# Linear Solvation Energy Relationships. Part 38.† An Analysis of the Use of Solvent Parameters in the Correlation of Rate Constants, with Special Reference to the Solvolysis of t-Butyl Chloride

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Arguments are advanced to show that at least four solvent parameters are needed in any general equation for solvent effects on rate constants and on Gibbs energies of individual solutes: the parameters we use in our general equation are $\pi^*$, the solvent dipolarity, $\alpha$, the solvent hydrogen-bond acidity, $\beta$, the solvent hydrogen-bond basicity, and $\delta_H^2$, the solvent cohesive energy density. Parameters such as $Y$ and $N$ cannot represent unique solvent properties, because there exists more than one set of $Y$ values and more than one set of $N$ values. It is shown that the various $Y$ values are 'blends' of $\pi^*$ and $\alpha$ in varying proportions, that the $N$ values are 'blends' of $\pi^*$ and $\beta$, and that $Y^+$ values are nearly pure $\beta$. Conditions for the collapse of the several $Y$ scales into one scale, and for the collapse of the ($mY + lN$) equation into just $mY$, are outlined, based on the collinearity of $\pi^*$, $\alpha$, and $\beta$ in certain sets of solvents.

Whenever rate constants for a given reaction are determined in a number of solvents, it is nowadays almost obligatory to construct plots of log $k$ (or the equivalent $\Delta G^‡$) against some solvent parameter, $P$, using a simple regression equation as in equation (1) or (2). General accounts of these simple regression

$$\log k = mP + c \qquad (1)$$

$$\Delta G^‡ = nP + d \qquad (2)$$

equations have been written,[1–6] and it is not our intention either to repeat these accounts, or to examine in detail the various solvent parameters that have been used. Reichardt, in 1979,[5] was able to refer to no fewer than 24 parameters that had been put forward at that time, and, no doubt, further solvent parameters will become available.

Out of all these solvent parameters, only few have any rigorous theoretical basis. Kirkwood,[7] however, established a relationship between the solvent dielectric constant, $\varepsilon$, and the electrostatic contribution to the free energy of transfer of a solute considered as a dipole of moment $\mu$ in a sphere of radius $r$. From Kirkwood's treatment it follows[8] that a solvent parameter can be defined as the Kirkwood function, $(\varepsilon - 1)/(2\varepsilon + 1)$, or as almost equivalent functions. More refined expressions, also based on reaction field theory, have been put forward by Abraham and Abraham[9,10] and by Beveridge and Schnuelle,[11] and it is clear that there will be a large electrostatic contribution to the free energy of transfer of a dipolar solute between solvents of different dielectric constants.

In another approach altogether, Hildebrand[12] showed that the primary medium activity coefficient of a nonelectrolyte solute can be expressed in terms of the solubility parameters of solute, $\delta_H^i$, and solvent, $\delta_H$, and of the solute molar volume, $V^i$. The corresponding free energy of transfer is then a function of the expression $V^i(\delta_H^i - \delta_H)^2$, and it is simple[2,13] to deduce a relationship between either log $k$ or $\Delta G^‡$ in equations (1) and (2) and the solvent solubility parameter. The Hildebrand approach is applicable to non-dipolar solutes, and includes not only the 'cavity' effect that arises through disruption of solvent–solvent bonds but probably also solute–solvent dispersion interactions.

Neither the Kirkwood nor the Hildebrand expression allows for specific solute–solvent interactions such as might arise through hydrogen bonding.‡ A general equation for solvent effects, either on a given solute or on reaction rates, must include provision for hydrogen bonding due to hydrogen-bond donor ($\alpha$) or hydrogen-bond acceptor ($\beta$) functions of the solvent. This requires an equation that contains at least four explanatory variables: a dipolarity term, a cavity term, and two hydrogen-bonding terms. One such general equation is equation (3), in

$$\text{XYZ} = (\text{XYZ})_0 + s\pi^* + a\alpha + b\beta + h\delta_H^2 \qquad (3)$$

which $\pi^*$, $\alpha$, and $\beta$ represent solvent dipolarity, hydrogen-bond acidity, and hydrogen-bond basicity, and $\delta_H^2$ is the solvent cohesive energy density. In order to provide for variable polarisability effects, a polarisability correction term, $(\pi^* + d\delta)$, is sometimes needed instead of $\pi^*$ alone,[15] and, as we have shown in the previous paper in this series,[16] the $\delta_H^2$ term may also include a contribution from solvent electrostriction/reorganisation. For the correlation of rate constants, XYZ is log $k$ (or $\Delta G^‡$) and for the correlation of solvent effects on the Gibbs energy of a single solute, XYZ is $\Delta G_t^\circ$, the transfer parameter for a solute. Of course, there are other general equations for solvent effects, such as the four-parameter equation of Koppel and Palm,[17] but the point we wish to emphasise is that there are so many possible interactions between a solute (or transition state) and solvents that no single solvent parameter can be expected to be applicable over a wide range of reaction types or processes.[18]

