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# Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XLIII.[1] Solvent Effect on Activation Parameters of Dehydrochlorination of 3-Chloro-3-methylbut-1-ene. Correlation Analysis of Solvation Effects

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**Abstract** — The influence of temperature on the rate of dehydrochlorination of 3-chloro-3-methylbut-1-ene in 17 aprotic and 13 protic solvents, $v = k[C_5H_9Cl]$, was studied by the verdazyl method. In aprotic solvents, the electrophilicity, ionizing power, and cohesion of solvents decrease $\Delta G^{\neq}$ by increasing $\Delta S^{\neq}$. The nucleophilicity and polarizability increase both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to equal extent and therefore do not affect $\Delta G^{\neq}$. In protic solvents, the solvent nucleophilicity increases $\Delta H^{\neq}$ to a greater extent than $\Delta S^{\neq}$, and the overall effect of the nucleophilic solvation is small and negative.
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In the previous papers of this series, we reported data on the kinetics of dehydrochlorination of 3-methyl-3-chloro-1-butene (**I**) at 25°C in 17 aprotic and 13 protic solvents [1, 2]. The reaction rate is satisfactorily described by a first-order rate equation (1), with the E1 mechanism realized in aprotic solvents and the E1 + SN1 mechanism, in protic solvents [1–3]:

$$v = k[\mathrm{I}]. \quad (1)$$

The rate of monomolecular heterolysis reactions (SN1, E1, solvolysis) is controlled by ionization of the covalent bond, which occurs via successive formation of three ion pairs: contact (**A**), spatially separated (**B**), and solvation-separated (**C**) [4, 5]:

$$\mathrm{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{A}}{\mathrm{R^+X^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\mathbf{B}}{\mathrm{R^+|\square|X^-}} \rightleftarrows \underset{\mathbf{C}}{\mathrm{R^+|Solv|X^-}}$$

$$\longrightarrow \text{Reaction products.} \quad (2)$$

In the limiting step, ion pair **A** interacts with the solvent cavity ( □ ); the cavities occupy about 10% of the liquid volume [6]. In the process, ion pair **B** is formed, which rapidly transforms into pair **C**. Pair **C**, in turn, also rapidly transforms into reaction products.

The majority of relevant studies deal with the solvent effect on the logarithm of the heterolysis rate constant or, which is equivalent, on the activation free energies [4, 5, 7–10]. In these studies, however, data for a single temperature (usually 25°C) are considered, because $\log k$ and $\Delta G^{\neq}$ are strongly temperature-dependent. The activation free energy is determined by the activation enthalpy and entropy ($\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$), which are virtually temperature-independent in the ranges usually examined. A study of the solvent effect on the activation parameters of the heterolysis would allow better understanding of the solvation effects and reaction mechanism.

Protic and aprotic solvents affect the activation parameters of the heterolysis differently. The formation of an ion pair is accompanied by solvent structuring around this intermediate (electrostriction effect [11]), which decreases $\Delta S^{\neq}$. In protic solvents, this effect is superimposed by break-up of the solvent structure ($\Delta S^{\neq}$ increases). In aprotic nonstructured solvents, the nature of solvation of the transition state can be judged from the sign and value of $\Delta S^{\neq}$, whereas in protic solvents it is difficult to make such conclusions.

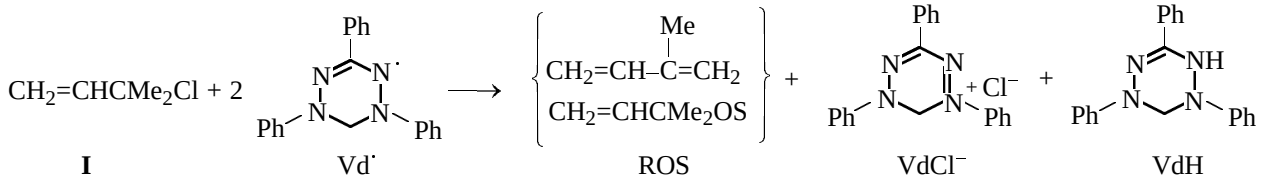
The electrostriction effect is readily identified when performing heterolysis in a binary mixture consisting of a polar solvent and a low-polarity solvent, e.g., of

[1] For communication XLII, see [1].

water and dioxane [12, 13]. The dependence of the reaction rate on the mixture composition allows determination of the number of polar solvent molecules participating in solvation of the transition state (so-called solvate number). For SN1 (E1) reactions with a polar transition state, the solvate number is usually 6–8, and for SN2 reactions occurring via low-polarity transition state, it is 2–3.

Data on the solvent effect on $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are very important for understanding the nature of solvation effects, but these data are few and insufficiently reliable. Abraham et al. [14], when performing correlation analysis of solvation effects in the heterolysis of *t*-BuCl and *t*-BuBr, used data for protic and aprotic solvents in combination. The experimental data were available for only 14 solvents. The other values (nine solvents) were estimated; in most cases, not only $\Delta H^{\neq}$ and $\Delta S^{\neq}$, but also $\Delta G^{\neq}$ were estimated. The data set on the activation parameters of the heterolysis of 1-methyl-1-halocycloalkanes was insufficient for correct correlation analysis using multiparameter equations of the linear free energy relationship. The most reliable data were obtained in the correlation analysis of the reactivity of *tert*-butyl halides separately in protic and aprotic solvents [15, 16]. However, the experimental data considered in these papers were obtained by different authors using different procedures.

