

Linear Solvation Energy Relationships. Part 37.† An Analysis of Contributions of Dipolarity–Polarisability, Nucleophilic Assistance, Electrophilic Assistance, and Cavity Terms to Solvent Effects on t-Butyl Halide Solvolysis Rates

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Solvolysis/dehydrohalogenation rates of t-butyl chloride in 21 hydrogen bond donor (HBD) and non-HBD solvents are well correlated ($r = 0.9973$, s.d. = 0.24) by the equation:

$$\log k = -14.60 + 0.48\delta_{\text{H}}^2/100 + 5.10\pi^* + 4.17\alpha + 0.73\beta$$

where δ_{H}^2 is the solvent cohesive energy density, and π^* , α , and β are the solvatochromic parameters that scale solvent dipolarity–polarizability, HBD acidity (electrophilicity), and hydrogen-bond acceptor basicity (nucleophilicity). In the corresponding equation over the same solvent set for t-butyl bromide, the terms in δ_{H}^2 and α are smaller and the term in β is not statistically significant, whereas for t-butyl iodide, the term in α is smaller still, and the terms in δ_{H}^2 and β are not statistically significant. It is shown that a trifluoroethanol (TFE)–ethanol plot, wherein Bu^tCl and 1-adamantyl chloride (1-AdCl) solvolysis rates are compared, can be interpreted as evidence for electrophilic assistance of 1-AdCl in TFE rather than the more usual interpretation of nucleophilic assistance to Bu^tCl in $\text{EtOH-H}_2\text{O}$.

The solvolysis of t-butyl halides has long been a key reference reaction in physical organic chemistry, especially as regards theories of solvent effects on organic reaction rates. Thus, solvolysis rates for t-butyl chloride have served as the basis for scales of solvent ionizing power,^{1–3} and conversely, attempts have been made to correlate rates for the unimolecular heterolysis of the t-butyl halides with various solvent property scales.^{4–6} The latter include an earlier effort by several of us to correlate solvent effects on t-butyl halide solvolysis/heterolysis rates with the solvatochromic parameters, π^* , α , and β .^{5,7} In the present paper we stress again that it is necessary to consider solvent electrophilicity as an important solvent property, separate from solvent ionizing power and nucleophilicity. We show also that there is a statistically significant dependence of reaction rates on the square of the Hildebrand solubility parameter, δ_{H}^2 , a term here related to the differential energies required to produce cavities in a solvent for reactant and transition state.^{8,9}

The original assumptions in our earlier analysis of t-butyl halide solvolysis/heterolysis rates⁵ had been that a term in π^* would measure the effect of solvent dipolarity–polarizability (which is only one of the contributors to the frequently used term, solvent ionizing power); a term in β (the ability of the solvent to donate a share of an electron pair in a hydrogen bonding or weak Lewis acid–base interaction) would measure the effect of solvent nucleophilic assistance; and a term in α (the ability of the solvent to accept an electron pair) would measure the effect of solvent electrophilic assistance. Our equating the

α measure of solvent hydrogen-bond donor acidity with electrophilicity and the β measure of hydrogen-bond acceptor basicity with nucleophilicity was consonant with Swain's later definitions of solvent 'acidity' and 'basicity' properties.‡ Following Koppel and Palm,⁴ and Abraham,¹⁰ we assumed that transition states for dehydrohalogenations in aprotic solvents and solvolysis in hydroxylic solvents were highly similar, so that hydroxylic and nonprotogenic solvents could be included in the same correlations.

Our earlier correlations involved fifteen solvents (nos. 1–3, 5, 7, and 13–21 of Table 1, and pentane, some less reliable data for which we have not included in the present correlations) and, using slightly different values for some of the solvatochromic parameters than those used here, gave equation (1) for t-butyl

$$\log k(\text{Bu}^t\text{Cl}) = (-15.06 \pm 0.22) + (6.94 \pm 0.33)\pi^* + (5.15 \pm 0.23)\alpha \quad (1)$$

$n = 15 \qquad r = 0.9949 \qquad \text{s.d.} = 0.363$

chloride. Including a term in β gave no improvement in the goodness of statistical fit ($r = 0.9950$, s.d. = 0.365), and on this basis we concluded that the effect of solvent nucleophilic assistance was negligible. The strong dependence on solvent electrophilicity was noteworthy, as solvent effects had typically been separated into only the two parameters for nucleophilicity and ionizing power.^{1,3,6,11–13} The data point for trifluoroethanol solvent was not included in the correlation because of its strong deviation from equation (1) ($\log k$ was 1.1 unit more negative than calculated); this was suggested as a possible result of an unusual amount of ion-pair return in this solvent.

These conclusions were justly criticized by Bentley and Carter¹¹ because our correlation excluded weakly nucleophilic solvents such as trifluoroethanol, and because we had offered no evidence that transition states for solvolysis and dehydrohalogenation were the same, and therefore no justification for

† Part 36, M. J. Kamlet, R. M. Doherty, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Pharm. Sci.*, 1986, **75**, 338.

‡ Swain and his co-workers⁶ characterized 'acidity' and 'basicity' as measures of cation and anion solvating ability. Hydrogen-bond acceptor basicity and nucleophilicity were also included in the 'basicity' definition; hydrogen-bond donor acidity and electrophilicity were included in the 'acidity' definition.

including hydroxylic and nonprotogenic solvents in the same correlation equation. This latter criticism was strengthened by our subsequent observation that correlation for the hydroxylic solvents alone gave quite a different result from that obtained for the full fifteen solvents. Significantly, the results for trifluoroethanol and hexafluoropropan-2-ol fit the latter equation quite well.