Because there are so many possible interactions on transfer of a species between solvents to consider, it is now clear why so many solvent scales have been devised, and why they will all, in general, fail.[18] A solvent parameter will correlate with some

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† Part 37, ref. 16.

‡ There are several modifications of the original Hildebrand expression that incorporate effects due to dipolarity and hydrogen bonding; see ref. 14.

**Table 1.** Values of log $k$ for solvolysis of t-butyl chloride, and solvent parameters in water and simple alcohols[a]

| Solvent | $-\log (k/s^{-1})$ | $\pi^*$ | $\alpha$ | $\beta$ | $\delta_H{}^2/100$ | $E_T$ | $f(\varepsilon)$[b] |
|---|---|---|---|---|---|---|---|
| Water | 1.54 | 1.09 | 1.17 | 0.18 | 5.490 | 63.1 | 0.4905 |
| Methanol | 6.10 | 0.60 | 0.93 | 0.62 | 2.052 | 55.5 | 0.4774 |
| Ethanol | 7.07 | 0.54 | 0.83 | 0.77 | 1.621 | 51.9 | 0.4698 |
| Propan-1-ol | 7.33 | 0.52 | 0.78 | 0.84 | 1.432 | 50.7 | 0.4642 |
| Propan-2-ol | 7.74 | 0.48 | 0.76 | 0.95 | 1.331 | 48.6 | 0.4623 |
| Butan-1-ol | 7.52 | 0.47 | 0.79 | 0.88 | 1.295 | 50.2 | 0.4582 |
| 2-Methylpropan-2-ol | 8.27 | 0.41 | 0.68 | 1.01 | 1.119 | 43.9 | 0.4423 |
| $r$: |  | 0.997 | 0.980 | 0.984 | 0.994 | 0.942 | 0.862 |

[a] Values taken from M. H. Abraham, A. Nasehzadeh, J. J. Moura Ramos, and J. Reisse, *J. Chem. Soc., Perkin Trans. 2*, 1980, 854. [b] $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$.

other process over a set of solvents only if (*a*) the coefficients (*s*, *a*, *b*, *h*) in equation (3) are exactly the same for the parameter and the process, or (*b*) if over the solvent set there is such collinearity of the variables in equation (3) that, by chance, equation (3) collapses to equation (1), or (*c*) if all but one of the coefficients in equation (3) are zero or nearly zero so that equation (3) reduces to equation (1) for both the solvent parameter and the process concerned.

Similar arguments apply to regression equations containing only two explanatory variables (for example the parameters $A$ and $B$ of Swain *et al.*[19] or the parameters $Y$ and $N$ often used to describe solvolysis reactions). Any of the possibilities (*a*)—(*c*) can clearly be amended so as to reduce a general equation (3) to a double regression equation.

*Application to the Solvolysis of Alkyl Halides.*—In the previous paper on the solvolysis of the t-butyl halides,[16] we showed that equation (3) allowed us, for the first time, to detail exactly the solvent effects that influenced log $k$ values for these reactions. We referred to the possibility of collinearity of variables over a reduced set of solvents, but did not explicitly show how such collinearity has hitherto prevented any adequate analysis of solvent effects on these important reactions. In Table 1 is given a selection of such variables, together with log $k$ values for the solvolysis of t-butyl chloride. The correlation coefficients, $r$, for simple regressions of log $k$ against each of these parameters are all quite good, no matter whether log $k$ is correlated with solvent acidity ($\alpha$), solvent basicity ($\beta$), solvent dipolarity [$\pi^*$ or $f(\varepsilon)$], or solvent cohesive energy density ($\delta_H{}^2$). Hence, in such a solvent set, it is totally impossible to come to any conclusion as to the factors that influence the variation of log $k$. Kevill *et al.*[20] refer to this extraordinary collinearity as 'nature's cruel trick'. Since the parameter $Y$ is defined in terms of log $k$ [equation (4)] the

