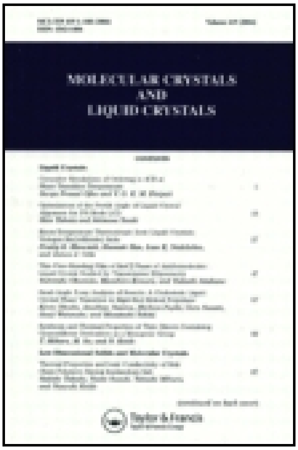

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Andrei P. Vorotnikov [a] , Boris A. Umanskii [b] , Evgenii Ya. Davydov [a] , Vladimir P. Pustoshnyi [a] & Israil I. Aliev [c]

[a] Institute of Biochemical Physics, Russian Academy of Science, Kosygina 4, Moscow, 117977, Russia

[b] SSC RF "NIOPIK" (Organic Intermediates & Dyes Institute), B. Sadovaya 1/4, Moscow, 103787, Russia

[c] Institute of Chemical Physics, Russian Academy of Science, Kosygina 4, Moscow, 117977, Russia

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The Influence of Liquid Crystal Ordering on Reversible Radical Dissociation

ANDREI P. VOROTNIKOV[a], BORIS A. UMANSKII[b], EVGENII YA. DAVYDOV[a], VLADIMIR P. PUSTOSHNYI[a] and ISRAIL I. ALIEV[c]

[a]*Institute of Biochemical Physics, Russian Academy of Science, Kosygina 4, Moscow 117977, Russia,* [b]*SSC RF "NIOPIK" (Organic Intermediates & Dyes Institute), B. Sadovaya 1/4, Moscow 103787, Russia and* [c]*Institute of Chemical Physics, Russian Academy of Science, Kosygina 4, Moscow 117977, Russia*

The influence of liquid crystal ordering in nematic, smectic and isotropic phases on thermodynamic parameters of a reversible thermal dissociation of dimeric 2,2-bis[2-(p-dimethylaminophenyl)indan-1,3-dione] into two stables 2-(p-dimethylaminophenyl)indan-1,3-dione-2-yl radicals was investigated.

Keywords: ESR; reversible thermal dissociation; liquid crystal ordering

INTRODUCTION

The problem of establishing of correlation between the character of molecular ordering of the medium and the dynamics of chemical reactions occurring in this medium is a fundamental problem of physical chemistry.

The chemical processes in liquid crystal LC mesomorphic phases attract a special interest due to the combination of opposite features of LC: the far ordering of molecular organization from one hand and high liability on the other hand. The interaction of reagents with mesomorfic environment of LC matrices results in anomalous kinetic and thermodynamic regularities of chemical reactions [1-3].

The aim of this work was the investigation of the effect of LC ordering on a temperature dependence of the equilibrium constant $K = [R]^2/[D]$ for model process of the reversible thermal dissociation of dimeric 2,2-bis[2-(p-di-methylaminophenyl)indan-1,3-dione] (D) into two stables 2-(p-dime-thyl-aminophenyl)indan-1,3-dione-2-yl radicals (R) in nematic smectic and isotropic phases of LC.

EXPERIMENTAL

Materials

The chemical reaction of reversible radical dissociation was investigated in liquid crystals 4-pentylcyanobiphenyl (5CB), 4-octylcyanobiphenyl (8CB), p-metoxybenziliden-p-butylaniline (MBBA) and eutectic mixture of MBBA with p-etoxybenzilidene-p-butylaniline (MBBA/EBBA). As a chemical reagent for radical dissociation we used dimer 2,2-bis[2-(p-di-methyl-aminophenyl)-indan-1,3-dion] (D).

Instrumentation

The cylindrical quartz ampoules of diameter 4 mm containing a solution of dimmer D in LC ($c = 10^{-4}$-10^{-2} mole/l) were placed in thermostable cavity of ESR-spectrometer Radiopan SE/X-2547. The temperature control was hold with accuracy of 1K at the temperature in the range of 293-353K.

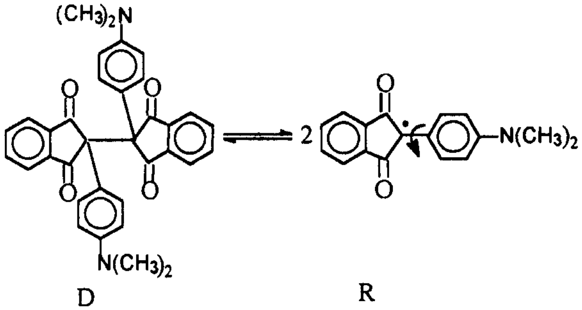
Measurements

The kinetics of radical dissociation was determined by measuring of ESR-spectra of stable radicals 2-(p-dimethyl-aminophenyl)indan-1,3-dione-2-yl (R) which appear as the result of thermal dissociation of dimmer D.

