Application of Reaction Field Theory to the Calculation of Solvent Effects on the Menschutkin Reaction of Tripropylamine with Methyl Iodide

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The reaction field theory previously applied to the calculation of solvent effects on $\Delta G^\ddagger$ values for the decomposition of t-butyl chloride has now been applied similarly to the Menschutkin reaction of tripropylamine with methyl iodide. Calculations have been carried out using a transition state model of $\mu = 7.60$ D, corresponding to a charge separation of 0.396 units, and cover reaction in 68 aprotic solvents. There is good agreement (± 0.2 kcal mol^{-1}) between calculated solvent effects and observed values of $\delta\Delta G^\ddagger$ for 28 solvents, and it is suggested that in this set of solvents specific solvent effects are small or absent. The remaining 40 solvents, including aromatic solvents and polyhalogenated solvents, generally lead to $\delta\Delta G^\ddagger$ values smaller than those calculated.

We have recently calculated[1] the effect of aprotic solvents on values of $\Delta G^\ddagger$ for the decomposition of t-butyl chloride, using the reaction field theory originally developed[2] for the calculation of solvent effects on rotational or conformational isomerism. The success of

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[1] M. H. Abraham and R. J. Abraham, *J.C.S. Perkin II*, 1974, 47.

[2] R. J. Abraham and R. Bretschneider, ' Internal Rotation in Molecules,' ed. W. J. Orville-Thomas, Academic Press, London, 1974, ch. 13.

the theory in the calculation of those $\Delta G^{\ddagger}$ values has prompted us to extend our studies to other reactions that also proceed through dipolar (but uncharged) transition states. The Menschutkin reaction is a typical bimolecular nucleophilic substitution that involves a transition state with a substantial dipole moment; values of between 5 and 9 D have been estimated for a number of Menschutkin reaction transition states (see ref. 3). Furthermore, one particular Menschutkin reaction, that between tripropylamine and methyl iodide, has been suggested [4-6] as the basis of a new parameter of solvent influence, S_{M}, defined as the logarithm of the rate constant of reaction (1). Since rate constants for this

$$\mathrm{Pr^{n}{}_{3}N + MeI \longrightarrow Pr^{n}{}_{3}NMe^{+} + I^{-}} \qquad (1)$$

reaction are known [7] for at least 78 solvents, it is clearly a convenient one to choose for our calculations. Drougard and Decroocq [4] have shown that the logarithms of rate constants for reaction (1) in a number of aprotic solvents are linearly related to various solvent parameters, and from the simple Kirkwood equation it has been estimated [3] that the transition state in reaction (1) has a dipole moment of *ca.* 8.7 D.

The reaction field theory has been derived elsewhere,[2] and its application to the unimolecular decomposition of t-butyl chloride described in detail.[1] We therefore discuss now only the treatment of a bimolecular reaction in terms of the reaction field theory. In essence, the theory yields the energy of transfer of a solute from a solution (s) to the vapour (v), E_{v}-E_{s}, in terms of the solute dipole moment, quadrupole moment, radius, and refractive index; the only solvent parameter used is the solvent dielectric constant, ε. Then if two such transfers are considered, from solvent 1 to vapour, and from solvent 2 to vapour, subtraction yields an expression (2) for the energy of transfer of a solute from solvent 1 to solvent 2. Now for the bimolecular reaction (1) we may

$$\Delta E_{\mathrm{t}} = E_{\mathrm{s2}} - E_{\mathrm{s1}} = (E_{\mathrm{v}} - E_{\mathrm{s1}}) - (E_{\mathrm{v}} - E_{\mathrm{s2}}) \qquad (2)$$

write (3) where $\Delta G_{\mathrm{t}}^{0}(\mathrm{X})$ denotes the standard free

$$\Delta G_{\mathrm{t}}^{0}(\mathrm{Tr}) = \Delta G_{\mathrm{t}}^{0}(\mathrm{Pr^{n}{}_{3}N}) + \Delta G_{\mathrm{t}}^{0}(\mathrm{MeI}) + \delta\Delta G^{\ddagger} \qquad (3)$$

energy of transfer of species X from solvent 1 to solvent 2; Tr is the transition state, and $\delta\Delta G^{\ddagger} = \Delta G_{2}^{\ddagger} - \Delta G_{1}^{\ddagger}$. Following a number of workers,[8] we may separate the $\Delta G_{\mathrm{t}}^{0}$ terms into electrostatic contributions, $\Delta G_{\mathrm{e}}^{0}$, and nonelectrostatic contributions, $\Delta G_{\mathrm{n}}^{0}$ [equation (4)].

