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Solvation Effects and the Mechanism of the Heterolysis of t-Butyl Halides

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Data on the kinetics and mechanism of the heterolysis of t-BuX (X = Cl, Br, I) in the gas phase and in individual solvents are surveyed. The mechanism of the unimolecular heterolysis of t-BuX and the role of the solvent in this process are discussed. The bibliography includes 192 references.

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I. INTRODUCTION

The reactions involving the unimolecular heterolysis of t-BuX (unimolecular solvolysis, S_N1, $E1$) have attracted the attention of chemists for more than 40 years[1-6]:

$$\text{t-BuX} \longrightarrow \begin{cases} \xrightarrow{\text{ROH}} \text{t-BuOR} + \text{HX} \\ \longrightarrow \text{Me}_2\text{C}{=}\text{CH}_2 + \text{HX} \end{cases}$$

Both substitution and elimination products are formed in proton-donating solvents, while in the gas phase and in aprotic solvents only elimination products are obtained. These reactions have been widely used in the study of the mechanism of the heterolytic cleavage of a covalent bond and of the influence of the solvent on the process. The principal data on the mechanisms of these reactions can be found in any modern text-book or monograph on organic or physical organic chemistry (see, for example, Refs.7-13). More detailed data are available in reviews of the solvolysis of organic substrates[1,5,14-17] and of the influence of the solvent on heterolytic reactions[4,6,18-24]. The number of publications on this problem has rapidly increased recently, novel research techniques have appeared, and new approaches to the interpretation of the results have been devised; at the same time contradictions have also accumulated.

The aim of the present review is a critical survey of modern ideas concerning the mechanism of the heterolysis of t-BuX. Attention has been concentrated on the effect of the solvent. Virtually all the available experimental kinetic parameters for the heterolysis of t-BuX (X = Cl, Br, I, or F) and certain other t-butyl derivatives in the gas phase and in individual solvents have been compiled and tabulated in the present review. A correlation analysis of the influence of various solvent parameters (nucleophilicity, electrophilicity, polarity, polarisability, and the energy of the self-association of the solvent) on the rate of heterolysis of t-BuX (X = Cl, Br, or I) has been carried out. This permits a critical approach to the interpretation of the solvent effect and certain new conclusions about the reaction mechanism.

II. THE NATURE OF THE TRANSITION STATE

The very extensive data on the heterolytic reactions of t-BuX are usually surveyed on the basis of the same, at first sight simple, mechanism, according to which a cationoid intermediate (an ion pair or a carbonium ion) is formed in the rate-limiting stage from t-BuX and is then rapidly converted into the reaction products.

The rates of these reactions increase rapidly with increase of solvent polarity; in the case of t-BuCl, the increase is by ~15 orders of magnitude on passing from n-heptane to water (Table 1) (t-BuCl is used as a standard in the correlation of the rates of solvolysis of other substrates—see the Grunwald–Winstein equation[1-3,14,15,18,21,23,25]).

Marked charge separation takes place in the transition state of the heterolysis of t-BuX:[1-6,10,23,26,27] 0.8 of an electron[4,26,28], $\mu^{\neq} = 8.8$ D, $d^{\neq} = 2.3$ Å.[26] In hydroxyl-containing solvents $\mu^{\neq}$ increases markedly[4,23]. On passing from the initial to the transition state, the volume of t-BuCl increases from 111 to 116 $cm^3\ mol^{-1}$;[6] however, the volume of activation diminishes as a result of electrostriction: $\Delta V^{\neq} \cong -20\ cm^3\ mol^{-1}$.[29] $Me_4N^+Cl^-$ is used as a model of the transition state[18]. The appreciable charge separation in the transition state is indicated by the reaction constant[30] for the heterolysis of $RCMe_2Cl$ in the Taft equation [$\rho = -3.3$ in 80% ethanol (EtOH) [31] and $\rho = -3.6$ in dimethylformamide (DMF) [32]]. The agreement between the experimental β-deuterium kinetic isotope effect in the solvolysis of t-BuCl [33] and the calculated H–D effect for the formation of t-Bu^+ ($k_{C_4H_9Cl}/k_{C_4D_9Cl} \cong 2.4$) [34] as well as the slope (~0.9) of the relation between the free energies of activation for the solvolytic reactions of alkyl chlorides and their heats of ionisation[35] are consistent with this finding.

The rate of solvolysis of t-BuCl depends on the nature of the solvent approximately in the same way as the rate of addition of Br_2 to styrene and phenylacetylene[36], which indicates a high polarity of the transition state in all cases. We may note that the calculations based on the ^{14}C and ^{37}Cl kinetic isotope effects lead to a less polar transition state[37-39], although it is believed[40] that the small isotope effect of chlorine (~1.01) in the solvolysis of t-BuCl is associated with the intense solvation of the anion formed and not with the low polarity of the transition state.

The effects of the solvent and salts[41,42] indicate the formation of a highly polar transition state[4,6,43], although in the case of Ph_2CHX these effects are more marked than for t-BuX.[16,44-46] The heterolysis of diphenylmethyl derivatives usually results in the formation of intermediate carbonium ions and solvent-separated ion pairs[16,45,47]. In the reaction involving t-BuX, less polar intermediates are apparently produced. Evidence has been adduced[6,18,19] in support of the view that the polarity of the transition state in the heterolysis of t-BuCl decreases with decrease of the polarity of the medium; however, other investigators believe[46,48] that the polarity of the transition state is independent of the nature of the medium. The possibility of the formation of a four-membered transition state in the heterolysis of t-BuCl in solvents of low polarity has been discussed[4,26,48,49].

Table 1. The logarithms of the rate constants for the heterolysis of t-BuX and solvent parameters.

No.	Solvent	$-\lg k^{25}$ (s^{-1})			ε^{20}	n_D^{20}	B	E	E_T	DN	AN	δ^2	Refs.
		X = Cl	X = Br	X = I									
1	Gas phase	19.3[a]	16.8[a]	14.3[a]	1.00	1.0000	0.00	0.00	0.00	—	—	0.00	[123]
2	H_2O	1.54	0.119	−0.188	80.1	1.3330	156	21.8	63.1	18.0	54.8	0.592	[124]
3	MeOH	6.06	4.46	3.90	32.7	1.3286	218	14.9	55.5	18.9[b]	41.3	0.196	[125]
4	EtOH	7.07	5.36	—	24.3	1.3614	235	11.6	51.9	19.2[b]	37.1	0.158	[126, 18]
5	n-BuOH	7.52[c]	—	—	17.3	1.3992	231	10.3	50.2	19.5[b]	—	0.112	[127]
6	iso-PrOH	7.80	6.07	—	18.3	1.3773	236	8.7	48.6	19.8[b]	33.5	0.130	[128, 71]
7	t-BuOH	8.30[t]	4.97	—	10.9	1.3848	247	5.2	43.9	21.5[d]	—	0.113	[128, 129]
8	n-HexOH	7.91[f]	—	—	12.5	1.4182	230	10.5	51.5	—	—	0.112	[127]
9	n-OctOH	8.18[g]	—	—	10.3	1.4291	230	10.8	51.8	—	—	0.111	[127]
10	CF_3CH_2OH	3.98	2.62	—	26.5	1.2907	—	—	59.5	—	23.3	—	[84, 130]
11	CH_2OHCH_2OH	4.60	—	—	38.7	1.4318	224	15.0	56.3	—	—	0.318	[128]
12	Glycerol	4.10	—	—	42.5[e]	1.4735[e]	—	—	57.0	—	—	—	[131]
13	PhOH	4.65[h]	—	—	10.3	1.5418	130	13.7	54.8	—	—	0.107	[62, 132]
14	HCO_2H	2.96	2.02	—	57.9	1.3714	131	16.7	57.9	11.4[d]	83.6	0.138	[25, 126]
15	CF_3CO_2H	3.19	—	—	39.0	1.2850	—	—	—	—	105.3	—	[133]
16	CH_3CO_2H	6.70	5.52	—	6.15	1.3716	139	14.6	51.2	12.1[d]	52.9	0.154	[128, 127, 134]
17	NH_3	7.26	—	—	16.9	1.3250	443	10.6	51.7	59	—	0.242	[135]
18	$PhNH_2$	6.13	—	—	6.89	1.5855	346	6.2	44.3	26.3[d]	—	0.107	[136]
19	$HCONH_2$	4.33	—	—	112	1.4475	270	14.5	56.6	22.2[d]	39.8	0.400	[137]
20	HCONHMe	6.54	—	—	190	1.4310	287	11.9	54.1	—	—	0.255	[106]
21	MeCONHMe	7.33	—	—	179[i]	1.4301	338	9.9	52.0	—	—	0.250	[106]
22	EtCONHMe	8.00	5.65[j]	—	166	1.4350	—	—	—	—	—	—	[41, 128]
23	DMF	8.62	5.62[k]	—	36.7	1.4272	291	2.6	43.8	26.6	16.0	0.198	[106, 113]
24	Dimethylacetamide	9.31	—	—	37.8	1.4356	343	2.4	43.7	27.8	13.6	0.199	[106]
25	*N*-Methylpyrrolidinone	8.97[l]	6.00[m]	—	32.2[e]	1.4680	319	1.3	42.2	27.3	—	0.121	[65]
26	Propylene carbonate	8.29	5.50	4.02	70.0	1.4189	180	6.1	46.6	15.1	18.3	0.138	[102]
27	$MeNO_2$	8.12	5.44[n]	—	38.6	1.3819	65	5.1	46.3	2.7	20.5	0.170	[62, 138]
28	MeCN	8.64	5.90[o]	4.28	37.5	1.3416	160	5.2	46.0	14.1	19.3	0.150	[119]
29	Me_2CO	9.61[p]	7.13[r]	5.21	20.7	1.3588	224	2.1	42.2	17.0	12.5	0.095	[139]
30	Ac_2O	8.32	—	—	20.5	1.3904	100	3.7	43.9	10.5	—	0.141	[128]
31	$PhNO_2$	9.72[s]	6.95	5.52	34.8	1.5546	67	0.0	42.0	4.4	14.8	0.113	[140, 141]
32	PhCN	—	7.11	5.43	25.2	1.5282	155	0.0	42.0	11.9	15.5	0.123	[141]
33	$PhCF_3$	—	—	6.10	9.18[i]	1.4146	—	0.0	—	—	—	—	[141]
34	C_6H_6	—	—	6.56	2.28	1.5011	48	2.1	34.5	0.1	8.2	0.085	[141]
35	PhF	—	—	6.58	5.42	1.4657	38	0.0	38.1	—	—	0.076	[141]
36	PhCl	—	—	6.58	5.62	1.5218	38	0.0	37.5	0.6	—	0.087	[141]
37	PhBr	—	—	6.59	5.40	1.5560	40	0.0	37.5	0.2	—	0.096	[141]
38	PhI	—	—	6.51	4.62	1.6212	38	0.0	37.9	0.0	—	0.084	[141]
39	PhOMe	—	—	6.37	4.33	1.5170	255	1.4	37.2	19.8	—	0.097	[141]
40	$PhCH_3$	—	—	7.04	2.38	1.4969	58	1.3	33.9	2.9	—	0.080	[141]
41	CH_2Cl_2	9.54	7.21	6.12	9.08	1.4246	23	2.7	41.1	1.1[d]	20.4	0.095	[142]
42	CH_2ClCH_2Cl	—	7.75	6.15	10.4	1.4451	40	3.0	41.9	0.1	—	0.108	[142]
43	CH_2BrCH_2Br	—	—	7.09	4.78[e]	1.5387	—	—	—	—	—	—	[142]
44	t-BuCl	13.6[u]	—	—	9.96	1.3856	64	—	—	—	—	—	[143]
45	Dioxan	10.8	8.52	6.78	2.21	1.4424	237	4.2	36.0	14.8[v]	10.8	0.110	[71, 128, 144]
46	THF	—	—	6.57	7.39	1.4076	287	0.0	37.4	20.0	8.0	0.076	[144]
47	Et_2O	12.7[w]	—	—	4.35	1.3527	280	0.0	34.6	19.2	3.9	0.057	[18]
48	$(CO_2Et)_2$	—	7.54	6.18	8.08	1.4112	—	—	—	—	—	—	[144]
49	$PhCO_2Et$	—	—	6.83	6.02	1.5052	142	—	—	—	—	—	[144]
50	$MeCO_2Et$	—	—	7.02	6.02	1.3724	181	1.6	38.1	17.1	—	0.082	[144]
51	n-Heptane	16.0[x]	—	—	1.92	1.3877	0.0	0.0	30.9	0.0	0.0	0.060	[145]

