Substitution at Saturated Carbon. Part XX.[1] The Effect of 39 Solvents on the Free Energy of Et_3N, EtI, and the Et_3N–EtI Transition State. Comparison with Solvent Effects on the Equilibria $Et_3N + EtI \rightleftharpoons Et_4\overset{+}{N}\overset{-}{I}$ and $Et_3N + EtI \rightleftharpoons Et_4\overset{+}{N} + \overset{-}{I}$

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Limiting values of the Raoult's law activity coefficient of triethylamine in five solvents and of ethyl iodide in 32 solvents have been determined. When combined with previous data. these results yield values of the standard free energy of transfer of the Et_3N–EtI transition state from dimethylformamide to 31 other aprotic solvents and to 7 hydroxylic solvents (including water). It is shown that although solvent effects on $\Delta G^‡$ for the reaction of Et_3N with EtI are often the result of mainly transition-state effects, there are numerous solvents in which initial-state effects are large. Combination of the present data with previous data on the ion pair $Et_4\overset{+}{N}\overset{-}{I}$ and the pair of ions $Et_4\overset{+}{N} + \overset{-}{I}$ enables the solvent effect on values of $\Delta G°$ for the title equilibria to be calculated. Comparison of values of $\Delta G°_t(\mathrm{Tr})$ with $\Delta G°_t(Et_4\overset{+}{N}\overset{-}{I})$ and $\Delta G°_t(Et_4\overset{+}{N} + \overset{-}{I})$, and comparison of $\delta\Delta G^‡$ with $\delta\Delta G°$ values for the equilibria shows conclusively that the Et_3N–EtI transition state lies between the reactants and the ion pair, rather closer to the reactants than to the latter. The pair of ions is far away from the transition state on the reaction co-ordinate.

THE Menschutkin reaction of tertiary amines with alkyl halides has aroused considerable attention,[2] both because it is a classic example of a bimolecular reaction in which uncharged reactants proceed to polar products, and because the particular reaction (1) has been suggested [3,4] as

$$Pr^n_3N + MeI \longrightarrow Pr^n_3\overset{+}{N}Me + I^- \qquad (1)$$

a standard process in the examination of solvent effects on chemical reactivity. A number of investigators have suggested that although the Menschutkin reaction leads to polar products (either the ion pair, $R_4\overset{+}{N}X^-$, or the pair of ions, $R_4\overset{+}{N} + X^-$) the transition state resembles the reactants rather than the products. Reported work includes evidence from solvent effects on reaction

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[1] Part XIX, M. H. Abraham and P. L. Grellier, *J.C.S. Perkin II*, 1975, 1856.

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

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

[4] K. F. Wong and C. A. Eckert, *Ind. and Eng. Chem.*, 1970, **62** (*No* **9**), 16.

rates,[1,2,5–8] kinetic isotope effects,[9] calculations of solvent effects on reaction (1) through the reaction field theory,[10] the effect of pressure on reaction rates,[11] and comparisons of solvent effects on rate constants and equilibrium constants.[12]

Part of the above work [5,6] involved the dissection of solvent effects on $\Delta G^{\ddagger}$ for reaction (2) into initial-state and transition-state contributions, followed [8] by comparison of solvent effects on the transition state with

$$\mathrm{Me_3N} + p\text{-}\mathrm{NO_2C_6H_4CH_2Cl} \longrightarrow \mathrm{Me_3\overset{+}{N}CH_2C_6H_4NO_2}\text{-}p + \mathrm{Cl^-} \quad (2)$$

those on a model ion pair, $\mathrm{Et_4\overset{+}{N}Cl^-}$. However, it is clearly desirable to compare transition state properties with those of the actual product ion pair, but this has been achieved only for a few solvents (two protic and two aprotic) in the $\mathrm{Me_3N}$–MeI reaction,[2] and for protic solvents in the case of reaction (3).[1] Since it is known that hydroxylic solvents exert anomalous effects on the Menschutkin reaction, we set out to determine the influence of aprotic solvents on initial-state and transition-state contributions to $\delta\Delta G^{\ddagger}$ for reaction (3), and also on

$$\mathrm{Et_3N} + \mathrm{EtI} \longrightarrow \mathrm{Et_4\overset{+}{N}} + \mathrm{I^-} \quad (3)$$

$\delta\Delta G^{\circ}$ values for the equilibria (4) and (5); initial state

$$\mathrm{Et_3N} + \mathrm{EtI} \rightleftharpoons \mathrm{Et_4\overset{+}{N}I^-} \quad (4)$$

$$\mathrm{Et_3N} + \mathrm{EtI} \rightleftharpoons \mathrm{Et_4\overset{+}{N}} + \mathrm{I^-} \quad (5)$$

effects on (4) and (5) are of course identical to initial state effects on reaction (3).[*]

Although our results are confined to reaction (3), our conclusions should be generally applicable to Menschutkin reactions of tertiary amines, since we have verified that there are extremely good linear correlations between solvent effects on rate constants for different reactions, especially if aprotic solvents only are considered. In Table 1 are details of the correlation coefficient, *r*, and slope, *m*, obtained on plotting log (k/l mol^{-1} s^{-1}) for Menschutkin reactions against log *k* for reaction (1). Drougard and Decroocq [3] carried out a similar analysis; their values of *m* are close to those we find, but they did not record any correlation coefficients.

