Substitution at Saturated Carbon. Part 26.† A Complete Analysis of Solvent Effects on Initial States and Transition States for the Solvolysis of the t-Butyl Halides in Terms of *G*, *H*, and *S* using the Unified Method

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The influence of 20—30 solvents on $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ for the solvolysis of t-butyl chloride and t-butyl bromide has been dissected into initial-state and transition-state contributions. Using the unified method in which the general equation (i) is applied to both these contributions, it is shown that the decrease in $\Delta G^\ddagger$ due to solvent dipolarity (π_1^*) and to solvent hydrogen-bond acidity (α_1) is primarily a transition-state effect, that there is little effect of solvent hydrogen-bond basicity (β_1) on either initial-state or transition-state, and that large effects of solvent Hildebrand solubility parameter (δ_H) on initial-state and transition-state partly cancel out.

$$XYZ = XYZ_0 + s(\pi_1^* + d\delta) + a\alpha_1 + b\beta_1 + h\delta_H^2/100 \qquad \text{(i)}$$

A similar analysis carried out on the transition-state transfer quantities, ΔH_t° and ΔS_t°, yields the surprising results that the influence of solvent π_1^* and α_1 values on the transition-state is primarily an entropic effect and that there is a very large influence of solvent hydrogen-bond basicity in increasing both ΔH_t° and ΔS_t° for the transition-state in an almost exactly compensatory way. It is suggested that this latter effect, previously unsuspected, may arise through solute/solvent lone pair/lone pair repulsions.

For many years, most studies of solvent effects on reaction rates were limited to simple regressions of rate constants (as $\log k$ or $\Delta G^\ddagger$) against some particular solvent parameter. More sophisticated methods of analysis are now available, and we consider two particular such methods that have been applied to the t-butyl halide solvolysis reactions. Firstly, multiparameter equations have been used to correlate rate constants, the earliest successful application being that of Koppel and Palm[1] who used the four-parameter equation (1), where f(ε) is a

$$\log k = \log k_0 + yf(\varepsilon) + pf(\eta) + eE + bB \qquad (1)$$

dielectric constant function such as $(\varepsilon - 1)/(2\varepsilon + 1)$, $f(\eta)$ is the refractive index function $(\eta^2 - 1)/(\eta^2 + 2)$, and E and B are measures of electrophilic solvation ability and nucleophilic solvation ability of the solvent respectively. An even more successful equation is the general equation (2) advocated by Abraham, Kamlet, Taft, and co-workers,[2–4] and applied not only to the solvolysis of the t-butyl halides[2,3] but to non-kinetic phenomena such as the Gibbs energies of transfer of ions and ion-pairs.[4] Here, π_1^* is a measure of solvent dipolarity, δ is a polarisability correction term, α_1 is the solvent hydrogen-bond acidity, β_1 the solvent hydrogen-bond basicity, and δ_H the Hildebrand solubility parameter of the solvent. The variable XYZ may be a $\log k$ or $\Delta G^\ddagger$ value, but can also be a Gibbs energy of transfer, ΔG_t^0, for non-kinetic processes. When applied to the t-butyl halide reactions in 21 non-aromatic solvents,‡ the full equation (2) took the form[3] of equations (3)—(5).

$$XYZ = XYZ_0 + s(\pi_1^* + d\delta) + a\alpha_1 + b\beta_1 + h\delta_H^2 \qquad (2)$$

We denote the number of data points as n, the standard deviation as s.d., and the multiple correlation constant as r. The correlations, equations (3)—(5), are the best ever reported for the t-butyl halide reactions when a wide range of solvents is used. It is immediately obvious that $\log k$ is increased by solvents that are dipolar (large π_1^* values) and are hydrogen-bond acids (large α_1 values), and clearly, much valuable information can be obtained by the use of multiparameter regression equations.

$$\log k\,(\mathrm{Bu^tCl}) = -14.60 + 5.10\,\pi_1^* + 4.17\,\alpha_1 + 0.73\,\beta_1 + 0.0048\,\delta_H^2 \qquad (3)$$
$$n = 21 \qquad \text{s.d.} = 0.242 \qquad r = 0.9973$$

$$\log k\,(\mathrm{Bu^tBr}) = -11.97 + 5.77\,\pi_1^* + 3.16\,\alpha_1 + 0.46\,\beta_1 + 0.0031\,\delta_H^2 \qquad (4)$$
$$n = 21 \qquad \text{s.d.} = 0.280 \qquad r = 0.9947$$

$$\log k\,(\mathrm{Bu^tI}) = -9.80 + 6.07\,\pi_1^* + 2.43\,\alpha_1 - 0.34\,\beta_1 + 0.0003\,\delta_H^2 \qquad (5)$$
$$n = 21 \qquad \text{s.d.} = 0.311 \qquad r = 0.9905$$

The second method that has been applied to the t-butyl halide reactions is the method of model solutes, used extensively by Abraham and co-workers.[5–13] In this procedure, the solvent effect on the initial-state is obtained by some thermodynamic method, and then the solvent effect on the transition-state is calculated *via* equation (6), where $\Delta G_t^0(i)$ represents the Gibbs

$$\Delta G_t^0(\mathrm{Tr}) = \Delta G_t^0(\mathrm{Bu^tX}) + \delta\Delta G^\ddagger \qquad (6)$$

energy of transfer of species i from a reference solvent to some

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† Part 25, M. H. Abraham and J. Andonian-Haftvan, *Bull. Soc. Chim. Belg.*, 1980, **89**, 819.

‡ Note that since δ is zero for non-aromatic and non-polyhalogenated solvents (*e.g.* solvents 1—21), the term in $d\delta$ drops out of equations (3)—(5).

other solvent, Tr denotes the transition state, and $\delta\Delta G^{\ddagger} = \Delta G^{\ddagger}$ (solvent) $-$ $\Delta G^{\ddagger}$ (reference solvent). The deduced values of ΔG_t^0(Tr) are then compared with ΔG_t^0 values for solutes that might serve as models for the transition-state. In the case of the t-butyl chloride reaction, comparison of ΔG_t^0(Tr) with ΔG_t^0 for the ion-pair Me_4NCl led to the conclusion that the t-butyl chloride transition state was quite ion-pair like in character, with a charge separation of about 0.8 units.[6—8,12,13]

Both of the methods described above have advantages and disadvantages. Although the application of equation (2) is straightforward, it does require a knowledge of the solvent parameters over a wide range of solvents. But then, information as to the effect of specific solvent properties is obtained. The one great disadvantage of equation (2) and, indeed, of any equation that is used to correlate rate constants, is that there is no rigorously logical process that can be used to assign the influences of specific solvent effects to the transition-state or the initial-state. Thus in equations (3)—(5), for example, it is intuitively reasonable to assign the accelerating influence of dipolar solvents to an effect on the transition-state.[3] But it is not so intuitively obvious that the progression in the β_1 term is due to a slight accelerating transition-state effect (nucleophilic solvent assistance) in the case of t-butyl chloride and to an almost-zero transition-state effect for t-butyl bromide and t-butyl iodide. It might just as well be the case that there is a constant transition-state accelerating effect, but that there is an initial-state decelerating effect with t-butyl bromide and t-butyl iodide.

