The Effect of Hydroxylic Solvents on the Solvolysis of t-Butyl Chloride; Calculation of the Cavity Terms

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The effects of water and alcohols on values of $\Delta G^\ddagger$ for the solvolysis of t-butyl chloride have been correlated with various solvent parameters. It is shown, however, that neither simple nor multiple correlations yield information about the nature of the solvolysis because in these solvents the parameters are usually collinear. Transfer free energies of the transition state, ΔG_t°(Tr), have been correlated with ΔG_t° values for α-amino-acids and the $Me_4N^+Cl^-$ ion-pair. For transfers to water, these correlations are improved by correction for the size or cavity effect, using scaled particle theory, the Sinanoglu–Reisse–Moura Ramos method, or the division into neutral and electrostatic contributions. Plots of the corrected ΔG_t° values, corresponding to the solute–solvent interaction terms, for the transition state against the α-amino-acids and the ion-pair show that the transition state is very polar, though not so polar as the ion-pair, and that α-amino-acids are excellent models for the solvolysis transition state.

Two main approaches have been used recently in the study of solvent effects on reaction rates. One method, applied especially by Koppel and Palm,[1] by Chapman and Shorter,[2] and by Fawcett and Krygowski,[3] involves multiple correlation of rate constants (as log *k* or as $\Delta G^\ddagger$ values) with various solvent parameters. The latter are chosen so as to reflect specific solvent properties such as nucleophilic or electrophilic character, or general solvent properties such as polarity or polarisability.[1-4] The second method, developed by Abraham,[5-9] involves determination of the effect of solvents on the free energy of solutes that might be considered as reasonable models for a given transition state. If the free energy of transfer of a species from a reference solvent to any other solvent is denoted as ΔG_t°, then the ΔG_t° (model solute) values are compared with $\Delta G^\ddagger$ values or, more usually, with ΔG_t° (Tr) values for the given reaction. In the latter case, the solvent effect on the free energy of the transition state, Tr, has to be obtained separately.[6,10]

Both the above methods have been applied to the solvolysis or decomposition of t-butyl chloride. However, although the solvolysis in hydroxylic solvents is straightforward, it is not clear if the unimolecular decomposition to isobutene in aprotic solvents should be regarded as the same ' reaction ' as the solvolysis process. In order to minimise difficulties in interpretation of results, we shall deal only with the solvolysis of t-butyl chloride in pure hydroxylic solvents. We apply both methods to the same sets of experimental data, and we hope to reach conclusions as to the nature of the transition state and the usefulness of the methods in this particular system.

Correlations of $\Delta G^\ddagger$ *with Solvent Parameters.*—In Table 1 are given the values of $\delta\Delta G^\ddagger = \Delta G^\ddagger$ (solvent) $- \Delta G^\ddagger$ (methanol) that we shall use.[6,7] Following other workers [1,4] we chose the solvent parameters E_T, Gutmann's donor number DN, and Kamlet and Taft's [11] α- and β-parameters as examples of specific solvent properties, E_T and the α-parameter as measures of solvent acidity, and DN and the β-parameter as solvent basicity parameters. As general solvent parameters we selected the Kirkwood dielectric constant function $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ and the refraction function [1] $f(\eta^2) = (\eta^2 - 1)/(\eta^2 + 2)$. We therefore have $\delta\Delta G^\ddagger$ as the dependent variable and six solvent parameters as explanatory or independent variables. There is no point in including in any multiple correlation analysis any explanatory variables that are themselves strongly related. Unfortunately, over the solvents used in this work, most of the six explanatory variables are collinear. Against E_T, for example, the other explanatory variables yield the following correlation constants, ρ, in linear analysis : DN-(0.981 4), α-parameter (0.960 7), β-parameter (0.961 7), f(ε) (0.970 6), and $f(\eta^2)$ (0.785 0). Thus in any multiple analysis, it is reasonable only to combine $f(\eta^2)$ with one other explanatory variable. Furthermore, there are difficulties in the interpretation of even simple linear correlations. Previous workers [1,3] have stressed the importance of solvent acidity (as measured for example by E_T) in the t-butyl chloride reaction. But we see for the present hydroxylic solvents that if $\delta\Delta G^\ddagger$ is well correlated with E_T, it will also be well correlated with the basicity functions DN and the β-parameter. In these circumstances it is impossible even to deduce a causal relationship between $\delta\Delta G^\ddagger$ and any one of the collinear variables. Nevertheless, since E_T has been suggested as important,[3] we give in Table 2 details of a simple correlation with E_T and of a correlation with E_T and $f(\eta^2)$.† For all the listed solvents in Table 1, the value of ρ is barely affected by the incorporation of $f(\eta^2)$, and the level of significance, α, as judged by the *F* test, is actually reduced. If water is excluded (Table 2B) the multiple correlation constant is increased but the level of significance remains the same. Thus the additional variable, $f(\eta^2)$, is not really warranted.

