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Kinetics of the reduction of nitroxyl radicals by hydrazo compounds in a nematic liquid crystal

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The kinetics of thermal bimolecular reactions of nitroxyl radicals with hydrazo compounds have been studied in a nematic liquid crystal. The experimental reaction rate constant in the pretransition region of the isotropic phase and in the mesophase has been found to show a positive deviation from the Arrhenius dependence obtained in the isotropic phase at higher temperatures. A method is proposed for a quantitative description of the temperature dependence of the experimental rate constant in the mesophase, based on the assumption of a decrease in the activation energy in the nematic phase, as compared with the isotropic phase. Consideration is given to the influence of nematic ordering on the activation energy of the reactions studied, conforming to the values of the parameters found from the experimental data. Models accounting for the existence of local ordering fluctuations are proposed for a quantitative description of the temperature dependence of the experimental rate constant in the isotropic phase. These are based on an approximate representation of a liquid crystal above the clearing point as a combination of isotropic and nematic regions. This makes it possible to estimate the size of the minimal region of nematic ordering that a given reaction is sensitive to.

1. Introduction

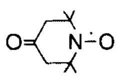
Investigation of chemical processes in liquid crystals is undoubtedly of interest for chemical kinetics as it can provide information on the elementary act in condensed media. This makes it possible to trace the influence of the mutual orientation of reagents in an ordered mesophase on the rate constant of the elementary stage and from this to make assumptions about the structure of the transition state. Analysing the changes in the reaction kinetics, taking place in the mesophase, as compared with the isotropic phase, especially when combined with a study of the molecular dynamics of solutes, is also a method of investigating the effect of the liquid-crystalline media on the processes conducted in them. It can also show promise in forecasting the feasibility of stereospecific synthesis. At present kinetic data on reactions in liquid crystals have only been obtained by a few authors and even then mainly for photochemical processes. The results are explained at a qualitative level see, for example, [1–4].

It is important to estimate the minimum size of the region of nematic ordering, able to influence the kinetics of a given reaction to understand the mechanism of the influence of mesophases on chemical processes. This information can be obtained by studying the kinetic effects in the pretransitional region of the isotropic phase prior to the formation of the nematic, where fluctuations of local ordering are known to be of significance [5, 6].

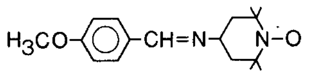
The study of the effect of nematic ordering of the mesophase and fluctuations of the nematic ordering in the isotropic phase on the kinetics of thermal bimolecular reactions is the main topic of this paper. The reduction of nitroxides by hydrazo compounds in 4-methoxybenzylidene-4'-*n*-butylaniline(MBBA) has been chosen as an example.

2. Experimental

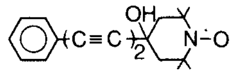
The nitroxyl radicals:



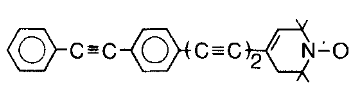
I. $S' = 0$



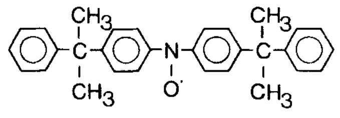
II. $S' \simeq 0{\cdot}70$



III. $S' \simeq 0{\cdot}25$



IV. $S' \simeq 0{\cdot}95$



V. $S' \simeq 0{\cdot}55$

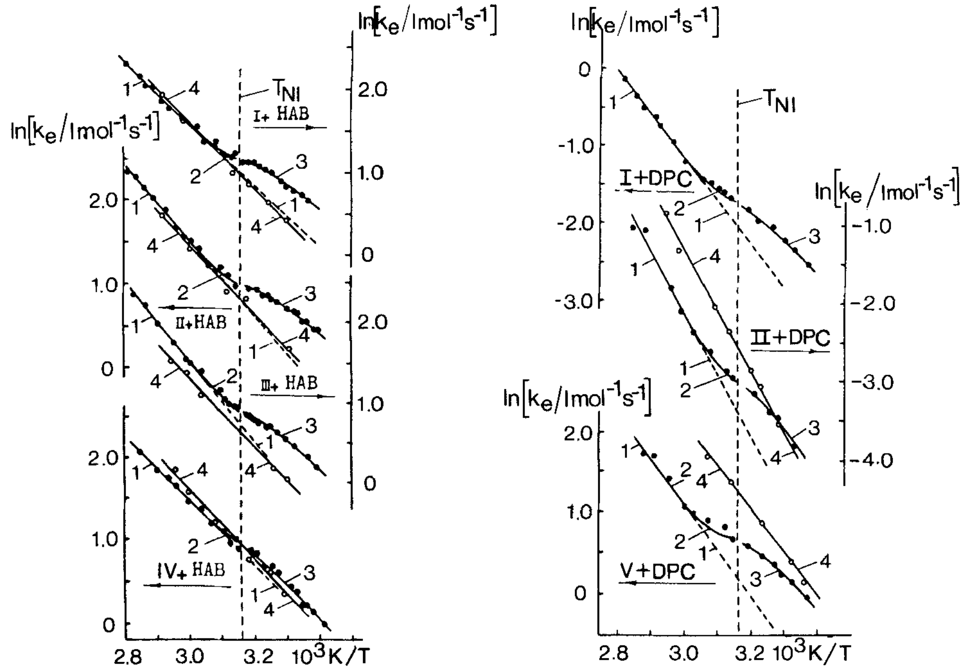
characterized by a different degree of ordering S' in the MBBA mesophase [7] were used. Here $S' = S_{\text{mol}}/S$ is the ratio of the orientational order parameter of the long axis for the nitroxyl radical, S_{mol}, to the order parameter of liquid crystal, S. Nitroxyl I was recrystallized from hexane, II was synthesized using the procedure described in [8], radicals III–IV were used without additional purification. Hydrazobenzene (HAB) was purified by recrystallization from heptane, diphenylcarbazone (DPC) was isolated from the commercial preparation by the method described in [9]. MBBA was distilled in an inert gas flow at 2 torr. A mixture of MBBA with benzene (5 : 1 volume fractions), which does not form a mesophase, was also used as the solvent. The benzene was of the "for chromatography" grade. The concentrations of nitroxyl radicals and hydrazo compounds in the reaction mixture were (5–7) × 10^{-5} and (2–3) × 10^{-4} mol/l, respectively. The X-band electron spin resonance was used to study the reaction kinetics to measure the spin-exchange rate constants, K_e, and the nitroxyl radical order parameter. The E.S.R. spectrometer, equipped with a temperature control unit (the accuracy of temperature control in the cavity was $\pm 0{\cdot}3$–$0{\cdot}5$°C) is part of an automated system. The reaction was observed directly by a decreasing nitroxyl radical concentration in the E.S.R. cavity. The procedure used to measure the kinetics in the reaction with hydrazo compounds is described in [10]. K_e and the order parameters of the nitroxyl radicals were determined in accordance with [11, 12].