The method of model solutes also has its own advantages and disadvantages. Because initial-state effects are subtracted out, all the information gleaned refers only to the transition-state, a decided advantage. On the other hand, it is not easy to deduce specific effects of the solvent simply by comparing ΔG_t^0(Tr) with ΔG_t^0 for a model solute, and in some cases it is difficult even to suggest a suitable model solute. Thus in the Menschutkin reaction of triethylamine with ethyl iodide, it can be demonstrated that the transition-state does not resemble the Et_4NI ion-pair,[10] but so far it has proved impossible to obtain the necessary thermodynamic data for a model solute that the transition-state might resemble.

There therefore seems to be scope for a method of analysis of solvent effects that does not suffer from all the disadvantages mentioned. It is the purpose of this paper to show that the method of multiple linear regression and the method of model solutes can be amalgamated into a 'unified method' that can be used to obtain information about specific interactions of solvents with transition-states, and can be used to compare such results with those for various solutes. In the unified method, initial-state effects are first subtracted out *via* equations such as (6) in order to obtain values of ΔG_t^0(Tr). Then the multiple linear regression procedure is applied to these ΔG_t^0(Tr) values, and the resulting equation compared term-by-term to the kinetic regression equation, that is to equations such as (3)—(5) where log *k* is replaced by $\Delta G^{\ddagger}$. In this way it should be possible to take each term in equation (3), for example, and to conclude exactly how the term arises through some combination of initial-state and transition-state effects.

In an extension of this procedure, we also examine solvent effects on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, and separate these into initial-state and transition-state values *via* the complementary equations (7) and (8). To this effect we have measured the

$$\Delta H_t^0(\mathrm{Tr}) = \Delta H_t^0(\mathrm{Bu^tX}) + \delta\Delta H^{\ddagger} \qquad (7)$$

$$\Delta S_t^0(\mathrm{Tr}) = \Delta S_t^0(\mathrm{Bu^tX}) + \delta\Delta S^{\ddagger} \qquad (8)$$

thermodynamics of t-butyl chloride and t-butyl bromide in a wide range of solvents.

Experimental

The solutes t-butyl chloride (H and W) and t-butyl bromide (BDH) were distilled, and the middle cut collected and stored in the dark. All the solvents were purified by standard methods and then distilled either under nitrogen or *in vacuo*. The middle fraction was then percolated through a column of molecular sieve (4 Å) and collected under nitrogen. When used for calorimetric work, the solvents were transferred from the collection vessel to the calorimeter *via* a glass connection under a stream of nitrogen.

Calorimetric measurements were carried out exactly as described before.[14,15] Since the calorimetric ampoules were not completely filled with the solutes, corrections were made both for the condensation of the solute vapour in the empty space in the ampoule and for the evaporation of the solvent into the empty space. These two corrections tend to cancel out, and in the event the sum total of the corrections was quite small. The corrected ΔH_s^0 values are given in Table 1; in all cases two to four measurements were made on each system. In the case of trifluoroethanol, a value of ΔH_s^0 for t-butyl chloride could just be obtained, but it was not possible to obtain a value for t-butyl bromide. In hexafluoropropan-2-ol, reaction with the solvent was so rapid that no ΔH_s^0 values could be determined.

Raoult's law activity coefficients were obtained by the gas–liquid chromatographic head-space method described in detail before.[15] The only problems occurred with the solvents trifluoroethanol and hexafluoropropan-2-ol due to rapid reaction of the solutes with solvents. In the case of trifluoroethanol, values were obtained by successively sampling the head-space vapour and the solvent, and hence deducing the concentrations of solute in the head-space and in the solvent at the same instant in time. With hexafluoropropan-2-ol, reaction with the solvent was so rapid that no γ^{∞} values could be obtained. The obtained γ^{∞} values are given in Table 2.

Discussion

Solvent Effects in Terms of Gibbs Energies.—Values of ΔG_t^0, ΔH_t^0, and ΔS_t^0 for transfer of the t-butyl halides from the standard solvent dimethylformamide (DMF) are given in Table 2, on the mol fraction scale. In the calculation of ΔH_t^0 we have used our own ΔH_s^0 values, but use of ΔH_s^0 values obtained by Goncalves and Simoes[16] (see Table 1) would not significantly alter any of our conclusions. As is generally found for rather inert non-electrolytes, for example tetramethyltin,[15] solvent effects on these transfer functions are quite small, except in the case of water (and aqueous organic media). Because the variations in the transfer function are rather small, we have estimated a few extra values by comparison with related solvents, see Table 2.

It is often useful to have thermodynamic functions for the solution of gaseous solutes. These can be obtained from combination of γ^{∞} and ΔH_s^0 values with parameters for the vaporisation of the pure liquid solutes to the ideal gas. In Table 3 are given these parameters, together with our calculated ΔG_s^0 (gas, 1 atm), ΔH_s^0 (gas, 1 atm), and ΔS_s^0 (gas, 1 atm) values for solution in the standard solvent, DMF. From the transfer parameters in Table 2, the thermodynamics of solution of the gaseous solutes in any other solvent may simply be calculated.

The initial-state effects, as transfer values, can be analysed using the general equation (2). Initial-state ΔG_t^0 values are available for all the 21 solvents studied previously,[3] these being solvents 1—21 in Table 2. The solvent parameters for these 21 solvents were taken as exactly those listed before, and the resulting regression equations are:

Table 1. Enthalpies of solution of t-butyl chloride and t-butyl bromide in cal mol^{-1} at 298 k[a]

Solvent	Bu^{t}Cl		Bu^{t}Br	
Methanol	360[b]	373[c]	475[b]	525[c]
Ethanol	339[b]	359[c]	401[b]	418[c]
Propan-1-ol	427[b]	387[c]	451[b]	478[c]
Propan-2-ol	836[b]	853[c]	881 ± 30	985[c]
Butan-1-ol	530[b]	502[c]	521 ± 30	566[c]
2-Methylpropan-2-ol	1 635[b]	1 510[c]	1 603 ± 22	1 735[c]
Trifluoroethanol	1 152 ± 80			
Acetic acid	385 ± 30		487 ± 20	
Dimethyl sulphoxide	1 331 ± 15		1 340 ± 10	
Propylene carbonate	725 ± 5		831 ± 30	
Nitromethane	1 244 ± 10		1 443 ± 15	
Dimethylformamide	522 ± 10		530 ± 5	
Dimethylacetamide				
Acetonitrile	729 ± 10		906 ± 5	
N-Methylpyrrolidinone	273 ± 5		334 ± 5	
Nitrobenzene	458 ± 10		505 ± 5	
Diethyl oxalate	449 ± 15		430 ± 5	
Acetone	400 ± 5		535 ± 15	
1,2-Dichloroethane	390 ± 10		343 ± 10	
Dichloromethane	195 ± 5		159 ± 5	
Ethyl acetate	239 ± 5		257 ± 15	
Diethyl ether	45 ± 30		190 ± 50	
Cyclohexane	628 ± 40		564 ± 5	

[a] This work except where indicated. [b] Ref. 11. [c] Ref. 16.