Our simple correlation of $\delta\Delta G^\ddagger$ with E_T, significant at

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† Simple and multiple regression analyses were carried out using the MREG package at the University of Surrey.

the 0.998 level, may be compared with the analysis of Fawcett and Krygowski [3] who reported a multiple regression correlation constant of 0.909 for log *k* against E_T and DN as explanatory variables for five unspecified (but probably hydroxylic) solvents. Apart from the theoretical point that E_T and DN could be collinear, the above value of ρ 0.909 corresponds only to a level of significance between 0.9 and 0.95, *i.e.* much less than our simple correlation using E_T. On the other hand, Dougherty's [12] multiple correlation of log *k* with three explanatory variables that are combinations of solvent ionisation potential and solvent electron affinity yields an *F* value of 4×10^4 for five hydroxylic solvents; this corresponds to an 0.995 level of significance. Earlier work of Koppel and Palm [13] showed that log *k* values in aliphatic alcohols were well correlated with σ^* values (the inductive substituent constants for the alkyl group in the alcohols); as might now be expected, σ^* is also [13] linearly related to E_T for alcoholic solvents.

TABLE 1

Solvent effects on the $\Delta G^\ddagger$ values for solvolysis of t-butyl chloride and free energies of transfer (on the mole fraction scale) from methanol, in kcal mol^{-1} at 298 *K* [a]

		ΔG_t^0					
Solvent	$\delta\Delta G^\ddagger$	Glycine	α-Aminocaproic acid	α-Phenylalanine	Bu^tCl	$Me_4\overset{+}{N}Cl^-$	Tr
Water	−6.22	−3.41	−0.90	−0.93	4.57	−3.0	−1.65
Methanol	0	0	0	0	0	0	0
Ethanol	1.32	1.22	1.03	0.86	−0.26	1.5	1.06
n-Propanol	1.68	1.39		1.29	−0.34	1.9	1.34
n-Butanol	1.94	1.65	1.44	1.32	−0.46	2.2	1.48
Propan-2-ol	2.24	1.52		1.53	−0.30	2.3	1.94
t-Butyl alcohol	2.96	1.74		1.88	−0.46	3.9	2.50

[a] Values taken from refs. 6—8.

TABLE 2

Correlation of $\delta\Delta G^\ddagger$ with solvent parameters

A All solvents in Table 1			
Explanatory variables	ρ [a]	*F* [b]	α [c]
E_T	0.9422	39.5	0.998
$E_T + f(\eta^2)$	0.9423	15.8	0.980
ΔG_t^0 (Glycine)	0.9938	401	0.999 99
ΔG_t^0 (α-Aminocaproic acid) [d]	0.9230	11.5	0.900
ΔG_t^0 (α-Phenylalanine)	0.9365	33.7	0.998
ΔG_t^0 (Me_4NCl)	0.9648	67.4	0.999
B Alcohols in Table 1			
E_T	0.9667	57.1	0.998
$E_T + f(\eta^2)$	0.9924	97.8	0.998
ΔG_t^0 (Glycine)	0.9362	28.4	0.990
ΔG_t^0 (α-Aminocaproic acid) [e]	0.9993	683	0.975
ΔG_t^0 (α-Phenylalanine)	0.9915	232	0.999
ΔG_t^0 (Me_4NCl)	0.9826	112	0.999

