Substitution at Saturated Carbon. Part XIV.[1] Solvent Effects on the Free Energies of Ions, Ion-pairs, Non-electrolytes, and Transition States in Some S_N and S_E Reactions

By **M. H. Abraham,** Department of Chemistry, University of Surrey, Guildford, Surrey

Standard free energies of transfer from methanol to various other solvents are reported for dissociated species $R_4N^+ + X^-$ (20—30 solvents). ion pairs R_4NX (20—30 solvents). t-butyl chloride (20 solvents). t-butyl bromide (10 solvents). tetramethyltin (15 solvents). tetraethyltin (15 solvents). and tetraethyl-lead (10 solvents). A dissection on solvent influences on $\Delta G^{\ddagger}$ into initial-state and transition-state contributions has been accomplished for the decomposition of t-butyl chloride (18 solvents). the decomposition of t-butyl bromide (10 solvents). the Menschutkin reaction of *NN*-dimethylaniline with methyl iodide (3 solvents). and the iododemetallation of tetra-alkyl-leads (8 solvents).

A comparison of solvent effects on the free energies of ion pairs with solvent effects on the free energies of transition states suggests that transition states carry the following units of charge separation: $[Bu^tCl]^{\ddagger}$ 0·70 (polar solvents). ≏0·5 (non-polar solvents): $[Bu^tBr]^{\ddagger}$ 0·68 (polar solvents): $[p\text{-}NO_2\cdot C_6H_4\cdot CH_2Cl\text{–}Me_3N]^{\ddagger}$ 0·35. Charge separation in the $[R_4Pb\text{–}I_2]^{\ddagger}$ transition states is probably rather higher than in the transition state of the Menschutkin reaction.

SOLVENT influences on activation parameters for substitution reactions can be dissected into initial-state and transition-state contributions in terms of the standard free energy, enthalpy, and entropy of transfer of a species (either a reactant or a transition state) from a given solvent to some other solvent. The determined values of $\Delta G_t^{\circ}(\mathrm{Tr})$, where Tr represents a transition state, can then be compared with ΔG_t° values for solutes

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[1] Part XIII, M. H. Abraham, F. Behbahany, and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 2566.

TABLE 1

Molar solubilities of tetra-alkylammonium iodides, and free energies of solution (on the molar scale) of the dissociated species ($R_4N^+ + I^-$) and the ion pairs ($R_4N^+I^-$) in kcal mol^{-1} at 298 K

Solvent	C^t	K_A	a°	ΔG_s^c/kcal mol^{-1}	
				($R_4N + I^-$)	$R_4N^+I^-$
A. R = Me [a]					
Water	0·2314 [b]	1·5 [c]	γ = 0·605 [b]	2·33	2·09
Methanol	1·519 × 10^{-2}	18 [d]	3·5	5·58	3·87
Ethanol	1·760 × 10^{-3}	190 [d]	4·2	7·99	4·88
n-Propanol	5·650 × 10^{-4}	800 [d]	4·5	9·34	5·38
Propan-2-ol	2·295 × 10^{-4}	1900 [d]	4·8	10·36	5·88
n-Butanol	2·200 × 10^{-4}	2200 [d]	5·0	10·44	5·88
Dimethyl sulphoxide	6·408 × 10^{-2}	2·2 [f]	4·0	3·84	3·38
Nitromethane	1·793 × 10^{-2} [e]	12 [g]	3·5	5·30	3·83
Acetonitrile	7·875 × 10^{-3}	19 [g]	3·5	6·16	4·42
Dimethylformamide	1·731 × 10^{-2}	14·5 [h]	3·5	5·38	3·79
N-Methylpyrrolidone	1·060 × 10^{-2} [i]	15 [c]	3·5	5·91	4·31
Nitrobenzene	1·027 × 10^{-3}	97 [j]	3·7	8·38	5·67
Acetone	5·200 × 10^{-4}	325 [k]	4·8	9·29	5·86
Ethyl methyl ketone	1·682 × 10^{-4}	969 [l]	4·8	10·57	6·50
1,2-Dichloroethane	3·956 × 10^{-4}	4·90 × 10^{4} [m]	5·8	11·21	4·81
Dichloromethane	1·50 × 10^{-4}	1·79 × 10^{5} [n]	5·8	12·52	5·35
Ethyl benzoate	2·40 × 10^{-6}	3·18 × 10^{7} [n]	6·8	17·97	7·74
Ethyl acetate	2·20 × 10^{-6}	2·45 × 10^{7} [n]	6·8	17·88	7·80
Chlorobenzene	7·00 × 10^{-7}	7·40 × 10^{7} [n]	6·8	19·22	8·48
Ether	1·0 × 10^{-9}	1·54 × 10^{10} [n]	7·3	26·33	12·43
B. R = Et [a]					
Water	1·927 [b]	1·5 [c]	γ = 0·197 [b]	1·15	0·91
Methanol	0·362 [o]	18 [d]	3·6	3·00	1·29
Ethanol	3·40 × 10^{-2} [e]	133 [d]	4·3	5·45	2·55
n-Propanol	1·187 × 10^{-2}	466 [d]	4·7	6·70	3·06
Propan-2-ol	3·565 × 10^{-3}	1300 [d]	5·0	7·97	3·72
n-Butanol	5·950 × 10^{-3}	1410 [d]	6·0	7·65	3·36
3-Methylbutanol	2·75 × 10^{-3} [e]	4500 [n]	7·0	8·72	3·74
t-Butyl alcohol	2·760 × 10^{-4}	4·00 × 10^{4} [n]	7·0	11·34	5·06
Dimethyl sulphoxide	0·1214	0 [f]	4·0	3·16	—
Nitromethane	0·2090 [e]	2 [g](?)	3·9	2·92	2·51
Acetonitrile	0·1153 [e]	5 [g]	3·6	3·61	2·65
Dimethylformamide	0·1150	12·2 [h]	3·7	3·69	2·21
Propiononitrile	3·00 × 10^{-2} [e]	38 [n]	4·5	5·17	3·02
Nitrobenzene	1·96 × 10^{-2} [e]	27 [j]	3·9	5·35	3·40
Benzonitrile	1·76 × 10^{-2} [e]	51 [n]	4·5	5·73	3·40
Acetone	9·68 × 10^{-3} [e]	150 [k]	5·0	6·53	3·57
Ethyl methyl ketone	2·035 × 10^{-3}	411 [l]	5·0	8·10	4·53
Acetophenone	5·05 × 10^{-3} [e]	250 [n]	5·5	7·25	3·98
1,2-Dichloroethane	9·19 × 10^{-3} [p]	1·00 × 10^{4} [m]	6·0	8·39	2·93
Dichloromethane	3·77 × 10^{-2}	3·65 × 10^{4} [n]	6·0	8·23	2·01
1,1,2,2-Tetrachloroethane	4·82 × 10^{-2} [q]	1·06 × 10^{5} [n]	6·5	8·68	1·83
1,1,2-Trichloroethane	1·83 × 10^{-3} [q]	5·82 × 10^{5} [n]	6·5	11·65	3·76
1,1-Dichloroethane	$\leqslant$1 × 10^{-4} [q]	4·50 × 10^{4} [m]	6·0	$\geqslant$12·13	$\geqslant$5·78
Methyl formate	1·20 × 10^{-3} [e]	8·44 × 10^{4} [n]	6·5	10·79	4·07
Bromobenzene	3·61 × 10^{-4}	2·92 × 10^{7} [n]	7·0	14·89	4·70
Ethyl benzoate	4·96 × 10^{-5}	6·50 × 10^{6} [n]	7·0	15·20	5·91
Ethyl acetate	1·56 × 10^{-5} [e]	5·00 × 10^{6} [n]	7·0	15·77	6·63
Chlorobenzene	2·21 × 10^{-5}	1·51 × 10^{7} [n]	7·0	16·18	6·39
Ether	4·0 × 10^{-8}	3·14 × 10^{9} [n]	7·5	23·10	10·15
Benzene	3·87 × 10^{-7} [o]	3·41 × 10^{17} [n]	8·0	32·67	8·75
Benzene [e]	$\leqslant$1 × 10^{-6}	C^i = 2 × 10^{-11}		29·19	$\geqslant$8·19
C. R = Pr^n					
Water	0·5075 [b]	1·5 [c]	γ = 0·326 [b]	2·13	1·89
Methanol	1·789 [e]	16·3 [d]	3·8	1·78	0·13
Ethanol	0·641 [e]	120 [d]	4·1	3·42	0·58
n-Butanol	0·157	1160 [d]	5·5	5·42	1·25
Nitromethane	0·710 [e]	1 [g](?)	4·0	1·79	1·79
Acetonitrile	0·597 [e]	5 [g]	3·8	2·23	1·27
Propiononitrile	0·308 [e]	27 [n]	4·7	3·28	1·33
Nitrobenzene	0·182 [e]	20 [j]	4·1	3·45	1·67
Benzonitrile	0·272 [e]	37 [n]	4·7	3·54	1·40
Acetone	0·126 [e]	160 [g]	5·2	4·67	1·66
1,2-Dichloroethane	0·252 [q]	7·08 × 10^{3} [m]	6·2	6·27	1·02
1,1,2,2-Tetrachloroethane	1·256 [q]	7·70 × 10^{4} [n]	6·7	6·62	−0·05
1,1,2-Trichloroethane	0·689 [q]	4·20 × 10^{5} [n]	6·7	7·94	0·27
1,1-Dichloroethane	2·01 × 10^{-2} [q]	3·40 × 10^{4} [m]	6·2	8·55	2·37
Ethyl bromide	8·65 × 10^{-3} [e]	2·17 × 10^{4} [n]	6·3	8·84	2·92
Ethyl acetate	2·01 × 10^{-4} [e]	3·60 × 10^{6} [n]	7·2	14·01	5·07
Chlorobenzene	6·94 × 10^{-4} [q]	1·10 × 10^{7} [n]	7·2	13·92	4·32

