Application of Reaction Field Theory to the Calculation of Solvent Effects on the t-Butyl Chloride Solvolysis, and on the $Me_4N^+Cl^-$ Ion Pair

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The reaction field theory previously developed to calculate solvent effects on equilibria involving rotational or conformational isomers has been applied to the calculation of solvent effects on values of $\Delta G^‡$ for the decomposition of t-butyl chloride in aprotic solvents and the gas phase. Calculations in terms of a transition state of dipole moment μ = 7·40 D lead to good agreement between calculated and observed values over the entire solvent range including the gas phase. Even better agreement is obtained by calculations in terms of a transition state of μ = 8·80 D in polar solvents and a less polar, four-centred, transition state of μ = 7·29 D in less polar solvents and the gas phase. Calculations are also reported of solvent effects on the free energy of the $Me_4N^+Cl^-$ ion pair, again in good agreement with the observed values in aprotic solvents.

THE decomposition of t-butyl chloride proceeds through a transition state that is generally agreed to be highly polar in nature, not only for solvolyses in polar solvent media [1,2] but also for the homogeneous gas-phase elimination.[3-5] Results of quantitative investigations have often been presented [6-11] in terms of a transition state model consisting of point charges, $\pm z$ units, separated by a distance, d, usually taken as 2·3 Å at 298 K. For reactions in polar solvents, z has been variously estimated as between 0·7 and 0·9 units at 298 K, *viz.* 0·82 from a study of salt effects on the aqueous hydrolysis,[6] 0·84 from comparison of the effect of methanol–water mixtures on the free energies of the solvolysis reaction transition state and of ion pairs,[7,8] 0·70 from a comparison of the effect of several pure

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[1] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[2] E. M. Arnett, in 'Physico-chemical Processes in Mixed Aqueous Solvents,' ed. F. Franks, Heinemann, London, 1967, p. 105.

[3] A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, 1967, **4**, 119.

[4] A. Maccoll, *Chem. Rev.*, 1969, **69**, 33.

[5] S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 1963, **39**, 3463.

[6] G. A. Clarke and R. W. Taft, *J. Amer. Chem. Soc.*, 1962, **84**, 2295.

[7] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 1610.

[8] M. H. Abraham, *Progr. Phys. Org. Chem.*, 1974, in the press.

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

[10] M. H. Abraham, *J.C.S. Perkin II*, 1973, 1893.

[11] I. A. Koppel and V. A. Palm, *Reakts. spos. org. Soedinenii*, 1967, **4**, 862.

solvents on the free energies of the transition state and of the $Me_4N^+Cl^-$ ion pair,[9] 0·80 from a similar comparison involving calculated values for the $Bu^{t+}Cl^-$ ion pair,[10] and *ca.* 0·9 from correlations using the Kirkwood function $(\varepsilon-1)/(2\varepsilon+1)$, where ε is the solvent dielectric constant, in a number of pure alcoholic solvents.[8] The ' best ' value for z in polar solvents seems to be 0·80, which corresponds to a dipole moment of $\mu = 8{\cdot}8$ D for the transition state if d is taken as 2·3 Å. In solvents of moderate or low polarity (especially aprotic solvents), charge separation in the transition state seems to be rather less. From a comparison of the effect of such solvents on the free energies of the transition state and of the $Me_4N^+Cl^-$ ion pair it was suggested[9] that $z = 0{\cdot}45$—$0{\cdot}55$ at 298 K; these values correspond to $\mu = 5{\cdot}0$—$6{\cdot}1$ D if the dipolar distance is again taken as 2·3 Å. Analyses of solvent effects on $\log k_1$ (where k_1 is the observed first order rate constant for the decomposition of t-butyl chloride) in terms of the Kirkwood function tend to confirm this suggestion; Koppel and Palm[11] deduce dipole moments for the transition state of *ca.* 5·8 at 298 K and *ca.* 6·0 D at 393 K using data for the gas phase and for aprotic solvents. These results[11] thus support the proposition[3,4] that the transition state for the gas-phase decomposition is moderately polar or quasi-heterolytic in nature.