Recently, further reports have been published on nucleophilic solvent assistance in the solvolysis of *t*-butyl chloride: Kevill *et al.*^{11,14} suggest that there is a statistically significant effect, and Farcasiu *et al.*¹⁵ suggest that there is no such effect at all. With a more extensive set of reaction rates for the *t*-butyl halide heterolyses available, it seemed timely to reinvestigate the question of nucleophilic solvent assistance. In addition to testing our earlier two- and three-parameter equations, we have also examined a four-parameter equation [equation (2)], in

$$\log k = (\log k)_0 + h\delta_H^2 + s\pi^* + a\alpha + b\beta \quad (2)$$

which the square of the Hildebrand solubility parameter, δ_H^2 (the solvent cohesive energy density)^{16,*} is included as an explanatory variable. In a number of previous reports,^{8,9,17} we have used δ_H , or better δ_H^2 , as a measure of solvent-solvent interactions that are interrupted in creating a cavity for a solute molecule. Hence in the transfer of a solute molecule from one solvent to another, a term in δ_H^2 is always needed to accommodate this so-called cavity effect. In general, the larger the solute, the larger will be the cavity effect, and the more negative will be the sign of h in the equation (3) that correlates $\log K$ for transfer of a solute.†

$$\log K = (\log K)_0 + h\delta_H^2 + s\pi^* + a\alpha + b\beta \quad (3)$$

The only cases in which the h -coefficients in equation (3) did not agree with all our expectations were in the transfer of the dissociated ions ($R_4N^+ + X^-$) or of the ion pairs ($R_4N^+X^-$) between solvents.¹⁷ Thus for the ($Me_4N^+X^-$) ion pairs, values of h were: I^- (-0.016), Br^- (-0.020), Cl^- (-0.021), and for the dissociated ions ($Me_4N^+ + X^-$) values were I^- (-0.046), Br^- (-0.049), and Cl^- (-0.050). The magnitude of the term in h is $Cl^- > Br^- > I^-$, whereas for a term depending only on cavity volume, the order of anion size, $Cl^- < Br^- < I^-$ would be expected. We rationalised¹⁷ these effects on the value of h in terms of a solvent reorganisation/electrostrictive effect ($Cl^- > Br^- > I^-$) that opposed the usual sequence of purely cavity effects ($Cl^- < Br^- < I^-$). It is well known that electrostrictive effects of solvents¹⁸ and reorganisation of hydrogen bonds in self-associated solvents¹⁹ both contribute to the observed partial molar volumes of ions in solution.

However, not only ions but also polar but electrically neutral species can lead to electrostriction. Thus standard entropies of the ion pair $Et_4N^+I^-$ become increasingly negative with decrease in solvent polarity,²⁰ and for the hypothetical equilibrium between $RCH(NH_2)CO_2H$ and $RCH(NH_3^+)CO_2^-$ in water ΔV^0 is around²¹ $-15 \text{ cm}^3 \text{ mol}^{-1}$. Since the *t*-butyl chloride transition state is certainly highly polar, with considerable charge separation,^{11,22-24} it is quite possible that electrostriction/solvent reorganisation also takes place in the interaction of the transition state with various solvents. Thus,

* The Hildebrand solubility parameter is defined by $\delta_H = [(\Delta H_v - RT)/\bar{V}]^{1/2}$, where ΔH_v is the molar heat of vaporisation to a gas at zero pressure, and \bar{V} is the molar volume.

† We write equation (3) in terms of the equilibrium constant K rather than the standard free energy of transfer ΔG_t , in order to show exactly how equation (2) relates to equation (3). In subsequent discussion, the original h terms calculated¹⁷ using ΔG_t values have been divided by -1.364 so as to obtain h terms relevant to $\log K$ in equation (3).

although the intrinsic volume of the *t*-butyl chloride ground state and transition state will be very close²⁴ and by themselves will lead to a cavity term that is small or nonexistent, other effects as already noted may lead to reaction rates being dependent, at least in part, on solvent cohesive energy densities.

Results and Discussion

Assembled in Table 1 are literature rate constants for *t*-butyl chloride, bromide, and iodide reactions in 21 hydroxylic and nonprotogenic aliphatic solvents. Aromatic and polychloroaliphatic solvents are not included, in order to avoid variable polarizability effects. Also not included are several relatively less reliable results in pentane and propylene carbonate solvents, as well as data for carboxylic acid solvents, for which dimerization in the liquid and vapour states has made impossible the estimation of a meaningful Hildebrand solubility parameter (meaningful in the sense that it measures the endoergic process of separating the solvent molecules to provide a cavity for the solute).

The other Hildebrand solubility parameters in Table 1 have been determined, where possible, from calorimetrically determined enthalpies of vaporization at 298 K. Although complete data sets were not available for the bromide and iodide, we have estimated a number of values (from separate linear regressions with chloride reaction rates in hydroxylic and nonhydroxylic solvents) in the expectation that comparisons amongst the three sets of reaction rates would be statistically more valid if they involved the same solvent sets. The results of the correlation by equation (2) for the three halides are given in Table 2. We will discuss first the key points for the chloride.

(a) First, it is seen that correlation of all 21 data points by equation (2) (equation A of Table 2) shows a better correlation coefficient (0.9973 *vs.* 0.9949) and a significantly lower standard deviation (0.242 *vs.* 0.363) than equation (1).

(b) Of particular relevance to the present work, equation A indicates that electrostriction/solvent reorganisation leads to acceleration which, in some solvents, cannot be ignored. On the basis of Student's *t*-test, the $0.0048\delta_H^2$ term is statistically significant at the >99.99% confidence level.