[a] Solubilities from this work. [b] Molal values from ref. 11. [c] See text. [d] Ref. 10. [e] Ref. 8. [f] D. E. Arrington and E. Griswold, *J. Phys. Chem.*, 1970, **74**, 123. [g] D. Evans, C. Zawoyski, and R. L. Kay, *J. Phys. Chem.*, 1965, **69**, 3878. [h] P. G. Sears, E. D. Wilhoit, and L. R. Dawson, *J. Phys. Chem.*, 1955, **59**, 373. [i] P. O. I. Virtanen and R. Kirkelä, *Suomen. Kem.*, 1969, **42**, *B*, 29. [j] From data in footnote *g* and in C. R. Witschonke and C. A. Kraus, *J. Amer. Chem. Soc.*, 1947, **19**, 2472 [k] W. A. Adams and K. J. Laidler, *Canad. J. Chem.*, 1968, **46**, 1977. [l] S. R. C. Hughes and D. H. Price, *J. Chem. Soc.* (*A*), 1967, 1093; 1968, 1464. [m] From data in V. Plichon, *Bull. Soc. chim. France*, 1969, 3369. [n] Extrapolated or interpolated values (see text). [o] Using the value of 0·428 mol per 1000 g solution from G. M. Goldberg and A. A. Vernon, *J. Amer. Chem. Soc.*, 1951, **73**, 2845, and the density of 0·8463 for the saturated solution in ref. 8. [p] Ref. 15. [q] Ref. 9.

that might be regarded as suitable models for the transition state.[2-4] Alternatively, as suggested by Haberfield,[5] values of $\Delta H_t°(\mathrm{Tr})$ can be compared with $\Delta H_t°$ values for the corresponding reactants and products, but the method of comparison with model solutes seems more generally to have been employed.[6]

For substitutions that involve only neutral molecules as reactants, model solutes could include non-electrolytes, ion pairs, and dissociated pairs of ions. It is important [4] that the model solute should be of about the same size as, and structurally similar to, the transition state with which it is to be compared; hence for substitutions involving organic substrates, the tetra-alkylammonium halides may often be used as transition-state models. Preliminary results [2,7] have shown that for a limited number of solvents, values of $\Delta G_t°$ for the Me_4NCl ion pair match those for the transition state in the decomposition of t-butyl chloride whereas neither of the ion pairs Et_4NCl and Et_4NI are entirely suitable models for the transition state in the Menschutkin reaction of trimethylamine with *p*-nitrobenzyl chloride. The present work seeks to compare values of $\Delta G_t°$ for transition states with values of $\Delta G_t°$ for non-electrolytes, ion pairs, and dissociated pairs of ions, with use of as wide a range of solvents as possible, in order to derive suitable transition-state models and hence to be able to deduce the nature of the various transition states.

Solvent Effects on Ions and Ion Pairs.—Molar solubilities, C^t, of tetra-alkylammonium halides are in Table 1; these solubilities have either been determined in the present work or are from the work of Walden [8] or Houckgeest.[9] From values of C^t together with ion-pair association constants, K_A, it is possible (*cf.* ref. 2) to calculate standard free energies of solution, ΔG_s^c, of the dissociated species $(R_4N^+ + X^-)$ and of the ion pairs (R_4NX); as before,[2] the superscripts c, m, and x indicate molar, molal, and mol-fraction standard states respectively. Values of K_A in alcohols are from Evans

TABLE 2

Free energies of transfer (on the molar scale) from methanol to other solvents of the dissociated species $(R_4N^+ + I^-)$, in kcal mol^{-1} at 298 K

		ΔG_t^c		Increment [a]		
No.	Solvent	$Me_4N^+ + I^-$	$Et_4N^+ + I^-$	$I^- \longrightarrow Br^-$	$I^- \longrightarrow Cl^-$	Δ [b]
1	Water	−3·3	−1·8	−0·7 [e]	−1·4 [c]	−1·0
2	Methanol	0	0	0	0	0
3	Ethanol	2·4	2·5	0·5	1·0	0·4
4	n-Propanol	3·8	3·7	0·5	1·0	0·7
5	Propan-2-ol	4·8	5·0	0·6	1·2	0·8
6	n-Butanol	4·9	4·7	0·6	1·2	1·0
7	3-Methylbutanol	(5·9) [d]	5·7	0·7	1·4	1·2
8	t-Butyl alcohol	(8·5) [d]	8·3	0·7	1·4	1·0
9	Dimethyl sulphoxide	−1·7	0·2	2·8 [e]	5·0 [e]	0·7
10	Nitromethane	−0·3	−0·1	2·6 [e]	4·7 [e]	0·3
11	Acetonitrile	0·6	0·6	2·5 [f]	5·3 [f]	0·3
12	Dimethylformamide	−0·2	0·7	3·1 [f]	5·3 [f]	0·8
13	*N*-Methylpyrrolidone	0·3		3·5 [g]	6·0 [g]	1·0
14	Propiononitrile		2·2	(3·5) [d]	(6·0) [d]	0·7
15	Nitrobenzene	2·8	2·4	(3·5) [d]	(6·0) [d]	1·1
16	Benzonitrile		2·7	(3·5) [d]	(6·0) [d]	1·1
17	Acetone	3·7	3·5	3·1	6·0	0·7
18	Ethyl methyl ketone	5·0	5·1	(3·6) [d]	(7·0) [d]	0·9
19	Acetophenone		4·3			1·3
20	1,2-Dichloroethane	5·6	5·4			0·8
21	Dichloromethane	6·9	5·2 [h]			0·5
22	1,1,2,2-Tetrachloroethane		5·7			1·1
23	1,1,2-Trichloroethane		8·6			1·0
24	1,1-Dichloroethane		9·1			0·9
25	Methyl formate		7·8			0·5
26	Bromobenzene	(12·3) [d]	11·9			1·4
27	Ethyl benzoate	12·4	12·2			1·5
28	Ethyl acetate	(13·0) [i]	12·8			1·0
29	Chlorobenzene	13·6	13·2	(5·0) [d]	(8·0) [d]	1·1
30	Ether	20·8	20·1	(5·0) [d]	(8·0) [d]	1·1
31	Benzene	(27·0) [d]	26·2	(5·0) [d]	(8·0) [d]	0·9
	Gas phase [j]	97	93	8·0	14·0	

[a] These increments when added to the values of $\Delta G_t^c(R_4N^+ + I^-)$ yield values of $\Delta G_t^c(R_4N^+ + Br^-)$ and $\Delta G_t^c(R_4N^+ + Cl^-)$. [b] To be subtracted from the given ΔG_t^c values to obtain the corresponding values of ΔG_t^x. [c] Ref. 18. [d] Estimated values. [e] J. Courtot-Coupez, M. le Démézet, A. Laouenan, and C. Madec, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **29**, 21. [f] Ref. 29. [g] M. Bréant, *Bull. Soc. chim. France*, 1971, 725. [h] This value is probably too low. [i] Estimated by comparison with values for $(Et_4N^+ + I^-)$ and $(Pr_4N^+ + I^-)$ and preferred to the calculated value of 12·3 kcal mol^{-1}. [j] See text.

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

[3] M. H. Abraham, *J. Chem. Soc. (A)*, 1971, 1061.

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

[5] P. Haberfield, *J. Amer. Chem. Soc.*, 1971, 2091.

[6] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 1541.

[7] M. H. Abraham, *Tetrahedron Letters*, 1970, 5233.

[8] P. Walden, *Z. phys. Chem.*, 1908, **61**, 633; 1906, **55**, 698.

[9] J. P. W. A. van Braam Houckgeest, *Rec. Trav. chim.*, 1941, **60**, 433.

