Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 725–730. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 791–796.
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Influence of the Kind of the Halogen on Solvation Effects in Hydrolysis of 2-Methylbenzenesulfonyl Chloride and Bromide in Water-Rich H_2O–Dioxane Mixtures

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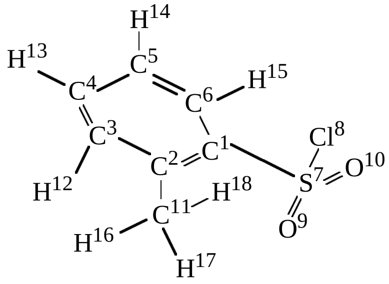
Received May 7, 2002

Abstract—The structural and energy parameters of 2-methylbenzenesulfonyl chloride and bromide were calculated by *ab initio* (B3LYP/6-311G**) and semiempirical (PM3) methods and were correlated with the kinetic parameters of hydrolysis of these compounds in aqueous dioxane (mole fraction of dioxane X_2 0–0.15). The concentration dependences of the activation parameters of hydrolysis of these compounds, which are essentially nonmonotonic and are strongly influenced by the kind of the halogen, were accounted for by specific structural features of sulfonyl chloride and bromide groups.

Previously we determined the activation parameters of hydrolysis of 2-methylbenzenesufonyl chloride (**I**) [1] and bromide (**II**) [2] in water-rich water–dioxane mixtures. In both cases, the activation parameters showed essentially nonmonotonic dependences of the activation parameters on the dioxane mole fraction X_2. Figure 1a shows the plots of $\Delta H^{\neq}$ of hydrolysis of **I** and **II** vs. X_2, constructed using data from [1, 2]. The role of the entropy factor is illustrated by the contribution ϑ (%) of the term ($-T\Delta S^{\neq}$) to $\Delta G^{\neq}$ as a function of X_2 (Table 1, Fig. 1b). The dependences of the activation parameters of hydrolysis on X_2 are similar for **I** and **II**, proving that the interactions of *o*-methylbenzenesulfonyl halides with solvents have much in common. However, there are certain specific features associated with the molecular structures of **I** and **II**. In this connection, our goal was to reveal a correlation of the structural characteristics of **I** and **II** with the specific features of the concentration dependences of the activation parameters of their hydrolysis and to elucidate the influence of particular halogen on solvation effects in the elementary event of nucleophilic substitution at the sulfonyl sulfur atom.

We calculated some structural and energy parameters of the substrates. Below is the structural formula of 2-methylbenzenesulfonyl chloride with the atom numbering.



The *ab initio* calculations of the molecular structure of sulfonyl halides were performed by the DFT B3LYP method [3] in the 6-311G** basis set using the GAUSSIAN 98 program package, as in [4]. Semiempirical calculations were performed by the PM3 method using the MOPAC 6.0 program [5], as in [6, 7]. The calculated parameters are listed in Tables 2 and 3. For comparison, we also give in Table 2 the structural data for 4-methylbenzenesulfonyl chloride, determined in [8] by gas-phase electron diffraction. The calculation results reasonably agree with the experimental data; therefore, in further analysis, it is quite justified to use the calculated values only.

In 2-methyl- and 4-methyl-substituted sulfonyl chlorides (Tables 2, 3), the interatomic distances, bond angles, and atomic charges in the sulfonyl group differ insignificantly. At the same time, in 2-methyl-substituted compounds, compared to 4-methyl-substituted derivatives, the dihedral angles $X^8S^7C^1C^2$, $O^9S^7C^1C^2$, and $O^{10}S^7C^1C^6$ change appreciably (by ~15°), the barrier to rotation of the sulfonyl group increases by a factor of 3, the barrier to rotation of the methyl group increases by a factor of 40–50, and the dipole moment somewhat decreases. The high barriers to rotation of functional groups in **I** and **II** are due to considerable steric hindrance arising in mutual turn