$$\Delta G_{\mathrm{t}}^{0} = \Delta G_{\mathrm{e}}^{0} + \Delta G_{\mathrm{n}}^{0} \qquad (4)$$

Substitution of three equations of type (4) into equation (3) yields (5) after rearrangement. Now since the dipole

$$\delta\Delta G^{\ddagger} = \Delta G_{\mathrm{e}}^{0}(\mathrm{Tr}) + \Delta G_{\mathrm{n}}^{0}(\mathrm{Tr}) - \Delta G_{\mathrm{e}}^{0}(\mathrm{Pr^{n}{}_{3}N}) - \Delta G_{\mathrm{n}}^{0}(\mathrm{Pr^{n}{}_{3}N}) - \Delta G_{\mathrm{e}}^{0}(\mathrm{MeI}) - \Delta G_{\mathrm{n}}^{0}(\mathrm{MeI}) \qquad (5)$$

moment of tripropylamine is small, and its molar volume is rather large, $\Delta G_{\mathrm{e}}^{0}(\mathrm{Pr^{n}{}_{3}N})$ is always negligibly small and equation (5) is reduced to (6).

$$\delta\Delta G^{\ddagger} = [\Delta G_{\mathrm{e}}^{0}(\mathrm{Tr}) - \Delta G_{\mathrm{e}}^{0}(\mathrm{MeI})] + [\Delta G_{\mathrm{n}}^{0}(\mathrm{Tr}) - \Delta G_{\mathrm{n}}^{0}(\mathrm{Pr^{n}{}_{3}N}) - \Delta G_{\mathrm{n}}^{0}(\mathrm{MeI})] \qquad (6)$$

If the nonelectrostatic effect cancels between reactants and transition state we may write (7) and hence derive the

$$\Delta G_{\mathrm{n}}^{0}(\mathrm{Tr}) - \Delta G_{\mathrm{n}}^{0}(\mathrm{Pr^{n}{}_{3}N}) - \Delta G_{\mathrm{n}}^{0}(\mathrm{MeI}) = 0 \qquad (7)$$

simple equation (8). Since only the electrostatic

$$\delta\Delta G^{\ddagger} = \Delta G_{\mathrm{e}}^{0}(\mathrm{Tr}) - \Delta G_{\mathrm{e}}^{0}(\mathrm{MeI}) \qquad (8)$$

contribution to the free energy of transfer is calculated by the reaction field theory,* equation (9) follows. Thus

$$\delta\Delta G^{\ddagger} = \Delta G_{\mathrm{e}}^{0}(\mathrm{Tr}) - \Delta G_{\mathrm{e}}^{0}(\mathrm{MeI}) = \Delta E_{\mathrm{t}}(\mathrm{Tr}) - \Delta E_{\mathrm{t}}(\mathrm{MeI}) = \delta\Delta E_{\mathrm{t}} \qquad (9)$$

values of $\delta\Delta E_{\mathrm{t}}$ calculated from reaction field theory should be directly comparable to the observed values of $\delta\Delta G^{\ddagger}$ when a suitable reference solvent is chosen. As before,[1] we shall use *NN*-dimethylformamide (DMF) as our reference solvent 1. One difficulty in dealing with a bimolecular reaction is that although values of ΔE_{t} are independent of the solute standard state, values of $\delta\Delta G^{\ddagger}$ do depend on the concentration units specified. We shall use $\delta\Delta G^{\ddagger}$ values derived from rate constants recalculated in units of mol-fraction^{-1} s^{-1}, although use of the more familiar units of mol^{-1} s^{-1} would not significantly alter any of our conclusions. The cancellation of nonelectrostatic effects between reactants and transition state follows from previous work; in particular, it has been shown [1,8] that values of $\Delta G_{\mathrm{n}}^{0}$ depend on the molar volume, V, of the species transferred. To a first approximation, $V(\mathrm{Tr}) = V(\mathrm{Reactants})$ so that $\Delta G_{\mathrm{n}}^{0}(\mathrm{Tr}) \simeq \Delta G_{\mathrm{n}}^{0}(\mathrm{Reactants})$. Should the assumptions implied by equations (4) and (7) break down, agreement between $\delta\Delta G^{\ddagger}$ and $\delta\Delta E_{\mathrm{t}}$ will no longer be expected. This will occur when there are marked solute–solvent interactions other than those calculated using the electrostatic continuum model of the reaction field theory. Since the transition state is more polar (and more polarisable) than the reactants, these effects are more likely to involve the transition state than the reactants, so that $\delta\Delta G^{\ddagger}$ will then be lower in value than expected. Hence a negative value for the term ($\delta\Delta G^{\ddagger} - \delta\Delta E_{\mathrm{t}}$) will imply a lowering of the transition state free energy by some factor other than the reaction field effect. Whether or not such a negative value has any quantitative or semi-quantitative significance is a moot point. It could be argued that in cases where the electrostatic continuum model has broken down, no quantitative interpretation is possible. On the other hand, proponents of the