TABLE 3

Free energies of transfer (on the molar scale) from methanol to other solvents of the ion pairs (R_4NX), in kcal mol^{-1} at 298 K

		ΔG_t^c						
No.	Solvent	Me_4NI	Me_4NBr	Me_4NCl	Et_4NI	Et_4NBr	Et_4NCl	Δ [a]
1	Water	−1·8	−2·5	−3·5	−0·4	−1·2	−2·3	−0·5
2	Methanol	0	0	0	0	0	0	0
3	Ethanol	1·0	1·5	1·7	1·3	1·6	1·8	0·2
4	n-Propanol	1·5	2·0	2·3	1·8	2·0	2·3	0·4
5	Propan-2-ol	2·0	2·5	2·7	2·4	2·7	3·0	0·4
6	n-Butanol	2·0	2·5	2·7	2·1	2·3	2·6	0·5
7	3-Methylbutanol	2·4	2·9	3·2	2·5	2·8	3·1	0·6
8	t-Butyl alcohol	3·6	4·2	4·4	3·8	4·1	4·4	0·5
9	Dimethyl sulphoxide	−0·5	1·7	3·3	(0·5) [b]			0·3
10	Nitromethane	0	1·8	3·3	1·2	3·5	5·2	0·2
11	Acetonitrile	0·6	2·4	4·7	1·4	3·1	5·3	0·2
12	Dimethylformamide	−0·1	2·3	3·9	0·9	3·5	5·0	0·4
13	*N*-Methylpyrrolidone	0·4	3·3	5·2	(1·0) [b]	(3·8) [b]	(5·9) [b]	0·5
14	Propiononitrile				1·7	4·5		0·3
15	Nitrobenzene	1·8	4·9	6·8	2·1	4·8	6·7	0·5
16	Benzonitrile				2·1	4·9		0·5
17	Acetone	2·0	4·7	7·0	2·3	4·7	7·0	0·4
18	Ethyl methyl ketone	2·6	5·2		3·2	6·0		0·5
19	Acetophenone				2·7			0·6
20	1,2-Dichloroethane	0·9			1·6			0·4
21	Dichloromethane	1·5			(2·0) [c]			0·3
22	1,1,2,2-Tetrachloroethane				0·6			0·6
23	1,1,2-Trichloroethane				2·5			0·5
24	1,1-Dichloroethane				4·5			0·4
25	Methyl formate				2·8			0·3
26	Bromobenzene				3·4			0·7
27	Ethyl benzoate	3·9			4·6			0·7
28	Ethyl acetate	4·6			5·3			0·5
29	Chlorobenzene	4·6	9·2	11·6	5·1	9·3	12·0	0·5
30	Ether	8·6	13·1	15·7	8·9	13·3	15·7	0·6
31	Benzene	6·4 [d]	11·0 [d]	13·4 [d]	6·9	11·1 [d]	13·8 [d]	0·5
32	Carbon tetrachloride [e]	11	16	19	11	16	19	0·5
33	Cyclohexane [e]	13	18	21	13	18	21	0·6
34	Hexane [e]	14	19	22	14	19	22	0·7

[a] To be subtracted from the given ΔG_t^c values to obtain the corresponding value of ΔG_t^x. [b] Estimated values. [c] Estimated by comparison with the value for Me_4NI and preferred to the calculated value of 0·7 kcal mol^{-1}. [d] Taken as 1·8 kcal mol^{-1} greater than the corresponding value for chlorobenzene. [e] Values for these solvents estimated from plots of $\Delta G_t^c(R_4NX)$ against E_T and against $(\varepsilon - 1)/(2\varepsilon + 1)$.

TABLE 4

Molar solubilities of tetra-alkylammonium perchlorates, and free energies of solution (on the molar scale) of the dissociated species ($R_4N^+ + ClO_4^-$) and the ion pairs ($R_4N^+ClO_4^-$) in kcal mol^{-1} at 298 K

					ΔG_s^c/kcal mol^{-1}	
	Solvent	C^t	K_A	a°	$R_4N^+ + ClO_4^-$	$R_4N^+ClO_4^-$
A.	R = Me					
	Water	$7{\cdot}440 \times 10^{-2}$ [a]	2 [b]	3·8	3·45	3·04
	Methanol	$5{\cdot}626 \times 10^{-3}$ [a]	47 [c]	3·8	6·61	4·33
	Ethanol	$8{\cdot}900 \times 10^{-4}$ [d]	330 [e]	3·8	8·72	5·29
	Acetonitrile	$6{\cdot}260 \times 10^{-2}$ [f]	7 [g]	3·8	4·15	2·99
B.	R = Et					
	Water	0·2170 [b]	2 [b]	3·9	2·40	1·99
	Methanol	0·1072 [c]	41 [c]	3·9	4·10	1·90
	Ethanol	$1{\cdot}140 \times 10^{-2}$ [d]	290 [e]	3·9	6·51	3·15
	Acetonitrile	1·061 [f]	2 [g]	3·9	1·61	1·20
C.	R = Pr^n					
	Water	$1{\cdot}950 \times 10^{-2}$ [a]	2 [b]	4·0	4·86	4·45
	Methanol	$9{\cdot}462 \times 10^{-2}$ [a]	36 [c]	4·0	4·15	2·03
	Ethanol	$1{\cdot}490 \times 10^{-2}$ [d]	250 [e]	4·0	6·26	2·99
	Acetonitrile	0·7235 [f]	1·5 [g]	4·0	1·90	1·65
D.	R = Bu^n					
	Water	$1{\cdot}026 \times 10^{-2}$ [a]	3 [b]	4·1	5·58	4·93

[a] Ref. 21. [b] R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, *J. Chem. Soc.* (*A*), 1969, 45; R. Bury and J. C. Justice, *J. Chim. phys.*, 1967, **64**, 1491. [c] Ref. 10 and R. L. Kay, D. F. Evans, and G. P. Cunningham, *J. Phys. Chem.*, 1969, **73**, 3322; F. Conti, P. Delogu, and G. Pistoia, *ibid.*, 1968, **72**, 1396. [d] N. C. Deno and H. E. Berkheimer, *J. Org. Chem.*, 1963, **28**. 2143. [e] Estimated values. [f] This work. [g] J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, 1965, **87**, 2529: C. H. Springer and J. F. Coetzee, *J. Phys. Chem.*, 1969, **73**, 471.

and his co-workers;[10] other sources are shown in Table 1. Data on molal solubilities and molal activity coefficients in water are from Lindenbaum and Boyd,[11] and K_A values in water are averages from various estimates.[12-14] From data given by Vernon and Sheard[15] an extrapolated value of $3{\cdot}87 \times 10^{-7}$ mol l^{-1} for the solubility of tetraethylammonium iodide in benzene can be calculated; this value confirms the earlier estimate[16] of $C^t \leqslant 1 \times 10^{-6}$ mol l^{-1}.

Table 2 gives the calculated free energies of transfer, $\Delta G_t^c(R_4N^+ + I^-)$ based on methanol as the reference solvent. The values for transfer from the gas phase to methanol have been calculated (R = Me) or estimated (R = Et and Pr^n) from Boyd's data.[17] Also in Table 2 are the increments required to correct the $\Delta G_t^c(R_4N^+ + I^-)$ values to values for the corresponding chlorides and bromides. The data for water are from Strehlow's review[18] and data for the alcohols[19] and acetone[20] have been calculated from known solubilities of the alkali-metal halides, with corrections for ion-pair association and activity coefficients. Values of ΔG_t° for various ion pairs are in Table 3. The values for the R_4NI ion pairs have been calculated from data in Table 1, and values of $\Delta G_t^c(R_4NCl)$ and $\Delta G_t^c(R_4NBr)$ have been obtained through equation (1); K_A^M and K_A^S are ion-pair association constants in methanol and in another solvent, respectively.

$$\Delta G_t^c(R_4NX) = \Delta G_t^c(R_4N^+ + X^-) + RT \ln (K_A^M/K_A^S) \quad (1)$$

The consistency of the calculated values of $\Delta G_t^c(R_4N^+ + I^-)$ can be tested by comparison with similar data for tetra-alkylammonium perchlorates. Table 4 gives values of C^t and the derived values of $\Delta G_s^c(R_4N^+ + ClO_4^-)$ and $\Delta G_s^c(R_4NClO_4)$, calculated in the same way as for the iodides (*cf.* also ref. 21). Values for the differences $\Delta G_t^c(R_4N^+ + X^-) - \Delta G_t^c(Me_4N^+ + X^-)$ are in Table 5. These differences should be independent of the counter-anion, X^-, and for the range of solvents studied this is found to be so to within *ca.* 0·1 kcal mol^{-1}. The single anomalous result is that for $\Delta G_t^c(Pr^n{}_4N^+ + X^-) - \Delta G_t^c(Me_4N^+ + X^-)$ for transfer to ethanol, and the value of $\Delta G_t^c(Pr^n{}_4N^+ + I^-)$ in ethanol is considered to be in error.

TABLE 5

Test for consistency in free energies of transfer (on the molar scale) from methanol to other solvents of tetra-alkylammonium iodides and perchlorates [a]

	$\Delta G_t^c(Et_4N^+ + X^-) - \Delta G_t^c(Me_4N^+ + X^-)$		$\Delta G_t^c(Pr^n{}_4N^+ + X^-) - \Delta G_t^c(Me_4N^+ + X^-)$	
Solvent	X : ClO_4	I	ClO_4	I
Water	+1·5	+1·5	+3·9	+3·7
Methanol	0	0	0	0
Ethanol	+0·3	+0·1	0·0	−0·8 [b]
Acetonitrile	0·0	0·0	+0·2	−0·1

[a] Values in kcal mol^{-1} at 298 K from Tables 2, 3, and 4.
[b] This value is considered to be in error (see text).

Solvent Effects on Non-electrolytes.—The limiting value of the Raoult's law activity coefficient, γ^∞, of a solute in a given solvent is defined by equation (2), in which P is the vapour pressure of the solute above a solution of N mol fraction solute and P^0 is the vapour pressure of the pure solute.

$$\gamma^\infty = (P/P^0 \,.\, N)_{N\to O} \quad (2)$$

Since $\Delta G_t^x = RT \ln (\gamma_2^\infty/\gamma_1^\infty)$, where the subscripts refer to solvents 1 and 2, equation (3) follows for a given solute. The ratio $(P_2/N_2) : (P_1/N_1)$ can be determined[3] by g.l.c. analysis of the vapour above dilute solutions of the solute in solvents 1 and 2, and values of ΔG_t^x thus calculated.

$$\Delta G_t^x = RT \ln \left[\frac{(P_2/N_2)_{N\to O}}{(P_1/N_1)_{N\to O}}\right] \quad (3)$$

Table 6 gives values of ΔG_t^x for a number of volatile non-electrolytes in a variety of solvents. Although the absolute values of γ^∞ are not required in order to calculate ΔG_t^x values, these values were determined by comparison of the detector response to the vapour above a dilute solution of the solute with the detector response to the pure solute. Values of γ^∞ for the various solutes in solvent methanol are also in Table 6.