The goal of this study is correlation analysis of the influence of solvent parameters on the activation parameters of the heterolysis of 3-chloro-3-methylbut-1-ene (**I**) whose carbocation has two electrophilic centers (positions 1 and 3) for nucleophilic solvation. We examined the influence of temperature on the rate of heterolysis of chloride **I** in 13 protic and 17 aprotic solvents. Kinetic experiments were performed by the verdazyl method [17]. As internal indicator we used 1,3,5-triphenylverdazyl (Vd$^{\cdot}$), which rapidly and quantitatively reacts with the solvation-separated ion pair of the substrate after the limiting step to form in an aprotic medium isoprene, verdazylium chloride $Vd^+Cl^-$, and leucoverdazyl VdH (E1 reaction). In a protic medium (SOH), the reaction occurs in part along the SN1 pathway with the formation of the solvolysis product (ROS) instead of isoprene [3]. The reaction follows the stoichiometric equation




Irrespective of the reaction pathway (E1 and/or SN1), 2 mol of Vd$^{\cdot}$ is always consumed per mole of the substrate, and 1 mol of $Vd^+Cl^-$ is formed. The reaction rate was monitored spectrophotometrically, by a decrease in the Vd$^{\cdot}$ concentration ($\lambda_{max}$ ~720 nm). It is satisfactorily described by a first-order rate equation (3):

$$v = -d[\mathrm{Vd}^{\cdot}]/2dt = k[\mathrm{I}]. \quad (3)$$

The $\log k_{25}$ values, activation parameters of the heterolysis of **I** in 30 solvents, and solvent parameters are given in the table. Comparison of $\log k_{25}$ from this table with the related data for *t*-BuCl [10, 15] and cumyl chloride [18, 19] show that the reaction rate in the series of substrates (4) increases by three orders of magnitude.

$$\underset{1}{t\text{-BuCl}} < \underset{\sim 100}{CH_2{=}CH{-}CMe_2Cl} < \underset{\sim 1000}{PhCMe_2Cl}. \quad (4)$$

The increase in the reaction rate in series (4) is mainly associated with an increase in the stability of the forming carbocationic intemediate. Indeed, the increase in the rate is mainly due to a decrease in $\Delta H^{\neq}$. For example, $\Delta H^{\neq}$ (kJ mol$^{-1}$) for the heterolysis in γ-butyrolactone decreases in going from *t*-BuCl (103) to 3-chloro-3-methylbut-1-ene (88) and then to cumyl chloride (82), with $\Delta S^{\neq}$ remaining essentially the same (–73 J mol$^{-1}$ K$^{-1}$) [15, 19].

The figure illustrates two separate compensation effects $\Delta H^{\neq}$–$\Delta S^{\neq}$ (for protic and aprotic solvents) in the heterolysis of **I**. For aprotic solvents, the correlation is satisfactory ($R$ 0.954), and for protic solvents it is approximate ($R$ 0.934).

The compensation effect is apparently caused by the uniformity of solvation effects: dipolar solvation in aprotic solvents and electrophilic solvation in protonic solvents. Analysis of the $\log k$–$1/T$ dependences shows that the isokinetic relationship is not observed in the heterolysis of **I**.

Solvent effect on the rate and activation parameters of heterolysis of chloride **I**

| Comp. no. | Solvent | $-\log k_{25}$ | $\Delta G^{\neq}$, kJ mol$^{-1}$ | $\Delta H^{\neq}$, kJ mol$^{-1}$ | $-\Delta S^{\neq}$, J mol$^{-1}$ K$^{-1}$ | $E$ | $E_T$ | $B$ | $\delta^2/100$ | ε | $n$ | π* | α | β |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | MeOH | 3.83 | 94 ± 2 | 80 ± 4 | 49 ± 3 | 62 | 232 | 2.61 | 8.58 | 32.7 | 1.329 | 0.6 | 0.98 | 0.66 |
| **2** | $CH_2$=CH–$CH_2$OH | 4.19 | 97 ± 1 | 75 ± 4 | 75 ± 4 | 49 | 218 | 2.55 | 5.83 | 20.6 | 1.414 | 0.52 | 0.84 | 0.9 |
| **3** | EtOH | 4.48 | 99 ± 2 | 78 ± 5 | 69 ± 4 | 49 | 217 | 2.81 | 6.78 | 24.3 | 1.361 | 0.54 | 0.86 | 0.75 |
| **4** | *n*-BuOH | 5.23 | 103 ± 2 | 78 ± 4 | 81 ± 4 | 43 | 210 | 2.76 | 5.41 | 17.1 | 1.399 | 0.47 | 0.84 | 0.84 |
| **5** | *i*-BuOH | 5.24 | 103 ± 1 | 71 ± 5 | 107 ± 7 | 37 | 203 | 2.75 | 5.91 | 17.7 | 1.396 | 0.4 | 0.79 | 0.84 |
| **6** | *n*-PentOH | 5.45 | 104 ± 1 | 85 ± 4 | 64 ± 4 | 41 | 205 | 2.8 | 5.01 | 13.9 | 1.41 | 0.4 | 0.84 | 0.86 |
| **7** | *n*-PrOH | 5.52 | 104 ± 1 | 53 ± 4 | 174 ± 9 | 39 | 206 | 2.82 | 5.56 | 18.3 | 1.377 | 0.48 | 0.76 | 0.84 |
| **8** | *n*-HexOH | 5.53 | 105 ± 1 | 96 ± 5 | 28 ± 3 | 40 | 204 | 2.84 | 4.85 | 12.5 | 1.418 | 0.4 | 0.8 | 0.84 |
| **9** | Cyclohexanol | 5.62 | 105 ± 1 | 95 ± 5 | 32 ± 3 | 29 | 196 | 2.89 | 5.15 | 15 | 1.467 | 0.45 | 0.66 | 0.84 |
| **10** | *n*-OctOH | 5.65 | 105 ± 1 | 91 ± 5 | 48 ± 3 | 40 | 202 | 2.82 | 4.44 | 10.3 | 1.429 | 0.4 | 0.77 | 0.81 |
| **11** | 2-BuOH | 5.73 | 106 ± 1 | 79 ± 5 | 89 ± 5 | 30 | 197 | 2.82 | 5.19 | 16.6 | 1.398 | 0.4 | 0.69 | 0.8 |
| **12** | *t*-BuOH | 6.45 | 110 ± 1 | 88 ± 6 | 72 ± 5 | 21 | 183 | 2.95 | 4.6 | 10.9 | 1.385 | 0.41 | 0.42 | 0.93 |
| **13** | *t*-PentOH | 6.78 | 112 ± 1 | 64 ± 6 | 159 ± 8 | 19 | 172 | 3.03 | 4.6 | 5.8 | 1.386 | 0.4 | 0.28 | 0.93 |
| **14** | Sulfolane | 6.06 | 108 ± 1 | 90 ± 5 | 59 ± 5 | 10 | 184 | 1.88 | 6.9 | 42.1 | 1.481 | 0.98 | 0 | 0.39 |
| **15** | Propylene carbonate | 6.15 | 108 ± 1 | 96 ± 4 | 40 ± 4 | 21 | 195 | 2.18 | 7.4 | 62.9 | 1.421 | 0.83 | 0 | 0.4 |
| **16** | γ-Butyrolactone | 6.44 | 110 ± 1 | 88 ± 5 | 73 ± 6 | 12 | 185 | 2.48 | 6.95 | 41 | 1.437 | 0.87 | 0 | 0.49 |
| **17** | MeCN | 6.56 | 110 ± 1 | 98 ± 4 | 42 ± 4 | 21 | 191 | 1.91 | 5.86 | 35.9 | 1.344 | 0.75 | 0.19 | 0.4 |
| **18** | $PhNO_2$ | 7.76 | 117 ± 1 | 85 ± 6 | 110 ± 7 | 0 | 173 | 0.8 | 5.11 | 36.1 | 1.551 | 1.01 | 0 | 0.3 |
| **19** | PhCN | 7.91 | 118 ± 1 | 94 ± 6 | 80 ± 6 | 0 | 173 | 1.85 | 5.15 | 25.2 | 1.528 | 0.9 | 0 | 0.37 |
| **20** | PhCOMe | 7.96 | 118 ± 1 | 87 ± 5 | 106 ± 6 | 0 | 170 | 2.42 | 4.33 | 18.2 | 1.534 | 0.9 | 0.04 | 0.49 |
| **21** | 1,2-Dichloroethane | 8.02 | 119 ± 1 | 63 ± 5 | 186 ± 9 | 9.6 | 173 | 0.48 | 4.12 | 10.4 | 1.551 | 0.81 | 0 | 0.1 |
| **22** | Acetone | 8.30 | 120 ± 1 | 53 ± 4 | 225 ± 10 | 8.5 | 176 | 2.68 | 3.88 | 21.4 | 1.359 | 0.71 | 0.08 | 0.43 |
| **23** | MeCOEt | 8.34 | 121 ± 1 | 71 ± 5 | 166 ± 9 | 5.4 | 173 | 2.5 | 3.61 | 18.9 | 1.379 | 0.67 | 0.06 | 0.48 |
| **24** | Cyclohexanone | 8.34 | 121 ± 1 | 68 ± 8 | 177 ± 9 | 0 | 166 | 2.89 | 4.08 | 16 | 1.451 | 0.76 | 0 | 0.53 |
| **25** | *o*-Dichlorobenzene | 8.79 | 123 ± 1 | 52 ± 7 | 237 ± 10 | 0 | 159 | 0.33 | 4.2 | 10.4 | 1.551 | 0.8 | 0 | 0.03 |
| **26** | PhBr | 8.89 | 124 ± 1 | 63 ± 9 | 203 ± 10 | 0 | 153 | 0.48 | 4 | 5.55 | 1.56 | 0.79 | 0 | 0.06 |
| **27** | PhCl | 9.24 | 126 ± 1 | 65 ± 5 | 204 ± 10 | 0 | 154 | 0.45 | 3.76 | 5.74 | 1.524 | 0.71 | 0 | 0.07 |
| **28** | Dioxane | 9.53 | 127 ± 1 | 66 ± 7 | 207 ± 9 | 0 | 150 | 2.84 | 4.2 | 2.27 | 1.422 | 0.55 | 0 | 0.37 |
| **29** | THF | 9.64 | 128 ± 1 | 73 ± 8 | 185 ± 9 | 0 | 156 | 3.43 | 3.61 | 7.39 | 1.408 | 0.58 | 0 | 0.55 |
| **30** | AcOEt | 10.29 | 132 ± 1 | 90 ± 8 | 140 ± 9 | 6.7 | 159 | 2.17 | 3.39 | 6 | 1.372 | 0.55 | 0 | 0.45 |