In order to measure the quantity of radicals their ESR-spectra were compared with ESR-spectrum of stable nitroxyle radical. The measurement error of absolute and relative radical concentration did not exceed 20% and 10 % accordingly.

RESULTS AND DISCUSSION

The reversible thermal dissociation of dimer D into two radicals R happens to the following scheme:



The thermal equilibrium between dimer D and radical R in the different mesophases and in ordinary solvents is became rather promptly and [R] is proportional to $[D]^{1/2}$ in this equilibrium state [2, 4].

Figure 1 shows the dependence of logarithm of equilibrium constant K on the reverse temperature T in LC matrices MBBA and 5CB. As it seen from Figure 1 these dependences have complicated, non-linear forms, and the constant K in mesophases has anomalous high value, which is higher than in acetonitryl (CH_3CN) by approximately 2 orders:

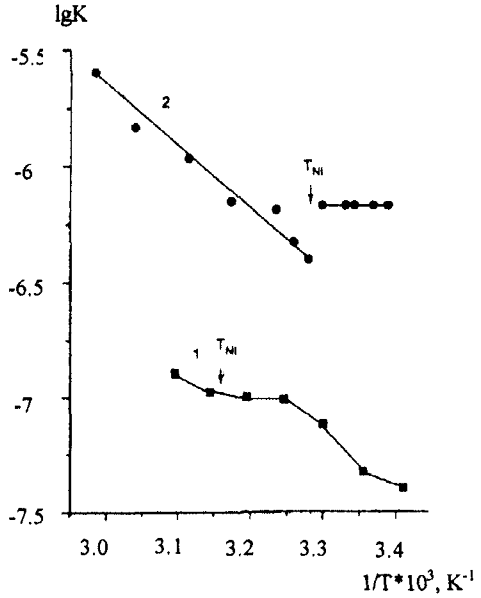


Figure 1. The temperature dependence of logarithm of equilibrium constant K on reverse temperature 1/T in MBBA (1) and 5CB (2).

$K = 6.7*10^{-7}$ in 5CB and $K = 4.4*10^{-9}$ in CH_3CN [2] for 295K. It should be noticed that the value of K for 5CB within the temperature region of nematic phase existence varies insignificantly, but at clearing point the essential falling of its value (approximately in 1.5 times) is observed.

The values of thermodynamic parameters: the enthalpy $H = 46 \pm 5$ kJ/mole and the entropy $S = 23 \pm 10$ kJ/mole for reversible thermal dissociation D into two free radicals R in isotropic phase of 5CB are calculated. These parameters are much lower by absolute value, than in ordinary isotropic solvents, that indicates the strong solvation of LC environment in isotropic phase, which considerably raising stability of the radical R.

In order to clarify the mechanism of the LC ordering influence on a relative radical output the temperature dependence of the radical ESR spectrum forms in nematic, smectic and isotropic phases was studied (Figures 2 and 3).

It is necessary to point out, that during phase transition from nema-tic to isotropic phase the additional splitting of each main component of radical ESR spectra completely disappears. The alignment of LC molecules in an external magnetic field results to partial orientation of radical R by the long axis along the LC director, and the anisotropic splitting in spectra ESR on nitrogen atom is exhibited.

The high degree of non-coupled electron delocalization of radical R in LC matrices results to high value of hyperfine coupled constant on nitrogen atom, which anisotropic character is exhibited in spectra ESR in nematic phase for high order parameter values at temperature region which is far from clearing point (Figure 2).

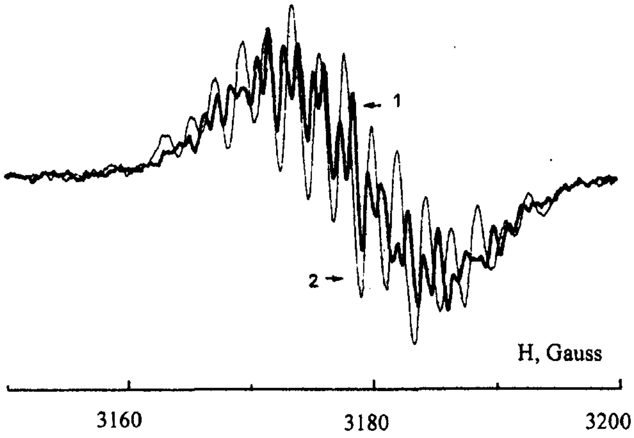


Figure 2. ESR spectra of radical R in MBBA;
1 – nematic phase at 295 K;
2- isotropic phase at 335 K.

