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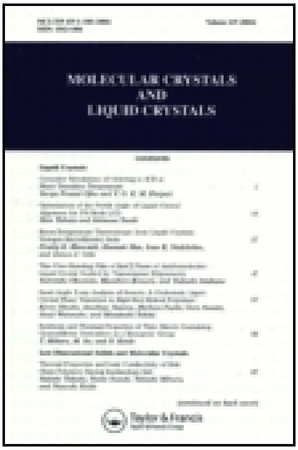

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Kinetic and Diffusion Regimes of the Reduction of Nitroxide by Hydrazobenzene in Frozen Liquid Crystal Materials

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Version of record first published: 22 Sep 2006.

To cite this article: V. A. Batyuk , T. N. Boronina & G. B. Sergeev (1990): The Kinetic and Diffusion Regimes of the Reduction of Nitroxide by Hydrazobenzene in Frozen Liquid Crystal Materials, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 186:1, 93-98

To link to this article: http://dx.doi.org/10.1080/00268949008037197

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Mol. Cryst. Liq. Cryst., 1990, vol. 186, pp. 93–98
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THE KINETIC AND DIFFUSION REGIMES OF THE REDUCTION OF NITROXIDE BY HYDRAZOBENZENE IN FROZEN LIQUID CRYSTAL MATERIALS

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Abstract A kinetic model of thermal bimolecular reactions in frozen nonhomogeneous liquid crystalline systems has been proposed.

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INTRODUCTION

Chemical reactions in the solid frozen state of liquid crystal materials have been studied even less than in mesophases and those investigated were mainly of photochemical reactions[1]. In the present work, a quantitative approach to the description of the kinetics of the nitroxide (2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl) reduction by hydrazobenzene in frozen nematic liquid crystal 4-methoxybenzylidene-4'-n-butylanyline (MBBA) and in its mixtures with the ethoxy homologue (EBBA) in 9:1 mol. ratio (mixture I) and in 2:1 mol. ratio (mixture II) is proposed. The specimens were prepared by rapid freezing in liquid nitrogen of nematic solutions in ESR-ampules. These were then heated at the rate about 80 K/min to the experimental temperatures (from 233 to 288 K). Isothermal reaction kinetics were determined by an ESR-method. The kinetic data and experimental details can be found in reference 2.

DISCUSSION

The principal experimental features were found to be the isothermal kinetic curves were S-shaped and could be subdivided into three consecutive parts (Fig.1). The S-shape was sensitive to the liquid crystalline systems capacity to crystallize, to overcool and to form glass and was more distinctive for mixture I; ESR-spectra showed phase heterogeneity of the sample and formation of zones with high molecular mobilities as a result of solute diffusion and

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the mediums structure relaxation. The relative amount of the radicals with high molecular mobility increases in time during annealing of fast cooled samples.

In order to describe the experimental data the following kinetic model has been suggested. When a liquid crystalline sample of reaction mixture is placed into liquid nitrogen, a liquid like glassy structure with solute distribution close to uniform is predominantly formed. This quenched solid is thermodymamically unstable and subsequent annealing is accompanied by different processes such as sample structure relaxation, nucleation, crystallization, and formation of heterogeneous structures with high molecular mobility in some zones. As a result of diffusion the reagent concentrations in such zones can increase and chemical reaction can proceed more rapidly. A heterogeneous system is thermodynamically stable at temperatures below solid - mesophase transition. Because of the tendency of liquid crystals to form glass and their high viscosity in the supercooled state, the approach of the system to equilibrium is much slower than in the case of isotropic solvents[3]. As a result characteristic time for heterogeneous structure formation and reagent diffusion to zones with high molecular mobility (τ_D), and characteristic time for chemical reaction (τ_R) taking place in such zones can become comparable. In such case, nitroxide consumption rate would be determined by both mentioned processes.

