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Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XXXVI.[1] Solvent Effect on the Activation Parameters of Heterolysis of 1-Methyl-1-chlorocyclohexane. Correlation Analysis of Solvation Effects in Heterolysis of 1-Methyl-1-chlorocyclohexane and 1-Methyl-1-chlorocyclopentane

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Abstract—The kinetics of heterolysis of 1-methyl-1-chlorocyclohexane in six protic and eight aprotic solvents at 25–50°C was studied by the verdazyl method; $v = k[\mathrm{RCl}]$, $E1$ mechanism. The correlation analysis of the solvent effects on the activation free energy $\Delta G^{\neq}$, enthalpy $\Delta H^{\neq}$, and entropy $\Delta S^{\neq}$ of heterolysis of 1-methyl-1-chlorocyclohexane and 1-methyl-1-chlorocyclopentane was performed for the same sets of solvents.

The heterolysis kinetics of 1-methyl-1-chlorocyclohexane was studied at 25°C in 80% aqueous ethanol [2, 3], and also in nine individual protic and 25 aprotic solvents [4]. The reaction occurs by the E1 mechanism in aprotic solvents and by the SN1 + E1 mechanism in protic solvents. In all the cases, the reaction rate is satisfactorily described by a first-order reaction equation:

$$v = k[\mathrm{RCl}]. \qquad (1)$$

The rates of the S_N1 and $E1$ reactions are determined by ionization of the covalent bond, which occurs via successive formation of contact, spatially separated, and solvation-separated ion pairs [5]:

$$\mathrm{RX} \rightleftarrows \mathrm{R^+X^-} \rightleftarrows \mathrm{R^+\cdots X^-} \rightleftarrows \mathrm{R^+}\,|\,Solv\,|\,\mathrm{X^-} \longrightarrow \text{Reaction products.}$$

In the limiting stage, the contact ion pair interacts with the solvent cavity [5, 6]. A spacially separated ion pair is formed, which rapidly transforms into a solvation-separated ion pair; the latter, in turn, rapidly transforms into reaction products.

The correlation analysis of the solvent effects on the activation parameters of heterolysis of t-BuCl [7, 8], 1-methyl-1-chlorocyclopentane [9], 1-bromo-1-methylcyclopentane, and 1-bromo-1-methylcyclohexane [1] showed that the quantities $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ depend on the solvent effects differently, which allows detailed elucidation of how the solvent affects the reaction rate.

Proceeding with studies of the solvent effects on the activation parameters of monomolecular heterolyses, we examined heterolysis of 1-chloro-1-methylcyclohexane **I** in six protic and eight aprotic solvents. The kinetic experiments were performed by the verdazyl method. The values of $\log k_{25}$ (k_{25} is the rate constant at 25°C, s^{-1}), $\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and correlation coefficient of the dependence $\log(k/T)$–$1/T$ are listed in the table together with the solvent parameters.

Correlation analysis of the solvent effects on the activation parameters of heterolysis of **I** was performed in comparison with 1-chloro-1-methylcyclopentane **II** in the same sets of solvents. Calculations were performed using Koppel–Palm equations [11], with additionally included cohesion energy density parameter δ^2 [12] [Eq. (2)], and Eq. (3):

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

$$\varphi = a_0 + a_1E_T(Z) + a_2B + a_3\delta^2, \qquad (3)$$

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

Solvent effect on the rate and activation parameters of heterolysis of 1-methyl-1-chlorocyclohexane

