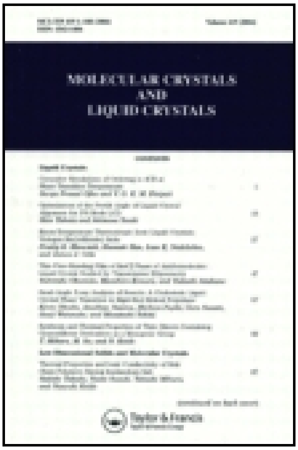

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Phenomenological Approach to the Description of the Dimerization Kinetics in Nematic Mesophase

V. A. Batyuk [a] , T. I. Shabatina [a] & G. B. Sergeev [a]
[a] Department of Chemistry, Moscow State University, Lenin Hills, Moscow, 119899, USSR

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Phenomenological Approach to the Description of the Dimerization Kinetics in Nematic Mesophase

V. A. BATYUK, T. I. SHABATINA and G. B. SERGEEV
Department of Chemistry, Moscow State University, Lenin Hills, Moscow 119899, USSR

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The expression has been obtained, which determines the observed reaction rate constant in the nematic mesophase as a function of scalar liquid crystal order parameter. The expression includes the experimentally obtained parameters. It has been used for the estimation of the rate constants for 2-methyl-2-nitrosopropane at selected temperatures in nematic liquid crystal MBBA.

At present liquid crystals and liquid-crystalline compositions have been exploited in numerous technical and scientific applications. The ordered structure in conjunction with high molecular mobility makes liquid crystals a promising medium for conducting chemical reactions. Characteristic of chemical reactions in a condensed phase is that the reagents molecules being surrounded by molecules of a medium interact in a cage of a solvent.[1] Liquid-crystalline medium is anisotropic and it is therefore insufficient to treat it as an isotropic viscous medium.[2-4]

The long axes of liquid crystal molecules in nematic mesophase have a predominant orientation ($\bar{n}$) and the averaged value of an experimental bimolecular reaction rate constant can be expressed as:

$$k_{\text{exp}} = \int k'(\theta,\varphi) \cdot f'(\theta,\varphi)\, d\Omega = \int k(\theta) \cdot f(\theta)\, d\theta \tag{1}$$

where $f(\theta)$ is the distribution function that accounts for the orientations of reagent molecules and θ is the angle between the molecular axis and $\bar{n}$. An integration is conducted over the macroscopic volume. The expression (1) holds true for the interaction between the species of one type, e.g. for dimerization, and nematic mesophase with axial symmetry.

As a probe function the dependence of $k(\theta)$ of the type:

$$k(\theta) = k_{\parallel} \cdot \cos^2\theta + k_{\perp} \sin^2\theta, \tag{2}$$

where $k_{\|,\perp}$—the reaction rate constants for the reagent molecules oriented parallel and perpendicular to $\bar{n}$ respectively, was considered. This dependence has among others the following properties: an integral (1) does not turn into zero and in case $k_{\|} = k_{\perp} = k$, $k_{\text{exp}} = k$.

The ordering of molecules in the volume of liquid crystal is characterised by a macroscopic value—the scalar liquid crystal order parameter S[5]:

$$S = \int f(\theta) \cdot 1/2\,(3\cos^2\theta - 1)d\theta = 1/2\,\langle(3\cos^2\theta - 1)\rangle \tag{3}$$

where θ is the angle between the long molecular axis and $\bar{n}$.

By using (3) the equation (1) can now be rewritten as:

$$k_{\text{exp}} = 2/3\,S(k_{\|} - k_{\perp}) + 1/3\,k_{\|} + 2/3\,k_{\perp} \tag{4}$$

It should be noted that here S is the order parameter for reagent molecules that is unknown in the majority of cases but very often as a first approximation the liquid crystal order parameter can be used.

Let us consider the extreme cases:

for the ideally ordered liquid-crystalline system ($S = 1$)

$$k_{\text{exp}} = k_{\|} = k_N \tag{5}$$

for the isotropic system ($S = 0$)

$$k_{\text{exp}} = 1/3\,k_{\|} + 2/3\,k_{\perp} = k_I \tag{6}$$

Taking into account the definitions of k_N and k_I, the expression (4) for the reaction rate constant in the mesophase of the nematic liquid crystal at $0 < S < 1$ can be written as:

$$k_{\text{exp}} = k_N \cdot S + k_I\,(1 - S) \tag{7}$$

or

$$k_{\text{exp}} = k_I[1 - S(1 - Z)], \quad \text{where } Z = k_N/k_I \tag{8}$$

It should be noted that expression (7) can be obtained on the basis of the statistical meaning of S as a scalar value that characterises the effective molar fraction of liquid crystal molecules with corresponding long molecular axes orientations. The expression (7) or (8) determines the observed reaction rate constant in the mesophase as a function of the nematic liquid crystal order parameter (S) and includes also k_N and k_I, which can be experimentally obtained [k_N is a rate constant for reaction in an ideally ordered system ($S = 1$) and k_I is a rate constant in an isotropic disordered system ($S = 0$)].