Remarks. The main bulk of the values of ε, n, B, E, E_T, DN, AN, and δ^2 were taken from Refs. 6, 11, 21, 22, 90, and 91 (see Section IV).

[a] Calculated from the values of k at 230–680 °C. [b] Taken from Kanevskii and Zarubina[146]. [c] $\lg k^{25} = -7.26$ in the paper of Rudakov and Kozhevnikov[48]. [d] Taken from Makitra and Pirig[147]. [e] At 25 °C. [f] $\lg k^{25} = -7.43$ in the paper of Rudakov and Kozhevnikov[48]. [g] $\lg k^{25} = -7.52$ in the paper of Rudakov and Kozhevnikov[48]. [h] Calculation from the values of k at 40°, 50°, and 55 °C. [i] At 30 °C. [j] Calculation from the values at 24.8°, 39.2°, and 50.7 °C. [k] $\lg k^{25} = -5.66$ in the paper of Peters and Anteunis[32]. [l] Estimate from $k^{60} = 9.1 \times 10^{-8}$ s^{-1}, $\Delta H^{\neq} = 102.1$ kJ mol^{-1}.[18] [m] Calculation from the values of k at 20°, 40°, and 60 °C for [HBr] ≅ 0.0275 M. [n] $\lg k^{25} = -5.36$ in the paper of de la Mare et al.[118] [o] $\lg k^{24.5} = -5.92$ in Hoffman's paper[117]. [p] $\lg k^{25} = -9.9$ in Rudakov's paper[128]. [r] Calculation from the values of k at 20°. 40°, 44.4°, 50°, and 60 °C, taken from Winstein et al.[68], yields $\lg k^{25} = -7.16$. [s] Calculation from the values of k at 39°, 53°, and 70 °C.[140] [t] Calculation from the values of k at 27–60 °C, taken from Viana and Concalves[129], yields $\lg k^{25} = -5.3$. [u] Calculation from the values of k at 100° and 120 °C, taken from Koppel[145], yields $\lg k^{25} = -10.0$. [v] Taken from Gutman[90]. [w] Estimate in Abraham's paper[18] from data for 120 °C.[4] $\lg k^{25} = -10.4$ in the paper of Pocker and Buchholz[148] and $\lg k^{120} = -7.0$ in the paper of Koppel and Palm[4]. If $\lg k^{25} = -12.7$ is used, then $\Delta H^{\neq} = 132.3$ kJ mol^{-1} and $\Delta S^{\neq} = -52.8$ J mol^{-1} K^{-1} (realistic values). If one uses $\lg k^{25} = -10.4$, then $\Delta H^{\neq} = 77.9$ kJ mol^{-1} and $\Delta S^{\neq} = -191.3$ J mol^{-1} K^{-1} (improbable values). [x] Estimate in Abraham's paper[6]: $\lg k^{25} = -13.5$.

The interpretation of the solvent effect is complicated by the fact that the solvent influences both the initial state of the substrate and the transition state and a difference between these effects has been observed[6,10,15,48]. The separate effects of the medium on the solvation of the initial and transition states are taken into account using a thermodynamic approach to the analysis of kinetic data[6,48,50]. Unfortunately this method does not differentiate the ionic intermediates formed in the heterolysis of a covalent bond; the polarity of the transition state is usually assumed to be constant for all media.

Comparative analysis of the Henry coefficients for the ground state and the rate constants for the solvolysis of t-BuCl showed[48] that the change in the rate of reaction in a medium of low polarity depends greatly on the degree of solvation of the transition state, while in a polar medium it depends on the degree of solvation of the substrate in the initial state. The use of the solubility parameter δ in combination with the free energies of activation enabled Abraham[6] to determine the free energies of the transition state in the heterolysis of t-BuCl(Br) in various solvents. It was shown that the decrease of the free energies of activation with increase of the polarity of the medium is due both to the increase of the energy of the initial state and the decrease of the energy of the transition state, the latter making the main contribution.

The correlation between the relative free energies of the transition state and the free energies of the model compound $Me_4N^+Cl^-$ showed that the polarity of the transition state is much higher in polar solvents than in solvents of low polarity. However, after the determination of the contribution of the energy of formation of a cavity (cage) in the solvent, Abraham recently abandoned this conclusion; he now believes that the polarity of the transition state is independent of the nature of the medium. On the basis of the concept of S_N1 transition states as ternary species formed from $t\text{-}Bu^+X^-$ and solvent molecules ($R^+...X^-...Solv$) or metal ions ($R^+...X^-...M^+$), Rudakov[50,51] analysed the influence of the medium on the rate of heterolysis of t-BuX and, having separated the effects of the solvation proper and the Coulombic interaction in the transition state, showed that the solvent effect is due mainly to the solvation of the transition state.

It is noteworthy that the solvation of the substrate in the initial state can greatly influence $\Delta H^{\neq}$ and $\Delta S^{\neq}$.[15] The initial state is less polar than the transition state and its solvation therefore depends greatly on the solvent structure[52,53].

It is usually believed that the heterolysis of t-BuX, interpreted within the framework of Winstein's scheme, stops at the stage involving the formation of a contact ion pair[54-57]:

$$t\text{-}BuX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} t\text{-}Bu^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} t\text{-}Bu^+ \mid Solv \mid X^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} t\text{-}Bu^+ + X^-.$$

However, this is not always so. Since the solvolysis of t-BuX in proton-donating solvents proceeds via the S_N1 mechanism, t-BuOR should be formed from an intermediate carbonium ion or a solvent-separated ion pair (attack by the nucleophile on the contact ion pair would lead to S_N2 substitution)[14,16]. In water the yield of the olefin (~5%) is independent[58] of the nature of the departing group in t-BuX (X = Cl, Br, I, or SMe_2I), which indicates the formation of an intermediate carbonium ion; in acetic acid, ethanol[58], and methanol[59], the yield of the olefin increases with the basisity of the departing group, which indicates the formation of the olefin from intermediate ion pairs.

It is believed[60] that in solution in CF_3CH_2OH the contact ion pair is converted into a solvent-separated ion pair in the rate-limiting stage of the ionisation of t-butyl halide. The contact ion pairs were generated in solution in CF_3CH_2OH by the addition of HCl to isobutene[14,61]:

$$t\text{-}BuCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} t\text{-}Bu^+Cl^- \overset{k_2}{\rightsquigarrow} \begin{matrix} t\text{-}Bu^+ \mid Solv \mid Cl^- \\ \downarrow \\ t\text{-}BuOCH_2CF_3 \end{matrix}$$
$$Me_2C{=}CH_2 + HCl$$

The yield of the product of the reaction involving the reconversion of the ion pair (t-BuCl) was higher by a factor of two than the yield of the substitution product ($t\text{-}BuOCH_2CF_3$). Consequently $k_{-1} > k_2$ and the rate-limiting stage in the heterolysis of t-BuCl in CF_3CH_2OH should be the formation of a solvent-separated ion pair. The phenolysis of t-BuCl apparently proceeds partly via a carbonium ion—the rate of reaction diminishes in the presence of a salt with a common ion[62]. This is apparently a unique case, since the salt effect, associated with the operation of the Law of Mass Action, is not as a rule manifested in the solvolysis of t-BuX.[14,16] Possibly this effect may be important in methanol and dioxan[63].