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* We are grateful to a referee for noting that in general the energy derived from electrostatic theories is related to work of charging, and must therefore be a free energy.

[3] M. H. Abraham, *Progr. Phys. Org. Chem.*, 1974, **11**, 1.

[4] Y. Drougard and D. Decroocq, *Bull. Soc. chim. France*, 1969, 2972.

[5] K. F. Wong and C. A. Eckert, *Ind. and Eng. Chem.*, 1970, **62**(9), 16.

[6] O. B. Nagy, J. B. Nagy, and A. Bruylants, *J.C.S. Perkin II*, 1972, 968.

[7] C. Lassau and J.-C. Jungers, *Bull. Soc. chim. France*, 1968, 2678.

[8] M. Alfenaar and C. L. de Ligny, *Rec. Trav. chim.*, 1967, **86**, 929; M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 1610.

analysis of solvent effects through multiple regression methods generally assume[9] that a number of separate solute–solvent interactions all act quite independently. We take an intermediate view and suggest that the term ($\delta\Delta G^‡ - \delta\Delta E_t$) is capable of semi-quantitative interpretation. Our reason is that this term is seldom more negative than 2 kcal mol^{-1}, so that if several solvent molecules are involved in solute–solvent interactions each solvent molecule is restricted by an energy $<RT$, and the continuum model has thus not completely broken down.

The solute parameters used in the calculations are in Table 1; they are as defined before.[1] The transition state parameters correspond to the model shown in Figure 1. A tetrahedral arrangement about nitrogen is maintained, and each n-propyl group has been assumed to adopt a conformation in which the $CH_3CH_2CH_2N$ system is *trans* and the CH_2CH_2N . . C group is *gauche*. This preserves the time-averaged three-fold symmetry of the transition state. An alternative model with a *trans-trans*-orientation of the propyl groups gives rise to a much larger quadrupole moment, due to the ' volume centre of gravity ' (*cf*. ref. 2) being far removed from the charged atoms, and hence not so good agreement between the calculated and observed results.

TABLE 1

Solute parameters used in the calculations

Solute	μ^a/D	M_v/ml ^{b}	n_D ^{c}	k ^{d}	h ^{d}	l ^{e}
MeI	1.64	63	1.529	1.57	0.02	0.617
$Pr^n{}_3N$	0.70	190	1.418	0.09	0.03	0.504
Tr	7.60	235	1.550	8.94	7.08	0.637

^{a} Dipole moment. ^{b} Molar volume. ^{c} Refractive index. ^{d} μ^2/a^3 and q^2/a^5 respectively, in kcal mol^{-1}. ^{e} $2(n_D{}^2 - 1)/(n_D{}^2 + 2)$.

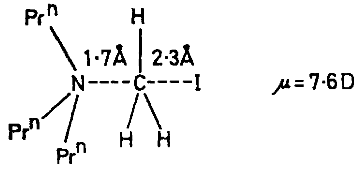

FIGURE 1

Most of the rate constants and the solvent dielectric constants are those reported by Lassau and Jungers.[7]

RESULTS AND DISCUSSION

For the calculations we fixed the values of the transition state molar volume, refractive index, and also the geometry, so that the transition state dipole moment was left as the only adjustable parameter. A value of 7.6 D for this moment was found to give good agreement between our calculations and the experimental results. Such a value is well within the range of dipole moments previously suggested for Menschutkin reaction transition states, and is not far from the value of 8.7 D that has been estimated for the Pr_3N–MeI transition state.[3] With the geometry shown in Figure 1, the dipole moment of 7.6 D corresponds to a charge separation of ±0.396 units located at the nitrogen and iodine atoms of the transition state. This is in exact accord with our earlier proposition[10] that ' transition states in Menschutkin reactions behave towards change of solvent as though they carried a charge separation of only *ca*. 0.4 unit.'