Values of ΔG_t^x for the solutes in Table 6 generally decrease with decrease in the polar character of the solvent, but except for transfer to water, solvent effects on the free energies of the solutes are not exceptionally large. All the solutes in Table 6 are relatively non-polarisable, and it is of interest to compare solvent effects on these solutes with solvent effects on a polarisable non-electrolyte. Figure 1 shows plots of ΔG_t^x for t-butyl chloride and *p*-nitrobenzyl chloride against $\Delta G_t^x(Me_4NCl)$. Whereas the plot of $\Delta G_t^x(Bu^tCl)$ against $\Delta G_t^x(Me_4NCl)$ yields a single smooth curve which includes points for both hydroxylic and aprotic solvents, a plot of $\Delta G_t^x(p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH_2Cl)$ against $\Delta G_t^x(Me_4NCl)$ results in two distinct curves, that for hydroxylic solvents being about 1·5 kcal mol^{-1} above the curve for aprotic solvents.

These results suggest that information on the nature of a neutral transition state can be obtained through a plot of values of $\Delta G_t^\circ(Tr)$ against ΔG_t° values for a model ion pair. If the transition state resembles an ion pair, a straight line of unit positive slope should be obtained

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[10] R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, 1965, **69**, 4208; D. F. Evans and P. Gardam, *ibid.*, 1968, **72**, 3281; 1969, **73**, 158; M. A. Matesich, J. A. Nadas, and D. F. Evans, *ibid.*, 1970, **74**, 4568.

[11] S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, 1964, **68**, 911.

[12] B. J. Levien, *Austral. J. Chem.*, 1965, **18**, 1161.

[13] D. F. Evans and R. L. Kay, *J. Phys. Chem.*, 1966, **70**, 366.

[14] V. E. Bower and R. A. Robinson, *Trans. Faraday Soc.*, 1963, **59**, 1717.

[15] A. A. Vernon and J. L. Sheard, *J. Amer. Chem. Soc.*, 1948, **70**, 2035.

[16] N. Bjerrum and E. Jozefowicz, *Z. phys. Chem.*, 1932, **159***A*, 194.

[17] R. H. Boyd, *J. Chem. Phys.*, 1969, **51**, 1470.

[18] H. Strehlow, in 'The Chemistry of Non-Aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1966, vol. I, p. 147.

[19] R. G. Larson and H. Hunt, *J. Phys. Chem.*, 1939, **43**, 417.

[20] A. Lannung, *Z. Phys. Chem.*, 1932, **161**, *A*, 255.

[21] C. L. de Ligny, D. Bax, M. Alfenaar, and M. G. L. Elferink, *Rec. Trav. chim.*, 1969, **38**, 1183.

with both hydroxylic and aprotic solvents. If the transition state resembles a non-polarisable non-electrolyte, a single curve with negative slope as in Figure 1(a) should be obtained, and if the transition state resembles a polarisable non-electrolyte then the double curves in Figure 1(b) should be observed. Naturally, these three divisions are extreme examples and various combinations are obviously possible.

TABLE 6

Free energies of transfer (on the mol-fraction scale) from methanol to other solvents of some non-electrolytes at 298 K [a]

		ΔG_t^x/kcal mol^{-1}					
No.	Solvent	Bu^tCl	Bu^tBr	Me_4Sn	Me_4Pb	Et_4Sn	Et_4Pb
1	Water	4·57 [b]	4·55 [e]	5·60 [c]	5·38 [c]	8·28 [d]	8·18 [e]
2	Methanol	0	0	0	0	0	0
3	Ethanol	−0·26 (−0·24) [f]	−0·39	−0·43	−0·5 [g]	−0·53	−0·77
4	n-Propanol	−0·34		−0·78	−0·8 [g]	−0·87	−1·09
5	Propan-2-ol	−0·30	−0·48				
6	n-Butanol	−0·46 (−0·46) [f]					
8	t-Butyl alcohol	−0·46	−0·60	−1·33		−1·56	
	Acetic acid	−0·29 (−0·26) [b]	−0·38	−0·20	−0·2 [g]	−0·13	−0·1 [g]
9	Dimethyl sulphoxide	+0·08 (−0·2) [h]	+0·15	+0·41	−0·5 [g]	+0·52	+0·61
10	Nitromethane	−0·18 (−0·14) [f]	−0·23	+0·09		+0·49	
11	Acetonitrile	−0·39		−0·07	0 [g]	+0·18	+0·24
12	Dimethylformamide	−0·54 (−0·55)	−0·73 (−0·8)	−0·42		−0·39	
13	*N*-Methyl-2-pyrrolidone	−0·50 [h]					
15	Nitrobenzene	−0·75					
17	Acetone	−0·83	−0·84	−0·80	−0·8 [g]	−0·93	−0·90
29	Chlorobenzene	−1·12		−1·56		−2·19	
	Dioxan	−0·81					
30	Ether	−0·95 [g]					
31	Benzene	−1·06		−1·55	−1·8 [g]	−2·16 [g]	−2·39
32	Carbon tetrachloride			−1·78	−2·1 [g]	−2·27 [g]	−2·63
	Pentane	−0·93 [f]					
	Decane	−1·03		−1·79		−2·27 [g]	
	γ^{∞} [j]	10	13	31		65	85

[a] Determined by the g.l.c. method (present work) unless indicated otherwise. [b] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937. [c] Estimated by the method given in ref. 4. [d] Ref. 4. [e] Using data by C. J. Feldhake and C. D. Stevens, *J. Chem. and Eng. Data*, 1963, **8**, 196; estimation by the method of ref. 4 gives a value of 8·11. [f] E. S. Rudakov and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1965, **2**, 135, 142. [g] Estimated value. [h] Ref. 29. [i] Ref. 41. [j] Rault's law activity coefficient of the non-electrolyte in methanol solvent.

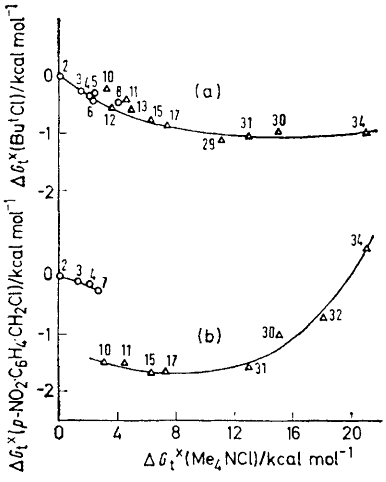

FIGURE 1 Plot of (a) $\Delta G_t^x(Bu^tCl)$ and (b) $\Delta G_t^x(p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH_2Cl)$ against $\Delta G_t^x(Me_4NCl)$; ○ hydroxylic solvents, △ aprotic solvents; solvents are numbered as in the Tables

Solvent Effects on the Decomposition of t-Butyl Chloride.—The rate of production of acid from t-butyl chloride in a variety of solvents has been investigated by numerous sets of workers. With non-polar solvents, the reaction is normally [22,23] carried out in the presence of various quantities of a base such as pyridine and the rate constant extrapolated to zero concentration of base. In both polar and non-polar solvents, however, the rate of production of acid is found to be proportional to the concentration of t-butyl chloride and it may therefore be deduced that (apart from an indeterminate number of solvent molecules) the transition state for the decomposition has the molecular formula C_4H_9Cl. Even though the decomposition follows a simple first-order rate law, the overall reaction may be kinetically complex; a possible reaction scheme is given in equation (4). The steady-state approximation yields for the observed first-order rate constant for production of acid, k_1^{obs}, the expression (5). Thus if equation (4) holds, in general

$$\mathrm{Bu^tCl} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Ion pair} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Bu^{t+}} + \mathrm{Cl^-} \xrightarrow{\text{fast}} \text{Products} \qquad (4)$$

$$k_1^{obs} = k_1 \cdot k_3/(k_2 + k_3) \qquad (5)$$

the observed free energy of activation, $\Delta G^{\ddagger}_{obs}$, will be a complex quantity. If $k_2 \ll k_3$ there is no problem, for then $k_1^{obs} = k_1$ and values of $\Delta G^{\ddagger}_{obs}$ can be taken as those for the elementary act of ionisation of t-butyl chloride; the transition state referred to in equation (6)

$$\Delta G^{\ddagger}_{obs} = \Delta G_f^{\circ}(Tr) - \Delta G_f^{\circ}(Bu^tCl) \qquad (6)$$

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[22] E. S. Rudakov, G. P. Valueva, and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1967, **4**, 150.