The correlation analysis of the effect of solvent parameters on the activation parameters of the heterolysis of **I** was performed using the Koppel–Palm equation [20] with additionally included cohesion energy density parameter $\delta^2$ [21] [Eq. (5)], Eq. (6), and Kamlet–Taft equation (7) [22]:

$$\Delta = a_0 + a_1\frac{\varepsilon - 1}{\varepsilon + 1} + a_2\frac{n^2 - 1}{n^2 + 1} + a_3E + a_4B + a_5\delta^2, \quad (5)$$

$$\Delta = a_0 + a_1E_T + a_2\frac{n^2 - 1}{n^2 + 1} + a_3B + a_4\delta^2, \quad (6)$$

$$\Delta = a_0 + a_1\pi^* + a_2\alpha + a_3\beta + a_4\delta^2. \quad (7)$$

Here Δ is the parameter being correlated ($\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$); ε, dielectric constant of the solvent; $n$, refractive index; $E$ and α, empirical parameters of electrophilicity; $B$ and β, empirical parameters of nucleophilicity; π*, dipolarity parameter (polarity + polarizability); $E_T$, solvatochromic parameter of the solvent ionizing power; $\delta^2 = (\Delta H_m - RT)/V_m$ reflects the energy of solvent self-association, $\Delta H_m$ is the molar heat of vaporization, and $V_m$, molar volume. The solvent parameters were taken from [23–25].

In aprotic solvents, application of Eq. (5) to the activation free energy leads to a satisfactory five-parameter correlation:

$$\Delta G^{\neq} = (163 \pm 12) - (0.0306 \pm 0.0091)\delta^2 - (15.3 \pm 5.0) f(\varepsilon) - (0.280 \pm 0.213)E - (36.3 \pm 34.8) f(n) - (0.765 \pm 1.19)B;$$
$$R\ 0.959,\ S\ 2.43,\ F\ 25\ (2.8),\ N\ 17.$$

Here and hereinafter, $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 1)$; $f(n) = (n^2 - 1)/(n^2 + 1)$; $F$ is the calculated and critical (in parentheses) Fisher test [26]. The model is reliable if the calculated Fisher test is higher than the critical value.

