JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 341–345 (1991)

ACTIVATION AND THERMODYNAMIC PARAMETERS OF NUCLEOPHILIC SUBSTITUTION. REACTION OF ALKYL HALIDES WITH SOLID SALTS UNDER PHASE-TRANSFER CATALYSIS CONDITIONS

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The paper is concerned with the effect of temperature and the nature of a solid ionophore (MCl, where M = Li, Na, K, Rb or Cs) on the rate and equilibrium constants in the process of substitution of chlorine for bromine in hexyl bromide. The non-linearity of the log k vs $1/T$ dependence is shown to be linked with a change in the physical meaning of the constants with temperature variations. This is attributed to the occurrence of a strong exothermic process consisting in the formation of a kinetically independent intermediate, that precedes the limiting stage. A mechanism including the formation of two stable ternary complexes coordinated on the solid-phase surface, one of which is structurally close to the starting reagents and the other to the final reaction products, is proposed. The observed activation energies, enthalpies of formation of the ternary complex and activation energies of the limiting stages for the forward and reverse substitution processes were calculated. Thermal effects of the substitution in the presence of various solid MCl species were determined from the thermodynamic data and observed activation energies for both reaction types. The substitution is shown to involve a limiting stage represented by a transition between the ternary complexes. A linear relationship between the activation energy for the limiting stage and the solid ionophore crystalline lattice was established, suggesting incorporation of the solid salt molecule into the transition reaction state. Potential energy changes in the course of substitution in the presence of the various MCl solid salts are discussed. The Bell–Evans–Polyani principle is shown to hold for these studies.

INTRODUCTION

Earlier we reported on the kinetic principles governing the nucleophilic replacement of bromine with chlorine in hexyl bromide under phase-transfer catalysis (PTC) conditions in a solid ionophore liquid system:[1-3]

$$n\text{-}C_6H_{13}Br + MCl \underset{}{\overset{QX}{\rightleftharpoons}} n\text{-}C_6H_{13}Cl + MBr$$

A considerable effect of the kinetics of the process has been shown to result from a preliminary solid salt activation.[1] After activation of the ionophore, the kinetics of the process obey the laws of a pseudo-first-order reaction with respect to the alkyl halide and exhibits a variable order with respect to both the catalyst and the ionophore.[3] This paper deals with the effect of the MCl ionophore, where M = Li, Na, K, Rb or Cs, on the rate and activation parameters of the nucleophilic substitution.

EXPERIMENTAL

The quality of the reagents and the methods used for the kinetic studies, product analysis and constant calculations have been described elsewhere.[3]

The reaction was carried out in the temperature range 60–106 °C with solid salts such as LiCl, NaCl, KCl, RbCl and CsCl. The dry, solid alkali metal chlorides (0·05–0·071 mm fractions) were preactivated by crushing against the glass reactor walls just prior to the experiments.[1] The phase-transfer catalyst used was Bu_4NBr (m.p. 118–119 °C). The MCl/RBr molar ratio was 7. The kinetic curves for all the experiments were identical and consistent with a reversible pseudo-first-order reaction. The values of the observed constants ($k_{for.}$, $k_{rev.}$ and $K_{eq.}$), are listed in Table 1.

The thermal effect of the reaction

$$RBr_l + MCl_s = RCl_l + MBr_s$$

was calculated by different methods as follows.

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0894–3230/91/060341–05$05.00

Received 31 May 199
Revised 12 November 199

Table 1. Effect of the nature of the solid ionophore and temperature on the rate and equilibrium constants in the bromine–chlorine substitution reaction in hexyl bromide[a]

