Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XLII.¹ Effect of Aprotic Solvent on the Rate of 3-Methyl-3-chloro-1-butene Dehydrochlorination. Correlation Analysis of Solvation Effects

N. E. Ponomarev, V. V. Zaliznyi, and G. F. Dvorko

Kiev Polytechnic Institute, National Technical University of Ukraine, Kiev, Ukraine

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Abstract — The kinetics of 3-methyl-3-chloro-1-butene dehydrochlorination in propylene carbonate, γ -butyrolactone, sulfolane, acetone, MeCN, PhNO₂, PhCN, PhCOMe, MeCOEt, cyclohexanone, *o*-dichlorobenzene, PhCl, PhBr, 1,2-dichloroethane, dioxane, and AcOEt were studied; $v = k[C_5H_9Cl]$, *E*1 mechanism. The reaction rate is satisfactorily described by the parameters of the polarity, electrophilicity, and cohesion of the solvent; the solvent nucleophilicity and polarizability exert no effect on the reaction rate.

The rate of monomolecular heterolysis $(S_N 1, E1, E1)$ solvolysis) strongly depends on the solvent, which is due to intense solvation of the polar transition state. The nature of the solvation effects depends on the substrate structure. As shown for 15 tertiary substrates (t-BuX, 1-AdX, 1-halo-1-methylcycloalkanes, ArCCl₃, PhCMe₂Cl, Ph₂CCl₂, 2-bromo-2-methyladamantane), the heterolysis rate increases with an increase in the polarity and electrophilicity of the solvent or in its ionizing power and decreases with an increase in the solvent nucleophilicity and polarizability [2–7]. The heterolysis rate of secondary substrates is independent of the solvent nucleophilicity and is satisfactorily described by the parameters of the solvent polarity and electrophilicity, or of its ionizing power [2, 3]. This was demonstrated by the examples of Ph₂CHBr [8], 1-phenyl-1-chloroethane [9], 7- α bromocholesterol benzoate [10], and 3-bromocyclohexeane [11]. The solvent cohesion usually increases the rate of heterolysis of tertiary substrates and exerts no effect on that of secondary substrates.

Monomolecular heterolysis usually occurs via successive formation of three ion pairs: contact (A), spacially separated (B), and solvation-separated (C) [2, 3].

In the limiting step, ion pair A interacts with the solvent cavity (cavities account for $\sim 10\%$ of the liquid volume [12]) to form ion pair B, which rapidly transforms into ion pair C and then, also rapidly, into reaction products.

The difference between secondary and tertiary substrates is associated with the steric hindrance to nucleophilic solvation of the substrate from the rear side. In secondary substrates this solvation is sterically possible, whereas in tertiary substrates it is hindered or impossible. In heterolysis of tertiary substrates, it is ion pair A forming before the limiting step that is subject to nucleophilic solvation. The solvation stabilizes this intermediate and hinders formation of the transition state. In heterolysis of secondary substrates, equilibrium solvation of the transition state is observed, with the solvation shells of the initial and transition states having similar structure (one of solvates of the initial state reaches the transition state [13]). In the case of tertiary substrates, we can speak of nonequilibrium solvation, because the solvation shells of the initial and transition states have different structures [14].

A kinetic study of the solvolysis of 3-methyl-3chloro-1-butene **I** showed that the solvation effects observed with this compound in protic solvents differ essentially from those observed with the previously studied tertiary substrates [1]. The rate of heterolysis of **I** in 13 alcohols (MeOH, EtOH, BuOH, CH₂=CH · CH₂OH, *i*-BuOH, *i*-PrOH, PentOH, HexOH, OctOH,

¹ For communication XLI, see [1].

cyclohexanol, s-BuOH, t-BuOH, t-PentOH) grows with an increase in the solvent ionizing power E_T and is virtually independent of its nucleophilicity. Such trends are typical of secondary substrates.