The polarizability, electrophilicity, and nucleophilicity parameters are insignificant, and on their exclusion we obtain a satisfactory two-parameter correlation:

$$\Delta G^{\neq} = (153 \pm 3) - (17.6 \pm 4.6) f(\varepsilon) - (0.0399 \pm 0.0054)\delta^2;$$
$$R\ 0.952,\ S\ 2.3,\ F\ 68\ (2.5),\ N\ 17.$$

The correlation analysis of the effect of solvent paameters on $\Delta H^{\neq}$ and $\Delta S^{\neq}$ leads to correlations of lower quality. Satisfactory correlation for $\Delta S^{\neq}$ was obtained only after exclusion of three points (**17, 25**, and **30**; here and hereinafter, the solvent numbering is the same as in the table):

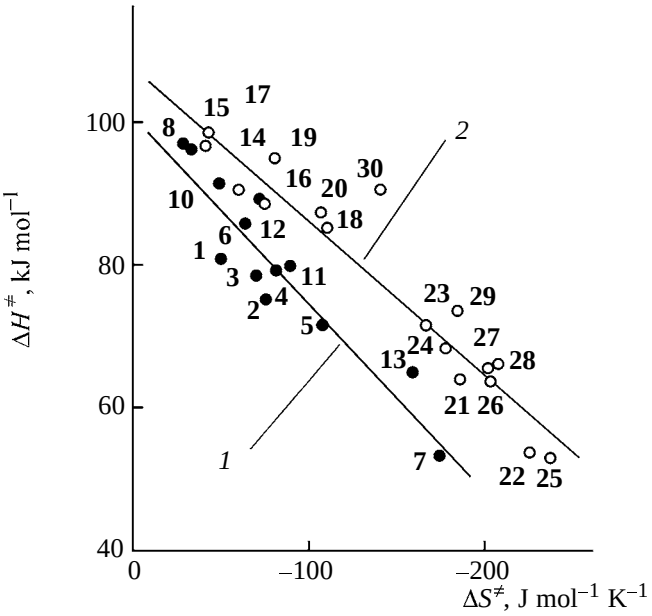
$$\Delta S^{\neq} = -(853 \pm 100) + (1090 \pm 290) f(n) + (38.7 \pm 10.0)B + (0.466 \pm 0.052)\delta^2;$$
$$R\ 0.950,\ S\ 2.4,\ F\ 31\ (3.1),\ N\ 14.$$

For the whole set of 17 solvents, $R$ 0.858. The electrophilicity and polarity parameters affect the correlation quality insignificantly; their inclusion increases $R$ only to 0.961.

Even after exclusion of four points (**17, 23, 25, 30**), we obtained for $\Delta H^{\neq}$ only an approximate correlation:

$$\Delta H^{\neq} = -(97.7 \pm 31.0) + (302 \pm 72) f(n) + (9.82 \pm 2.67)B + (0.0879 \pm 0.0127)\delta^2;$$
$$R\ 0.934,\ S\ 5.9,\ F\ 21\ (3.3),\ N\ 13.$$

Thus, in aprotic solvents, the polarizability, nucleophilicity, and cohesion increase both $\Delta H^{\neq}$ and $\Delta S^{\neq}$, and only the cohesion affects the reaction rate, increasing it. This fact indicates that the nucleophilicity and polarizability affect both activation parameters to similar extent, which leads to the compensation effect, whereas the cohesion affects $\Delta S^{\neq}$ more strongly than $\Delta H^{\neq}$. It is unclear why the reaction rate depends on the solvent polarity if this parameter affects neither $\Delta H^{\neq}$ nor $\Delta S^{\neq}$. The cause may be the fact that, when constructing correlations for $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$, we used different sets of solvents. To eliminate this inconsistency, we performed a correlation analysis for $\Delta G^{\neq}$ and $\Delta S^{\neq}$ in the same set of solvents as for $\Delta H^{\neq}$:




$\Delta H^{\neq}$–$\Delta S^{\neq}$ plots for (*1*) protic and (*2*) aprotic solvents. For solvent numbering, see table.

$$\Delta G^{\neq} = (150 \pm 2) - (13.9 \pm 3.3) f(\varepsilon) - (0.0398 \pm 0.0091)\delta^2;$$
$$R\ 0.978,\ S\ 1.6,\ F\ 104\ (3.1),\ N\ 13,$$

$$\Delta S^{\neq} = -(610 \pm 113) + (136 \pm 33) f(\varepsilon) + (449 \pm 262) f(n) + (19.1 \pm 9.4)B + (0.319 \pm 0.051)\delta^2;$$
$$R\ 0.963,\ S\ 2.0,\ F\ 26\ (3.6),\ N\ 13.$$

Thus, an increase in the heterolysis rate with an increase in the solvent polarity and cohesion is due to the effect of these paameters on $\Delta S^{\neq}$, and the independence of the rate from the solvent nucleophilicity and polarizability means that these parameters increase $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to the same extent (full compensation effect). Similarly, after exclusion of four points (**17, 20, 23, 30**), application of Eq. (6) leads to the following correlations:

$$\Delta G^{\neq} = (176 \pm 9) - (0.261 \pm 0.067)E_T - (0.0253 \pm 0.0071)\delta^2;$$
$$R\ 0.976,\ S\ 1.7,\ F\ 99\ (3.1),\ N\ 13,$$

$$\Delta S^{\neq} = -(1010 \pm 136) + (1.29 \pm 0.65)E_T + (33.7 \pm 7.8)B + (1130 \pm 210) f(n) + (0.346 \pm 0.066)\delta^2;$$
$$R\ 0.978,\ S\ 17,\ F\ 43\ (3.6),\ N\ 13,$$

$$\Delta H^{\neq} = -(98.0 \pm 37.0) + (302 \pm 17) f(n) + (9.82 \pm 1.67)B + (0.0879 \pm 0.0127)\delta^2;$$
$$R\ 0.934,\ S\ 5.9,\ F\ 21\ (3.3),\ N\ 13.$$

Thus, the heterolysis rate increases with an increase in the ionizing power and cohesion of the solvent. The effect of the solvent ionizing power is due to an increase in $\Delta S^{\neq}$, and the effect of cohesion, due to a more pronounced increase in $\Delta S^{\neq}$ than in $\Delta H^{\neq}$. The

solvent nucleophilicity and polarizability do not affect the reaction rate, because they increase both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to an equal extent.