$$\log(k/k_0)^{\mathrm{Bu^tCl}} = Y \qquad (4)$$

foregoing comments on log $k$ refer exactly to $Y$ values as well. Thus for the type of solvent used for many years to obtain $Y$ values, it is not possible to deduce the solvent property (or properties) that influence $Y$. The term 'ionising power' used to describe $Y$ is misleading, because (see Table 1) for many solvents $Y$ might be a function of solvent acidity, or solvent basicity, *etc.*, or any combination of parameters. Interestingly, the authors who originally set up the $Y$ scale were probably aware of this difficulty, because they refer to $Y$ as being a combination of general and specific effects,[21] and, indeed, attempted[22] to dissect $Y$ into an ionising power based on general solvent functions ($Y_G$) and ionising power based on specific short-range hydrogen-bonding electrophilic functions of the solvent ($Y_H$). Unfortunately, these ideas seem to have been completely overlooked in recent years.

If the solvent set in Table 1 is expanded to include hydroxylic solvents such as the fluoro-alcohols or carboxylic acids, collinearity between solvent parameters is reduced, and it becomes possible to investigate the origin of the $Y$ parameter. But for just these solvents, there are now numerous sets of $Y$ values, each set defined in terms of a different alkyl halide. In Table 2 are given the various $Y$ parameters† that have been suggested.[23–30] These $Y$ parameters cannot all be measures of some unique solvent property such as 'ionising power', and it is clear that the various sets of parameters must themselves be combinations of two or more solvent properties, the 'mix' of which depends on the particular alkyl halide used. It would be useful to analyse the sets of $Y$ values with the general equation (3), but unfortunately, for the adamantyl (Ad) solutes, there are far too few solvents for which data are available. We have therefore had to reduce equation (3) to a two-parameter equation, and give only the best double regressions that we have obtained with the results in Table 2. A summary of the coefficients of $\pi^*$, $\alpha$, or $\beta$ is in Table 3, together with the correlation coefficients. In order to compare $Y$ and $Y_{\mathrm{AdOTs}}$ more carefully with $Y$ for adamantyl halides, we have repeated the correlations for $Y$ and $Y_{\mathrm{AdOTs}}$ using only the seven common solvents.

It must be emphasised that the correlations of Table 3 refer to only a limited solvent set, with a curtailed version of equation (3).‡ However, they do yield reasonable graduations in the coefficients with $\alpha$ = 4.9, 4.3, and 3.4 for adamantyl chloride, bromide, and iodide, and with $\alpha(\mathrm{AdCl}) - \alpha(Y) = 2.1$, within the range of the previously suggested values of 2.0—2.4 units.[16] We can, therefore, use these correlations, at least as a first step, to examine solvent effects on the $Y$ values themselves. Nature's cruel trick is now exposed: the $Y$ values for solvolysis of t-butyl and adamantyl substrates are combinations of solvent dipolarity ($\pi^*$) and solvent acidity ($\alpha$). Because $\pi^*$ and $\alpha$ are linearly related for water and the simple alcohols ($r$ = 0.969 for the seven solvents in Table 1), there appears to be one solvent parameter only governing solvolysis in these solvents. Only when a solvent set is chosen in which $\pi^*$ and $\alpha$ are not so related ($r$ = 0.444 for the nine solvents in Table 2) can $Y$ values be broken down into their constituent parameters.

The $\log(k/k_0)$ values for solvolysis of methyl tosylate are of considerable interest in that $\pi^*$ and $\beta$ (and not $\pi^*$ and $\alpha$) are now significant. Here we have a demonstration that solvent

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† We include in Table 2 rate constants for solvolysis of methyl tosylate, which are of some interest, even though these are not $Y$ values, as such, and $Y^+$ values which are actually nucleophilic parameters (see later).

‡ Hence the coefficients of $\pi^*$ and $\alpha$ in Table 3 for the $Y$ parameter are not the same as those we have found before, using 21 solvents and the full equation (3).[16] Also, it must be pointed out that the errors in the coefficients are so large that only an indication of graduations can be given.