$$\Delta G_t^0(\text{Bu}^t\text{Cl}) = -0.856 - 0.542\,\pi_1^* - 0.032\,\alpha_1 - 0.308\,\beta_1 + 1.130\,\delta_H^2/100 \quad (9)$$
$$n = 21 \qquad \text{s.d.} = 0.231 \qquad r = 0.9857$$

$$\Delta G_t^0(\text{Bu}^t\text{Br}) = -0.912 - 0.529\,\pi_1^* + 0.038\,\alpha_1 - 0.279\,\beta_1 + 1.156\,\delta_H^2/100 \quad (10)$$
$$n = 21 \qquad \text{s.d.} = 0.227 \qquad r = 0.9871$$

In both equations (9) and (10), only the term in $\delta_H^2/100$ is significant, as might be expected for the transfer of rather non-dipolar solutes that have little or no hydrogen-bonding properties. In Table 4 are listed ΔG_t^0 values for a more extensive set of solvents for which initial-state and transition-state effects can be obtained. The solvents 1—21 are those mentioned above, but solvent parameters are also available for the extra solvents 22—30. These parameters are given in Table 5, and application of the general equation (2) to all 30 solvents yields equations (11) and (12). Again, we note that since δ is not zero for some of the solvents 22—30, the $d\delta$ term is now required.

$$\Delta G_t^0(\text{Bu}^t\text{Cl}) = -0.727 - 0.851\,(\pi_1^* + 0.107\,\delta) - 0.014\,\alpha_1 - 0.382\,\beta_1 + 1.151\,\delta_H^2/100 \quad (11)$$
$$n = 30 \qquad \text{s.d.} = 0.319 \qquad r = 0.9633$$

$$\Delta G_t^0(\text{Bu}^t\text{Br}) = -1.239 - 0.161\,(\pi_1^* + 1.124\,\delta) + 0.041\,\alpha_1 - 0.060\,\beta_1 + 1.111\,\delta_H^2/100 \quad (12)$$
$$n = 30 \qquad \text{s.d.} = 0.260 \qquad r = 0.9771$$

Finally, application of equation (2) to all 37 solvents in Table 2 for which solvent parameters are available* (Table 5) yields the equations:

$$\Delta G_t^0(\text{Bu}^t\text{Cl}) = -1.175 - 0.175\,(\pi_1^* + 0.943\,\delta) - 0.014\,\alpha_1 - 0.110\,\beta_1 + 1.081\,\delta_H^2/100 \quad (13)$$
$$n = 37 \qquad \text{s.d.} = 0.225 \qquad r = 0.9783$$

$$\Delta G_t^0(\text{Bu}^t\text{Br}) = -1.222 - 0.190\,(\pi_1^* + 0.926\,\delta) + 0.038\,\alpha_1 - 0.055\,\beta_1 + 1.114\,\delta_H^2/100 \quad (14)$$
$$n = 37 \qquad \text{s.d.} = 0.239 \qquad r = 0.9776$$

The more extensive set of results included in equations (11)—(14) confirms the conclusions from equations (9) and (10), namely that only the term in δ_H^2 is significant, in all cases at more than 99.99% confidence level (CL). But note that in equations (9), (10), and (11) CL for the β_1 term is around 85%.

The $\Delta G_t^0(\text{Bu}^t\text{X})$ values may now be combined with $\delta\Delta G^\ddagger$ values through equation (6) to yield corresponding transition-state quantities. Rate constants required to calculate $\delta\Delta G^\ddagger$ for solvents 1—21 are as set out before,[3] and other rate constants have been taken from the compilations of Abraham,[7] and of Dvorko *et al.*[17] Results are collected in Table 4, both for the previous set of 21 solvents, and for a more extensive set. Using the solvent parameters given before for solvents 1—21, and those in Table 5 for solvents 22—30, equation (1) can now be applied to the $\delta\Delta G^\ddagger$ values, the $\Delta G_t^0(\text{Tr})$ values and the $\Delta G_t^0(\text{Bu}^t\text{X})$ values to explain how each term in the general equation arises from a combination of initial-state and transition-state effects. The error in the $\Delta G_t^0(\text{Bu}^t\text{X})$ values is around 0.1 kcal mol^{-1}; that in $\delta\Delta G^\ddagger$ is not easy to estimate but is not likely to be less than 0.2 kcal mol^{-1} for the solvent set 1—21 and could be as large as 0.4 kcal mol^{-1} for the extended set 1—30.† The corresponding error in $\delta G_t^0(\text{Tr})$ will then be around 0.3 and 0.5 kcal mol^{-1}, respectively. The standard deviation found in the various correlations are reasonably in accord with these estimated errors.

Details of all the equations are collected in Table 6. Equations A3 and C3 are exactly equivalent to those given before when the dependent variable was log k instead of $\delta\Delta G^\ddagger$, but each term in the log k equations has to be multiplied by -1.3642 to yield the constants in the $\delta\Delta G^\ddagger$ equations. However, the correlation constants for the $\delta\Delta G^\ddagger$ and log k equations are exactly the same. Application of equation (2) to the $\Delta G_t^0(\text{Tr})$ values yields quite reasonable correlations, especially for the restricted set of solvents 1—21. There is very little difference between the constants obtained for correlations with solvents 1—21 and those with solvents 1—30, except that the latter correlation must perforce include the polarisability correction term, δ.

Table 6A yields a breakdown of solvent effects on $\Delta G_t^0(\text{Tr})$, $\Delta G_t^0(\text{Bu}^t\text{Cl})$, and $\delta\Delta G^\ddagger$ term-by-term in the general equation (2) for the 21 solvents used before.[3] There is no doubt that the influence of solvent dipolarity (π_1^*) and solvent hydrogen-bond acidity (α_1) are almost exclusively transition-state effects, the interpretation of which was detailed previously.[3] The influence of solvent hydrogen-bond basicity, taken as a measure of solvent nucleophilicity,‡ is interesting in that there does seem to be a slight initial-state effect that tends to lower $\Delta G_t^0(\text{Bu}^t\text{Cl})$. Hence the solvent influence on $\Delta G_t^0(\text{Tr})$ is somewhat larger than on $\delta\Delta G^\ddagger$ and indicates that there is a definite (although rather small) effect of nucleophilic solvent assistance at the transition state. The breakdown into initial-state and transition-state effects is very informative in the $\delta_H^2/100$ term. The negative (*i.e.* rate accelerating) term in the $\delta\Delta G^\ddagger$ correlation can now be shown to be the result of a positive (*i.e.* rate retarding) effect on the transition-state, that is totally overcome by a very positive effect on the initial-state that by itself is rate accelerating. Now transfer of a large, rather non-polar, solute such as t-butyl chloride will result in a positive coefficient in the $\delta_H^2/100$ term largely due to the increased work in creating a cavity in solvents with high internal pressures. In the case of the transition-state that is of about the same intrinsic volume as the initial-state, the

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* Only diethyl oxalate in Table 2 is not included, because of lack of the required solvent parameters.

† 1 kcal = 4.184 kJ.

‡ Note that Bentley[18] has pointed out that this is an assumption.