In Table 2 are values of the rate constant, in conventional units of l mol^{-1} s^{-1}, for reaction (3). Most of the data is from the work of Hartmann and his colleagues,[15,16] a few rate constants we have determined (see Experimental section), and a number of rate constants have been estimated using the correlations shown in Table 1. Also in Table 2 are the derived $\Delta G^{\ddagger}$ values after conversion of the rate constant units to mol-fraction^{-1} s^{-1}. We use equation (6) to calculate the solvent effect on the free energy of the transition state, Tr, and define $\delta\Delta G^{\ddagger}$ as $\Delta G^{\ddagger}$ (solvent 2) − $\Delta G^{\ddagger}$ (solvent 1).

TABLE 1

Correlation of log *k* values for Menschutkin reactions in aprotic solvents with those for the $\mathrm{Pr_3N}$–MeI reaction [a]

Reactants	*T*/K	No. of solvents	*m*	*r*
$\mathrm{Et_3N + BrCH_2CO_2Et}$	293	30 [b]	0.840	0.988
$\mathrm{Et_3N + ICH_2CO_2Et}$	293	30 [b]	0.774	0.992
$\mathrm{Et_3N + EtI}$	298	29 [c]	0.912	0.946
Pyridine + $\mathrm{C_{12}H_{25}Br}$	348	13 [d]	1.119	0.988
Pyridine + MeI	373	12 [e]	0.713	0.950
$\mathrm{Et_3N + EtI}$	373	12 [f]	0.882	0.978
$\mathrm{PhCH_2NMe_2 + MeI}$	303	11 [g]	1.028	0.985
$\mathrm{Me_3N} + p\text{-}\mathrm{NO_2C_6H_4CH_2Cl}$	298	10 [h]	1.195	0.977
Pyridine + $\mathrm{PhCH_2Br}$	303	10 [i]	1.206	0.952
$\mathrm{Et_3N + EtI}$	373	8 [j]	0.827	0.988

[a] log*k* Values at 293 K for the standard reaction taken from C. Lassau and J.-C. Jungers, *Bull. Soc. chim. France*, 1968, 2678, and from G. Berrebi and D. Decroocq, *J. Chim. Phys.*, 1974, **71**, 673. The point for solvent hexane has been excluded. [b] Ref. 3. [c] Table 2. [d] K. Murai and C. Kimura, *Nippon Nogei-Kagaku Kaishi*. 1972, 2209. [e] N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1936, 1353. [f] N. Menschutkin, *Z. phys. Chem.*, 1890, **6**, 41. [g] T. Matsui and N. Tokura, *Bull. Chem. Soc. Japan*, 1971, **44**, 756. [h] Refs. 5 and 20. [i] Ref. 11. [j] H. J. Grimm, H. Ruf, and H. Wolff. *Z. phys. Chem.*, 1931, **13B**, 301; E. A. Moelwyn-Hughes and C. N. Hinshelwood, *J. Chem. Soc.*, 1932, 230.

$$\Delta G^{\circ}_{\mathrm{t}}(\mathrm{Tr}) = \Delta G^{\circ}_{\mathrm{t}}(\mathrm{Et_3N}) + \Delta G^{\circ}_{\mathrm{t}}(\mathrm{EtI}) + \delta\Delta G^{\ddagger} \quad (6)$$

The standard solvent 1 is dimethylformamide (DMF), and all free energies of activation and of transfer will be expressed on the mol-fraction scale. Both reactants are volatile solutes, so that their $\Delta G^{\circ}_{\mathrm{t}}$ values can be obtained from the limiting Raoult's law activity coefficients, γ^{∞}, of the solute in various solvents through the relation $\Delta G^{\circ}_{\mathrm{t}} = RT\ln(\gamma_2^{\infty}/\gamma_1^{\infty})$. Most of the γ^{∞} values for triethylamine have already been determined,[17] but a few more values (Table 3) have been obtained in the present work. Values of γ^{∞} for ethyl iodide in 26 aprotic solvents have now been determined by our gas chromatographic method and are in Table 4, together with a few other values taken from the literature. The γ^{∞} values for ethyl iodide are not exceptional, and in general solvent effects on γ^{∞}(EtI) and hence on $\Delta G^{\circ}_{\mathrm{t}}$(EtI) are quite small. Details of the calculation of $\Delta G^{\circ}_{\mathrm{t}}$(Tr) for 32 aprotic solvents are in Table 5. Also given are previous

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[*] Absolute values of K_4 and K_5 (*i.e.* ΔG°_4 and ΔG°_5) are not known, but the position of equilibrium must lie well over to the right. For some other Menschutkin reactions, kinetic studies indicate that the reaction is definitely reversible (see *e.g.* refs. 12—14).

[5] M. H. Abraham, *Chem. Comm.*, 1969, 1307.

