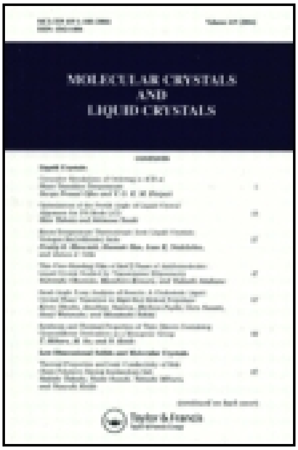

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Structure Effects on the Thermal Bimolecular Reaction Kinetics in Frozen MBBA and MBBA: EBBA Mixtures

V. A. Batyuk [a] , T. N. Boronina [a] , G. E. Chudinov [a] & G. B. Sergeev [a]

[a] Moscow State University, Moscow, 119899, USSR

To cite this article: V. A. Batyuk , T. N. Boronina , G. E. Chudinov & G. B. Sergeev (1990): The Structure Effects on the Thermal Bimolecular Reaction Kinetics in Frozen MBBA and MBBA: EBBA Mixtures, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 191:1, 289-293

To link to this article: http://dx.doi.org/10.1080/00268949008038607

Mol. Cryst. Liq. Cryst. 1990, Vol. 191, pp. 289-293
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

THE STRUCTURE EFFECTS ON THE THERMAL BIMOLECULAR REACTION KINETICS IN FROZEN MBBA AND MBBA:EBBA MIXTURES

V.A.BATYUK, T.N.BORONINA, G.E.CHUDINOV, G.B.SERGEEV
Moscow State University, Moscow 119899, USSR

Abstract. The reduction of the nitroxyl radical by hydrazobenzene has been studied in frozen nematic liquid crystals by ESR method. The spectral and kinetic data are evidence that heterophase samples with nonuniform reagents distribution are formed at the experiment temperatures. The reaction kinetics depends on sample phase structure transformation.

INTRODUCTION

Only several chemical processes, generally, photoinduced, have been studied in the solid liquid crystalline systems (LCS)[1]. The presence of non-mesomorphic guest molecules complicates the solid-state polymorphism and can lead to the heterophase system[1,2] Recent studies on ^{2}H NMR and the photochemical behaviour of a number of aromatic ketones in BCCN[1,3] confirms the assumption[4] that in LCS the reaction under certain conditions proceeds in a solute-rich isotropic zones. Concentration of the reagents in the zones of higher molecular mobility, which is formed in the course of crystallization of isotropic solvents, and its manifestation in the kinetics of chemical processes are well known[5]. In all the indicated studies the reaction proceeded in the formed heterophase sample since easily crystallizing liquids were used as isotropic solvents and in the case of photoinduced processes the sample formation is completed before irradiation begins. The present paper is devoted to studying the bimolecular thermal reaction- the reduction of the nitroxyl radical by hydrazobenzene - in liquid crystalline MBBA and MBBA:EBBA mixtures, which tend to glassing and have a higher, as compared to isotropic solvents, viscosity. It is known that MBBA fast cooled (< 40 K/min) down to 77 K forms glass which transforms to a crystalline modification above 203 K.[6] In such systems one can expect a simultaneous occurrense of the reaction isothermal kinetics and of the relaxation processes accompanying the LCS sample formation.

EXPERIMENTAL

The nitroxyl radical 2,2,6,6-tetramethyl-4- oxopiperidine-1-oxyl was recrystallized from hexane (T_m=309 K) and hydrazobenzene from heptane (T_m=400.5 K). The temperature of crystal-nematic (T_{CN}) phase transitions determined by DSC were found to be 293±0.5 K for MBBA, 278±0.5 K for 90:10 mol.% ratio MBBA:EBBA (mixture I) and 261±0.5 K for 67:33 mol.% ratio MBBA:EBBA (mixture II). The concentrations of nitroxyl radical and hydrazobenzene in the sample were respectively $(6\div7)\cdot10^{-5}$ and $(4\div5)\cdot10^{-4}$ mol/l in MBBA, $(1.1\div1.5)\cdot10^{-4}$mol/l in the mixture I $(6\div7)\cdot10^{-4}$ and $(1.8\div2;6)\cdot10^{-3}$mol/l in the mixture II. Solutions were deoxygenated with dry argon. The X-band ESR method was used to study the reaction kinetics and to control the molecular mobility of nitroxide in frozen LCS. "Rubin" ESR spectrometer was equipped with automatic home-made system on the base of PC D3-28. Temperature was controllable to within ±0.5 K. A sample in 4 mm ESR tube was fast cooled to 77 K from the temperature some degrees over T_{CN} and then it was kept during 40 s, heated up to the experimental temperature at a rate of 80 K/min and thermostated in the ESR cavity over 2 min. Meaurements were taken every 20-30 min. The accuracy of determination of relative nitroxyl radical concentration was ± 1%.

RESALTS AND DISCUSSION

The kinetic curves of nitroxide consumption were obtained for MBBA, mixtures I and II in the range of 233-288 K. They are S-shaped(Fig.1), viz., at the initial section the reaction rate gradually increases and then exponentially decreases. The initial duration depends on the temperature and the solvent used. It grows in the sequence MBBA - mixture I - mixture II from 1- 2 to 2-6 and 6-10 min., respectively. Shapes of ESR spectra at the experiment temperatures and their change in time suggest the formation of heterophase samples and the increase in the nitroxide concentration in the zones of a higher molecular mobility (Fig.2). The characteristic time of ESR spectrum changes at a specific temperature in a particular liquid crystall corresponding to the initial duration for slow nitroxide consumption.