Table 2. Raoult's law activity coefficients and thermodynamics of transfer from dimethylformamide of t-butyl halides at 298 K mol fraction scale[a]

		$\mathrm{Bu^tCl}$				$\mathrm{Bu^tBr}$			
		γ^∞	ΔG_t^0	ΔH_t^0	ΔS_t^0	γ^∞	ΔG_t^0	ΔH_t^0	ΔS_t^0
1	Water	2.2×10^4	5.11^b	1.53^c	−12.0	3.0×10^4	5.28^b	1.00^d	-14.0^d
2	Methanol	10.0	0.54^b	-0.16^e	−2.3	14.0	0.73^b	-0.06^e	−2.6
3	Ethanol	6.40	0.28^b	-0.18^e	−1.5	7.25	0.34^b	-0.13^e	−1.6
4	Propan-1-ol	5.59	0.20^b	-0.10^e	−1.0	6.43	0.27	-0.08^e	−1.2
5	Propan-2-ol	6.04	0.24^b	0.31^e	0.2	6.20	0.25^b	0.35	0.3
6	Butan-1-ol	4.62	0.08^b	0.01^e	−0.2	5.46	0.17	−0.01	−0.6
7	2-Methylpropan-2-ol	4.60	0.08^b	1.11^e	3.5	5.04	0.13^b	1.07	3.2
8	Ethylene glycol	34.9	1.28			43.3	1.40		
9	Formamide	130.2	2.06			159.0	2.17		
10	Trifluoroethanol	6.33	0.27	0.63	1.2	7.36	0.35	0.70^d	1.2
11	Hexafluoropropan-2-ol	3.02^d	−0.17			3.63^d	−0.07		
12	Nitromethane	7.38	0.36^b	0.72	1.2	9.50	0.50^b	0.91	1.4
13	Dimethylformamide	4.02	0.00	0.00	0.0	4.08	0.00	0.00	0.0
14	Dimethylacetamide	3.63	−0.06	-0.06^d	0.0	3.88	-0.03^b	−0.03	0.0
15	Acetonitrile	5.18	0.15	0.21	0.2	3.94	−0.02	0.38	1.3
16	*N*-Methylpyrrolidinone	4.30	0.04^b	−0.25	−1.0	4.29	0.03	−0.20	−0.8
17	Acetone	2.46	-0.29^b	−0.12	0.6	2.73	−0.24	0.00	0.8
18	Tetrahydrofuran	2.42	−0.30			2.46	−0.30		
19	Dioxane	2.55	-0.27^b			2.58	−0.27		
20	Ethyl acetate	1.59	−0.55	−0.28	0.9	1.50	−0.59	−0.27	1.1
21	Diethyl ether	2.01	-0.41^b	−0.48	−0.2	1.97	−0.43	−0.34	0.3
22	Acetic acid	6.13	0.25	−0.14	−1.3	7.37	0.35^b	−0.04	−1.3
23	Dimethyl sulphoxide	11.45	0.62^b	0.81	0.6	18.03	0.88^b	0.81	−0.2
24	Propylene carbonate	6.90	0.32	0.20	−0.4	6.01	0.23	0.30	0.2
25	Nitrobenzene	2.82	-0.21^b	−0.06	0.5	2.93	−0.20	−0.02	0.6
26	Benzonitrile	3.02	−0.17	-0.06^d	0.4	2.85	−0.21	-0.02^d	0.6
27	1,2-Dichloroethane	1.88	−0.45	−0.13	1.1	1.84	−0.47	−0.18	1.0
28	Dichloromethane	2.92	−0.19	−0.33	−0.5	2.01	−0.42	−0.37	0.2
29	Chlorobenzene	1.51	-0.58^b			1.71	−0.51		
30	Benzene	1.67	-0.52^b			1.61	−0.55		
31	Ethyl benzoate	2.08	−0.39			1.87	−0.46		
32	Bromobenzene	1.79	−0.48			1.83	−0.47		
33	Hexane	1.85	−0.46			1.78	−0.49		
34	Decane	1.76	-0.49^b			2.24	−0.35		
35	Hexadecane	1.30^f	−0.67			1.18^f	−0.74		
36	Cyclohexane	1.95	−0.43	0.11	1.8	1.75	−0.50	0.03	1.8
37	Tetrachloromethane	1.35^g	−0.65			1.27^d	−0.69		
38	Diethyl oxalate	2.60	−0.26	−0.07	0.6	2.26	−0.35	−0.10	0.8

[a] This work unless indicated otherwise. Values of ΔG_t^0 and ΔH_t^0 in kcal $\mathrm{mol^{-1}}$ and ΔS_t^0 in cal $\mathrm{K^{-1}\ mol^{-1}}$. [b] Ref. 7. [c] Approximate value from ref. 8. [d] Estimated value. [e] Ref. 11. [f] M. H. Abraham, P. L. Grellier, and R. A. McGill, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, 797. [g] M. M. Valle, G. C. Calero, and C. G. Losa, *Rev. Real. Ac. Nat. Madrid*, 1969, **63**, 533.

Table 3. Thermodynamics of vaporisation of t-butyl halides and of solution of the gaseous halides in DMF at 298 K

	$\mathrm{Bu^tCl}$	$\mathrm{Bu^tBr}$
ΔG_v^0	0.56^a	1.00^a
ΔH_v^0	6.93^b	7.60^b
ΔS_v^0	21.4	22.1
ΔG_s^0 (gas ⟶ DMF)	0.26	−0.16
ΔH_s^0 (gas ⟶ DMF)	−6.41	−7.07
ΔS_s^0 (gas ⟶ DMF)	−22.4	−23.2

[a] R. R. Driesbach, 'Physical Properties of Chemical Compounds,' Vol. III, ACS, Washington DC, 1961. Values in kcal $\mathrm{mol^{-1}}$. [b] I. Wadsö, *Acta Chem. Scand.*, 1968, **22**, 2438. Values in kcal $\mathrm{mol^{-1}}$.

much lower coefficient in the $\delta_H^2/100$ term must be a result of some extra exoergic interactions involving the highly dipolar transition-state and the solvent. Previously, just on the basis of a log *k* ($G^\ddagger$) correlation, it was suggested that solvent reorganisation/electrostriction took place round the transition-state, and our results are in complete accord with such a suggestion.

The additional range of solvents 1—30, results for which are in Table 6B, just confirm all the equations listed in Table 6A. One of the criteria of the stability of a multiple regression equation is that the coefficients do not alter appreciably when subsets of data are used. Results in Table 6A and 6B show that the three regression equations in Table 6A (or 6B) are firmly based.

Results for t-butyl bromide in the 21 solvents are given in Table 6C, and follow closely those for t-butyl chloride in terms of π_1^* and α_1. The influence of solvent dipolarity and hydrogen-bond acidity are undoubtedly transition-state effects.

The effect of solvent hydrogen-bond basicity, or nucleophilic power, is not quite so straightforward. In the case of $\delta\Delta G^\ddagger$, the term in β_1 is significant at only the 92% confidence level, and on this basis it was concluded previously that nucleophilic solvent assistance is not significant. But for solvents 1—21, the slight effect of solvent basicity on the initial-state results in the β_1 term for the t-butyl bromide transition state now being statistically significant, at the 96.8% confidence level. The solvent set 1—30 yields appreciably poorer correlations than does the reduced set, and we feel that solvent nucleophilic participation at the t-butyl bromide transition state, although small, is just about significant.