3. Results and discussion

The kinetics of the reduction of nitroxyl radicals I–IV with hydrazobenzene and of I, II, V with diphenylcarbazone have been studied in the isotropic and nematic phases of MBBA, as well as in a mixed isotropic MBBA-benzene solvent, in the range 20–80°C. The experimental rate constant of the limiting stage

$$\text{RNO}^{\cdot} + \text{-NH-NH-} \xrightarrow{k_e} \text{RNOH} + \text{-NH-N}^{\cdot}\text{-}$$

was calculated from the kinetic curves of nitroxyl radical consumption assuming a bimolecular reaction. Preliminary careful investigation of the mechanism and the



(*a*) (*b*)

Figure 1. The temperature dependence of the experimental reaction rate constant k_e for the reduction of radicals I–IV with hydrazobenzene (HAB) (*a*) and of radicals I, II, V with diphenylcarbazone (DPC) (*b*) in the isotropic and nematic phases of MBBA and in an MBBA-benzene mixture. ●, in experiment in MBBA; ○, experiment in the MBBA-benzene mixture; 1,4, Arrhenius dependence in the MBBA isotropic phase and in the MBBA-benzene mixture; 2, k_e in the isotropic phase pretransitional region, calculated from equation (18) with $m = 400$; 3, k_e in the mesophase, calculated from equation (7).

kinetics of the reaction was undertaken [10]. The accuracy of the determination of k_e is ±3 per cent.

The temperature dependence of k_e is qualitatively similar for all the reactions studied (see figure 1). In the isotropic phase of MBBA between 60 to 80°C the increase in k_e with temperature is described by the Arrhenius equation. These constants, as well as the values obtained by extrapolating the Arrhenius dependence to $T < 60°$ are denoted by k_I. The values of the activation energies, E_a, and the preexponential factors for the reduction of nitroxyl radicals with HAB and DPC lie within the range 31–42 kJ/mol, (2·80–9·35) × 10^5 l/mol s and 41–54 kJ/mol, 7·35 × 10^5–1·0 × 10^9 l/mol s, respectively. The mean error in the determination of E_a is ±1·6 kJ/mol. In the pretransitional region of the isotropic phase (T_{NI} for the MBBA-reagents mixture is 43°C), starting from 55–60°C, a positive deviation of the k_e values from an Arrhenius dependence is observed. The relative variation of the constant, $\Delta k = k_e - k_I$, is maximal near T_{NI}, reaching 30 per cent for reactions with DPC and 15 per cent with HAB. In going from the isotropic to the nematic phase a practically continuous change in k_e is observed. In the nematic phase k_e is higher than the values obtained by extrapolating the $\ln k_I$ versus $1/T$ dependence. Δk is maximal for the reaction involving nitroxyls II and III–up to 50 per cent for the reaction with DPC and up to ~40 per cent with HAB, and minimal for nitroxyl IV. The highest Δk values in the phase pretransitional region conform to the highest Δk in the mesophase. The temperature dependences of k_e in the nematic phase are not described by the Arrhenius equation. For the nitroxyl II reaction with HAB this is confirmed by checking the linearity hypothesis according to Fisher's statistical criteria.

In the mixed solvent, where the mesophase is destroyed by the addition of benzene the $\ln k_e$ versus $1/T$ dependence is linear, and the activation energy of this reaction is close to that determined in the isotropic phase of MBBA at $T > 60°$ (see figure 1). Thus, as seen from figure 1, the MBBA mesophase and the isotropic phase in the vicinity of T_{NI} affect the kinetics of the reactions in question: a positive deviation of k_e from an Arrhenius' dependence, obtained in the isotropic phase at $T > 60°C$, is observed.

3.1. *The influence of nematic ordering on the kinetics of nitroxyl radical reduction with hydrazo compounds in the liquid-crystalline phase*

The kinetic regularities observed in the mesophase could be caused by a change in the molecular transitional mobility of the reactants or by the formation of regions with increased local concentrations of reagents. However, a study of spin exchange for nitroxyl I, characterizing its transitional diffusion, has shown the K_e values determined in the isotropic and the nematic phases on Arrhenius' coordinates to lie on a single straight line within the experimental error. Moreover, the spin exchange activation energy, of $9{\cdot}6 \pm 1{\cdot}2$ kJ/mol, is close to that obtained for the isotropic MBBA-benzene solvent of $10{\cdot}0 \pm 0{\cdot}4$ kJ/mol (see figure 2). It is seen therefore that in the mesophase there is neither a significant change in transitional diffusion nor the formation of regions with an increased local concentration of reagents.

The influence of the mesophase on the kinetics of bimolecular chemical reactions can also be associated with the orientation of reagents, with a change in the entropy and activation energy of the elementary steps. On the basis of existing kinetic concepts and physical models of the liquid-crystalline state we can form some ideas on the kinetics of bimolecular reactions in liquid crystals and the magnitude of the mesophase effects expected.