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

[7] M. H. Abraham, *Chem. Comm.*, 1970, 293.

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

[9] C. G. Swain and N. D. Hershey, *J. Amer. Chem. Soc.*, 1972, **94**, 1901; T. M. Bare, N. D. Hershey, H. O. House, and C. G. Swain, *J. Org. Chem.*, 1972, **37**, 997.

[10] M. H. Abraham and R. J. Abraham, *J.C.S. Perkin II*, 1975, 1677.

[11] Y. Kondo, M. Ohnishi, and N. Tokura, *Bull. Chem. Soc. Japan*, 1972, **45**, 3579.

[12] T. Matsui and N. Tokura, *Bull Chem. Soc. Japan*, 1970, **43**, 1751.

[13] H. Essex and O. Gelormini, *J. Amer. Chem. Soc.*, 1926, **48**, 882.

[14] J. B. Rossell, *J. Chem. Soc.*, 1963, 5183.

[15] H. Hartmann, H. D. Brauer, and G. Rinck, *Z. phys. Chem.*, (*Frankfurt*), 1968, **61**, 47.

[16] H. Hartmann and A. P. Schmidt, *Z. phys. Chem.* (*Frankfurt*), 1969, **66**, 183.

[17] M. H. Abraham, P. L. Grellier, and J. Mana, *J. Chem. Thermodynamics*, 1974, **6**, 1175.

results on hydroxylic solvents,[1] after conversion to DMF as the standard solvent, so that we now have ΔG°_t(Tr) values for 39 solvents, by far the largest number of pure solvents ever used in such transition state calculations.

TABLE 2

Solvent effects [a] on rate constants for the Et_3N–EtI reaction at 298 K

Solvent	10^6k/ l mol^{-1} s^{-1}	$\Delta G\ddagger$	$\delta\Delta G\ddagger$	Ref.
Hexane	0.0135	26 988	6 050	15
Cyclohexane	0.0216	26 596	5 658	*b*
Ether	0.359	24 909	3 971	*b*
Carbon tetrachloride	0.422	24 768	3 830	*b*
1,1,1-Trichloroethane	3.14	23 597	2 659	16
Toluene	3.37	23 594	2 656	*b*
Cyclohexyl chloride	5.21	23 406	2 468	16
Cyclohexyl bromide	6.15	23 319	2 381	16
Benzene	5.37	23 212	2 274	*c*
Ethyl acetate	7.78	23 050	2 112	This work
Dioxan	11.8	22 720	1 782	*d*
Tetrahydrofuran	11.7	22 695	1 757	*e*
Ethyl benzoate	23.8	22 612	1 674	This work
Chlorobenzene	19.5	22 528	1 590	16
Bromobenzene	34.4	22 365	1 427	16
1,1-Dichloroethane	23.7	22 301	1 363	16
Chloroform	30.1	22 129	1 191	16
Butan-2-one	39.6	22 033	1 095	16
Iodobenzene	50.2	22 021	1 083	16
Acetone	65.4	21 620	682	*f*
1,2-Dichloroethane	94.1	21 466	508	16
Dichloromethane	79.9	21 419	481	16
Acetophenone	164.0	21 348	410	*b*
Benzonitrile	152.0	21 317	379	16
Propiononitrile	118.0	21 246	308	16
Nitrobenzene	184.0	21 200	262	*g*
Dimethylformamide	216.0	20 938	0	*b*
1,1,2,2-Tetrachloroethane	312.0	20 904	−34	*b*
Acetonitrile	227.0	20 638	−255	This work
Nitromethane	333.0	20 468	−470	*h*
Propylene carbonate	684.0	20 308	−630	*i*
Dimethyl sulphoxide	873.0	20 062	−876	*j*

[a] Values of $\Delta G\ddagger$ in cal mol^{-1}, after conversion of the rate constants to units of mol-fraction^{-1} s^{-1}. [b] Values calculated from linear correlations in Table 1. [c] Average value from data by (i) E. Tommila and P. Kaurenen, *Acta Chem. Scand.*, 1954, **8**, 1152; (ii) E. Tommila and L. Hämäläinen, *ibid.*, 1963, **17**, 1985; and (iii) Y. Kondo, personal communication. [d] Average value from footnote *c*(i) and *c*(iii). [e] Footnote *c*(ii). [f] Average value from refs. 16, 17, and H-D. Brauer and H. Kelm, *Z. phys. Chem.* (*Frankfurt*), 1972, **79**, 96. [g] Average value from refs. 16, 17, and footnote *c*(iii). [h] Footnote *c*(iii). [i] I. S. Lyuborskii, A. L. Shapiro, V. I. Romanova, and S. Z. Levin, *Zhur. obshchei Khim.*, 1969, **39**, 478. [j] Footnote *c*(ii).

TABLE 3

Limiting activity coefficients [a] of triethylamine in solvents at 298 K

Solvent	γ^∞
1,1,1-Trichloroethane	1.10
Cyclohexyl chloride	1.63
Cyclohexyl bromide	1.53
Propylene carbonate	24.5
Propan-2-ol	1.45

[a] This work.