Table 4. Initial-state and transition-state solvent effects in terms of Gibbs energy at 298 K mol fraction scale, in kcal mol^{-1}

	Solvent	$\mathrm{Bu^tCl}$			$\mathrm{Bu^tBr}$		
		$\Delta G_t^0(\mathrm{Bu^tCl})$	$\delta\Delta G^{\ddagger}$	$\Delta G_t^0(\mathrm{Tr})$	$\Delta G_t^0(\mathrm{Bu^tBr})$	$\delta\Delta G^{\ddagger}$	$\Delta G_t^0(\mathrm{Tr})$
1	Water	5.11	−9.56	−4.45	5.28	−7.50	−2.22
2	Methanol	0.54	−3.34	−2.80	0.73	−1.58	−0.85
3	Ethanol	0.28	−2.02	−1.74	0.34	−0.37	−0.03
4	Propan-1-ol	0.20	−1.66	−1.46	0.27	0.01	0.28
5	Propan-2-ol	0.24	−1.10	−0.86	0.25	0.52	0.77
6	Butan-1-ol	0.08	−1.40	−1.32	0.17	0.25	0.42
7	2-Methylpropan-2-ol	0.08	−0.38	−0.30	0.13	1.20	1.33
8	Ethylene glycol	1.28	−5.37	−4.09	1.40	−3.41	−2.01
9	Formamide	2.06	−5.66	−3.60	2.17	−3.78	−1.61
10	Trifluoroethanol	0.27	−6.23	−5.96	0.35	−4.09	−3.74
11	Hexafluoropropan-2-ol	−0.17	−7.98	−8.15	−0.07	−5.28	−5.35
12	Nitromethane	0.36	−0.59	−0.23	0.50	−0.25	0.25
13	Dimethylformamide	0.00	0.00	0.00	0.00	0.00	0.00
14	Dimethylacetamide	−0.06	1.04	0.98	−0.03	1.20	1.17
15	Acetonitrile	0.15	0.18	0.33	−0.02	0.38	0.36
16	*N*-Methylpyrrolidinone	0.04	0.57	0.61	0.03	0.52	0.55
17	Acetone	−0.29	1.84	1.55	−0.24	2.06	1.82
18	Tetrahydrofuran	−0.30	3.34	3.04	−0.30	3.66	3.36
19	Dioxane	−0.27	3.08	2.81	−0.27	3.96	3.69
20	Ethyl acetate	−0.55	4.02	3.47	−0.59	4.20	3.61
21	Diethyl ether	−0.41	5.72	5.31	−0.43	5.97	5.54
22	Acetic acid	0.25	−2.52 [b]	−2.27	0.35	−0.14 [b]	0.21
23	Dimethyl sulphoxide	−0.84	0.62 [b]	−0.22	0.88	−0.64 [c]	0.22
24	Propylene carbonate	0.32	0.35 [b]	0.67	0.23	−0.16 [b]	0.07
25	Nitrobenzene	−0.21	1.60 [b]	1.39	−0.20	1.81 [b]	1.61
26	Benzonitrile	−0.17	1.75 [c]	1.58	−0.21	2.03 [b]	1.82
27	1,2-Dichloroethane	−0.45	1.35 [b]	0.90	−0.47	2.17 [b]	1.70
28	Dichloromethane	−0.19	2.59 [c]	2.40	−0.42	2.91 [b]	2.49
29	Chlorobenzene	−0.58	3.81 [b]	3.23	−0.51	4.16 [c]	3.65
30	Benzene	−0.52	4.92	4.40	−0.55	5.32 [c]	4.77
38	Diethyl oxalate	−0.26	2.31 [c]	2.05	−0.35	2.62 [b]	2.27

[a] Values of $\Delta G_t^0(\mathrm{Bu^tCl})$ and $\Delta G_t^0(\mathrm{Bu^tBr})$ from Table 2, $\delta\Delta G^{\ddagger}$ values from rate constants in ref. 3, except where shown. [b] From rate constants in refs. 7 and 17. [c] Estimated from rate constants for the other t-butyl halides in aprotic solvents.

Table 5. Additional solvent parameters used in the correlations[a]

	Solvent	$\delta_H^2/100$	π_1^*	δ	α_1	β_1
22	Acetic acid	2.035 [b]	0.64	0	1.12	0.45 [c]
23	Dimethyl sulphoxide	1.688	1.00	0	0	0.76
24	Propylene carbonate	1.769	0.83	0	0	0.40
25	Nitrobenzene	1.222	1.01	1.0	0	0.30
26	Benzonitrile	1.229	0.90	1.0	0	0.37
27	1,2-Dichloroethane	0.983	0.81	0.5	0	0
28	Dichloromethane	0.977	0.82	0.5	0.30	0
29	Chlorobenzene	0.936	0.71	1.0	0	0.07
30	Benzene	0.838	0.59	1.0	0	0.10
31	Ethyl benzoate	0.917 [d]	0.74	1.0	0	0.41
32	Bromobenzene	0.974	0.79	1.0	0	0.06
33	Hexane	0.528	−0.08	0	0	0
34	Decane	0.597	0.03	0	0	0
35	Hexadecane	0.641	0.08	0	0	0
36	Cyclohexane	0.672	0	0	0	0
37	Tetrachloromethane	0.738	0.28	0.5	0	0

[a] Values for solvents 1—21 are exactly those given before.[3] [b] From ΔH_v^0 at 298 K for vaporisation to monomeric solute vapour, M. H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 153. [c] Taken as that for ethyl acetate. [d] From a calorimetrically determined value of ΔH_v^0 at 298 K, 13.8 kcal mol^{-1}, by M. H. Abraham and R. J. Irving, unpublished work.

Our conclusions as to the nature of the t-butyl halide transition states, especially the dipolar character, are quite consistent with previous work by us and by other groups of workers. For example, Clark and Taft[19] through salt effect studies, and Arnett[20] through his classical work on solvent effects, both showed that the t-butyl chloride transition state was highly dipolar in character.

The unified method, as we have shown above, enables the influence of solvents on rate constants (as $G^{\ddagger}$ values) to be broken down into initial-state and transition-state contributions term-by-term in the general regression equation (2). The unified method will also allow transition-state effects to be compared with effects on a variety of solutes, not just model solutes, again term-by-term in the general equation (2). We refrain from such an analysis at this point, because we shall summarise all our results on transition-states and various solutes in a later paper.