Salt	Temperature (°C)	$K_{eq.}$	$k_{for} \cdot 10^5$ (s^{-1})	$k_{rev} \cdot 10^5$ (s^{-1})
LiCl	70	0·064	0·28	4·37
	76	0·057	0·38	6·68
	84	0·125	1·44	11·51
	94	0·084	0·8	9·54
	106	0·08	0·61	7·66
NaCl	61	0·351	0·167	0·476
	70	0·451	0·645	1·43
	84	0·43	2·87	6·68
	94	0·36	3·58	8·52
	106	0·36	3·26	9·07
KCl	66	1·08	2·1	1·95
	84	3·22	7·46	2·3
	106·5	3·19	9·25	2·9
KCl[b]	62	0·92	0·8	0·87
	69	1·63	1·72	1·05
	77·5	2·75	3·4	1·24
	89	3·5	4·3	1·23
	104·5	3·86	5·2	1·34
RbCl	61	2·57	2·11	0·82
	70	3·48	4·4	1·27
	84	2·9	10·04	3·46
	94	2·2	18·4	8·36
	100	2·14	19·04	8·92
	106	1·94	39·56	19·37
CsCl	61	5·67	2·32	0·41
	70	5·39	4·61	0·86
	84	2·74	9·32	3·58
	96	3·58	34·8	9·71
	106	3·17	58·2	17·10

[a] Toluene, $[RBr]_0 = 0{\cdot}9–1$ M, $[Bu_4NBr]_0 = 0{\cdot}04$ M, MCl = 0·17 mol, MCl/RBr = 7.
[b] $[Bu_4NBr] = 0{\cdot}02$ M.

Method A. From the thermodynamic cycle:

$$RBr_l = RBr_g + Q_p^I$$
$$Q_p^I = -8{\cdot}99 \text{ kcal mol}^{-1} \text{ (1 kcal} = 4{\cdot}184 \text{ kJ)}$$
$$RBr_g = R^{\cdot} + Br^{\cdot} + Q_p^{II}$$
$$Q_p^{II} = -66{\cdot}4 \text{ kcal mol}^{-1} \text{ (Ref 4) } (R = C_5H_{11}{}^*)$$
$$Br^{\cdot} + e^- = Br^- + Q_p^{III}$$
$$Q_p^{III} = 77{\cdot}7 \text{ kcal mol}^{-1} \text{ (Ref. 4)}$$
$$MCl_{cryst.latt.} = M^+ + Cl^- + Q_p^{IV}$$
$$Cl^- = Cl^{\cdot} + e^- + Q_p^V$$
$$Q_p^V = -83{\cdot}25 \text{ kcal mol}^{-1} \text{ (Ref. 4)}$$
$$M^+ + Br^- = MBr_{cryst.latt.} + Q_p^{VI}$$
$$R^{\cdot} + Cl^{\cdot} = RCl_g + Q_p^{VII}$$
$$Q_p^{VII} = 79{\cdot}7 \text{ kcal mol}^{-1} \text{ (Ref 4) } (R = C_5H_{11}{}^*)$$
$$RCl_g = RCl_l + Q_p^{VIII}$$
$$Q_p^{VIII} = 8{\cdot}27 \text{ kcal mol}^{-1}$$

The energies of the crystalline MCl and MBr lattices have been reported elsewhere.[5] The Q_p^I and Q_p^{VIII} values were calculated by Trouton's rule ($\Delta H_{ev} = T_{boil.} \Delta S_{ev.}$). The thermal effect of the reaction was taken to be equal to the algebraic sum of those for all the stages of the $Q_p = \Sigma Q_p^i$ cycle.

Method B. From the difference between the enthalpies of formation of the starting reagents and the final products. The heat of formation of RCl, were $R = C_5H_{11}$,* is $-50{\cdot}9$ kcal mol^{-1} and that of RBr, where $R = C_5H_{11}$,* is $-40{\cdot}68$ kcal mol^{-1}.[6] Published ΔH values for the formation of MCl and MBr were taken;[6] $Q_p = (\Delta H_{RCl} + \Delta H_{MBr}) - (\Delta H_{RBr} + \Delta H_{MCl})$.

Method C. From the difference between the observed activation energies for the forward and reverse reactions in the temperature range 80–106 °C. The calculated results are given in Table 2.

Table 2. Effect of the nature of the solid ionophore on the thermal behaviour of the reaction $MCl + RBr \rightleftharpoons MBr + RCl + Q_p$

	Crystal lattice energy (kcal mol^{-1})		Enthalpy of formation (kcal mol^{-1})		Thermal effect, Q_p (kcal mol^{-1})		
M	ΔH_{MCl}	ΔH_{MBr}	$-\Delta H_{MCl}$	$-\Delta H_{MBr}$	Method A	Method B	Method C
Li	205·66	195·48	97·6	83·9	−3·15	−3·48	−2·85
Na	188·12	179·66	98·3	86·3	−1·43	−1·78	−0·87
K	171·32	164·56	104·3	94·0	+0·28	+0·08	+0·80
Rb	165·3	159·15	104·0	94·4	+0·88	+0·62	+1·80
Cs	159·42	154·16	105·7	96·9	+1·70	+1·42	+2·10

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*We took Q_p for $C_5H_{11}Hal$ because Q_p for $C_6H_{13}Hal$ is unknown.