The solvolysis of t-BuCl in formic acid proceeds at the same rate as the unimolecular exchange of the anion[64], which indicates the formation of an intermediate carbonium ion or a solvent-separated ion pair. The solvolysis of t-BuCl in *N*-methylpyrrolidinone in the presence of radioactive LiCl* is accompanied by the unimolecular exchange of the anion (~3%); the usual salt effect of the chloride observed under these conditions indicates the formation of an intermediate solvent-separated ion pair. The same intermediate is apparently formed in the solvolysis of 2-bromo-2-methylpentane in DMF.[32] The intermediate solvent-separated ion pair is apparently also formed in the methanolysis of 2,4-dimethylhex-4-yl phthalate, which proceeds with 54% retention of the configuration[66]. The exchange of the anion in t-BuCl, catlaysed by $FeCl_3$, apparently proceeds in benzene solution via a solvent-separated ion pair[67]. In acetone[68], $MeNO_2$,[69] and acetic acid[14], the anion derived from t-BuCl(Br) does not exchange; the specific salt effect of perchlorate is not manifested in acetic acid. Consequently in these and less polar solvents the main intermediates are contact ion pairs†.

Evidence showing that the reaction proceeds via a rate-limiting stage involving the formation of a contact ion pair in the heterolysis of t-BuBr in acetonitrile was obtained by a comparative study of the influence of added water and salts on the rates of the reactions of t-BuBr and Ph_2CHBr.[45] It is evident from the foregoing that in aprotic solvents the rate of reaction is as a rule limited by the stage involving the formation of a contact ion pair, while in proton-donating solvents the rate-limiting stage involves the conversion of the contact ion pair into a solvent-separated ion pair. The increase of the dipole moment of $[t\text{-}BuCl]^{\neq}$ on passing from aprotic to proton-donating solvents[4,23,26] and also Abraham's conclusion that the polarity of the transition state increases with increase of the polarity of the medium[6,18] are satisfactorily consistent with this finding.

The above view has been confirmed in a study[70] where the logarithms of the rate constants for the heterolysis of t-BuBr and Ph_2CHBr in various solvents were compared with the Kosower solvent polarities, *Z*. It was shown that in aprotic solvents the rates of heterolysis of both substrates are similar, while in proton-donating solvents t-BuBr reacts at a rate lower by 2.5 orders of magnitude (see Figure).

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†The heterolysis of t-BuCl(Br) in acetic acid apparently proceeds partly also via a solvent-separated ion pair, which is indicated by the formation of t-BuOAc in ~30% yield[58].

The Figure also shows that there is a linear relation between $\lg k_{Ph_2CHBr}$ and Z for the entire set of solvents, while the rate of heterolysis of t-BuBr deviates sharply from this relation in the region of the transition from aprotic to proton-donating solvents as a result of the decrease of the rate of reaction in isopropyl alcohol. The $\lg k_{Ph_2CHBr}$ are satisfactorily correlated with the values of Z (correlation coefficient 0.978), while in the case of t-BuBr the correlation is unsatisfactory[71]. This can be explained by a change of mechanism of the heterolysis of t-BuBr: in aprotic solvents the rate of the process is limited by the formation of a contact ion pair, while in proton-donating solvents it is limited by the formation of a solvent-separated pair. In the heterolysis of Ph_2CHBr the rate-limiting stage involves in all cases the formation of a solvent-separated ion pair[45,72]. Analogous features were manifested on comparing a more restricted set of data for t-BuCl and Ph_2CHCl: in proton-donating solvents Ph_2CHCl reacts faster by ~3 orders of magnitude than t-BuCl,[73] while in acetonitrile the rates are similar[74].

Thus the heterolysis of t-BuX proceeds via the formation of intermediate solvent-separated and contact ion pairs. The former predominate in proton-donating solvents, while the latter predominate in aprotic solvents. A contact ion pair is apparently formed in the gas phase[75,76]. In a few individual instances (in phenol and water) the reaction can proceed partly via a carbonium ion.

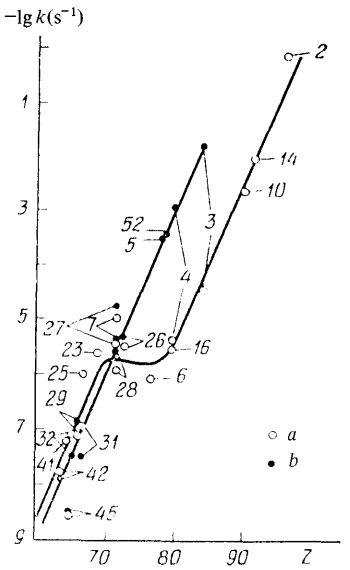
t-Butyl halides do not enter into a reaction via the S_N2 mechanism owing to the strong repulsion in the transition state between the nucleophile and the methyl groups[1,3,10,15]. In 1959 Winstein et al.[68] showed that the conclusion by Ingold[77] and other workers[78,79] according to which the substitution in t-BuCl(Br) in solution in acetone proceeds via the S_N2 mechanism must be treated merely as an unsuccessful hypothesis. However, when one of the methyl groups in t-BuX is substituted by a more electron-accepting group ($ArSO_2CH{=}CH{-}$) substitution via the S_N2 mechanism (more precisely via an S_N2 ion pair) at a tertiary carbon atom becomes possible[80]. Consequently the different reactivities of tertiary carbon in reactions involving the S_N1 and S_N2 mechanisms are due to both steric and electronic effects of the substituents.

The possibility of the operation of the $E2$ mechanism has been discussed[41,65,81,82]. The evidence against this reaction mechanism is that the yield of the olefin and the deuterium isotope effect in the solvolysis of t-BuCl are almost independent of the basicity of the mixed solvent[40], although in the presence of strong bases this reaction pathway is possible[59,83].

It is believed[84,85] that the smallness of the kinetic isotope effect and the deviation of the rate of heterolysis of t-BuCl in CF_3CH_2OH from the linear relation between $\lg k_{t\text{-}BuCl}$ and $\lg k_{1\text{-}AdBr}$ (where 1-AdBr is 1-adamantyl bromide) show that the elimination of HCl from the ion pair $t\text{-}Bu^+Cl^-$ is rate-limiting. However, comparison of the rates of heterolysis of t-BuCl, 1-AdCl, and 2-chloro-2-methyladamantane in various solvents, including fluorinated alcohols, shows[54,55] that all these substrates react via the same mechanism. This rules out the possibility of dehydrohalogenation as the rate-limiting stage.

According to Hammett[3], analysis of the kinetics of solvolysis of t-BuX is complicated by the reaction involving the internal return of the ion pair (with a rate constant k_{-1}). Harris[14] believes that the return reactions (k_{-1}, k_{-2}, and k_{-3}) are unimportant for t-BuX; elimination, dissociation of ion pairs, (k_2, k_3), or the interaction of the intermediates with the solvent predominate for these substrates. The absence of mixing of the oxygen in the solvolysis of t-BuOCAr[1,16] and 2,4-dimethylhex-4-yl phthalate[86] is used as an argument against the occurrence of the internal ion pair return. However, it is believed[40] that, absence of the mixing of ^{18}O in t-alkyl derivatives can be caused by steric effects in the presence of which the reconversion takes place without mixing.

The occurrence of internal return is indicated by the formation of a sulphone on solvolysis of t-BuOSOAr.[87] The possibility of external return is indicated by the unimolecular exchange of the anion in t-BuX [26,32,64,65] and the salt effect based on the Law of Mass Action[62]. Analysis of the dependence of the heat capacities of activation on the composition of the medium (H_2O–EtOH) and on temperature led Blandamer et al.[88] to the conclusion that at ~20 °C the rates of internal return and of the elimination of HCl from $t\text{-}Bu^+Cl^-$ are approximately the same. Bentley and co-workers[54,55] and Harris et al.[85] believe that the observed deviations in weakly nucleophilic solvents such as CF_3CH_2OH and $(CF_3)_2CHOH$ are due to reactions involving the ion pair return and are not caused by the rate-limiting dehydrochlorination. As mentioned above, the proportions of the products following the addition of HCl to isobutene in CF_3CH_2OH clearly indicate the occurrence of the stage involving internal ion pair return[14,16,60].



Dependence of $\lg k_{t\text{-}BuBr}$ (*a*) and $\lg k_{Ph_2CHBr}$ (*b*) on Z (data from Table 1 and Refs.70 and 71). The numbering of the solvents is the same as in Table 1; 52 = n-PrOH.

The influence of the solvent on the rate of reaction is attributed to its electrostatic and acid–base properties[2-5,20,22-89,90,91]. When the reaction is carried out in solution, it is always necessary to take into account the effect of non-specific solvation[4,20,23], although recently attempts have been made frequently to reduce the influence of the solvent on the kinetic parameters solely to its acid–base properties[22,90,92,93]. It is believed[94] that the high rate of solvolysis in water is caused by the presence of a small amount of OH groups not bound by a hydrogen bond and of unshared electron pairs (~6%).