An ordered mesophase creates an anisotropy of orientation and rotation of solute molecules. It seems that the orientation effect will play the greatest role in diffusion-controlled reactions ($E_a \leqslant kT$), when the reaction starts with the very first collisions of reagents. In consequence the orientation at the moment of contact determines the probability of the reaction taking place and the direction of the reaction. This seems to govern the effectiveness and selectivity of photochemical dimerization processes in mesophases, see for example [1], the reactions of the t-butyl radical [13]. It is possible that analogous effect takes place for the rearrangement of *n*-(dimethylamino)-benzene sulphonate into a zwitter-ion [14]. When the activation energy is considerably high ($E_a \gg kT$) the orientation of reagents at the moment of contact is unimportant as the reaction takes place after a large number of collisions in the cage. This will be most probable when the most favourable orientation of the reagents is realized, preceding the formation of the transition state with the lowest energy. However, as a result of solute ordering and the transition state, their rotational partition functions can decrease, which must result in a decrease in the absolute value of the activation entropy, $\Delta S^{\neq}$, and an increase in the preexponential factor of bimolecular reactions, as compared with the isotropic phase. The possibility of this effect was noted in [15]. Proceeding from the Maier–Saupe theory of the nematic state [5, 6], we can estimate the maximum value of the $\Delta S^{\neq}$ variation. In the most favourable situation, when

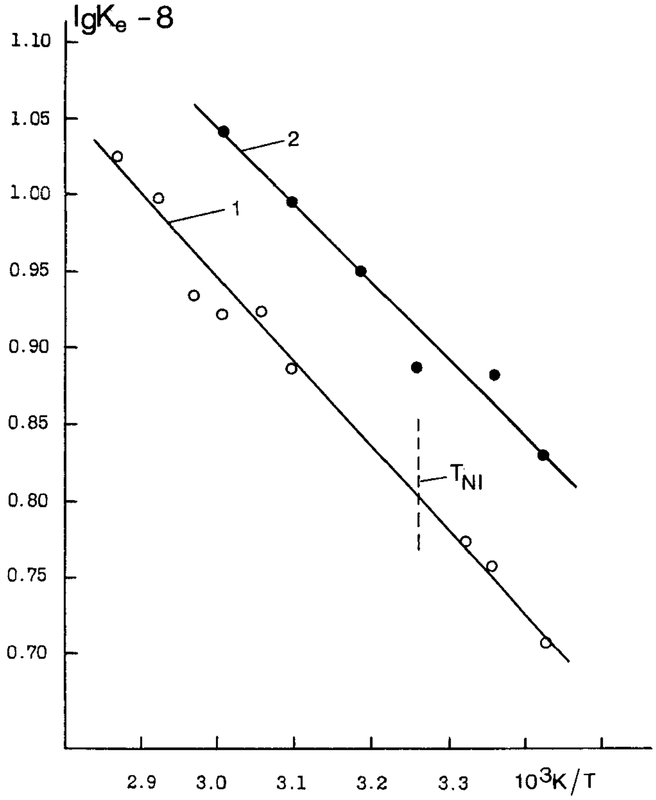


Figure 2. The temperature dependence of the spin-exchange rate constants, K_e, of nitroxyl radical I in the isotropic and nematic phases of MBBA (1) and in the MBBA-benzene mixture (2).

both the reagents are fully oriented, and the transition state is not oriented at all, it does not exceed 12–17 J K^{-1}mol^{-1} and in reality should be even smaller. On the whole, when making such estimates, the entropy variation in the ordered liquid-crystalline host should be taken into account which results from the transition state formation. This can exceed the variation of the activation entropy of the reaction itself and can have either sign. That is why chemical reactions in the mesophase can, in principle, proceed both with an increase or a decrease in $\Delta S^{\neq}$.

In some cases, e.g. in monomolecular reactions, it seems that we should take into account the influence of the mesomorphic phases on the conformation of the solute, since this can cause a substantial change in activation parameters.

The activation energy for the reaction in the mesophase can also change in comparison with the isotropic phase. If the transition state interacts specifically with the molecules of the medium, then, when it is favourably oriented with respect to the anisotropic environment, the interaction can be increased and lead to a decrease in E_a in the mesophase, as compared with the isotropic phase. The amount of energy gained must depend in this case on the type of interaction.

If both the reagents are oriented, but their orientation is unfavourable for the formation of the transition state this leads, on the one hand, to an increase in the preexponent and, on the other, to an increase in the activation energy, since for the transition state to be formed it is required that a certain energy should be needed to rotate the molecules. In this case the E_a variation in the nematic phase should not exceed the energy of the interaction of liquid crystal molecules with one another, i.e., according to [5], about 8–12 kJ/mol. We expect, therefore, that the influence of the nematic both on the energy and the entropy of activation will manifest itself in the reactions with a small activation barrier. In smectics, characterized by a higher ordering and a higher energy of intermolecular interaction, the orientation, energy and entropy effects can be higher, for example [4, 14].

Activation parameters of chemical reactions are dependent on hydrodynamical, electrodynamical (dipole–dipole), and dispersive interaction of the solute molecules with the solvent. Characteristic relaxation times of the solvent structural rearrangements are much longer in liquid crystal mesophases in comparison with isotropic low molecular weight liquids. So the situation when elementary chemical reaction steps are taking place in unrelaxed solvent is highly probable in liquid crystals. It is of great importance the preceding mutual structural arrangements and interactions as well of solvent and reagents molecules are favourable or not for transition state formation and for elementary reaction step as a whole. In particular transition state formation is accompanied by volume changes. We expect solvent effects in cases when the volume of the transition state is larger than the volumes of the reagent molecules. Solvent hydrodynamical effects on reaction kinetics should be small or even negligible for the opposite case. Such arguments lead to a conclusion about the important role of structural fluctuations in liquid crystals on the reaction kinetics. Depending on the structural and energetic requirements for transition state formation the fluctuations in the liquid crystal and changes of liquid crystal ordering will promote or retard a particular chemical reaction. Proceeding from this, the reactions of nitroxyl radicals with hydrazo compounds, having small activation energies, were chosen as the subject of this study.