**Table 2.** $Y$ Parameters derived from the solvolysis of alkyl halides[a]

| Solvent | $\pi^*$ | $\alpha$ | $\beta$ | $Y^b$ | $Y_{AdOTs}{}^c$ | $Y_{AdCl}{}^c$ | $Y_{AdBr}{}^c$ | $Y_{AdI}{}^c$ | $Y_{AdClO_4}{}^c$ | $Y_{AdPic}{}^c$ | $Y_{AdOTf}{}^c$ | $Y_{NOTf}{}^d$ | $Y^{+e}$ | $\log(k/k_0)_{MeOTs}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | 1.09 | 1.17 | 0.18 | 3.49 | 4.1 | 4.57 | 4.44 | 4.24 | | | | | 0.257 | 0.79 |
| Methanol | 0.60 | 0.93 | 0.62 | −1.09 | −0.92 | −1.20 | −1.12 | −0.84 | −0.84 | −0.97 | −0.88 | | 0.037 | −0.32 |
| Ethanol | 0.54 | 0.83 | 0.77 | −2.03 | −1.75 | −2.50 | −2.40 | −2.20 | −1.84 | −1.37 | −1.84 | −1.50 | −0.024 | −0.53 |
| Propan-2-ol | 0.48 | 0.76 | 0.95 | −2.73 | −2.83 | | | | | | −2.39 | | −0.131 | −0.73 |
| Trifluoroethanol | 0.73 | 1.51 | 0.00 | 1.045 | 1.80 | 2.83 | 2.53 | 2.22 | 1.21 | | 1.23 | 0.40 | 0.456 | −2.47 |
| Hexafluoropropan-2-ol | 0.65 | 1.96 | 0.00 | 2.46 | 3.61 | 5.08 | 4.51 | 3.84 | | | | | | −3.19 |
| Acetic acid | 0.64 | 1.12 | 0.45[f] | −1.64 | −0.61 | −1.60 | −2.10 | −2.20 | −1.40 | −0.90 | −1.68 | −1.78 | 0.072 | −2.55 |
| Formic acid | 0.75[g] | 1.88[g] | 0.36[f] | 2.05 | 3.04 | 3.20 | 2.47 | 1.60 | | | | 1.49 | 0.035 | −1.43 |

[a] Values of $\pi^*$, $\alpha$, and $\beta$ from refs. 15 and 16 unless shown otherwise. [b] From ref. 27. [c] Refs. 23—30. [d] These are values from solvolysis of 7-norbornyl tosylate.[28] [e] From solvolysis of 1-$AdSMe_2{}^+$, reflecting nucleophilic solvation of the reactant (see text). Another value is −0.319 for t-butyl alcohol.[29b] [f] These are values for methyl esters. [g] O. Kolling, *Anal. Chem.*, 1984, **56**, 2988.

**Table 3.** Constants in regressions of $Y$ values against $\pi^*$, $\alpha$, and $\beta$

| Parameter | $\pi^*$ | $\alpha$ | $\beta$ | $r$ | $n$ |
|---|---|---|---|---|---|
| $Y$ | 7.94 ± 1.17 | 2.70 ± 0.48 | | 0.979 | 8 |
| $Y$ | 8.38 ± 1.57 | 2.86 ± 0.63 | | 0.967 | 7 |
| $Y_{AdOTs}$ | 8.58 ± 0.87 | 3.58 ± 0.36 | | 0.991 | 8 |
| $Y_{AdOTs}$ | 8.44 ± 1.20 | 3.53 ± 0.48 | | 0.984 | 7 |
| $Y_{AdCl}$ | 9.67 ± 2.58 | 4.95 ± 1.04 | | 0.957 | 7 |
| $Y_{AdBr}$ | 9.72 ± 3.03 | 4.33 ± 1.21 | | 0.934 | 7 |
| $Y_{AdI}$ | 9.39 ± 3.24 | 3.45 ± 1.30 | | 0.904 | 7 |
| $\log(k/k_0)_{MeOTs}$ | 7.30 ± 1.65 | | 4.18 ± 0.88 | 0.916 | 8 |

nucleophilic participation is important, and, furthermore, taking all the regressions into account, that at least three parameters ($\pi^*$, $\alpha$, and $\beta$) are needed.