TABLE 4

Limiting activity coefficients [a] of ethyl iodide in solvents at 298 K

Solvent	γ^∞	Solvent	γ^∞
Hexane	1.90	Iodobenzene	0.89
Cyclohexane	1.34 [b]	Acetone	2.10
Ether	2.26	1,2-Dichloroethane	1.44
Carbon tetrachloride	1.23 [c]	Dichloromethane	2.06
1,1,1-Trichloroethane	1.23 [d]	Acetophenone	1.28
Toluene	1.10	Benzonitrile	1.63
Cyclohexyl chloride	1.00	Propiononitrile	2.54
Cyclohexyl bromide	1.02	Nitrobenzene	1.59
Benzene	1.07	Dimethylformamide	1.92
Ethyl acetate	1.42 [c]	1,1,2,2-Tetrachloroethane	0.78
Dioxan	1.34	Acetonitrile	4.25
Tetrahydrofuran	0.93	Nitromethane	4.81
Ethyl benzoate	1.15	Propylene carbonate	3.13
Chlorobenzene	1.01	Dimethyl sulphoxide	3.11
Bromobenzene	1.05	Water	2 165
1,1-Dichloroethane	1.44 [d]		
Chloroform	0.96		
Butan-2-one	1.42		

[a] This work except where indicated. [b] See J. A. V. Butler and P. Harrower, *Trans. Faraday Soc.*, 1937, **31**, 171. [c] Value at 323 K from J. von Zawidzki, *Z. phys. Chem.*, 1900, **35**, 129. [d] Estimated value.

TABLE 5

Calculation of free energies of transfer [a] (on the mol-fraction scale) from dimethylformamide to other solvents of the Et_3N–EtI transition state, in kcal mol^{-1} at 298 K

		ΔG°_t		
Solvent	$\delta\Delta G\ddagger$	Et_3N	EtI	Tr
Hexane	6.05	−1.28	−0.01	4.76
Cyclohexane	5.66	−1.26	−0.21	4.19
Ether	3.97	−1.06	0.10	3.01
Carbon tetrachloride	3.83	−1.39	−0.26	2.18
1,1,1-Trichloroethane	2.66	−1.22	−0.26	1.18
Toluene	2.66	−1.29	−0.33	1.04
Cyclohexyl chloride	2.47	−0.99	−0.39	1.09
Cyclohexyl bromide	2.38	−1.02	−0.37	0.99
Benzene	2.27	−1.12	−0.35	0.80
Ethyl acetate	2.11	−0.74	−0.18	1.19
Dioxan	1.78	−0.56	−0.21	1.01
Tetrahydrofuran	1.76	−1.06	−0.43	0.27
Ethyl benzoate	1.67	−0.86	−0.30	0.51
Chlorobenzene	1.59	−1.16	−0.38	0.05
Bromobenzene	1.43	−1.09	−0.36	−0.02
1,1-Dichloroethane	1.36	−1.35	−0.17	−0.16
Chloroform	1.19	−1.92	−0.41	−1.14
Butan-2-one	1.10	−0.68	−0.18	0.24
Iodobenzene	1.08	−0.99	−0.46	−0.37
Acetone	0.68	−0.30	0.05	0.43
1,2-Dichloroethane	0.51	−0.83	−0.17	−0.49
Dichloromethane	0.48	−1.31	0.04	−0.79
Acetophenone	0.41	−0.61	−0.24	−0.44
Benzonitrile	0.38	−0.66	−0.10	−0.38
Propiononitrile	0.31	−0.42	0.17	0.06
Nitrobenzene	0.26	−0.52	−0.11	−0.37
Dimethylformamide	0	0	0	0
1,1,2,2-Tetrachloroethane	−0.03	−2.51	−0.53	3.07
Acetonitrile	−0.25	0.13	0.47	0.35
Nitromethane	−0.47	0.21	0.54	0.28
Propylene carbonate	−0.63	0.62	0.29	0.28
Dimethyl sulphoxide	−0.88	0.74	0.29	0.15
t-Butyl alcohol	2.41	−0.93	0.44	1.92
Propan-2-ol	2.49	−1.06	0.41	1.84
n-Butanol	2.90	−1.38	0.29	1.81
n-Propanol	2.65	−1.34	0.42	1.73
Ethanol	2.32	−1.14	0.57	1.75
Methanol	2.00	−1.29	0.84	1.55
Water	0.22	1.22	4.16	5.60

[a] All values for hydroxylic solvents from ref. 1, after change of reference solvent from methanol to DMF.

For the aprotic solvents, effects on $\Delta G\ddagger$ are generally due mainly to transition state influences, and thus for many solvents values of ΔG°(Tr) follow those of $\delta\Delta G\ddagger$; there are, however, a number of exceptions. Quite recently, calculations of solvent effects on $\Delta G^{\ddagger}$ for reaction (1) have been carried out [10] in terms of the reaction field theory. Results suggested that (a) for many solvents initial-state effects were comparatively small, and (b) the free energy of the transition state was lower than expected in aromatic solvents (especially the less polar ones) and in many polyhalogenated solvents. Our present results are in accord with these predictions; solvents such as benzene, carbon tetrachloride, 1,1- and 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, *etc.* all lower the values of $\Delta G^{\circ}_{t}(Tr)$ (see Figure 1). In addition, results for the hydroxylic solvents confirm that the anomalous effect of these solvents is due largely to transition-state effects, with $\Delta G^{\circ}_{t}(Tr)$ much higher than for aprotic solvents of similar dielectric constant.