In these reactions the entropy contribution to k_e, associated with the liquid crystal ordering, is small because of a weak orientation of the hydrazo compound and this does not explain the observed Δk values. We can suggest the feeble orientation of HAB and DPC by analogy with the ordering data for azobenzene [16] and nitroxides of similar chemical structures [7]. In fact the entropy variation with transition state formation in the isotropic and the nematic phases can be expressed as

$$\left.\begin{aligned} \Delta S_I^{\neq} &= S_I^{\neq} - S_I^A - S_I^R, \\ \Delta S_N^{\neq} &= S_N^{\neq} - S_N^A - S_N^R, \end{aligned}\right\} \tag{1}$$

where $S_I^{\neq}$, S_I^A, S_I^R and $S_N^{\neq}$, S_N^A, S_N^R are the entropies of the transition state, hydrazo molecules, and nitroxyl radical in the isotropic and the nematic phases, respectively. A decrease in entropy caused by the ordering of the medium may be estimated from [5]

$$S_I - S_N = R \int f(\theta) \cdot \ln(4\pi f(\theta))\, d\Omega, \tag{2}$$

where $f(\theta)$ is the singlet angular distribution function, θ is the angle between the long axis of a solute molecule and the director. It is supposed that the molecules reagent are sufficiently rigid and can be considered to have cylindrical symmetry. It is evidently reasonable for nitroxides II–IV and is good approximation for the nitroxide V, HAB and DPC. The order parameter of nitroxide I $S' \approx 0$ [7, 12], and so $f(\theta)$ is a constant and $S_I^R \approx S_N^R$. So the reaction entropy activation difference in isotropic and nematic phases is

$$\Delta S_{\mathrm{I}}^{\neq} - \Delta S_{\mathrm{N}}^{\neq} = R\int f^{\neq}(\theta)\cdot\ln(4\pi f^{\neq}(\theta))\,d\Omega - Rf^{\mathrm{A}}(\theta)\ln(4\pi f^{\mathrm{A}}(\theta))\,d\Omega$$

$$- R\int f^{\mathrm{R}}(\theta)\ln(4\pi f^{\mathrm{R}}(\theta))\,d\Omega, \qquad (3)$$

where $f^{\neq}(\theta)$, $f^{\mathrm{A}}(\theta)$, $f^{\mathrm{R}}(\theta)$ are the distribution functions for the long axes of the transition state, the hydrazo compound molecules and the nitroxyl radicals, which determine respectively the values of the orientational ordering for the transition state $S'^{\neq}$, hydrazo compound S'^{A} and nitroxyl radical S'^{R} in the mesophase. The S'^{R} values can be determined from experiment. To estimate $S'^{\neq}$, in all reactions, except those with nitroxyl I, the orientational order of the hydrazo compound was assumed to be lower and that of transition state equal to or somewhat lower than the ordering of the radical. In this case

$$|\Delta S_{\mathrm{I}}^{\neq} - \Delta S_{\mathrm{N}}^{\neq}|/R \leqslant \int f^{\mathrm{A}}(\theta)\ln(4\pi f^{\mathrm{A}}(\theta))\,d\Omega.$$

The S'^{A} value can be evaluated approximately based on the data from [7]: $S'^{\mathrm{A}} \leqslant$ 0·10–0·15, the entropy contribution to the rate constant, resulting from the liquid-crystalline ordering, will then amount to

$$|\Delta S_{\mathrm{I}}^{\neq} - \Delta S_{\mathrm{N}}^{\neq}|/R \leqslant 2\times 10^{-2},$$

i.e. the influence exerted by the nematic mesophase on the activation entropy for the reduction of nitroxyl radicals with hydrazo compounds is small and does not explain the observed Δk values.

In our opinion, a relative increase in the experimental rate constant of the reactions studied and the nature of its temperature variation not adhering to an Arrhenius dependence are associated with a decrease in the activation energy in the ordered mesophase, caused by a stabilisation of the transition state. In the nematic phase a decrease in the activation energy must depend on the orientation of the reaction centre of the transition state with respect to the director. This can be determined having assigned the position of one of the transition state reaction centre fragments, e.g. the nitroxyl $\mathrm{N}\dot{-}\mathrm{O}$ bond. To express the activation energy variation (ΔE_{a}) in the mesophase as a function of the angle ε between the N–O bond orientation and the director, we shall use the first non-zero member in the multiple energy function expansion as adopted in the theory of liquid crystals [5, 6]:

$$\Delta E_{\mathrm{a}}(\varepsilon) = \tfrac{1}{2}[3\cos^2(\varepsilon-\varepsilon_0) - 1]\,US(T).$$

Here the angle ε_0 characterizes the most favourable transition state orientation with respect to the director, $S(T)$ is the order parameter of liquid crystal, U is the decrease in the reaction activation energy in a fully ordered mesophase ($S = 1$) at $\varepsilon = \varepsilon_0$. For the reactions studied, the hydrazo molecules are poorly ordered in nematic MBBA and, therefore, the transition state position with respect to the director is determined by the more ordered nitroxyl radicals. We shall characterize the nitroxyl radical orientation, and thereby that of the transition state, by means of two parameters: the angle θ between the long axis of the nitroxyl and the director and the angle η for the rotation of nitroxyl radical about its long axis (see figure 3). The angle between the long axis and the N–O bond is denoted by γ. Then from geometric considerations we

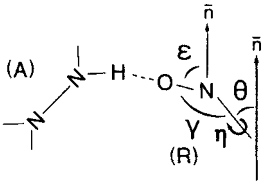


Figure 3. A schematic presentation of the transition state in the reaction of a nitroxyl radical (R) with a hydrazo compound (A) in the mesophase of a liquid crystal.