Results of our calculations for 68 aprotic solvents are in Table 2, with the calculated solvent effect given as $\delta\Delta E_t$ and the observed solvent effect as $\delta\Delta G^‡$, both expressed relative to the standard solvent, DMF. For 28 of these solvents (Table 2A), there is good agreement between $\delta\Delta E_t$ and $\delta\Delta G^‡$, the difference ($\delta\Delta G^‡ - \delta\Delta E_t$) averaging only ±0.2 kcal mol^{-1}. We suggest that in the case of these 28 solvents, specific solvent effects on $\Delta G^‡$ must be small or nonexistent, so that the variation in $\Delta G^‡$ with solvent is due very largely to the electrostatic continuum effect (as calculated by the reaction field theory). In our previous calculation[1] of solvent effects on the decomposition of t-butyl chloride, eight solvents for which there was good agreement between theory and experiment are common to the solvents studied in the present work. It is interesting that all eight solvents are members of the set of 28 solvents in Table 2A. It is noteworthy that this set of ' normal ' solvents excludes not only hydroxylic solvents but also, in general, aromatic solvents and polyhalogenated solvents. It is thus evident that extreme care must be taken in the selection of solvents for studies that seek to relate rate constants or equilibrium constants to, for example, functions of solvent dielectric constant.

In Table 2B are results for 20 aromatic solvents. It is known[1] that reaction field theory is not usually applicable to these solvents, because of the incursion of effects such as polarisability[11-13] that are outside the scope of reaction field theory. These effects, by the argument outlined in the introduction, should result in marked negative values for ($\delta\Delta G^‡ - \delta\Delta E_t$) due to a lowering of the free energy of the transition state. Inspection of Table 2B shows that this is indeed the case, and also that this effect is much more marked for solvents of lower dielectric constant, as suggested previously.[11,13]

Eliel and Hofer,[14] in a study of solvent effects on the conformational equilibrium of a 1,3-dioxan found a good correlation of their ΔG^0 values with the E_T (30) scale,[15] but that benzene and toluene, but not mesitylene or t-butylbenzene were anomalous. They suggested that the orientation of the solute dipole with respect to the anisotropic solvent molecules may be of importance.

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[9] I. A. Koppel and V. A. Palm in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972; see especially equation (5.23), p. 222.

[10] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

[11] M. H. Abraham, *J. Chem. Soc.* (*B*), 1971, 299.

[12] E. F. Caldin and J. Peacock, *Trans. Faraday Soc.*, 1955, **51**, 1217; J. D. Reinheimer, J. D. Harley, and W. W. Meyers, *J. Org. Chem.*, 1963, **28**, 1575; H. Hartmann and A. P. Schmidt, *Z. phys. Chem.* (*Frankfurt*), 1968, **62**, 312.

[13] K. B. Wiberg, ' Physical Organic Chemistry,' Wiley, New York, 1964, pp. 379—388.

[14] E. L. Eliel and O. Hofer, *J. Amer. Chem. Soc.*, 1973, **95**, 8041.

[15] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.

When the solute dipole is parallel to the aromatic ring plane the polarisability interaction will be maximised, and this cannot occur with bulky side groups. However, they found no evidence of this orientation effect from n.m.r. data, although the anomalous high-field shifts (ASIS) of many solutes in aromatic solvents are well documented.[16]

The excess high-field shifts of methyl iodide in aromatic solvents have been detailed [17] and we observed a correlation between these shifts and our ($\delta\Delta G^{\ddagger} - \delta\Delta E_t$) values. We therefore extended the n.m.r. measurements to a wider range of aromatic solvents, particularly alkylbenzenes, and these results are given in Table 3 and plotted against the corresponding ($\delta\Delta G^{\ddagger} - \delta\Delta E_t$) values in Figure 2. In order to include the solvents n-propylbenzene and t-butylbenzene, we have estimated $\delta\Delta G^{\ddagger}$ values from data [18] on the related reaction of triethylamine and methyl iodide.