TABLE 6

Solvent effects on the free energy of $(Et_4N^+I^-)$ and of $(Et_4N^+ + I^-)$, and calculation [a] of solvent effects on the standard free energy change for reactions (4) and (5), in kcal mol^{-1} on the mol-fraction scale at 298 K

Solvent	$\Delta G^{\circ}_{t}(Et_4N^+I^-)$ [b]	$\delta\Delta G^{\circ}_{4}$	$\Delta G^{\circ}_{t}(Et_4N^+I^-)$ [b]	$\delta\Delta G^{\circ}_{5}$
Hexane	12.8	14.0		
Cyclohexane	11.9	13.3		
Ether	7.8	8.7		
Carbon tetrachloride	9.9	11.6		
Benzene	5.9	7.4	25.3	26.8
Ethyl acetate	4.27	5.19	11.80	12.72
Ethyl benzoate	3.33	4.49	10.78	11.94
Chlorobenzene	4.01	5.55	12.16	13.70
Bromobenzene	2.15	3.60	10.52	11.97
1,1-Dichloroethane	2.28 [c]	3.80	7.32 [c]	8.84
Butan-2-one	2.23	3.09	4.23	5.09
Acetone	1.38	1.63	2.90	3.15
1,2-Dichloroethane	0.62 [c]	1.62	4.64 [c]	5.64
Dichloromethane	1.18	2.45	4.76	6.03
Acetophenone	1.52	2.37	3.07	3.92
Benzonitrile	1.02	1.78	1.70	2.46
Propiononitrile	0.86	1.11	1.59	1.84
Nitrobenzene	1.02	1.65	1.33	1.96
Dimethylformamide	0	0	0	0
1,1,2,2-Tetrachloroethane	−0.57	2.47	4.62	7.66
Acetonitrile	0.66	0.06	0.37	−0.23
Nitromethane	0.51	−0.24	−0.34	−1.09
Dimethyl sulphoxide	−0.38	−1.41	−0.43	−1.46
t-Butyl alcohol	2.72	3.21	7.41	7.90
Propan-2-ol	1.51	2.16	4.29	4.94
n-Butanol	1.04	2.13	3.76	4.85
n-Propanol	0.86	1.78	3.05	3.97
Ethanol	0.50	1.07	2.09	2.66
Methanol	−0.54	−0.09	0.07	0.52
Water	−0.44	−5.82	−0.82	−6.20

[a] Calculation through equation (7). [b] Values from ref. 8. [c] Recently determined values by M. H. Abraham and A. F. Danil de Namor.

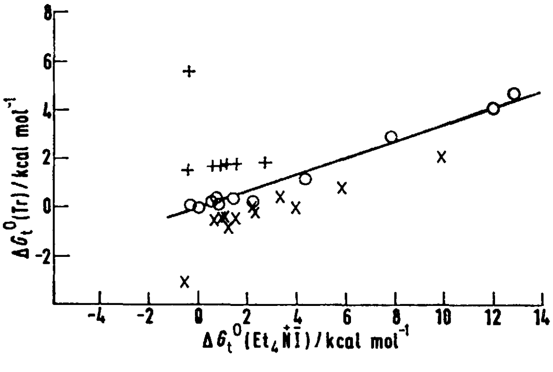

FIGURE 1 Plot of $\Delta G^{\circ}_{t}(Tr)$ against $\Delta G^{\circ}_{t}(Et_4N^+I^-)$: +, hydroxylic solvents; ○, 'normal' solvents; ×, polyhalogenated and aromatic solvents

In order to deduce the position of the transition state along the reaction co-ordinate, we may plot $\Delta G^{\circ}_{t}(Tr)$ against [2,8] $\Delta G^{\circ}_{t}(Et_4\overset{+}{N}I^-)$ and $\Delta G^{\circ}_{t}(Et_4\overset{+}{N} + I^-)$. The plot of $\Delta G^{\circ}_{t}(Tr)$ against ΔG°_{t} for the ion pair is in Figure 1; there is a reasonable line of slope 0.365 when a selection of aprotic solvents is taken. These solvents are those described [10] as 'normal' solvents and exclude aromatic solvents and polyhalogenated solvents. When the slight negative slope of the plot (not shown) of $\Delta G^{\circ}_{t}(Reactants)$ against $\Delta G^{\circ}_{t}(Et_4\overset{+}{N}I^-)$ is taken into account, these results agree well with the previous estimate [2] of 0.4 for the extent of charge separation in the transition state, and show that the transition state lies rather nearer to the reactants than to the product ion pair. However, a plot (not shown) of $\Delta G^{\circ}_{t}(Tr)$ against $\Delta G^{\circ}_{t}(Et_4\overset{+}{N} + I^-)$ yields for the 'normal' solvents a line of slope only 0.081, so that the product pair of ions is far removed from the transition state along the reaction co-ordinate.