(c) The nucleophilic assistance term in equation A (0.73β) is statistically significant at the 99.5% confidence level, whereas in our original equation (1) this term was not significant. It should be noted that the $b\beta$ term in equation (2) does not arise merely through incorporation of the solubility parameter as another explanatory variable, since the $b\beta$ term in equation C is also significant. It is possible that the nucleophilic assistance term in equations A and C has been identified because we have results for 21 solvents rather than 15 as used before. In any case, as we shall discuss later, the $b\beta$ term in equation A is certainly the smallest of the contributing terms.

(d) Comparing equation B with C, it is seen that the cavity term has a somewhat greater influence on the reaction rate than the nucleophilic assistance term. Dropping the former leads to a somewhat greater deterioration of correlation than dropping the latter.‡ Inclusion of the cavity term, however, has two important effects.

(e) Unlike equation (1) the 21-solvent correlation equation accommodates the fluoro-alcohol results quite well; the trifluoroethanol datum fits equation A to within 0.07 log unit and

‡ Use of Student's *t*-test prevents any *ad hoc* accumulation of explanatory variables. Only if a parameter is significant at a certain level (often taken as 95%) can it be retained in a multiparameter regression. Hence although a four-parameter equation is required to account for the *t*-butyl chloride solvolysis (A), only a three-parameter equation is needed for the *t*-butyl bromide solvolysis (H), as explained later.

Table 1. *t*-Butyl halide solvolysis/dehydrohalogenation rates and solvatochromic parameters used in the correlations; rates are at 25 °C^a

Solvent	$\delta_H^2/100$	π^*	α	β	$-\log (k/s^{-1})$		
					RCl	RBr	RI
1 Water	5.490	1.09	1.17	0.18	1.54	0.12	0.19
2 Methanol	2.052	0.60	0.93	0.62	6.10	4.46	3.90
3 Ethanol	1.621	0.54	0.83	0.77	7.07	5.35	4.76
4 Propan-1-ol	1.432	0.52	0.78	0.83	7.33	5.63 ^b	5.00 ^b
5 Propan-2-ol	1.331	0.48	0.76	0.95	7.74	6.00	5.36
6 Butan-1-ol	1.295	0.47	0.79	0.88	7.52	5.80 ^b	5.17 ^b
7 2-Methylpropan-2-ol	1.119	0.41	0.68	1.01	8.27	6.50	5.84
8 Ethylene glycol	2.740	0.92	0.90	0.52	4.61	3.12 ^b	2.56 ^b
9 Formamide	3.617	0.97	0.71	(0.60) ^c	4.40	2.85 ^b	2.30 ^b
10 Trifluoroethanol	1.371	0.73	1.51	(0.00) ^{c,h}	3.98 ^d	2.62 ^e	2.01 ^f
11 Hexafluoropropan-2-ol	0.893	0.65	1.96	(0.00) ^c	2.70 ^f	1.75	0.85 ^b
12 Nitromethane	1.585	0.85	0.22	0.25	8.12	5.44	3.9 ^b
13 Dimethylformamide	1.389	0.88	0	0.69	8.55	5.62	4.20
14 Dimethylacetamide	1.166	0.88	0	0.76	9.31	6.50	5.00
15 Acetonitrile	1.378	0.75	0.19	0.37	8.68	5.90	4.28
16 <i>N</i> -Methylpyrrolidone	1.276	0.92	0	0.77	8.97	6.00	4.55
17 Acetone	0.906	0.71	0.08	0.48	9.90	7.13	5.21
18 Tetrahydrofuran	0.864	0.58	0	0.55	11.00	8.30	6.78
19 Dioxane	1.000	0.55	0	0.37	10.81	8.52 ^g	6.78
20 Ethyl acetate	0.792	0.55	0	0.45	11.50	8.70	7.02
21 Diethyl ether	0.562	0.27	0	0.47	12.74	10.00	8.2 ^b

^a Values of $\log k$ from refs. 5 and M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1893; solvatochromic parameters from ref. 7. ^b Rates obtained from separate linear correlations in hydroxylic and nonhydroxylic solvents of $\log k(\text{Bu}^t\text{Br})$ and $\log k(\text{Bu}^t\text{I})$ with $\log k(\text{Bu}^t\text{Cl})$. ^c Estimated values. ^d V. J. Shiner, W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, 1969, **91**, 4838. ^e F. L. Scott, *Chem. Ind. (London)*, 1959, 224. ^f Estimated from corresponding values in 97% trifluoroethanol and 97% hexafluoropropan-2-ol: T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1244; B. G. Cox and H. Maskill, *ibid.*, 1983, 1901. ^g E. A. Ponomareva, G. F. Dvorko, N. I. Kulik, and N. Yu Evtushecko, *Dokl. Akad. Nauk. SSSR*, 1983, **273**, 373. ^h More recent results indicate that the β values for these solvents may be somewhat higher than indicated here, *i.e.*, water *ca.* 0.4; trifluoroethanol *ca.* 0.1. These alternative values would not materially change either the correlation equations or the conclusions arrived at here.

the hexafluoropropan-2-ol datum fits to within 0.03 log unit (*cf.* 0.24 log unit standard deviation of equation A).

(*f*) Again, unlike the earlier correlations, the equations for the 11 hydrogen-bond donor (HBD) solvents (1–11 of Table 1) and for the 21 HBD and non-HBD solvents (equations A and E) show agreements between the coefficients of the independent variables and the intercepts which are well within the combined uncertainties of the estimates.