RESULTS AND DISCUSSION

Analysis of previously reported kinetic data[1-3] was instrumental in selecting a feasible scheme of bromine–chlorine substitution in alkyl halides (RBr) in the presence of a solid ionophore and a phase-transfer catalyst (QBr). According to Scheme 1, proposed elsewhere,[7] the process runs through the formation of the ternary complex (TC1) incorporating a substrate and a catalyst and also through a surface-coordinated solid ionophore. The equilibrium nature of the process under study has made it possible to obtain a kinetic equation for the observed reaction rate constant[3]:

$$k_{\mathrm{for}} = \frac{k_+ K_{\mathrm{TC1}}[\mathrm{KCl}]_0[\mathrm{QBr}]_0}{1 + K_{\mathrm{TC1}}[\mathrm{RBr}]_0([\mathrm{KCl}]_0 + [\mathrm{QBr}]_0)} \qquad (1)$$

where $[\mathrm{KCl}]_0$ is the concentration of the ionophore molecules in the starting reaction mixture, equal to the ratio of the number of salt molecules on the solid phase surface to the organic phase volume; $k_{\mathrm{for.}}$ is the observed pseudo-first-order reaction rate constant for the process $\mathrm{RBr} \rightarrow \mathrm{RCl}$; K_{TC1} is the equilibrium constant of TC1 formation; k_+ is the rate constant for TC1 decomposition.

The complex dependence of $k_{\mathrm{for.}}$ on the parameters of the starting mixture and constants of the individual process stages is responsible for the non-linear nature of the Arrhenius-type plots, observed for the reactions involving the various solid MCl species such as LiCl, NaCl, KCl, RbCl and CsCl (Figure 1). The values of the observed activation energy (K_{obs}) calculated for high and low temperatures are presented in Table 3.

It is evident from Figure 1 that the saddle point on the Arrhenius-type plot corresponds to *ca* 80–84 °C. Using the published value of K_{TC1} and $[\mathrm{KCl}]_0$,[7] we calculated a numerical value of the denominator in equation (1) and found that $K_{\mathrm{TC1}}[\mathrm{RBr}]_0([\mathrm{KCl}]_0 + [\mathrm{QBr}]_0) \approx 1$. Changes in the numerical value of K_{TC1} and reagent concentration can affect not only the denominator but also the form and physical meaning of equation (1). Thus, for example, the E_{obs} value may vary with temperature as a result of large K_{TC1} changes with temperature variations. In the low-temperature region, if

$$K_{\mathrm{TC1}}[\mathrm{RBr}]_0([\mathrm{KCl}]_0 + [\mathrm{QBr}]_0) \gg 1,$$

$$k_{\mathrm{for.}} = \frac{k_+[\mathrm{KCl}]_0[\mathrm{QBr}]_0}{[\mathrm{RBr}]_0([\mathrm{KCl}]_0 + [\mathrm{QBr}]_0)} \qquad (2)$$

$$\mathrm{KCl} + \mathrm{QBr} \underset{K_1}{\overset{K}{\rightleftharpoons}} \mathrm{D1} \qquad \mathrm{D1} = \boxed{\mathrm{KCl}\cdot\mathrm{QBr}}$$

$$\mathrm{D1} + \mathrm{RBr} \rightleftharpoons \mathrm{TC1} \qquad \mathrm{TC1} = \boxed{\mathrm{KCl}\cdot\mathrm{QBr}\cdot\mathrm{RBr}}$$

$$\mathrm{TC1} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{RCl} + \mathrm{D2} \qquad \mathrm{D2} = \boxed{\mathrm{KBr}\cdot\mathrm{QBr}}$$