Since the free energy of activation, $\Delta G^\ddagger$, is given by equation (1), in which Tr refers to the transition state,

$$\Delta G^\ddagger = \Delta G_f^0(\mathrm{Tr}) - \Delta G_f^0(\mathrm{Bu^tCl}) \qquad (1)$$

then solvent effects on $\Delta G^\ddagger$ and on the free energy of the transition state are related through equation (2). In

$$\Delta G_t^0(\mathrm{Tr}) = \Delta G_t^0(\mathrm{Bu^tCl}) + \delta\Delta G^\ddagger \qquad (2)$$

this equation, ΔG_t^0 represents the free energy of transfer of a species from the reference solvent 1 to any other solvent 2, and $\delta\Delta G^\ddagger = \Delta G_2^\ddagger - \Delta G_1^\ddagger$ is the difference in the free energy of activation in solvents 1 and 2. As the transition state is highly polar and t-butyl chloride is rather nonpolar, it is to be expected that solvent effects on $\Delta G_t^0(\mathrm{Tr})$ and on $\delta\Delta G^\ddagger$ (or on $\log k_1$) would be very large, as indeed is observed.[9,11] Thus values of $\Delta G_t^0(\mathrm{Tr})$ and $\delta\Delta G^\ddagger$ may usefully be compared[8,9] with ΔG_t^0 values for the ion pair $Me_4N^+Cl^-$, and are to some extent correlated with solvent parameters such as E_T and the Kirkwood function, $(\varepsilon - 1)/(2\varepsilon + 1)$.[8] Koppel and Palm[11] have obtained rather better correlations of $\log k_1^{393}$ for decomposition in aprotic solvents and the gas phase through various empirical equations that include functions of the solvent dipole moment, dielectric constant, refractive index, and molar volume. In the present work we seek to calculate values of $\delta\Delta G^\ddagger$, using various transition state models and to compare the properties of the model that gives the best agreement between the calculated and observed values with the transition state properties deduced previously[6-11] (see above).

The reaction field theory that we use has been derived elsewhere,[12,13] thus we give here only the necessary outline with emphasis on those aspects of direct relevance to the present application. On this theory, the energy of transfer of a solute from a solvent(s) to the vapour (v) is given by equation (3). In this equation, $k = \mu^2/a^3$,

$$E_v - E_s = kx/(1 - lx) + 3hx/(5 - x) + bf[1 - \exp(-bf/16\,.\,RT)] \qquad (3)$$

$h = q^2/a^5$, and $l = 2(n_D^2 - 1)/(n_D^2 + 2)$ where μ, q, a, and n_D are the solute dipole moment, quadrupole moment, radius, and refractive index respectively; $b = 4{\cdot}35(T/300)^{\frac{1}{2}}(a^{3/2}/r^3)(k + ha^2/r^2)^{\frac{1}{2}}$ where r is the solvent–solute distance and is taken from previous studies[13] as $(a + 1{\cdot}8)$ Å. The solute radius, a, is defined by $4\pi a^3/3 = M_v/N$ where M_v is the molar volume of the solute and N is the Avogadro number. The only solvent parameter in the equation is the solvent dielectric constant which occurs in $x = (\varepsilon - 1)/(2\varepsilon + 1)$ and also in $f = [(\varepsilon - 2)(\varepsilon + 1)/\varepsilon]^{\frac{1}{2}}$ for $\varepsilon > 2$; $f = 0$ when $\varepsilon \leqslant 2$.

If two equations of the type (3) are written for a given solute in the case of solvents 1 and 2, subtraction will yield equation (4) for the energy of transfer of the given solute from solvent 1 to solvent 2.

$$\Delta E_t = E_{S_2} - E_{S_1} \qquad (4)$$

It is of interest to consider briefly the basis of the theory. The first two terms in equation (3) are merely the result of calculating the solute electric field including both the dipolar and quadrupolar contributions, and also the solute polarisability (l). If the first-order approximation of zero quadrupole moment and polarisability is made, then these terms in equation (3) reduce to the familiar Kirkwood equation (5). The theoretical basis of the first two terms in equation (3) is exactly the

$$E_v - E_s = \frac{\mu^2}{a^3}(\varepsilon - 1)/(2\varepsilon + 1) \qquad (5)$$

same as in the Kirkwood equation, and no new principles are involved. However, the inclusion of the solute quadrupole moment and polarisability gives rise to important consequences. The plot of $E_v - E_s$ (or any associated parameter) against $(\varepsilon - 1)/(2\varepsilon + 1)$ is now no longer a straight line, as required by equation (5), but a smooth curve. Thus deviations from linearity in plots of E against $(\varepsilon - 1)/(2\varepsilon + 1)$ do not necessarily imply a breakdown of the electrostatic formalism. However, use of the first two terms only in equation (3) does result in the treatment becoming more approximate for very polar solvents. In particular, the solvation energy $(E_v - E_s)$ should theoretically[14] approach infinity as ε approaches infinity whereas this is not predicted by the first two terms of equation (3). This is due to direct solvent–solute polar interactions that are accounted for by the third term in equation (3), obtained by a generalised integration of the solute dipolar and quadrupolar interactions with the solvent dipoles. This

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[12] R. J. Abraham and M. A. Cooper, *J. Chem. Soc.* (*B*), 1967, 202.