(*g*) As a final test of the correlations, we have excluded the datum for water, which has the largest π^* and by far the largest δ_H^2 value, and hence exerts considerable 'leverage' on the correlation. It is seen that the resulting equation D again agrees quite well with equation A. Thus, with the expansion of the data set and the inclusion of the $h\delta_H^2$ term, everything fits. The criticisms by Bentley and Carter¹¹ appear to be answered, and the small but statistically significant $b\beta$ term is consistent with the conclusions of Bentley¹¹ and Kevill¹⁴ regarding the involvement of solvent as nucleophile in *t*-butyl chloride solvolysis. The powerful dependence on π^* and α is consistent with a transition state that is well on its way to a fully developed ion pair, as suggested by Abraham.^{10,24} (It deserves mention at this point that the statistical quality of the correlations with the solvatochromic parameters is significantly better than any of the numerous correlations reported²⁵ with other solvent property scales.)

Collinearity of the Independent Variables.—Some problems raised by collinearity of the independent variables in equation (2) deserve discussion. For the 21-solvent data set, the strongest collinearity is between δ_H^2 and π^* ; $r(\delta_H^2/\pi^*) = 0.657$. For the 11 ROH solvent data set there is a strong collinearity between α and β ($r = 0.887$) and between δ_H^2 and π^* ($r = 0.874$) and a moderate collinearity between π^* and β ($r = 0.606$).

The much stronger collinearity between the independent variables for the 11 ROH solvent data set as compared with the 21-solvent data set has two important consequences.

(*a*) The uncertainties in the $(\log k)_0$, h , s , a , and b terms are much greater for equation E than for equation A. Therefore, although equation E has the higher correlation coefficient and the lower standard deviation, equation A is by far the more reliable and reproducible, *i.e.* it is less susceptible to change by inclusion of additional data points, and more likely to be matched by correlation of an independent data set.

(*b*) Small changes in the input data or composition of the ROH data set can lead to extraordinarily large changes in the coefficients of the independent variables, coupled with relatively minor changes in the statistical measures of goodness of fit (this will be seen in the discussion, later of *t*-butyl bromide heterolysis.)

***t*-Butyl Bromide and Iodide Reactions.**—Turning next to the 21-solvent correlations for *t*-butyl bromide and iodide, equations G and N, we observe a number of systematic progressions:

(*a*) The s terms (dependence on solvent dipolarity–polarizability) increase from Bu^tCl to Bu^tBr to Bu^tI, whereas in our earlier correlations⁵ the order had been Bu^tBr > Bu^tCl > Bu^tI. This new order is of some interest, because the negative s coefficients in the correlations for free energies of transfer of the tetramethylammonium halide ion pairs (which have been invoked as models for the *t*-butyl halide transition state)¹⁰ are in the order Cl[−] > Br[−] > I[−].¹⁷

(*b*) The a coefficients (measures of electrophilic assistance) decrease from Bu^tCl to Bu^tBr to Bu^tI. As discussed earlier,⁵ this is consonant with the relative free energies of transfer of the halide ions from DMF to methanol,²⁶ and with free energies of

Table 2. Correlations of *t*-butyl halide solvolysis/dehydrohalogenation rates
$$\log k = (\log k)_o + h\delta_H^2 + s\pi^* + ax + b\beta$$

Eqn. Solvent set ^a	(log <i>k</i>) _o (±)	100 <i>h</i> (±)	<i>s</i> (±)	<i>a</i> (±)	<i>b</i> (±)	<i>r</i>	s.d.
<i>t</i>-Butyl chloride							
A 21 aliphatic solvents	-14.60 (0.29)	0.48 (0.07)	5.10 (0.37)	4.17 (0.11)	0.73 (0.21)	0.9973	0.242
B 21, exclude <i>bβ</i> term	-13.88 (0.25)	0.53 (0.09)	4.63 (0.44)	4.02 (0.13)		0.9954	0.305
C 21, exclude <i>hδ_H²</i> term	-15.38 (0.50)		6.84 (0.50)	4.53 (0.19)	1.04 (0.39)	0.9898	0.453
D 20 solvents, excl. H ₂ O	-14.55 (0.29)	0.58 (0.11)	4.94 (0.39)	4.14 (0.12)	0.63 (0.23)	0.9968	0.237
E 11 ROH solvents	-14.07 (0.96)	0.48 (0.07)	4.77 (0.60)	3.97 (0.40)	0.56 (0.53)	0.9992	0.118
F 11, exclude <i>bβ</i> term	-13.08 (0.14)	0.49 (0.07)	4.34 (0.43)	3.58 (0.12)		0.9990	0.119
<i>t</i>-Butyl bromide							
G 21 aliphatic solvents	-11.97 (0.34)	0.31 (0.08)	5.77 (0.43)	3.16 (0.13)	0.46 (0.25)	0.9947	0.280
H 21, exclude <i>bβ</i> term	-11.51 (0.25)	0.35 (0.09)	5.47 (0.43)	3.06 (0.13)		0.9935	0.299
I 21, exclude <i>hδ_H²</i> term	-12.48 (0.41)		6.91 (0.41)	3.39 (0.16)	0.67 (0.32)	0.9900	0.371
J 20 solvents excl. H ₂ O	-11.98 (0.35)	0.28 (0.14)	5.83 (0.48)	3.17 (0.14)	0.50 (0.28)	0.9928	0.288
K 11 ROH solvents	-10.58 (0.70)	0.54 (0.05)	3.72 (0.44)	3.01 (0.29)	-0.11 (0.39)	0.9995	0.086
L 11, exclude <i>bβ</i> term	-10.78 (0.10)	0.53 (0.05)	3.81 (0.30)	3.09 (0.09)		0.9995	0.084
M 7 ROH solvents, exclude secondary values	-8.34 (0.40)	0.89 (0.86)	0.12 (0.58)	2.92 (0.07)	-1.19 (0.20)	1.0000	0.021
<i>t</i>-Butyl iodide							
N 21 aliphatic solvents	-9.80 (0.37)	0.03 (0.09)	6.07 (0.48)	2.43 (0.15)	-0.34	0.9905	0.311
O 21, exclude <i>bβ</i> term	-10.13 (0.26)	0.00 (0.09)	6.29 (0.46)	2.50 (0.14)		0.9896	0.316
P 21, exclude also <i>hδ_H²</i> term	-10.14 (0.24)		6.30 (0.32)	2.50 (0.12)		0.9896	0.307