$$\mathrm{D2} \rightleftharpoons \mathrm{KBr} + \mathrm{QBr}$$

$$K_{\mathrm{TC1}} = KK_1$$

Scheme 1

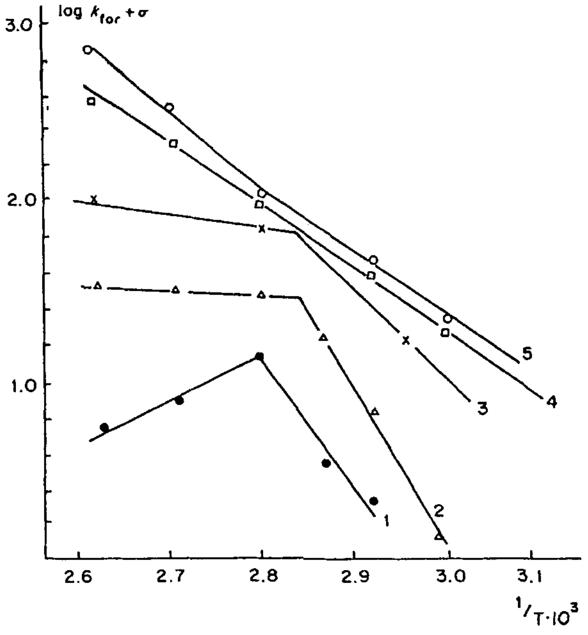

Figure 1. Changes in log $k_{\mathrm{for.}}$ with respect to temperature and nature of the solid ionophore (MCl): 1 = LiCl; 2 = NaCl; 3 = KCl; 4 = RbCl; 5 = CsCl

According to equation (2), the E_{obs} value in the low-temperature region corresponds to the activation energy for TC1 decomposition (E_+). With increasing temperature the K_{TC1} value is expected to decrease so that $K_{\mathrm{TC1}}[\mathrm{RBr}]_0([\mathrm{KCl}]_0 + [\mathrm{QBr}]_0) \ll 1$. Then in the high-temperature region

$$k_{\mathrm{for.}} = k_+ K_{\mathrm{TC1}}[\mathrm{KCl}]_0[\mathrm{QBr}]_0 \qquad (3)$$

Hence in this region E_{obs} is equal to the sum of the enthalpies of formation of TC1 (ΔH_{TC1}) and the activation energy for TC1 decomposition $E_{\mathrm{obs}} = \Delta H_{\mathrm{TC1}} + E_+$.

Estimating ΔH_{TC1} as a difference between the E_{obs} values in the low- and high-temperature regions for the various solid salts (Table 3) indicates that the enthalpy of TC1 formation increases in the order LiCl < NaCl < KCl < RbCl < CsCl.

It should be borne in mind that ΔH_{TC1} is a composite parameter and, according to the published scheme,[7] incorporates the enthalpy of formation of the binary complex (MCl·QBr) and that of the ternary complex proper (QBr·RBr·MCl). For LiCl, NaCl and KCl the TC1 species is formed exothermally, for RbCl ΔH_{TC1} is equal to zero and for CsCl it is positive.

Table 3. Observed activation energies (E_{obs}) at low and high temperature, enthalpy of TC formation (ΔH_{TC}) and energies of its decomposition (E^{*}) as a function of the nature of the ionophore

	E_{obs} (kcal mol^{-1})			
Salt reaction	Low temperature	High temperature	$E^{*}_{\pm}$ (kcal mol^{-1})	ΔH_{TC} (kcal mol^{-1})
LiCl Forward	30·4	−8·55	30·4	−38·95
NaCl	26·5	+2·5	26·5	−24·0
KCl	17·6	5·9	17·6	−11·7
RbCl	14·9	14·9	14·9	0·0
CsCl	13·9	19·9	13·9	6·0
LiBr Reverse	17·1	−5·7	17·1	−22·8
NaBr	24·8	1·63	24·8	−22·17
KBr	6·7	6·7	6·7	0·0
RbBr	16·7	16·7	16·7	0·0
CsBr	22·0	22·0	22·0	0·0

Analysis of the dependence of $k_{for.}$ on $[QBr]_0$ and $[RBr]_0$[7] for KCl gave $K_{TC1} = 20{\cdot}48$ mol^{2}l^{-2} at 84 °C. Estimating the entropy of TC1 formation by the equation $-RT \ln K_{TC1} = \Delta H_{TC1} - T\Delta S_{TC1}$ for KCl · RBr · QBr indicates that TC1 represents a strongly ordered species ($\Delta S_{TC1} = -26{\cdot}8$ e.u.).