Solvent Effects in Terms of Enthalpy and Entropy.—Equations (7) and (8) are used to dissect the solvent effect on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ into transition-state and initial-state contributions. Activation enthalpies are collected in Table 7; values are also given[17] for the t-butyl iodide reaction in order that a number of estimations can be made. Usually, it seems as though $\Delta H^{\ddagger}(\mathrm{Bu^tCl}) - \Delta H^{\ddagger}(\mathrm{Bu^tBr})$ is around 1.7 kcal mol^{-1}, and $\Delta H^{\ddagger}(\mathrm{Bu^tBr}) - \Delta H^{\ddagger}(\mathrm{Bu^tI})$ is 1.5 kcal mol^{-1}. The dissection *via* equation (7) is given in Table 8. Initial-state effects as $\Delta H_t^0(\mathrm{Bu^tX})$, are rather small and so $\Delta H_t^0(\mathrm{Tr})$ tends to follow $\delta\Delta H^{\ddagger}$. There is no need for a separate dissection in terms of entropy, equation (8), because the entropic terms can be calculated from G and H, but we can state that $\Delta S_t^0(\mathrm{Bu^tX})$ values are again rather small, except for transfer to water, see Table 2. Errors in $\Delta H_t^0(\mathrm{Bu^tX})$ are very small, less than 0.1 kcal mol^{-1}, because these values have been determined calorimetrically (see Table 1). However, errors in $\Delta H^{\ddagger}$ and hence in $\Delta H_t^0(\mathrm{Tr})$ are likely to be quite large, possibly as high as 1 kcal

Table 6. Analysis of initial-state and transition-state effects in terms of Gibbs energy, in kcal mol^{-1} at 298 K, mol fraction scale

	n	s.d.	r	CL%			
				π_1^*	α_1	β_1	$\delta_H^2/100$
A Bu^{t}Cl, solvents 1—21							
$\Delta G_t^0(\text{Tr}) = 7.39 - 7.50\,\pi_1^* - 5.72\,\alpha_1 - 1.29\,\beta_1 + 0.48\,\delta_H^2/100$	21	0.45	0.9925	100^a	100^a	99.5	99.7
$\Delta G_t^0(\text{Bu}^t\text{Cl}) = -0.86 - 0.54\,\pi_1^* - 0.03\,\alpha_1 - 0.31\,\beta_1 + 1.13\,\delta_H^2/100$	21	0.23	0.9856	86	22	84	100^a
$\delta\Delta G^\ddagger = 8.25 - 6.96\,\pi_1^* - 5.70\,\alpha_1 - 0.99\,\beta_1 - 0.65\,\delta_H^2/100$	21	0.33	0.9973	100^a	100^a	99.6	100^a
B Bu^{t}Cl, solvents 1—30							
$\Delta G_t^0(\text{Tr}) = 7.22 - 7.34\,(\pi_1^* - 0.16\,\delta) - 5.46\,\alpha_1 - 1.21\,\beta_1 + 0.42\,\delta_H^2/100$	30	0.66	0.9805	100^a	100^a	97.5	96.5
$\Delta G_t^0(\text{Bu}^t\text{Cl}) = -0.73 - 0.85\,(\pi_1^* + 0.11\,\delta) - 0.01\,\alpha_1 - 0.38\,\beta_1 + 1.15\,\delta_H^2/100$	30	0.32	0.9633	95	8	87	100^a
$\delta\Delta G^\ddagger = 7.95 - 6.49\,(\pi_1^* - 0.20\,\delta) - 5.45\,\alpha_1 - 0.83\,\beta_1 - 0.73\,\delta_H^2/100$	30	0.68	0.9863	100^a	100^a	83	99.9
C Bu^{t}Br, solvents 1—21							
$\Delta G_t^0(\text{Tr}) = 7.75 - 8.40\,\pi_1^* - 4.27\,\alpha_1 - 0.91\,\beta_1 + 0.73\,\delta_H^2/100$	21	0.43	0.9822	100^a	100^a	96.8	100^a
$\Delta G_t^0(\text{Bu}^t\text{Br}) = -0.91 - 0.53\,\pi_1^* + 0.04\,\alpha_1 - 0.28\,\beta_1 + 1.16\,\delta_H^2/100$	21	0.23	0.9871	85	27	81	100^a
$\delta\Delta G^\ddagger = 8.66 - 7.87\,\pi_1^* - 4.31\,\alpha_1 - 0.63\,\beta_1 - 0.43\,\delta_H^2/100$	21	0.38	0.9947	100^a	100^a	92	99.8
D Bu^{t}Br, solvents 1—30							
$\Delta G_t^0(\text{Tr}) = 7.55 - 8.23\,(\pi_1^* - 0.19\,\delta) - 3.96\,\alpha_1 - 0.81\,\beta_1 + 0.66\,\delta_H^2/100$	30	0.66	0.9672	100^a	100^a	88	99.8
$\Delta G_t^0(\text{Bu}^t\text{Br}) = -1.24 - 0.16\,(\pi_1^* + 1.12\,\delta) + 0.04\,\alpha_1 - 0.06\,\beta_1 + 1.11\,\delta_H^2/100$	30	0.26	0.9771	36	27	23	100^a
$\delta\Delta G^\ddagger = 8.78 - 8.06\,(\pi_1^* - 0.22\,\delta) - 4.00\,\alpha_1 - 0.75\,\beta_1 - 0.45\,\delta_H^2/100$	30	0.68	0.9799	100^a	100^a	84	97.4

[a] $\geqslant$ 99.999.

Table 7. Activation enthalpies for the t-butyl halide reactions^a in kcal mol^{-1}

		Bu^{t}Cl	Bu^{t}Br	Bu^{t}I
1	Water	23.2	21.9	
2	Methanol	25.1	23.0	22.0
3	Ethanol	26.1	24.4	
4	Propan-1-ol	26.0	(24.3)	
5	Propan-2-ol	23.6	(22.0)	
6	Butan-1-ol	24.5	(22.8)	
9	Formamide	22.4	(20.7)	
10	Trifluoroethanol	19.7^b	(18.0)	
11	Hexafluoropropan-2-ol	(17.9)	16.2^c	
12	Nitromethane	23.2	20.0	
13	Dimethylformamide	25.2	21.9^d	
15	Acetonitrile	23.9	22.4	17.1
16	*N*-Methylpyrrolidinone	(23.8)	22.1^d	
17	Acetone	20.4	19.5	19.0
18	Tetrahydrofuran	(23.1)	(21.4)	19.9
20	Ethyl acetate	(20.3)	(18.6)	17.1
22	Acetic acid	25.8	24.1	
24	Propylene carbonate	20.5	20.2	16.9
25	Nitrobenzene	25.7	20.3	19.2
26	Benzonitrile	(23.2)	21.5	20.0
27	1,2-Dichloromethane	(22.0)	18.4	19.8
28	Dichloromethane	(19.5)	16.6	17.4
29	Chlorobenzene	(21.7)	(20.0)	18.5
30	Benzene	(21.2)	(19.5)	18.0
31	Ethyl benzoate	(20.5)	(18.8)	17.3
32	Bromobenzene	(24.2)	(22.5)	21.0
33	Heptane	39.2	(37.5)	
38	Diethyl oxalate	(16.8)	14.9	13.8

[a] All values from refs. 11 and 17, unless otherwise shown. Parenthesised values are estimates, see text. [b] T. W. Bentley and P. von R. Schleyer, unpublished work. [c] T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1244. [d] P. O. I. Virtanen, *Suomen Kem.*, 1967, **40B**, 179.

mol^{-1} over all the solvents studied, with corresponding errors in $\Delta S^\ddagger$ and $\Delta S_t^0(\text{Tr})$ of around 3—4 cal K^{-1} mol^{-1}. Again, the obtained standard errors in the correlations (Table 9) are in accord with these estimated errors.