The rate of heterolysis of t-BuX is known to depend strongly on the electron-accepting properties of the solvent[4,23]. This is indicated by the increase of the rate of reaction owing to the formation of hydrogen-bonded complexes with the departing group[1,4,5,15,95] and also by the catalysis by metal ions[5,96–99], which is described by an equation analogous to the Brønsted equation[5,100]. The great importance of electrophilic solvation in the heterolysis of t-BuX is indicated by the comparison of the rates of elimination of HBr from t-BuBr in a weakly polar ($\varepsilon = 15$) but electrophilic solvent such as SO_2 and in propylene carbonate, which is a strongly polar solvent ($\varepsilon = 70$). In the former case[101] at −15 °C we have $k = 5.2 \times 10^{-5}$ s^{-1}, while in the latter case[102] $k = 9.4 \times 10^{-7}$ s^{-1} (calculated from the temperature variation of k).

The question of the nucleophilic cooperation of the solvent in the heterolysis of t-BuX is still controversial[55,92,93,103]. On the basis of data for Ph_3CCl, Swain suggested in 1948 a push-pull character of the effect of the solvent on the heterolysis of t-BuCl.[104] Thornton[40] developed this hypothesis into the concept of a continuous spectrum of S_N1–S_N2 mechanisms. In 1970 Schleyer and co-workers[105] compared the rates of solvolysis of t-BuCl and 1-AdBr in various solvents and concluded on the basis of the observed deviations in a weakly nucleophilic medium ($CF_3CH_2OH + H_2O$) that the heterolysis of t-BuCl in other solvents proceeds with the nucleophilic cooperation of the sovlent. However, the same deviations are observed on comparing the rates of heterolysis of 1-AdBr and 1-AdOTos [106] and the rates of heterolysis of t-BuCl and 1-AdCl are poorly correlated with one another[15], although the correlation observed on comparing 1-AdBr and t-BuBr was on the whole satisfactory[54] and the deviations were the same as in the comparison of t-BuCl and 1-AdBr.

Other examples of the correlation between the rates of solvolysis of t-BuCl with the rates of solvolysis of various substrates can be found in the literature[15,107]; some of these lead to the conclusion that nucleophilic cooperation by the solvent takes place, while others indicated their absence. All this demonstrates the unreliability of the conclusions based on such comparisons. One of the causes may be the formation of different intermediates depending on the nature of the substrate and the solvent[108]. Thus it follows from a comparison of the rates of solvolysis[109] that the stability of the cations decreases in the sequence $Ph_3C^+ > t\text{-}Bu^+ > 1\text{-}Ad^+$, although it has been shown[110,111] that $1\text{-}Ad^+$ is more stable than $t\text{-}Bu^+$. The cause of the observed differences between the rates may consist in the fact that the rate of heterolysis of t-BuX is limited by the stage involving the formation of a contact ion pair, while in other instances more polar intermediates are produced[16,112,113]. However, to a first approximation, the rate of solvolysis reflects the stability of the cationic intermediate[35].

Evidence in support of the nucleophilic involvement of the solvent has been obtained in the case of DMF.[32,114] It has been shown[115] that the heterolysis of the bond at a tertiary carbon atom can proceed with the nucleophilic cooperation of a neighbouring group [the solvolysis of $PhSO-(CH_2)_nCR_2Cl$]. The conclusion that the cation formed in the solvolysis of t-BuBr undergoes nucleophilic solvation was based on the analysis of the dependence of $\Delta C_p^{\neq}$ on m (where $\Delta C_p^{\neq}$ is the heat capacity of activation and m is the sensitivity of the solvolysis to the influence of the solvent in the Grunwald–Winstein equation) for certain substrates in different media[116]. It is believed[32] that the higher value of $\Delta S^{\neq}$ in the heterolysis of t-BuBr in acetonitrile (amounting to −42 J mol^{-1} K^{-1}) [117] compared with that in $MeNO_2$ (−67 J mol^{-1} K^{-1}) [118] is due to the fact that the tendency towards nucleophilic solvation, of the charges separated in the transition state, by acetonitrile is smaller. Comparison of the nucleophilicity parameters of these solvents (see Table) shows that acetonitrile is more nucleophilic. In addition it has been shown[119,120] that $\Delta S^{\neq} = -84$ J mol^{-1} K^{-1} in acetonitrile. It is believed[14] that the heterolysis of t-alkyl substrates proceeds without the nucleophilic cooperation of the solvent. Fairly convincing evidence has been adduced[10] against the nucleophilic involvement of the solvent in the heterolysis of t-BuX. Indeed a solvent molecule can hardly attack the carbonium ion formed "from the rear" if even a charged nucleophile is incapable of it.

In 1972 Koppel and Palm[20] carried out a correlation analysis of the solvation effects in the heterolysis of t-BuCl and showed that the rate of reaction is independent of the nucleophilic properties of the medium. Later Fawcett and Krygowski[93] concluded that the basicity of the solvent influences the rate of heterolysis of t-BuCl—its influence on the rate constant is to the extent of ~20%. Other workers[22,92], who used the donor (DN) and acceptor (AN) numbers of the solvents, arrived at an analogous conclusion.

Bentley and Carter[121] recently summarised the available evidence in support of nucleophilic cooperation of the solvent in the heterolysis of t-BuX. They believe that this reaction proceeds via the mechanism involving an S_N2-intermediate (its rate is limited by the stage in which an ion pair is formed on treatment of the covalent substrate with a nucleophile[15]). The main evidence adduced by the above workers[121] reduces to the fact that in weakly nucleophilic solvents [acetic acid, formic acid, trifluoroacetic acid, CF_3CH_2OH, and $(CF_3)_2CHOH$] the rate of heterolysis of 1-AdCl(Br) is higher than would follow from the linear relation between $\lg k_{t\text{-BuX}}$ and $\lg k_{1\text{-AdX}}$ and that the rates of heterolysis of 1-AdX and t-BuX in these solvents are similar, while in a nucleophilic medium (80% ethanol) t-BuX reacts faster by ~3 orders of magnitude than 1-AdX. Bearing in mind that the $1\text{-}Ad^+$ cation is more stable in the gas phase than $t\text{-}Bu^+$,[110,111] the authors[121] conclude that the observed differences between the rates of reaction in 80% ethanol can be explained by the nucleophilic cooperation of the solvent in the heterolysis of t-BuX. The authors[121] ignore the fact that the weakly nucleophilic solvents which they enumerated are at the same time comparatively strong acids; the cause of the observed differences can therefore be the fact that the adamantyl substrates are more susceptible to electrophilic catalysis than the t-butyl substrates[15,16].

We may note that, when $\lg k_{1\text{-AdBr}}$ is plotted against $\lg k_{1\text{-AdCl}}$ on the basis of the values quoted by Bentley and Carter[121], deviations from linearity are also observed in the weakly nucleophilic (strongly electrophilic) medium owing to the increase of the rate of heterolysis of 1-AdCl. If one follows the reasoning of Bentley and Carter[121], one must conclude that the heterolysis of 1-AdBr proceeds with nucleophilic cooperation by the solvent, while the heterolysis of 1-AdCl takes place without such cooperation, which is absurd. As in the comparison of the rates of heterolysis of t-BuX and 1-AdX, here the differences between the reactivities of the substrate decrease with increase of the electrophilicity (or with decrease of the nucleophilicity) of the medium). From our point of view, the natural explanation is that the chlorides, forming more stable hydrogen-bonded complexes with proton-donating solvents than the bromides, are more sensitive to electrophilic catalysis. In addition, one must bear in mind that in the heterolysis of 1-AdX and t-BuX different intermediates can be formed in the rate-limiting stage and, even when the same intermediate is formed in both cases, for example, a solvent-separated ion pair, the energies of the solvation of the cation and anion by the internal ligand in $1\text{-}Ad^+|Solv|X^-$ and $t\text{-}Bu^+|Solv|X^-$ can vary greatly as a function of the nature of the solvent.

As a second argument in support of S_N2-substitution in t-BuX, Bentley and Carter[121] point to the formation, noted by Bunton and Nayak[122], of radioactive t-BuCl* in the solvolysis of t-BuCl in aqueous methanol (the authors erroneously state that aqueous acetone was used) in the presence of NaCl*. This example cannot serve as evidence in support of the S_N2 mechanism since in aqueous methanol there is a possibility of the formation of solvent-separated ion pairs and a carbonium ion, which leads to the exchange of the anion via the S_N1 mechanism involving the external return of the ion (k_{-3}) or the ion pair (k_{-2}).

Thus, the examination of the entire set of data, including the publications of recent years, shows that the question of the nucleophilic involvement of the solvent in the heterolysis of t-BuX still remains controversial.

In the interpretation of the solvent effects, one must bear in mind that the time required for t-BuX to pass from the initial to the transition state is usually shorter than the orientational relaxation time of the solvent molecules (the lifetime of the transition state is 10^{-13} s and the orientational relaxation time of the dipole is 10^{-10}–10^{-11} s).[23] Evidence has been presented[50] in support of the view that the maximum stabilisation of the transition state and the highest rate of the process are attained only under the conditions of equilibrium solvation of the transition state.

III. KINETIC PARAMETERS OF THE HETEROLYSIS OF t-BuX IN THE GAS PHASE AND IN INDIVIDUAL SOLVENTS

Table 1 presents the logarithms of the rate constants for the heterolysis of t-BuCl(Br, I) at 25 °C and the parameters of the solvents which we used for the correlation analysis. The heterolysis rate constants have been determined for all three alkyl halides in only 8 of the 50 solvents and in the gas phase; t-BuCl was investigated mainly in proton-donating solvents (21 out of 35), t-BuI in aprotic solvents (21 out of 23), and t-BuBr approximately to equal extents in both groups of solvents (9 out of 13). This restricts the scope of comparative analysis.

Table 2. The activation parameters of the heterolytic reactions of t-BuX.