In this study we examined how the rate of heterolysis of I depends on the nature of the aprotic solvent. It is known [2, 3, 11] that, in cases when the solvent nucleophilicity exerts no effect on the reaction rate (secondary substrates), a satisfactory linear correlation $\log k - E_T$ (k is the reaction rate constant), common for protic and aprotic solvents, is observed. In cases when the solvent nucleophilicity exerts a negative effect on the reaction rate (tertiary substrates), two separate linear correlations $\log k - E_T$ are observed for protic and aprotic solvents. This is due to the fact that the negative effect of the nucleophilic solvation is manifested in protic solvents considerably more strongly; therefore, the values of $\log k$ in protic solvents are lower than those estimated from the $\log k - E_T$ correlations for aprotic solvents.

We studied the kinetics of heterolysis of I in 17 aprotic solvents. The kinetic experiments were performed by the verdazyl method [15]. As internal indicator we used 1,3,5-triphenylverdazyl (Vd), which rapidly and quantitatively reacts with ion pair C of the substrate to form isoprene, verdazylium salt (Vd⁺Cl⁻), and leucoverdazyl (VdH). The reaction follows the equation

$$CH_{2}=CHCMe_{2}Cl+2 \xrightarrow[N]{N} \stackrel{N}{\longrightarrow} CH_{2}=CH-C=CH_{2} + \underbrace{N}_{Ph} \stackrel{N}{\longrightarrow} \stackrel{N}{\longrightarrow}$$

The reaction rate was monitored spectrophotometrically by a decrease in the Vd concentration (λ_{max} ~720 nm). It is satisfactorily described by a first-order kinetic equation, *E*1 mechanism.

$$v = -\frac{d[\mathrm{Vd}^{\,}]}{2d\tau} = k[\mathbf{I}].$$

The substrate concentration in kinetic experiments was 0.01-0.7 M; concentration of the verdazyl indicator, $(0.8-2.4) \times 10^{-4}$ M; substrate conversion, 0.1-0.001%; and verdazyl conversion, 10-30%.

The rate constants at 25°C and the solvent parameters required for the correlation analysis of the solvation effects are given in the table. The correlation analysis was performed using the Koppel–Palm equations based on the linear free energy relationship [16] with additional inclusion of the cohesion energy density parameter δ^2 [17] [Eq. (1)], Kamlet–Taft equation [Eq. (2)] [18], and Eq. (3):

$$\log k = a_0 + a_1 \frac{\varepsilon - 1}{\varepsilon + 1} + a_2 \frac{n^2 - 1}{n^2 + 1} + a_3 E + a_4 B + a_5 \delta^2 / 100, \qquad (1)$$

$$\log k = a_0 + a_1 \pi^* + a_2 \alpha_2 + a_3 \beta + a_4 \delta^2 / 100, \quad (2)$$

$$\log k = a_0 + a_1 E_T + a_2 \frac{n^2 - 1}{n^2 + 1} + a_3 B + a_4 \delta^2 / 100, \qquad (3)$$

where ε is the dielectric permittivity of the solvent; *n*, refractive index; *E* and α , empirical parameters of the electrophilicity; *B* and β , empirical parameters of the nucleophilicity; π^* , dipolarity (polarity + polarizability) parameter; E_T , solvatochromic parameter of the solvent ionizing power; $\delta^2 = (\Delta H_M - RT)/V_M$, parameter characterizing the energy of interaction of solvent molecules with each other; ΔH_M , molar heat of vaporization; V_M , molar volume; and a_i , coefficients characterizing the contributions of the corresponding parameters. The solvent parameters were taken from [16, 19, 20].

The use of Eq. (1) leads to a satisfactory threeparameter correlation (4):

$$log k = -(12.3 \pm 0.7) + (2.83 \pm 0.98) f(\varepsilon) + (0.0653 \pm 0.0064) E + (0.322 \pm 0.108) \delta^{2},$$
(4)
R 0.960, S 0.52, F 101 (2.60), N 17.

Here $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 1)$; *F* is the observed and critical (in parentheses) Fisher test [21]; the fact that the observed Fisher test is higher than the critical value indicates that the model is reliable.

