Kinetics of the Synthesis of 1-Alkyl-3methylimidazolium Ionic Liquids in Dilute and Concentrated Solutions

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> ABSTRACT: The kinetics of the reactions of 1-methylimidazole with iodoethane, 1-iodobutane, 1-bromobutane, 1-bromohexane, 1-bromooctane resulting in the formation of corresponding 1-alkyl-3-methylimidazolium halide ionic liquids in acetonitrile and cyclopentanone solutions has been studied in a wide range of concentrations and degrees of conversion. The studied reactions were found to follow the $S_N 2$ rate law in the dilute solutions. The significant deviations from the simple S_N^2 rate law observed at higher concentrations of the reactants were assigned to the concentration dependence of activity coefficients for the reactants and the transition states. The experimental data were processed with the conductor-like screening model-segment activity coefficient (COSMO-SAC) model and the Scatchard-Hildebrand equation. The latter was found to provide somewhat better description of the experimental results; however, the former has a wider predictive ability. The Arrhenius activation energies and the activation enthalpies were calculated for the investigated systems. The rate constants at infinite dilution were obtained for a large number of 1-haloalkane + 1-methylimidazole + solvent systems with the use of the COSMO-SAC model. It was demonstrated that the rate constants of the studied reactions in various non-hydrogen-bonding solvents can be estimated from a correlation with the Hildebrand solubility parameter. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 1-9, 2013

INTRODUCTION

Room temperature ionic liquids (ILs) are salts with melting temperatures below T = 373 K [1]. Physico-

chemical properties of these liquids can be easily tailored by changing their structure: nature of the cations and the anions or the alkyl substituents in the cations, and it is possible to find IL possessing the required characteristics. A large number of potential applications of these compounds both in science and technology are considered nowadays [2].

Imidazolium ILs are among the most studied compounds of this class. They can be synthesized by

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quaternization of 1-methylimidazole (MeIm) with esters, such as diakyl sulfates, carbonates, and methyl triflate. However, in most cases imidazolium ILs are obtained in two stages through corresponding halides: and Scurto [10] obtained kinetic characteristics of the reaction between HexBr and MeIm in various solvents. Gro β e Böwing and Jess [11] studied homogeneous and heterogeneous reaction between



A chloride, bromide or iodide IL is obtained at the first stage (R1), and the anion is changed to the desired one at the second stage (R2). The highly exothermic stage (R1) [3,4] can be realized by either continuous or periodic methods. In the continuous method, the reactants are mixed in a microreactor and then the reaction proceeds in a flow mode [5-9]. At the beginning, the rate of the process is rather high; however, it may take a few days to achieve the degree of conversion of more than 99%. High quality of the obtained product due to the good temperature control is the advantage of this method. The second method is normally used if a small amount of ILs is required. The possibilities of scaling up for this method are limited due to problems with temperature control. These problems are partly solved if the solvent is used.

The existing methods of the synthesis should be improved for further promotion and wide usage of ILs. The quantitative description of kinetics and thermodynamics of the IL synthesis is one of important steps in this process. The reaction rate constants and activation energies as well as the enthalpies of the proceeding reactions are necessary for the development of new production units. These data can also be used for development of procedures quantifying the effect of various factors on the rate of these reactions.

In this work, the systems with a solvent were chosen for the kinetic study of the reaction (R1) with a number of haloalkanes. The solvent allowed us to keep the reaction mixture homogeneous in the course of the reaction and perform the process isothermally. Acetonitrile and cyclopentanone were used as solvents since the rate constants for the reactions between MeIm and 1bromohexane HexBr in these solvents were found to be higher than those in other conventional solvents [10].

The kinetics of the synthesis of other 1-alkyl-3-methylimidazolium ILs has been considered in a number of studies [5–13]. The kinetics of formation of 1-ethyl-3-methylimidazolium ethylsulfate $[C_2mim]EtSO_4$ was studied in [8] and [9]. Schleicher 1-chlorobutane and MeIm in the presence of ethanol and without it. Alkylation of MeIm with 1bromobutane BuBr without solvent in the temperature range 348–363 K was considered by Hu et al. [13]. The energy of activation of reaction (R1) for R = 1-butyl and Hal = Br was reported [3].