Although absolute values of ΔG° for the equilibria (4) and (5) are not known, it is possible to calculate the solvent effect on these standard free energies of reaction through equation (7); Pr here refers to the product $Et_4\overset{+}{N}I^-$ in (4) and to the product $Et_4\overset{+}{N} + I^-$ in (5). In

$$\delta\Delta G^{\circ} = \Delta G^{\circ}_{t}(Pr) - \Delta G^{\circ}_{t}(Et_3N) - \Delta G^{\circ}_{t}(EtI) \quad (7)$$

Table 6 are given details of the calculation of $\delta\Delta G^\circ_4$ and $\delta\Delta G^\circ_5$. It is now possible to compare values of $\delta\Delta G^\ddagger$ for reaction (3) with the corresponding values for the overall equilibria, using 30 solvents for the ion pair equilibrium (4) and 26 solvents for equilibrium (5). A plot of $\delta\Delta G^\ddagger$ against $\delta\Delta G^\circ_4$ (Figure 2) yields a good straight line of slope 0.449 for the 'normal' solvents. As usual, the hydroxylic solvents are anomalous, but, surprisingly, many of the solvents that are abnormal in terms of Figure 1 are much less so in terms of Figure 2. If we denote the reactants as R, then relationship (8) holds.

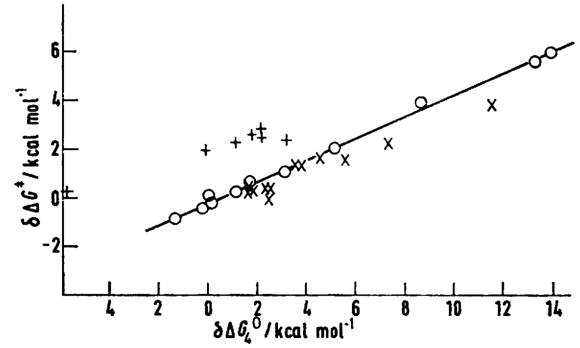

FIGURE 2 Plot of $\delta\Delta G^\ddagger$ against $\delta\Delta G^\circ_4$: +, hydroxylic solvents, ○, 'normal' solvents, ×, polyhalogenated and aromatic solvents

$$\frac{\delta\Delta G^\ddagger}{\delta\Delta G^\circ} = \frac{\Delta G^\circ_t(\mathrm{Tr}) - \Delta G^\circ_t(\mathrm{R})}{\Delta G^\circ_t(\mathrm{Pr}) - \Delta G^\circ_t(\mathrm{R})} \tag{8}$$

When $\Delta G^\circ_t(\mathrm{R})$ is significant, then clearly the ratios $\delta\Delta G^\ddagger/\delta\Delta G^\circ$ and $\Delta G^\circ_t(\mathrm{Tr})/\Delta G^\circ_t(\mathrm{Pr})$ will not be identical. The plot of $\delta\Delta G^\ddagger$ against $\delta\Delta G^\circ_5$ (not shown) results in a line of slope only 0.198 for the 'normal' solvents, so that again it is apparent that the transition state does not resemble the product pair of ions. Matsui and Tokura[12] have carried out a similar study with six aprotic solvents for the *NN*-dimethylaniline–methyl iodide reaction, but used equilibrium constants calculated from kinetic studies assuming a reversible reaction based on the ion pair equilibrium analogous to equation (4). It might be expected that for polar solvents, especially in the early stages of reaction, the product would contain the pair of ions as well as the ion pair; nevertheless, Matsui and Tokura obtained a reasonable line on plotting δ log *k* against δ log *K* for reactions in six aprotic solvents. From the small slope of the line (*ca.* 0.4) Matsui and Tokura[12] concluded that the transition state in the *NN*-dimethylaniline–methyl iodide reaction was not very similar to the final product.

Our results for the 'normal' solvents as defined in ref. 10 may be summarised as follows:

	No. of points	*m*	*r*
$\Delta G^\circ_t(\mathrm{Tr})$ *vs.* $\Delta G^\circ_t(\mathrm{Et_4N^+I^-})$	11	0.365	0.990
$\Delta G^\circ_t(\mathrm{Tr})$ *vs.* $\Delta G^\circ_t(\mathrm{Et_4N^+ + I^-})$	8	0.081	0.894
$\delta\Delta G^\ddagger$ *vs.* $\delta\Delta G^\circ_4$	11	0.449	0.998
$\delta\Delta G^\ddagger$ *vs.* $\delta\Delta G^\circ_5$	8	0.198	0.968