[13] R. J. Abraham and Z. L. Rossetti, *J.C.S. Perkin II*, **1973**, 582.

[14] R. J. Abraham, *J. Phys. Chem.*, 1969, **73**, 1192.

term is small for most solvents but does approach infinity as ε approaches infinity so that the entire equation (3) now satisfies this theoretical condition. Incorporation of the third term will of course also lead to curvature of the $(E_v - E_s)$ against $(\varepsilon - 1)/(2\varepsilon + 1)$ plot. Finally we note that the theory is unchanged from that derived initially for studies of solvent effects on molecules in the ground state. Application to the calculation of transition state properties thus requires that the transition state is in thermal equilibrium with the solvent(s).* Also, following the previous applications, the molecular dipole and quadrupole moments are simply calculated by placing point dipoles at the mid-point of the appropriate polar bonds pointing along the bond.

TABLE 1

Kinetic data [a] for the decomposition of t-butyl chloride

Solvent	$-\log k_1$		$\Delta G^‡$		E_A	
	298 K [b]	393 K [c]	298 K	393 K	Obs.	Equations (6) and (7)
Dimethyl sulphoxide		3·36		29·3		23·5
Nitromethane	8·12	3·91	28·5	30·2	23·8 [d]	24·4
Dimethylformamide	8·48	4·06	29·0	30·5	25·2 [e]	25·1
Dimethylacetamide	8·6 [f]		29·2			25·2
Acetonitrile	8·73	4·16	29·4	30·7	25·8 [g]	25·5
N-Methylpyrrolidone	8·97		29·7			25·9
Nitrobenzene	9·74	5·06	30·7	31·3	26·3 [h]	26·9
Acetone	10·20	5·22	31·4	32·6	(28·1) [i]	28·4
Dioxan	10·80		32·2			29·4
Chlorobenzene		6·1		34·2		30·9
Benzene	12·16	6·61	34·0	35·1		32·2
Ether	12·74	7·0	34·8	35·8		33·2
Triethylamine		7·3		36·4		34·2
t-Butyl chloride	13·60	7·41	36·0	36·6	35·0	34·9
Cyclohexane		8·1		37·8		36·4
n-Heptane [k]	16·0	9·0	39·3	39·4	39·8	39·2
n-Pentane	16·0		39·3			39·6
Perfluoro-octane		9·2		39·8		40·0
Gas phase [l]	19·3	11·3	43·7	43·5	45·0	45·4

[a] Units of k_1 are s^{-1}; $\Delta G^‡$ and E_A in kcal mol^{-1}. [b] Ref. 9. [c] Ref. 11. [d] From data by Y. Pocker, *J. Chem. Soc.*, 1960, 1972. [e] E. S. Rudakov and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1965, **2**, 142. [f] E. S. Rudakov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **127**, 1058. [g] From rate constants in ref. 11 and by D. N. Kevill and J. E. Dorsey, *Chem. and Ind.*, 1967, 2174. [h] I. A. Koppel and V. A. Palm, *Reakts. spos. org. Soedinenii*, 1964, **1**, 170. [i] From the tabulated rate constants. If $-\log k_1^{298} = 9·90$ (see ref. 9) then E_A would be calculated to be 26·4 kcal mol^{-1}. [j] Values of $-\log k_1$ and of E_A from E. S. Rudakov, G. P. Valueva, and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1967, **4**, 150. Other values for $-\log k_1$ are quite different, *viz.* 10·4 at 298 K (footnote *f*) and 6·1 at 393 K (ref. 11). [k] Values of $-\log k_1$ and of E_A from I. A. Koppel, *Reakts. spos. org. Soedinenii*, 1965, **2**, 162. Using the values of log A = 13·73 and E_A = 45·0 given in ref. 4.

Equations (3) and (4) are not applicable to hydroxylic solvents nor to anisotropic solvents such as aromatic ones. Furthermore, the energy term in these equations refers to internal energy, and not to the free energy, of the solute, so that it would seem more appropriate to compare the calculated values of ΔE_t with activation energies rather than with activation free energies. Unfortunately, only few activation energies for the decomposition of t-butyl chloride in aprotic solvents have been determined (*cf.* Table 1). We find, however, that E_A is linearly related to $\Delta G^‡$ by equations (6) and (7) to within 0·3—0·4 kcal mol^{-1}; Table 1 includes values of E_A estimated through these equations. The correlations shown in equations (6) and (7) indicate that there are

$$E_A = [\Delta G^‡(298\ K) - 11·6]/0·70 \qquad (6)$$

$$E_A = [\Delta G^‡(393\ \mathrm{K}) - 13·8]/0·66 \qquad (7)$$

no unusual entropy effects and that we may compare calculated values of ΔE_t with $\Delta G^‡$ without serious error.†