One can use the expression (7) or (8) in particular for the description of the reaction rate constant dependence on S-value at constant temperature, i.e. for the designated Z-value. At a fixed temperature we can alter the ordering (S-value) of liquid-crystalline system by introducing the chemically inert possible isotropic additives. Among others the following possibilities should be considered: a) if $k_N = k_I$, then the experimental rate constant is independent of the ordering in the liquid-crystalline system, i.e. for any values of liquid crystal order parameter (S) $k_{\text{exp}} = k_N = k_I$; b) if $k_N >> k_I$, then $k_{\text{exp}} \sim k_N \cdot S$; c) if $k_N << k_I$, then $k_{\text{exp}} \sim k_I(1 - S)$. It should be convenient to have the possibility to use the equation (7) or (8) for the description "reaction rate constant (k_{exp})—liquid crystal parameter order (S)" relationship in cases, where the S-values for given liquid-crystalline system vary as a result of temperature changes. However, in general the temperature dependence of the parameter $Z(T) = Z_0 \cdot e^{-\Delta E/RT}$ should be known, where Z_0 is ratio of pre-exponential factors of the reaction in the mesophase and isotropic phase of the liquid crystal, and ΔE—the difference between the corresponding activation energies. We attempted to dispense with this difficulty in the case of 2-methyl-2-nitrosopropane dimerization in nematic liquid crystal MBBA. Our previous spectroscopic study (by double-wavelength spectroscopy method) of the dimerization kinetics of the nitrosocompound in the mesophase of MBBA and in the isotropic system—binary mixture of MBBA and benzene† (5:1 by volumes) in temperature range 293–313 K revealed that the activation energies of the reaction in the nematic and isotropic phases are practically the same.[6] So we have that $\Delta E = E_N - E_I = 0$. For this particular case we suppose that parameter Z in Equation (8) is temperature independent and equal to $Z = k_N/k_I \approx k^{293}_{\text{MBBA}}/k^{293}_{\text{MBBA+benzene}}$, k^{293}_{MBBA} is the experimental rate constant for 2-methyl-2-nitrosopropane dimerization in the MBBA mesophase at 293 K. The temperature 293 K corresponds to the maximum experimentally attainable order of the liquid-crystalline system. $k^{293}_{\text{MBBA+benzene}}$ is the experimental rate constant for 2-methyl-2-nitrosopropane dimerization in the isotropic phase obtained at the same temperature by disordering of MBBA mesophase by addition of minimal amounts of benzene. The Z-value evaluated this way is 10.8. This value has been used for estimation of the rate constant for 2-methyl-2-nitrosopropane dimerization at selected temperatures over the range 293–313 K in the MBBA mesophase by Equation (8). The k_I-values for the same temperatures were determined experimentally as the dimerization rate constants in isotropic system (MBBA+benzene).[6] The S-values at these temperatures were taken for MBBA from Reference 7. The experimental values k_{exp} ($l\text{M}^{-1}\ \text{s}^{-1}$) assigned by Equation (8) are given in Table I.

It follows from Table I that there is a good agreement between the experimental and calculated values at temperatures close to phase transition crystal-nematic. At higher temperatures the deviation between the experimental and calculated data

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†The application of this binary mixture allowed us to investigate the reaction kinetics in the isotropic system in the same temperature range as in the nematic phase. The addition of minimal amounts of the chemically inert isotropic solvent lead to a complete shattering of nematic ordering of the system. As this took place the chemical nature of the system maintained practically invariable.

TABLE I

The experimental and calculated [Equation (8)] values of the rate constant for 2-methyl-2-nitrosopropane dimerization in the mesophase of the liquid crystal MBBA

			$k_{exp} \cdot 10^4$ /M^{-1} s^{-1}[b]	
T,K	S[a]	$k_l \cdot 10^4$, /M^{-1} s^{-1}[b]	Calculated	Experimental
298	0.65	16.0	117.9	115.0
303	0.58	21.1	141.0	157.0
308	0.56	26.6	173.0	195.0
313	0.50	38.2	225.0	279.0

[a] Data were taken from Reference 7.

[b] Experimental rate constants for 2-methyl-2-nitrosopropane dimerization in nematic and isotropic phases of MBBA have been measured by double-wavelength spectroscopy (Aminco DW-2, $\lambda_1 = 678$ nm, $\lambda_2 = 800$ nm) better than 15%.

slightly increases. It can be caused by difference of the order parameters for the pure liquid crystal (used in calculations) and for the liquid-crystalline-system with additives of the nitrosocompound. Moreover the accuracy of k_N-value (which should correspond to $S = 1$) approximation by experimental k^{293}_{MBBA}-value measured at $S \approx 0.7$ may be insufficient.

Thus in some cases Equation (7) or (8) can be of use for the description of chemical kinetics in nematic liquid crystalline systems.

References

1. E. A. Moelwin-Hughes, Chemical Statics and Kinetics of Solutions, Academic Press, London and New York (1971); S. G. Entelis, and R. P. Tiger, Kinetics of Liquid-Phase Reactions, Quantitative Assessment of the Effects of the Medium. Moscow, *Khimia* (1973); A. M. North, The Collision Theory of Chemical Reactions in Liquids, New York, Wiley (1964); R. M. Noyes, The effects of diffusion rates on chemical kinetics. In: Progress in Reaction Kinetics, London, Pergamon Press (1961).
2. G. B. Sergeev, V. A. Batyuk, M. B. Stepanov, and T. I. Shabatina, *Dok. Akad. Nauk. SSSR*, **246**(6), 1409–1413 (1979).
3. G. B. Sergeev, V. A. Batyuk, and T. I. Shabatina, *Vest. Mosk. Univ., Ser. 2, Khim.* **24**(1), 55–59 (1983).
4. G. B. Sergeev, V. A. Batyuk, and T. N. Boronina, *Dokl. Akad. Nauk. SSSR*, **279**(4), 935–938 (1984).
5. P. G. de Gennes. The Physics of Liquid Crystals, Clarendon Press, Oxford (1974).
6. G. B. Sergeev, V. A. Batyuk, and T. I. Shabatina, *Kinet. Katal.*, **24**(3), 538–541 (1983).
7. B. Kronberg, D. F. R. Gilson, and D. Patterson, *J. Chem. Soc. Faraday*, 11, **9**, 1673–1685 (1976).