Because, in the solvent set given in Table 2, the various $Y$ values are no longer linearly related, attempts have been made to expand the $mY$ equation (5) into a two-parameter equation

$$\log(k/k_0) = mY \qquad (5)$$

(6). In equation (6) $l$ is defined as unity for methyl solvolyses,

$$\log(k/k_0) = mY + lN \qquad (6)$$

and $m$ is arbitrarily given the value 0.30 for the methyl tosylate substrate.† Then $N$ may be obtained from equation (7) or (8), depending on whether $Y$ or $Y_{AdOTs}$ values are used.[23]

$$N = \log(k/k_0)_{MeOTs} - 0.3Y \qquad (7)$$

$$N_{OTs} = \log(k/k_0)_{MeOTs} - 0.3Y_{AdOTs} \qquad (8)$$

The two sets of $N$ values obtained in this way are given in Table 4. They represent the 'nucleophilic' power of a solvent, in contrast to the 'ionising' power of a solvent defined as $Y$. However, since there are two sets of $N$ values, they cannot both represent a single solvent parameter. Our comments about the various $Y$ values apply here as well, and so we have correlated the $N$ values against $\pi^*$, $\alpha$, and $\beta$ to determine the 'mix' of solvent parameters in the two $N$ value scales. The best double regressions are equations (9) and (10). On the basis of these

$$N = -7.27 + (5.43 \pm 1.65)\pi^* + (5.27 \pm 0.88)\beta \qquad r = 0.937 \qquad (9)$$

$$N_{OTs} = -7.68 + (5.54 \pm 1.75)\pi^* + (5.65 \pm 0.99)\beta \qquad r = 0.932 \qquad (10)$$

**Table 4.** $N$ Values for various solvents[a]

| Solvent | $N$ | $N_{OTs}$ |
|---|---|---|
| Water | −0.26 | −0.44 |
| Methanol | 0.01 | −0.04 |
| Ethanol | 0.09 | 0.00 |
| Propan-2-ol | 0.09 | 0.20 |
| Trifluoroethanol | −2.78 | −3.00 |
| Hexafluoropropan-2-ol | −3.93 | −4.27 |
| Acetic acid | −2.05 | −2.35 |
| Formic acid | −2.05 | −2.35 |

[a] Ref. 23.

equations, the relative contributions of $\pi^*$ and $\beta$ to $N$ and $N_{OTs}$ cannot be distinguished. It does seem, however, that for the solvent set in Table 4, the two $N$ values may be broken down into contributions from $\pi^*$ and $\beta$.

Kevill and Lin[27b] have devised a set of $N_{KL}$ values based on the solvolysis of $Et_3O^+$, but for only six of the solvents listed in Table 4. There are but poor correlations of $N_{KL}$ with $\pi^*/\alpha/\beta$ for these six solvents, but, as expected, the dominant factor is $\beta$.

The $Y^+$ values of Kevill and Anderson[29b] are based on rate constants for the solvolysis of the charged species 1-$Ad\overset{+}{S}Me_2$. As Kevill and Anderson pointed out, these $Y^+$ values are not at all comparable to the various sets of $Y$ values for neutral substrates, but reflect nucleophilic solvation of the initial state. A regression analysis of $Y^+$ values for eight pure solvents (values given in Table 2 together with $Y^+ = -0.319$ for t-butyl alcohol) leads to the best double regression (11). The $Y^+$ values,

$$Y^+ = 0.66 - (0.18 \pm 0.10)\alpha - (0.77 \pm 0.12)\beta \qquad r = 0.967 \qquad (11)$$

in agreement with Kevill and Anderson,[29b] thus reflect almost entirely solvent nucleophilic effects on the initial state (hence the negative sign of the coefficient of $\beta$). The $\alpha$ term in equation (11) is significant at only the 80% level, and a single regression based only on $\beta$ yields the equation (12), confirming $Y^+$ as an almost

$$Y^+ = 0.38 - (0.61 \pm 0.08)\beta \qquad r = 0.946 \qquad (12)$$

pure nucleophilic solvation parameter. There seems now to be little need for the parameters $N$, $N_{OTs}$, $N'_{OTs}$, or $N_{KL}$, in view of this new nucleophilic parameter, $Y^+$.

Our overall analysis shows that each of the components $Y$ and $N$ in equations (7) and (8) is composed of at least two parameters, $\pi^*$ and $\alpha$ in the case of $Y$, and $\pi^*$ and $\beta$ in the case of $N$. Hence, at least three parameters ($\pi^*$, $\alpha$, and $\beta$) are needed to account for the various sets of $\log(k/k_0)$ values, exactly as predicted by Winstein *et al.*,[32] who suggested that at least three terms on the right-hand side of equation (6) would be required

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† But Kevill and Rissmann[31] suggest that a better value for $m$ is 0.55, and use this to obtain a related scale of $N'_{OTs}$ values.