Through equations (3) and (4) we can calculate values of $\Delta E_t(\mathrm{Bu^tCl})$ and $\Delta E_t(\mathrm{Tr})$. The quantity $\Delta E_t(\mathrm{Tr}) - \Delta E_t(\mathrm{Bu^tCl}) = \delta\Delta E_t$ is then directly comparable with either δE_A or with $\delta\Delta G^‡$ provided that a suitable reference solvent is chosen. We shall mostly use *NN*-dimethylformamide (DMF) as the reference solvent 1 in our calculations. As well as dealing with the t-butyl chloride reaction, we thought it of interest to calculate ΔE_t for the ion pair $\mathrm{Me_4N^+Cl^-}$ and to compare these values with the known [8,9] values of $\Delta G_t^0(\mathrm{Me_4N^+Cl^-})$. In this case there is a difficulty over the appropriate standard state, since ΔG_t^0 for a given solute depends to some extent on the standard state adopted; we shall use the mole fraction standard state. These considerations do not apply in the case of E_A or of $\Delta G^‡$ because these two quantities are independent of any such standard state in the present case.

For the solute t-butyl chloride, the dipole moment, molar volume, and refractive index are known (Table 2) and these together with standard geometry give the calculated parameters in Table 2. Note that because the C–Cl point dipole is not at the centre of the molecule,

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* As has been pointed out before,[8] this is not an additional assumption but follows from the assumptions made in the transition state theory itself. On this theory, the transition state is assumed to be in chemical and thermal equilibrium with the reactants. Now since the reactants are in thermal equilibrium with the solvent, it follows from the zeroth law of thermodynamics that the transition state is in thermal equilibrium with the solvent.

† We compare ΔE_t with $\Delta G^‡$ rather than with E_A merely on the basis of more experimental data. However, we find that the correlation with E_A is just as good as that with $\Delta G^‡$, and use of E_A rather than $\Delta G^‡$ would not significantly affect our conclusions.

TABLE 2

Solute parameters used in the calculations

Solute	T/K	μ/D	M_v/ml [a]	n_D [b]	k [e]	l	h [e]
$Me_4N^+Cl^-$	298	8·48	107	1·6610	24·43	0·7392	8·48
Bu^tCl	298	2·13	111	1·3869	1·49	0·4707	0·63
Bu^tCl	393	2·13	127	1·3869	1·30	0·4707	0·50
Tr	298	7·29 [c]	116	1·3869	16·66	0·4707	10·62
		7·40	116	1·3869	17·16	0·4707	9·98
		8·80 [d]	116	1·3869	24·27	0·4707	14·12
Tr	393	8·00	132	1·3869	17·63	0·4707	6·65

[a] From ref. 7; the values at 393 K have been estimated. [b] Refractive index; the value for $Me_4N^+Cl^-$ has been calculated from the molar refraction of ammonium chloride (16·08) plus four CH_2 groups (with C = 2·591 and H = 1·028). [c] This corresponds to model (I). [d] This corresponds to model (II). [e] In kcal mol^{-1}.

the solute has a quadrupolar field as well as dipolar field. For the transition state we have estimated values for the molar volume and refractive index, and again use standard geometry. A similar procedure was adopted for the ion pair $Me_4N^+Cl^-$. The various parameters are in Table 2. Solvent dielectric constants at 298 K are from ref. 8; for the calculations at 393 K we have estimated a number of values of ε at 393 K from a plot of ε at 298 K against ε at 393 K using data for several solvents. The dielectric constants used in the calculations are given in Tables 4 and 5.

RESULTS AND DISCUSSION

The calculated values of $\Delta E_t(Me_4N^+Cl^-)$ and the observed values of $\Delta G_t^0(Me_4N^+Cl^-)$ are in Table 3; the former have been calculated with $\mu(Me_4N^+Cl^-)$ set equal to 8·48 D. Agreement between the calculated and observed solvent effects is very good, although the dipole moment that we have had to use is rather low. Table 3 gives a breakdown of the calculated ΔE_t values for $Me_4N^+Cl^-$, showing the contribution of the various terms. Although the dipole term is always predominant, the other two terms are significant, particularly in polar solvents. Results of breakdowns of calculated values of ΔE_t for the transition state and of $\delta\Delta E_t$ are very similar, so that in these cases only the total calculated energy will be given.