Exclusion of the most outlying point (ethyl acetate) appreciably improves the correlation [Eq. (5)]:

$$log k = -(11.7 \pm 0.6) + (2.52 \pm 0.87) f(\varepsilon) + (0.0660 \pm 0.0051) E + (0.267 \pm 0.009) \delta^{2},$$
(5)
R 0.972, S 0.41, F 143 (2.71), N 16.

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		T	г	r		r	т	т
Solvent	Solvent	$k_{25} \times 10^7$,	-log kar	<i>E_T</i> ,	8	$n_{\rm D}^{20}$	<i>E</i> ,	<i>B</i> ,
no.	Sorvent	s ⁻¹	108125	kJ mol ⁻¹	0	"D	kJ mol ⁻¹	kJ mol ⁻¹
1	Sulfolane	8.78	6.06	184	42.1	1.481	10	1.88
2	Propylene carbonate	7.08	6.15	195	62.9	1.421	21	2.18
3	γ-Butyrolactone	3.63	6.44	185	41	1.437	12	2.48
4	Acetonitrile	2.75	6.56	191	35.9	1.344	21	1.91
5	Nitrobenzene	0.174	7.76	173	36.1	1.551	0	0.8
6	Benzonitrile	0.123	7.91	173	25.2	1.528	8 0	1.85
7	Acetophenone	0.11	7.96	170	18.2	1.534	0	2.42
8	1,2-Dichloroethane	0.0955	8.02	173	10.4	1.551	9.6	0.48
9	Acetone	0.0501	8.30	176	21.4	1.359	8.5	2.68
10	Methyl ethyl ketone	0.0457	8.34	173	18.9	1.379	5.4	2.5
11	Cyclohexanone	0.0457	8.34	166	16	1.451	0	2.89
12	o-Dichlorobenzene	0.0162	8.79	159	10.4	1.551	0	0.33
13	Bromobenzene	0.0129	8.89	153	5.55	1.56	0	0.48
14	Chlorobenzene	0.00575	9.24	154	5.74	1.524	0	0.45
15	1,4-Dioxane	0.00295	9.53	150	2.27	1.422	2 0	2.84
16	Tetrahydrofuran	0.00229	9.64	156	7.39	1.408	8 0	3.43
17	Ethyl acetate	0.000513	10.29	159	6	1.372	6.7	2.17
Solvent no.	Solvent	δ ² /100,	, kJ l ⁻¹	π*	0	α		μ, D
1	Sulfolane	6.	9	0.98	()	0.39	4.81
2	Propylene carbonate	7.	7.4		()	0.4	4.38
3	γ-Butyrolactone	6.	6.95		()	0.49	4.12
4	Acetonitrile	5.	5.86		().19	0.4	3.44
5	Nitrobenzene	5.	5.11		()	0.3	4.03
6	Benzonitrile	5.	5.15		()	0.37	4.05
7	Acetophenone	4.	4.33		().04	0.49	2.96
8	1,2-Dichloroethane	4.	4.12		()	0.1	1.75
9	Acetone	3.	3.88		().08	0.43	2.64
10	Methyl ethyl ketone	3.	3.61		().06	0.48	2.76
11	Cyclohexanone	4.	4.08		()	0.53	3.01
12	o-Dichlorobenzene	4.	4.2		()	0.03	2.77
13	Bromobenzene	4		0.79	()	0.06	1.55
14	Chlorobenzene	3.	76	0.71	()	0.07	1.54
15	1,4-Dioxane	4.	4.2		()	0.37	0.45
16	Tetrahydrofuran	3.	61	0.58	()	0.55	1.75
17	Ethyl acetate	3.	39	0.55	()	0.45	1.88
		1			1			

Solvent effect on the rate of heterolysis of 3-methyl-3-chloro-1-butene I and solvent parameters

The effect of the polarizability and nucleophilicity parameters on the correlation quality is insignificant; with their inclusion, R 0.979.

The use of Eq. (2) leads to a similar result [Eq. (6)]:

$$log k = -(13.8 \pm 0.5) + (2.98 \pm 0.82)\pi^* + (6.85 \pm 1.81)\alpha + (0.672 \pm 0.087)\delta^2,$$
(6)
R 0.967. S 0.35. F 62 (2.71). N 17.