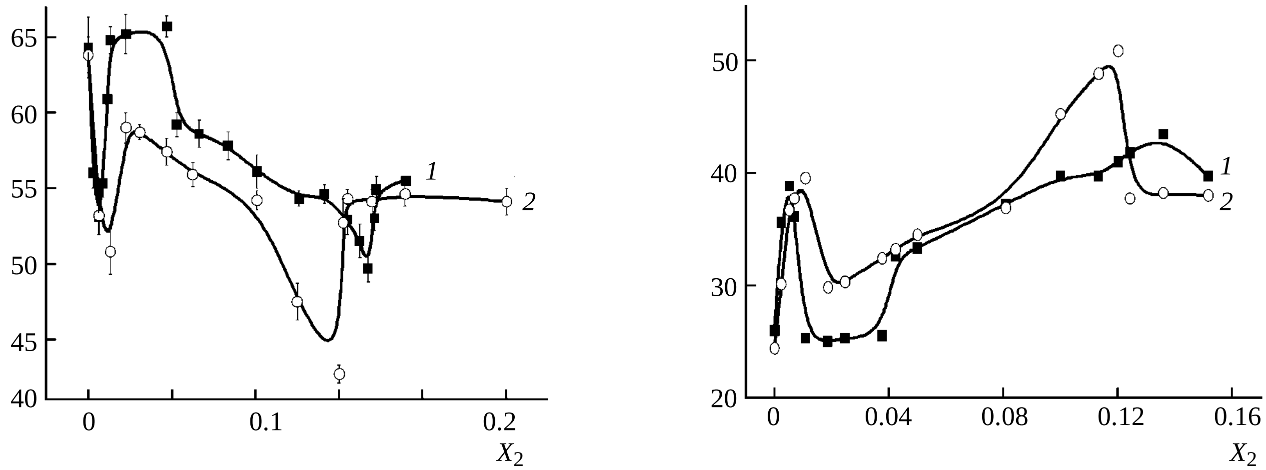


Fig. 1. (a) Activation enthalpy and (b) contribution ϑ for hydrolysis of 2-methylbenzenesulfonyl halides as functions of the dioxane mole fraction X_2. Compound: (*1*) **I** and (*2*) **II**.

of the sulfonyl and methyl groups owing to the nonbonded interactions $Hlg\cdots H_{Me}$, $O\cdots H_{Me}$, and $O\cdots H_{Ar}$ (where H_{Me} and H_{Ar} are the hydrogen atoms of the *o*-methyl group and benzene ring, respectively). Other manifestations of the steric effects are specific mutual orientation of the SO_2Hlg and CH_3 groups and also, as shown by calculations (Table 2), short distances $Hlg\cdots H_{Me}$ (3 Å), $O\cdots H_{Me}$ (2.5 Å), and especially $O\cdots H_{Ar}$ (~2.4 Å), typical of hydrogen bonding. These interactions result in that the molecule of **I** exists in a single conformation [6] but do not cause deformation of the benzene ring in *o*-toluenesulfonyl halides (decrease in the $C^2C^1C^6$ angle) and the corresponding decrease in the steric shielding of the S atom, as concluded in [10] on the basis of molecular-mechanics calculations.

The replacement of bromine by chlorine in the sulfonyl halide group causes shortening of the S–Hlg distance, a decrease in the rotation barriers of sulfonyl halide and especially methyl groups, an increase in the dipole moment of the molecule, and certain changes in the dihedral angles. This replacement is accompanied by an appreciable increase in the negative charge on the chlorine atom, with the positive charges on the S atom and negative charges on the O atoms changing insignificantly (Table 3).

Table 1. Entropy contributions ϑ and ratios of rate constants $k_{eff(II)}/k_{eff(I)}$ of hydrolysis of **I** and **II** in water–dioxane mixtures of the same compositions [1, 2]

X_2	$\vartheta_{(I)}$	$\vartheta_{(II)}$	$k_{eff(II)}/k_{eff(I)}$	X_2	$\vartheta_{(I)}$	$\vartheta_{(II)}$	$k_{eff(II)}/k_{eff(I)}$
0	26.0	24.4	2.7	0.0500	33.3	34.5	3.1
0.0024	35.6	30.1	2.8	0.0808	37.2	36.9	3.9
0.0052	38.8	36.7	2.8	0.100	39.7	45.2	3.9
0.0070	36.1	37.7	2.6	0.113	39.7	48.8	4.4
0.0107	25.3	39.5	3.2	0.120	41.0	50.8	4.8
0.0187	25.0	29.8	3.2	0.124	41.8	37.7	4.3
0.0247	25.3	30.3	3.8	0.136	43.4	38.2	3.6
0.0376	25.5	32.4	3.6	0.152	39.7	38.0	4.8
0.0424	32.6	33.2	3.2	0.328	43.4	37.7	6.1