After exclusion of three points (**19, 22, 30**), Eq. (7) takes the following forms:

$$\Delta H^{\neq} = (17.9 \pm 10.9) + (24.9 \pm 15.3)\pi^* + (90.3 \pm 32.0)\alpha + (29.5 \pm 9.3)\beta + (0.0551 \pm 0.0156)\delta^2;$$
$$R\ 0.944,\ S\ 5.8,\ F\ 17.3\ (3.3),\ N\ 14, \quad (8)$$

$$\Delta G^{\neq} = (150 \pm 3) - (15.3 \pm 5.2)\pi^* - (34.1 \pm 11.1)\alpha - (0.0387 \pm 0.0052)\delta^2;$$
$$R\ 0.968,\ S\ 2.0,\ F\ 49\ (3.1),\ N\ 14, \quad (9)$$

$$\Delta S^{\neq} = -(447 \pm 33) + (139 \pm 49)\pi^* + (413 \pm 102)\alpha + (108 \pm 30)\beta + (0.308 \pm 0.048)\delta^2;$$
$$R\ 0.974,\ S\ 19,\ F\ 42\ (3.3),\ N\ 14. \quad (10)$$

As the parameters of Eq. (7) are normalized, from correlations (8) and (10) we can calculate the relationship describing the effect of solvent parameters on $\Delta G^{\neq}$ [Eq. (11)]; this equation reasonably agrees with correlation (9) obtained using Eq. (7):

$$\Delta G^{\neq} = 151 - 16.5\pi^* - 32.7\alpha - 0.0360\delta^2. \quad (11)$$

The adequacy of relationships (9) and (11) confirms the correctness of our conclusions that the lack of the nucleophilic effect of a solvent in the heterolysis of chloride **I** is due to the compensation of the effects of nucleophilic solvation on $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

Thus, analysis of the solvation effects using three multiparameter equations shows that in an aprotic solvents the ionizing power and also the dipolarity and polarity of the solvent decrease $\Delta H^{\neq}$ and thus increase the heterolysis rate. The solvent cohesion also increases the reaction rate, as it affects $\Delta S^{\neq}$ more strongly than $\Delta H^{\neq}$.

The most important conclusion following from our study for aprotic solvents is as follows: In the heterolysis of chloride **I**, which, like secondary substrates, experiences no steric hindrance in nucleophilic solvation of the covalent substrate, the nucleophilicity and polarizability of the solvent increase both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to an equal extent and, therefore, do not affect the reaction rate. Abraham et al. [14] attributed this compensation effect to break-up of the solvent structure, accompanying formation of an ion pair, which leads to an increase in both $\Delta S^{\neq}$ and $\Delta H^{\neq}$. This explanation contradicts the modern views on the heterolysis mechanism, according to which the break of the solvent structure facilitates formation of cavities in liquids and thus increases the reaction rate [4, 5]. Furthermore, only in structured protic solvents the effect of structure break-up can be significant. The equal effect of the nucleophilic solvation on the activation entropy and enthalpy is apparently due to the occurrence of the compensation effect $\Delta H^{\neq}$–$\Delta S^{\neq}$ (see figure). Indeed, the quality of correlations obtained with Eqs. (5)–(7) increases upon exclusion of solvents that deviate from the $\Delta H^{\neq}$–$\Delta S^{\neq}$ correlation to the greatest extent (AcOEt, MeCOEt, MeCN).

Application of Eq. (5) to protic solvents, after exclusion of three points (**7, 11, 12**), leads to the following relationships:

$$\Delta G^{\neq} = (50.4 \pm 14.4) + (22.3 \pm 4.7)B - (0.0172 \pm 0.0051)\delta^2;$$
$$R\ 0.963,\ S\ 1.5,\ F\ 44\ (4.1),\ N\ 10, \quad (12)$$

$$\Delta S^{\neq} = -(1900 \pm 270) + (2100 \pm 320)f(n) + (5.85 \pm 0.91)E + (296 \pm 67)B + (0.140 \pm 0.075)\delta^2;$$
$$R\ 0.969,\ S\ 19,\ F\ 72\ (6.0),\ N\ 10, \quad (13)$$

$$\Delta H^{\neq} = -(41.8 \pm 3.9) + (515 \pm 81)f(n) + (1.64 \pm 0.30)E_T + (95.1 \pm 22.7)B;$$
$$R\ 0.938,\ S\ 4.5,\ F\ 15\ (4.8),\ N\ 10. \quad (14)$$

In all the three correlations, the nucleophilic effect of the solvent is significant: Upon exclusion of *B*, *R* decreases to 0.902, 0.728, and 0.830 in the first, second, and third cases, respectively.

Thus, the electrophilicity and polarizability of a protic solvent increase both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to an equal extent and therefore do not affect the solvolysis rate; the solvent nucleophilicity increases $\Delta H^{\neq}$ to a greater extent than $\Delta S^{\neq}$ and thus decreases the reaction rate; an increase in the reaction rate with increasing cohesion is due to the effect on $\Delta S^{\neq}$.

After exclusion of three solvents (**3, 7, 12**), Eq. (6) takes the following forms:

$$\Delta G^{\neq} = (82 \pm 20) - (0.107 \pm 0.043)E_T + (17.1 \pm 4.4)B - (0.00818 \pm 0.00308)\delta^2;$$
$$R\ 0.992,\ S\ 0.71,\ F\ 128\ (4.8),\ N\ 10,$$

$$\Delta H^{\neq} = -(636 \pm 121) + (1.32 \pm 0.23)E_T + (122 \pm 26)B - (354 \pm 68)f(n);$$
$$R\ 0.945,\ S\ 4.2,\ F\ 17\ (4.8),\ N\ 10,$$

$$\Delta S^{\neq} = -(2260 \pm 430) + (4.28 \pm 1.11)E_T + (1430 \pm 330)f(n) + (301 \pm 109)B;$$
$$R\ 0.959,\ S\ 15,\ F\ 19\ (4.8),\ N\ 10. \quad (15)$$

In this case, the polarizability increases both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to an equal extent and therefore does not affect $\Delta G^{\neq}$; the solvent ionizing power increases $\Delta S^{\neq}$ to a greater extent than $\Delta H^{\neq}$ and thus increases the reaction rate; and the nucleophilicity increases $\Delta H^{\neq}$ to a greater extent, so that the reaction rate decreases. The effect of the nucleophilicity of protic solvents on the reaction rate is significant: Exclusion of this

factor decreases $R$ to 0.703 for $\Delta H^{\neq}$ and to 0.885 for $\Delta S^{\neq}$. However, the compensation effect reduces the influence of the nucleophilicity on $\Delta G^{\neq}$.

With Eq. (7), no satisfactory correlations for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained.

Thus, in a protic medium the nucleophilic solvation exerts a weak negative effect, as $\Delta H^{\neq}$ increases to a greater extent than $\Delta S^{\neq}$.

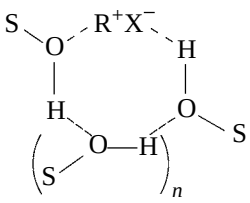
Application of Eqs. (5)–(7) to the whole set of protic and aprotic solvents gave satisfactory correlations only for $\Delta G^{\neq}$.