No.	Solvent	1-Methyl-1-chlorocyclohexane heterolysis					$\varepsilon(20)$	n_D^{20}	Z, kJ mol^{-1}	E_T, kJ mol^{-1}	E, kJ mol^{-1}	B, kJ mol^{-1}	δ^2, kJ mol^{-1} l^{-1}
		$-\log k_{25}$	$\Delta G^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	r							
1	MeOH	6.68	111 ± 3	105 ± 2	21 ± 5	0.9992	32.7	1.3286	350	232	62.3	2.61	941
2	*n*-BuOH	7.58	116 ± 2	87.5 ± 1.3	96 ± 4	0.9996	17.1	1.3992	325	210	43.1	2.76	552
3	Cyclohexanol	7.74	117 ± 2	70.8 ± 1.3	156 ± 4	0.9991	15.0	1.4674	314	196	28.9	2.89	515
4	*i*-PrOH	7.79	117 ± 2	101 ± 1	57 ± 4	0.9998	18.3	1.3773	319	203	33.6	2.82	565
5	*t*-BuOH	8.01	119 ± 2	78.4 ± 1.3	135 ± 4	0.9994	10.9	1.3848	298	184	21.8	2.95	460
6	*t*-AmOH	8.54	122 ± 2	89.4 ± 1.2	108 ± 3	0.9997	5.8[a]	1.3859	296	175	22.6	2.95	460
7	MeCN	7.98	119 ± 6	84.9 ± 3.0	113 ± 9	0.9970	37.5	1.3416	298	193	21.8	1.91	594
8	γ-Butyrolactone	8.22	120 ± 2	86.2 ± 1.3	113 ± 4	0.9995	39.0	1.4360	290	185	12.1	2.48	695
9	$PhNO_2$	8.60	122 ± 3	88.7 ± 1.5	112 ± 5	0.9993	34.8	1.5546	278	176	0.8	0.8	477
10	1,2-Dichloroethane	8.74	123 ± 1	68.7 ± 0.7	182 ± 2	0.9997	10.4	1.4451	265	175	12.6	0.48	411
11	Cyclohexanone	9.00	124 ± 4	72.7 ± 2.3	173 ± 7	0.9987	18.3	1.4510	271	171	2.1	2.89	431
12	Acetone	9.11	125 ± 5	69.2 ± 2.6	187 ± 8	0.9965	20.7	1.3588	275	177	8.8	2.68	393
13	PhCN	9.14	125 ± 4	94.9 ± 2.2	101 ± 7	0.9987	25.2	1.5282	272	176	3.3	1.85	515
14	PhCOMe	9.23	126 ± 5	99.3 ± 2.7	88 ± 8	0.9985	17.4	1.5350	274	173	2.9	2.42	464

[a] At 25°C.

where φ is the reaction parameter ($\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$); ε, dielectric constant of the solvent; *n*, refractive index; *E* and *B*, empirical electrophilicity and nucleophilicity parameters [11]; E_T and *Z*, solvatochromic parameters of the solvent ionizing power, which are satisfactorily described by the first three parameters of Eq. (2) [6, 13]; and $\delta^2 = (\Delta H_m - RT)/V_m$, the parameter characterizing the energy of the solvent self-association (ΔH_m is the molar heat of vaporization, and V_m, molar volume).

In the whole set of 14 solvents, the $\Delta H^{\neq}$–$\Delta S^{\neq}$ compensation effect is observed in heterolysis of **I**:

$$\Delta H^{\neq}_{\mathbf{I}} = (114\,000 \pm 2620) + (246 \pm 21)\Delta S^{\neq}_{\mathbf{I}};$$

$$R\ 0.960,\quad S\ 3520,\quad n\ 14.$$

Here and hereinafter, the activation parameters are given in J mol^{-1}.

The correlation $\Delta H^{\neq}_{\mathbf{II}}$–$\Delta S^{\neq}_{\mathbf{II}}$ for **II** is poor: *R* 0.838.

For six protic solvents, we obtain the following correlation:

$$\Delta H^{\neq}_{\mathbf{I}} = (113\,000 \pm 2830) + (252 \pm 27)\Delta S^{\neq}_{\mathbf{I}};$$

$$R\ 0.978,\quad S\ 2980,\quad n\ 6.$$

The compensation effect is usually associated with the manifestation of the isokinetic dependence [14, 15], according to which there is a temperature at which the reaction occurs at equal rate in all the solvents. If this were the case, the $\log k$–$1/T$ straight lines for various solvents would intercept in one point corresponding to the isokinetic temperature. To check this assumption, we chose the best temperature dependences in aprotic solvents. Computer analysis showed that the $\log k$–$1/t$ straight lines intercept in the temperature range from –164 to –135°C, in which $\log k$ varies from –35.9 to –4.19. Hence, the isokinetic relationship is not valid for heterolysis of **I**. The same is observed for heterolysis of 1-methyl-1-chlorocyclopentane in protic and aprotic solvents [9] and of 1-bromo-1-methylcyclopentane and 1-bromo-1-methylcyclohexane in protic solvents [1].