The nucleophilicity parameter exerts no effect on the correlation quality: with its inclusion, R 0.968.

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Proceeding from Eq. (3), we obtain a satisfactory two-parameter correlation (7):

$$\log k = -(18.7 \pm 1.6) + (0.0490 \pm 0.0117) E_T + (0.465 \pm 0.123) \delta^2,$$
(7)
R 0.959, *S* 0.38, *F* 80 (2.52), *N* 17.

The correlation quality is considerably improved after exclusion of AcOEt [Eq. (8)]:

$$log k = -(18.4 \pm 1.1) + (0.0494 \pm 0.0080)E_T + (0.403 \pm 0.086)\delta^2, \qquad (8)$$

R 0.978, S 0.26, F 140 (2.60), N 16.



Effect of the solvent ionizing power E_T on the rate of heterolysis of 3-methyl-3-chloro-1-butene I (25°C). (1–17) Figures are solvent numbers in the table; (18) MeOH, (19) CH₂=CHCH₂OH, (20) EtOH, (21) BuOH, (22) *i*-BuOH, (23) PentOH, (24) *i*-PrOH, (25) HexOH, (26) cyclohexanol, (27) OctOH, (28) *s*-BuOH, (29) *t*-BuOH, and (30) *t*-PentOH; (*a*–*c*) for comments, see text.

After exclusion of AcOEt and sulfolane, we obtain a satisfactory one-parameter correlation (9):

$$\log k = -(20.7 \pm 1.1) + (0.0743 \pm 0.0066)E_T, \quad (9)$$

R 0.953, S 0.34, F 12.7 (2.62), N 15.

Thus, the rate of heterolysis of chloride I in aprotic solvents, as in protic solvents, depends on the polarity (dipolarity) and electrophilicity of the solvent, or on its ionizing power. In aprotic solvents, the solvent cohesion makes a significant contribution. When this parameter is excluded, the correlation becomes considerably worse or is broken at all.

In an aprotic medium, the major factor is electrostatic (dipolar) solvation occurring via formation of linear or cyclic quadrupoles from the substrate and solvent dipoles. In this case, there should be a strong correlation between the heterolysis rate and dipole moment of the solvent (μ). Indeed, we found that these quantities in 14 solvents (1–3, 5–7, 9–16; here and hereinafter, the solvent numbering is the same as in the table) are correlated [Eq. (10)]:

$$log k = -(10.5 \pm 0.3) + (0.805 \pm 0.102)\mu,$$
(10)
R 0.916, S 0.49, F 63 (2.75), N 14.

The heterolysis rate in ethyl acetate is considerably lower than that estimated from the $\log k-E_T$ correlation for the other solvents (see figure); therefore, exclusion of this point substantially improves the quality of the correlations obtained using Eqs. (1) and (3). The quantity $\log k_{25}$ for this solvent (see table) was calculated by extrapolation of the dependence $\log (k/T)-1/T$ (R 0.992) obtained for higher temperatures and is beyond question. The observed deviation is apparently caused by steric hindrance arising in solvation of the substrate with solvents containing acetyl group. Indeed, the points for acetone (no. 9) and methyl ethyl ketone (no. 10) also lie below the $\log k-E_T$ straight line (see figure).

In protic solvents, the contribution of the dipolar solvation is apparently insignificant. Indeed, in 13 alcohols studied, the rate of solvolysis of chloride **I** varies by three orders of magnitude at virtually constant dipole moment of the solvent (1.7–1.8 D). The major contribution in protic solvents is made by electrophilic solvation via H-bonding of the nucleofuge. The solvation effects in protic solvents are more uniform than in aprotic solvents. This is manifested in the fact that the variance in the log $k-E_T$ correlation for protic solvents is considerably smaller than for aprotic solvents (see figure).