^a The correlation coefficients for the major covariances between the explanatory variables are as follows: for the 21 solvent data set, $r(\delta_H^2/\pi^*) = 0.657$. For the 11 ROH solvent set $r(\delta_H^2/\pi^*) = 0.874$; $r(\pi^*/\beta) = 0.606$; $r(\alpha/\beta) = 0.887$.

the reactions $X^- + 4H_2O \longrightarrow X(H_2O)_4^-$ in the gas phase.²⁷ The free energies of transfer of the $Me_4N^+X^-$ ion pairs¹⁷ also show the same order and almost the same ratios of dependences on solvent HBD acidity, *i.e.* $a(\text{Bu}^1\text{Cl}/\text{Br}/\text{I}) = 1.00/0.73/0.60$; $-a(\text{Me}_4\text{N}^+\text{Cl}^-/\text{Br}^-/\text{I}^-) = 1.00/0.78/0.47$.

(c) The *b* coefficients (measures of nucleophilic assistance) decrease from Bu¹Cl to Bu¹Br, and change sign on going to Bu¹I. Further, by the *t*-test the *bβ* term may be included at only the 92% confidence level for Bu¹Br and only the 77% confidence level for Bu¹I. Usually 95% is the minimal confidence level that warrants inclusion of an additional term in a multiple parameter linear solvation energy relationship. On this basis we conclude that nucleophilic assistance does not influence *t*-butyl bromide or iodide solvolysis rates to any significant extent.

(d) The *h* coefficient (cavity term) also decreases from Bu¹Cl to Bu¹Br to Bu¹I. The $h\delta_H^2$ parameter remains statistically significant at the 99.9% confidence level for Bu¹Br, but *h* is not statistically distinguishable from zero for Bu¹I. Hence the cavity term is somewhat less important for Bu¹Br than for Bu¹Cl, and drops out completely for Bu¹I.

(e) On the basis of the foregoing, we consider that the four-parameter equation A is the statistically preferred correlation

equation for Bu¹Cl; the three-parameter equation H is preferred for Bu¹Br; and the two-parameter equation P is preferred for Bu¹I.

That we may take the 21-solvent correlation for *t*-butyl bromide as being reasonably reliable is evidenced by the quite small changes in the intercept and the coefficients when the high leverage datum for water is excluded; compare equation J with G. The same cannot be said for the 11 ROH solvent correlation, however. The major differences between equations K and G are a consequence of the collinearity problem already touched on, because the 11 ROH solvents still fit equation G with a smaller standard deviation than for the full 21-solvent data set. A more extreme example of this collinearity problem is seen when we restrict the correlation to the seven ROH solvents for which primary data are available (*i.e.* excluding the data in solvents 4, 6, 8, and 9 which were estimated from linear correlations of Bu¹Br with Bu¹Cl reaction rates). The correlation is then given by equation M which, despite the correlation coefficient of 1.0000 and the standard deviation of 0.021 log unit, bears no relationship to any of the earlier correlation equations. Equation M amounts almost to a *reductio ad absurdum*, and exemplifies the cruel trap that the correlational chemist can fall

Table 3. Contributing terms to t-butyl chloride reaction rate differences between solvents

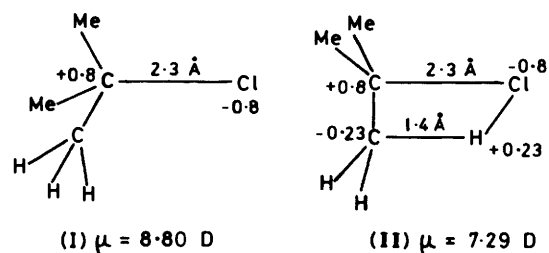
From solvent	To solvent	Experimental $\Delta \log k$	Dipolarity-polarizability term $5.10\Delta\pi^*$	Electrophilic assistance term $4.17\Delta\alpha$	Nucleophilic assistance term $0.73\Delta\beta$	Cavity/electrostriction term $0.48\Delta(\delta_H^2/100)$
MeOH	H ₂ O	4.56	2.49	1.00	-0.31	1.65
EtOH	H ₂ O	5.53	2.80	1.42	-0.42	1.88
TFE	H ₂ O	2.44	1.83	-1.42	0.13	1.98
HFP	H ₂ O	1.16	2.24	-3.29	0.13	2.21
EtOH	TFE	3.09	0.97	2.84	-0.57	-0.12

into when he encounters strong collinearities between presumably independent variables in multiple parameter correlations involving limited data sets. Kevill and his co-workers¹⁴ have characterized the strong reciprocal collinearity between nucleophilicity and electrophilicity as 'nature's cruel trick'.* (No such problem arises when we exclude the secondary data from the 21-solvent set. The resulting equation agrees quite well with equation G.)

Solvolysis and Dehydrohalogenation Transition States.—Our treating hydroxylic and nonprotogenic solvents in the same correlations carries with it the implicit assumption that one of the following four conditions obtains: (a) transition states are identical in both sets of solvents; (b) transition states are quite similar in both sets of solvents; (c) transition state properties differ between solvents in a manner which is collinear with one or any linear combination of the solvent parameters used in the correlations; or (d) although the transitions states may not be similar in the two sets of solvents, they still provoke similar responses with respect to solvent dipolarity, electrophilicity, and nucleophilicity. We believe that (d) is the most likely possibility.