Application of Eq. (2) to 14 solvents gives approximate two-parameter correlations:

$$\Delta G^{\neq}_{\mathbf{I}} = (128\,000 \pm 1850) - (0.181 \pm 0.033)E$$
$$- (0.00\,666 \pm 0.00\,400)\delta^2;\ R\ 0.945,\ S\ 1490,$$
$$F\ 45.5\ (2.91),\ n\ 14.$$
$$\Delta G^{\neq}_{\mathbf{II}} = (123\,000 \pm 3110) - (0.279 \pm 0.056)E$$
$$- (0.00\,915 \pm 0.00\,700)\delta^2;\ R\ 0.932,\ S\ 2500,$$
$$F\ 36.6\ (2.91),\ n\ 14.$$

Here F is the observed and critical (in parentheses) Fisher test at 95% confidence level [16]. The solvent parameters are given in J mol^{-1}. The polarity, polarizability, and nucleophilicity parameters of the solvents are insignificant.

The ratio of the observed Fisher test to the critical value shows that the two-parameter models are highly reliable. Since these dependences were obtained for the same set of solvents, we can evaluate the relative effect of each parameter from the ratio of the coefficients at the solvent parameters. It is seen that the logarithm of the heterolysis rate constant of **II**, compared to **I**, is more strongly affected by the electrophilicity and cohesion (by factors of 1.5 and 1.4, respectively).

Application of Eq. (3) gives satisfactory one-parameter correlations:

$$\Delta G^{\neq}_{\mathbf{I}} = (168\,000 \pm 4470) - (0.160 \pm 0.015)Z;\ R\ 0.950,$$
$$S\ 1350,\ F\ 112\ (2.69),\ n\ 14.$$
$$\Delta G^{\neq}_{\mathbf{II}} = (185\,000 \pm 6790) - (0.244 \pm 0.023)Z;$$
$$R\ 0.951,\ S\ 2060,\ F\ 112\ (2.69),\ n\ 14.$$

The solvent ionizing power affects the logarithm of the heterolysis rate constant of **II** by a factor of 1.5 more strongly compared to **I**.

Thus, in the set of six protic and eight aprotic solvents, enhancement of the ionizing power, electrophilicity, and cohesion of the solvent accelerates heterolysis of **I** and **II**.

The solvent parameters in Eqs. (2) and (3) for 14 solvents are independent variables. A slight mutual correlation [17] is observed for the following pairs: δ^2–E_T (r 0.819), δ^2–Z (r 0.747), E–$f(n)$ (r 0.674), and δ^2–E (r 0.712); the other correlation coefficients are less than 0.5. Here, $f(n) = (n^2 - 1)/(n^2 + 2)$.

Application of Eq. (2) to six protic solvents gives good two-parameter correlations:

$$\Delta G^{\neq}_{\mathbf{I}} = (146\,000 \pm 4570) - (49\,700 \pm 11900)f(\varepsilon)$$
$$- (0.0117 \pm 0.0020)\delta^2;\ R\ 0.988,\ S\ 687,\ F\ 63.0\ (9.01),\ n\ 6.$$
$$\Delta G^{\neq}_{\mathbf{II}} = (137000 \pm 5470) - (45700 \pm 4260)f(\varepsilon)$$
$$- (0.0157 \pm 0.0030)\delta^2;\ R\ 0.988,\ S\ 822,\ F\ 59.7\ (9.01),\ n\ 6.$$

Here, $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$. In protic solvents, the polarity affects the heterolysis rates of **I** and **II** similarly, whereas the effect of cohesion is by a factor of 1.3 stronger in the case of **II**.

Application of Eq. (3) to protic solvents gives one-parameter correlations:

$$\Delta G^{\neq}_{\mathbf{I}} = (151\,000 \pm 4230) - (0.168 \pm 0.021)E_T;$$
$$R\ 0.970,\ S\ 948,\ F\ 63.8\ (6.26),\ n\ 6. \quad (4)$$
$$\Delta G^{\neq}_{\mathbf{II}} = (146\,000 \pm 5950) - (0.193 \pm 0.030)E_T;$$
$$R\ 0.956,\ S\ 1340,\ F\ 42.4\ (6.26),\ n\ 6. \quad (5)$$

In protic solvents, the solvent ionizing power affects the heterolysis of **II** by a factor of 1.15 more strongly compared to **I**.

