The calculated curves are

Table 1
Parameters of the distribution of compound I molecules over dark isomerization rate constants

Initial <i>cis</i> isomer fraction ^a (%)	Weights			Isomerization rate constants (min ⁻¹)		
	<i>p</i> ₁	<i>p</i> ₂	<i>p</i> ₃	<i>k</i> ₁	<i>k</i> ₂	<i>k</i> ₃
30	0.41	0.35	0.24			
60	0.31	0.40	0.29	0.56	0.08	0.0091
90	0.25	0.40	0.35			
100	0.22	0.36	0.42			

^a 100% corresponds to 405 nm photoequilibrium fraction.

depicted in Fig. 3 by solid lines. Table 1 summarizes parameters of distributions obtained for compound I.

As follows from the Table 1, even at the shortest irradiation time the 'slow' *cis* molecules originate. Their number is comparable with number of 'fast' *cis* molecules that contradicts the concept that the less-reactive *cis* molecules are obtained only from the less-reactive *trans* molecules.

To remove this contradiction we suggested that the appearance of 'slow' *cis* molecules from the 'fast' *trans* molecules be caused by rearrangement of the local structure of the matrix. The reason for rearrangement is that the energy transfer from excited *cis* molecule to the matrix follows the act of *trans*→*cis* isomerization [7] that can cause a change in the local structure of the matrix. Therefore, a 'fast' *trans* molecule can give a 'slow' *cis* molecule.

The energy dissipated to the matrix leads to 'heating' and changes in the structure of some restricted matrix region. It is expected that the degree of correlation between the rates of direct and inverse conversions will depend on the size of an isomerizing molecule. Indeed, when the molecule size is smaller than the 'heated' zone, the rate correlation must be absent because the configuration of the cage, containing *cis* molecule, differs from that involving predecessor *trans* molecule. To verify this assumption, we have performed experiments using 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene.

Fig. 3 demonstrates a weak difference in the kinetic curves of the 1,1'-azonaphthalene dark isomerization for the initial *cis* isomer contents, equal to 24 and 100% of 405 nm photoequilibrium value. The kinetic curves can be described to within good accuracy by the sum of two exponents because the distribution of the particles of this compound over isomerization rate constants is more narrow

than that of compound I. A more narrow distribution is a result of smaller size of 1,1'-azonaphthalene molecules.

Finally, the dependence of the kinetics of dark *cis*→*trans* isomerization of 1-naphthyl-azomethoxybenzene on the initial number of *cis* isomer particles is not observed (Fig. 3, bottom curve). Obviously, a change of azo molecule's matrix environment due to *trans*→*cis* isomerization is drastic in this case. Probably, the 'heated' zone completely includes the molecule of this compound.

Table 2 presents parameters of biexponential distribution for the *cis*→*trans* isomerization of 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene. As follows from Tables 1 and 2 the ratio between the maximum and minimum rate constants of dark isomerization is about 62 for compound I, 13 for 1,1'-azonaphthalene, and 7 for 1-naphthyl-azomethoxybenzene. This ratio characterizes a width of distribution over rate constants. The width of particle distribution over effective rate constants of *trans*→*cis* 405 nm photoisomerization is much smaller than that of particle distribution over the rate constants of dark *cis*→*trans* isomerization for all compounds. The *trans*→*cis* photoisomerization kinetics is well approximated by the sum of two exponents (Fig. 2). A ratio between the exponents indices for compound I is 17 and those for 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene are 7 and 4, respectively.

We think that a more narrow distribution in the case of photoreaction is caused by a change in the environment structure of azo molecule after unsuccessful absorption of a photon. The initial quantum yield of *trans*→*cis* isomerization of 1-naphthyl-azomethoxybenzene in PMMA measured at 290 K under 405 nm light is 0.07 ± 0.02 and for 1,1'-azonaphthalene it is 0.02 ± 0.005 . Thus, before *trans*→*cis* isomerization the azo molecule absorbs several photons.

Table 2
Parameters of the distributions of 1,1'-azonaphthalene and 1-naphthyl-azomethoxybenzene molecules over dark isomerization rate constants

Compound	Initial <i>cis</i> isomer fraction ^a (%)	Weights		Isomerization rate constants (min ⁻¹)	
		<i>p</i> ₁	<i>p</i> ₂	<i>k</i> ₁	<i>k</i> ₂
1,1'-azonaphthalene	24	0.35	0.65		
	100	0.30	0.70	0.16	0.012
1-naphthyl-azomethoxybenzene	20	0.25	0.75		
	100	0.25	0.75	0.02	0.0029

^a 100% corresponds to 405 nm photoequilibrium fraction.

Due to the small quantum yield of luminescence (10^{-4} [14]) this energy is emitted almost completely into the matrix and is used for matrix rearrangement near the azo compound molecule. Thus, the reactivity of a given molecule is averaged over the cages of different configurations but the averaging is incomplete. Isomerization kinetics remains nonexponential. Probably, after energy transfer to the cage some cage configurations are not realized.

Thus, photon energy dissipation into the matrix leads to rearrangement of its local structure. The rearrangement results from the increase in molecular mobility in the limited region. The size of this region is smaller than the size of compound I but does not exceed or is comparable with the size of the 1-naphthyl-azomethoxybenzene molecule.

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