Combination of the kinetic and ESR data point to the formation of heterophase samples and to the reaction taking place mainly in the higher molecular mobility zones enriched with reagents, as well as in the frozen solutions of isotropic solvents. In our opinion, the S-shape of the kinetic curves, not observed earlier in the frozen isotropic and liquid crystalline solvents, is due to the fact that in the studied systems the solvent crystallization and the sample formation do not end by the beginning of kinetics registration and at least one of the relaxation processes in the matrix proceeds with the characteristic time τ_D comparable with the characteristic time of chemical interaction τ_R. It is assumed that the diffusion of the reagents towards the zones of higher molecular mobility is such a relaxation process as suggested in[7].

Clearly, then a faster process discontinues to influence the kinetics of the reaction, the nitroxide consumption is determined by one characteristic time and the kinetic curve has the exponential form. Assuming that this was the chemical interaction time we attempted to determine the observed rate constant of bimolecular reaction k_e from the exponential (second, Fig.1) section of the kinetic curves. The calculated rate constants proved to be stable to the borders of selected sections. Uncertainties in k_e determination were in 5-15% limits. The ln k_e - 1/T dependences have extrema for MBBA and mixture I as well as for the frozen solutions of the isotropic solvents. The mixture II k_e

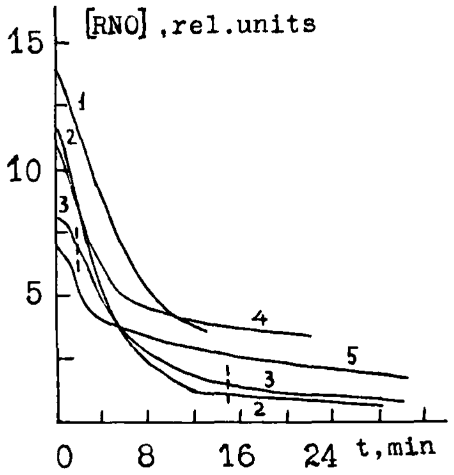

FIGURE 1. The kinetic curves of nitroxyl radical consumption in reaction with hydrazobenzene in MBBA at 249 K (1), in mixture I at 250 K (2) and 248 K (3), in mixture II at 240 K (4) and 233 K (5).

Figure 2. The ESR spectrum of the nitroxyl radical at concentration $4 \cdot 10^{-4}$ mol/l at 241 K in mixture I with azobenzene (this being the concentration of hydrazobenzene in reaction media). Microwave power 3mW, modulation amplitude 1 Gs, time constant 0.1 s, scan time 4 min..

values were by 2-3 times smaller and varied little in the temperature range of 233-253 K. The varying k_e behaviour was due to the fact that in MBBA and mixture I the crystallization processes proceed fast enough and $\tau_D < \tau_R$. In mixture II the kinetics is determined not by chemical interaction but by diffusion of reagents towards the reaction zones ($\tau_D > \tau_R$). A slow-down of the diffusion process in the eutectic mixture II is due to, in our opinion, a comparatively higher stability of its glass-like state and, also to a slower crystallization.

Thus, it is shown that in the system studied the reaction proceeds along with the formation of the heterophase sample which manifests itself in the kinetics. The kinetic curve shape is determined by the relationship between the characteristic time of chemical interaction and that of the relaxation process, i.e. diffusion of the rea-

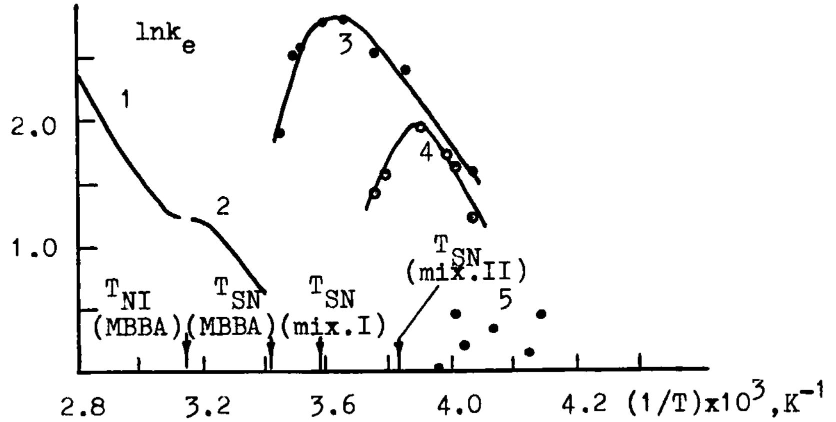

FIGURE 3. Temperature k_e dependences in isotropic(1) and nematic (2)MBBA phases[8], in frozen states of MBBA (3), mixture I (4) and mixture II(5).

gents towards the reaction zones with higher molecular mobility. One of these processes is limited depending on the properties of a liquid crystalline solvent.

REFERENCES

1. R.G.Weiss, Tetrahedron, 44, 3413 (1988).
2. S.Limmer, S.Grande and A.Lösche, Phys. Stat. Solidi, B 84, 283 (1977).
3. B.J. Fahie, D.S Mitchell, M.S.Workentin and W;J. Leigh J. Am. Chem. Soc., 111, 2916 (1989)
4. G.B.Sergeev, V.A.Batyuk and T.N.Boronina, Kinet. Katal., 24, 283 (1983).
5. G.B.Sergeev and V.A.Batyuk, Cryochemistry, (Mir Publishers, Moscow, 2-nd., 1986).
6. L.Rosta and V.K.Dolganov, Mol. Cryst. Liq. Cryst., 146, 77 (1987).
7. V.A.Batyuk, T.N.Boronina, and G.B.Sergeev, Mol. Cryst. Liq. Cryst., 1990, in press
8. V.A.Batyuk, T.N.Boronina, G.E.Chudinov and G.B.Sergeev, Liquid Crystals, 4(2), 181 (1989).