[23] Y. Pocker and R. F. Buchholz, *J. Amer. Chem. Soc.*, 1970, **92**, 4033.

will lie between the t-butyl chloride reactant and the ion pair. Even if $k_2 \gg k_3$ there is no difficulty, because it can be shown quite easily that equation (6) again applies, although now the transition state will lie between the ion pair and the dissociated pair of ions. The real difficulty occurs if $k_2 \simeq k_3$; in the least favourable case in which $k_2 = k_3$, then $k_1^{\text{obs}} = k_1/2$ and it follows that, at 298 K, $\Delta G^{\ddagger}_{\text{obs}} = \Delta G^{\ddagger}_1 + 0{\cdot}41$ kcal mol^{-1}. Hence if the reaction scheme (4) is valid, use of equation (6) will result in a maximum possible error of $+0{\cdot}41$ kcal mol^{-1} in the calculated value of $\Delta G_f{}^{\circ}(\text{Tr})$. Since the various $\Delta G_f{}^{\circ}(\text{Tr})$ values span a range of 14 kcal mol^{-1} over the solvents studied, this maximum error is not significant. The decomposition of t-butyl chloride, especially in aprotic solvents, can also take place by the single elementary elimination reaction (7); in this case, however, equation (6) will still apply.

TABLE 7

Calculation of free energies of transfer (on the mol-fraction scale) from methanol to other solvents of the transition state in the decomposition of t-butyl chloride at 298 K

				$\Delta G_t{}^x$/kcal mol^{-1}			
No.	Solvent	$-\log k$ [a]	$\delta\Delta G^{\ddagger}$	Bu^{t}Cl	[Bu^{t}Cl]‡	Me$_4$NCl	Me$_4$N$^+$ + Cl$^-$
1	Water	1·54 [c]	−6·22	4·57	−1·65	−3·0	−3·7
2	Methanol	6·10 [d]	0	0	0	0	0
	Acetic acid	6·71 [e]	0·83	−0·29	0·54		
3	Ethanol	7·07 [e]	1·32	−0·26	1·06	1·5	3·0
4	n-Propanol		1·68 [f]	−0·34	1·34	1·9	4·1
6	n-Butanol	7·26 [g] 7·52 [h]	1·58 1·94	−0·46 −0·46	1·12 1·48	2·2	5·1
5	Propan-2-ol		2·24 [i]	−0·30	1·94	2·3	5·2
8	t-Butyl alcohol		2·96 [i]	−0·46	2·50	3·9	8·9
10	Nitromethane	8·12 [j]	2·76	−0·18	2·58	3·1	4·1
12	Dimethylformamide	8·48 [g]	3·25	−0·54	2·71	3·5	4·3
11	Acetonitrile	8·73 [k]	3·59	−0·39	3·20	4·5	5·6
13	*N*-Methylpyrrolidone	8·97 [l]	3·92	−0·50	3·42	4·7	5·3
15	Nitrobenzene	9·72 [m]	4·94	−0·75	4·19	6·3	7·7
17	Acetone	9·9 [n]	5·18 5·59 [o]	−0·83 −0·83	4·35 4·76	6·6	9·0
	Dioxan	10·8 [n]	6·41 6·43 [o]	−0·81 −0·81	5·60 5·62		
29	Chlorobenzene	11·34 [m]	7·15	−1·12	6·03	11·1	20·5
31	Benzene	12·16 [m]	8·27	−1·06	7·21	12·9	34·1
30	Ether	10·38 [p] 12·74 [m]	5·84 9·06	−0·95 −0·95	4·89 8·11	15·1	27·7
34 [q]	Pentane	16·0 [g]	13·51	−1·0	12·51	21·3 [q]	

[a] Observed rate constant/s^{-1}. [b] Ion pair. [c] Ref. 26. [d] Recorded values are 6·12,[24] 6·10,[25] and 6·06.[26] [e] Ref. 24. [f] Estimated through a plot of $\delta\Delta G^{\ddagger}$ against E_T for alcohols. [g] Table 6, footnote *f*. [h] E. S. Rudakov and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1964, **1**, 114. [i] From Y values in ref. 24. [j] Y. Pocker, *J. Chem. Soc.*, 1960, 1972. [k] From data at 45 °C by D. N. Kevill and J. E. Dorsey, *Chem. and Ind.*, 1967, 2174, with $E_A = 25$ kcal mol^{-1}. [l] From data at 60 °C by P. O. I. Virtanen, *Suomen Kem.*. 1967. **40**, *B*, 1 with $E_A = 25$ kcal mol^{-1}. [m] Estimated from high-temperature data in ref. 27. [n] Ref. 25. [o] From Y values given by P. R. Wells, ' Linear Free Energy Relationships,' Academic Press, London, 1968. [p] Ref. 23. [q] Solvent hexane.

$$\text{Bu}^t\text{Cl} \longrightarrow \text{Me}_2\text{C:CH}_2 + \text{HCl} \qquad (7)$$

If equation (6) is applied to reactions taking place in the reference solvent (usually methanol, in the present work) and in some other solvent, equation (8) results. In this equation, $\delta\Delta G^{\ddagger}$ is the observed free energy of activation in the other solvent less the observed free

$$\Delta G_t{}^{\circ}([\text{Bu}^t\text{Cl}]^{\ddagger}) = \Delta G_t{}^{\circ}(\text{Bu}^t\text{Cl}) + \delta\Delta G^{\ddagger} \qquad (8)$$

energy of activation in the reference solvent. It should be noted that the validity of equation (8) does not depend on any assumptions about the nature of the [Bu^{t}Cl]‡ transition state or about the mechanism of the decomposition. Solvent effects on values of $\Delta G^{\ddagger}_{\text{obs}}$ can thus be dissected into initial-state and transition-state contributions through equation (8); details are in Table 7. Rate constants at 298 K have been taken from a number of previous investigations [24-26] and in addition a few rate constants have been estimated from the high-temperature data of Koppel and Palm.[27] Since the units of the rate constant are s^{-1}, values of $\Delta G_t{}^{\circ}$ in equation (8) can be expressed on any convenient concentration scale. The mol-fraction standard state is the most fundamental such scale, and the standard free energies of transfer in Table 7 are based on this scale. The $\Delta G_t{}^x(\text{Me}_4\text{NCl})$ values in Table 7 have been derived from the $\Delta G_t{}^c(\text{Me}_4\text{NCl})$ values in Table 3; they differ from the values given in a preliminary account [7] because the new values have been calculated from the solubilities determined in the present work and from more recent ancillary data.

In Figure 2 are plotted values of $\Delta G_t{}^x([\text{Bu}^t\text{Cl}]^{\ddagger})$ against $\Delta G_t{}^x(\text{Me}_4\text{NCl})$. Points for the more polar solvents 1—13 fall on a line of slope $0{\cdot}67 \pm 0{\cdot}02$ whereas a plot (not shown) of $\Delta G_t{}^x([\text{Bu}^t\text{Cl}]^{\ddagger})$ against $\Delta G_t{}^x$-$(\text{Me}_4\text{N}^+ + \text{Cl}^-)$ yields a poor line of slope only $0{\cdot}39 \pm 0{\cdot}05$ for the same polar solvents. Thus for solvents

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[24] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**. 2770.

[25] E. S. Rudakov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **127**, 1058.

[26] J. Biordi and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1962, 4291; E. A. Moelwyn-Hughes, *ibid.*, p. 4301.

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

1—13, it follows that the transition state does not lie between the $Bu^{t+}Cl^-$ ion pair and the dissociated pair of ions, $Bu^{t+} + Cl^-$, but lies between the t-butyl chloride reactant and the $Bu^{t+}Cl^-$ ion pair. Hence if scheme (4) applies to reaction in these solvents, then $k_3 > k_2$ and $k_1^{obs} \simeq k_1$. The value of the slope, 0·67, provides an estimate of the *minimum* degree of charge separation in the transition state because a plot of $\Delta G_t^x(Bu^tCl)$ against $\Delta G_t^x(Me_4NCl)$ for solvents 2—13 results in a line of slope *ca.* —0·11 (see Figure 1). A correction for this negative non-electrostatic effect yields a value of 0·70 for the average degree of charge separation in the $[Bu^tCl]^‡$ transition state over the range of solvents 1—13. This conclusion that the transition state markedly resembles an ion pair is in accord with results of previous workers who are agreed[4,6] that the transition state is ion-pair-like in character.

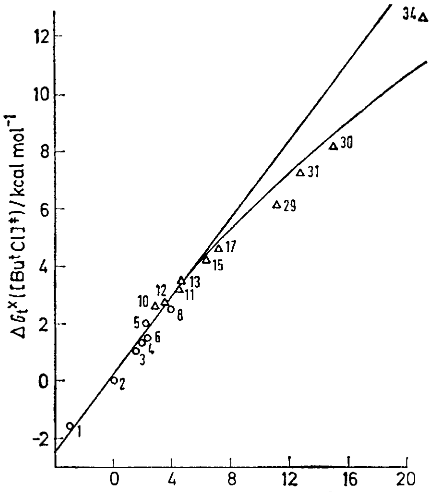

FIGURE 2 Plot of $\Delta G_t^x([Bu^tCl]^‡)$ against $\Delta G_t^x(Me_4NCl)$; ○ hydroxylic solvents, △ aprotic solvents; solvents are numbered as in the Tables

As seen from Figure 2, the slope of the line for the less polar solvents 15, 17, 29—31, and 34 is substantially less than that for the polar solvents, being only 0·55 (if solvent 34, hexane, is excluded the slope falls to 0·45). Over the range of non-polar solvents used, no correction is necessary for the non-electrostatic effect, so that the average degree of charge separation in the transition state can be estimated as 0·45—0·55 when the non-polar solvents are used. Whatever the geometry and structure of the transition state in the less polar solvents, it may be concluded that the transition state still behaves as though it carried a substantial separation of charge, although the degree of charge separation is not as high as in the polar solvents.