In aprotic solvents, it is difficult to reveal the effect of the solvent nucleophilicity on the reaction rate [3]. Chloride I in aprotic solvents behaves in some cases as a secondary substrate and in other cases, as a tertiary substrate. Indeed, a satisfactory correlation of the reaction rate with E_T [Eq. (9)] in both protic and aprotic solvents is characteristic of heterolysis of secondary substrates [2, 3, 8–11], and the effect of the cohesion on the reaction rate [Eqs. (5)–(8)] is usually observed in the heterolysis of tertiary substrates [2–7].

In some cases, the effect of the solvent nucleophilicity on the heterolysis rate can be revealed when only dipolar aprotic solvents are considered in the correlation analysis of the solvation effects. For example, the activation free energy of heterolysis of 1-methyl-1-chlorocyclopentane in eight solvents (nos. 3–9, 11) grows with an increase in the solvent nucleophilicity and polarizability [22]:

 $\Delta G^{\neq} = 122\,000 + 35\,700f(n) + 1.72B - 0.0357\delta^2, \quad (11)$ R 0.993, S 0.64, F 94 (6.1), N 8;

$$\Delta G^{\neq} = 176\,000 - 0.288E_T + 1.03B - 0.0216\delta^2, (12) R 0.989, S 0.18, F 61 (6.1), N 8.$$

A decrease in the reaction rate with an increase in the solvent polarizability is associated with the negative effect of the nucleophilic solvation, since an increase in the solvent polarizability favors the nucleophilic solvation of the contact ion pair.

With log k used instead of ΔG^{\neq} , we obtain for the same substrate in the same solvents similar correlations (13) and (14) based on Eqs. (1) and (3):

$$log k_{C_5H_9Cl} = -(8.06 \pm 0.50) - (5.37 \pm 0.97)f(n) + (0.243 \pm 0.055)B - (0.564 \pm 0.039)\delta^2,$$
(13)
R 0.993, S 0.11, F 97 (8.89), N 8;

$$\log k_{\rm C_5H_9Cl} = -(7.63\pm0.67) - (6.07\pm1.42)f(n) - (0.253\pm0.083)B + (0.535\pm0.046)\delta^2, \quad (14) R 0.987, S 0.14, F 52 (8.89), N 8,$$

where $f(n) = (n^2 - 1)/(n^2 + 1)$.

A similar pattern is observed in the heterolysis of cumyl chloride. In a wide range of aprotic solvents (N 20), the reaction rate is independent of the solvent nucleophilicity, and in dipolar aprotic solvents (nos. 2–4, 7–9, MeNO₂, DMF) the solvent nucleophilicity decreases the reaction rate. Using Eqs. (1) and (3), we obtain relationships (15) and (16):

$$\log k_{\text{PhCMe}_2\text{Cl}} = -(15.8 \pm 0.4) + (0.077 \pm 0.0249)E$$

- (0.186 ±0.113)B + (0.285 ±0.175)\delta^2, (15)
R 0.969, S 0.29, F 20 (8.89), N 8;
$$\log k_{\text{PhCMe}_2\text{Cl}} = - (15.7 \pm 3.8) + (0.0476 \pm 0.0249)E_T$$

+ (0.282 ±0.175)\delta^2 - (0.186 ±0.113)B, (16)
R 0.969, S 0.29, F 20 (8.89), N 8.

Application of Eqs. (1) and (3) to the correlation analysis of the heterolysis of chloride I in nine dipolar aprotic solvents (nos. 1-6, 8, 9, 11) shows that the solvent nucleophilicity exerts no effect on the reaction rate.

Thus, the negative effect of the nucleophilic solvation in the heterolysis of chloride **I** in aprotic solvents is not revealed. Manifestation of this effect strongly depends on the solvent set chosen, substrate structure (including the nature of the nucleofuge), and choice of the correlation equation [3]. This effect is more pronounced in protic solvents than in aprotic solvents. It is frequently revealed by combined consideration of data for protic and aprotic solvents [3, 8, 23, 24].

