Free Radical Generation during Thermal Decomposition of Azoisobutyronitrile in Nematic Liquid Crystal Mixtures[†]

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Free radical generation during the thermal decomposition of azoisobutyronitrile (AIBN) in nematic 5CB:5OCB mixtures has been studied by electron paramagnetic resonance (EPR) at 308–343 K. The kinetic model of primary radical cage escape in nematic mesophases is considered from the point of view of rotational and translational evolution of primary radical pairs ordered by anisotropic intermolecular energy potentials. An expression has been obtained to describe the cage effect of free radicals escaped into the bulk as a function of the order parameter of a nematic matrix.

The investigation of free radical reactions in liquid crystals is of great interest, particularly in respect of means of effective chemical stabilization of liquid-crystalline materials. This problem is especially acute for a number of cholesteric and nematic liquid crystals.[1,2]

The effects of molecular orientational ordering on the kinetics of some photo-induced free radical reactions in nematic and smectic liquid crystals has been discussed previously.[3-5] In the present work we analyse the specific features of active radicals generated thermally in a nematic matrix during thermal decomposition of a model azocompound, i.e. AIBN which is widely used as a free-radical initiator.[6] The factors which determine the radical reaction kinetics in a molecular organized mesophase are considered.

Experimental

Materials

AIBN was purified twice by recrystallization from ethanol. The liquid crystals, 4-pentyl-4'-cyanobiphenyl (5CB) and 4-pentyloxy-4'-cyanobiphenyl (5OCB) of highest purity grade were employed without further purification. The stable radical 2,2,6,6-tetramethyl-4-piperidine-N-oxide (TEMPO) was purified by sublimation under vacuum conditions.

Kinetic Investigation

The kinetics of free radical formation during the thermal decomposition of the azocompound dissolved in a liquid-crystalline 5CB:5OCB mixture of varying component ratios has been studied by EPR using an EPR Rubin spectrometer (made in Russia) of 3 cm range over a temperature range of 308–343 K. The free radicals in the sample volume were determined by measuring the expenditure of stable TEMPO which was used as a counter of active cyanoisopropyl radicals.

The rate constant of free radical generation (k_i) during thermal decomposition of AIBN was measured using the kinetics of the expenditure of the TEMPO via its interaction with primary radicals escaped in the sample's bulk.

The value of the cage effect (e) was determined from the relationship

$$e = W_i/2k_D[\text{In}], \qquad (1)$$

where W_i is the free radical generation rate measured from the initial decrease of the TEMPO EPR signal during thermal
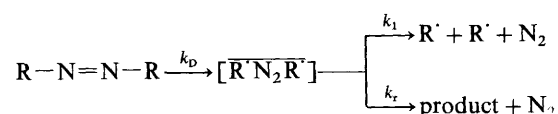
decomposition of the azocompound; [In] is the initial AIBN concentration and k_D is the rate constant of AIBN decomposition. The last value was measured in different matrices, and it was found that k_D is independent of the nature of the matrix at a given temperature and can be described as $k_D = 1.58 \times 10^{15} \exp(-129 \text{ kJ}/RT)$.[7]

Dynamic Investigation

The stable nitroxide radical TEMPO was used in our investigation as a free radical acceptor ('counter' of active radicals) and as a spin probe, which characterized, by means of EPR, the molecular dynamics of the system. The evaluation of micro-viscosity values (Q) of the reactive system of different compositions and at different temperatures has been described previously.[8] The stable radical has almost globular shape[8] and was not oriented by the liquid-crystalline matrix. Hence its EPR spectra were not influenced by matrix anisotropy and reflect the effective value of Q at given temperature.

Results and Discussion

Thermal decomposition of AIBN takes place as a simultaneous break of two C—N bonds and corresponding formation of a geminal radical pair:

$$\text{R—N}{=}\text{N—R} \xrightarrow{k_D} [\overline{\text{R}^{\cdot}\text{N}_2\text{R}^{\cdot}}] \begin{cases} \xrightarrow{k_1} \text{R}^{\cdot} + \text{R}^{\cdot} + \text{N}_2 \\ \xrightarrow{k_r} \text{product} + \text{N}_2 \end{cases}$$

where R is $(\text{CH}_3)_2{-}\text{C}^{\cdot}{-}\text{CN}$. The translational and rotational evolution of these radical pairs in an isotropic or anisotropic solvent cage determines the relationship between the probabilities of primary cyanoisopropyl radicals to recombine or to escape into the bulk.

We have determined the rate constant of cyanoisopropyl radical generation (k_i) and the value of the cage effect in a liquid-crystalline 5CB:5OCB system of different component ratios and at different temperature conditions, including isotropic and nematic phase states. Temperature dependences of the initial free radical generation rate constant in the nematic system 5CB:5OCB (70:30 wt./wt.) matrix are presented in Fig. 1. It was shown that a decrease in temperature is accompanied by the transition of the system from an isotropic to a nematic state and leads to a sharp decrease in the value of k_i.