Since (see Figure 2) $\Delta G_t^x([Bu^tCl]^‡)$ correlates very well with $\Delta G_t^x(Me_4NCl)$ for polar solvents, interaction of the transition state with these solvents, Nos. 1—13, must be qualitatively and semiquantitatively similar to interaction of these solvents with the Me_4NCl ion pair. There is no need (*cf.* also ref. 28) to invoke concepts such as special nucleophilic solvent assistance or nucleophilic solvent participation in order to account for the present results.

With the exception of transfer to water, initial-state solvent effects on $\delta\Delta G^‡$ are small in comparison with the values of $\delta\Delta G^‡$. Hence $\delta\Delta G^‡ \simeq \Delta G_t^x([Bu^tCl]^‡)$, and a plot (not shown) of $\delta\Delta G^‡$ or of —log k against $\Delta G_t^x(Me_4NCl)$ yields a result similar to that shown in Figure 2 when values of $\delta\Delta G^‡$ or of —log k at 298 K are used. Koppel and Palm[27] have determined values of —log k at 393 K for a slightly different range of solvents than that shown in Figure 2, and a plot of —log k at 393 K against $\Delta G_t^x(Me_4NCl)$ is shown in Figure 3. In spite of the 95 K difference, the values of —log k at 393 K are correlated exactly as would be predicted, with a high value for the slope in the polar solvent range and a lower value in the non-polar solvent range.

The suggestion (above) that charge separation in the $[Bu^tCl]^‡$ transition state in non-polar solvents is appreciably less than in polar solvents is based, of course, on the values of $\Delta G_t^\circ(Me_4NCl)$ in these non-polar solvents. Although such values are much less reliable than values in polar solvents, only very large errors in $\Delta G_t^\circ(Me_4NCl)$ will significantly affect this conclusion. For example, in order for the points for solvents hexane and benzene in Figure 3 to lie on the line for the polar solvents, values of $\Delta G_t^\circ(Me_4NCl)$ would have to be reduced from 21 to 12 kcal mol^{-1} (hexane) and from 13 to 8 kcal mol^{-1} (benzene); such reductions seem to be outside any possible errors.

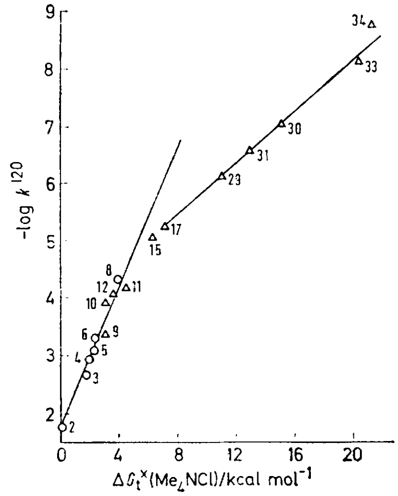

FIGURE 3 Plot of —log k for the decomposition of t-butyl chloride at 120 °C against $\Delta G_t^x(Me_4NCl)$; ○ hydroxylic solvents, △ aprotic solvents; solvents are numbered as in the Tables

In Table 7 two values are given for —log k in solvent ether, 10·38 being a direct determination[23] at 25 °C, and 12·74 being an estimated value from high-temperature data. The value of 10·38 leads to a value for $\Delta G_t^x([Bu^tCl]^‡)$ that seems too low by over 3 kcal mol^{-1},

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[28] D. J. Raber, R. C. Bingham, J. M. Harris. J. L. Fry. and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 5977.

whereas the estimated value appears to be quite reasonable. However, I have no explanation for this anomaly.

Solvent Effects in the Decomposition of t-Butyl Bromide.—An analysis of solvent effects on $\Delta G^{\ddagger}$ for the rate of acid production from t-butyl bromide can be carried out for a number of polar solvents; results are in Table 8.

TABLE 8

Calculation of free energies of transfer (on the mol-fraction scale) from methanol to other solvents of the transition state in the decomposition of t-butyl bromide at 298 K

				ΔG_t^x/kcal mol^{-1}		
No.	Solvent	$-\log k$ [a]	$\delta\Delta G^{\ddagger}$	Bu^tBr	$[Bu^tBr]^{\ddagger}$	Me_4NBr [b]
1	Water	0·119 [c]	−5·92	4·55	−1·37	−2·0
2	Methanol	4·46 [c]	0	0	0	0
3	Ethanol	5·35 [d]	1·21	−0·39	0·82	1·3
	Acetic acid	5·52 [e]	1·45	−0·38	1·07	
5	Propan-2-ol		2·10 [f]	−0·48	1·62	2·1
8	t-Butyl alcohol		2·78 [f]	−0·60	2·18	3·7
10	Nitromethane	5·44 [g]	1·34	−0·23	1·11	1·6
12	Dimethylformamide	5·62 [h]	1·59	−0·73	0·86	1·9
13	*N*-Methylpyrrolidone	6·00 [i]	2·10	−0·7 [j]	1·40	2·8
17	Acetone	7·13 [k]	3·64	−0·84	2·80	4·3

[a] Observed rate constant/s^{-1}. [b] Ion pair. [c] Ref. 26. [d] M. L. Dhar, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1948, 2065. [e] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1602. [f] From *Y*-values in ref. 24, with $m = 0·94$. [g] S. Winstein, S. Smith, and D. Darwish, *Tetrahedron Letters*, 1959, No. 16, 24. [h] N. Kornblum and R. K. Blackwood, *J. Amer. Chem. Soc.*, 1956, **78**, 4037. [i] P. O. I. Virtanen, *Suomen Kem.*, 1967, **40**, *B*, 1. [j] Estimated value. [k] From data in footnote *g*.

The only previous calculation on these lines is that of Parker[29] who finds that $\Delta G_t^x([Bu^tBr]^{\ddagger}) = 1·1$ kcal mol^{-1} for transfer from methanol to dimethylformamide as compared with the present value of 0·9 kcal mol^{-1}. Just as for the t-butyl chloride reaction, solvent effects on $\Delta G^{\ddagger}$ (Table 8) are largely due to solvent effects on the transition state. Only for transfer to water does the value of $\Delta G_t^x(Bu^tBr)$ become large in comparison with the value of $\Delta G_t^x([Bu^tBr]^{\ddagger})$.

A plot (not shown) of $\Delta G_t^x([Bu^tBr]^{\ddagger})$ against $\Delta G_t^x(Me_4NBr)$ yields a reasonable straight line of slope $0·61 \pm 0·03$; correction for the non-electrostatic effect raises this value to 0·68. Hence the transition state must again lie between the reactant and the ion pair, $Bu^{t+}Br^-$, and must carry the considerable charge separation of *ca.* 0·68 unit. This value is only slightly less than the corresponding value for the $[Bu^tCl]^{\ddagger}$ transition state, 0·70, and indicates the close similarity in the two transition states when polar solvents are used as the reaction media. The ratio of charge separation in the transition states in polar media, 0·68 : 0·70, is 0·97 from the present results as compared with a ratio of 0·96 found for reactions in the methanol–water system.[4]

Solvent Effects in the Menschutkin Reaction.—A separation of solvent influences on the rate of the Menschutkin reaction (9; Ar = p-$NO_2{\cdot}C_6H_4$) into initial-state and transition-state contributions has already been

$$Me_3N + ArCH_2Cl \longrightarrow ArCH_2\overset{+}{N}Me_3 + Cl^- \quad (9)$$

carried out,[2] and values of $\Delta G_t^x([Me_3N\text{-}ArCH_2Cl]^{\ddagger})$ have been compared with values of $\Delta G_t^x(Et_4NI)$. However, the Et_4NI ion pair is not a very good model for the $[Me_3N\text{-}ArCH_2Cl]^{\ddagger}$ transition state, and Figure 4 shows a plot of $\Delta G_t^x([Me_3N\text{-}ArCH_2Cl]^{\ddagger})$ against $\Delta G_t^x(Et_4NCl)$. The similarity between Figure 4 and Figure 1(b) is striking, and confirms the previous conclusion[2] that $[Me_3N\text{-}ArCH_2Cl]^{\ddagger}$ transition state more resembles a polarisable non-electrolyte than an ion pair. The slope of the line in Figure 4 for the aprotic solvents is 0·43 and this value also indicates that charge separation in the transition state is not very large. The value of 0·43 for the slope may be taken as a maximum value for the degree of charge separation, because the 'polarisability or non-electrostatic effect' now makes a positive contribution to the slope [see Figure 1(b)]. Indeed, values of $\Delta G_t^x([Me_3N\text{-}ArCH_2Cl]^{\ddagger})$ for both hydroxylic and aprotic solvents can be correlated quite well by use of the two-parameter equation (10), as shown by Table 9.