Inspection of the $\Delta H_t^0(\text{Tr})$ values in Table 8 and Table 9 reveals very little in the way of regular behaviour, quite unlike the corresponding $\Delta G_t^0(\text{Tr})$ values. It might be thought that on transfer from a polar aprotic solvent (DMF) to less polar aprotic solvents, both $\Delta G_t^0(\text{Tr})$ and $\Delta H_t^0(\text{Tr})$ would increase regularly. However, this is not necessarily so. There will be a quite large dipolar contribution to such a transfer, indicated in equation (2) by a large $s\pi_1^*$ term. Now the transfer of a dipole of moment μ and radius r can be approached through the Kirkwood equation (15),[8] where ε is the solvent dielectric

$$G = -\frac{A\mu^2}{r^3}\cdot\frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \tag{15}$$

constant and A is a known constant. Although not commonly used, analogous equations can be developed in terms of enthalpy and entropy:

$$H = -\frac{A\mu^2}{r^3}\cdot\frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{3T}{(2\varepsilon + 1)^2}\cdot\frac{\delta\varepsilon}{\delta T} \tag{16}$$

$$S = \frac{3A\mu^2}{r^3}\cdot\frac{1}{(2\varepsilon + 1)^2}\cdot\frac{\delta\varepsilon}{\delta T} \tag{17}$$

It turns out that the dipolar contribution to the enthalpy of a species becomes slightly more negative as the solvent becomes less polar, and then considerably positive in very non-polar solvents. The entropic term, equation (17), becomes steadily more negative, again until the solvent is very non-polar when the entropic term becomes positive. For the solvents listed in Tables 8 and 9, the variations in $\Delta H_t^0(\text{Tr})$ and $\Delta S_t^0(\text{Tr})$ amongst the aprotic solvents can certainly be accounted for, qualitatively at least, in terms of the Kirkwood equations for transfer of a dipole.

We give in Table 10 an analysis of the transition-state transfer parameters using the general equation (2). The constants in the equations for $\Delta G_t^0(\text{Tr})$ with both Bu^{t}Cl and Bu^{t}Br are very nearly the same as before (see Table 6), but the equations in Table 10 are appreciably poorer, no doubt because of the particular selection of solvents in Table 9. The main interest,

Table 8. Initial-state and transition-state solvent effects[a] in terms of enthalpy at 298 K in kcal mol^{-1}

	Solvent	Bu^{t}Cl			Bu^{t}Br		
		ΔH_t^0(Bu^{t}Cl)	$\delta\Delta H^‡$	ΔH_t^0(Tr)	ΔH_t^0(Bu^{t}Br)	$\delta\Delta H^‡$	ΔH_t^0(Tr)
1	Water	1.5	−2.0	−0.5	1.0	0.0	1.0
2	Methanol	−0.2	−0.1	−0.3	−0.1	1.1	1.0
3	Ethanol	−0.2	0.9	0.7	−0.1	2.5	2.4
4	Propan-1-ol	−0.1	0.8	0.7	−0.1	2.4	2.3
5	Propan-2-ol	0.3	−1.6	−1.3	0.3	0.1	0.4
6	Butan-1-ol	0.0	−0.7	−0.7	0.0	0.9	0.9
10	Trifluoroethanol	0.6	−5.5	−5.5	0.7	−3.9	−3.2
11	Hexafluoropropan-2-ol	(0.3)	−7.3	−7.0	(0.2)	−5.7	−5.5
12	Nitromethane	0.7	−2.0	−1.3	0.9	−1.9	−1.0
13	Dimethylformamide	0	0	0	0	0	0
14	Acetonitrile	0.2	−1.3	−1.1	0.4	0.5	0.9
16	*N*-Methylpyrrolidinone	−0.2	−1.4	−1.6	−0.2	0.2	0.0
17	Acetone	−0.1	−4.8	−4.9	0	−2.4	−2.4
18	Tetrahydrofuran	(−0.3)	−2.1	−2.4	(−0.3)	−0.5	−0.8
20	Ethyl acetate	−0.3	−4.9	−5.2	−0.3	−3.3	−3.6
22	Acetic acid	−0.1	0.6	0.5	0.0	2.2	2.2
24	Propylene carbonate	0.2	−4.7	−4.5	0.3	−1.7	−1.4
25	Nitrobenzene	−0.1	0.5	0.4	0.0	−1.6	−1.6
26	Benzonitrile	−0.1	−2.0	−2.1	0.0	−0.4	−0.4
27	1,2-Dichloroethane	−0.1	−3.2	−3.3	−0.2	−3.5	−3.7
28	Dichloromethane	−0.3	−5.7	−6.0	−0.4	−5.3	−5.7
29	Chlorobenzene	(−0.6)	−3.5	−4.1	(−0.5)	−1.9	−2.4
30	Benzene	(−0.5)	−4.0	−4.5	(−0.5)	−2.4	−2.9

[a] From Tables 2 and 7, parenthesised values have been estimated.

Table 9. Thermodynamic parameters for solvent effects on the t-butyl chloride and t-butyl bromide transition states at 298 K mol fraction scale[a]

	Solvent	Bu^{t}Cl			Bu^{t}Br		
		ΔG_t^0	ΔH_t^0	ΔS_t^0	ΔG_t^0	ΔH_t^0	ΔS_t^0
1	Water	−4.45	−0.5	13.2	−2.22	1.0	10.8
2	Methanol	−2.80	−0.3	8.4	−0.85	1.0	6.2
3	Ethanol	−1.74	0.7	8.2	−0.03	2.4	8.2
4	Propan-1-ol	−1.46	0.7	7.2	0.28	2.3	6.8
5	Propan-2-ol	−0.86	−1.3	−1.5	0.77	0.4	−1.2
6	Butan-1-ol	−1.32	−0.7	2.1	0.42	0.9	1.6
10	Trifluoroethanol	−5.96	−5.5	1.5	−3.74	−3.2	1.8
11	Hexafluoropropan-2-ol	−8.15	−7.0	3.9	−5.35	−5.5	−0.5
12	Nitromethane	−0.23	−1.3	−3.6	0.25	−1.0	−4.2
13	Dimethylformamide	0	0	0	0	0	0
15	Acetonitrile	0.33	−1.1	−4.8	0.36	0.9	1.8
16	*N*-Methylpyrrolidinone	0.61	−1.6	−7.4	0.55	0.0	−1.8
17	Acetone	1.55	−4.9	−21.6	1.82	−2.4	−14.2
18	Tetrahydrofuran	3.04	−2.4	−18.2	3.36	−0.8	−14.0
20	Ethyl acetate	3.47	−5.2	−29.1	3.61	−3.6	−24.2
22	Acetic acid	2.27	0.5	−5.9	0.21	2.2	6.7
24	Propylene carbonate	0.67	−4.5	−17.3	0.07	−1.4	−4.9
25	Nitrobenzene	1.39	0.4	−6.0	1.61	−1.6	−10.8
26	Benzonitrile	1.58	−2.1	−12.3	1.82	−0.4	−7.4
27	1,2-Dichloroethane	0.90	−3.3	−14.1	1.70	−3.7	−18.1
28	Dichloromethane	2.40	−6.0	−28.2	2.49	−5.7	−27.5
29	Chlorobenzene	3.23	−4.1	−24.6	3.65	−2.4	−20.3
30	Benzene	4.40	−4.5	−29.9	4.77	−2.9	−25.7