[a] Single or multiple correlation constant. [b] *F* statistic. [c] Level of significance of the correlation. This takes into account the number of explanatory variables and the number of data points so that the values of α are directly comparable with each other. [d] Only four data points. [e] Only three data points.

Our conclusion is that because nearly all the common solvent parameters are collinear within the set of solvents water and alcohols, neither simple linear regression nor multiple regression analysis can yield any definitive information about the nature of the reaction or of the transition state.

If it is necessary to predict $\delta\Delta G^\ddagger$ values in other alcohols, a simple linear regression against E_T can be used.† We give in Table 2 details of correlations of $\delta\Delta G^\ddagger$ against ΔG_t° values for a number of solutes. The α-amino-acids glycine (α 0.999 99 for water and alcohols) or α-phenylalanine (α 0.999 for alcohols) yield excellent correlations, and it would be of interest to see if these correlations could be extended. We remark finally that the recent method of Parker,[14] in which $\Delta G^\ddagger$ or ΔG_t°(Tr) is correlated with $\Delta G_t^\circ(Cl^-)$ or Gutmann's acceptor number, AN, cannot be applied because of lack of data on $\Delta G_t^\circ(Cl^-)$ and AN for the aliphatic alcohols.

Method of Model Solutes.—Several workers [15] have compared solvent effects on $\Delta G^\ddagger$ or on ΔG_t°(Tr) with effects on 1 : 1 electrolytes. However, ion-pairs are much more suitable model solutes, and in Table 1 are values for $\Delta G_t^\circ(Me_4N^+Cl^-)$,[6,7] this particular ion-pair being chosen because it is about the same size as the transition state and it contains the appropriate anion. The zwitterionic α-amino-acids might also be useful models for polar transition states,[16-18] and in Table 1 are ΔG_t° values for three such α-amino-acids. If a model solute resembles the transition state in charge separation, polarity, *etc.*, then it should respond to change of solvent similarly to the response of the transition state, and ΔG_t°(Tr) might be expected to be linearly related to ΔG_t° (model solute) with a slope near unity. Details of the linear correlations are in Table 3, where *m* and *c* are the slope and intercept respectively, and ρ, *F*, and α are defined before. Although the correlations are all very good, it is noticeable that the values of *m* for the α-amino-acids in Table 3A vary considerably with the size of the amino-acid. Several workers [19-21] have emphasised that values of ΔG_t° for various solutes depend on the solute size, especially for transfers involving water or aqueous-organic solvent mixtures, and that some correction for the size effect is necessary when comparing ΔG_t° values for species that are not of exactly the same size. The nature of the size or volume effect may be

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† Or indeed a linear regression against any of the collinear explanatory variables. Correlation constants for $\delta\Delta G^\ddagger$ against the Taft α acidity function are −0.9601 (all solvents) and −0.8192 (alcohols), and against the Taft β basicity function are 0.9857 (all solvents) and 0.9929 (alcohols). This illustrates again how regression analysis with collinear variables sheds no light on the nature of the reaction or the transition state.