The aim of this work is to study the kinetics of the reactions between MeIm and haloalkanes including iodoethane EtI, 1-iodobutane BuI, 1-bromobutane BuBr, 1-bromohexane HexBr, and 1-bromooctane OctBr in acetonitrile and cyclopentanone media in a wide range of concentrations and degrees of conversion and to evaluate the performance of theoretical methods toward quantitative description of the observed kinetic dependences.

EXPERIMENTAL

Commercial samples of MeIm (99%; Fluka, Switzerland), BuBr (99%; Acros Organics, Belgium), and acetonitrile (>99.99%; Khimmed, Russia) were used without further purification. Commercial samples of EtI (99%; Sigma-Aldrich, Germany), BuI (98%; Fluka), HexBr (pure grade; Reakhim, Russia), and OctBr (pure grade; Reakhim) were washed with the solutions of Na₂S₂O₃ and NaCl, then dried over P₂O₅ and distilled. Cyclopentanone (pure grade; Reakhim) was dried over K₂CO₃ and distilled twice. The mixtures of 1-butyl-3-methylimidazolium halides [C₄mim]Hal with MeIm were obtained by mixing BuHal and the 1.1 to 1.2-fold excess of MeIm and keeping the solution at T = 338 K for 8 h.

A 4–25 cm³ amount of acetonitrile or cyclopentanone and 0.5–15 cm³ of RHal were mixed in a roundbottomed flask. The amount of RHal was adjusted in such a way as to get its initial concentration within $0.3-3.6 \text{ mol} \cdot \text{dm}^{-3}$. The flask was thermostated within ± 0.1 K for 30 min in a liquid thermostat. 0.3–4.0 mL of MeIm or MeIm + IL solution in a syringe was thermostated within ± 2 K in an air thermostat for 30 min. The amount of MeIm was adjusted to get its initial concentration in the range $0.3-3.6 \text{ mol} \cdot \text{dm}^{-3}$. After that, MeIm or MeIm + IL solution was introduced into the flask held in the liquid thermostat. During the experiment, the reaction mixture was continuously stirred. Periodically, samples of 0.2-5.0 cm³ volume were taken and immediately poured into cold water to stop the reaction. The amount of MeIm in the samples was determined by titration with a 0.1 mol \cdot dm⁻³ acid solution. The equivalent point was found potentiometrically using a glass electrode. The uncertainty of the titration was evaluated from the titration of MeIm aqueous solutions to be $\pm 0.3\%$. All the reported uncertainties correspond to the confidence interval of 95%.

The amounts and concentrations of components in the solutions were calculated from the mass of the components determined with the maximum error of $\pm 5 \times 10^{-4}$ g. Based on the experimental data, the amount of substances at the initial points and at the time of sampling was calculated. The volume of the solutions was assumed to be equal to the sum of volumes of pure components. In the calculations, the molar volumes of molecular liquids [14] were used. The molar volume of 1-ethyl-3-methylimidazolium iodide [C₂mim]I was found from the linear extrapolation of the molar volumes of $[C_n \min]I$ (n = 4, 6,8) [15] to n = 2. The molar volumes of 1-alkyl-3methylimidazolium bromides $[C_4 mim]Br, [C_6 mim]Br,$ and $[C_8 mim]$ Br were found from the molar volume of [C₃mim]Br [16] increased by the contribution to the molar volume per the CH2 group evaluated from the recommended data for 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides $[C_n mim]NTf_2$ (n = 2, 4, 6, 8 [14].