can obtain the relationship between the value of $\cos(\varepsilon - \varepsilon_0)$ and the parameters θ and η, namely

$$\cos(\varepsilon - \varepsilon_0) = \cos\eta\sin\theta\sin(\varepsilon_0 - \gamma) - \cos\theta\cos(\varepsilon_0 - \gamma) \tag{5}$$

and express the dependence of ΔE_a on the nitroxyl radical orientation. We introduce the elementary rate constant $k(\theta, \eta)$ determining the reaction rate at a given orientation of the nitroxyl radical by

$$k(\theta, \eta) = k_1 \exp(\Delta E_a(\theta, \eta)/kT). \tag{6}$$

The experimental rate constant is obtained by averaging this value over all angles. All the values of η are in this case equally probable and the angular distribution for θ is given by the distribution function $f(\theta)$, hence

$$k_e = \iint k(\theta, \eta) f(\theta) \sin\theta \, d\theta \, d\eta. \tag{7}$$

For the distribution function $f(\theta)$ we have used the simple relation [5]:

$$f(\theta) = (1/Z)\exp(m(T)\cos^2\theta), \tag{8}$$

where Z is the normalization constant, and the parameter $m(T)$ is determined from the condition

$$S_{\text{mol}}(T) = \frac{1}{Z}\int \frac{3\cos^2\theta - 1}{2} f(\theta)\sin\theta \, d\theta. \tag{9}$$

In equation (9) $S_{\text{mol}}(T)$ is the order parameter for the long axis of the nitroxyl radical, determined experimentally as a function of temperature.

When deriving equation (7) the orientation of the transition state was assumed to be determined by the orientation of the nitroxyl radical. This seems to hold for all the radicals except I, whose ordering in MBBA is close to zero [12]. However, in this case too, equation (7) remains valid if we take $f(\theta) = 1$, which corresponds to the interaction of two completely unoriented molecules. In this case the value of k_e does not depend on the angle ε_0.

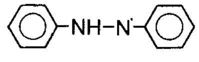
Expression (7) establishes the relationship between the experimental rate constant and the physical characteristics of the liquid crystal-reagents mixture: the parameters of the ordering of the nematogenic molecules in the mesophase, $S(T)$, and of the nitroxyl radical, $S_{\text{mol}}(T)$, the energy U of the stabilizing effect exerted by the mesophase on the transition state, the angles ε_0 and γ characterizing the structure of the transition state and of the nitroxyl radical. The non-linear variation of the order parameter $S(T)$ with temperature [5, 6] leads to a deviation of the $\ln k_e$ versus $1/T$ from an Arrhenius dependence in the nematic phase.

The $S_{\mathrm{mol}}(T)$ and $m(T)$ values were calculated from the order parameter S_{33} for the N∸O nitrogen $2p\pi$ orbital of the nitroxyl fragment, determined by ESR spectroscopy [12]. The liquid crystal order, $S(T)$, in the presence of the reagents (azobenzene was used instead of HAB) were determined as $1{\cdot}05 \times S_{\mathrm{mol}}(T)$ where $S_{\mathrm{mol}}(T)$ is the corresponding values for nitroxide IV which in the MBBA mesophase, is close to 1 [7]. The $S(T)$ data obtained were 10–15 per cent lower than those given in [16] for pure MBBA which is attributed to the presence of the solutes.

The values of parameters entering into equation (7).

System	U/kJ mol^{-1}	$(\varepsilon_0 - \gamma)^\circ$	$\gamma/^\circ$	$\varepsilon_0/^\circ$
I + HAB	8·5	0	0	0
II + HAB	8·5	42	~15	~55
III + HAB	8·5	22	~35	~55
IV + HAB	8·5	57	0	57
I + DPC	11·1	0	0	0
II + DPC	11·1	42	~15	~55
V + DPC	11·1	35	90	55

After estimating the angle γ from literature data or Stewart-Briegleb models (cf. the table) and determination of $S(T)$ and $m(T)$ the unknown parameters in equation (7) are U and ε_0. The order parameter for nitroxyl I is close to zero, and so the rate constant of the reaction of this radical with hydrazo compounds is a function of U only. The best agreement with the experimental $\ln k_e$ versus $1/T$ dependences for the reactions of I with HAB and DPC has been obtained for U equal to 8·5 and 11·1 kJ/mol, respectively (see figure 1, and the table). Since all the nitroxyls are characterized by the same reaction centre it is natural to assume that the value of U should not depend significantly on the structure of the radical. Therefore, when calculating k_e for the reactions of the other nitroxyls with a given hydrazo compound the same U values were used, and for them the natural optimized parameter was the angle $(\varepsilon_0 - \gamma)$. As we can see from the table, the calculated values of ε_0 are close to one another and equal to approximately 55–60°, i.e. the greatest activation energy gain is reached when the angle between the >N˙–O bond and the director in the transition state amounts to ~60°. It can be assumed that with such an orientation of the transition state the long axis of the hydrazo fragment proves to be oriented parallel to the director, and in this case the mechanism of mesophase influence is as follows. Dispersive interactions are claimed to be important for the formation of the nematic mesophase and the energy gain due to the ordering of nematogenic molecules along one direction increases with the anisotropy of the molecular polarizability [5, 6, 17]. For the reactions in question the transition state fragment of the limiting step probably has a structure close to that of the product, for hydrazobenzene it is



and its polarizability and polarizability anisotropy are higher than in the initial hydrazo compound, because of the increased length of the conjugation chain. It is, therefore, possible that a decrease in E_a in the mesophase, as compared with the isotropic phase, results from the increase of the dispersive interaction of the transition state with the nematogenic molecules in the ordered solution. The energy gain is a maximum in this case if the hydrazo fragment in transition state is oriented parallel to the director. When it has the unfavourable perpendicular orientation the energy gain decreases, as compared with the isotropic phase, with the value of the maximum energy gain being twice as large as the maximum loss, which is in agreement with equation (4). The U values obtained are somewhat smaller than the energy of the dispersive interaction of MBBA molecules in the mesophase which is approximately 12 kJ/mol [5], which corresponds to their physical meaning for the proposed mechanism of the influence of the liquid crystal on the reaction activation energy.

