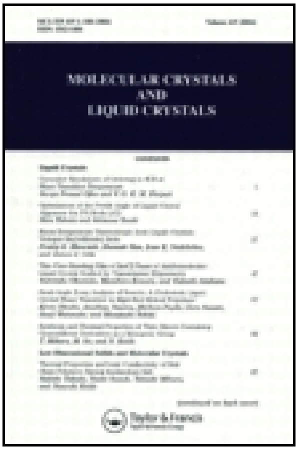

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INFLUENCE OF MOLECULAR STRUCTURE AND MOLECULAR ORDERING TYPE ON NITROXIDE FORMATION KINETICS IN SOME LOW TEMPERATURE SOLID STATES OF CYANOBIPHENYLS

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Abstract The influence of solid specimens' formation conditions on test photoinduced reactions of nitroxide generation has been studied in mesogenic cyanobiphenyls: 7OCB, 8OCB, 5CB, 8CB. Reaction kinetics appears to be a very sensitive instrument for investigation of the changes in local ordering and molecular dynamics which accompany solid structure formation before and during the course of reaction itself.

Chemical reactions in the solid state of frozen liquid crystals (LC's) are of great interest. The tendency of LC's for deep supercooling, for formation of ordered phases of different types and the existence of fluctuations of more ordered liquid crystalline structures in less organized phases, and, as a result, the ability to form diversly organized solid states at low temperatures must have a pronounced effect on reaction kinetics.

The influence of a solid specimen's formation conditions on the test photoinduced reaction of nitroxide generation:

$$tC_4H_9NO \underset{\Delta}{\overset{h\nu\ (\lambda>650\ \mathrm{nm})}{\rightleftarrows}} [tC_4H_9{}^{\bullet}\uparrow + \uparrow{}^{\bullet}NO]_s \xrightarrow{+tC_4H_9NO} (tC_4H_9)_2NO^{\bullet}$$

has been studied by ESR*) in mesogenic cyanobiphenyls 4-heptyloxy-4'-cyanobiphenyl (7OCB), 4-octyloxy-4'-cyanobiphenyl (8OCB), 4-pentyl-4'-cyanobiphenyl (5CB) and 4-octyl-4'-cyanobiphenyl (8CB).

Primary tert-butyl radicals resulting from the nitrosocompound photolysis practically do not possess any excess energy. The difference between C-N bond cleavage and the photon energy does not exceed 20 kJ/mole. The kinetics of nitroxide formation has been found to be sensitive to the structural organization of the medium and to the changes in molecular mobility within the systems[1-3]. The reaction product, di-tert-butyl nitroxide also served as spin probes and characterized the molecular mobility directly in the regions where

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*) The experimental conditions can be found in [1,2].

reaction took place [4].

It appears that the temperature dependences of the initial reaction rates (W_o , relative units) in the studied states of cyanobiphenyls (obtained by varying the thermal prehistory and the crystallization conditions of the samples) differ greatly. It was shown, in particular, that liquid crystalline alkoxycyanobiphenyls 7OCB and 8OCB exist at low temperatures in two different solid states K_1 (T_m= 326 and T_m= 324.5 K respectively) and K_2 (T_m=321 and 317 K respectively)*).

Different solid modifications of alkoxycyanobiphenyls, K_1 and K_2, were obtained using various conditions of crystallization. Rapid crystallization of the samples during fast cooling (~100 K/min) from the isotropic state to liquid nitrogen temperature led to K_1-phase formation. The reaction rate in this state sharply dropped with decrease of temperature and was practically equal to zero at 295 K (Figure 1).

Isothermal crystallization of the samples in the supercooled state at temperatures close to the temperature of the crystal-mesophase transition led to K_2-phase formation. The reaction rate in this state differed from zero over a wide temperature range up to 223 K in the case of 8OCB and up to 203 K in the case of 7OCB, and depended on temperature in a complicated manner (Figure 1). The tumbling mobility of nitroxides also remained high in those temperature ranges .

So the kinetics of nitroxide formation was sensitive to the differences in the microstructure and local molecular ordering in those phases.

The investigation of the solid systems by DTA methods has shown that, for all the LC's, the formation of solid solutions of the nitrosocompound in cyanobiphenyl matrixes took place. It was shown that in the case of the isotropic system[3] $tC_4H_9NO-CCl_4$, the formation of the solid solution structure by the components of the system upon freezing resulted in an abrupt decrease of nitroxide formation rate due probably to great hindrance of cage escape and translational diffusion processes for primary tert-butyl radicals. These processes

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*) Phase transition temperatures in the systems were obtained by DTA

were necessary for reaction product formation (di-tert-butylnitroxide) The formation of the solid solution structure was also accompanied by a deep decrease of molecular mobility in the system.

The data obtained have shown that the crystallization processes of liquid crystalline compositions based on cyanobiphenyls are very complex. The observed temperature dependence of the W_0 -values in the K_2-state can probably be assigned to the microheterogeneous distribution of the nitrosocompound molecules in the cyanobiphenyl crystalline matrix. Unlike the statistically uniform distribution of 2-methyl-2-nitrosopropane molecules in the isotropic CCl_4-matrix (guest and host molecules have similar volumes) crystallization of the liquid crystalline systems in supercooled states led to formation of solids with differing structures.

The degree of dimerization of mesogenic alkyl- and alkoxycyanobiphenyl molecules in the supercooled states was more than 90% [5-7]. The crystalline structure of the cyanobiphenyl matrix is formed by dimers having an antiparallel arrangement of "head-to-tail" type [8,9]. In this case the size of the structural element of the host is almost four times greater than the diameter of 2-methyl-2-nitrosopropane molecule. The nitrosocompound molecules can occupy space in common with the flexible hydrocarbon chains of alkoxycyanobiphenyls, only slightly affecting the packing character of the rigid aromatic cores. The temperature dependence of the reaction rate and the tumbling mobility of nitroxides (see Figure 1) are determined in this case by the mobility of hydrocarbon chains of alkoxycyanobiphenyl molecules, which is maintained at a high enough level even at low temperatures.