The heterolysis of a covalent bond involves formation of a polar transition state; therefore, it is commonly believed that all types of solvation should favor this process. The recently identified negative effect of nucleophilic solvation in heterolysis of tertiary substrates [4, 5] contradicts this rule and requires detailed consideration. Analysis of solvent effect on activation parameters offers such an opportunity.

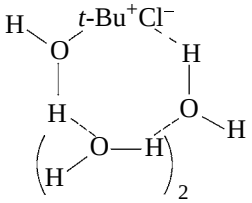
The solvent nucleophilicity increases both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of heterolysis of **I**. As the first factor decreases the reaction rate and the second factor increases it, a compensation effect is observed. In aprotic solvents, there is full compensation, and the solvent nucleophilicity does not affect the heterolysis rate. In protonic solvents, a weak negative effect of nucleophilic solvation is observed, i.e., the solvent nucleophilicity affects $\Delta H^{\neq}$ more strongly than $\Delta S^{\neq}$. The negative effect of nucleophilic solvation is observed only in heterolysis of tertiary substrates [4, 5, 9, 10, 27, 28]. This effect increases with an increase in the steric hindrance to nucleophilic solvation from the rear side and reaches a maximum in heterolysis of adamantyl substrates in which the nucleophilic solvation from the rear side is impossible. In heterolysis of **I**, the decrease in the reaction rate with increasing solvent nucleophilicity is relatively weak.

The negative effect of nucleophilic solvation is better manifested in protic than in aprotic solvents. This fact can be accounted for as follows. Apparently, in protic solvents the nucleophilic solvation of pair **A** yields cyclic solvate **II** in which hydrogen bonds are formed between the molecules that nucleophilically solvate the carbocation and electrophilically solvate the anion, which hinders ion separation in the transition state [4, 5].

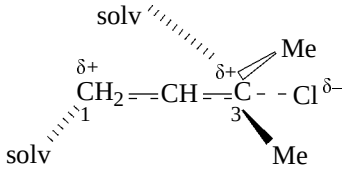
McLennan and Martin [29] analyzed the solvent effect on the rate of solvolysis of benzhydryl derivatives. They concluded that transformation of pair **A** into pair **B** is accompanied by cleavage of hydrogen bonds between the solvent molecules solvating pair **A**.



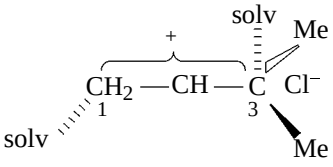
**II**



**III**



**IV**



**V**

An ab initio analysis of the mechanism of *t*-BuCl hydrolysis made McLennan and Martin [29] to suggest intermediate formation of a ten-membered cyclic solvate of contact ion pair **III** with four water molecules one of which nucleophilically solvates the carbocation from the rear side and another, the chloride ion [30]. Similar conclusions were made by Yamabe and Tsuchida [31] who studied the reaction of *t*-BuCl with a water cluster. It follows from [32] that solvate **III** is formed by reorganization of the solvation shell of the covalent substrate, suggesting nonequilibrium solvation.

Owing to delocalization of the partial positive charge in positions 1 and 3, the nucleophilic solvation of covalent chloride **I** occurs at both sites, with the formation of solvate **IV**. In position 1, there is no steric hindrance to nucleophilic solvation, and the solvent molecule is in the direct contact with the electrophilic center, whereas in position 3, in which there is strong steric hindrance, the nucleophilically solvating solvent molecule is remote from the electrophilic center. When the covalent substrate transforms into pair A, the arrangement of the nucleophilically solvating molecule at position 1 does not change, whereas the nucleophilically solvating solvent molecule at position 3 comes in direct contact with the electrophilic center, possible because of the planar structure of the carbocation [33]; in the process, solvate **V** is formed.

Without steric hindrance, the relative contributions of the enthalpy and entropy terms of the energy of nucleophilic solvation change only slightly in going from the covalent substrate to pair **A**, full compensation is observed, and the reaction rate is independent of the solvent nucleophilicity. At a strong steric hindrance, the relative contributions of the enthalpy and entropy terms of the energy of nucleophilic solvation change appreciably in going from the covalent substrate to pair **A**, because of additional decrease in the entropy upon reorientation of the solvent molecule toward the electrophilic center in position 3. Since the nucleophilic solvation of a carbocation is entropy-controlled [34], this reorientation will result in a weaker increase in $\Delta S^{\neq}$, compared to $\Delta H^{\neq}$, and hence in a decrease in the reaction rate with increasing nucleophilicity of the solvent.

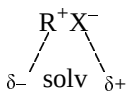
In aprotic solvents, the negative effect of nucleophilic solvation is considerably more difficult to reveal than in protic solvents. In a broad set of aprotic solvents ($N$ 26), it was found only for 2-bromo-2-methyladamantane [5] in which the nucleophilic solvation from the rear side is impossible, and also for *p*-methoxyneophyl tosylate in ten solvents [35]. However, this effect can be relatively readily revealed when only dipolar aprotic solvents are considered. This was demonstrated for heterolysis of cumyl chloride [5], $Ph_2CCl_2$ [36], and 1-chloro-1-methylcyclopentane [37].

This trend can be illustrated by the heterolysis of 1-AdOTs. As shown in [7], in a set of 22 aprotic solvents the reaction rate is independent of the solvent nucleophilicity. We found that, in a set of eight aprotic solvents (propylene carbonate, MeCN, $PhNO_2$, PhCN, PhCOMe, acetone, cyclohexanone, 1,2-dichloroethane), the rate of this reaction decreases with an increase in the solvent polarizability and nucleophilicity.

$$\log k = 0.0289E_T - 0.55f(n) - 0.399B;$$
$$R\ 0.987,\ N\ 8.$$

Exclusion of $B$ decreases $R$ to 0.928, and exclusion of $f(n)$, to 0.697.

The negative effect of nucleophilic solvation in dipolar aprotic solvents can be accounted for by electrostatic solvation of pair **A**, leading to the formation of cyclic quadrupole **VI** by interaction of the dipole of pair **A** with that of the solvent molecule. Such interaction stabilizes the intermediate and hinders the ion separation in the transition state.