The direct proof of radical orientation in LC mesophases is the obviously expressed anisotropic character of ESR spectrum in smectic phase of 8CB, measured for the sample cooled from nematic to smectic phase in a magnetic field. The fixation of the initial direction of radicals R in smectic phase results to angular dependence in spectra ESR (Figure 3). The ESR spectra in oriented smectic phase, sharply distinguishing in initial and orthogonal positions of the sample, are characterized by small width of components, that is stipulated by the limited molecular mobility of the radical R introduced into smectic matrix. On the contrary, the ESR spectrum components at approaching to clearing point are strongly widened and anisotropic splitting on nitrogen atom is faintly expressed and disappears above clearing point.

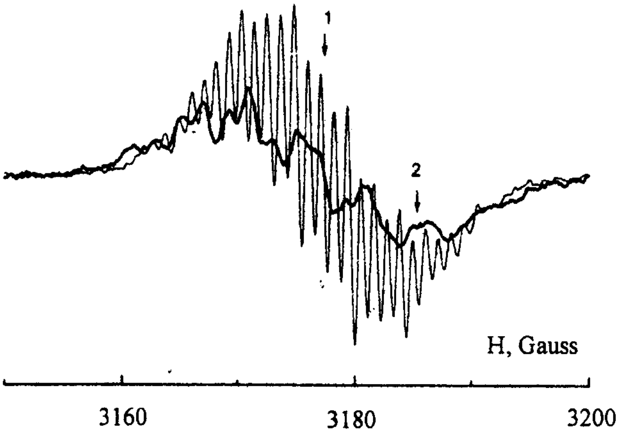


Figure 3. ESR spectra of radical R in smectic phase of 8 CB, obtained by cooling of the sample in magnetic field;

1 – initial orientation of LC director is parallel to magnetic field;

2 – orientation of LC director is perpendicular to magnetic field.

The sharp difference of thermodynamic features of chemical reactions in mesomorphic phases on a comparison with isotropic solutions is stipulated by specific character of interaction of reagents with mesophase environment. The volumetric molecules of dimer D unlike from elongated rod-shaped molecules of radicals R hardly distort LC matrix, what leads to the enhancing energy of such structure. In order to increase energy, the system tends to lower the concentration of dimers so that equilibrium shifts to radical form and equilibrium constant increases. Another words, the steric obstacles for a mutual recombination of radicals R can arise.

CONCLUSION

The common feature for all investigated LC systems is the nonlinear dependence of lgK vs (1/T), especially in the temperature region of phase transition from nematic phase to isotropic one, which stipulated by changing of effective thermodynamic parameters ΔH and ΔS of dimer dissociation with temperature growth, as the decrease of order parameter means the reduction of mentioned above steric influence on the equilibrium constant.

The noticeable growth of the constant K is observed in MBBA and MBBA/EBBA mixture, which have a rather broad nematic temperature interval and rather poorly exhibiting of solvation effect. However, this dependence has not enough linear character far from clearing point, and close to the clearing point the dependence curve has the bent.

Especially interesting is the significant decrease of K at heating in the temperature region of clearing point for 5CB. With transition from nematic to isotropic phase the macroscopic ordering of LC matrix disappears, that results to significant growth of effective value of an enthalpy of dimmer dissociation due to reducing of steric obstacles for its embedding in LC environment.

Acknowledgements

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References

[1] R.G. Weiss, Tetrahedron, **44**, 3413 (1988).
[2] A.P. Vorotnikov, V.P. Pustoshnyi, E. Ya. Davydov, L.S Pustoshnaya, Russ. J. Phys. Chem., **72**, 736 (1998).
[3] T.I. Shabatina, Yu. K. Yarovoi, V.A. Batyuk, G.B. Sergeev, Chem. Phys. Rep., **16**, 1159 (1997).
[4] L.M. Pisarenko, V.I. Nikulin, M.P. Blagorazumov, O. Ya. Neiland, L.L. Paulin'sh, Izv. Akad. Nauk SSSR, Ser. Khim., 1525 (1990) (in Russian).
[5] M.A. Morsy, G.A. Oweimreen, A.M. Al-Tawfig, *J. Phys. Chem.*, **B 102**, 3684 (1998).