In the protic solvents examined in this study, some of the solvent parameters show strong mutual correlation, especially the following pairs of parameters: B–E (r 0.995), B–E_T (r 0.980), B–Z (r 0.987), δ^2–E (r 0.943), δ^2–E (r 0.927), δ^2–Z (r 0.926), δ^2–E_T (r 0.898), $f(\varepsilon)$–B (r 0.758), $f(\varepsilon)$–E (r 0.720), $f(n)$–δ^2 (r 0.657), and δ^2–$f(\varepsilon)$ (r 0.644). This complicates interpretation of the solvation effects in protic solvents. For example, correlations (4) and (5) may mean that $\Delta G^{\neq}$ depends on the solvent electrophilicity or nucleophilicity. However, with these parameters, we obtain only approximate correlations suggesting that $\Delta G^{\neq}$ is determined not only by these effects.

$$\Delta G^{\neq}_{\mathbf{I}} = (125\,000 \pm 1540) - (0.213 \pm 0.041)E;$$
$$R\ 0.934,\ S\ 1390,\ F\ 27.5\ (6.26),\ n\ 6.$$
$$\Delta G^{\neq}_{\mathbf{II}} = (116\,000 \pm 1840) - (0.247 \pm 0.048)B;$$
$$R\ 0.931,\ S\ 1660,\ F\ 26.0\ (6.26),\ n\ 6.$$
$$\Delta G^{\neq}_{\mathbf{I}} = (46\,800 \pm 13\,800) + (24.8 \pm 4.9)B;$$
$$R\ 0.931,\ S\ 1420,\ F\ 26.0\ (6.26),\ n\ 6. \quad (6)$$
$$\Delta G^{\neq}_{\mathbf{II}} = (24\,400 \pm 14\,800) + (29.2 \pm 5.2)B;$$
$$R\ 0.942,\ S\ 1530,\ F\ 31.2\ (6.26),\ n\ 6. \quad (7)$$

The latter dependences show that an increase in the solvent electrophilicity results in decreased $\Delta G^{\neq}$, and an increase in its electrophilicity, in increased $\Delta G^{\neq}$; both parameters affect **II** by a factor of 1.2 more strongly than **I**. In protic solvents, the effect of nucleophilic solvation is negative, which is due to nucleophilic solvation of the contact ion pair formed before the limiting stage [5]. The occurrence of this effect in protic solvents and in the whole set of protic and aprotic solvents is also indicated by an increase in the reaction rate with increasing solvent cohesion: The higher the cohesion, the more difficult is withdrawal of the solvent molecule from the bulk of the solvent for nucleophilic solvation [5].

Application of Eq. (2) to seven aprotic solvents (nos. 7, 8, 10–14; solvent numbering as in the table) led to the following correlations:

$$\Delta G^{\neq}_{\mathbf{I}} = (131\,000 \pm 1730) - (0.268 \pm 0.057)E$$

$$- (0.0113 \pm 0.0040)\delta^2; \; R\ 0.966,\ S\ 892,\ F\ 27.6\ (6.16),\ n\ 7.$$

$$\Delta G^{\neq}_{\mathbf{II}} = (133\,000 \pm 1790) - (0.287 \pm 0.060)E$$

$$- (0.0270 \pm 0.0040)\delta^2; \; R\ 0.985,\ S\ 925,\ F\ 64.6\ (6.16),\ n\ 7.$$

The electrophilicity of aprotic solvents affects the heterolysis rate of both substrates to a similar extent, whereas the effect of cohesion on **II** is by a factor of 2.4 stronger than that on **I**. The solvent parameters in Eq. (2) for seven aprotic solvents are independent variables. The greatest mutual correlation was observed for the following pairs: δ^2–Z (r 0.808), δ^2–E_T (r 0.741), δ^2–$f(\varepsilon)$ (r 0.741), $f(\varepsilon)$–B (r 0.610), and E–$f(n)$ (r 0.757).

Thus, in protic solvents the reaction rate grows with increasing solvent polarity and cohesion, and in aprotic solvents it grows with increasing solvent electrophilicity and cohesion. The effect of nucleophilic solvation is negative.

Application of Eqs. (2) and (3) to correlation analysis of the solvent effects on the activation enthalpy and entropy only seldom gives satisfactory results, especially in the case of $\Delta H^{\neq}$.