**VI**

In heterolysis of **I** in any specially selected set of dipolar aprotic solvents, the reaction rate is independent of the solvent nucleophilicity. Presumably, in an aprotic medium only the nucleophilic solvation in position 1 is significant. In protic solvents, where the solvent nucleophilicity decreases the heterolysis rate, the nucleophilic solvation in position 3 is also significant. Hence, heterolysis of **I** in aprotic and protonic solvents models the effect of solvent nucleophilicity in heterolysis of secondary and tertiary substrates, respectively.

Four types of solvolysis reactions occurring with the nucleophilic assistance of the solvent are known: SN2-classical (one-step reaction of a nucleophile with a covalent substrate), SN2-intermediate (reaction of a nucleophile with a covalent substrate with intermediate formation of a contact ion pair), SN2-ion pair (the limiting step is the reaction of a nucleophile with a contact ion pair), and SN2($C^+$) (the limiting step is the reaction of a nucleophile with a solvation-separated ion pair or, according to Ingold, with a free carbocation) [4, 5, 38, 39]. In these reactions, the solvent as a nucleophile participates in the formation of the transition state.

The heterolysis of secondary substrates, apparently, is also accompanied by nucleophilic assistance by the solvent through nucleophilic solvation of the covalent substrate from the rear side [40, 41], but it is compensated by solvation effects hindering the ion separation (solvates **II** and **VI**). In the heterolysis of tertiary substrates in which the nucleophilic solvation from the rear side is impossible or strongly hindered, a negative effect of the nucleophilic solvation is observed, caused by formation of solvates **II** and **VI**.

Entelis and Tiger [42] conclude that in nonpolar solvents the solvation of the transition state in heterolysis is equilibrium, whereas in dipolar aprotic and especially in protic solvents nonequilibrium solvation of the transition state prevails. Our results render this assumption more concrete: Only nucleophilic solvation is nonequilibrium in protic and dipolar aprotic solvents, because just this kind of solvation involves break-up of the solvent structure. However, electrophilic and dipolar solvation is equilibrium. Gorodynskii and Morachevskii [43], and Kim and Hynes [44] believe that the solvation of the transition state is nonequilibrium. This is caused by orientation polarization, which changes sufficiently rapidly (in ~$10^{-16}$ s) to affect the formation of the transition state (~$10^{-13}$ s) [45]. This idea is convenient for quantum-chemical analysis of heterolysis products, but it is difficult to prove. We believe that the nonequilibrium solvation is caused by the multistep course of heterol-

ysis of a covalent bond. The nonequilibrium solvation of the transition state is suggested by low values of $\Delta S^{\neq}$. Coordination of one monodentate ligand decreases the entropy by ~45 J mol$^{-1}$ K$^{-1}$ [46]. As seen from the table, in heterolysis of **I** from one to five solvent molecules additionally participate in formation of the transition state. Similar pattern is observed in heterolysis of secondary substrates [47].

Conclusions about the occurrence of the nucleophilic assistance by the solvent are based either on application of the Grunwald–Winstein dependences unsuitable for this purpose or on incorrect interpretation of experimental data on relative rate constants [4, 5, 17]. The nucleophilicity parameter in the Grunwald–Winstein equation is a complex quantity determined by the polarity, electrophilicity, and nucleophilicity parameters [27, 48]. Its application leads to contradictory, and in some cases to absurd results [11]. Correct interpretation of the experimental data shows that the nucleophilic assistance by the solvent is lacking [4, 5, 27, 48–50].

The idea of nucleophilic assistance by the solvent is based in incorrect conclusions of Ingold and Winstein that the return from the product-forming intermediate exerts a significant effect on the heterolysis rate [4, 5, 39, 51]. It was assumed that the nucleophilic solvation of a carbocation (free or incorporated in an ion pair) should increase the reaction rate by shifting the equilibrium toward reaction products. These conclusions were based on erroneous interpretation of the so-called salt effect of the law of mass action [52] and special salt effect [53]. At that time, another interpretation of these effects could not be offered, but now there is a good reason to offer a correct interpretation [4, 5, 52, 53]. Nevertheless, even relatively recent papers [54, 55] refer only to "classical" studies.

Search for nucleophilic assistance by a solvent was started more than 50 years ago and still continues with increasing intensity [56–58]. Following a Russian proverb, this search resembles catching a black cat in a dark room in which this cat is absent. And since it is believed that this "cat" (nucleophilic assistance) does exist, any deviations from common trends are attributed to the nucleophilic assistance by the solvent. For example, comparison of the solvolysis rates of adamantyl and *tert*-butyl substrates in various solvents reveals decreased values of $\log k_{t\text{-BuX}}$ in a weakly nucleophilic (strongly electrophilic) medium, and this trend is attributed to nucleophilic assistance by the solvent in heterolysis of *t*-BuX in strongly nucleophilic solvents [59–61].

The erroneous conclusion about nucleophilic assistance by a solvent originates from the use of relative quantities. The observed differences between framework and *tert*-alkyl substrates show that the influence of the solvent nucleophilicity on the rate of solvolysis of these compounds is different, but give no information about the causes of their difference. Direct evaluation of the influence of the solvent nucleophilicity on the heterolysis rate confirmed that the nucleophilic effect of the solvent, indeed, depends on the steric factor, but an increase in the steric hindrance leads to an increase in the negative effect of nucleophilic solvation, rather than to a decrease in the nucleophilic assistance by the solvent [4, 5, 7, 9, 10, 27, 35–37, 49, 50, 62–64]. In other words, the solvent nucleophilicity decreases, rather than increases, the heterolysis rate and this effect becomes stronger with an increase in the steric hindrance to nucleophilic solvation.

Abboud et al. [65, 66] showed that the rate of solvolysis of various framework substrates well correlates with the stability of their carbocations in the gas phase. They believed that the solvent nucleophilicity did not affect the solvolysis rate of these compounds and therefore suggested to use the "framework line" for revealing the occurrence or lack of nucleophilic assistance by a solvent with other substrates. The deviation from the "framework line" for *tert*-alkyl substrates was attributed to the nucleophilic assistance by the solvent in solvolysis of these compounds [61, 67]. This conclusion was confirmed by the fact that deviations from the "framework line" decreased with an increase in the steric hindrance to nucleophilic solvation from the rear side [61].