explained in terms of cavity theories of solution, and the process of dissolution of a solute may be broken down into stages as follows: (a) creation of a cavity of the appropriate solute size in the bulk solvent, (b) reorganisation of solvent molecules round the cavity, and (c) introduction of the solute into the cavity, with concomitant interaction of the solute with the correctly organised solvent molecules. With each of these processes these will be an associated energy term, G_{CAV}, G_{REORG}, and G_{INT}, respectively. At least to a first approximation, it seems as though the term G_{REORG} can be taken as zero,[22] there evidently being considerable compensation between H_{REORG} and S_{REORG}. If the total free energy of dissolution of a solute is given by G_{CAV} and G_{INT}, then for transfer of the solute from a given reference solvent to some other solvent we can write equation (1). The two

$$\Delta G_t^\circ = \Delta G_{CAV} + \Delta G_{INT} \qquad (1)$$

terms on the right-hand side represent the differences in the energy terms between a solvent and the reference solvent, with respect to a given solute. It may be argued that if we wish to compare two solutes with each other, it is the ΔG_{INT} terms that should be compared and not the overall ΔG_t° terms. Equation (1) is also useful in that if the ΔG_{CAV} terms can be obtained, the correction for any size difference in the solutes is automatically carried out.

TABLE 3

Correlations of transition state functions with α-amino-acids and with the ion-pair $Me_4N^+Cl^-$

A All solvents in Table 1					
ΔG_t^0	m [a]	c [b]	ρ	F	α
Glycine	0.7058	0.538	0.9472	43.7	0.998
α-Aminocaproic acid [c]	1.0310	−0.291	0.9888	87.6	0.98
α-Phenylalanine	1.3943	−0.232	0.9931	357	0.999 99
$Me_4N^+Cl^-$	0.6236	0.169	0.9930	353	0.999 99
ΔG_{INT} (SPT)					
Glycine	0.9651	0.207	0.9892	228	0.9999
α-Aminocaproic acid [c]	1.1158	−0.073	0.9999	8 697	0.999
α-Phenylalanine	1.1069	0.105	0.9988	2 013	>0.999 999
$Me_4N^+Cl^-$	0.7899	−0.138	0.9967	756	0.999 99
ΔG_{INT} (SRMR)					
Glycine	1.2410	−0.304	0.9967	749	0.999 99
α-Aminocaproic acid [c]	1.0287	−0.011	0.9999	8.1×10^5	0.999 99
α-Phenylalanine	0.9854	0.268	0.9994	3 894	>0.999 999
$Me_4N^+Cl^-$	0.8985	−0.360	0.9983	1 421	>0.999 999
ΔG_E					
Glycine	1.1258	0.176	0.9961	633	0.999 99
α-Aminocaproic acid [c]	1.0631	−0.081	0.9999	9 648	0.999
α-Phenylalanine	1.0144	0.161	0.9984	1 521	>0.999 999
$Me_4N^+Cl^-$	0.8335	−0.139	0.9978	1 150	>0.999 999
B Alcohols only in Table 1					
ΔG_t^0					
Glycine	1.2008	−0.118	0.9092	19.1	0.980
α-Aminocaproic acid [d]	1.0280	0.000	0.9999	9.6×10^5	0.999
α-Phenylalanine	1.2764	−0.077	0.9843	124	0.999
$Me_4N^+Cl^-$	0.6557	0.097	0.9790	92.1	0.999
ΔG_{INT} (SPT)					
Glycine	1.2733	−0.260	0.9300	25.6	0.990
α-Aminocaproic acid [d]	1.0337	−0.001	0.9999	8 759	0.990
α-Phenylalanine	1.2193	−0.058	0.9937	314	0.9999
$Me_4N^+Cl^-$	0.7143	0.041	0.9769	83.8	0.999
ΔG_{INT} (SRMR)					
Glycine	1.1155	−0.071	0.9356	28.1	0.990
α-Aminocaproic acid [d]	1.0193	0.002	0.9999	1.4×10^5	0.998
α-Phenylalanine	1.1516	−0.022	0.9976	820	0.999 99
$Me_4N^+Cl^-$	0.7428	0.052	0.9861	150	0.999
ΔG_E					
Glycine	1.3054	−0.138	0.9714	66.8	0.998
α-Aminocaproic acid [d]	1.0080	−0.001	0.9999	8.2×10^5	0.999
α-Phenylalanine	1.1295	−0.066	0.9897	190	0.999
$Me_4N^+Cl^-$	0.7370	0.131	0.9886	173	0.999

[a] Slope. [b] Intercept. [c] Only four data points. [d] Only three data points.