Solvent	$\Delta H^{\neq}_{25}$, kJ mol^{-1}	$\Delta S^{\neq}_{25}$, J mol^{-1}K^{-1}	$\Delta G^{\neq}_{25}$, kJ mol^{-1}	Refs.
t-BuCl				
Gas phase	185.9	10.0	183.4	[123]
H_2O	97.1	51.1	81.6	[137]
MeOH	104.3	−13.0	107.6	[137]
EtOH	109.3	−13.4	113.5	[140]
n-BuOH	118.1	6.3	116.0	[127]
t-BuOH	110.5[b]	8.4[b]	108.0[b]	[129]
n-HexOH	120.2	6.7	118.1	[127]
n-OctOH	121.4	6.7	119.7	[127]
PhOH	69.5[c]	−100.9[c]	99.7	[92, 132]
HCO_2H	87.9	−7.1	90.0	[137]
CH_3CO_2H	108.0	−10.5	111.4	[137]
$PhNH_2$	79.1	−100.5	108.0	[136]
$HCONH_2$	93.8	−15.9	97.6	[137]
DMF	105.5	−56.1	122.3	[41]
Propylene carbonate	85.8	−115.1	120.2	[102]
$MeNO_2$	97.1	−75.4	119.3	[149]
MeCN	100.1	−74.9	122.3	[119]
Me_2CO	85.4	−153.7	127.7	[139]
t-BuCl	144.0[e]	−22.6[e]	150.7	[143]
$PhNO_2$	107.6[f]	−71.2[f]	128.5	[140]
n-Heptane	164.1	−1.3	164.5	[145]

Table 2 (contd.).

Solvent	$\Delta H^{\neq}_{25}$, kJ mol^{-1}	$\Delta S^{\neq}_{25}$, J mol^{-1}K^{-1}	$\Delta G^{\neq}_{25}$, kJ mol^{-1}	Refs.
t-BuBr				
Gas phase	170.0[a]	7.1[a]	169.1	[123]
H_2O	91.7	58.6	73.7	[126]
MeOH	98.0	−2.1	98.4	[126]
EtOH	103.0	−1.7	103.8	[126]
t-BuOH OH	97.6	−14.7	102.2	[129]
CH_3CO_2H	100.9	−8.0	103.4	[126]
EtCONHMe	93.8[d]	−38.5[d]	105.1	[41]
DMF	87.1	−59.9	105.1	[41]
N-Methylpyrrolidinone	92.5[g]	−47.7[g]	107.2	[65]
Propylene carbonate	84.6	−66.6	104.3	[102]
$MeNO_2$	83.7	−65.7	103.8	[118]
MeCN	81.6[h]	−83.7[h]	106.8	[119]
Me_2CO	81.6[i]	−119.3[i]	113.9	[139]
PhCN	90.0	−78.3	113.5	[141]
CH_2Cl_2	69.5	−149.5	114.3	[142]
Dichloroethane	77.0	−134.8	117.2	[142]
$(CO_2Et)_2$	62.4	−180.0	116.0	[144]
$PhNO_2$	85.0	−93.0	112.6	[141]
t-BuI				
Gas phase	154.9[a]	0.8[a]	154.5	[123]
CH_3OH	92.1	−9.6	95.5	[125]
Propylene carbonate	70.8	−84.6	95.9	[102]
MeCN	71.6	−86.7	97.6	[119]
Me_2CO	79.5	−77.0	102.6	[139]
$PhNO_2$	80.4	−81.2	104.7	[141]
PhCN	83.7	−68.3	103.8	[141]
$PhCF_3$	117.7	33.1	108.0	[141]
C_6H_6	75.4	−117.7	110.5	[141]
PhF	98.4	−40.6	110.5	[141]
PhCl	77.5	−97.6	110.5	[141]
PhBr	88.3	−75.4	111.0	[141]
PhI	78.3	−107.6	110.1	[141]
PhOMe	81.2	−94.6	109.3	[141]
$PhCH_3$	82.1	−104.3	113.0	[141]
CH_2Cl_2	72.9	−117.7	108.0	[142]
CH_2ClCH_2Cl	82.9	−85.4	108.4	[142]
CH_2BrCH_2Br	92.1	−71.6	113.5	[142]
Dioxan	49.8	−207.7	111.8	[144]
THF	83.3	−89.6	110.5	[144]
$(CO_2Et)_2$	57.8	−169.6	108.4	[144]
$PhCO_2Et$	72.4	−132.7	112.2	[144]
$MeCO_2Et$	71.6	−139.4	113.0	[144]
Other substrates				
Gas phase, t-BuF[j]	208.5[j]	14.2[j]	203.9	[150]
H_2O, t-BuF[k]	100.5	−32.2	110.1	[151]
Gas phase, t-BuOEt[l]	213.5	−28.1	219.4	[152]
CH_3CN, t-BuONO$_2$[m]	92.1	−35.6	102.6	[149]
MeCN, t-BuOTos[n]	79.5	−20.9	85.4	[153]
H_2O, t-BuOAc[o]	108.9	23.4	101.7	[154]
H_2O, t-BuOP(O)EtH[o]	91.7	−33.5	101.7	[155]
H_2O, t-BuOP(O)(OH)$_2$[o]	97.6	−16.7	102.6	[156]
H_2O, t-BuS$^+$Me$_2$I$^-$[p]	108.4	−12.6	112.2	[157]

Remarks. [a]Calculated from the values of k at 230–680 °C; $\Delta H^{\neq} = 188.8$ kJ mol^{-1} and $\lg A = 19.93$ have been obtained by Hegtman et al.[158] for t-BuCl. [b]At 27 °C; $\Delta H^{\neq}$ and $\Delta S^{\neq}$ depend greatly on temperature; $\Delta H^{\neq}_{60°} = 19.7$ kJ mol^{-1} and $\Delta S^{\neq}_{60°} = -268.0$ J mol^{-1} K^{-1}. [c]Calculation from the values of k at 45°, 50°, and 55 °C. [d]Calculation from the values of k at 24.8°, 39.2° and 50.7 °C. [e]Calculation from the values of k at 100° and 120 °C [145] yields $\Delta H^{\neq} = 89.2$ kJ mol^{-1} and $\Delta S^{\neq} = -145.7$ J mol^{-1} K^{-1}. [f]Calculation from the values of k at 39°, 53°, and 70 °C.[140] [g]At 20°, 40°, and 60 °C; [HBr] ≅ 0.0275 M. [h]$\Delta H^{\neq} = 93.8$ kJ mol^{-1} and $\Delta S^{\neq} = -41.9$ J mol^{-1} K^{-1} are quoted by Hoffman[117]. [i]Calculation from the values of k at 20°, 40°, 44.4°, 50°, and 60 °C [68] yields $\Delta H^{\neq} =$ 78.7 kJ mol^{-1} and $\Delta S^{\neq} = -126.4$ J mol^{-1} K^{-1}. [j]Calculation from the values of k at 315–370 °C; $\lg k^{25} = -22.9$. [k]$\lg k^{25} = -6.49$. [l]$\lg k^{25} = -25.6$. [m]$\lg k^{25} = -5.16$. [n]$\lg k^{25} = -2.20$. [o]$\lg k^{25} = -5.00$. [p]$\lg k^{25} = -6.71$.

Simple comparison of the rate constants shows that the sensitivity of t-BuX to changes in the nature of the solvent on passing from one proton-donating solvent to another (H_2O–MeOH) or from a proton-donating solvent to another solvent (MeOH–propylene carbonate) decreases in the sequence Cl > Br > I, which can be explained by the fact that in the series of departing groups indicated the capacity of the solvent for electrophilic cooperation in the heterolysis diminishes. Indeed the sensitivity of t-BuX to the change of the aprotic solvent depends comparatively little on the nature of the halogen.

The rate of heterolysis of t-BuX decreases in the leaving-group order (Table 2):

$$OTos > I > ONO_2 > Br > Cl > OAc \approx OPOEtH \approx OPO(OH)_2 > F > SMe_2I.$$

The differences between the rates diminish with increase of the acidity of the proton-donating solvent; for example, $\lg(k_{t\text{-BuBr}}/k_{t\text{-BuCl}})$ decreases monotonically from 1.6 to 1.0 in the series MeOH–H_2O–HOAc–HCO_2H (the increasing influence of the formation of hydrogen-bonded complexes abolishes the effect of the departing group). In the gas phase and in aprotic solvents the above ratio is higher ($\lg k^{Br}/k^{Cl} \cong 2.7$; $\lg k^{I}/k^{Cl} \cong 4.3$) and depends little on the nature of the solvent. In CH_2Cl_2 these quantities are lower (2.3 and 3.4 respectively)—here the influence of the formation of hydrogen-bonded complexes is also manifested[142].

Table 2 presents a compilation of the activation parameters for the heterolytic reactions of t-BuCl, t-BuBr, and t-BuI and presents certain data for the heterolysis of t-BuF, t-$BuONO_2$, t-BuOTos, t-BuOAc, t-BuOEt, t-BuOP(O)EtH, t-$BuOP(O)(OH)_2$, and t-$BuS^+Me_2I^-$.

Analysis of the relations between $\Delta H^{\neq}$ and $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$, and $\lg k^{25}$ and $\lg k^{50}$ for t-BuCl(Br, I) in various solvents[159] indicates the non-uniformity of the interaction[11] in the series considered, as shown by the failure of the isokinetic relation and the absence of the compensation effect. This may be due to the different degrees of charge separation in the transition state in various media, in agreement with the earlier conclusion that the rate-limiting stage is the formation of a contact ion pair in aprotic solvents and of the solvent-separated ion pair in proton-donating solvents.