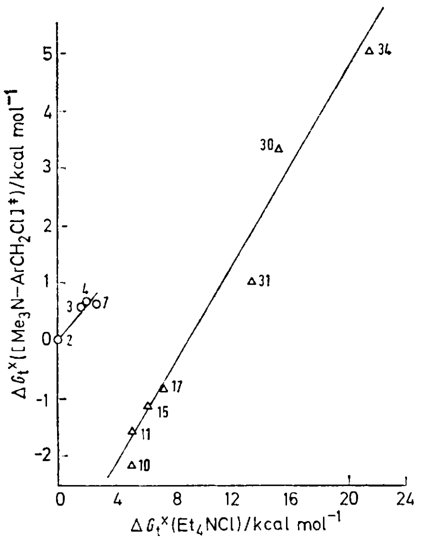

FIGURE 4 Plot of $\Delta G_t^x([Me_3N\text{-}p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH_2Cl]^{\ddagger})$ against $\Delta G_t^x(Et_4NCl)$; ○ hydroxylic solvents, △ aprotic solvents; solvents are numbered as in the Tables

$$\Delta G_t^x([Me_3N\text{-}ArCH_2Cl]^{\ddagger}) = 0·35\Delta G_t^x(Et_4NCl) + 2·0\Delta G_t^x(ArCH_2Cl) \quad (10)$$

With the exception of the point for solvent hexane, equation (10) reproduces the ΔG_t^x values to within

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[29] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

±0·4 kcal mol^{-1}. On the above analysis, the transition state $[Me_3N{-}ArCH_2Cl]^‡$, where Ar = p-$NO_2{\cdot}C_6H_4$, may be said to behave as though it carried a separation of only 0·35 unit of charge and was considerably more polarisable than the non-electrolyte *p*-nitrobenzyl chloride.

Table 9

Solvent	$\Delta G_t^x([Me_3N{-}ArCH_2Cl]^‡)$/kcal mol^{-1} Observed[2]	Calc. *via* equation (10)
Nitromethane	−2·2	−1·3
Acetonitrile	−1·6	−1·2
Nitrobenzene	−1·2	−1·3
Acetone	−0·9	−0·8
Methanol	0	0
Ethanol	0·5	0·3
3-Methylbutanol	0·6	0·4
n-Propanol	0·7	0·4
Benzene	1·0	1·4
Ether	3·3	3·2
Hexane	5·0	8·7

Although initial-state solvent effects can be quite large in reaction (9; Ar = p-$NO_2{\cdot}C_6H_4$), values of $\delta\Delta G^‡$ still tend to parallel values of $\Delta G_t^x([Me_3N{-}ArCH_2{-}Cl]^‡)$ for many aprotic solvents. Hence a plot of $\delta\Delta G^‡$ against $\Delta G_t^x(Et_4NCl)$ also yields a straight line, this time of slope 0·36, when only aprotic solvents are included. For all Menschutkin reactions that have been studied in both hydroxylic and aprotic solvents (*e.g.*, see refs. 2 and 30—33) plots of $\delta\Delta G^‡$ against ΔG_t°(Ion pair) are similar to the one shown in Figure 4. Table 10 summarises the results of plotting $\delta\Delta G^‡$ for various Menschutkin reactions against ΔG_t° for the simple tetra-alkylammonium halide ion pairs, with data restricted to aprotic solvents only. For bimolecular reactions with rate constants in units of l mol^{-1} s^{-1}, values of $\delta\Delta G^‡$ should be compared with ΔG_t^c values for an ion pair. Alternatively [2] the rate constant units can be converted to mol-fraction^{-1} s^{-1} and the derived values of $\delta\Delta G^‡$ then compared with ΔG_t^x values. In practice, results from the two methods of treatment are very similar.

Table 10

Correlation of solvent effects on values of $\delta\Delta G^‡$ for Menschutkin reactions with corresponding solvent effects on the free energy of ion pairs

Reactants	t/°C	Abscissa	Slope [a]	Solvents
$Et_3N + EtI$ [b]	30	$\Delta G_t^c(Et_4NI)$	0·42	9. 14—18, 20, 21, 24, 26, 29, 31, 34
$Et_3N + EtI$ [c]	100	$\Delta G_t^c(Et_4NI)$	0·42	17, 19, 26—31, 34
$Et_3N + EtI$ [d]	100	$\Delta G_t^c(Et_4NI)$	0·47	15, 16, 26, 29, 31, 33, 34
$Pr^n_3N + MeI$ [e]	20	$\Delta G_t^c(Et_4NI)$	0·45	10—12, 14—24, 26—34
Me_3N + p-$NO_2C_6H_4CH_2Cl$ [f]	25	$\Delta G_t^x(Et_4NCl)$	0·36	10, 11, 15, 17, 30, 31, 34
X-$C_6H_4{\cdot}CH_2NMe_2 + MeI$ [g]	30	$\Delta G_t^c(Et_4NI)$	0·46 [h]	11, 15, 17, 26, 29, 31, 33
$C_5H_5N + MeI$ [i]	25	$\Delta G_t^x(Et_4NI)$	0·41	10, 15—17, 26, 29, 31, 32
$C_5H_5N + MeI$ [i]	25	$\Delta G_t^x(Me_4NI)$	0·40	10, 15, 17, 29, 31, 32
X-$C_6H_4NMe_2 + MeI$ [j]	30	$\Delta G_t^c(Et_4NI)$	0·44 [k]	11, 15, 17, 18, 31
$Et_3N + ICH_2CO_2Et$ [l]	20	$\Delta G_t^c(Et_4NI)$	0·31	10, 11, 13—20, 31—33
$Et_4N + BrCH_2CO_2Et$ [l]	20	$\Delta G_t^c(Et_4NBr)$	0·27	10, 11, 13—18, 31—33

[a] Standard deviations in the values for the slopes ranged from 0·01 to 0·02. [b] Ref. 32. [c] Ref. 30. [d] H. G. Grimm, H. Ruf, and H. Wolff, *Z. phys. Chem.*, 1931, **13**, *B*, 301. [e] Ref. 31. [f] H. von Halban. *Z. phys. Chem.*. 1913, **84**. 129; see also ref. 2. [g] Ref. 33. [h] Value for X = H; values for other substituents are in the text. [i] H. Hartmann, H. Kelm, and G. Rinck, *Z. phys. Chem.* (*Frankfurt*), 1965, **44**, 335; H. Hartmann and A. P. Schmidt, *ibid.*, 1968, **62**, 312; K. Kalliorinne and E. Tommila, *Suomen Kem.*. 1967, **40**, *B*, 109. [j] Ref. 34. [k] Value for X = H; values for other substituents are 0·43 (*p*-Me), and 0·45 (*m*-Me). [l] Y. Drougard and D. Decroocq, *Bull. Soc. chim. France*, 1969, 2972.

For the nine sets of data that refer to experiments at near room temperature (Table 10) the average value of the slope of the line obtained on plotting $\delta\Delta G^‡$ against ΔG_t°(Ion pair) is 0·39. The two reactions involving the substrates $ICH_2{\cdot}CO_2Et$ and $BrCH_2{\cdot}CO_2Et$ give rise to significantly lower slopes, and if data on these reactions are omitted the average value for the remaining seven sets of data rises to 0·42. In general, therefore, transition states in Menschutkin reactions behave towards change of solvent as though they carried a charge separation of only about 0·4 unit. It is noteworthy that reasonable correlations of $\delta\Delta G^‡$ with $\Delta G_t^\circ(Et_4NI)$ or $\Delta G_t^\circ(Et_4NCl)$ are obtained even for Menschutkin reactions that involve aromatic compounds as one or other of the reactants. The Et_4NI ion pair, for example, must therefore be a suitable comparative standard not only for the $[Et_3N{-}EtI]^‡$ transition state but also (perhaps surprisingly) for the $[PhCH_2NMe_2{-}MeI]^‡$ and $[PhNMe_2{-}MeI]^‡$ transition states.

When values [33] of $\delta\Delta G^‡$ for the Menschutkin reactions of the amines X–$C_6H_4{\cdot}CH_2NMe_2$ with methyl iodide in solvents **11**, **15**, **17**, **26**, **29**, **31**, and **33** are plotted against $\Delta G_t^c(Et_4NI)$ values, there is a significant increase in the slope of the resulting lines with increase in the electron-attracting character of the group X (Table 11). It is possible that the degree of charge separation in the $[X{-}C_6H_4CH_2NMe_2{-}MeI]^‡$ transition states gradually increases along the above series.

Table 11

X	*p*-OMe	*m*-Me	H	*p*-Cl	*m*-Cl	*m*-NO_2	*p*-NO_2
Slope	0·43	0·45	0·46	0·51	0·51	0·56	0·61

The ratio $\delta\Delta G^‡/\Delta G_t^\circ$ (Ion pair) seems to be a reason-

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[30] N. Menschutkin, *Z. phys. Chem.*, 1890, **6**, 41.

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

[32] S. Eagle and J. C. Warner, *J. Amer. Chem. Soc.*, 1939. **61**. 488; H. Hartmann, H. D. Brauer, and G. Rinck, *Z. phys. Chem.* (*Frankfurt*), 1968, **61**, 47; H. Hartmann and A. P. Schmidt. *ibid.*, 1969, **66**, 183.