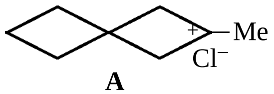
For seven aprotic solvents (nos. 7, 8, 10–14), Eq. (2) gives the following correlation:

$$\Delta H^{\neq}_{\mathbf{I}} = (151\,000 \pm 72\,300) - (451\,000 \pm 172\,000)f(\varepsilon)$$

$$+ (476\,000 \pm 55\,400)f(n) + (2.37 \pm 0.38)E;$$

$$R\ 0.982,\ S\ 2900,\ F\ 27.4\ (8.94),\ n\ 7.$$

The activation enthalpy decreases with increasing solvent polarity and grows with increasing electrophilicity and polarizability. Increase in the solvent polarity favors stabilization of the cationoid intermediate; the effect of polarizability suggests the occurrence of the negative effect of nucleophilic solvation: higher polarizability favors nucleophilic solvation of the contact ion pair. The effect of the solvent electrophilicity is apparently associated with the resolvation [1, 18] in the course of formation in the transition state of ion-pair *twist* conformer **A** [3, 19]; the electrophilicity favors solvation of the earlier cationoid intermediate.



A

In five protic solvents (nos. 1–4, 6), $\Delta H^{\neq}_{\mathbf{I}}$ decreases with increasing polarizability.

$$\Delta H^{\neq}_{\mathbf{I}} = -(203\,000 \pm 18\,800) - (475\,000 \pm 78\,500)f(n);$$

$$R\ 0.961,\ S\ 4210,\ F\ 36.6\ (9.12),\ n\ 5.$$

Application of Eq. (2) to $\Delta S^{\neq}$ in six protic solvents gives the following two-parameter correlations:

$$\Delta S^{\neq}_{\mathbf{I}} = (711 \pm 210) - (1200 \pm 489)f(n) - (0.185 \pm 0.089)B;$$

$$R\ 0.943,\ S\ 21.5,\ F\ 11.9\ (9.01),\ n\ 6.$$

$$\Delta S^{\neq}_{\mathbf{II}} = (876 \pm 175) + (1460 \pm 407)f(n) - (0.460 \pm 0.075)B;$$

$$R\ 0.963,\ S\ 17.9,\ F\ 19.0\ (9.01),\ n\ 6.$$

Increased nucleophilicity of the solvent results in decreased activation entropy of the heterolysis of both substrates, which is associated with the solvation of the contact ion pair. Increased polarizability of the solvent results in increased $\Delta S^{\neq}$ for **II** and decreased $\Delta S^{\neq}$ for **I**, which is probably also associated with the resolvation effect.

In six aprotic solvents (nos. 7–9, 11, 13, 14), the polarizability and electrophilicity increase $\Delta S^{\neq}$ of both substrates.

$$\Delta S^{\neq}_{\mathbf{I}} = -(618 \pm 78) + (1590 \pm 248)f(n)$$

$$+ (0.00776 \pm 0.00100)E;$$

$$R\ 0.966,\ S\ 9.76,\ F\ 21.0\ (9.01),\ n\ 6.$$

$$\Delta S^{\neq}_{\mathbf{II}} = -(447 \pm 68) + (1070 \pm 217)f(n)$$

$$+ (0.00654 \pm 0.00100)E;$$

$$R\ 0.961,\ S\ 8.54,\ F\ 18.2\ (9.01),\ n\ 6.$$

In aprotic solvemnts, the positive effect of the polarizability and electrophilicity on $\Delta S^{\neq}$ of heterolysis of **I** is by factors of 1.5 and 1.2, respectively, stronger as compared to **II**.

In aprotic solvents, the resolvation effect in heterolysis of **I** is apparently insignificant; therefore, the solvent polarizability affects mainly the solvation of the transition state and facilitates the reaction.

Thus, increases in the ionizing power, electrophilicity, polarity, and cohesion of solvents result in decreased activation free energy of the heterolysis of both substrates. The negative effects of polarizability and nucleophilicity, manifested in heterolysis of 1-bromo-1-methylcyclohexane and 1-bromo-1-methylcyclopentane [1], are not observed in heterolysis of **I** and **II**. This may be due to the stronger effect of the solvent electrophilicity on the heterolysis rate in the case of chlorides. The indirect negative effect of the nucleophilic solvation in heterolysis of chlorides is manifested in the growth of $\Delta G^{\neq}$ with increasing solvent cohesion. Indeed, we showed previously that, when a larger set of solvents is considered, the negative effect of the nucleophilicity on the heterolysis rate is revealed for both chlorides [4, 20]. In our case, the negative effect of the polarizability is associated with the activation enthalpy, and the negative effect of the nucleophilicity, with the activation entropy.