The plots involving $\Delta G^\circ_t(\mathrm{Tr})$, $\delta\Delta G^\circ_4$, and $\delta\Delta G^\circ_5$ can only be constructed if initial-state effects are known, but various solvent parameters can be used to correlate $\delta\Delta G^\ddagger$ values without the necessity of determining initial-state effects. Three of the most common parameters are[2] E_T, the Kirkwood dielectric constant function $Q = (\varepsilon - 1)/(2\varepsilon + 1)$, and Hildebrand's solubility parameter, δ_H. In Table 7 are given the correlation constants for plots of $\delta\Delta G^\ddagger$ against these parameters.* The hydroxylic solvents are particularly anomalous, and their exclusion greatly improves the correlations; restriction of the remaining 26 aprotic solvents to the 'normal' solvents also increases the value of *r*. From the slopes of lines in the plots involving Q and δ_H, it is possible to calculate the transition state dipole moment of 8.2 D and the transition state solubility parameter of 12.2 (in both cases, these values refer to the normal solvents) using methods described[2] previously. If the above analysis is carried out for $\Delta G^\circ_t(\mathrm{Tr})$, values of *r* for the E_T and Q plots are no better than in the case of $\delta\Delta G^\ddagger$ values. Hence dissection into initial- and transition-state free energies has not aided interpretation in terms of these parameters. From the plot of $\Delta G^\circ_t(\mathrm{Tr})$ against Q, a value of 6.5 D for the transition-state dipole moment is obtained (again using the normal solvents). For a given solute, it is not appropriate to plot ΔG°_t against δ_H, but it is better to use a function of the form $(\delta_\mathrm{H} - \delta'_\mathrm{H})^2$ where δ_H is the solvent solubility parameter and δ_H' the solute solubility parameter. By trial and error we found that a value of 11.5 for δ'_H gave the best fit, but the correlation constant value does not depend greatly on the actual value of δ'_H, and values between 11.0 and 12.0 yielded essentially the same values of *r*. In Table 8 are summarised the properties of the transition state as calculated in this work; there is reasonable agreement between the extent of charge separation, *Z*, in the transition state as calculated directly in Table 8 and as obtained from the dipole moment by the assumption of a dipolar distance of 4.0 Å.[2]

TABLE 7

Correlation coefficients for plots of $\delta\Delta G^\ddagger$ and $\Delta G^\circ_t(\mathrm{Tr})$ against solvent parameters [a]

Plot	All solvents (32)	All aprotic solvents (26)	Normal solvents (12)
$\delta\Delta G^\ddagger$ *vs.* E_T	0.459	0.935	0.990
$\delta\Delta G^\ddagger$ *vs.* Q	0.757	0.898	0.978
$\delta\Delta G^\ddagger$ *vs.* δ_H	0.576	0.850	0.888
$\Delta G^\circ_t(\mathrm{Tr})$ *vs.* E_T	0.242	0.713	0.943
$\Delta G^\circ_t(\mathrm{Tr})$ *vs.* Q	0.578	0.751	0.985
$\Delta G^\circ_t(\mathrm{Tr})$ *vs.* $(\delta_\mathrm{H} - 11.5)^2$	0.642	0.858	0.929

[a] Values of $\delta\Delta G^\ddagger$ and $\Delta G^\circ_t(\mathrm{Tr})$ from Table 5, omitting in all cases the solvents cyclohexyl chloride, cyclohexyl bromide, dioxan, tetrahydrofuran, chloroform, 1,1,2,2-tetrachloroethane, and water; either these solvents are anomalous in some way or else there is not data available on the solvent parameters.

In all the above correlations, the hydroxylic solvents behave 'anomalously', and result in an increase in $\delta\Delta G^\ddagger$ (and hence a decrease in the rate constant) by comparison to aprotic solvents of similar E_T, Q, or δ_H value. We show here (see also refs. 2 and 6) that the effect of

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* The plots of $\delta\Delta G^\ddagger$ against δ_H are definitely curved.

hydroxylic solvents is to increase the free energy of the transition state, and not to lower the initial-state free energy. It is known [2] that the free energy of polarisable nonelectrolytes that carry only partial charges is also higher in hydroxylic solvents than in polar aprotic solvents. The transition state, with a high solubility parameter (*ca.* 12) and rather low charge separation (*ca.* 0.4), is thus exhibiting the thermodynamic behaviour one might predict from its properties; the effects of hydroxylic solvents can no longer be regarded as ' anomalous ' but are quite comparable with solvent effects on various other solutes. A similar explanation accounts for the accelerating effect of aromatic solvents, since the free energy of the polarisable transition state will now tend to be reduced in value by such solvents.

TABLE 8

Deduced properties of the Et_3N–EtI transition state

Quantities plotted	Property deduced	Value
$\delta\Delta G\ddagger$ *vs.* ΔG°_4 [a]	Charge separation Z	0.45
ΔG°_t(Tr) *vs.* ΔG°_t ($Et_4N^+I^-$) [b]	Charge separation Z	0.37
$\delta\Delta G\ddagger$ *vs.* Q [c]	Dipole moment μ and Z	μ 8.2, Z 0.43 [d]
ΔG°_t(Tr) *vs.* Q [c]	Dipole moment μ and Z	μ 6.5, Z 0.34 [d]
$\delta\Delta G\ddagger$ *vs.* δ_H [c]	Solubility parameter δ_H	12.0
ΔG°_t(Tr) *vs.* $(\delta_H - 11.5)^2$ [e]	Solubility parameter δ_H	11.5

[a] Figure 2. [b] Figure 1. [c] Using values for the normal solvents (see Table 7). [d] With the dipolar distance taken as 4.0 Å. [e] Plots using the quantities $(\delta_H - 11.0)^2$ and $(\delta_H - 12.0)^2$ gave correlation coefficients only slightly lower.