The revealed differences in the molecular structures of **I** and **II** cause differences in the concentration dependences of the activation parameters of hydrolysis in the range of X_2 0–0.15. These differences can be explained within the framework of the mechanism suggested in [1] on the basis of results of quantum-chemical simulation of hydrolysis of benzenesulfonyl chloride in the gas phase [11] and in aqueous clusters [12]. The calculations show that the hydrolysis of benzenesulfonyl chloride is a two-step exothermic reaction proceeding via unstable five-coordinate intermediate $PhSO_2(H_2O)Cl$ containing, along with the water molecule acting as nucleophile, also the water dimer acting as bifunctional catalyst [1]:

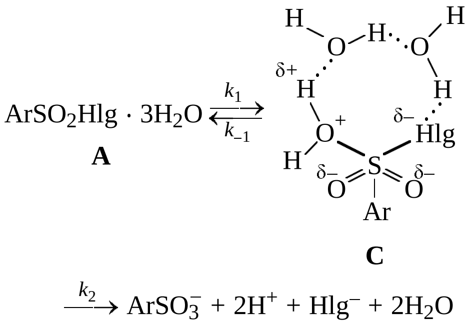


Table 2. Some structural and energy parameters[a] of 2-methylbenzenesulfonyl halide and 4-methylbenzenesulfonyl chloride molecules

Parameter	$2\text{-}CH_3C_6H_4SO_2Cl^b$	$2\text{-}CH_3C_6H_4SO_2Br^b$	$4\text{-}CH_3C_6H_4SO_2Cl$	
			calculation[b]	published data [8]
$r_{C–S}$	1.797	1.802	1.783	1.758(6)
$r_{S–Hlg}$	2.161	2.333	2.161	2.049(5)
$r_{S–O}$	1.450	1.454	1.450	1.419(3)
$r_{O\cdots H(Me)}$	2.480	2.442	–	–
$r_{Hlg\cdots H(Me)}$	2.971	3.102	–	–
$r_{O\cdots H(Ar)}$	2.388	2.379	2.597	–
$\angle C^1S^7O^9$	111.03	110.71	109.86	110.5(6)
$C^1S^7O^{10}$	109.53	109.08		
$\angle C2C1C6$	123.05	123.03	122.06	–
$\angle C^1S^7X^8$	100.82	101.60	100.56	101.3(6)
$\angle X^8S^7O^9$	106.04	106.49	105.85	106.9(3)
$\angle O^9S^7O^{10}$	121.47	121.15	122.44	120.5(9)
$\angle F^8S^7C^1C^2$	–75.52	–76.23	–91.34	–
$\angle O^9S^7C^1C^2$	36.49	36.57	19.93	–
$\angle O^{10}S^7C^1C^6$	–4.41	–6.17	–20.90	–
μ, D	5.519	5.322	6.471	–
$\Delta H_{f,298}$,[c] kJ mol^{-1}	–226.0	–170.4	–240.8	
$\Delta H_{dis\ S–Hlg}$,[c] kJ mol^{-1}	643.4[d]	566.9	–	
ΔE_{sh},[c] kJ mol^{-1}	19.3	21.7	6.7	
ΔE_{Me},[c] kJ mol^{-1}	3.9	5.8	0.11	

[a] ($r_{i–j}$) Interaromic distances, Å; ($\angle ijk$) bond angles, deg; ($\angle ijkl$) torsion angles, deg; (ΔE_{sh}, ΔE_{Me}) barriers to internal rotation of sulfonyl halide and methyl groups, respectively. [b] Calculated *ab initio*, B3LYP/6-311G** method. [c] Calculated semiempirically, PM3 method. [d] 668 kJ mol^{-1} [9].

The structure of intermediate[1] **C**, determined quantum-chemically, is similar to the most energetically favorable configurations of water clusters $(H_2O)_n$ at $3 < n < 5$, corresponding to planar homodromic rings [13], among which the most stable are the rings with $n = 3$ [7, 14, 15].

The experimental activation parameters of hydrolysis of sulfonyl halides are determined by the strength of the H bonds in aqueous bridges of cyclic clusters, and an increase in the energy of H bonds due to one or another factor should cause the activation parameters to decrease [12].