In the conductor-like screening model-segment activity coefficient (COSMO-SAC) [17], properties of molecules or ions in solution are found from the results of quantum mechanical COSMO calculations. The activity coefficients are determined by molecular surface interactions, which are supposed to be dominated by local electrostatic interactions. Surface charge distribution in the species is characterized by their hydrogen-bonding σ^{hb} profiles and nonhydrogen-bonding σ^{nhb} profiles. In the COSMO calculations, the GAMESS (US) quantum chemistry package (version 24, March 2007 (R1)) [18] was used. The source code of this program was modified according to Wang et al. [19]. The calculations were performed at the B3LYP/6–311G(d,p) theory level. The atomic radii [20] were used. The radii for the bromide and iodide ions were assumed to be 2.25 and 2.53 Å, respectively, which exceed their crystallographic radii of

 Table I
 Values of Parameters in COSMO-SAC (CA)

Parameter	Value
$a_{\rm eff}$ (Å ²)	7.25
$r_{\rm av}$ (Å)	0.804
$\sigma_0 (e \cdot \dot{A}^{-2})$	0.007
$r(Å^3)$	66.69
q (Å ²)	79.53
Z	10
$\alpha' (kJ \cdot mol^{-1} \cdot Å^4 \cdot e^{-2})$	84,282.5
$C_{\rm hb} (\mathrm{kJ} \cdot \mathrm{mol}^{-1} \cdot \mathrm{\AA}^4 \cdot \mathrm{e}^{-2})$	11,702.7

1.96 and 2.20 Å [21] by 15%. The solvent radius was set to 1.2 Å. The latter value was found to provide good agreement for the σ profiles obtained with GAMESS and those obtained with D-Mol3 package [19]. The most stable TT conformation was considered for BuI and the GT conformation for BuBr [22]. For HexBr, calculations for the similar GTTT conformation were carried out. These conformations were also adopted as the starting points for the transition state geometry optimizations. σ profiles for the most stable conformers of the particles and their geometries are presented in the Supporting Information. COSMO-SAC calculations for the MeIm + OctBr + acetonitrile systems were not performed since the number of surface segments in MeIm…Oct…Br particles exceeded the software limitations.

The σ profiles were generated from the GAMESS output files using the homemade software based on the program source codes provided by the Virginia Tech group [23] and equations from [20]. Each calculated σ profile was divided into non-hydrogen-bonding and hydrogen-bonding σ profile. The σ^{hb} profile was found based on the segments that belong to fluorine, oxygen, and nitrogen atoms having a nonbonding electron pair and hydrogen atoms attached to these atoms. The σ^{hb} profile was calculated as a difference between the σ and the σ^{hb} profiles. The empirical parameters used in these calculations (Table I) were obtained from the COSMO-SAC (CA) version [17,20,24].

The methods for calculation of activity coefficient used in this work provide the rational activity coefficients based on the symmetric convention of normalization $\gamma_{x,\text{sym}}$. The transformation of the activity coefficients to the asymmetric convention was performed using the equation [25]

$$\gamma_x = \frac{\gamma_{x,\text{sym}}}{\gamma_{x,\text{sym}}^\infty} \tag{1}$$

where $\gamma_{x,\text{sym}}^{\infty}$ is the activity coefficient at infinite dilution based on the symmetric convention. γ_x were

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converted into γ_c , with the use of the equation

$$\gamma_c = \frac{x \cdot \gamma_x}{V_{\rm m,sol} C} \tag{2}$$

where *C* and *x* are the concentration and the mole fraction of the solute and $V_{m,sol}$ is the molar volume of the solvent.

EXPERIMENTAL

Formal Kinetics. One would expect that the studied reactions follow the $S_N 2$ kinetics, since this mechanism is typical for similar reactions [10,26]. The differential kinetic equation for this mechanism is

$$-\frac{dn\,(\text{MeIm})}{dt} = k\frac{n\,(\text{MeIm}).n\,(\text{RHal})}{V}$$
(3)

where k is the reaction rate constant, V is the volume of the reaction mixture, and n(MeIm) and n(RHal) are the current amount of the reactants. If the volume of the mixture remains unchanged in the course of the reaction and the amount of reagents is not equal, Eq. (3) corresponds to the integral kinetic equation

$$\theta = \frac{1}{C_0 \,(\text{MeIm}) - C_0 \,(\text{RHal})} \ln \frac{C \,(\text{MeIm}) \cdot C_0 \,(\text{RHal})}{C_0 \,(\text{MeIm}) \cdot C \,(\text{RHal})}$$
$$= kt \tag{4}$$

where C_0 (MeIm), C_0 (RHal) and C(MeIm), C(RHal) are the initial and current concentrations of the reactants.

