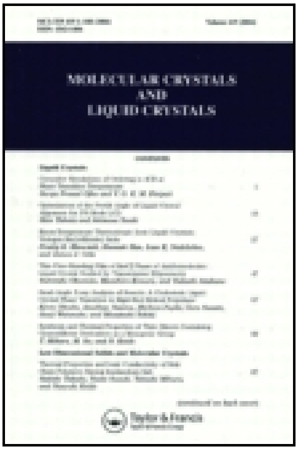

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Kinetics of Photochromic Reactions of Substituted Azobenzenes in Solutions, and in Liquid Crystalline and Polymer Matrices

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Kinetics of Photochromic Reactions of Substituted Azobenzenes in Solutions, and in Liquid Crystalline and Polymer Matrices

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Kinetics of photochromic reactions was studied in azobenzene derivatives: azobenzene-containing crown ethers, and 4-methoxy-4′-halogen-substituted azobenzenes capable of forming liquid crystalline phases. The photoactive materials were dissolved in alkanes, and in polymer and liquid-crystalline matrices. The isomerisation reactions follow the first order kinetics, in some polymer matrices, however, a dispersion of the rate constants was found. Thermal cis-trans isomerisation rates of halogen-substituted azobenzenes in n-heptane were found practically independent of the substitutent. Kinetics of the same reactions in liquid crystalline matrices seems to exhibit anomalies near phase transitions of the matrices.

Keywords: photochromism; isomerisation; kinetics; crown ether; azobenzene derivative; liquid crystal

INTRODUCTION

A photochromic process can be defined as a reversible reaction in which at least the first step ('forward reaction') is photochemically driven. Azobenzenes are one of the most extensively studied groups of photochromic materials owing to their emerging applications in data storage and processing. Although attention of most researchers has been focused on the applications, fundamental studies of such systems seem nevertheless necessary in order to optimize their photochemical activity. The materials under study, when excited with UV light, undergo a reversible trans-cis isomerisation (see Fig. 1). Since such reactions are space-demanding, one can expect the photochromic behaviour of substituted azobenzenes depend on both, chemical nature of substituents and constraints induced by matrices [1,2]. This feature opens a possibility of controlling the kinetics of photochemical reactions in substituted azobenzenes by a suitable tailoring of substituents and/or by a modification of the matrices.

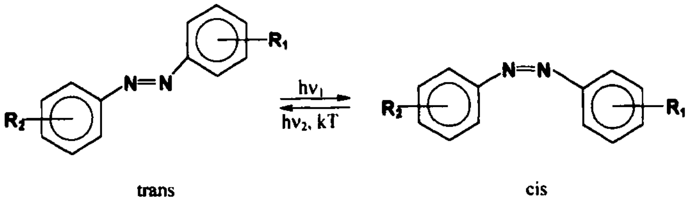

FIGURE 1 Isomerisation of azobenzene derivatives.

In this paper we present results of measurements of the isomerisation kinetics of two groups of substituted azobenzenes: crown ethers containing the azobenzene moiety built into the crown (Ia-Ic) [3], and asymmetrically substituted azobenzenes which can form liquid crystalline (LC) phases (IIa – IId) [4]. The formulae of the molecules are presented in Figure 2.

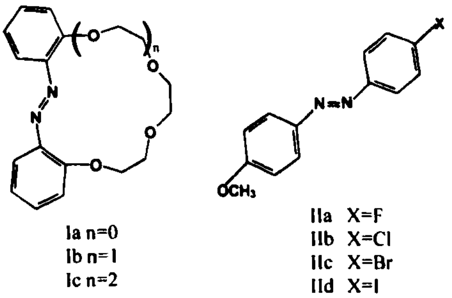

FIGURE 2 Formulae of photochromic azobenzene derivatives used in the present study

The measurements were performed in alkane (isooctane or n-heptane) solutions, as well as in polymer (Ia – Ic) and liquid crystalline (IIa – IId) matrices.

EXPERIMENTAL

Details of the synthesis of the materials under study can be found in [3,4]. Liquid solutions were prepared with n-heptane or isooctane (Merck, spectroscopic grade), their concentrations being of the order of 10^{-5}M. Polymer (PMMA or polystyrene) films were obtained by casting solutions of the crown ethers and PMMA in chloroform (or the ethers and polystyrene in toluene) on glass plates, the concentrations of the ethers amounting to ca 0.2% w/w. Liquid crystalline matrices used throughout this work were n-pentylcyanobiphenyl (5CB) or E7 commercial LC mixture (Merck). The cells were 5 μm thick, filled with 10^{-2} M solutions of IIa – IIb in LC.

The isomerization kinetics was monitored spectrophotometrically, by following the absorbance of the trans forms of the substituted azobenzenes at ca. 350 nm. The absorption spectra were measured with Perkin Elmer Lambda 20 and Shimadzu UV-2101PC spectrophotometers. The photoisomerisation of the samples was performed at 298K, using a 200 W Hg lamp and appropriate combinations of colour filters. In all samples, a good reproducibility of the spectra and of the kinetic curves was observed after several experimental cycles.