Our results in general are consistent with those of Eliel.[14] The n.m.r. experiments show unequivocally that in the interaction of methyl iodide with aromatic solvents, the position of the methyl iodide molecule with respect to the solvent is of importance. Since values of ($\delta\Delta E_t - \delta\Delta G^{\ddagger}$) correlate smoothly with the excess high-field shifts of methyl iodide, this implies that in the interaction of the transition state with the aromatic solvents, a positional effect is also important. When the aromatic solvent is moderately polar, the positional effect becomes less significant, and for polar

TABLE 2

Calculated and observed solvent effects on $\delta\Delta G^{\ddagger}$ for the reaction of tripropylamine with methyl iodide, in kcal mol^{-1} at 293 K

Solvent		$E_v - E_s$			
A Normal solvents	ε [a]	MeI	Tr	$\delta\Delta E_t$	$\delta\Delta G^{\ddagger}$ [b]
n-Hexane	1.886 [c]	0.331	2.701	5.9	5.8 [d]
Cyclohexane	2.024 [c]	0.366	2.981	5.6	5.5
Di-n-butyl ether	3.12	0.574	4.590	4.2	4.7
Diethyl ether	4.35	0.713	5.632	3.3	3.8
n-Hexyl chloride	5.90	0.822	6.439	2.6	2.9 *
Ethyl acetate	6.20	0.839	6.558	2.5	2.1
Ethyl fumarate	7.19	0.885	6.894	2.2	2.2
n-Butyl chloride	7.35	0.892	6.941	2.2	2.4 *
n-Butyl bromide	7.40	0.894	6.956	2.2	2.4
Tetrahydrofuran	7.61	0.902	7.015	2.1	1.8 [e]
Ethyl malonate	8.02	0.918	7.124	2.0	1.7
Ethyl trichloroacetate	8.80	0.944	7.309	1.9	1.9 *
Ethyl bromide	9.50	0.965	7.455	1.8	1.9
Heptan-3-one	12.90	1.044	7.984	1.3	1.9
Cyclopentanone	13.50	1.055	8.057	1.2	0.7
Cyclohexanone	18.20 [f]	1.127	8.507	0.9	0.9
Butan-2-one	18.35	1.129	8.519	0.9	1.1
Acetone	21.07	1.162	8.716	0.7	0.8
Hexane-2,5-dione	21.80	1.170	8.764	0.7	0.6
1-Nitropropane	24.20	1.196	8.910	0.5	0.5
Butyronitrile	24.90	1.203	8.950	0.5	0.7
Nitroethane	29.11	1.243	9.169	0.3	0.1
Proprionitrile	29.42	1.246	9.184	0.3	0.4
Acetonitrile	37.50 [g]	1.314	9.535	0.0	−0.1 *
DMF	38.42	1.321	9.571	0	0
Nitromethane	38.57 [h]	1.322	9.577	0.0	−0.6
DMSO	47.12 [i]	1.386	9.889	−0.3	−0.6 [d]
Propylene carbonate	66.10 [j]	1.516	10.485	−0.7	−0.6 [d]
B Aromatic solvents					
p-Xylene	2.27	0.424	3.433	5.2	3.0
Mesitylene	2.28	0.426	3.450	5.2	3.6
Benzene	2.28	0.426	3.450	5.2	2.1
m-Xylene	2.37	0.446	3.599	5.1	3.0
Toluene	2.39	0.450	3.631	5.1	2.6
Isopropylbenzene	2.41	0.454	3.662	5.0	3.2
Ethoxybenzene	4.25	0.704	5.564	3.4	1.7
Methoxybenzene	4.39	0.716	5.658	3.3	1.3
Iodobenzene	4.65	0.738	5.820	3.2	1.1 *
m-Dichlorobenzene	5.08	0.770	6.060	3.0	1.9 *
Bromobenzene	5.46	0.796	6.247	2.8	1.3 *
Chlorobenzene	5.70	0.811	6.355	2.7	1.4 *
Ethyl benzoate	6.03	0.829	6.492	2.6	1.5
o-Dichlorobenzene	10.07	0.981	7.562	1.7	1.3 *
4-Phenylbutan-2-one	10.75	0.998	7.678	1.6	0.7
Phenylpropanone	11.85	1.023	7.845	1.4	0.7
Acetophenone	17.65	1.120	8.463	0.9	0.5
Benzaldehyde	17.85	1.122	8.479	0.9	0.5
Benzonitrile	25.65	1.211	8.991	0.5	0.4
Nitrobenzene	35.75	1.300	9.464	0.1	0.3
C Other solvents					
Isoprene	2.10	0.385	3.129	5.5	4.1
trans-1,2-Dichloroethylene	2.14	0.395	3.203	5.4	2.8 *
Cyclohexene	2.23	0.415	3.364	5.3	4.8
Carbon tetrachloride	2.24	0.418	3.382	5.3	3.7 *
Tetrachloroethylene	2.30	0.431	3.484	5.2	4.2
Carbon disulphide	2.64	0.498	4.001	4.7	3.0
Trichloroethylene	3.42	0.615	4.895	4.0	2.5
Pentachloroethane	3.73	0.651	5.171	3.7	2.0 *
Bromoform	4.40	0.717	5.665	3.3	0.5
1,2-Dibromoethane	4.80	0.750	5.908	3.1	1.0
Chloroform	4.80	0.750	5.908	3.1	0.9 *
1,1,2-Trichloroethane	7.16	0.884	6.885	2.3	0.5
Allyl chloride	7.65	0.904	7.026	2.1	1.5
1,1,2,2-Tetrachloroethane	8.50	0.934	7.241	1.9	0.0 *
Dichloromethane	9.08	0.953	7.369	1.8	0.3
cis-1,2-Dichloroethylene	9.25	0.958	7.405	1.8	0.8 *
1,4-Dichlorobutane	9.60	0.968	7.474	1.7	0.9
1,1-Dichloroethane	10.15 [k]	0.983	7.576	1.7	1.3 *
1,2-Dichloroethane	10.52 [k]	0.992	7.640	1.6	0.3 *
Acetylacetone	27.10	1.225	9.068	0.4	1.1