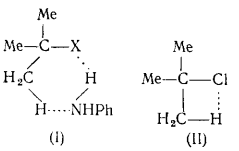
The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ vary marketdly as a function of the nature of the solvent—from 164.1 kJ mol^{-1} (n-heptane, t-BuCl) to 49.8 kJ mol^{-1} (dioxan, t-BuI) and from −207.7 kJ mol^{-1} (dioxan, t-BuI) to 58.6 kJ mol^{-1} K^{-1} (water, t-BuBr); therefore the conclusions that $\Delta S^{\neq} \geqslant 0$ [160,161] or that $\Delta H^{\neq}_{S_N1} > \Delta H^{\neq}_{S_N2}$ and $\Delta S^{\neq}_{S_N1} > \Delta S^{\neq}_{S_N2}$ [2,12,13] for reactions involving the S_N1 mechanism have little justification. The $\Delta S^{\neq}$ as a rule decreases in the series of solvents H_2O > proton-donating solvents > aprotic solvents; in the first case $\Delta S^{\neq} > 0$, in the second case $\Delta S^{\neq} \cong 0$, and in the third case $\Delta S^{\neq} < 0$. This can be explained by the fact that on formation of the transition state in water the effect of structure breaking in the solvent[162] predominates over the ordering of the latter as a result of the solvation of the ion pair produced; in other proton-donating solvents these effects are approximately identical, while in polar aprotic solvents the decrease of $\Delta S^{\neq}$ is due mainly to structure formation in the solvent around the ion pair formed.

The disruption of the structure of a proton-donating solvent with the aid of ultrasound increases the rate of solvolysis of t-BuCl.[103] The addition of small amounts of H_2O_2, ROH, tetrahydrofuran (THF), or acetonitrile also leads to the destabilisation of the water structure and hence to an increase of the rate of solvolysis of t-BuX.[163,164] The increase of the stability of the water structure on passing from H_2O to D_2O entails a decrease of the rate of solvolysis of t-BuCl ($k_{H_2O}/k_{D_2O} = 1.3$ was obtained at 25 °C [165]) with a simultaneous increase of $\Delta S^{\neq}$.[166] The negative value of $\Delta S^{\neq}$ for t-BuF in H_2O is associated with the formation of strong hydrogen bonds in the transition state, while $\Delta S^{\neq} \cong 0$ in n-heptane indicates an insignificant solvation of the transition state. Indeed, in the gas phase $\Delta S^{\neq}$ is also close to zero. $\Delta S^{\neq} = 33.1$ J mol^{-1} K^{-1} for t-BuI in $PhCF_3$ can be explained by the preferential solvation of the initial state as a result of the dipole–dipole interaction

$$(C^{\delta+}—F^{\delta-},\ C^{\delta+}—I^{\delta-}).$$

On formation of the transition state the dimensions of the $C^{\delta+}$–$I^{\delta-}$ dipole greatly increase, which leads to desolvation (disruption of the quadrupole).

The values $\Delta S^{\neq} \cong -80$ J mol^{-1} K^{-1} in certain proton-donating solvents (aniline, phenol) can be explained by the formation of a cyclic solvate complex of type (I) in the transition state[48,136]:



In aprotic solvents containing groups with a high dipole moment (CN, NO_2, CO), the formation of a quadrupole between the substrate and the solvent molecule is to be expected[3,4,141,167], which should reduce $\Delta S^{\neq}$ by ~80 J mol^{-1} K^{-1}; [12,120] the lower values of $\Delta S^{\neq}$ (from −125 to −210 J mol^{-1} K^{-1}) [dioxan, $(CO_2Et)_2$, CH_2Cl_2, RCO_2Et)] are apparently associated with the formation of complex cyclic associated species in the transition state[142,144]. This also applies to t-BuCl in propylene carbonate and acetone. The low value of $\Delta S^{\neq}$ in benzene is probably caused by the interaction of the substrate with the induced dipole of the C_6H_6 molecule[168].

In the gas phase and in non-polar aprotic solvents, $\Delta S^{\neq}$ is close to zero or has a low positive value. This conflicts with the hypothesis of the formation of a four-membered transition state of type (II) [6,18,48,49,142] in a medium of low polarity, since an appreciable decrease of $\Delta S^{\neq}$ is in fact to be expected precisely under the given conditions on formation of a cyclic transition state; this occurs, for example, on decomposition of t-BuOEt (Table 2). The increase of $\Delta S^{\neq}$ in acetonitrile in the sequence t-BuX < t-$BuONO_2$ < t-BuOTos can be explained by the decrease of the steric requirements in the dipolar solvation of the transition state, while the increase of $\Delta S^{\neq}$ in water in the sequence t-BuF < t-BuOAc < t-BuCl < t-BuBr is probably caused by the decrease of the solvation energy of the departing group.

It is noteworthy that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can vary markedly with temperature; for example, in the solvolysis of t-BuCl in t-BuOH, $\Delta H^{\neq}$ decreases by ~84 kJ mol^{-1} and $\Delta S^{\neq}$ by ~290 J mol^{-1} K^{-1} on raising the temperature from 27° to 60 °C (Table 2).[129,169] In this case the heat capacity of activation is $\Delta C_p^{\neq} = -2760$ J mol^{-1} K^{-1}; in water $\Delta C_p^{\neq} = -347$ J mol^{-1} K^{-1}.[170] The values of $\Delta C_p^{\neq}$ ranging from −125 to −625 J mol^{-1} K^{-1} for S_N1 reactions are usually accounted for by the necessity for the reorganisation of the solvation shell when the substrate passes to the activated state[170,171] or more precisely by the temperature variation of the solvation of the anion formed[172,173]. Indeed $\Delta C_p^{\neq}$ can depend greatly not only on the solvent but also on the nature of the departing group ($\Delta C_p^{\neq} = -255$ J mol^{-1} K^{-1} for t-BuBr in t-BuOH [129]). $\Delta C_p^{\neq} < -650$ J mol^{-1} K^{-1} and its marked decrease on passing from t-BuBr to t-BuCl cannot be explained either by the influence of temperature on the solvation of the anion generated[173], or by the presence

of a stage involving ion pair return[165,174,175], or by large errors in the determination of the temperature variation of the rate constant[176]. The above effects are apparently associated with the structure of the solvent and its temperature variation[173,177]. This may be confirmed to some extent by the fact that in the hydrolysis of the compound RX the quantity $\Delta C_p^{\neq}$ in D_2O is always lower than in H_2O.[166] The significant role of the solvent structure is indicated by the fact that the rate of solvolysis of t-BuCl in the $(CF_3)_2CHOH-H_2O$ mixture passes through a minimum when the solvent composition corresponds to the dihydrate $(CF_3)_2CHOH.2H_2O$,[178] while the rate of hydrolysis of $PhCH_2Cl$ passes through a minimum at the temperature of the maximum density of water[179].

IV. SOLVATION EFFECTS

We carried out a correlation analysis of the influence of solvent parameters on $\lg k$ [71,180] on the basis of the equation

$$\lg k = a_0 + a_1 DN + a_2 AN + a_3\delta^2 \qquad (1)$$

and the Koppell–Palm equation[11,20] with inclusion of the Hildebrand parameter[6] δ^2:

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

where DN is the donor number[21,90], AN the acceptor number[22,90], n the refractive index, ε the dielectric constant, B an empirical parameter of the basicity (nucleophilicity)[11,20], E empirical parameter of the electrophilicity calculated[11,20] from the Dimroth–Reichardt polarity parameter[91] E_T by the formula $E = E_T - 25.10 - 14.84f(\varepsilon) + 9.59f(n)$, and $\delta^2 = (\Delta H_M - RT)/V_M$ the Hildebrand parameter which characterises the energy of interaction of solvent molecules with one another; ΔH_M is the molar heat of evaporation and V_M is the molar volume. The solvent parameters are listed in Table 1. The Hildebrand parameter has been used in a number of studies for the interpretation of kinetic data[6,22,46,181], although it is frequently employed in the relatively unsuitable form of the solubility parameter δ.[6,46] For comparison with the data of Fawcett and Krygowski[93], we also carried out a calculation by Eqn.(2) with E replaced by E_T. In order to determine the influence of each parameter, the calculation was performed with successive inclusion of the parameters in accordance with the procedure of Chapman et al.[182] (the solvents for which the error exceeded the average error by a factor greater than or equal to 2.5 were rejected). The calculation was carried out on a Mir-2 computer.

The application of Eqn.(2) to t-BuCl in 28 solvents (solvents 2–9, 11, 13, 16–21, 23–31, 41, 45, 47) # yields the expression:

$$\lg k = -18.2 + 16.6f(n) + 7.06f(\varepsilon) + \\ + 4.77\delta^2 + 0.293E \quad (r=0.960,\ S=0.664).$$

When account is taken of B, we obtain $r = 0.961$. When the parameters δ^2, $f(n)$, $f(\varepsilon)$, and E are excluded, the values of r decrease respectively to 0.946, 0.945, 0.928, and 0.749. Thus the rate of hydrolysis of t-BuCl depends mainly on the electrophilicity of the solvent, to a lesser extent on its polarity, and depends little on the polarisability and self-association energy of the solvent. The nucleophilicity of the solvent does not influence the rate of reaction. These conclusions are consistent with the results of the calculations for t-BuCl by the Koppel–Palm equation[20,159].

In order to deduce the specific features of the solvation effects in proton-donating and aprotic solvents, we carried out calculations by Eqn.(2) separately for each group of solvents. In 15 proton-donating solvents (solvents 2–8, 11, 13, and 16–21), we obtained the equation

$$\lg k = -15.4 + 19.7f(n) + 5.10\delta^2 + 0.263E \quad (r=0.962,\ S=0.554).$$

When account is taken of B and $f(\varepsilon)$, we obtain $r = 0.964$; without taking into account δ^2, $f(n)$, and E, the values of r are respectively 0.934, 0.878, and 0.877. Thus in proton-donating solvents the rate of solvolysis of t-BuCl depends equally on the electrophilicity and polarisability of the solvent and to a lesser extent on its self-association energy; the basicity and polarity of the solvent do not affect the rate of reaction.