One method of calculating the ΔG_{CAV} terms is the scaled particle theory (SPT) as set out by Pierotti,[23] and we use exactly the method described, in this work. Although it has been suggested [24] that the method does not work very well for large solutes in non-aqueous solvents, we were interested in results for a series of similar alcoholic solvents. The parameters necessary for the calculation of ΔG_{CAV} by SPT are σ_1 and σ_2, the hard-sphere solvent and solute diameters, respectively. The best method of obtaining σ_1 values is through a plot of log K^H for rare gases against their polarisability [23] (K^H is the Henry's law constant for a rare gas in the particular solvent), and we have used this method whenever possible. Values of σ_2 were obtained from solute molar volumes using the Stearn–Eyring formula,[6] and in Table 4 are given the σ values we used. Values of ΔG_{CAV} can also be calculated using the method developed by Reisse and Moura Ramos,[25,26] based on the original work of Halicioglu and Sinanoglu[27] (SRMR method). In the SRMR method, molar volumes are used instead of solute diameters, and in Table 4 are the volumes we have used; values of ΔG_{CAV} were computed exactly as detailed before.[25,26]

TABLE 4

Parameters used in the calculations

Solvent	σ/Å	$\tilde{v}$/ ml mol^{-1}	γ/dyn cm^{-1}	ΔG_v^0/ kcal mol^{-1}
Water	2.77	18	71.97	+2.06
Methanol	3.71	41	22.20	+0.90
Ethanol	4.36	59	21.85	+1.47
n-Propanol	4.85	75	23.30	+1.84
n-Butanol	5.32	92	24.16	+2.49
Propan-2-ol	4.87	77	21.24	+1.63
t-Butyl alcohol	5.33	95	20.02	+1.70
Solute				
Glycine	4.56	57		
α-Aminocaproic acid	5.87	122		
α-Phenylalamine	6.07	135		
t-Butyl chloride	5.69	111		
$Me_4N^+Cl^-$	5.62	107		
Transition state	5.78	116		

TABLE 5

Values of the constants[a] in equation (3) used in calculating $\Delta G_N°$. $\Delta G_N° = a_0 + a_1V + a_2V^2 + a_3V^3$

Solvent	a_0		a_1		a_2		a_3	
Water	0.148 36	E + 1	0.504 82	E − 2	0.271 01	E − 3	−0.596 93	E − 6
Methanol	0		0		0		0	
Ethanol	0.464 73	E − 1	−0.583 99	E − 2	0.117 44	E − 4		
n-Propanol	0.145 09	E − 1	−0.882 41	E − 2	0.192 14	E − 4		
n-Butanol	−0.119 68	E − 1	−0.118 19	E − 1	0.295 33	E − 4		
Propan-2-ol	−0.289 92		−0.229 45	E − 2	−0.807 93	E − 5		
t-Butyl alcohol	−0.454 89		−0.528 80	E − 2	0.430 36	E − 5		

[a] Constants for use with V in ml mol^{-1} and ΔG_N^0 in kcal mol^{-1} on the mole fraction scale. Note that with the given constants, equation (3) may not be value for $V \geqslant 200$ ml mol^{-1}.