[a] Solvent dielectric constant at 293 K from ref. 7, except where indicated. [b] From rate constants given in ref. 7 (after correction to the mol-fraction scale) except where indicated. [c] R. H. Stokes, *J. Chem. Thermodynamics*, 1973, **5**, 379. [d] Estimated from data for other Menschutkin reactions (see text). [e] The value of $\delta\Delta G^{\ddagger}$ for dioxan is 1.7 kcal mol^{-1}; this solvent usually behaves as though it has an effective dielectric constant of that of tetrahydrofuran. [f] G. J. Janz and R. P. T. Tomkins, 'Nonaqueous Electrolytes Handbook,' Academic Press, New York, 1972, vol. I, p. 23. [g] From data at other temperatures. [h] R. Philippe and A. M. Piette, *Bull. Soc. chim. belges*, 1955, **64**, 600; Note that in refs. 1 and 3 this value was incorrectly given at 298 K. [i] R. Garnsey and J. E. Prue, *Trans. Faraday Soc.*, 1968, **64**, 1206. [j] J. Simeral and R. L. Amey, *J. Phys. Chem.*, 1970, **74**, 1443. [k] J. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, 1955, **77**, 2615.

* Using more recent data in ref. 18.

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[16] P. Laszlo, 'Progress in N.M.R. Spectroscopy,' eds. J. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon, Oxford, 1967, ch. 6.

[17] R. J. Abraham, *Mol. Phys.*, 1961, **4**, 369.

[18] G. Berrebi and D. Decroocq, *J. Chim. phys.*, 1974, **71**, 673.

aromatic solvents such as benzonitrile and nitrobenzene, both the excess high-field shift of methyl iodide and values of ($\delta\Delta E_t - \delta\Delta G^\ddagger$) are small or essentially zero.

TABLE 3

Proton chemical shifts of methyl iodide in various solvents *versus* ($\delta\Delta E_t - \delta\Delta G^\ddagger$)

Solvent	Observed shift [a]	Excess high-field shift [c]	$\delta\Delta E_t - \delta\Delta G^\ddagger$ (kcal mol^{-1})
Benzene	88.0	32.0	3.1
Toluene	90.7	29.3	2.5
m-Xylene	92.2	27.8	2.1
p-Xylene	92.3	27.7	2.2
Isopropylbenzene	93.0	27.0	1.8
n-Propylbenzene	95.0	25.0	1.9 [d]
Mesitylene	94.1	25.9	1.6
t-Butylbenzene	94.1	25.9	1.6 [d]
Chlorobenzene	105.6	23.6	1.2
o-Dichlorobenzene	116.9 [b]	12.2	0.4
Benzaldehyde	121.5 [b]	8.5	0.4
Benzonitrile	125.7 [b]	3.0	0.1
Nitrobenzene	127.7 [b]	1.0	−0.2
Cyclohexane	120.0	0.0	0.1