Taking into account Eq. (4), one would expect that θ versus t dependence is linear for all concentration ranges. This behavior was observed at low degrees of conversion if the concentration of the reactants was about 0.5 M in all the studied systems (Fig. 1 for the MeIm + BuI + CH₃CN system and Figs. S12, S14, S20, and S24 in the Supporting Information for other systems). However, the systematic deviations from the line occurred at higher concentrations of the reactants, in the presence of the products in the initial reaction mixture, and at high degrees of conversion. At a given moment of time, the increase in the RHal concentration leads to the decrease in the θ values and the rate of the reactions. The opposite trend was observed when the concentration of MeIm increased or the product was introduced to the initial reaction mixture.

If k varies in the course of the reaction, then θ is not equal to kt. However, if one differentiates θ with



Figure 1 Typical kinetic curves for the reaction MeIm + BuI → [C₄mim]I at T = 318.2 K in acetonitrile media: \circ , C_0 (MeIm) = 0.605 mol·dm⁻³, C_0 (BuI) = 0.626 mol·dm⁻³; \blacksquare , C_0 (MeIm) = 1.105 mol·dm⁻³, C_0 (BuI) = 0.485 mol·dm⁻³; \blacklozenge , C_0 (MeIm) = 0.550 mol·dm⁻³, C_0 (BuI) = 0.964 mol·dm⁻³; \Box , C_0 (MeIm) = 3.078 mol·dm⁻³, C_0 (BuI) = 0.555 mol·dm⁻³; \diamondsuit , C_0 (MeIm) = 0.575 mol·dm⁻³, C_0 (BuI) = 2.951 mol·dm⁻³; \bullet , C_0 (MeIm) = 0.875 mol·dm⁻³, C_0 (BuI) = 1.042 mol·dm⁻³, and C_0 ([C₄mim]I) = 1.316 mol·dm⁻³.

respect to *t* and combines the results with Eq. (3), it becomes clear that at a moment of time $k(t) = d\theta/dt$. To provide further processing of the experimental data, the experimental $\theta(t)$ points for each experiment were smoothed by a second-order polynomial and the apparent rate constants were calculated for each point.

It was found that the k(0) values for the same system could differ more than twice at different concentrations of the participants (Fig. 1 for the MeIm + BuI + CH₃CN system and Figs. S12, S14, S20, S24, and S28 in the Supporting Information). In some experiments, the apparent rate constants doubled in the course of the reaction.

Transition State Theory. For the $S_N 2$ reaction, where the reactants are uncharged but the transition state has built up a charge, the polarity of media has strong influence on the reaction rate [26]. The strong dependence *k* on the composition of the reaction mixture can be quantitatively described by changes in the activity coefficients for the reactants and the transition state in the course of the reaction. The following equation relates the apparent rate constant and the true rate



Figure 2 Typical kinetic curves for the reaction MeIm + BuI \rightarrow [C₄mim]I at T = 318.2 K in acetonitrile media after COSMO-SAC processing. For symbols, see Fig. 1.

constant k_0 :

$$k = k_0 \frac{\gamma_c \text{ (MeIm)} \cdot \gamma_c \text{ (RHal)}}{\gamma_c \text{ (MeIm} \cdots R \cdots \text{Hal)}}$$
(5)

where γ_c (MeIm) and γ_c (RHal) are the activity coefficients of the reactants and γ_c (MeIm…R…Hal) is the activity coefficient of the transition state.