A rather different approach to that summarised by equation (1) involves the breakdown of the $\Delta G_t°$ values into a nonelectrostatic and an electrostatic term [equation (2)].[6,20,21] As a measure of ΔG_N, it is usual[6,20,21] to

$$\Delta G_t° = \Delta G_N + \Delta G_E \qquad (2)$$

take the overall $\Delta G_t°$ value for a non-polar solute of the same molar volume as the solute in question. Values of $\Delta G_t°$ for rare gases, alkanes, and compounds of the type R_4M were taken from recent compilations,[8,28] and were fitted to polynomials in solute molar volume V [equation (3)]. Details of the constants in equation (3) are in Table 5. We also fitted the $\Delta G_t°$ values to polynomials $V^{1/3}$, but generally the more convenient polynomials in V yielded better fits. For transfers from methanol to water, the equation used in the present work (third order in V) gives results very close to those obtained from our previous equation[21] (fifth order in $V^{1/3}$), after conversion

$$\Delta G_N = \Delta G_t° \text{ (nonpolar solute)} = a_0 + a_1V + a_2V^2 + a_3V^3 \qquad (3)$$

from the mole fraction to the molar scale. Using equation (3), values of ΔG_N were calculated and then ΔG_E values were obtained from equation (2).

Results of the calculation are in Tables 6—8, given as $\Delta G_{\mathrm{INT}} = \Delta G_t° - \Delta G_{\mathrm{CAV}}$ and $\Delta G_E = \Delta G_t° - \Delta G_N$. Now it should be pointed out that ΔG_{INT} is not necessarily identical to ΔG_E. The interactions covered by the ΔG_{INT} term include any electrostatic effects and also the dispersive part of the interaction. However, in the calculation of ΔG_E, these dispersive interactions are largely covered by the ΔG_N term, so that if the solvent reorganisation term is small or zero, the ΔG_E term covers only the electrostatic part of the solute–solvent interactions. Thus if for a given transfer, $\Delta G_E = \Delta G_{\mathrm{INT}}$, it can be deduced that the dispersive part of the transfer term is zero. In other words, the solute–solvent dispersive interaction is the same in the reference solvent as in the other solvent. Comparison of the two sets of ΔG_{INT} terms (Tables 6 and 7) for transfer from methanol to the other alcohols, with the corresponding ΔG_E terms, shows that all three sets are numerically very similar, and it follows from the above argument that the major contribution to ΔG_{INT} must be the electrostatic term. For transfer to water, values of ΔG_{INT} calculated by SPT are in fair agreement with the ΔG_E values, but the SRMR

TABLE 6

Values of ΔG_{INT}, as calculated by scaled particle theory, in kcal mol^{-1}

Solvent	Glycine	α-Aminocaproic acid	α-Phenylalanine	Bu^{t}Cl	$Me_4\overset{+}{N}Cl^-$	Tr
Water	−6.05	−4.86	−5.13	0.81	−6.69	−5.51
Methanol	0	0	0	0	0	0
Ethanol	1.35	1.16	0.99	−0.13	1.63	1.19
n-Propanol	1.58		1.47	−0.16	2.08	1.52
n-Butanol	1.65	1.29	1.14	−0.59	2.08	1.34
Propan-2-ol	1.96		2.11	0.24	2.83	2.49
t-Butyl alcohol	2.17		2.39	0.03	4.38	2.99

calculations yield ΔG_{INT} values that differ quite considerably from the other two sets of data. Thus for the nonpolar solute, Bu^{t}Cl itself, $\Delta G_{\mathrm{INT}} = -5.2$ (SRMR), +0.8 (SPT), and 0.0 kcal mol^{-1} (ΔG_N method). These differences cannot be due merely to solvent reorganisation in water or to dispersive forces in water, because the SRMR and SPT calculations should still yield the same values for ΔG_{INT}. It does seem that for aqueous solutions there is some fundamental difference between the SRMR and SPT calculations of the cavity term.