[a] In Hz at 60 MHz from Me_4Si. Measured on a Varian A-60 spectrometer, probe temperature 35°, using *ca.* 0.03M solutions of methyl iodide and tetramethysilane in the neat solvents. [b] Measured from C_6H_{12} (ref. 17) converted using $C_6H_{12} - Me_4Si = 84.5$ Hz. [c] Observed shift in aromatic solvent minus observed shift in similar aliphatic solvent. [d] Values of $\delta\Delta G^\ddagger$ estimated from data on the Et_3N–MeI reaction.[18]

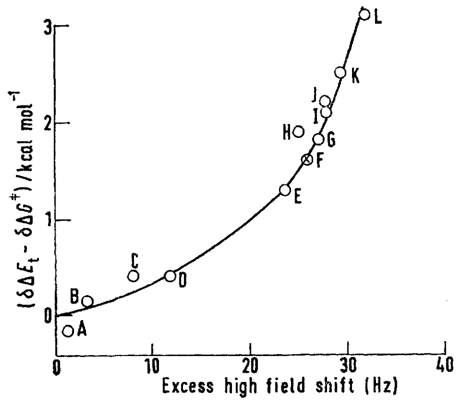

FIGURE 2 Plot of ($\delta\Delta E_t - \delta\Delta G^\ddagger$) against the excess high-field shift of MeI in aromatic solvents at 60 MHz: A, $PhNO_2$; B, PhCN; C, PhCHO; D, *o*-$C_6H_4Cl_2$; E, PhCl; F, 2,4,6-$C_6H_3Me_3$, $PhBu^t$; G, $PhPr^i$; H, $PhPr^n$; I, *m*-$C_6H_4Me_2$; J, *p*-$C_6H_4Me_2$; K, PhMe; L, C_6H_6

Finally, in Table 2C, we assemble data on the 19 other solvents for which values of ($\delta\Delta G^\ddagger - \delta\Delta E_t$) are sufficiently negative to indicate the presence of solvent effects other than electrostatic ones, and one solvent (acetylacetone) for which ($\delta\Delta G^\ddagger - \delta\Delta E_t$) is positive by 0.7 kcal mol^{-1}. Unsaturated compounds tend to result in low values of $\Delta G^\ddagger$ (compare the aromatic compounds), but more interestingly, nearly all the polyhalogenated aliphatic compounds markedly reduce the value of $\delta\Delta G^\ddagger$ whereas the simple alkyl halides behave normally. In Table 4 are given values of ($\delta\Delta G^\ddagger - \delta\Delta E_t$) for a number of chlorinated methanes and ethanes. There seems, however, to be no simple reason for the negative values of ($\delta\Delta G^\ddagger - \delta\Delta E_t$) that imply additional stabilisation of the transition state.

TABLE 4

Values of ($\delta\Delta G^\ddagger - \delta\Delta E_t$) (kcal mol^{-1}) for chloromethane and chloroethane solvents

CH_4	≃0.0 [a]	CH_3CH_3	≃0.0 [a]
CH_3Cl	≃0.0 [a]	CH_3CH_2Cl	≃0.0 [a]
CH_2Cl_2	−1.5	CH_3CHCl_2	−0.4
$CHCl_3$	−2.2	CH_3CCl_3	−0.2 [b]
CCl_4	−1.6		
		$CH_2Cl{\cdot}CH_2Cl$	−1.3
		$CH_2Cl{\cdot}CHCl_2$	−1.8
		$CHCl_2{\cdot}CHCl_2$	−1.9
		$CHCl_2{\cdot}CCl_3$	−1.7

[a] Estimated by comparison with values for other alkanes and alkyl chlorides (Table 2A). [b] From data on the Et_3N–EtI reaction (unpublished calculations).

Our conclusion is that for just under half the solvents studied in this work, solvent effects on values of $\Delta G^\ddagger$ for the Menschutkin reaction (1) may be interpreted simply in terms of the electrostatic continuum effect calculated by the reaction field theory; these solvents, following Rosseinsky, may be termed Onsager liquids (compare the treatment in ref. 19). For the remaining solvents, other effects such as polarisability, hydrogen-bonding, charge-transfer interactions, *etc.*, may play an important part in reducing the free energy of the transition state, decreasing the value of $\Delta G^\ddagger$, and therefore increasing the reaction rate constant.

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[19] D. R. Rosseinsky, *Nature*, 1970, **227**, 944.