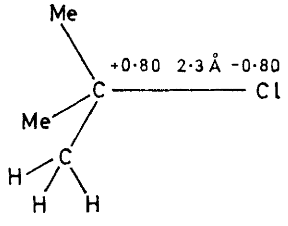
TABLE 3

Calculated and observed solvent effects on the ion pair $Me_4N^+Cl^-$, in kcal mol^{-1} at 298 K

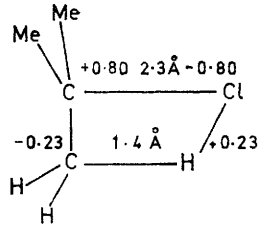
	Calculated energies					Observed energy [a]
Solvent	Dipole term	Quadrupole term	Polar term	Total $E_v - E_s$	ΔE_t	ΔG_t^0
Dimethyl sulphoxide	18·4	2·7	3·5	24·6	−0·9	−0·5
Nitromethane	18·2	2·7	3·0	23·9	−0·2	−0·4
Dimethylformamide [b]	18·2	2·7	2·8	23·7	0·0	0·0
Acetonitrile	18·1	2·7	2·8	23·6	0·1	1·0
N-Methylpyrrolidone	18·0	2·7	2·5	23·2	0·5	1·2
Acetone	17·3	2·6	1·7	21·6	2·1	3·1
Ether	11·1	1·9	0·3	13·3	10·4	11·6
Carbon tetrachloride	6·6	1·2	0·0	7·8	15·9	15·0
Cyclohexane	5·8	1·0	0·0	6·8	16·9	16·9
n-Hexane	5·3	1·0	0·0	6·3	17·4	17·8
Gas phase	0·0	0·0	0·0	0·0	23·7	

[a] Mole fraction scale values from refs. 8 and 9. [b] The reference solvent.

As a first step in the calculation of $\delta\Delta G^\ddagger$ values for the decomposition of t-butyl chloride, we chose a transition state model of geometry similar to that of (I), with a C–Cl bond distance of 2·3 Å. The dipole moment of the transition state, μ(Tr), was regarded as constant over the entire solvent range and treated as an adjustable parameter. In Tables 4 and 5 are the calculated values of $\delta\Delta E_t$ and the observed values of $\delta\Delta G^\ddagger$. We have not included aromatic solvents because these always give rise to anomalous results in calculations based on equation (3). However, with the single exception of t-butyl chloride itself as solvent, calculated and observed values in Tables 4 and 5 are in quite good agreement. The values of μ(Tr) used in the calculations, 7·40 at 298 K and 8·00 D at 393 K, correspond to charge separations of 0·67 and 0·72 units respectively acting over the dipolar distance of 2·3 Å. These values of μ(Tr) and z agree reasonably well with values deduced previously, *viz* μ(Tr) = 8·8 in polar solvents and μ(Tr) = 5·0—6·0 D in moderately polar and nonpolar solvents (see Introduction).*



(I) μ = 8·80 D



(II) μ = 7·29 D

A refinement of the above procedure is to use more than one transition state model in the calculations, since it has been suggested [8,9] that μ(Tr) is larger in value in polar solvents than in nonpolar solvents. We therefore carried out another set of calculations in which we used the two transition state models (I) and (II). Over the polar solvent range nitromethane to *N*-methylpyrrolid-

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* Care should be exercised when comparing values of μ calculated through equation (3) with values calculated through the simple Kirkwood equation. Because of the quadrupole and polar terms in equation (3), plots of E against $(\varepsilon - 1)/(2\varepsilon + 1)$ will yield different slopes on the two equations. In addition, there is no uniform method of assigning the radii of the species in the term μ^2/a^3; we have used the formula $a^3 = 3M_v/4\pi N$, but the formula $a^3 = M_v/8N$ has been used before,[8] and Koppel and Palm[11] in their analysis of the t-butyl chloride reaction take a as the C–Cl bond distance (2·3 Å in the transition state).

Table 4

Calculated and observed solvent effects on $\Delta G^{\ddagger}$ for the decomposition of t-butyl chloride, in kcal mol^{-1} at 298 K

Solvent	ε [a]	$E_v - E_s$		$\delta\Delta E_t$	$\delta\Delta G^{\ddagger}$ [c]
		Bu^{t}Cl	Tr [b]		
Nitromethane	38·6	1·36	16·17	−0·1	−0·5
Dimethylformamide [d]	36·71	1·34	16·03	0·0	0·0
Dimethylacetamide	38·93	1·36	16·20	−0·1	0·2
Acetonitrile	36·02	1·34	15·98	0·1	0·4
N-Methyl-pyrrolidone	32·2	1·31	15·69	0·3	0·7
Acetone	20·49	1·20	14·55	1·3	2·4 [e]
Dioxan	7·39 [f]	0·95	11·67	4·0	3·2
Ether	4·22	0·76	9·37	6·1	5·8
t-Butyl chloride	9·90	1·03	12·61	3·1	7·0 [g]
n-Heptane	1·90	0·38	4·70	10·4	10·3
n-Pentane	1·84	0·36	4·48	10·6	10·3
Gas phase	1	0·00	0·00	14·7	14·7

[a] Solvent dielectric constants from ref. 8. [b] Calculated with μ(Tr) = 7·40 D. [c] Observed values (Table 1). [d] The reference solvent. [e] An alternative value is 1·9 (see ref. 9 and footnote *i* in Table 1). [f] This dielectric constant for tetrahydrofuran was used in the calculation. [g] An alternative value is 2·6 (see footnote *j* in Table 1).