The energies of H bonds in bridges are influenced by the specific interactions HO–H···Hlg–S and HO–H···O=S) and by hydrophobic hydration of hydrocarbon moieties. Both types of interaction depend on the structural and energy state of "bulk" water molecules

Table 3. Mulliken atomic charges in 2-methylbenzenesulfonyl halide and 4-methylbenzenesulfonyl chloride molecules (*ab initio* B3LYP/6-311G** calculation)

Atom	$4\text{-}CH_3C_6H_4SO_2Cl$	$2\text{-}CH_3C_6H_4SO_2X$	
		X = Cl	X = Br
C^1	–0.36	–0.37	–0.36
C^2	0.01	0.02	0.01
C^3	–0.06	–0.06	–0.06
C^4	–0.09	–0.07	–0.07
C^5	–0.06	–0.08	–0.08
C^6	0.01	0.00	–0.00
S^7	1.01	1.00	0.96
X^8	–0.20	–0.20	–0.16
O^9, O^{10}	–0.43	–0.43	–0.43
H_{Ar}	0.10–0.14	0.10–0.14	0.10–0.14
C_{Me}	–0.26	–0.27	–0.27
H_{Me}	0.12–0.14	0.11–0.15	0.11–0.16

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[1] In [11], we determined the structures and energies of all the states in the gas-phase process $\mathbf{A} \overset{\mathbf{B}^{\neq}}{\rightleftarrows} \mathbf{C} \overset{\mathbf{D}^{\neq}}{\rightleftarrows} \mathbf{E}$.

[16], and the specific interactions depend also on particular halogen. The molecules of the dissolved nonaqueous component (dioxane) cause reorganization of the surrounding water molecules, leading, owing to the cooperative effect, to changes in the local structure of the solution [16, 17] and to steric optimization of the whole hydrogen bond network. As a result of filling of the available cavities with dioxane molecules [18], the solvent undergoes structuring without break of the hydrogen bond network [19–22], and the water structure becomes more “openwork” [23]. Owing to the cooperative effect, the structuring improves the tetrahedral ordering, decreases the mobility of water molecules in the hydration shell of the sulfonyl halide group [1], enhances the strength of hydrogen bonds in the cyclic fragments of intermediate **C**, and ultimately decreases the activation parameters.

Figure 1 shows that, although the activation parameters of hydrolysis of sulfonyl halides, on the whole, tend to decrease with increasing X_2 owing to the structural stabilization of the solvent, there are two sharp minima in the $\Delta H^{\neq} = f(X_2)$ curves [and two maxima in the $\vartheta = f(X_2)$ curves]. The trends in variation of ϑ and activation Gibbs energy coincide (both increase with increasing X_2). Therefore, the hydrolysis of sulfonyl halides can be regarded as an entropy-controlled process.

The first minima in the range of X_2 0.005– 0.01 are due to particular enhancement of the strength of the H bonds in the water bridges of the cyclic clusters. This is favored by formation of supramolecular structures (*V* configurations) or peculiar “solvation niches” (“quasiclathrate” [1, 2, 12, 24, 25] or quasicrystalline [26] shells). The probability of formation of “solvation niches” is determined by the nature and mole fraction of the nonelectrolyte, and the probability that intermediate **C** will occupy these niches, in accordance with the complementariness principle [25, 27], by the size and shape of sulfonyl halide molecules. We believe that the first minima of the activation parameters in the range of X_2 0.005– 0.02 are characteristic evidences of the occurrence of the substitution in the tetrahedral sulfonyl group.

The solvation effects are largely determined by the steric factor [16, 24], in our case by the size of the sulfonyl halide group, and also by the capability of molecules to assume conformations favorable for hydrophobic hydration. The smaller volume of the sulfonyl chloride group compared to the sulfonyl bromide group, and also less hindered rotation of the methyl and sulfonyl groups in **I** compared to **II** (Table 2) enhance the hydrophobic properties of the methyl group in **I** compared to **II**. These factors improve the conditions for hydrophobic hydration of molecules of **I** and increase the probability of their getting into “solvation niches” in less structured water owing to the fact that the hydration shells of **I** and bulk water become complementary at lower values of X_2 compared to **II**. Our observations are consistent with the observed trend that the stability of clathrates formed by $(C_4H_9)_4N^+Hlg^-$ decreases in going from F to I [24].