Different models are used for the prediction of activity coefficients in solution. However, most of them cannot be applied to calculation of activity coefficients for the transition state because of either undeveloped computational procedures or the absence of the required empirical parameters. The two methods used in this work are free from these drawbacks. The COSMO-SAC model [17] does not use the system-specific adjustable parameters. The Scatchard– Hildebrand equation (SHE) [27] has some adjustable parameters, which, however, can be found from the obtained experimental data.

COSMO-SAC. The processing with COSMO-SAC, whose typical results are presented in Fig. 2 for the MeIm + BuI + CH₃CN system and Figs. S13, S17, S21, and S25 in the Supporting Information for the other systems, improved convergence of the curves, which are expected to coincide in the ideal case. However, at high concentrations of the reactants or high degrees of conversion the rate constants significantly deviated from the average value. The statistical characteristics of the solutions are reported in Table II. The results of this processing may be further improved by reparameterization of COSMO-SAC.

SHE. This equation, the basic equation of the theory of regular solutions [27], has the following form:

$$\ln \gamma_{i,x} = \frac{V_{m,i}}{RT} \left(\delta_i - \frac{\sum_j x_j V_{m,j} \delta_j}{\sum_k x_k V_{m,k}} \right)^2 \tag{6}$$

where *R* is the gas constant, *T* is the temperature, δ_i is the Hildebrand solubility parameter, and x_i is the mole fraction of the *i*th component. The mole fraction of the transition state was assumed to be zero. The δ_i parameters for the reactants and the solvent were calculated from the following equation:

$$\delta_i = \sqrt{\frac{\Delta_{\rm vap} H_{\rm m,i}^{\rm o} - RT}{V_{\rm m,i}}} \tag{7}$$

where $\Delta_{vap}H_{m,i}^{\circ}$ is the standard molar vaporization enthalpy of the component. In the calculations, we used the recommended values of the enthalpies of vaporization for molecular compounds [14].

The δ_i parameters for the product and the transition state were determined from the nonlinear fit of the experimental kinetic data. First, the δ_{IL} and δ_{TS} values were determined individually for each system. SHE provides better description of the obtained experimental data than COSMO-SAC (Table II) that can be explained by the presence of two adjustable parameters for each system in this approach. With individual parameters for each system, SHE can be used only for interpolation of the experimental kinetic data for the studied systems. To improve the predictive ability of this approach, we assumed that the δ_{IL} and δ_{TS} parameters for different systems are related by the following equations:

$$\delta_{\rm IL} = \delta_{\rm [C_1 mim]Hal} + (n-1) \cdot \delta_{\rm CH_2} \tag{8}$$

$$\delta_{\rm TS} = \delta_{\rm MeIm\cdots CH_3\cdots Hal} + (n-1) \cdot \delta_{\rm CH_2} \tag{9}$$

where $\delta_{[C1mim]Hal}$, $\delta_{MeIm...CH3...Hal}$, and δ_{CH2} are the Hildebrand parameters for [C₁mim]Hal, MeIm...CH₃...Hal, and CH₂ fragments, *n* is the number of carbon atoms in RHal. Equations (8) and (9) allow one to use only three adjustable parameters for description of the kinetics of all the studied systems as well as the systems with other bromo- and iodoalkanes. The following parameters were found to provide the best description of the experimental data: $\delta_{MeIm...CH3...Hal} = 24.1 \text{ MPa}^{1/2}$, $\delta_{[C1mim]Hal} =$ 28.4 MPa^{1/2}, and $\delta_{CH2} = -0.38 \text{ MPa}^{1/2}$.