TABLE 7

Values of ΔG_{INT} as calculated by SRMR theory, in kcal mol^{-1}

Solvent	Glycine	α-Aminocaproic acid	α-Phenylalanine	Bu^{t}Cl	$Me_4\overset{+}{N}Cl^-$	Tr
Water	−9.17	−11.41	−12.27	−5.21	−12.51	−11.75
Methanol	0	0	0	0	0	0
Ethanol	1.38	1.23	1.06	−0.07	1.69	1.26
n-Propanol	1.46		1.24	−0.35	1.90	1.32
n-Butanol	2.97	2.58	2.42	0.70	3.38	2.63
Propan-2-ol	2.14		2.26	0.40	2.99	2.65
t-Butyl alcohol	2.66		3.04	0.70	4.98	3.55

TABLE 8

Values of ΔG_E, as calculated via equation (2), in kcal mol^{-1}

Solvent	Glycine	α-Aminocaproic acid	α-Phenylalanine	Bu^{t}Cl	$Me_4\overset{+}{N}Cl^-$	Tr
Water	−5.95	−5.95	−6.57	0.00	−7.40	−6.43
Methanol	0	0	0	0	0	0
Ethanol	1.47	1.52	1.39	0.20	1.94	1.53
n-Propanol	1.82		2.12	0.39	2.61	2.09
n-Butanol	2.24	2.45	2.39	0.50	3.14	2.47
Propan-2-ol	1.97		2.28	0.34	2.93	2.60
t-Butyl alcohol	2.48		2.97	0.53	4.87	3.51

Results from plots of ΔG_{INT}(Tr) against ΔG_{INT} (model solute) and from plots of ΔG_E(Tr) against ΔG_E (model solute) are in Table 3A. The significance levels, α, of these plots are extraordinarily high and from the plots themselves there seems little to choose between the three methods of correcting for the ' size effect '. On all three methods, the slopes of the plots when the amino-acids are the model solutes vary much less with amino-acid than do the uncorrected plots (Table 2A), the slopes of the corrected plots being 0.97—1.11 (SPT), 0.99—1.24 (SRMR), and 1.01—1.13 (ΔG_N method). It could be argued, however, that the excellent values of ρ and α, and also the rather high values of the slopes of the corrected plots are unduly affected by the point for water; for this point the ΔG_{INT} and ΔG_E values are very far from all the other points on the plots. This argument does not apply to transfers between the alcohols themselves. Results are in Table 3B; again, the ρ and α values are excellent, and the slopes, *m*, are reasonably constant with variation in amino-acid: 1.03—1.27 (SPT), 1.02—1.15 (SRMR), and 1.01—1.31 (ΔG_N method). If we give half weight to the values for α-aminocaproic acid, the average value of *m* when α-amino-acids are used as models in alcohols is 1.16, a value that seems very high and which suggests at first sight that the transition state is extraordinarily polar. It is of interest that Pople *et al.*[29] have recently calculated the molecular structure of zwitterionic glycine in the gas phase (Scheme). The separation of charge is appreciably less than unity, only *ca.* 0.7 units, so that an *m*-value of 1.16 (above) might correspond to a value of *ca.* 0.8 units for the transition state. Of course, the calculation by Pople *et al.* refers to the gas phase and not to solution, but it does provide a reasonable explanation. Plots for the transition state *versus* the ion-pair $Me_4N^+Cl^-$ gave slopes of *ca.* 0.73 (alcohols only) or 0.81 (SPT and ΔG_N values for all solvents), again indicating that the transition state is polar but not as polar as an ion-pair,* and confirming previous conclusions[6,7,21] about the nature of the t-butyl chloride solvolysis transition state.

Since the transition state carries a substantial charge separation, and since nucleophilic solvent assistance is generally thought to be of little importance,[14,31] it follows that electrophilic solvation must be considerable, even though we have seen that such solvation cannot be deduced by correlation analysis. Thus $\delta\Delta G^{\ddagger}$ is well correlated by E_T (see Table 3), but since no correction for size or cavity effects have been applied there is little that can be deduced from such a correlation; the slope of the plots of $\delta\Delta G^{\ddagger}$ against E_T are —0.49 (all solvents) or —0.25 (alcohols), and it is not clear if any meaning can be attached to these values. Parker *et al.*[14] have also shown that $\delta\Delta G^{\ddagger}$ or $\Delta G^{\ddagger}$(Tr) are linearly related to functions of solvent acidity such as $\Delta G_t^{\circ}(Cl^-)$ or Gutmann's acceptor number, AN. Whilst these correlations are useful empirically, it is again difficult to make any quantitative deduction about the nature of the transition state from the correlations; this is at least partly due to the size or cavity effect.