As the dioxane content grows, the hydrophobic interaction between the nonaqueous component molecules becomes stronger [24]. At X_2 0.12– 0.13 [18, 19, 28] (critical concentration of hydrophobic interaction [29]), additions of dioxane no longer exert a stabilizing effect on the water structure. The local ordering of the water structure in the hydration shells of associates like $ArSO_2Hlg\cdots1,4\text{-}C_4H_8O_2$ gives rise to the second minima of the activation parameters of hydrolysis of **I** and **II**, observed in the range of X_2 0.12– 0.13. Bromide **II** is characterized by a steeper and deeper minimum of $\Delta H^{\neq}$ compared to chloride **I**. This is due to higher probability of formation of associates $ArSo_2Hlg\cdots1,4\text{-}C_4H_8O_2$ by molecules of **II** compared to **I**, since the molecules of **II** are less polar (Table 2) and exhibit stronger affinity for dioxane.

At X_2 0.12– 0.15, after the critical concentration of hydrophobic interaction is exceeded, the activation parameters of hydrolysis start to grow, which is due to enhancement of hydrophobic interaction between the dioxane and sulfonyl halide molecules, accommodation of $ArSO_2Hlg$ molecules in dioxane clusters $(1,4\text{-}C_4H_8O_2)_n$, and hence to a sharp decrease in the standard enthalpies and entropies of the initial states of sulfonyl halides. As bromide **II** showes stronger affinity for dioxane, the activation parameters of its hydrolysis in this concentration range start to grow at lower concentrations than those of hydrolysis of **I** (Fig. 1).

Figure 1a shows that, for the majority of compositions of the mixed solvent, $\Delta H^{\neq}_{\mathbf{I}} > \Delta H^{\neq}_{\mathbf{II}}$, in full agreement with the enthalpies of dissociation of the S–Hlg bonds in gas-phase reactions $ArSO_2Hlg = ArSO_2^+ + Hlg^-$ (Table 1): $\Delta H_{\mathrm{dis(S–Cl)}} > \Delta H_{\mathrm{dis(S–Br)}}$. However, this relationship is not valid for pure water and some mixtures, in which $\Delta H^{\neq}_{\mathbf{I}} \cong \Delta H^{\neq}_{\mathbf{II}}$ and $\vartheta_{\mathbf{I}} < \vartheta_{\mathbf{II}}$ (Fig. 1b). This anomaly can be accounted for as follows.

The close values of $\Delta H^{\neq}_{\mathbf{I}}$ and $\Delta H^{\neq}_{\mathbf{II}}$ in the ranges of X_2 0 – 0.007 and 0.04 – 0.08 suggest enhanced hydration of sulfonyl halide groups in these ranges, leveling off the difference in the dissociation energies of the S–Cl and S–Br bonds. The charge distribution on atoms of sulfonyl halide groups (Table 3) should favor formation of stronger H bonds in the water bridges of the cyclic transition states in hydrolysis of **I**, compared to **II**, owing to higher energy of the specific interaction $Cl^{\delta-}\cdots H–O–H$ compared to $Br^{\delta-}\cdots H–O–H$. Therefore, in water and in the mixed solvent in these ranges of X_2 (i.e., at compositions at which the complicating hydrophobic effects are not manifested), the hydrate clusters around sulfonyl bromide molecules should be less structured than those around sulfonyl chloride molecules, which, according to calculations [12], should result in increased activation parameters of hydrolysis of **II** compared to **I**. As a result, $\Delta H^{\neq}_{\mathbf{II}} \cong \Delta H^{\#}_{\mathbf{I}}$ and $\Delta S^{\neq}_{\mathbf{II}} > \Delta S^{\#}_{\mathbf{I}}$. It should be noted that hydrolysis of a series of substituted benzenesulfonyl halides (substituents H, 4-Cl, 4-NO_2, 2-NO_2) in water is also characterized by the relationships $\Delta H^{\neq}_{\mathbf{II}} > \Delta H^{\#}_{\mathbf{I}}$ and $\Delta S^{\neq}_{\mathbf{II}} > \Delta S^{\#}_{\mathbf{I}}$ [30], which could not be attributed to differences in the strengths of the S–Br and S–Cl bonds.