For the reaction under study we can assume that in frozen liquid crystalline systems the reaction scheme is just the same as in isotropic and nematic phases of MBBA[4] with the rate limiting stage being the formation of intermediate active radicals as a result of hydrogen atom elimination:

$$R_1NO^{\cdot} + R_2\text{-}NH\text{-}NH\text{-}R_2 \longrightarrow R_1NOH + R_2\text{-}NH\text{-}N^{\cdot}\text{-}R_2 \qquad (1)$$

Reagent diffusion can be taken into account as follows. Some phase nucleation centers in zones with high molecu-

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lar mobility arise initially during sample freezing. Let us suppose that they are distributed uniformly with concentration L. Let us imagine the sample to consist of spherical volumes of radius R centered on nuclei with radius ρ . The reagents diffuse to nuclei from the sphere. Change in concentration $C_i(t)$ of i-th component is described by a diffusion equation with the diffusion coefficient D_i. With boundary conditions $C_i=0$ at the surface of the nucleus and concentration derivative $(dC_i/dn)_R = 0$ normal to the surface of the sphere (i.e. there is no diffusion from the sphere), the diffusion equation can be solved in analytical form if $R \gg \rho$. Then the quantity of i-th component $Q_i(t)$ transfered in the unit sample volume to zones of high molecular mobility is given by the expression:

$$Q_i(t) \sim C_{oi}(1 - \exp(-t/\tau_{D_i})) \qquad (2)$$

where C_{oi} = the initial concentration of the i-th component, $\tau_{D_i} = (4\pi D_i \cdot \rho L)^{-1}$, D_i = the diffusion coefficient of the i-th component in the bulk solid phase, ρ = the diameter of the zone with high molecular mobility. For the rate of chemical reaction in zones with high molecular mobility one can write the following differential equations (assuming that for these zones liquid phase kinetics is valid):

$$\frac{1}{V_m}\frac{dN_R}{dt} = -k\frac{N_R N_{HB}}{V_m^2} + \frac{1}{V_m}\frac{dQ_R(t)}{dt}$$
$$\frac{1}{V_m}\frac{dN_{HB}}{dt} = -k\frac{N_R N_{HB}}{V_m^2} + \frac{1}{V_m}\frac{dQ_{HB}(t)}{dt} \qquad (3)$$

where V_m = the whole volume of zones with high molecular mobility in the unit sample volume; N_R and N_{HB} = the amounts of nitroxyl radical and hydrazobenzene, respectively, in zones of high molecular mobility in the unit sample volume. For the case when $C_{oHB} \gg C_{oR}$ and $D_{HB} \approx D_R = D$, the solution of equations (3) is possible in analytical form:

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$$C_R(t) = C_{oR}\left(\frac{1/\tau_D}{1/\tau_D - 1/\tau_R}e^{-t/\tau_R} - \frac{1/\tau_R}{1/\tau_D - 1/\tau_R}e^{-t/\tau_D}\right) \quad (4)$$

where $C_R(t)$ = the amount of nitroxyl radical in the unit sample volume at time t, $\tau_R = V_m/2k(C_{oHB})^2$. It should be noted that characteristic times τ_R and τ_D appear in the

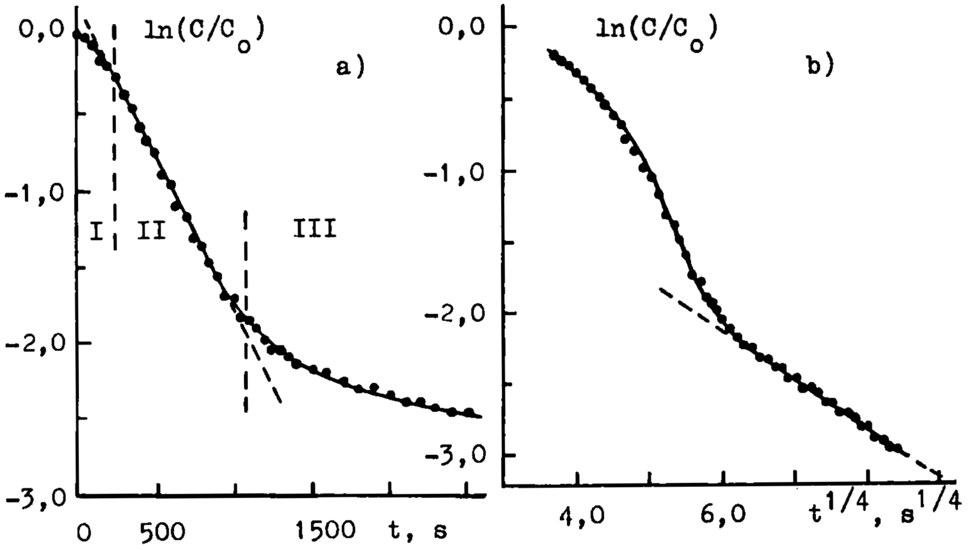

FIGURE 1. a) Kinetic curve of the nitroxyl radical consumption in the reaction with hydrazobenzene in mixture I at 248 K; b) The kinetic curve in lnC/C$_o$ – $t^{1/4}$ coordinates.