We performed a correlation analysis of the solvation effects in 17 aprotic (nos. 1–17) and 13 protic (nos. 18–30) solvents. The correlation $\log k = f(E_T)$ for the heterolysis of I in protic and aprotic solvents is shown in the figure. The numbering of the protic solvents is given in the figure caption. We can distinguish two separate linear correlations: one for protic solvents (straight line a) and another one for aprotic solvents (straight line b), as in the case of tertiary substrates. Straight line c corresponding to the whole set of data virtually coincides with the straight line for aprotic solvents, as in the case of secondary substrates.

Application of Eqs. (1)–(3) to the whole set of the solvents shows that the nucleophilicity and polarizability exert no effect on the reaction rate [Eqs. (17)–(19)]:

$$\log k_{\mathbf{I}} = -(12.3 \pm 0.7) + (0.0653 \pm 0.0064)E + (2.83 \pm 0.98)f(\varepsilon) + (0.322 \pm 0.108)\delta^{2}, \quad (17)$$

$$R \ 0.960, \ S \ 0.52, \ F \ 101 \ (1.95), \ N \ 30;$$

$$\log k_{\mathbf{I}} = -(11.8 \pm 0.6) + (1.12 \pm 0.99)\pi^{*} + (3.52 \pm 0.56)\alpha + (0.600 \pm 0.114)\delta^{2}, \quad (18)$$

$$R \ 0.958, \ S \ 0.53, \ F \ 97 \ (1.95), \ N \ 30;$$

$$\log k_{\mathbf{I}} = -(2.11 \pm 0.80) + (0.0770 \pm 0.0041)E_{T}, \quad (19)$$

Thus, in contrast to the previously studied tertiary substrates, the solvent nucleophilicity exerts no effect on the rate of the heterolysis of **I**. This does not mean that the nucleophilic solvation does not take place in the heterolysis of this substrate: it occurs always. There are stoichiometric evidences of the nucleophilic solvation of the initial state of substrates reacting by the $S_N 1$ or E1 mechanism [25]. In particular, such solvation causes partial or complete retention of the configuration in the phenolysis of optically active substrates [26]. Experiments on the effect of neutral salts on the rate of heterolysis of 3-bromocyclohexene in MeCN revealed a strong influence of the nucleophilic solvation of the covalent substrate on the manifestation of the salt effects [27].

R 0.962, S 0.49, F 344 (1.93), N 30.

In the heterolysis of **I**, as in the case of secondary substrates, specifically the covalent substrate (initial state) is subject to the nucleophilic solvation, and the solvation does not change on reaching the transition state. Such a pattern is possible only when the solvation is not hindered sterically. Since our substrate is an allyl derivative, the nucleophilic solvation of the hydrocarbon radical can occur at positions 1 and 3, with no steric hindrance to the solvation at position 1 (*Solv*...CH₂=CHCMe₂Cl); therefore, this tertiary substrate behaves as a secondary substrate.

Comparative analysis of solvation effects is usually performed with *tert*-butyl halides as reference substrates. However, the rate of their heterolysis depends

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on the solvent nucleophilicity, which complicates the analysis of the solvation effects. With adamantyl substrates [28, 29], the pattern is still more complex, since these substrates are still less active, and the rate of their heterolysis depends on the solvent nucleophilicity still more strongly [2, 3]. Chloride I is more suitable as reference substrate. It is by two orders of magnitude more active than *t*-BuCl, and the rate of its heterolysis in protic and aprotic solvents is virtually independent of the solvent nucleophilicity and is satisfactorily described by the solvatochromic parameter of the solvent ionizing power.

EXPERIMENTAL

3-Methyl-3-chloro-1-butene **I** was prepared according to [30] from isoprene in an ether solution by treatment with dry HCl at -20° C; the product was purified by double distillation under reduced pressure (bp 43– 44°C/230 mm Hg); $n_{\rm D}^{20}$ 1.4192 (published data [30]: bp 40–41°C/200 mm Hg; $n_{\rm D}^{20}$ 1.4190).

1,3,5-Triphenylverdazyl was prepared and purified according to [31].

The aprotic solvents were purified according to [32], and the alcohols, according to [1]. The kinetic experiments were performed in a temperature-controlled cell of an SF-26 spectrophotometer. The mathematical treatment of the experimental data was performed with Excel-97 software; confidence level 95%.

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