Table 5

Calculated and observed solvent effects on $\Delta G^{\ddagger}$ for the decomposition of t-butyl chloride, in kcal mol^{-1} at 393 K

Solvent	ε [a]	$E_v - E_s$		$\delta\Delta E_t$	$\delta\Delta G^{\ddagger}$ [c]
		Bu^{t}Cl	Tr [b]		
Dimethyl sulphoxide	30·2 [d]	1·11	14·67	−0·6	−1·2
Nitromethane	25·0 [e]	1·07	14·21	−0·1	−0·3
Dimethylformanide [f]	23·8 [d]	1·06	14·09	0·0	0·0
Acetonitrile	23·4 [d]	1·06	14·05	0·0	0·2
Acetone	13·4 [d]	0·95	12·70	1·3	2·1
	11·8	0·92	12·37	1·6	
Ether	2·89	0·51	6·92	6·6	5·3
Triethylamine	2·20 [d]	0·40	5·30	8·1	5·9
t-Butyl chloride	6·72 [d]	0·79	10·67	3·1	6·1 [g]
Cyclohexane	1·87	0·32	4·30	9·0	7·3
n-Heptane	1·78	0·30	3·99	9·3	8·9
Perfluoro-octane	1·70 [d]	0·27	3·69	9·6	9·3
Gas phase	1·00	0·00	0·00	13·0	13·0

[a] Solvent dielectric constants at 393 K from data in Landolt–Bornstein, Zahlenwerte and Funktionen, Sechste Auflage, Band II, Teil 6, and International Critical Tables. [b] Calculated with μ(Tr) = 8·00 D. [c] Observed values (Table 1). [d] Estimated from plots of ε at 393 K against ε at 298 K (see text). [e] Using data in footnote *a* and by R. Philippe and A. M. Piette, *Bull. Soc. chim. belges*, 1955, **64**, 600. [f] The reference solvent. [g] An alternative value is 3·7 (see footnote *j* in Table 1).

Table 6

Calculated [a] and observed solvent effects on $\Delta G^{\ddagger}$ for the decomposition of t-butyl chloride using transition state models (I) and (II), in kcal mol^{-1} at 298 K

Solvent	$E_v - E_s$		$\delta\Delta E_t$	$\delta\Delta G^{\ddagger}$ [b]
	Model (I)	Model (II)		
Nitromethane		22·72	−0·6	−1·2
Dimethylformamide		22·53	−0·4	−0·7
Dimethylacetamide		22·75	−0·6	−0·5
Acetonitrile		22·46	−0·3	−0·3
N-Methylpyrrolidone [c]	15·56	22·06	0·0	0·0
Acetone	14·44		1·0	1·7 [d]
Dioxan [e]	11·58		3·6	2·5
Ether	9·31		5·7	5·1
n-Heptane	4·74		9·9	9·6
n-Pentane	4·45		10·2	9·6
Gas phase	0·00		14·2	14·0

[a] Values of $E_v - E_s$ for t-butyl chloride are the same as those in Table 4. [b] Observed values (Table 1). [c] The reference solvent. [d] An alternative value is 1·2 (*cf.* Table 4). [e] As before, the dielectric constant for tetrahydrofuran (7·39) was used.