In one of their later studies [68], Abboud et al. showed that using the "framework line" for revealing the nucleophilic effect of a solvent leads to absurd conclusions. They showed that data for $PhCH_2Cl$ are well fitted by the "framework line", whereas data for $Ph_2CHCl$ strongly deviate from it. However, an opposite effect should be expected, because the solvolysis of $PhCH_2Cl$ occurs with a strong nucleophilic assistance by a solvent, as the rate of this reaction is limited by interaction of the solvent with the contact ion pair (SN2-ion pair mechanism) [69, 70], whereas the rate of heterolysis of benzhydryl halides is independent of the solvent nucleophilicity [4, 70, 71]. Thus, application of the "framework line" to revealing the nucleophilic assistance by a solvent leads to results opposite to those expected.

## EXPERIMENTAL

3-Chloro-3-methylbut-1-ene was prepared by the reaction of isoprene with HCl [72] and was purified

by double distillation, bp 42–44°C/230 mm Hg, $n_D^{20}$ 1.4192. 1,3,5-Triphenylverdazyl was prepared and purified as described in [73]. The majority of alcohols were dried by prolonged refluxing over calcined CaO, distilled, and fractionated from sodium metal. Allyl alcohol was dried over calcined $K_2CO_3$. Viscous hexanol and octanol were kept at 100°C over sodium metal grains and fractionated in a vacuum. Aprotic solvents were dried and fractionated.

Kinetic experiments were performed in a temperature-controlled cell of an SF-26 spectrophotometer. The substrate concentration in kinetic experiments was 0.01–0.5 M, and the verdazyl indicator concentration, $(1–3) \times 10^{-4}$ M. The substrate conversion in kinetic experiments was 0.001–1%, and the indicator conversion, 5–50%. The rate constants *k* were determined with an accuracy of ±3%.

Below are given the solvent, temperature (°C), and $k \times 10^7$ ($s^{-1}$). MeOH. 11.6, 283; 16.7, 605; 21.2, 1050; 25.0, 1470; 25.6, 1460; 30.2, 2560. Allyl alcohol. 22.0, 452; 25.0, 643; 27.0, 825; 32.4, 1310; 38.0, 2840; 46.2, 4800. EtOH. 18.5, 146; 22.0, 228; 25.0, 328; 26.7, 464; 32.6, 779; 39.8, 1380. BuOH. 22.0, 40.2; 25.0, 58.4; 25.5, 60.2; 30.6, 123; 36.3, 192; 41.5, 312. *i*-BuOH. 23.5, 53.3; 25.0, 57.4; 28.5, 71.0; 38.5, 215; 46.2, 445; 51.2, 595. PentOH. 22.0, 23.9; 25.0, 35.1; 27.2, 48.3; 33.7, 93.3; 40.8, 201; 46.33, 383. *i*-PrOH. 25.0, 30.5; 27.0, 39.1; 29.1, 39.3; 35.5, 65.8; 39.0, 87.7; 47.5, 138. HexOH. 19.3, 13.4; 22.0, 19.8; 25.0, 29.7; 28.7, 46.4; 34.8, 123; 41.3, 214. Cyclohexanol. 25.0, 24.2; 26.1, 28.2; 33.3, 71.0; 40.5, 152; 48.4, 458. OctOH. 22.4, 16.0; 25.0, 22.4; 27.5, 31.2; 32.5, 54.4; 38.3, 120.0; 42.3, 170.0. 2-BuOH. 22.0, 13.6; 25.0, 18.8; 29.2, 28.7; 38.1, 80.5; 42.5, 113. t-BuOH. 22.0, 2.50; 25.0, 3.57; 27.5, 4.77; 31.0, 7.18; 34.8, 11.1; 39.7, 20.8. *t*-PentOH. 22.0, 1.15; 25.0, 1.67; 28.4, 2.38; 35.4, 4.71; 43.0, 7.87; 48.6, 11.1. Sulfolane. 25.3, 8.22; 29.9, 18.3; 32.7, 23.3; 36.7, 34.9; 40.9, 55.8. Propylene carbonate. 22.4, 5.26; 27.1, 8.99; 32.4, 18.6; 36.2, 27.3; 40.8, 56.9. γ-Butyrolactone. 22.0, 2.21; 30.6, 8.02; 37.0, 17.7; 43.5, 33.5; 52.0, 61.8. MeCN. 22.0, 1.80; 25.0, 2.75; 26.3, 3.72; 32.6, 7.58; 39.8, 19.7; 47.0, 42.8. $PhNO_2$. 18.0, 0.0758; 21.6, 0.104; 25.0, 0.174; 27.2, 0.249; 33.8, 0.515; 39.4, 0.808. PhCN. 21.4, 0.0775; 24.4, 0.134; 30.6, 0.261; 35.3, 0.417; 39.8, 0.839. PhCOMe. 20.5, 0.0589; 25.0, 0.109; 25.2, 0.118; 29.3, 0.193; 34.6, 0.315. 1,2-Dichloroethane. 17.0, 0.100; 31.2, 0.167; 40.4, 0.377; 48.5, 0.866; 56.3, 0.945. Acetone. 25.0, 0.0497; 29.5, 0.0686; 38.4, 0.137; 44.0, 0.179; 50.4, 0.299. MeCOEt. 23.1, 0.0379; 27.5, 0.0598; 32.6, 0.0996; 39.2, 0.155; 53.5, 0.642. Cyclohexanone. 22.3, 0.0341; 28.4, 0.0674; 33.7, 0.0973; 41.2, 0.200; 47.9, 0.342. 1,2-Dichlorobenzene. 34.8, 0.0349; 42.6, 0.0518; 47.3, 0.0784; 53.0, 0.100; 60.0, 0.180. PhBr. 25.5, 0.0127; 30.4, 0.0248; 33.3, 0.0292; 37.9, 0.0342; 40.9, 0.0410; 52.5, 0.137. PhCl. 29.4, 0.0844; 33.4, 0.0114; 38.0, 0.0198; 50.4, 0.0477; 55.5, 0.0710. Dioxane. 28.8, 0.00424; 34.0, 0.00613; 40.1, 0.0118; 46.5, 0.0184; 50.9, 0.0262. THF. 34.0, 0.00548; 37.2, 0.00801; 45.2, 0.0161; 54.1, 0.0349. AcOEt. 40.8, 0.00321; 44.4, 0.00474; 52.2, 0.0135; 56.0, 0.0179; 60.2, 0.0233.

Calculation by Eqs. (6)–(8) was performed using the EXCEL 97 program package, confidence level 95%.

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