E_{obs} for the process, determined for low temperatures and corresponding to E_{+}, depends linearly on the crystalline MCl lattice energy (Figure 2) and decreases in the order LiCl > NaCl > KCl > RbCl > CsCl. This points to the participation of the solid salt molecules in the transition state.

Although there are no data on the effect of KBr, QBr and RCl concentrations on the specific rate of the reverse reaction, it can be assumed that such a reaction also passes through a similar ternary complex QBr · RCl · MBr (TC2) and is described by the kinetic equation

$$k_{rev.} = \frac{k_{-}K_{TC2}[KBr]_0[QBr]_0}{1 + K_{TC2}[RCl]_0([KBr]_0 + [QBr]_0)} \tag{4}$$

where K_{TC2} is the equilibrium constant for TC2 formation and k_{-} is the rate constant for TC2 decomposition. The reverse process also displays non-linearity of the Arrhenius-type plots for the lithium and sodium salts.

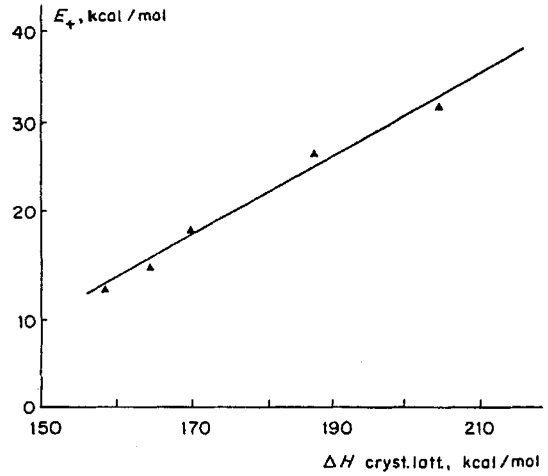

Figure 2. E_{+} as a function of crystalline lattice energy ($\Delta H_{cr.lat.}$) for MCl

Analysis (see Table 3) of the $k_{rev.}$–temperature dependence allows E_{-} and ΔH_{TC2} to be estimated.

If the energy of the initial and final state terms in the substitution reaction is calculated as the sum of the heats of formation of the starting and final products, respectively (see Table 2), then, knowing ΔH_{TC1} and E_{+}, one can estimate the energy of the saddle point. However, a correlation of these terms for LiCl indicates that the activation enthalpy is lower than the energy of the final substitution products term. This suggests directly that the reaction rate gives rise to one more kinetically independent state represented by TC2.

Consequently, the system includes the two ternary complexes QBr · RBr · MCl (TC1) and QBr · RCl · MBr (TC2) the transition between them occurring through a potential barrier controlling the rates of both the forward and reverse processes. The substitution seems to take place as follows:

$$RBr + MCl + QBr \xrightleftharpoons{K_{TC1}} TC1 \xrightleftharpoons[k_{-}]{k_{+}}$$
$$\xrightleftharpoons{K_{TC2}} RCl + MBr + QBr$$

The data obtained suggest that the substitution involves a limiting stage. Therefore, the kinetic equations (1) and (4) do not have constants for the stages that follow the limiting stage.

Because the process under study is equilibrated,[3] the direction of the mutual transitions between the complexes will depend on the MCl – MBr and RBr – RCl bond strength differences. Table 2 lists the results of thermodynamic calculations for the reaction

$$\mathrm{MCl} + \mathrm{RBr} \rightleftharpoons \mathrm{MBr} + \mathrm{RCl} + Q_P$$

with participation of the various MCl species. The main contribution to the thermal effect of the substitution (Q_P) is due to the difference between the energies of MBr and MCl formation. It can be clearly seen that when passing from LiCl and NaCl to KCl, RbCl and CsCl, there will be a change in both the magnitude and the sign of the Q_P values.

The thermal effect of the substitution was also estimated from the experimental data by correlating the E_{obs} values for the forward and reverse processes in the high-temperature regions. The resulting Q_P values correlate well with the thermal effects calculated by using methods A and B (see Table 2). This corroborates the validity of our assumptions on the occurrence of the reverse process and the correctness of equation (4).