The quantity $\Delta G^{\neq}_{\mathbf{I}}$ in protic solvents is independent of the polarizability. This is due to the fact that the parameter $f(n)$ has a negative effect on both $\Delta H^{\neq}_{\mathbf{I}}$ and $\Delta S^{\neq}_{\mathbf{I}}$. Acceleration of the heterolysis of **I** in aprotic solvents with increasing E is due to the effect of the solvent electrophilicity on the activation entropy.

EXPERIMENTAL

The procedures for synthesis of chlorides and purification of the solvents were reported elsewhere [2, 4]. Kinetic experiments were run in a temperature-controlled cell of an SF-26 spectrophotometer. The concentration of **I** in kinetic experiments was 0.01–0.8 M, and that of verdazyl indicator, $(1–2) \times 10^{-4}$ M. The conversion of the substrate in kinetic experiments was 0.01–0.0005%. Below are given the solvent, temperature (°C), and mean values of $k \times 10^8$ (s^{-1}) from 2–3 replicate runs. MeOH: 25.0, 21.1±0.1; 31.0, 51.3±0.1; 35.0, 90.5±0.3; 39.0, 158±2; 44.0, 276±1. BuOH, 25.0, 2.61±0.04; 30.0, 4.98±0.02; 35.0, 8.60±0.02; 39.0, 13.6±0.1; 45.0, 24.9±0.1; 50.0, 45.5±0.2. Cyclohexanol: 25.0, 1.81±0.01; 30.5, 3.38±0.01; 33.5, 4.28±0.02; 40.5, 7.69±0.05; 43.0, 10.3±0.1; 45.0, 12.3±0.3; 47.0, 14.2±0.1; 49.5, 17.7±0.3. *i*-PrOH: 25.0, 1.61±0.01; 30.0, 2.99±0.03; 41.0, 13.3±1.0; 45.0, 22.2±0.1; 50.0, 38.7±0.3; 50.5, 41.2±0.2. *t*-BuOH: 25.0, 0.978±0.002; 31.5, 1.87±0.05; 35.5, 3.06±0.03; 40.5, 4.86±0.05; 45.5, 7.89±0.01. *t*-PentOH: 25.0, 0.288±0.002; 33.5, 0.849±0.001; 40.5, 1.83±0.01; 45.5, 3.10±0.05; 50.0, 5.25±0.02. γ-Butyrolactone: 25.0, 0.597±0.003; 31.0, 1.17±0.03; 35.0, 1.95±0.02; 40.0, 3.48±0.01; 45.0, 5.68±0.02; 49.5, 8.85±0.01. CH_3CN: 25.0, 1.05±0.01; 30.0, 1.76±0.10; 35.0, 3.04±0.05; 40.0, 5.03±0.03; 44.5, 9.51±0.10. PhCN: 25.0, 0.0726±0.0016; 30.5, 0.132±0.003; 36.0, 0.296±0.002; 40.0, 0.460±0.010; 45.5, 0.877±0.007. $PhNO_2$: 25.0, 0.250±0.010; 31.0, 0.514±0.001; 35.5, 0.933±0.005; 40.5, 1.51±0.01; 45.5, 2.69±0.09. Acetone: 25.0, 0.0782±0.0001; 25.5, 0.0860±0.0015; 30.0, 0.126±0.010; 34.0, 0.166±0.020; 40.0, 0.319±0.001; 44.5, 0.476±0.006. Cyclohexanone: 25.0, 0.100±0.002; 30.5, 0.179±0.004; 40.0, 0.478±0.008; 46.0, 0.727±0.001; 50.5, 1.11±0.09. Acetophenone: 25.0, 0.0595±0.0002; 27.0, 0.0668±0.0014; 35.5, 0.231±0.004; 40.0, 0.399±0.010; 44.5, 0.688±0.012. 1,2-Dichloroethane: 25.0, 0.180±0.001; 30.0, 0.293±0.004; 35.0, 0.470±0.001; 39.5, 0.675±0.002; 43.5, 0.976±0.010.

Calculations with Eqs. (2) and (3) were performed by the least-squares method using the Spss software; confidence level 95%.

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