One of us pointed out a number of years ago²³ that when the Gibbs energy of transfer for the t-butyl chloride transition state, $\Delta G^\circ_1(\text{Tr})$ was plotted against ΔG°_1 for the $\text{Me}_3\text{N}^+\text{Cl}^-$ ion pair, the transition state appeared to be more dipolar in hydroxylic solvents than in aprotic solvents, especially the nondipolar aprotic solvents. There seems no doubt from a variety of investigations¹⁰ that in hydroxylic solvents the t-butyl chloride transition state behaves as a very dipolar species, with a charge separation of about 0.80–0.84 unit, corresponding to a dipole moment of about 9D [see model (I), suggested by Abraham and Abraham¹⁰]. Electrostatic calculations indicated¹⁰ that model (I) might also apply to reaction in the more dipolar aprotic solvents, but that in the less dipolar aprotic solvents model (II) was more probable (*cf.* results in ref. 10).

Whether or not reactions in the hydroxylic solvents and in the less dipolar aprotic solvents can be considered together depends on two main factors. First, rather imprecise methods may not be able to distinguish between transition states such as (I) and (II), and hence only one 'average' transition state would be postulated, whereas more refined methods might lead to different results for the two sets of solvents. Secondly, the nature of the investigation may itself lead to different con-



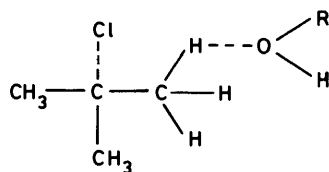
clusions. Thus, an investigation that yields the transition state dipole moment could, in principle, distinguish between (I) and (II), but a method that (for example) yields the C...Cl bond length or charge separation could not. Whereas the original work of Abraham²³ and subsequent calculations¹⁰ seemed to discriminate between (I) and (II), the present findings are very adequately rationalized in terms of an average transition state, a continuously varying transition state, or two transition states which show similar responses to solvent properties. Thus, although the criticisms of Bentley and Carter¹¹ regarding probable non-identity of the transition states in the two types of solvents have merit, and warrant the foregoing detailed discussion, we do not consider that they obviate or serve as a bar toward the present findings.

Mechanistic Implications.—Solvolysis reactions have long been studied because of their importance in synthesis and because of the wealth of fundamental mechanistic information provided that is applicable to organic chemistry in general. Among the most important advances in the understanding of solvolysis mechanisms in the past 15 years has been the appreciation that nucleophilic solvent assistance (NSA) is powerful and will probably be significant in all except highly hindered or internally stabilised carbocation systems. In the present work we have provided evidence for weak NSA in t-butyl chloride solvolysis. Our present analysis, if correct, suggests that for Bu'Cl the maximal possible acceleration due to NSA amounts to 0.73 β or 0.74 log unit in t-butyl alcohol, the most nucleophilic (strongest HBA) solvent considered. For the mixed solvents usually dealt with in solvolysis studies (MeOH-H₂O, EtOH-H₂O, TFE-H₂O) the $\beta\beta$ terms should amount to 0.5 log unit or less.^{15,25} For Bu'Br and Bu'I, the NSA effects are certainly smaller, and most probably not statistically significant.

Further, NSA is the weakest of the four contributing solvent effects. In Table 3, we have dissected $\Delta \log k(\text{Bu}'\text{Cl})$ values between solvents into dipolarity-polarizability, cavity electrophilic assistance, and nucleophilic assistance contributions. As a typical example, in going from ethanol to water, the total $\Delta \log k$ is +5.53 log units; the NSA contribution is -0.42 log unit. These findings are in close accord with the estimates by Kevill and his co-workers¹⁴ that NSA contributes about 10% to the rate in aqueous ethanolic system.¹⁴ However, we point out that the small $\beta\beta$ term in equation A does not necessarily confirm that there is partial S_N2 character to t-butyl chloride

* We are taking some minor liberties here. As set forth by Kevill and co-workers,¹⁴ the 'cruel trick' is that over wide composition ranges for the commonly used mixed solvents, the solvent nucleophilicities increase approximately linearly with decrease in solvent 'ionizing power'. Since solvent 'ionizing power', as commonly used, has both dipolarity-polarizability and electrophilicity components (which co-vary linearly in most mixed solvent systems), it is fair to say (and true) that the 'cruel trick' derives mainly from the reciprocal relationship between solvent nucleophilicity and electrophilicity (as was recognized by Farcasiu *et al.*).¹⁵

solvolysis. Jorgensen²⁸ has pointed out that when sufficient carbocation charge is delocalised to neighbouring carbon atoms, the α -hydrogen atoms take on some hydrogen-bond-donor characteristics, so that minor nucleophilic assistance might arise from hydrogen bonding of the type shown (III).



(III)

The present work also emphasises the importance of solvent electrophilic assistance, which varies even when the leaving groups are the same, and it will be shown that several of the important methods used for detecting NSA are flawed because they ignore variable solvent electrophilic assistance. A similar restriction, albeit to a lesser extent, applies to failure to consider cavity/electrostriction effects. Most mechanistic probes must be applied intelligently; the point of the following section is not that these flawed methods are invalid, but rather that there is new reason for caution in their use. In the following discussion we show specifically how this failure occurs for one such method, and we deal in a more general way with several other methods.

Re-examination of Trifluoroethanol-Ethanol Plots.—The trifluoroethanol-ethanol (TFE-EtOH) method of Raber and Harris has been proposed as a tool for detecting NSA.^{13,29} This method is based on the log-log plot of rates in aqueous trifluoroethanols and ethanols for 1-adamantyl bromide and some test substrate being non-collinear if the test substrate undergoes solvolysis with NSA, or collinear if this assistance is absent. The assumption is made that effects of solvent ionizing power and electrophilicity, but not nucleophilicity, are modelled by the 1-adamantyl rate; deviations from the collinearity in the rate plots are then taken as evidence for NSA to solvolysis of the test substrate. The approach of Bentley and Carter¹¹ is similar, in the NSA for Bu^tCl is invoked to explain deviations for weakly nucleophilic acetic and formic acids and for fluorinated alcohols from a log-log plot of rates for 1-adamantyl and t-butyl chlorides (Figure).