Hence the nature of the ionophore has a considerable effect on the activation and thermodynamic properties of the nucleophilic substitution parameters under PTC conditions in the solid–liquid system. This can be clearly seen in Figure 3, which shows the potential energy changes in the system throughout the reaction. In compliance with the Bell–Evans–Polyani principle, the loosening of the MCl bond, on passing from Li to Cs salts, results in a decrease in the activation energy. Moreover, the potential barrier for the forward reaction, for virtually all the salts, is higher than that for the reverse reaction, which is due to the fact that the breaking bond is stronger than the resulting bond.

Analysis of the transition between TC1 and TC2 suggests that such a transition will take place inside the cyclic transition state. Therefore, the ternary complexes (TC1 and TC2) can be treated as occupying the extreme positions of a six-membered cycle when moving along the reaction coordinate. The transition state appears to be a six-membered cycle with a delocalized electronic system. In addition, it should be pointed out that TC1 and TC2 are thermodynamically stable intermediates.

Hence it can be stated that nucleophilic substitution involving a solid ionophore proceeds by a scheme including the formation of ternary complexes QBr·RBr·MCl and QBr·RCl·MBr coordinated on the solid-phase surface. Overall these kinetic data provide support for the theory that the transition state of the reaction incorporates a solid ionophore leading to an influence of the solid salt on the activation and thermodynamic substitution parameters.

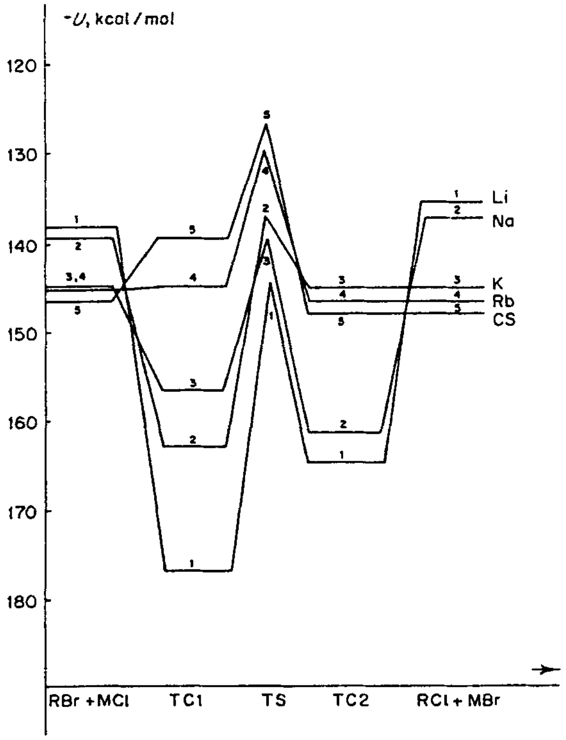

Figure 3. Changes in the potential energy of the system during the reaction $\mathrm{MCl} + \mathrm{RBr} \rightleftharpoons \mathrm{MBr} + \mathrm{RCl} + Q_P$ in the presence of various salts: 1 = LiCl; 2 = NaCl; 3 = KCl; 4 = RbCl; 5 = CsCl

REFERENCES

1. O. I. Danilova, I. A. Esikova and S. S. Yufit, *Izv. Akad. Nauk SSSR, Ser. Khim.* **11**, 2422 (1986).
2. O. I. Danilova, I. A. Esikova and S. S. Yufit, *Izv. Akad. Nauk SSSR, Ser. Khim.* **2**, 314 (1988).
3. I. A. Esikova and S. S. Yufit, *Izv. Akad. Nauk SSSR, Ser. Khim.* **7**, 1520 (1988).
4. V. N. Kondrayev (Ed.), *The Breaking Energy of Chemical Bonds, Ionization Potentials and Electron Affinity*, Nauka, Moscow (1974).
5. *The Thermodynamic Properties of Individual Substances*, Nauka, Moscow, Vol. I (1978); Vol. IV (1982).
6. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, New York (1970).
7. I. A. Esikova and S. S. Yufit, *J. Phys. Org. Chem.* **4**, 336–340 (1991).