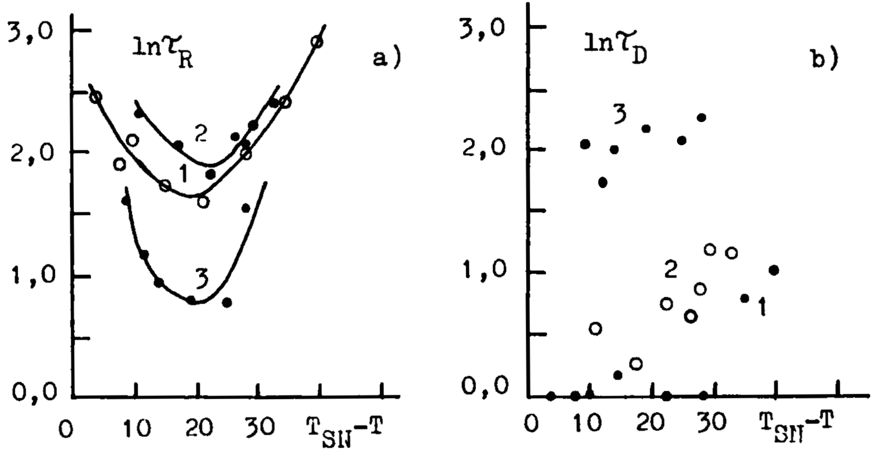

FIGURE 2. Temperature dependence of lnτ_R, (a), and lnτ_D, (b), in MBBA (1), mixture I (2) and mixture II (3).

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equation (4) in symmetrical form. If $\tau_D \ll \tau_R$, then at time $t \gg \tau_D$ mono exponential kinetics with characteristic time τ_R would be observed.

As one can judge from the experimental results in MBBA and mixture I $\tau_R > \tau_D$. The experimental bimolecular rate constants $k_e=2kC_{oHB}/V_mC_{oR}$ have been obtained from the second part of the S-shaped kinetic curves. In these liquid crystalline solvents the $\ln k_e(\ln \tau_R) - 1/T$ dependences in frozen samples have extrema (Fig.2a), as in the frozen solutions of isotropic solvents[3]. As obtained with the use of equation (4), absolute values of k_e in MBBA and mixture I are comparable to the determined k_e values in isotropic MBBA phases[4]. In mixture II we have $\tau_D > \tau_R$ (Fig.2). One can see from Fig.2 that τ_R and τ_D vary differently with temperature. The increase of τ_D values in the sequence MBBA $\longrightarrow$ mixture I $\longrightarrow$ mixture II is due in all probability to the increase of the tendency towards glass formation and, correspondingly to the decrease of L since only big nuclei are stable in glass forming solvents.

As for the third part of the S-shaped kinetic curves, they can be described in our opinion by diffusion polychronous kinetics methods[5]. We consider the slow reaction rate at $t \gg \tau_R, \tau_D$ to be connected with chemical reaction between diffusing reagent molecules in solid like bulk medium. It should be noted that, for the systems under study, kinetics for $t \gg \tau_R, \tau_D$ obeys the expression $\exp(-kt^{\alpha})$ with parameter α equal to 1/4 (Fig.1b).

CONCLUSION

In liquid crystalline azomethines, the solute diffusion affects reaction kinetics because diffusion (τ_D) and reaction (τ_R) characteristic times become comparable. Depending on the relation between τ_R and τ_D, the kinetic (in MBBA and mixture I) or diffusion (in mixture II) regimes are realized. At degrees of nitroxide consumption more than 70%, the reagent diffusion in the bulk solid like matrix becomes the limiting stage of the chemical process.

A quantitative kinetic model has been proposed for the description of S-shaped kinetic curves in frozen liquid crystalline systems.

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