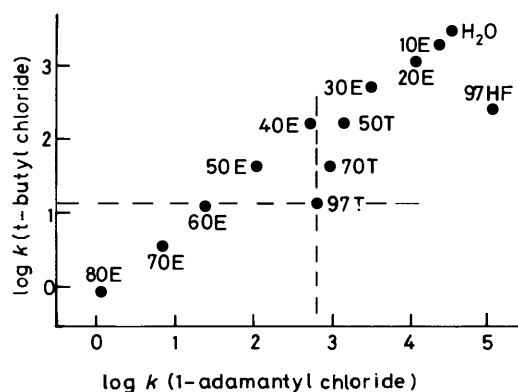


Figure. Correlation of logarithms of solvolysis rates for 1-adamantyl chloride versus t-butyl chloride at 25°C: 80E = 80% ethanol, 97T = 97% trifluoroethanol, 97HF = 97% hexafluoropropan-2-ol

The present results, however, emphasize the importance of solvent electrophilicity (α) in determining solvolysis rates, and they show that substrate sensitivity to solvent electrophilicity, a , need not parallel substrate sensitivity to solvent dipolarity-polarizability, s (compare t-butyl chloride and iodide, Table 2). Consequently, it is possible that non-collinearity of the TFE and EtOH data points in the TFE-EtOH plot could result not only from a difference in NSA, but also from a difference in electrophilic assistance for the adamantyl model and the test substrate. This possibility is especially interesting now that McManus and Harris³⁰ have observed a non-collinear plot for a substrate that has been shown not to react with nucleophilic solvent assistance.

We can demonstrate the consequences of the 'cruel trick' and the two possible methods of interpreting the data with the aid of a slightly modified version of a plot first published by Bentley and Carter,¹¹ wherein log adamantyl chloride solvolysis rates are compared with log t-butyl chloride rates (Figure). It is seen (vertical line) that the AdCl rates are similar in 97% TFE and 40% EtOH (presumably, therefore, according to the earlier model, these solvents have similar 'ionizing power'), but that the Bu^tCl reaction is 1.0 log unit faster in 40% EtOH than in 97% TFE. This has been interpreted as being due to acceleration for Bu^tCl relative to AdCl by virtue of enhanced nucleophilic assistance in EtOH-H₂O. However the β value of 40% EtOH is unlikely to be higher than 0.5, and if the analysis in Table 2 is correct, not more than 0.4 log unit acceleration could then be attributed to the total effect of NSA in this solvent. This is significantly lower than the 1.0 log unit observed.

It is also seen in the plot (horizontal line) that the Bu^tCl reaction rates are similar in 60% EtOH and 97% TFE, but that the AdCl reaction is about 1.4 log unit faster in 97% TFE than in 60% EtOH. This leads to the alternative interpretation of the plot wherein Bu^tCl is considered to model the solvent dipolarity-polarizability and cavity effects on the AdCl rate (in the same sense that the AdCl rates had earlier been considered to model solvent 'ionizing power' effects on the Bu^tCl rates). According to this model, the 1.4 log unit rate difference in AdCl rates in 60% EtOH and 97% TFE is mainly due to acceleration for AdCl (relative to the Bu^tCl model) in 97% TFE by virtue of enhanced electrophilic assistance in the stronger HBD solvent (*i.e.* *ca.* 0.2–0.4 log unit would be attributed to enhanced nucleophilic assistance to Bu^tCl in 60% EtOH, and *ca.* 1.0–1.2 log unit would be attributed to enhanced electrophilic assistance to AdCl in 97% TFE). Fortunately the information is available to test this alternative possibility.

The α value for 97% TFE is about 1.5, and that for 60% EtOH can be estimated as being about 1.0; $\Delta\alpha$ is therefore *ca.* 0.5. The 1.0–1.2 log unit acceleration which we attribute to enhanced electrophilic assistance of AdCl solvolysis in 97% TFE [= (Δa)-($\Delta\alpha$)] could then be rationalized if the a coefficient in equation (2) were 2.0–2.4 units higher for AdCl solvolysis than for Bu^tCl solvolysis.

The relative a values for Bu^tCl and AdCl can be estimated from their reaction rates in a common set of HBD solvents. The relevant data are available for five HBD solvents: water, methanol, ethanol, trifluoroethanol, and hexafluoropropan-2-ol (HFP). Unfortunately, there are insufficient pure solvent data points and too many independent variables to determine the a values from a statistically justifiable multiple linear regression correlation by equation (2). We have therefore made one important assumption and estimated the a values as follows.

Insofar as the AdCl rate is considered to be modelled by Bu^tCl and insofar as solvent dipolarity-polarizability and cavity effects are concerned, the s and h terms in equation A will apply to both systems. Using $h = 0.0048$ and $s = 5.10$ for both AdCl and Bu^tCl, $b = 0.73$ for Bu^tCl, and $b = 0.0$ for AdCl, one can rearrange equation (2) to give expressions (4) and (5) for the

$$[\log k(\text{Bu}^t\text{Cl}) - 0.73 - 0.0048\delta_{\text{H}}^2 - 5.10\pi^*] = (\log k)_0 + a\alpha \quad (4)$$

$$[\log k(\text{AdCl}) - 0.0048\delta_{\text{H}}^2 - 5.10\pi^*] = (\log k)_0 + a\alpha \quad (5)$$

rates which depend only on α . The least-squares fit of the data for the five HBD solvents according to equations (4) and (5) gives a values of 4.11 and 6.46 for Bu^tCl and AdCl, respectively, which values fit the requirement ($\Delta a = 2.0$ – 2.4) for the enhanced electrophilic assistance interpretation of the TFE–EtOH plot. We shall show in another paper³¹ that a method of double differences, which obviates the need to assume similar dipolarity–polarizability effects for the two substrates compared, leads to similar estimates of the a values for AdCl and Bu^tCl.