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RHal	EtI	BuI	BuI	BuBr	HexBr	OctBr
Solvent	Acetonitrile	Acetonitrile	Cyclopentanone	Acetonitrile	Acetonitrile	Acetonitrile
<i>T</i> (K)	318.6	318.2	318.6	328.4	328.4	328.2
Experimental data						
$k (\times 10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1})$	30.7 ± 1.7	12.0 ± 0.5	13.1 ± 1.0	8.9 ± 0.5	6.8 ± 0.6	5.9 ± 0.6
RMS (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	6.0	2.8	3.8	2.9	2.1	1.9
ME (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	13.0	7.1	7.9	10.1	4.3	3.1
COSMO-SAC						
$k_0 (\times 10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1})$	28.8 ± 1.5	10.6 ± 0.2	8.2 ± 0.4	7.2 ± 0.2	6.9 ± 0.3	_
RMS (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	5.3	0.9	1.3	1.5	1.1	_
$ME (\times 10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1})$	13.0	3.2	2.6	6.8	2.3	_
SHE						
Individual parameters for each	system					
$\delta_{\rm IL}$ (MPa ^{1/2})	31.3	26.3	24.4	29.5	26.9	23.9
$\delta_{\rm TS}~({\rm MPa}^{1/2})$	23.6	22.8	24.3	22.4	22.1	21.7
$k_0 \ (\times \ 10^5 \ \mathrm{dm}^{-3} \cdot \mathrm{mol} \cdot \mathrm{s}^{-1})$	26.2 ± 0.7	10.0 ± 0.1	10.5 ± 0.2	6.7 ± 0.1	7.0 ± 0.1	6.7 ± 0.1
RMS (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	2.5	0.5	0.7	0.6	0.2	0.2
ME (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	6.1	1.3	1.5	2.5	0.4	0.5
General parameters						
$k_0 (\times 10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1})$	27.3 ± 0.8	9.8 ± 0.1	10.8 ± 0.4	7.3 ± 0.1	7.2 ± 0.1	6.4 ± 0.1
RMS (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	2.6	0.7	1.4	0.7	0.3	0.4
ME (× $10^5 \text{ dm}^{-3} \cdot \text{mol} \cdot \text{s}^{-1}$)	4.9	2.2	3.1	2.1	0.6	0.9

Table II Results of Experimental Data Processing with COSMO-SAC and SHE

The δ values for $[C_n \text{mim}]$ Hal ILs determined in both case and δ_{CH2} value are close to the values for $[C_n \text{mim}]$ NTf₂ and $[C_n \text{mim}]$ PF₆ (n = 2,4,6,8), which were determined by the intrinsic viscosity method [28]. This fact can be used for estimation of the δ values for other 1-alkyl-3-methylimidazolium ILs. It should also be mentioned that the δ values for reagents, transition state, and products are consistent with overall characteristic of the S_N2 reaction with uncharged reactant and ionic product [26] since the δ values for the transition state are lower than those for products and higher than those for reactants.

It is seen from the results presented in Table II that statistical characteristics of the solution with three adjustable parameters are similar to those obtained for individual processing of each system, whereas the predictive ability of the former is higher. The kinetic curves after processing with SHE are demonstrated in Figs. 3 and 4 for the MeIm + BuI + CH_3CN system and in the Supporting Information for other systems.

Temperature Dependence of Rate Constants. A series of experiments at different temperatures with the initial reagent concentration of 0.3–0.6 mol·dm⁻³ was carried out for each system. The temperature dependence of the rate constant in dilute solution, k was described by the Arrhenius equation:

$$\ln k = -\frac{E_A}{RT} + A \tag{10}$$



Figure 3 Typical kinetic curves for the reaction MeIm + BuI \rightarrow [C₄mim]I at T = 318.2 K in acetonitrile media after SHE processing with individual parameters. For symbols, see Fig. 1.

where A is the preexponential factor and E_A is the energy of activation in the dilute solution. The obtained E_A values (Table III) are in good agreement with the values obtained for similar systems with the solvent [10] and without it [3,10].