RESULTS AND DISCUSSION

Figure 3 presents absorption spectra of the studied materials in both, thermodynamically stable (trans) and metastable (cis) forms. All spectra contain bands in UV resulting from π–π^* transitions and less intense bands in the visible due to n–π^* transitions. A splitting of the π–π^* peak was observed in the crown ethers, probably caused by an asymmetry of the azobenzene moiety. The intensity ratio of the components of the UV band depends on the size of the crown (cf. Fig. 3). Under irradiation in the UV region, all compounds convert to their cis isomers. The reaction manifests itself in a strong decrease of the intensity of the UV band and an increase of the intensity of the VIS band accompanied by a red shift.

The kinetics of the thermally driven reverse (cis-trans) reaction was studied in detail for all compounds, in several matrices. In all 'conventional' solutions, as well as in some matrices, semilogarithmic decays were observed, indicative of the first order kinetics (cf. Fig. 4a). Im some polymers and LC matrices, however, deviations from the expected behaviour were found though the reactions have obviously been the same. This feature can be attributed to distributions of rate constants accociated with distributions of micorenvironments of reacting species [5,6]. We assumed that the former distribution can be described by a single pre-exponential factor and a Gaussian distribution of activation energies in the Arrhenius equation. Under such an assumption, the non-exponential decays have been well fitted with model curves (e.g. Fig. 4b, see also [7]). A comparison of results obtained for various matrices, given in Table 1, shows that the activation energies determined for the three crown ethers vary little between the compounds, being also practically independent of the matrix used.

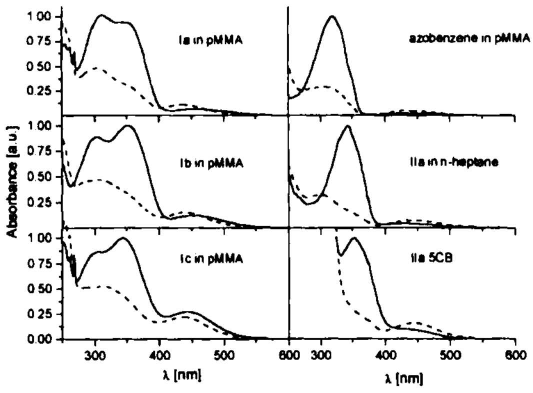

FIGURE 3 Absorption spectra of the molecules under study. The spectrum of parent azobenzene is shown for comparison. Full lines – pristine samples containing mostly trans isomers, dashed lines – the same samples after irradiation into the UV band, containing mostly cis isomers.

The thermal isomerisation of compounds IIa-IId in n-heptane is well fitted by the first order kinetics, with parameters of the Arrhenius equation being practically independent of the halogen atom: within an experimental uncertainty, all experimental points fall onto a master curve, with ν = 1.9×10^{11} s^{-1} and E_a = 93 kJ/mol. The thermal isomerisation of the same molecules dissolved in the liquid crystalline

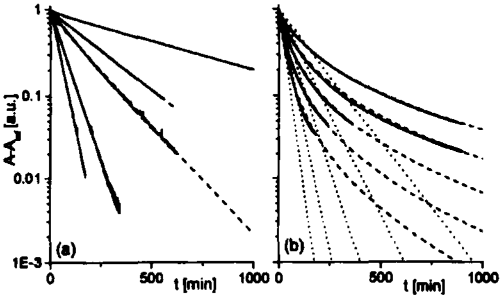

FIGURE 4 Typical decays of the absorbance at 350 nm: (a) Ic in PMMA, (b) Ic in polystyrene. Full lines, experimental data; dashed lines, fits performed with the following sets of experimental results: (a) ν = 1.3×10^{10} s^{-1}, E_a = 94 kJ/mol; (b) ν = 3.3×10^{9} s^{-1}, E_a = 88 kJ/mol, dispersion of E_a = σ = 3 kJ/mol The dotted lines in (b) have been calculated for the same values of the pre-exponential factor and activation energy, neglecting the dispersion.

TABLE 1 Activation energies (E_A) and preexponential factors (ν) of the cis-trans isomerisation of crown ethers in the isooctane solution and in polymer films.

Cpd.	Isooctane		PMMA		Polystyrene	
	E_A [kJ/mol]	ν[s^{-1}]	E_A [kJ/mol]	ν[s^{-1}]	E_A [kJ/mol]	ν[s^{-1}]
Ia	105	4.2×10^{11}	97	1.4×10^{10}	-	-
Ib	98	1.7×10^{11}	92	8.7×10^{9}	95 disp.	2.9×10^{10}
Ic	104	6.9×10^{11}	94	1.3×10^{10}	88 disp., $\sigma \cong$3kJ/mol	3.3×10^{9}

matrices seems to be faster than in n-heptane, in spite of the viscosity of the latter matrix exceeding that of the hydrocarbon: our measurements performed in IIa and IIb in 7E yielded $\nu = 4\times10^9$ s^{-1} and E_a = 82 kJ/mol. It should also be mentioned that the isomerization rates seem to exhibit an anomalous behaviour in the vicinity of phase transitions occurring in LC matrices.

FINAL REMARKS

The kinetics of thermally driven reverse photochromic reactions was measured in two groups of azobenzene derivatives. The rate constants in crown ethers are almost independent of the matrix used, probably due to the shapes of the molecules. The isomerisation kinetics of halogen-containing azobenzenes was found to be influenced by use of LC matrices and by phase situation of the matrices. This feature seems to create interesting prospects from the point of view of applications in, e.g., real time holography.

Acknowledgements
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