Nor should these relative a values be completely unexpected. The amounts of electrophilic assistance should depend on the amounts of ionic character in the transition states, which should depend in turn, on the relative stabilities of t-butyl and adamantyl carbocations. Gas-phase free energies of transfer of bromide ion³² and hydride ion³³ do indeed indicate that 1-adamantyl cation is more stable than t-butyl cation. (On the other hand, enthalpies of ionization in SO₂ClF–SbF₅ and in CH₂Cl₂–SbF₅ are lower for Bu^tCl than for AdCl.)³⁴

The foregoing results lend support both to those who suggest the existence of NSA for t-butyl chloride solvolysis, and to those who claim that the effect of electrophilic assistance is large and variable even when leaving groups are the same. In future papers additional TFE–EtOH plots will be analysed and re-interpreted, in the same way.

Further Mechanistic Implications.—The same lack of consideration of solvent electrophilicity which weakens the Raber-Harris and Bentley-Carter approaches applies also to several other methods for identifying nucleophilic solvent assistance. If the method involves a model compound, and if solvent electrophilicity is not estimated or controlled, the variations in model or substrate sensitivity to solvent electrophilicity can lead to failure of the method. This stricture applies to the use of the following probes and methods of estimating NSA: (1) Grunwald–Winstein m values;^{3,35} (2) the Bentley–Schleyer $l - m$ method; (3) the α -methyl/hydrogen ratio (the problem is accentuated here and in several other instances by the need to use different leaving groups);^{3,35} (4) the σ^* method;³⁶ (5) the $k_{\text{RX}}/k_{2\text{A}0\text{T}5}$ method;^{3,35} and (6) the $(k_{\text{EtOH}}/k_{\text{AcOH}})_Y$ method.^{3,35}

The present results also have implications regarding a recent paper by Bentley and his co-workers¹² in which Y values are given for adamantyl chloride, bromide and iodide. We have noted that in the t-butyl halide series there was an increasing dependence on solvent electrophilicity on going from iodide to bromide to chloride. We feel (and shall later confirm by the method of double differences)³¹ that the trend is the same in the adamantyl series, and is responsible for the observations of Bentley *et al.* that points for the fluoro-alcohols and acetic and formic acids deviate from the plots of Y_{Cl} against Y_{Br} and Y_{I} , with the deviations being larger for the iodide than for the bromide. The deviations are consistently in the direction of Y_{Cl} being too large.

Thus, these deviations probably result from the enhanced response of the chloride to the high electrophilicity of these particular solvents, a conclusion which is further supported by the observation that Y_{Cl} is higher for HFP than for water. There

* But note that more recently, Bentley and Roberts³⁸ have suggested that there are at least three contributing effects in solvolyses, namely electrostatic solvation, electrophilic solvation, and lipophilic solvation effects. They thus arrive at a position not far from that represented by our general equation (2).

have been several measures of the ionizing power of water and HFP,³⁷ but prior to the Bentley study none have indicated HFP to be more highly ionizing than water. Again, this relationship can be explained on the basis of the high response of 1-adamantyl chloride to the high electrophilicity of HFP.

Our approach is quite different to that of Bentley *et al.*¹² who feel that solvent effects on solvolysis rates can be treated empirically with only two parameters.* In a future paper³⁹ we set out theoretical arguments to show that at least four explanatory variables will be needed to account for solvent effects in general, and we show how these four variables can collapse into two, or sometimes even into just one, explanatory variable owing to collinearity in certain sets of solvents. Whether two empirical parameters or four parameters, for which there is some theoretical justification, are used depends entirely on the aim of the investigation. A referee has kindly pointed out that if $\log k$ for one t-butyl halide is plotted against $\log k$ for another t-butyl halide, there results a simple pattern of two parallel straight lines—one for protogenic and one for non-protogenic solvents. The referee therefore suggests that only two factors are needed to explain the solvent dependence of the t-butyl halide rate constants. This is perfectly correct, but only if the analysis is restricted to the effect of solvents on the t-butyl chloride reaction *vs.* the effect of solvents on the t-butyl bromide and t-butyl iodide reactions. Our aim, however, is much more general. It is to describe solvent effects on various reactions of different charge type, on equilibria, and on individual species by the *same* general equation and, eventually, to be able to understand and to predict how the different terms in the general equation, equation (2), vary between correlations for quite different processes. Thus we have already shown how (2) can be applied to the effect of solvents on the Gibbs energy of nonelectrolytes,⁸ the Gibbs energy of dissociated electrolytes and of ion pairs,¹⁷ the Menshutkin reaction of tertiary amines with alkyl halides,⁴⁰ and the Finkelstein reaction of anions with alkyl halides.⁴⁰ We can already categorically state that two parameters are not sufficient to deal with the range of solvent effects we have so far encountered. In our view, it will eventually be much more simple to use the same four (or five, *etc.*) parameters to investigate a wide range of solvent effects than to deal with each particular type of process separately. Indeed, much previous work on solvent effects on solvolysis reactions can be criticised on the grounds that these effects have been considered in isolation from general effects in organic chemistry. In the following paper we shall attempt to show how solvolysis reactions can be studied in the context of a general solvent effect theory.

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