The rate of decomposition of t-BuCl in 13 aprotic solvents (solvents 23–31, 41, 45, 47, and 51) is described by the equation

$$\lg k = -20.8 + 14.1f(n) + 14.2f(\varepsilon) + 0.523E \quad (r=0.956,\ S=0.754).$$

When account is taken of B and δ^2, we obtain $r = 0.961$; when $f(n)$, $f(\varepsilon)$, and E are disregarded, the values of r are respectively 0.941, 0.743, and 0.856. Thus the ionisation of t-BuCl in aprotic solvents depends most on the polarity of the solvent, greatly on its electrophilicity, and depends only slightly on its polarisability.

When E is replaced by E_T in Eqn.(2),[20] we obtain the following equation for t-BuCl in 28 solvents (solvents 2–9, 11, 13, 14, 16, 17, 19, 21, 23–31, 41, 45, and 47):

$$\lg k = -21.5 + 3.67\delta^2 - 0.00351B + 0.289E_T \quad (r=0.960,\ S=0.697). \qquad (3)$$

Taking into account $f(n)$ and $f(\varepsilon)$, we have $r = 0.961$; when δ^2, B, and E_T are disregarded, the values of r are respectively ~0.952, 0.949, and 0.730. Consequently the rate of heterolysis of t-BuCl actually depends on E_T (the nucleophilicity actually decreases somewhat the rate of reaction in this case). Our results conflict with the conclusion[93] that the rate of heterolysis of t-BuCl increases with increase of both the electrophilicity (E_T) and basicity (DN) of solvents. We may note that Fawcett and Krygowski[93] used only five solvents ($r = 0.909$), while we used 28 solvents.

The application of Eqn.(1) to the description of the rate of heterolysis of t-BuCl in 15 solvents (solvents 2–4, 6, 16, 19, 23, 24, 27–29, 31, 41, 45, and 47) yields the expression

$$\lg k = -12.4 + 0.0917AN + 10.6\delta^2 \quad (r=0.980,\ S=0.606). \qquad (4)$$

When account is taken of DN, we have $r = 0.800$; when AN and δ^2 are disregarded, the values of r are 0.897 and 0.899 respectively. Thus the rate of heterolysis of t-BuCl depends equally on AN and δ^2. The basicity of the solvent does not affect the rate of reaction, which conflicts with the conclusions[22,92] that the rate of reaction increases appreciably with increase of DN.

Following the replacement of δ^2 by δ in Eqn.(1), the correlation becomes appreciably worse[180].

The application of Eqn.(2) to t-BuBr leads to the following relation in 14 solvents (solvents 2, 4, 14, 16, 23, 25–29, 31, 32, and 41):

$$\lg k = -8.00 + 10.3\delta^2 + 0.0883E \quad (r=0.972,\ S=0.481).$$

When account is taken of $f(n)$, $f(\varepsilon)$, and B, we have $r = 0.984$; when δ^2 and E are disregarded, the values of r are respectively 0.871 and 0.960. Consequently the rate of heterolysis of t-BuBr is determined fairly completely by δ^2; the electrophilicity of the solvent promotes the reaction to a slight extent, while the polarisability, polarity, and nucleophilicity of the solvent have no importance.

#Here and henceforth the solvents are numbered as in Table 1.

When E is replaced by E_T in Eqn.(2), we obtain the following expression for t-BuBr in 14 solvents (solvents 2–4, 16, 23, 25–29, 31, 32, 41, and 42):

$$\lg k = -11.8 + 9.68\delta^2 + 0.0954E_T \quad (r = 0.969,\ S = 0.502). \qquad (5)$$

When account is taken of f(n), f(ε), and B, we have $r = 0.981$. When δ^2 and E_T are disregarded, the values of r are 0.900 and 0.960. Thus the rate of heterolysis of t-BuBr depends mainly on δ^2; allowance for E_T improves the correlation slightly.

The application of Eqn.(1) to t-BuBr yields the following relation for 12 points (solvents 2, 4, 16, 23, 26–29, 31, 32, 41):

$$\lg k = -8.53 + 0.0137DN + 0.0252AN + 11.7\delta^2 \quad (r = 0.976,\ S = 0.488). \qquad (6)$$

The exclusion of AN or DN has comparatively little influence on the correlation coefficient (r = 0.975 and 0.964 respectively), while the exclusion of δ^2 lowers r to 0.770. Thus the rate of heterolysis of t-BuBr depends virtually only on δ^2. The correlation of the rates taking into account only DN and AN (or E_T and B) leads to poor results.

The application of Eqn.(2) to t-BuI in 19 solvents (solvents 2, 3, 26, 28, 29, 31, 32, 34–42, 45, 46, and 49) yields the expression

$$\lg k = -9.69 + 6.32f(\varepsilon) + 11.8\delta^2 \quad (r = 0.965,\ S = 0.491).$$

When account is taken of f(n), B, and E, we have $r = 0.975$; when f(ε) is disregarded, r = 0.952. Consequently the rate of heterolysis of t-BuI depends mainly on δ^2.

Following the replacement of E by E_T, we obtain the following equation for the same 19 solvents:

$$\lg k = -12.5 + 5.72\delta^2 + 0.147E_T \quad (r = 0.973,\ S = 0.437).$$

Taking into account f(n), f(ε), and B, we obtain $r = 0.976$; when δ^2 and E_T are disregarded, the values of r are 0.953 and 0.952. Thus the rate of heterolysis of t-BuI is equally well correlated with both δ^2 and E_T. The nucleophilicity of the solvent does not affect the rate of reaction.

Application of Eqn.(1) to t-BuI in 11 solvents (solvents 2, 3, 26, 29, 31, 32, 34, 41, 45, and 46) leads to the relation

$$\lg k = -7.38 + 0.0455AN + 8.77\delta^2 \quad (r = 0.966,\ S = 0.668). \qquad (7)$$

Our correlation analysis showed that the rate of heterolysis of t-BuX is independent of the nucleophilic properties of the medium. In all cases the contribution of the parameters B or DN was close to or equal to zero with the exception of Eqn.(3), where B actually reduces slightly the rate of reaction. Consequently we conclude that the heterolysis of t-BuX proceeds without the nucleophilic cooperation by the solvent. This agrees with the conclusions of Koppel and Palm[20] and also Kulik[159] and conflicts with the conclusions of the authors of a number of studies[15,22,32,40,54,55,85,92–94,104,105,114,116,118], who believe that the formation of the transition state requires nucleophilic attack by the solvent. Our Eqns.(4), (6), and (7) showed that the conclusions[22,90,92–94] concerning the influence of the acid–base properties of the solvent on the rate of heterolysis of t-BuX are only half justified—only as regards the acid properties of the solvent.

Recently Abraham et al.[183] correlated the values of lg k for t-BuCl(Br, I) in 15 specially selected solvents (solvents 2–4, 7, 16, 23–26, 28, 29, 45, 47, 50, and 51) in terms of the Koppel–Palm equation and the equation

$$\lg k = a_0 + a_1\pi^* + a_2\alpha + a_3\beta, \qquad (8)$$

where π^* is the dipolarity parameter and α and β are the parameters of the electrophilicity and nucleophilicity of the solvents respectively[183]. In the former case the rate of reaction is described by a three-parameter equation including f(ε), f(n), and E with correlation coefficients of 0.975 (t-BuCl), 0.963 (t-BuBr), 0.934 (t-BuI), while in the latter case it is described by a two-parameter equation (the parameters π^* and α) with $r \cong 0.995$. This provided the authors[183] with grounds for the conclusion that Eqn.(8) describes the solvent effect better than the Koppel–Palm equation. Naturally a two-parameter equation is always better than a three-parameter equation, since the latter suffers from an uncertainty in its derivation[185,186], but the conclusions of Abraham et al.[183] provide only for the set of solvents indicated from which aromatic and organic polychloro-solvents have been excluded. Furthermore, out of the 45 values of lg K quoted by Abraham et al.[183], 14 had been calculated and four (t-BuBr in isopropyl alcohol, t-butyl alcohol, diethyl ether, and dioxan) had been taken from an unknown source—the values indicated are missing from Refs.6, 18, and 128 to which Abraham et al. refer[183]. Recently published data[129] on the solvolysis of t-BuBr in t-BuOH show that the value quoted by Abraham et al.[183] ($\lg k_1^{25} = -6.50$) is lower by 1.5 orders of magnitude than the experimental value (Table 1). It has been shown[159] that the correlation of the lg k for t-BuCl(Br, I) carried out for the entire set of solvents leads to better results. Consequently the set of solvents employed by Abraham et al.[183] on the one hand improved the correlation in terms of Eqn.(10) and on the other impaired the correlation in terms of the Koppel–Palm equation. In essence, the data obtained by Eqn.(10) agree well with the results of the correlation in terms of the Koppel–Palm equation, since it has been shown recently[187] that the parameter π^* is correlated with f(ε) and f(n). The main conclusion reduces in both cases to the rejection of the nucleophilic involvement of the solvent.