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RHal	Solvent	Temperature Range (K)	$E_{\rm A}$ (kJ·mol ⁻¹)	$\Delta^{\ddagger} H^{\circ}_{\text{COSMO-SAC}} \text{ (kJ-mol}^{-1})$	$\Delta^{\ddagger} H^{\circ}_{\text{SHE}} \text{ (kJ·mol}^{-1}\text{)}$
EtI	Acetonitrile	308-338	76 ± 4	72 ± 2	69 ± 1
BuI	Acetonitrile	298-338	70 ± 1	67 ± 1	67 ± 1
BuI	Cyclopentanone	308-338	67 ± 3	64 ± 1	64 ± 3
BuBr	Acetonitrile	321-343	72 ± 3	68 ± 2	65 ± 1
HexBr	Acetonitrile	321-343	72 ± 2	69 ± 2	66 ± 1
HexBr ^a	Acetonitrile	298-333	70 ± 3	68 ± 3	69 ± 3
OctBr	Acetonitrile	321-343	70 ± 1	_	68 ± 1

 Table III
 Activation Energy and Enthalpies of Activation for Different Systems

^aActivation parameters were calculated using the data from [10].



Figure 4 Typical kinetic curves for the reaction MeIm + BuI \rightarrow [C₄mim]I at T = 318.2 K in acetonitrile media after SHE processing with general parameters. For symbols, see Fig. 1.

According to the transition-state theory, the k_0 rate constant for a bimolecular reaction is related to the standard entropy of activation $\Delta^{\ddagger}S^{\circ}$ and the standard

enthalpy of activation $\Delta^{\ddagger} H^{\circ}$ by the equation

$$k_0 = \chi \frac{k_{\rm B}T}{h} \exp\left(\frac{\Delta^{\ddagger} S^{\circ}}{R}\right) \exp\left(-\frac{\Delta^{\ddagger} H^{\circ}}{RT}\right) \quad (11)$$

where χ is the transmission coefficient, $k_{\rm B}$ is the Boltzmann constant, and *h* is the Planck constant. The enthalpy of activation can be found from a slope of a line obtained from the experimental results in the $\ln(k_0 \cdot T^{-1})$ against T^{-1} coordinates. The $\delta_{\rm IL}$ and $\delta_{\rm TS}$ parameters were assumed to be independent of temperature. The values of $\Delta^{\ddagger}H^{\circ}$ for the same system found using both COSMO-SAC and SHE agreed within the uncertainties of their determination (Table III). The enthalpy of activation obtained for the HexBr + MeIm + acetonitrile system is in a good agreement with the previously reported value [10].

Rate Constants in Different Solvents. Both COSMO-SAC and SHE can be used to calculate the rate constants at different concentrations. However, if one needs to obtain the rate constants in an arbitrary solvent, COSMO-SAC should be used. To do this, only one experiment, preferably in dilute solutions, is required to evaluate k_0 , which will then be used to calculate the apparent rate constants at different concentrations:



RHal	Solvent	$k_{\text{dilute}} (\times 10^5 \text{ dm}^3 \cdot \text{mol} \cdot \text{s}^{-1})$	$k_0(\text{COSMO}) (\times 10^5 \text{ dm}^3 \cdot \text{mol} \cdot \text{s}^{-1})$
EtI	Acetonitrile	57.6 ± 3.0	55.2 ± 2.2
BuI	Acetonitrile	23.4 ± 1.0	22.6 ± 0.4
BuI	Cyclopentanone	24.0 ± 1.5	19.6 ± 0.3
BuBr	Acetonitrile	6.26 ± 0.19	6.01 ± 0.12
HexBr	Acetonitrile	7.47 ± 0.80	7.40 ± 0.79^{a}
HexBr	Acetonitrile	6.79 ± 0.19	6.40 ± 0.07
HexBr	Dimethyl sulfoxide	22.9 ± 1.7	$22.6 \pm 1.7 \ ^{a}$
HexBr	Cyclopentanone	5.30 ± 0.45	$4.69 \pm 0.40^{\ a}$
HexBr	Acetone	4.34 ± 0.39	$4.12\pm0.37~^{a}$
HexBr	2-Butanone	3.73 ± 0.54	3.40 ± 0.49^{a}
HexBr	Ethyl lactate	1.28 ± 0.13	1.30 ± 0.13 ^{<i>a</i>}
HexBr	Methanol	1.05 ± 0.18	1.06 ± 0.18 a
HexBr	Dichloromethane	2.80 ± 0.21	$4.03 \pm 0.31 \ ^{a}$
HexBr	Ethyl formate	3.42 ± 0.32	3.46 ± 0.32^{a}

Table IV Rate Constant for Different Systems at T = 328.2 K Obtained with COSMO-SAC

^aCalculated using the data from [10].