The positive differences $\Delta H^{\neq}_{\mathbf{I}} - \Delta H^{\#}_{\mathbf{II}}$ ($\Delta S^{\neq}_{\mathbf{II}} < \Delta S^{\#}_{\mathbf{I}}$, Fig. 1b) in the range of X_2 0.007–0.04 are due to lifting of “perturbations” from specific hydration and occupation of “solvation niches” by the substrates, and in the range of X_2 0.08–0.12, by enhancement of hydrophobic hydration of **II** due to selective solvation with dioxane.

In variation of the extent of structuring of aqueous clusters, variations in K_1 and k_2 compensate each other [12], since $k_{\mathrm{eff}} = K_1k_2$ and $K_1 = k_1/k_{-1}$ (see scheme). As the contribution from ΔG^0_1 determines $\Delta G^{\neq}_{\mathrm{eff}} = \Delta G^0_1 + \Delta G^{\neq}_2$ to more than 80% [11], the equilibrium constant K_1 exerts a decisive influence on k_{eff}. Therefore, changes in the hydration conditions affect the hydrolysis to virtually the same extent as they affect reversible formation of intermediate **C**. Since intermediate $\mathbf{C_I}$ is more structured than $\mathbf{C_{II}}$, $K_{1(\mathbf{II})}$ should be larger than $K_{1(\mathbf{I})}$, which leads to the relationship $k_{\mathrm{eff}(\mathbf{II})} > k_{\mathrm{eff}(\mathbf{I})}$ (Table 1).

The $k_{\mathrm{eff}(\mathbf{II})}/k_{\mathrm{eff}(\mathbf{I})}$ ratio gradually grows with increasing concentration of dioxane, which is due to weaker transfer of the structuring effect from bulk water to loose sulfonyl bromide clusters $\mathbf{C_{II}}$ compared to sulfonyl chloride clusters $\mathbf{C_I}$, which ultimately decelerates the decrease in $K_{1(\mathbf{II})}$ compared to $K_{1(\mathbf{I})}$. This conclusion is consistent with the fact that cyclic aqueous clusters of intermediate $\mathbf{C_{II}}$, compared to $\mathbf{C_I}$, require smaller number of water molecules for hydrolysis (2.72 and 3.36, respectively [1]).

Thus, differences in the structure of sulfonyl halide groups do not affect in general the essentially nonmonotonic concentration dependences of the activation parameters, determined by complex solvation effects in water-rich media. On replacement of the leaving groups, the main trend is preserved: a decrease in the enthalpy component and an increase in the entropy component with an increase in the content of the nonaqueous component. Also preserved are two minima of the activation parameters, though their positions on the concentration axis are shifted.

The above-presented concept is based on the results of numerous experimental studies [15, 16, 18–21, 28, 29]. Although the occurrence of local structuring of water on adding nonelectrolytes is subjected to questions in some papers [31], we believe that this process determines the solvation effects in hydrolysis of various substrates. The revealed trends in variation of the activation parameters on replacement of the leaving group and on variation of the composition of the medium should be general for different reaction systems.

ACKNOWLEDGMENTS

The study was financially supported by the International Soros Program of Education in the Field of Exact Sciences (grant no. d-98-504).

REFERENCES

1. Ivanov, S.N., Kislov, V.V., and Gnedin, B.G., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 1, p. 103.
2. Kislov, V.V., Ivanov, S.N., and Gnedin, B.G., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 3, p. 479.
3. Becke, A.D., *J. Chem. Phys.*, 1993, vol. 98, no. 24, p. 5648; Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. B*, 1988, vol. 37, no. 3, p. 785.
4. Lee, H.Y., Kislov, V.V., Lin, S.H., Mebel, A.M., and Neumark, D.M., *Chem. Eur. J.*, 2003, vol. 9, no. 3, p. 726.
5. Stewart, J.J.P., *J. Computer-Aided Mol. Des.*, 1990, vol. 4, p. 1; Stewart, J.J.P., MOPAC Manual, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO, 80840, 1990.
6. Kislov, V.V., Ivanov, S.N., and Petrov, V.M., *Zh. Strukt. Khim.*, 2000, vol. 41, no. 5, p. 914.
7. Kislov, V.V. and Ivanov, S.N., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 2, p. 208.
8. Petrov, V.M., Petrova, V.N., Kislov, V.V., Ivanov, S.N., Noskov, S.Yu., Krasnov, A.V., and Bylova, Z.M., *Zh. Strukt. Khim.*, 2000, vol. 41, no. 6, p. 1137.
9. Chatgilialoglu, C., Griller, D., Kanabus-Kaminska, J.M., and Lossing, F.P., *J. Chem. Soc., Perkin Trans. 2*, 1994, no. 2, p. 357.
10. Rubleva, L.I., Lyashchuk, S.N., Maksimenko, N.N., and Vizgert, R.V., *Zh. Org. Khim.*, 1994, vol. 30, no. 6, p. 261.
11. Kislov, V.V. and Ivanov, S.N., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, p. 791.