3.2. *Description of chemical reaction kinetics in the isotropic phase; the influence of nematic order fluctuations*

In the reduction of nitroxyl radicals by hydrazobenzene and diphenylcarbazone in the 8–10°C interval above T_{NI} k_e has been found to show a positive deviation from an Arrhenius dependence. This is similar to that in the mesophase. The deviation in the mesophase is caused by the liquid-crystalline ordering, and so when describing the reaction kinetics in the pretransitional region of the isotropic phase the existence of fluctuations in local ordering should be taken into account.

Making use of the concepts developed previously we extend equation (7) to include the interval $T > T_{NI}$ within the framework of the Landau–de Gennes model [5, 6]. For this purpose we expand equation (7) into a series in terms of the small order parameter S and confine ourselves to the terms of the order of S^2. In the general case the resulting equation is quite cumbersome, but it is substantially simplified if the radical is not oriented in the mesophase ($f(\theta)$ is constant), e.g. for nitroxyl I:

$$\frac{k_e}{k_I} = 1 + \frac{11}{64}\left(\frac{US}{RT}\right)^2. \tag{10}$$

According to the Landau–de Gennes model, in the pretransitional region of the isotropic phase $S^2 \sim 1/(T - T^*)$ [5, 6], where $T_{NI} - T^* \approx 1$ K and T^* is the critical temperature. As a result, we find

$$\begin{aligned}\Delta \ln k &= \ln \frac{k_e}{k_I}\\ &= \frac{B}{T - T^*}\left(\frac{U}{RT}\right)^2,\end{aligned} \tag{11}$$

where B is a proportionality factor. Equation (11) does not make it possible to obtain quantitative agreement, but qualitatively it conveys the nature of the temperature dependence of k_e in the isotropic phase of the liquid crystal (see figure 4). This seems to be associated with the Landau–de Gennes model adequately describing the isotropic phase structure only at distances of the order of tens or hundreds of molecules. These are the fluctuations determining the light scattering, electric and magnetic birefringence, etc., [5, 16, 18, 19]. However the regions essential for chemical interaction are of the size of several nematogenic molecules, since intermolecular forces decrease rapidly with distance.

For a quantitative description of the $k_e(T)$ dependence in the pretransitional region above T_{NI} two models are proposed here. In these models, as distinct from the Landau–de Gennes concepts, according to which the order parameter varies continuously from point to point, the isotropic phase is regarded, approximately, as consisting of two types of regions: the ordered (nematic) and the unordered (isotropic), with the fraction of the latter increasing with increasing temperature. If the

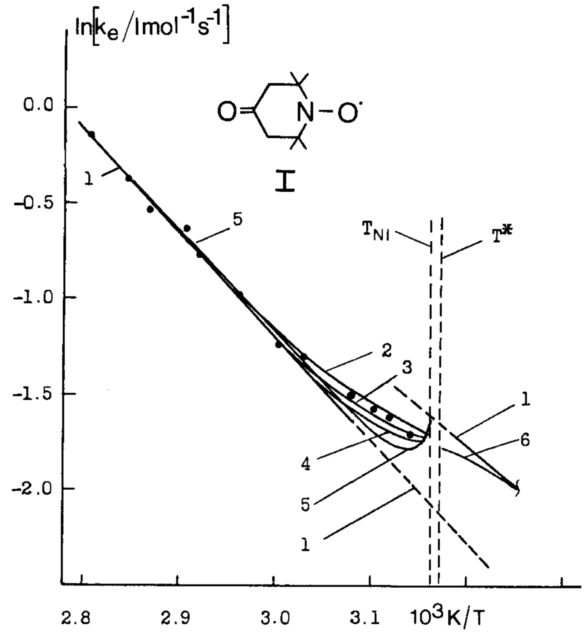


Figure 4. Temperature dependence of the rate constant, k_e, in the reduction of nitroxyl radical I with diphenylcarbazone (DPC) in the isotropic phase of MBBA. ●, experimental points; 1, Arrhenius dependence; 2,3,4, k_e calculated from equation (18) with m = 300, 400, 500, respectively; 5, k_e calculated from equation (11) with B = 0·12; 6, k_e in the mesophase, calculated from equation (7).

activation energy and the preexponential factors in these two regions are different, then the experimentally observed rate constant will deviate from an Arrhenius dependence which is obtained in the isotropic phase at higher temperatures. As the temperature moves away from T_{NI} the size of the nematic regions decreases, and the value of k_e approaches that of k_I.

We assume the distribution of reagents to be uniform within the whole volume ($C_N^R = C_I^R = C^R$, $C_N^A = C_I^A = C^A$); where C^R and C^A are the nitroxyl radical and the hydrazo compound concentrations), since no regions with an increased local concentration of dissolved species are formed in the mesophase. We can express the experimentally observed reaction rate as the sum of the rates in regions N and I ($V = V_N + V_I$, where V is the overall volume). We obtain an equation relating to k_e to the reaction rate constants in the isotropic (k_I) and the nematic (k_N) regions and to the ratio between the volumes of these regions [20], namely

$$-dR/dt = k_e C^R C^A V = k_N C^R C^A V_N + k_I C^R C^A V_I, \tag{12}$$

or

$$k_e = k_N(1 + V_I/V_N)^{-1} + k_I(V_I/V_N)(1 + V_I/V_N)^{-1}. \tag{13}$$

To express the temperature dependence of k_N, k_I, V_I/V_N, and thereby of k_e, in analytical form two approaches were used to describe the structure of the isotropic phase.