The crystalline K_1-phase, which has been obtained by rapid cooling from the isotropic state with a small degree of dimerization of the alkoxycyanobiphenyl molecules[10], seems to consist of the monomeric molecules. This probably provides a more uniform packing of the latter in the rigid crystalline structure which does not contain as much free volume as the K_2-phase. Therefore the processes of nitroxide formation is rather hindered at low temperatures. Only when the system is heated and a sufficient mobility of alkoxycyanobiphenyl molecules as a whole appears, the formation of nitroxides is observed at a measurable rate.

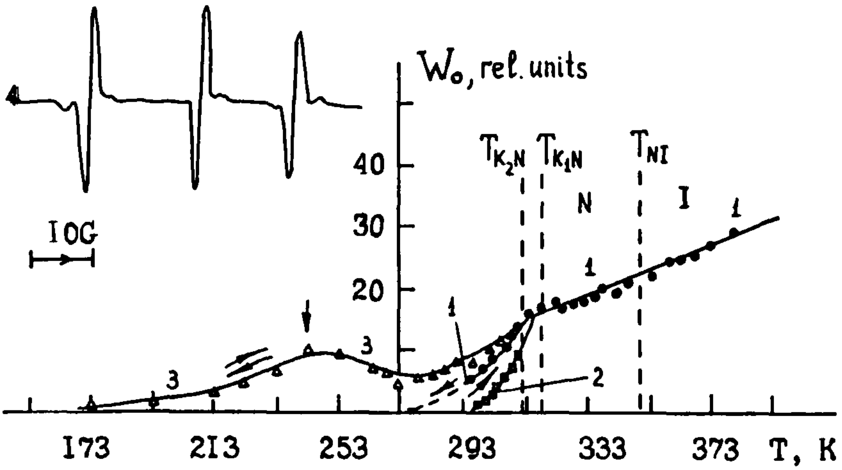

FIGURE 1. Temperature dependence of initial nitroxide formation rate, W_0, during photolysis of 2-methyl-2-nitrosopropane in 7OCB: 1 - in isotropic, nematic and supercooled states; 2 - in the solid K_1-phase; 3 - in the solid K_2-phase; 4 - ESR spectrum of the reaction product in the K_2-phase at the temperature indicated by ↓ .

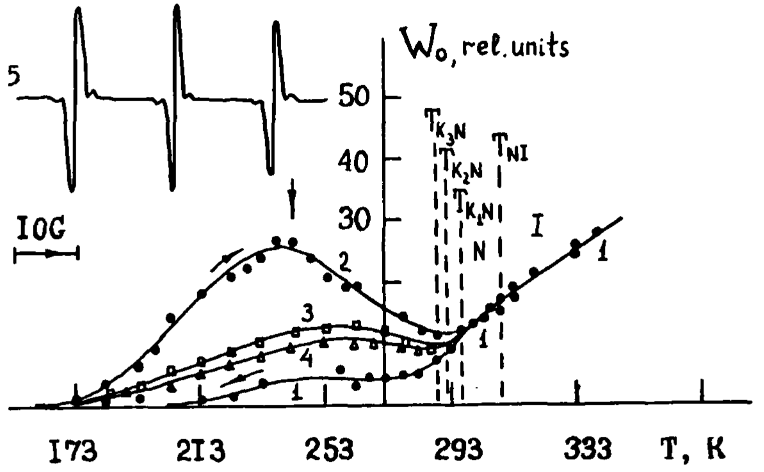

FIGURE 2. Temperature dependence of initial nitroxide formation rate, W_0, during photolysis of 2-methyl-2-nitrosopropane in 5CB: 1 - in isotropic, nematic, supercooled and glass like states; 2 - in the solid K_1-phase; 3 - in the solid K_2-phase; 4 - in the solid K_3-phase; 5 - ESR -spectrum of the reaction product in the K_1-phase at the temperature indicated by ↓ .

The kinetic data in the K_1- and K_2-phases of 7OCB and its next homologue 8OCB are similar. The absence of the marked differences in behaviour at low temperatures of nematogenic 7OCB and smectogenic 8OCB may be due to the existance of strong smectic fluctuations in the nematic and supercooled states of 7OCB [11].

Rapid cooling of the alkylcyanobiphenyls (5CB, 8CB) favours formation of glassy solid states . The reaction rates in these states were practically negligible (Figure 2). Heating of the samples to 223 to 233 K led to the crystallization and the formation of the K_1-phase (T_m =297 K in the case of 5CB). Nitroxide formation in this phase effectively took place in the range 173 to 297 K. K_1-phase formation gave rise to the reaction rates from 5 to 10 times higher compared to the reaction rate in glassy solid state (see Figure 2).

The isothermal crystallization at 253 to 263 K of the 5CB systems from the supercooled state led alternatively to K_2- (T_m= 291 K) or K_3- (T_m=287 K) phase formation and was accompanied by corresponding structure dependent reaction rates (Figure 2). These phases seem to have a similar type of molecular ordering as the K_2-phase of alkoxycyanobiphenyls. The correlations between temperature dependences of reaction rate and nitroxides tumbling frequencies were observed in all the systems.

Thus varying the crystallization conditions and thermal prehistory of the samples allows control of the reaction rate in liquid crystalline systems at low temperatures. On the other hand reaction kinetics appears to be a very sensitive tool for investigation of the changes in local ordering and molecular dynamics which accompany solid structure formation before and during the course of the reaction itself.

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