**Table 5.** Estimates of nucleophilic solvent assistance, in kcal mol$^{-1}$ (1 kcal = 4.184 kJ), for some solvolysis reactions[36,37]

| | Solvent | | | | |
|---|---|---|---|---|---|
| Substrate | Water | Methanol | Ethanol | Acetic acid | Trifluoroacetic acid |
| Methyl tosylate | | | 33 | 31 | 27 |
| Ethyl tosylate | | | 16 | 14 | 9 |
| Isopropyl tosylate | | | 6 | 3 | 0 |
| Methyl iodide | 41 | 43 | | | |
| Ethyl iodide | 16 | 19 | | | |
| Isopropyl iodide | 3 | 5 | | | |
| t-Butyl iodide | Small | Small | Small | | |
| t-Butyl chloride | Small | Small | Small | | |

for really successful fits. Our analysis also shows how equation (6) can collapse to the simple $mY$ equation with constant $Y$ in limited sets of solvents; for the solvent set in Table 1, $\pi^*$, $\alpha$, and $\beta$ are all linearly related; hence $N$ is collinear with $Y$ and equation (6) reduces to equation (5). It is quite possible (and indeed is required by our general correlative equation[16]) that $Y$ and $N$ are composed of more than two parameters. However, our analysis is restricted by the small number of solvents (Tables 2 and 4), and it would require rate constants to be obtained in very many more solvents before we could apply three- or four-parameter equations to $Y$ and $N$.

*Solvent Effects and Transition States.*—Related to the above is the question as to what, if any, quantitative information as to the nature of transition states can be obtained from solvent effect studies. For the solvolysis of t-butyl chloride, various estimates of the charge separation in the transition state, $z$, have been obtained by various electrostatic treatments, *e.g.* $z = 0.80$,[10] or $z = 0.81$.[33] Comparison of solvent effects on the t-butyl chloride transition state with those on ion-pairs gave a very similar value of $z = 0.84$;[34] these values of $z$ lead to a transition-state dipole moment of around 9 D; see ref. 10. Other solvent effect studies, following Hildebrand's treatment, lead to a solubility parameter for the t-butyl chloride transition state of 13.1, and a value of 10.8 for the t-butyl bromide transition state.[2]

However, use of equations such as (5) or (6) cannot lead to any such quantitative information, because these equations are based on relative solvent effects compared with some reference alkyl halide. Only by invoking some assumption about the reference alkyl halide, or by using some other treatment to obtain quantitative data on the reference alkyl halide, can equation (5) or (6) be used in a quantitative (absolute) sense. Hence solvolyses are often compared with those of adamantyl substrates, because the latter are assumed not to be prone to nucleophilic solvent assistance, or indeed, to any assistance at all. But quite recently, le Noble *et al.*[35] have discovered the existance of bridging and $\sigma$-participation in solvolyses of 2-adamantyl substrates, thus highlighting the inherent difficulty of obtaining any quantitative information through comparisons of rate constants only.

Estimates of nucleophilic assistance in other alkyl halides have been obtained from equations that contain only kinetic data, *e.g.* from equation (13), but only by invoking various

$$\text{solvent assistance} = k/k_c = \frac{k(\text{ROTs})/k(\text{2-AdOTs})^{\text{solvent}}}{k(\text{ROTs})/k(\text{2-AdOTs})^{\text{CF}_3\text{CO}_2\text{H}}} \quad (13)$$

assumptions: (i) the solvolysis of 2-adamantyl tosylate is not nucleophilically assisted in any solvent, (ii) the solvolysis of ROTs (all secondary tosylates) is not nucleophilically assisted in trifluoroacetic acid, and (iii) the increase in $k$(ROTs)/$k$(2-AdOTS) from trifluoroacetic acid to any other solvent is due entirely to nucleophilic assistance.[23]

**Table 6.** Comparison of the coefficient of $\pi$ ($s$) in equation (3) with the dipole moment of the solute or transition state[a]

| Species | $s$[b] | $\mu$/D |
|---|---|---|
| $CH_4$ | −0.04 | 0 |
| EtI | −0.44 | 1.8 |
| $Bu^tCl$ | −0.56 | 2.2 |
| MeCOEt | −1.51 | 2.9 |
| $MeNO_2$ | −3.44 | 3.5 |
| $p$-$NO_2C_6H_4CH_2Cl$ | −3.77 | 3.7 |
| $[Et_3N/EtI]^‡$ | −6.58[c] | 8.2[d] |
| $[Bu^tCl]^‡$ | −6.94[c] | 8.8[d] |

[a] Values from ref. 41 unless shown otherwise. [b] These values are for regressions of $\Delta G_t^\circ$ in kcal mol$^{-1}$. [c] These values are for regressions of $\Delta G^‡$ in kcal mol$^{-1}$. If the transition-state transfer energies themselves were used ($\Delta G_t^\circ$ values) the values would be expected to differ slightly. [d] Ref.18.