This phase transition can also be caused by changing the composition of the liquid-crystalline system. In varying
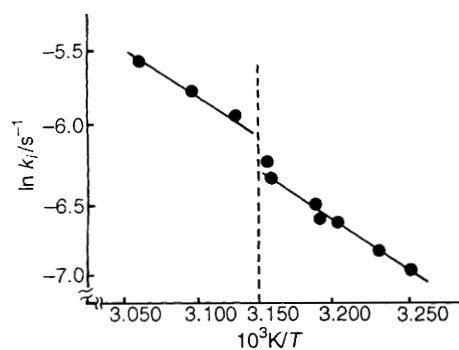
Fig. 1 Initial rate constant *versus* temperature for free cyanoisopropyl radical formation during thermal decomposition in a 5CB:5OCB (70:30) nematic mixture, [AIBN] = 2.8×10^{-2} mol dm^{-3}

Table 1 Cage escape (*e*) for free radical generation during thermal decomposition by chlorbenzene of AIBN in a nematic mixture 5CB:5OCB

chlorbenzene added (wt.%)	T_t^a/°C	Q/cP	S	$10e$
0	61.0	28.1	0.67	1.98
1.63	56.2	27.2	0.65	2.02
3.92	48.9	26.0	0.59	2.13
5.42	45.1	25.6	0.52	2.35
6.80	41.5	25.4	0.46	2.55
7.30	40.5	22.4	0.35	2.99
8.20	37.5	22.0	0	3.00
12.0	—	21.2	0	3.21
15.1	—	18.8	0	3.31
20.2	—	16.4	0	3.42
24.0	—	14.4	0	3.63
36.2	—	10.2	0	4.18
42.0	—	7.8	0	4.59

^{a} T_t = the temperature of the nematic–isotropic phase transition of the reactive system, determined by DTA.

the content of alkoxycyanobiphenyl from 10–20 wt.% to 30–50 wt.%, we also observed a decrease of k_i. The dynamic properties of the system do not change under these conditions to any practical extent. The results obtained are presented in Fig. 2.

The reaction rate of the thermal decomposition of AIBN does not depend on the chemical nature of the solvent[9] and it is almost constant for different temperatures across the range under investigation. Thus, the lowering of the yield of cyanoisopropyl radicals escaped into the bulk in the case of the nematic mesophase compared with the isotropic system probably occurs as a result of an increase in the probability of primary radicals recombining in an ordered solvent cage of the nematic matrix. Recently we have shown[10] that the phase transitions of cholesteric liquid-crystalline systems (with local molecular ordering the same as in nematic mesophases) influence free radical recombination kinetics. The transition of the system from an isotropic state to a mesophase was accompanied by a jump increase of the peroxide radical recombination rate.

A study of the kinetics of free radical escape (*e*) determined by molecular ordering (*S*) and micro-viscosity (*Q*) has been made for the liquid-crystalline system 5CB:5OCB (70:30). Alteration of the molecular order of this nematic system was achieved by adding increasing amounts of the solvent chlorobenzene. The results obtained are presented in Table 1. The data obtained show that the introduction of small amounts of chlorobenzene leads to a lowering of the temperature of the nematic–isotropic phase transition of the system under investigation. This is followed by a definite decrease in the order parameter of the nematic system. Adding chlorobenzene in amounts greater than 8 wt.% led to the destruction of the nematic order of the system. It can be seen in Table 1 that *Q* decreases slowly with the increase of chlorobenzene. This causes a corresponding increase in *e*. The
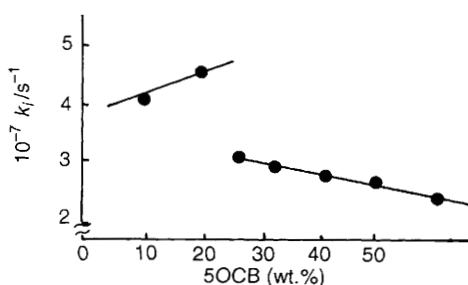
dependence of *e* on media micro-viscosity is presented in Fig. 3.

The data obtained show that in the isotropic phase a linear correlation exists between $(1 - e)^{-1}$ and T/Q according to Noyes' equation.[11] In the nematic phase there are strong deviations from linear dependence. It has been shown by the spin-probe method[12] that molecular-dynamic and bulk-viscosity properties of liquid-crystalline systems do not change significantly during the isotropic–nematic transition. Hence the deviations observed in the nematic mesophase can be caused only by a change in the molecular ordering of the system.

The process of free radical formation during thermal decomposition of AIBN can be examined using a model of rotational and translational evolution of primary geminal radical pairs[13]
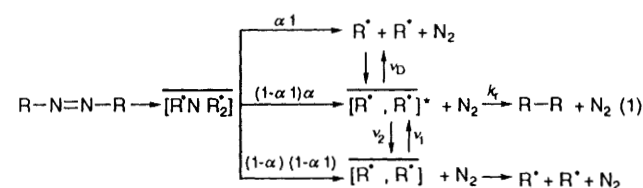
where R· is a primary radical escaped into bulk; $[\overline{R\cdot, R\cdot}]^*$ is a primary radical pair with a mutual orientation of radicals favouring their recombination; $[\overline{R\cdot, R\cdot}]$ is a primary radical pair with mutual orientation which does not favour their recombination; α is the probability of obtaining a primary radical pair with mutual orientation of radicals that favours their recombination; α1 is the probability of obtaining nitrogen and primary radicals escaped into bulk; v_1 and v_2 are the frequencies of transitions between primary radical-pair states of favoured and unfavoured radical recombination and v_D diffusion frequency of primary radicals. The value of *e* in this case can be obtained from