The first, based on concepts intermediate between the models of clusters [21] and the continuum model [5, 22], proceeds from the assumption that a cluster of the size of ξ consists of two regions: the internal ordered nematic phase (N) with a linear size of $(\xi - \beta)$ and the external isotropic layer (I) of β thickness, constituting a transition to the other clusters. To express the cluster size as a function of temperature we have used Landau's formula describing the temperature dependence of the correlation radius. This is a characteristic distance up to which the local ordering exists [5, 6],

$$\xi = \xi_0(T^*/(T - T^*))^{1/2}, \tag{14}$$

where ξ_0 characterizes the size of the nematogenic molecule. The external layer thickness β is assumed to be practically independent of temperature. Substituting equation (14) into equation (13) and taking into account the fact that the shape of the local ordering regions in MBBA is close to spherical [23] we find an expression describing the temperature variation of k_e in the isotropic phase:

$$\Delta \ln k = \ln[1 + (k_I/k_N - 1)(1 - n(T/T^* - 1)^{1/2})^3]. \tag{15}$$

Here the dimensionless parameter $n = \beta/\xi_0$ expresses the layer thickness in units of the nematogenic molecule size, and the constants k_I and k_N are determined by extrapolating the temperature dependence of k_e from the isotropic and the nematic phases to the pretransitional interval.

For calculations based on equation (15) the following relations were used

$$k_I = A_I \exp(-E_I/RT),$$
$$k_N = A_N \exp(-E_N/RT),$$

where A_N, E_N are the Arrhenius parameters obtained by approximating with a straight line the low-temperature portion ($T \leqslant 36°$) of the $\ln k_e$ versus $1/T$ dependence in the mesophase.

From the physical point of view, this model can be presented as follows. The reaction activation energy in the mesophase decreases owing to the dispersive interaction of the transition state with the ordered molecules of the liquid crystal. Dispersion forces are short-range and attenuate in accordance with the r^{-6} law or, with the additivity of dispersion forces and an increase in the number of interacting molecules with distance taken into account, as r^{-4}, i.e. a given transition state is affected only by neighbouring nematogenic molecules. In the isotropic phase in the vicinity of T_{NI} the transition state interaction with nematogenic molecules will decrease as the boundary of the cluster (i.e. the boundary of the correlation in the degree of orientation) is approached. We can approximate this dependence by a stepwise function with the lengths of the steps $(\xi - \beta)$ and β and consider β to be the external isotropic layer thickness and $(\xi - \beta)$ the internal nematic region radius. Then 2β is the distance at which the dispersive interaction drops to zero. As we have assumed, it should not depend on temperature, and $n = \beta/\xi_0$ yields the minimum number of nematogenic molecules forming a mesophase capable of influencing the kinetics of a given reaction. For all the reactions studied the best agreement with experiment is found for $n = 2$ (see figure 5), i.e. $2n = 4$, which is a reasonable quantity for dispersion forces.

The second approach to describing the kinetics of reactions in the isotropic phase, proposed in the present work, is based on successive application of Frenkel–Tsvetkov concepts. According to these above T_{NI} there exist nuclei of different size, characterized by a liquid–crystalline structure [21]. The expression for the number of nematic phase nuclei in the isotropic phase has the form

$$f_v = F \exp\left(-\frac{\lambda(T - T^*)v}{RT}\right), \tag{16}$$

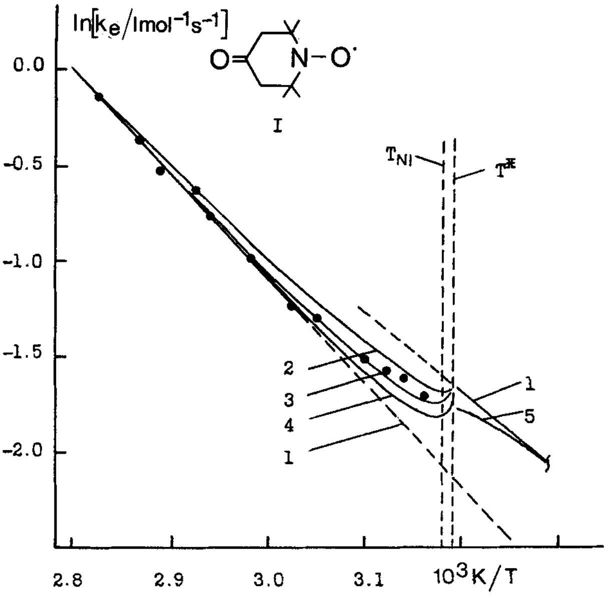


Figure 5. The temperature dependence of the rate constant k_e in the reduction of nitroxyl radical I with diphenylcarbazone (DPC) in the isotropic phase of MBBA. ●, experimental points; 1, Arrhenius dependences in the isotropic and nematic phases of MBBA; 2,3,4, k_e calculated from equation (15) with $n = 1, 2, 3$, respectively; 5, k_e in the mesophase, calculated from equation (7).

where f_v is the number of nuclei containing v molecules each, λ is the heat of the nematic–isotropic transition and F is the normalization constant. Let us assume that above T_{NI} the reaction proceeds in the volume constituting a combination of nuclei formed by a different number of nematogenic molecules and that in a nucleus there exists a minimum number m of nematogenic molecules which does not depend on temperature, whose influence on the reaction kinetics is similar to that of the nematic phase (i.e. the nuclei containing less than m molecules are regarded as isotropic). The volumes of isotropic and nematic regions in the sample will then amount to

$$\begin{aligned} V_I &= V_M \sum_{v=1}^{m} v f_v \\ &= V_M F\left(\frac{m\exp[a(m+2)] - m\exp[a(m+1)] - \exp[a(m+1)] - e^a}{(1-e^a)^2}\right), \\ V_N &= V_M \sum_{v=m+1}^{\infty} v f_v \\ &= V_M F\left(\frac{\exp(-am)}{m(1-e^a)+1} - 1\right), \end{aligned} \tag{17}$$

where $a = -[\lambda(T - T^*)/RT^2]$ and V_M is the volume of NLC molecules. After substituting equation (17) into (13) we find

$$\Delta \ln k = \ln[1 + (k_N/k_I - 1)(m(1 - e^a) + 1)e^{am}]. \tag{18}$$

Within the framework of Frenkel–Tsvetkov concepts it should be assumed that S is practically independent of temperature in the nematic nuclei in the isotropic phase.