Other estimates can be obtained through comparison of thermodynamic data with $\Delta G^‡$ values. Abraham[36] calculated $\Delta G^\circ$ values for ionisation of alkyl halides *via* a thermodynamic cycle. As a first approximation, we may take $\Delta G^\circ - \Delta G^‡$ as an indication of the solvent assistance necessary to promote the solvolysis reaction. Similarly, Arnett[37] later compared $\Delta G^‡$ for solvolysis with $\Delta H^\circ$ for ionisation in the solvent $SO_2$–$SbF_3$. In Table 5 are summarised the results of these two investigations. They are in remarkable agreement, and show how useful it is to combine kinetic with non-kinetic data. Once values such as those in Table 5 are established, it is then possible either to use these values as 'standards' in setting up scales based on kinetic data, or to examine the assumptions that necessarily have to be made when only kinetic data are used. Thus the nucleophilic assistance for isopropyl tosylate estimated by Bentley and co-workers.[23] (see before) is close to that observed by Arnett *et al.*[37] (Table 5), suggesting that the assumptions are reasonable.†

A considerable advantage of equation (3) over other solvent regression equations is that it can be applied to non-kinetic data. We have successfully used equation (3) to correlate, for example, the Gibbs energies of transfer of $R_4N^+X^-$ with solvent parameters.[39] We therefore now have the possibility of comparing coefficients in equation (3) for correlations of kinetic data ($\Delta G^‡$ values) with those for correlations of thermodynamic data ($\Delta G^\circ$ values), in order quantitatively to assess the role of $\pi^*$, $\alpha$, $\beta$, *etc.* in transition states. This, of course, is the multiparameter extension of the method of model solutes invented[40] several years ago with respect to simple regressions [equation (1) or (2)]. Thus, previously,[41] we have shown that there is a regular connection between the magnitude of the coefficient of $\pi^*$ ($s$) in equation (3) and the dipole moment of the solute under investigation, at least for solutes that carried a single dominant moment. Transition states in the t-butyl

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† But note that a recent analysis[38] of equations such as (6) and (9) indicates that in general these equations cannot distinguish between effects due to increased electrophilic assistance or decreased nucleophilic assistance (or *vice versa*). It is also concluded[38] that there is no nucleophilic assistance in solvolysis of t-butyl chloride, and that (as we have shown) a three-term correlation including solvent dipolarity, electrophilicity, and nucleophilicity is to be preferred over a two-term correlation such as equation (6). As regards nucleophilic assistance, our view[16] is that there is weak nucleophilic assistance in solvolysis of t-butyl chloride.

chloride solvolysis reaction, and in reactions of the Menschutkin type, also have a single dominant moment. As shown in Table 6, the very regular connection between μ and *s* extends also to these transition states. More results on different solutes and transition states are needed to establish the connection in a mathematical form so that values of μ can be predicted from the regression coefficient *s*, but the power of a general regression equation that will deal with solvent effects both on solutes (as $\Delta G^\circ$ transfer values) and on rate constants (as log *k* or $\Delta G^\ddagger$ values) is now clear. As also pointed out previously,[41] $\Delta G^\circ$ transfer values for the $R_4N^+X^-$ ion-pairs do not yield *s* coefficients that lie on the same line as that given by the values listed in Table 6, possibly because interaction of $R_4N^+X^-$ with solvents is more of the ion–dipole type, rather than the dipole–dipole type of interaction of the solutes and transition states listed in Table 6.

The overriding theme of this paper is the conviction that one aim of the study of a reaction mechanism must be to deduce the nature of the particular transition state. We conclude with the suggestion that application of a general solvent regression equation, for example our equation (3), to both rate constants and $\Delta G^\circ$ transfer values for solutes will enable quantitative estimates of transition-state properties to be made by a multiparameter extension of the method of model solutes.

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