one, model (I) was used with μ(Tr) fixed at 8·80 D but over the less polar solvent range *N*-methylpyrrolidone to the gas phase, model (II) was used with μ(Tr) now reduced to 7·29 D. Results of the refined treatment are in Table 6, where the calculated values of $\delta\Delta E_t$ have been compared with $\delta\Delta G^{\ddagger}$ values at 298 K. Calculated and observed solvent effects are in substantial agreement over the entire solvent range, so that the present calculations are compatible with the previous suggestion [8,9] that the transition state is less polar in the less polar solvents and more polar in the more polar solvents.* Model (I), with μ(Tr) = 8·80 D, corresponds to a transition state in which charge separation is 0·80 units at a dipolar distance of 2·3 Å, and hence is in exact agreement with results of previous work on the nature of the transition state in polar solvents. All the various salt and solvent effects observed to date from experiments in polar media are compatible with model (I) as a transition state structure. For solvents less polar than *N*-methylpyrrolidone, the four-centred model (II) well represents the medium effect on $\Delta G^{\ddagger}$ even as far as the gas-phase decomposition. On this basis, the transition state for the decomposition in the less polar aprotic solvents is similar to that for the gas-phase decomposition. Although it has proved difficult to put on a quantitative basis, there is agreement [3-5] that in the gas-phase decomposition the transition state is a polar, 'quasi-heterolytic,' four-centred species; model (II) is compatible with such a formulation. The dipole moment of model (II), μ = 7·29 D, is somewhat less than that of the model (I) again in agreement with the postulate that the transition state is less polar in the less polar solvents. Although charge separation in the C–Cl bond of model (II) is 0·80 units, the overall dipole moment of 7·29 D would correspond to a charge separation of only 0·64 units were a simple point-charge dipole at 2·3 Å to be assumed.

Our final results are therefore that solvent effects on values of $\Delta G^{\ddagger}$ for the decomposition of t-butyl chloride can be explained either in terms of a constant transition state with μ(Tr) = 7·40 D at 298 K, or we think perhaps more satisfactorily in terms of a more polar transition state (I) of μ(Tr) = 8·80 D in polar solvents and a less polar transition state (II) of μ(Tr) = 7·29 D in less polar solvents. Of course, there must be a rather gradual change from (I) to (II) at about solvents of the same polarity as *N*-methylpyrrolidone.

The good agreement between the calculated and observed values of $\delta\Delta G^{\ddagger}$ (see Tables 4—6) raises the intriguing possibility that the reaction field theory could be used in the determination of transition state properties for other reactions. In order to assess this possibility, however, it is necessary to show how the calculated solvent effects vary with change in the

* However it is not possible solely on the basis of the extent of the agreements between calculated and observed values in Tables 4—6 to differentiate between a fixed transition state model (Tables 4 and 5) and a variable transition state model (Table 6). Better agreement is expected in the latter case because there are now two adjustable parameters, μ(Tr-I) and μ(Tr-II), whereas in the simple calculations there is only one adjustable parameter, μ(Tr).

assumed transition state properties. In other words, how much variation in the assumed properties is allowed before the calculated and observed solvent effects differ significantly?

The two properties of the transition state that greatly affect the calculated solvation energies are the dipole moment and the molar volume; how the calculated energies depend on the values of these two properties can be illustrated with reference to the data in Table 4. For transfer from DMF to the gas phase, the calculated value of $\delta\Delta G^{\ddagger}$ is 14·7 kcal mol^{-1} with $\mu(\mathrm{Tr}) = 7{\cdot}4$ D and $V(\mathrm{Tr}) = 116$ ml. If $V(\mathrm{Tr})$ is kept constant, and $\mu(\mathrm{Tr})$ varied by $\pm 0{\cdot}5$ D, the calculated value of $\delta\Delta G^{\ddagger}$ varies by $\pm 2{\cdot}7$ kcal mol^{-1}, that is by nearly 20%.* Hence within any reasonable experimental errors in values of $\Delta G^{\ddagger}$, the calculated value of $\mu(\mathrm{Tr})$ is good to within $\pm 0{\cdot}5$ D. If the effect of variation in $V(\mathrm{Tr})$ is separately considered, it may be calculated that a 5% error in $V(\mathrm{Tr})$ leads to a *ca.* 5% error in $\delta\Delta G^{\ddagger}$; thus only a rather inexact value for $V(\mathrm{Tr})$ will greatly affect the result (providing that a self-consistent method for the calculation of molecular radii from molar volumes is used, see footnote on p. 50).

TABLE 7

Comparison of the calculated ΔE_t values with the electrostatic contribution to free energies of transfer of t-butyl chloride, in kcal mol^{-1} at 298 K

Solvent	$\Delta G_t^0(\mathrm{Bu^tCl})$ [a]	ΔG_t^0(n-Pentane) [b]	$\Delta G_e^0(\mathrm{Bu^tCl})$ [c]	$\Delta E_t(\mathrm{Bu^tCl})$ [d]
Dimethyl sulphoxide	0·62	0·87	−0·25	−0·06
Nitromethane	0·36	0·79	−0·43	−0·02
Dimethylformamide	0·00	0·00	0·00	0·00
Acetonitrile	0·15	0·22	−0·07	0·01
Acetone	−0·29	−0·58	0·29	0·15
n-Decane	−0·49	−1·58	1·09	0·95
Gas phase	−4·20 [e]	−5·26 [e]	1·06	1·34
Gas phase [f]	−3·91 [e]	−5·25 [e,g]	1·34 [h]	1·19