Our own conclusions are that α-amino-acids or the

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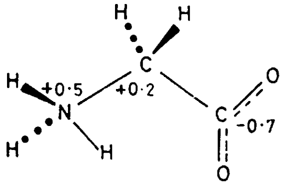
* It could be argued[30] that the slopes, *m*, should be proportional to Z^2, where *Z* is the charge separation.[6] If this were the case, *Z* for the transition state would be 0.85—0.90 (by comparison to $Me_4N^+Cl^-$) or 0.75 (if the α-amino-acids in alcohols had an effective charge separation of 0.7 units).

$Me_4N^+Cl^-$ ion-pair are good models for the t-butyl chloride solvolysis transition state, especially when corrections for size efforts or cavity effects are included. For alcoholic solvents the two methods of deducing cavity contributions to ΔG_t° values agree with each other and with the size correction *via* ΔG_N values. For these solvents it seems probable that the dispersion contribution to ΔG_t° is very small. If a wider range of solvents is chosen, then ΔG_{CAV} will not be the same as ΔG_N, since the dispersion contribution generally will not be small. We illustrate this by giving in Table 9 results for a variety of protic and aprotic solvents, with hexane taken as the reference solvent. If we compare ΔG_{CAV}(SPT) with ΔG_{CAV}(SRMR), then the sign of the terms and their order of magnitude are the same on the two theories. Numerically, there are differences, but for six out of the nine transfers, the SPT and SRMR ΔG_{CAV} calculations agree to within *ca.* 2 kcal mol^{-1}. For the solvents water, dimethyl sulphoxide, and nitromethane the SPT and SRMR results differ considerably. We have no real explanation for this behaviour, but it is possible that the SRMR approach leads to an overestimation of G_{CAV} in these solvents. On the other hand, the SPT calculations depend quite critically on the ratio $\sigma_2 : \sigma_1$; small variations in $\sigma_2 : \sigma_1$ can produce quite large variations in the calculated value of G_{CAV}.



SCHEME Charge separation in glycine (gas phase) [29]

TABLE 9

Cavity terms, ΔG_{CAV}, and ΔG_N terms calculated for Bu^tCl in some hydroxylic and aprotic solvents, in kcal mol^{-1}

Solvent	ΔG_{CAV} (SPT)	ΔG_{CAV} (SRMR)	ΔG_N
Hexane	0	0	0
Benzene	+2.2	+2.1	+0.4
Chlorobenzene	+2.7	+3.1	+0.4
Acetone	+1.2	+2.0	+1.0
Nitromethane	+3.0	+5.4	+2.1
Dimethylformamide		+5.1	
Dimethyl sulphoxide	+3.8	+7.0	+2.3
t-Butyl alcohol	+1.6	+2.1	+0.7
Ethanol	+1.9	+2.9	+1.2
Methanol	+2.0	+3.3	+1.7
Water	+5.8	+14.1	+6.3

It is clear that much work remains to be done before G_{CAV} can be estimated with any accuracy for all solvent systems. Nevertheless, we wish to emphasise that the procedure of isolating ΔG_{INT} (or ΔG_E) from the observed ΔG_t values is essential, not only for the determination of solute–solvent effects in ground states but also in excited states such as electronic excited states [32,33] or transition states.[25,34] In the first part of this paper, we have shown some limitations of methods based on correlation analysis, and it is our contention that the method of model solutes and/or the separation of ΔG_t° into cavity and interaction terms is in principle a much more powerful approach to the general problem of solvent effects on the chemical and physical properties of solutes.

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