12. Ivanov, S.N., Kislov, V.V., and Gnedin, B.G., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 1, p. 94.
13. Gonzales, E.Kh., Poltev, V.I., Teplukhin, A.V., and Malenkov, G.G., *Zh. Strukt. Khim.*, 1994, vol. 35, no. 6, p. 113; Malenkov, G.G., Tytik, D.L., and Zheligovskaya, E.A., *J. Mol. Liq.*, 1999, vol. 82, no. 1, p. 27.
14. Dang, L.X. and Chang, T.M., *J. Chem. Phys.*, 1997, vol. 106, no. 19, p. 8149.
15. Hantheas, S.S., *Chem. Phys. Lett.*, 2000, vol. 258, no. 2, p. 225.
16. Besseling, N.A.M. and Lyklema, J., *J. Phys. Chem. B*, 1997, vol. 101, p. 7604; Ikeguchi, M., Shimizu, S., Nakamura, S., and Shimizu, K., *J. Phys. Chem. B*, 1998, vol. 102, no. 30, p. 5891.
17. Noskov, S.Yu., Kiselev, M.G., and Kolker, A.M., *Zh. Fiz. Khim.*, 2001, vol. 75, no. 3, p. 446.
18. Naberukhin, Yu.I. and Shuiskii, S.I., *Zh. Strukt. Khim.*, 1967, vol. 8, no. 4, p. 606.
19. Glew, D.N., Mak, H.D., and Rath, N.S., *Chem. Commun.*, 1968, no. 5, p. 264.
20. Murthy, N.M. and Subrahmanyam, S.V., *Can. J. Chem.*, 1978, vol. 56, no. 20, p. 2412.
21. Matubayasi, N., *J. Am. Chem. Soc.*, 1994, vol. 116, no. 6, p. 1450.
22. Pchelkin, V.N. and Toryanik, A.I., *Zh. Strukt. Khim.*, 1991, vol. 32, no. 2, p. 88.
23. Bushuev, Yu.G., Davletbaeva, S.V., and Korolev, V.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1999, no. 5, p. 841.
24. Kessler, Yu.M. and Zaitsev, A.L., *Sol'vofobnye effekty* (Solvophobic Effects), Leningrad: Khimiya, 1989.
25. Lyashchenko, A.K., Khor'kin, V.S., Lileev, A.S., and Efremov, P.V., *Zh. Fiz. Khim.*, 2001, vol. 75, no. 2, p. 250; Lyashchenko, A.K., Lileev, A.S., Palitskaya, T.A., and Ostroushko, A.A., *Zh. Fiz. Khim.*, 2001, vol. 75, no. 2, p. 257.
26. Dakar, G.M. and Korableva, E.Yu., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 4, p. 662.
27. Lyashchenko, A.K., *Zh. Fiz. Khim.*, 1993, vol. 67, no. 7, p. 281.
28. Engberts, J.B.F.N., *Water: A Comprehensive Treatise*, Franks, F., Ed., New York: Plenum, 1979, vol. 6, p. 139.
29. Haak, J.R. and Engberts, J.B.F.N., *J. Am. Chem. Soc.*, 1986, vol. 108, no. 7, p. 1705.
30. Gnedin, B.G., Ivanov, S.N., and Spryskov, A.A., *Zh. Org. Khim.*, 1976, vol. 12, no. 9, p. 1939.
31. Blokzijl, W. and Engberts, J.B.F.N., *Angew. Chem., Int. Ed.*, 1993, vol. 32, p. 1545; Finney, J.L. and Soper, A.K., *Chem. Soc. Rev.*, 1994, no. 1, p. 1.