Nucleophilic attack by the solvent "from the rear" can actually hinder the unimolecular heterolytic reaction. Indeed the nucleophilic solvation of the carbonium ion generated leads to the stabilisation of the intermediates formed and hence can retard their subsequent migration along the reaction coordinate. It has been shown[32] that the nucleophilic involvement of a DMF molecule in the heterolysis of 2-bromo-2-methylpentane leads to the establishment of the dead-end equilibrium

$$\mathrm{DMF} \cdot \mathrm{R^+Br^-} \underset{-\mathrm{DMF}}{\overset{+\mathrm{DMF}}{\rightleftharpoons}} \underset{\mathrm{RBr}}{\mathrm{R^+Br^-}} \rightleftarrows \mathrm{R^+ \mid Solv \mid Br^-} \rightarrow \text{products}.$$

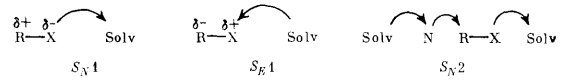
Consequently the intuitive hypothesis of Bentley and Schleyer[15] that the substrate should "make use" of the nucleophilic cooperation by the solvent does not occur on the main reaction pathway if it obtains at all.

In contrast to the nucleophilicity factor, other solvent parameters influence the rate of heterolysis of t-BuX and, depending on the nature of the leaving group or the set of solvents, any one of them can predominate.

The rate of heterolysis of t-BuCl in the entire set of proton-donating and aprotic solvents is determined mainly by the electrophilicity. The solvent polarity and polarisability promote the reaction to an appreciable extent. Calculation by the Koppel–Palm equation[129] shows that the solvent electrophilicity is also of decisive importance for t-BuBr and t-BuI.

It is possible to put forward the following picture of the mechanism of the unimolecular heterolysis of t-BuX: as a result of the action of the internal nucleophile (the t-butyl group), an electron is transferred to the departing group and this is sufficient for the rapid subsequent elimination of HX in the gas phase. In the condensed phase the reaction is to a large extent promoted by the delocalisation of the charge of the anion generated over the solvent molecule, i.e. by the electrophilic cooperation in the heterolysis. The positive charge generated does not require the nucleophilic cooperation by the solvent since it is sufficiently delocalised over the three methyl groups. Furthermore, the action of

the nucleophile is hindered by the pronounced steric hindrance. For reactions via the S_E1 mechanism, one can outline the opposite picture: in this case the nucleophilic cooperation in the heterolysis becomes decisive[188]. Reactions of the S_N2 type require both the nucleophilic and electrophilic cooperation by the solvent[93,189]. Hence follows a simple generalisation concerning the role of the solvent in substitution reactions:



S_N1 S_E1 S_N2

Analysis carried out separately in proton-donating and aprotic solvents[180] makes it possible to define and specify in greater detail the mechanism of the heterolysis of t-BuCl.

In proton-donating solvents the rate of reaction depends equally on the electrophilicity and polarisability of the solvent and is described by the two-parameter equation

$$\lg k = -(15.7\pm1.4) + (19.3\pm2.0)f(n) + (0.383\pm0.026)E \quad (r=0.934).$$

In aprotic solvents the decisive factor is the polarity and to a lesser extent the electrophilicity:

$$\lg k = -(17.7\pm1.7) + (15.5\pm1.4)f(\varepsilon) + (0.441\pm0.051)E \quad (r=0.941).$$

The dependence of the rate of heterolysis of t-BuCl in proton-donating solvents on the electrophilicity and polarisability factors can be explained by the fact that, as a result of the formation of hydrogen-bonded complexes by the anion generated, the negative charge is strongly delocalised over the solvent molecule, which leads to the formation of a readily polarisable transition state. In an aprotic medium the dependence of the rate of reaction mainly on the solvent polarity can be accounted for by the fact that in this instance the heterolysis occurs as a result of the dipole–dipole interaction of the t-BuCl molecules with solvent molecules[3,4,23,120,141]. If this is so, the rate of reaction should increase with increase of the dipole moment of the solvent. Indeed a satisfactory correlation has been observed between ε and μ (for solvents 23, 24, 26–32, 35–39, 41, 42, 45–47):

$$\mu = -13.0 + 13.4\varepsilon \quad (r=0.969,\ S=1.30).$$

The solvation of the anion generated should play a smaller role in this instance, which is in fact observed.

The differences between the rates of heterolysis of t-BuX in proton-donating and aprotic solvents are associated to some extent with the fact that in the former case a solvent-separated ion pair is formed in the rate-limiting stage, while in the latter case a contact ion pair is produced. It has been shown[44] that the formation of a solvent-separated ion pair depends much more on the formation of hydrogen-bonded complexes than the formation of a contact ion pair.

If *AN* is employed as the electrophilicity parmeter, the rate of heterolysis of t-BuCl is described satisfactorily by the two-parameter Eqn.(4), which also includes δ^2.

In contrast to t-BuCl, the rate of heterolysis of t-BuBr and t-BuI depends mainly on the self-association energy of the solvent, which is determined by the cohesive energy density and polarity of the solvent. We have

$$\lg k = -(8.06\pm0.28) + (13.9\pm1.2)\delta^2 \quad (r=0.963)$$

for t-BuBr and

$$\lg k = -(7.11\pm0.32) + (12.8\pm1.5)\delta^2 \quad (r=0.952)$$

for t-BuI.

One should note that δ^2 is an independent parameter. Indeed δ^2 is hardly correlated with the four parameters of Eqn.(2)—r = 0.72 for 41 solvents (solvents 2–9, 11, 13, 16–21, 23–32, 34–42, 45–47, 50, and 51). The maximum correlation coefficient among the one-parameter relations is observed for the δ^2–E relation (r = 0.70); allowance for the polarity parameter increases r to 0.72, while nucleophilicity and polarisability do not affect r. In proton-donating solvents (17 solvents) the multiple correlation coefficient is 0.83, while in aprotic solvents (24 solvents) it is 0.40.

The influence of the factor δ^2 on the rate of heterolysis of t-BuX can be explained by the fact that the residence time of the substrate in the solvent cage (10^{-8}–10^{-11} s) [23] and hence the probability of its ionisation increase with increase of the cohesion energy of the solvent. The migration of t-BuX relative to the solvent molecules leads to the dissipation of the energy required for the attainment of the transition state. If the influence of δ^2 is reduced solely to the energy required for the formation of the cage in the solvent, as is usually done[6,22,46], then it becomes incomprehensible why δ^2 should affect the rate of reaction if the process proceeds in the solution already formed. At the same time it is difficult to achieve a clear-cut interpretation of the dependence of the influence of δ^2 on the nature of the leaving group, since a different set of solvents has been used for each substrate.

In conformity with the rule of Richardson and Soper[190], the increase of the rate of heterolysis of t-BuBr with increase of the cohesion of the solvent shows that the products of the above reactions, or more correctly the transition state, have a greater cohesion than the initial reactants. The observed difference for t-BuCl can be hardly explained by the fact that in this case the cohesions of the reactants and reaction products, or more correctly $[\text{t-BuCl}]^{\neq}$, become equalised either due to the increase of the cohesion of t-BuCl or as a result of the decrease of the cohesion of the transition state. The explanation should apparently be sought in an increase of order in the solution[24] on passing from t-BuBr to t-BuCl. This conclusion is in good agreement with the latest interpretation of the low values of $\Delta C_p^{\neq}$ in S_N1 reactions[173], based on the concept that the solvent structure influences the solvation of the anion generated.

It is believed[129] that the marked decrease of $\Delta C_p^{\neq}$ in t-BuOH on passing from t-BuBr to t-BuCl is associated with the fact that the molecules of t-BuCl can enter freely into structural cavities or into the middle of the polymeric associated solvent species, while the molecules of t-BuBr are incapable of this. Cohesion therefore has apparently little influence on the heterolysis of t-BuCl, while a change in the solvent structure can lead to intense thermodynamic and kinetic effects[129,162,178]. It has been shown[191] that the stability of the solvation sphere around t-BuX depends on the nature of the halogen.

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Thus, the correlation analysis of the influence of solvent parameters shows that the rate of heterolysis of t-butyl halides depends mainly on the electrophilicity of the solvent and increases with its self-association energy. In all cases the heterolysis of t-BuX proceeds without the nucleophilic cooperation by the solvent.

In conclusion we may note that t-butyl halides are relatively unsuitable as standards for the comparative analysis of the influence of the solvent on solvolytic and other heterolytic reactions. Non-uniformity of the mechanism is characteristic of these substrates: a contact ion pair is formed in the rate-limiting stage in aprotic solvents, while a solvate-separated ion pair is formed in proton-donating solvents; in isolated instances (H_2O, phenol) carbonium ions are formed. Diphenylmethyl halides are more promising standards for the analysis of solvation effects.

During the preparation of the manuscript for the press, the paper of Swain et al.[192] was published and in it a correlation analysis has been carried out for 77 reactions in 61 solvents using the solvent electrophilicity (A) and nucleophilicity (B) parameters. The authors conclude that all the solvolytic reactions (26 systems) require both the nucleophilic and electrophilic cooperation of the solvent and that the influence of the nucleophilicity increases in the sequence Ph_2CHCl < t-BuCl < MeBr < 1-AdBr < t-BuBr. The series which they present[192] conflicts with modern ideas[14-16], according to which there should be no nucleophilic cooperation in 1-AdBr and such cooperation should be a maximum in MeBr. The reason for this discrepancy is that the parameters A and B of the solvents were calculated from the entire set of data on the basis of critical conditions arbitrarily selected by the authors[192]: $A = B = 1$ in water, $A = B = 0$ in hexane, and $A = 0$ in hexamethylphosphoramide and $B = 0$ in CF_3COOH. The parameters A and B obtained for other solvents as a result of the calculation[192] conflict with widely familiar experimental data. Thus, according to Swain et al.[192], acetic acid is less nucleophilic than formic acid and is less electrophilic than water. The lack of validity of the conclusions of Swain et al. [192] is associated also with the fact that they employed only an insignificant proportion of the experimental data. For example, out of the 35 known values of $\lg k$ for the heterolysis of t-BuCl in individual solvents only 6 were employed, while in the case of t-BuBr only 4 out of 21 were employed.

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