The values of rate constant in dilute solution (k_{dilute}) and k_0 obtained for different systems in this work and those from [10] and adjusted to a common temperature of 328.2 K are presented in Table IV. The k_0 rate constants for the HexBr + MeIm + acetonitrile system obtained in this work and in [10] agree very well. A good agreement between k_0 and k_{dilute} is observed for most systems. However, k_0 should be used instead of of k_{dilute} for theoretical analysis.

As expected, the iodides react more rapidly than the bromides, because iodide is a better leaving group than bromide due to its lower basicity. The increase in the alkyl chain from EtI to BuI significantly affects the rate constant, but only minor differences are observed for the BuBr–HexBr–OctBr series. This fact can be explained if one considers two circumstances. The alkyl group is an electron-releasing group (+I effect), which directly affects reactivity of RHal. The +I effect increases with the size of the alkyl group. At the same time, the inductive effect rapidly dies out and is significant only at short distances. As a result, changes in the inductive effect in the pair Et-Bu are more pronounced than in the Bu to Oct series.

The k_0 (acetonitrile)/ k_0 (cyclopentanone) quotient is very close for the systems with BuI and HexBr where it is available (Table IV). The constancy of these quotients for the reactions with similar transition states may be useful for the estimation of the rate constants in various solvents. The data from Table IV, which contains the information on the reactions with different RHals in acetonitrile and for the reaction with HexBr in various solvents, can be used for this purpose.

Stefani [29] demonstrated that the rate constant for the Menshutkin reaction correlates with the Hildebrand



Figure 5 Correlation of rate constants in dilute solutions with solvent Hildebrand parameters for the reaction MeIm + HexBr \rightarrow [C₆mim]Br at T = 328.2 K.

solubility parameters for the solvent. The linear dependence in the ln k versus δ coordinates was found for the non-hydrogen-bonding solvents. To check applicability of this correlation to the reactions studied in this work, we used the k_{dilute} rate constants for the HexBr + MeIm system from Table IV. The δ parameters for the solvents except methanol and ethyl lactate were calculated from the recommended data [14]. One can see (Fig. 5) that this correlation works satisfactory for the studied system, and the dependence is described by the equation

$$\ln \left(k_{\text{dilute}} \cdot 10^{5} / \text{dm}^{3} \cdot \text{mol} \cdot \text{s}^{-1} \right)$$

= -2.785 + 0.220 (\delta / MPa^{1/2}) (12)

CONCLUSIONS

Experimental investigation of kinetics of quaternization of MeIm with different RHals demonstrated that this reaction follows the expected S_N2 kinetic rate law only in the dilute solutions. Deviations from the simple dependence are caused by changes in the activity coefficients of the reactants and the transition state. It was demonstrated that both the COSMO-SAC model and SHE can be used for the description of the kinetic results over the whole studied range of concentrations. Moreover, these approaches allowed estimating the rate constants at any concentration of reagents and products. SHE provides better description of the experimental data but uses adjustable parameters. The COSMO-SAC model also performs satisfactorily and does not need system-specific adjustable parameters thus demonstrating wider predictive ability. The rate constants at infinite dilution were obtained for a large number of haloalkane + 1-methylimidazole + solvent systems with the use of the COSMO-SAC model.

SUPPORTING INFORMATION

 $\sigma^{\rm hb}$ and $\sigma^{\rm nhb}$ profiles for the studied species (Figs. S1–S11), optimized geometries of species for GAMESS/COSMO calculations, tables of experimental kinetic data (Tables S1–S6), and typical kinetics curves (Figs. S12–S30) are available as the Supporting Information.

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