[a] Mole fraction values from ref. 9. [b] Mole fraction values from data by J. A. Gerster, J. A. Gorton, and R.-B. Eklund, *J. Chem. Eng. Data*, 1960, **5**, 423. [c] Calculated as $\Delta G_t^0(\mathrm{Bu^tCl}) - \Delta G_t^0$(n-Pentane); these differences are independent of any standard state. [d] Values calculated through equations (3) and (4). [e] Values of $-RT\ln[P(\mathrm{mmHg})/N]$. [f] Transfer from acetone to the gas phase. [g] Value for neopentane, C. L. de Ligny and N. G. van der Veen, *Rec. Trav. chim.*, 1971, **90**, 984. [h] Calculated as $\Delta G_t^0(\mathrm{BuCl}) - \Delta G_t^0$(Neopentane).

We feel, therefore, that there is a real possibility of determining transition state properties, such as dipole moments, through application of the reaction field theory to solvent effects on reaction rates.

It remains to explain the success of the reaction field theory, equation (3), in the calculation of $\delta\Delta G^{\ddagger}(\delta\Delta E_t)$, especially since the observed values of $\Delta G_t^0(\mathrm{Bu^tCl})$ are not correlated at all by the calculated parameter $\Delta E_t(\mathrm{Bu^tCl})$ (see Table 7) (Note that in this Table the values of ΔG_t^0 for transfer to the gas phase have no absolute significance since they depend on the standard state adopted for the gas phase.) Now the values of ΔE_t for a solute calculated from equations (3) and (4) clearly refer to the electrostatic part of the energy of transfer whereas ΔG_t^0 values include a contribution from a nonelectrostatic term as well as from the electrostatic one. Following other workers (see ref. 7) we may write equation (8) and take the value of ΔG_n^0 as equal to the free energy of transfer of a nonpolar solute of about the same size as the solute under consideration.[7]

$$\Delta G_t^0 = \Delta G_n^0 + \Delta G_e^0 \qquad (8)$$

In Table 7 we have taken ΔG_t^0(n-Pentane) as an approximation to $\Delta G_n^0(\mathrm{Bu^tCl})$ and have then determined the values of $\Delta G_e^0(\mathrm{Bu^tCl})$. Within the experimental error these values of $\Delta G_e^0(\mathrm{Bu^tCl})$ follow reasonably closely the values of $\Delta E_t(\mathrm{Bu^tCl})$ calculated through equations (3) and (4), thus confirming the equivalence of ΔE_t and the electrostatic contribution even for transfers to the gas phase. From equations (2) and (8) it follows that $\delta\Delta G^{\ddagger} = \Delta G_t^0(\mathrm{Tr}) + \Delta G_n^0(\mathrm{Tr}) - \Delta G_e^0(\mathrm{Bu^tCl}) - \Delta G_n^0(\mathrm{Bu^tCl})$. But since the size of the transition state is nearly the same as that of t-butyl chloride, $\Delta G_n^0(\mathrm{Tr}) \approx \Delta G_n^0(\mathrm{Bu^tCl})$ and to a first approximation $\delta\Delta G^{\ddagger} = \Delta G_e^0(\mathrm{Tr}) - \Delta G_e^0(\mathrm{Bu^tCl})$. Since the reaction field theory yields reasonable values for the electrostatic contributions, it will also yield reasonable values for $\delta\Delta G^{\ddagger}$ even though the full terms ΔG_t^0 may not be so well calculated by the theory.†

The same reasoning applies to free energy differences between rotamers or between conformers, with $\delta\Delta G^0$ replacing $\delta\Delta G^{\ddagger}$ in the above equations. In these cases, the nonelectrostatic contribution will be the same for each isomer so that $\delta\Delta G^0 = \Delta G_e^0$ (isomer A) $- \Delta G_e^0$ (isomer B). Because the ΔG_e^0 values are well calculated by the reaction field equation, the success of the method in the calculation of $\delta\Delta G^0$ values is apparent.

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* For transfer from DMF to ether, the variation is 25%.

† The breakdown of ΔG_t^0 by equation (8) is perhaps better described as into *solute* electrostatic contributions (ΔG_e^0) and all other contributions (ΔG_n^0). These other contributions will include not only van der Waals contributions but also electrostatic contributions. Indeed the value of $\Delta G_t^0(\Delta G_n^0)$ for a nonpolar solute (such as n-pentane) in a polar solvent may be considered as due to the energy needed to create nonpolar ' holes ' in the polar solvent and this energy must include a contribution from solvent–solvent electrostatic interactions.