$$\frac{(\beta + 1)e - 1}{(\beta + 1)(e + 1)} = \frac{N}{k_r^*(gf + \alpha)} + \frac{1 - \alpha}{gf + \alpha} \quad (2)$$

where, $N = v_D + v_2$; $g = v_2/v_D$; k_r^* is the recombination rate constant for a primary radical pair with mutual orientations of radical particles favouring radical recombination; *f* is that part of primary radical pairs with mutual orientations favouring radical recombination; β is the ratio of the translational diffusion constant of N_2 and primary radicals. Eqn. (2) can be reduced to the following equation which is
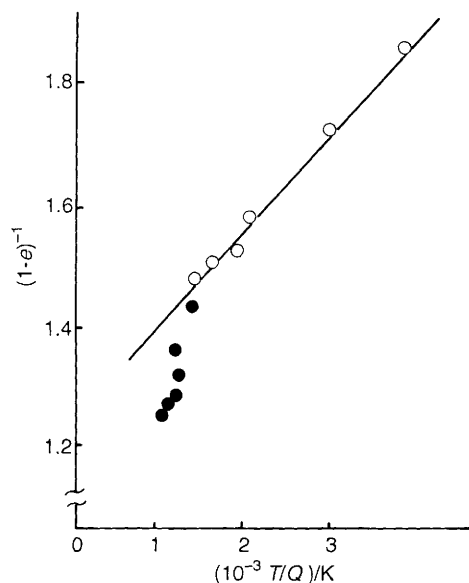

Fig. 2 The initial rate constant of free cyanoisopropyl radicals formation during AIBN thermal decomposition in a 5CB:50CB nematic mixture *versus* its composition $T = 313$ K, [AIBN] = 2.8×10^{-2} mol dm^{-3}

Fig. 3 The dependence of free radicals cage escape on media bulk viscosity
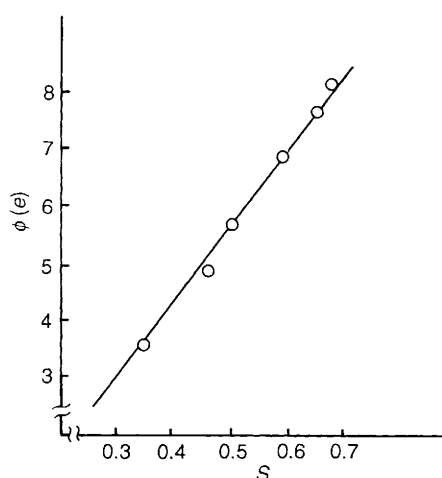

Fig. 4 The dependence of free radical cage escape on the order parameter of nematic systems

linear relative to f

$$\frac{1-e}{e-(1+\beta)^{-1}} = af + b \tag{3}$$

where $a = g/[(N/K_r^*) + (1-\alpha)]$; $b = \alpha a/g$.

In the nematic mesophase, radical diffusion contacts of primary radicals leading to their recombination are determined by nematic ordering of the system and f can be represented by

$$f = f_i + a_1 S \tag{4}$$

where, f_i is that part of a primary radical pair with mutual orientations of radical particles favouring their recombination in isotropic phase; a_1 is an empirical parameter, that reflects

the guest–host interactions; S is an order parameter of nematic systems. For a general case, a_1 can be positive if reagent ordering in the liquid-crystalline matrix favours the chemical interaction and negative if reaction molecule ordering hinders the reaction.

Using eqns. (3) and (4) we obtained eqn. (5) connecting the function of primary radical escape [$\phi(e)$] with a nematic order parameter (S):

$$\phi(e) = \frac{1-e}{e-(1-\beta)^{-1}} = A + BS \tag{5}$$

where A and B are correlation coefficients.

The dependence of the experimental function of free radical cage escape during thermal decomposition of AIBN in a nematic 5CB : 5OCB system, $\phi(e)$, on the order parameter of a nematic matrix is presented in Fig. 4. It can be seen that kinetic data obtained for free radical formation are well described by eqn. (5) for S from 0.35 to 0.67.

Conclusions

The formation of cyanoisopropyl radicals during the thermal decomposition of AIBN has been studied in nematic liquid-crystalline systems. It has been shown that the phase transition from isotropic to the nematic state leads to a lowering of primary radical escape in the bulk. This is probably due to an increased probability of primary radical recombination in ordered solvent cages of nematic matrices. The kinetic model of primary radical cage escape in a nematic mesophase is considered on the basis of rotational and translational evolution of primary radical pairs ordered by an anisotropic intermolecular energy potential. An expression has been obtained to describe the yield of free radicals escaped in volume as a function of the order parameter of a nematic matrix. It describes the experimental kinetic data for nematic order parameter values from 0.35 to 0.67.

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