[a] From Tables 4 and 8; ΔG_t^0 and ΔH_t^0 in kcal mol^{-1} and ΔS_t^0 in cal K^{-1} mol^{-1}.

however, is in the equations for ΔH_t^0(Tr) and ΔS_t^0(Tr). It must be borne in mind that the selection of solvents is not particularly good, and that the $\Delta H^‡$ (and hence $\Delta S^‡$) values used are much less reliable than the corresponding $\Delta G^‡$ values, so that only major features will be meaningful. The two halides may be taken together: the π_1^* term can be seen to be entirely an entropic phenomenon, explainable through the Kirkwood equations, above. Very surprisingly, the α_1 term is also entirely an entropic phenomenon. Although an entropic element, due to orientation of solvent molecules on forming hydrogen-bonds to the leaving halide atoms, would be expected, the observation of a zero enthalpic element is quite unexpected. Even more surprising is the very large β_1 coefficient in ΔH_t^0(Tr), and the almost compensating large coefficient in ΔS_t^0(Tr). Although the same phenomenon occurs in the Menschutkin reaction of triethylamine with ethyl iodide,[21] it is possible that these apparent compensating effects of ΔH_t^0(Tr) and ΔS_t^0(Tr) on β_1 arise through the compensation of $\Delta H^‡$ and $\Delta S^‡$. However, a plot of $\Delta H^‡$ *vs.* $\Delta S^‡$ for the 23 solvents in Table 9 leads to correlation constants of 0.554 (Bu^{t}Cl) and 0.644 (Bu^{t}Br) and the recommended[22]

Table 10. Analysis of transition-state transfer parameters for the solvents in Table 9

				CL%			
	n	s.d.	r	π_1^*	α_1	β_1	$\delta_H^2/100$
A Bu^{t}Cl							
$\Delta G_t^0(\mathrm{Tr}) = 7.37 - 7.98\,(\pi_1^* - 0.17\,\delta) - 5.10\,\alpha_1 - 1.22\,\beta_1 + 0.63\,\delta_H^2/100$	23	1.46	0.9086	99	100[a]	61	80
$\Delta H_t^0(\mathrm{Tr}) = -8.94 + 2.49\,(\pi_1^* + 0.81\,\delta) + 0.37\,\alpha_1 + 6.18\,\beta_1 + 0.94\,\delta_H^2/100$	23	1.62	0.8058	57	33	99.96	91
$\Delta S_t^0(\mathrm{Tr}) = -53 + 33\,(\pi_1^* + 0.004\,\delta) + 18\,\alpha_1 + 26\,\beta_1 + 1.2\,\delta_H^2/100$	23	6	0.8937	98	100[a]	99.93	42
B Bu^{t}Br							
$\Delta G_t^0(\mathrm{Tr}) = 7.65 - 8.65\,(\pi_1^* - 0.21\,\delta) - 3.88\,\alpha_1 - 0.93\,\beta_1 + 0.73\,\delta_H^2/100$	23	0.74	0.9599	100[a]	100[a]	80	99
$\Delta H_t^0(\mathrm{Tr}) = -4.85 - 1.08\,(\pi_1^* - 1.00\,\delta) + 0.03\,\alpha_1 + 6.03\,\beta_1 + 1.28\,\delta_H^2/100$	23	1.34	0.8658	32	4	99.98	99
$\Delta S_t^0(\mathrm{Tr}) = -44 + 25\,(\pi_1^* - 0.09\,\delta) + 13\,\alpha_1 + 23\,\beta_1 + 1.8\,\delta_H^2/100$	23	5	0.9066	97	100[a]	99.97	68

[a] $\geqslant$ 99.999.

plot of $\Delta H^\ddagger$ *vs.* $\Delta G^\ddagger$ to correlation constants of only -0.028 (Bu^{t}Cl) and -0.081 (Bu^{t}Br). Furthermore, there is no such compensating effect on the π_1^* or the α_1 term (above), so that the effect on the β_1 term seems unlikely to be due to a statistical artifact arising from any $\Delta H^\ddagger/\Delta S^\ddagger$ relationship. The only explanation we can offer is that the partially charged leaving halide ion interacts with hydrogen-bond bases, which all contain one or more electron lone pairs, by some type of endothermic lone pair/lone pair repulsion. The disruption of the solvent network leads to an entropic increase that almost exactly compensates for the increase in enthalpy, so that the Gibbs energy of the system remains unaffected. The only other piece of evidence we have in support of this argument is that a similar phenomenon is observed in transfer of the solute triethylamine[14] from DMF to a variety of other solvents:

$$\Delta G_t^0(\mathrm{Et_3N}) = -1.78 + 0.72\,(\pi_1^* - 0.85\,\delta) - 1.85\,\alpha_1 + 0.39\,\beta_1 + 0.08\,\delta_H^2/100 \quad (18)$$
$$n = 19 \qquad \text{s.d.} = 0.27 \qquad r = 0.963$$

$$\Delta H_t^0(\mathrm{Et_3N}) = -0.98 + 1.42\,(\pi_1^* - 0.47\,\delta) - 4.50\,\alpha_1 + 2.14\,\beta_1 - 0.88\,\delta_H^2/100 \quad (19)$$
$$n = 19 \qquad \text{s.d.} = 0.68 \qquad r = 0.970$$

$$\Delta S_t^0(\mathrm{Et_3N}) = 2.7 + 2.4\,(\pi_1^* - 0.06\,\delta) - 8.8\,\alpha_1 + 5.8\,\beta_1 - 5.6\,\delta_H^2/100 \quad (20)$$
$$n = 19 \qquad \text{s.d.} = 1.6 \qquad r = 0.987$$

Although triethylamine is far removed from a strongly dipolar species with a halide atom carrying a high partial charge, equations (18)—(20) still show an endothermic β_1 term in ΔH_t^0, counterbalanced by a positive β_1 term in ΔS_t^0. This does suggest that the similar situation shown in the equations given in Table 10 is not an artifact, but the consequence of hitherto unsuspected solute/solvent interactions. If this is so, it adds weight to our previous contention that only by use of a multiparameter equation containing at least four terms can one hope to be able to deal with all the possible solute/solvent interactions.[23]

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Addendum

Bridging and σ-Participation in Solvolyses of Adamantyl Substrates.—In a previous paper[1] dealing mainly with the solvolysis of t-butyl chloride, reference was made to the recent work of le Noble *et al.*,[2] on the existence of bridging and σ-participation in the solvolysis of 2-adamantyl substrates. Dr. M. C. Whiting has pointed out that such bridging and σ-participation was discovered by his group in the late 1970s;[3] it is a pleasure to acknowledge this initial work of Dr. Whiting.

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