Therefore, in the pretransitional region the k_N/k_I ratio varies but slightly with temperature and is equal to the ratio of these constants at T_{NI}. The best agreement with the experimental data for all the reactions studied is reached at $m \approx 400$ (see figure 1 and 4), i.e. the diameter of the minimal region of nematic ordering is equal to $\sqrt[3]{400}$ which is equivalent to 7–8 nematogenic molecules.

Three methods have been proposed to account for the influence of nematic ordering fluctuations in the isotropic phase on the kinetics of chemical reactions. They are used to describe the k_e temperature dependence in the reduction of nitroxyl radicals with hydrazo compounds.

Within the framework of Landau–de Gennes concepts we do not succeed in obtaining quantitative agreement with experiment (see figure 4). On the other hand, to calculate the reaction rate constant in the pretransitional region of the isotropic phase from equation (7) it is necessary to know the mechanism of the influence exerted by the mesophase on the reaction kinetics.

The models based on approximate representations of a liquid crystal above T_{NI} as a combination of isotropic and nematic regions quantitatively describe the temperature variation of k_e. They can be used without any assumptions regarding the mechanism of mesophase influence on the kinetics of a given process. Therefore, both these models seem to be applicable in describing various chemical reactions proceeding in the isotropic phase. In the first model certain elements of Landau–de Gennes theory were used, e.g. the expression for the temperature dependence of the coherence length ξ. However, $\xi(T)$ and the very notion of ξ were introduced by de Gennes on the assumption of a continuous variation of the order parameter throughout the sample volume [5, 6], whereas we consider here two types of regions whose ordering is different and at the boundary undergoes an abrupt change. That is why it is difficult to make any assumptions regarding the nature of the $S(T)$ dependence in nematic regions, and equation (7) cannot be used successfully in the pretransitional interval. When k_N is found by extrapolating the $\ln k_e$ versus $1/T$ dependence from the mesophase, an indeterminacy arises, associated with the non-linearity of this dependence. Nevertheless, the model is sufficiently descriptive, and the parameters β and n have a clear physical meaning. In the second model it is assumed that S in the nematic nuclei above T_{NI} is only slightly dependent on temperature, and, therefore, when calculations are made from equation (18) it is sufficient to know $\ln k$ at the clearing point. An important advantage of this model is the possibility of establishing the relationship between the kinetics of chemical reactions in liquid crystals and the thermodynamic characteristics of the medium. The proposed models make it possible to estimate the minimum number of nematogenic molecules which influences the kinetics of a given reaction. For instance, for the reduction of nitroxyl radicals by hydrazo compounds the estimates of the diameter of the minimum nematic region, performed within the framework of both these models, coincide and correspond to about 8 nematogenic molecules, which is in reasonable agreement with the distance at which dispersive interactions practically die away. They do not contradict the mechanism of nematic phase influence on the kinetics of the studied reactions, presented previously.

4. Conclusions

Nematic ordering has been established as affecting the kinetics of thermal bimolecular reactions of nitroxyl radical reduction by hydrazo compounds. Analysis of the experimental data allows us to assume that the observed relative increase in k_e

in the mesophase and its deviation from an Arrhenius temperature dependence are associated with a decrease in the reaction activation energy caused by the stabilization of the transition state in the ordered medium. The method of describing the temperature dependence of the experimental rate constant in the nematic phase, based on this assumption, seems also to be applicable to other thermal reactions with a different mechanism of mesophase influence, but, depending on the particular mechanism, the parameters entering into equation (7) may have another physical meaning. Comparison of the rate constant values obtained with those calculated from equation (7) makes it possible to determine the optimum transition state orientation relative to the director and, proceeding from this, to assume a mechanism for the mesophase effect. The results obtained show that a study of the kinetics of chemical reactions in liquid crystals allows us to estimate the limits of the applicability of transition state theory to describe the reactions in ordered media and expands our conception of the elementary step of chemical reactions. In our opinion, investigating chemical processes in liquid-crystalline media is of greatest interest from the point of view of the possibility of obtaining direct information on the transition state structure.

The existence of local ordering fluctuations in the istropic phase, influencing the kinetics of chemical reactions in a certain temperature range above T_{NI}, and the mesophase disordering with the temperature approaching T_{NI} from below must result in a practically continuous variation of the experimental reaction rate constant, which is actually observed in the reduction of nitroxyl radicals by hydrazo compounds (see figure 1). Such behaviour of the rate constant differs from the abrupt change in numerous thermodynamic and physical parameters, characteristic of first-order phase transitions, and is associated with the fact that the nematic–isotropic transition is a weak first order transition and by its nature is close to second order.

The data obtained indicate that the kinetics of chemical reactions can be sensitive to slight fluctuations in ordering. Hence, it is to be hoped that improved kinetic methods will provide information on the structure of small fluctuations in the isotropic phase of liquid crystals. On the other hand, accounting for the influence of liquid-crystal ordering fluctuations on the kinetics of chemical reactions allows us to describe the non-linear nature of the ln k_e versus $1/T$ dependence in the isotropic phase close to T_{NI} and to estimate the size of the minimal nematic region that a given reaction experiences. The latter is of great importance for understanding the mechanism of the influence of liquid-crystalline mesophases on the kinetics of chemical processes.

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