However, we can offer no convincing explanation for the accelerating effect of a number of polyhalogenated solvents. We know that these accelerations are due to the solvents reducing the free energy of the transition state by *ca.* 1—2 kcal mol^{-1}, but similar reductions in free energy do not seem to take place when these solvents interact with polarisable nonelectrolytes. On the other hand, ion pairs of type $R_4N^+I^-$ are lowered in free energy by solvents such as $CHCl_2{\cdot}CHCl_2$, CH_2Cl_2, and probably $CHCl_3$, to the extent of several kcal mol^{-1} by comparison with other solvents of similar dielectric constant.[8] Some form of solvent–solute interaction involving the iodide ion in the ion-pair and incipient iodide ion in the transition state is therefore possible. The interaction cannot be totally attributed to hydrogen bonding; although this would account for the fact that CH_3CCl_3 behaves normally, it cannot account for the anomalous behaviour of CCl_4 in reducing the value of ΔG°_t(Tr) by an estimated 1.5 kcal mol^{-1}.

In conclusion, the present results show that towards change of solvent, the transition state in the reaction of triethylamine with ethyl iodide behaves as a polarisable nonelectrolyte of solubility parameter *ca.* 12.0, dipole moment *ca.* 7.0 D, and which carries a charge separation of ≃0.4 units. Consideration of these properties enables the retarding effect of hydroxylic solvents on the rate of reaction to be understood, as well as the accelerating effect of aromatic solvents; the accelerating effect of many polyhalogenated solvents is, however, still not easily explained. It is now quite clear, though, that the above transition state lies between the reactants and the product ion pair, being rather closer to the reactants than to the ion pair. This latter conclusion is in agreement with results of several previous investigations [1,2,5-12,18,19] and seems to be quite general for the Menschutkin reaction of simple tertiary amines with primary alkyl halides.

EXPERIMENTAL

Ethyl iodide was stored over anhydrous sodium carbonate and anhydrous sodium sulphate, filtered, and distilled. The middle fraction, b.p. 344.6—345.6 K was collected and stored in the dark. Triethylamine and the aprotic solvents were as described before.[17]

Values of γ^∞ for triethylamine (Table 3) were determined as before. In a similar way γ^∞ values for ethyl iodide (Table 4) were obtained by g.l.c. analysis of the headspace above dilute solutions of ethyl iodide in the various solvents. Samples (1 ml) of headspace were analysed using either columns of 20% diglycerol on Celite or 10% Carbowax 4 000 on Celite, with a column temperature of 338 K. In all cases, solutions and headspace were thermostatted at 298.15 ± 0.1 K. There is little direct comparison that can be made between our γ^∞ values for ethyl iodide, and literature values obtained from conventional vapour–liquid equilibrium studies. von Halban [20] records data from which γ^∞ values at 338 K may be estimated in solvents hexane (1.8) and nitromethane (3.9); these values agree with ours at 298 K of 1.90 and 4.81 respectively. Also

TABLE 9

Rate constants (l mol^{-1} s^{-1}) for the reaction of triethylamine with ethyl iodide at 298 K

	a_0/mol l^{-1}	10^6k	10^6k (average)
Acetonitrile	0.302	218	227
	0.218	228	(v = 2%)
	0.201	227	
	0.201	225	
	0.201	227	
	0.145	233	
Ethyl benzoate	0.406	22.7	23.8
	0.406	23.5	(v = 3.6%)
	0.359	25.0	
	0.359	24.7	
	0.194	23.3	
Ethyl acetate	0.316	7.75	7.78
	0.258	7.56	(v = 1.5%)
	0.177	7.92	
	0.172	7.83	
	0.158	7.72	
	0.118	7.89	
Water	0.036 3	36.9	34.6
	0.028 8	31.7	(v = 9%)
	0.019 3	38.6	
	0.017 9	32.2	
	0.017 9	30.6	
	0.017 9	34.2	
	0.014 6	38.0	

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Smyth and Engel[21] list data in ethanol at 303 K from which a value for γ^{∞} of 5.1 may be deduced, as compared with our value at 298 K of 5.00 for γ^{∞}.

Kinetic measurements were carried out as before,[18] using reactant solutions equimolar in triethylamine and ethyl iodide, thermostatted at 298.15 ± 0.01 K. Results were analysed in terms of the modified second-order equation $kt = 1/(a - x) - 1/a$. Good straight lines were obtained, and details of the runs are in Table 9 where a_0 is the initial concentration of reactant, and v is the percentage variance; $v = 100\sigma/k$ where σ is the standard deviation and k the average value of the rate constant.

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