[33] T. Matsui and N. Tokura, *Bull. Chem. Soc. Japan*, 1971, **44**. 756.

able approximation to the fundamental ratio $\Delta G_t^\circ(\text{Tr})/\Delta G_t^\circ$ (Ion pair). In some circumstances, another method of approximation is possible, as follows. Rate constants for the Menschutkin reaction of dimethylanilines with methyl iodide usually decrease with the extent of reaction in any given kinetic run owing to[34,35] the incursion of the equilibrium process (11). If the rate constant for the forward (Menschutkin) reaction is denoted as k_{11} and if the equilibrium constant for reaction (11) is denoted as K_{11} equation (12) can easily be

$$X\text{–}C_6H_4NMe_2 + MeI \rightleftharpoons X\text{–}C_6H_4NMe_3I \qquad (11)$$

derived, where $\Delta \log k_{11}$ and $\Delta \log K_{11}$ refer to solvent

$$\frac{\Delta \log k_{11}}{\Delta \log K_{11}} = \frac{\Delta G_{11}^\ddagger}{\Delta G_{11}^\circ} = \frac{\Delta G_t^\circ(\text{Tr}) - \Delta G_t^\circ(\text{Reactants})}{\Delta G_t^\circ(\text{Ion pair}) - \Delta G_t^\circ(\text{Reactants})} \qquad (12)$$

effects on $\log k_{11}$ and $\log K_{11}$ respectively. For reactions in aprotic solvents, the term ΔG_t°(Reactants) is usually much smaller than either of the terms ΔG_t°(Tr) and ΔG_t°(Ion pair), so that the ratio $\Delta \log k_{11}/\Delta \log K_{11}$ (or $\Delta G_{11}^\ddagger/\Delta G_{11}^\circ$) should provide a good estimate of the required ratio $\Delta G_t^\circ(\text{Tr})/\Delta G_t^\circ(\text{Ion pair})$.

TABLE 12

Free energies of transfer (on the mol-fraction scale) from acetone to other solvents of the reactants and transition state in the Menschutkin reaction of *NN*-dimethylaniline with methyl iodide at 298 K

		ΔG_t^x/kcal mol^{-1}				
Solvent	$\delta\Delta G^{x\ddagger}$ [a]	MeI [b]	$PhNMe_2$ [c]	$[PhNMe_2\text{–}MeI]^\ddagger$	$PhNMe_3I$ [d]	Et_4NI [d]
Methanol	0·0	1·1	0·7	1·8		−1·9
Acetone	0	0	0	0	0	0
Benzene	2·2	−0·2	0·0	2·0	3·8—5·1 [e]	4·5
Methyl acetate			0·1			
Carbon tetrachloride		−0·1				

[a] Ref. 34. [b] From ref. 36 and data by D. I. R. Low and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1964, *A*. **281**. 366. [c] Calculated from data by G. Weissenberger, F. Schuster, and J. Lielacher, *Monatsh.*, 1925, **46**, 301. [d] Ion pair. [e] These values are based on different estimates of $K_{11}(X = H)$ at 25 °C.

Matsui and Tokura[34] have determined values of k_{11} and K_{11} for reaction (11) using 6 aprotic solvents, and a plot of $\Delta \log k_{11}$ against $\Delta \log K_{11}$ yields a line of slope 0·38 when both k_{11} and K_{11} are expressed in mol-fraction units. With additional data from Rossell[35] similar plots from use of eight aprotic solvents yield the following slopes: 0·40 (X = H, at 60 °C), 0·38 (X = H, at 50 °C), 0·43 (X = *m*-Me, at 60 °C) and 0·42 (X = *m*-Me, at 50 °C) with both constants now expressed in molar units. The results of this treatment are thus in excellent accord with those of the previous method, when $\delta\Delta G_{11}^\ddagger$ was plotted against $\Delta G_t^\circ(Et_4NI)$.

A dissection of solvent effects on values of $\Delta G_{11}^\ddagger$ into initial-state and transition-state contributions can be carried out for three solvents; details are in Table 12, where the reference solvent is now taken as acetone. Although data are limited, it seems clear from Table 12 that (i) solvent effects on the reactants in equation (11; X = H) are small when only aprotic solvents are considered, and hence the above approximation must be reasonable for such solvents; (ii) the value of the free energy of the $[PhNMe_2\text{–}MeI]^\ddagger$ transition state in methanol is much higher (≥2 kcal mol^{-1}) than in polar aprotic solvents (*cf.* Figure 4); (iii) the transition state resembles the reactants at least as much as it does the product ion pair; and (iv) solvent effects on the $PhNMe_3I$ ion pair are probably of the same magnitude as solvent effects on the Et_4NI ion pair. The success of the method (Table 10) in which values of $\Delta G_t^\circ(Et_4NI)$ are plotted against values of $\delta\Delta G^\ddagger$, not only for the reaction between triethylamine and ethyl iodide, but also for reactions involving aromatic substrates, is thus explained.

Table 12 contains one direct (but approximate) comparison of ΔG_t° values for a transition state with ΔG_t° values for the product ion pair. Similar comparisons are possible in only one other case, that of the reaction between trimethylamine and methyl iodide.[36] Details are in Table 13 and again it is evident that the transition state resembles the reactants rather more than it resembles the Me_4NI ion pair. The dissociated product ($Me_4N^+ + I^-$) is even further removed from the transition state than is the ion pair.

TABLE 13

A comparison of free energies of transfer (on the molar scale) from methanol to other solvents of the $[Me_3N\text{–}MeI]^\ddagger$ transition state with the corresponding reactants and products at 298 K

	ΔG_t^c/kcal mol^{-1}			
Solvent	Me_3N + MeI [a]	$[Me_3N\text{–}MeI]^\ddagger$ [a]	Me_4NI [b]	$Me_4N^+ + I^-$ [c]
Water	2·5	1·7	−1·8	−3·2
Methanol	0	0	0	0
Benzene	0·3	0·2	6·4	27
Carbon tetrachloride	0·4	1·8	11	Very large

[a] Values from ref. 36. [b] Ion pair, values from Table 3. [c] From Table 2.

All the free-energy data in the present work are commensurate with the suggestion that the transition state in the Menschutkin reaction of tertiary amines with organic halides quite generally resembles the reactants rather than the product ion pair, and behaves towards

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

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

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

change of solvent as though it carries a charge separation of *ca.* 0·4 unit.

TABLE 14

Calculation of second-order rate constants[a] for the substitution of tetramethyl-lead by iodine at 25 °C

No.	Solvent	k_2/K	K	$k_2(Me_4Pb)$	$k_2(Et_4Pb)$ [b]
11	Acetonitrile [c,d]	$9{\cdot}58 \times 10^{-3}$	$2{\cdot}52 \times 10^{7}$ [e]	$2{\cdot}4 \times 10^{5}$	$9{\cdot}3 \times 10^{4}$
17	Acetone [d]	$1{\cdot}9 \times 10^{-4}$ [f]	$2{\cdot}0 \times 10^{8}$ [g]	$3{\cdot}8 \times 10^{4}$	$1{\cdot}4 \times 10^{4}$
9	Dimethyl sulphoxide [h]	$3{\cdot}8 \times 10^{-2}$	$2{\cdot}5 \times 10^{5}$ [i]	$9{\cdot}5 \times 10^{3}$ $(1{\cdot}1 \times 10_4)$ [j]	$2{\cdot}6 \times 10^{3}$
2	Methanol [c]	$6{\cdot}16 \times 10^{-1}$	$1{\cdot}67 \times 10^{4}$ [k]	$1{\cdot}0 \times 10^{4}$	$4{\cdot}0 \times 10^{3}$
3	Ethanol [c]	$8{\cdot}44 \times 10^{-2}$	$3{\cdot}32 \times 10^{4}$	$2{\cdot}8 \times 10^{3}$	$1{\cdot}3 \times 10^{3}$
4	n-Propanol [c]	$6{\cdot}50 \times 10^{-2}$	$2{\cdot}48 \times 10^{4}$	$1{\cdot}6 \times 10^{3}$	$7{\cdot}3 \times 10^{2}$
31	Benzene [d]			$1{\cdot}1$ [l]	$1{\cdot}3 \times 10^{1}$
32	Carbon tetrachloride			$2{\cdot}6 \times 10^{-2}$ [m]	$7{\cdot}9 \times 10^{-1}$

[a] k_2/K in s^{-1}, K in l^{-1} mol, and k_2 in l mol^{-1} s^{-1}. [b] Calculated in the same way as $k_2(Me_4Pb)$. [c] Ref. 37. [d] Ref. 38. [e] J. Desbarres, *Bull. Soc. chim. France*, 1961, 502. [f] From the observed[38] value of $4{\cdot}36 \times 10^{-4}$ at 35 °C by assuming $E_a = 15$ kcal mol^{-1} (*cf.* data in ref. 39). [g] I. V. Nelson and R. T. Iwamoto, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1964, **7**, 218. [h] At 20 °C, ref 40. [i] At 22 °C, F. W. Hiller and J. H. Krueger, *Inorg. Chem.*, 1967, **6**, 528. [j] Corrected to 25 °C by assuming $E_a = 5$ kcal mol^{-1} (*cf.* data in ref. 39). [k] Ref. 39, and O. Buchman, M. Grosjean, and J. Nasielski, *Helv. Chim. Acta*, 1964, **47**, 1679. [l] From the observed[38] value of 1·9 at 35 °C by assuming $E_a = 10$ kcal mol^{-1}. [m] From the observed[38] value of $3{\cdot}55 \times 10^{-2}$ at 31 °C by assuming $E_a = 10$ kcal mol^{-1}.

Solvent Effects in the Iododemetallation of Tetra-alkylleads.—It seemed of interest to compare solvent effects on S_N1 and S_N2 reactions with solvent effects on a typical S_E2 reaction in which only neutral reactants are involved. Tagliavini and his co-workers[37,38] have studied the electrophilic substitution (13; R = alkyl). When polar solvents are used as the reaction medium, such

$$R_4Pb + I_2 \xrightarrow{k_2} RI + R_3PbI \qquad (13)$$

iododemetallations are usually carried out in the presence of iodide ion, and the observed data then analysed to give[39] the term k_2/K where K is the equilibrium constant for reaction (14) in the same solvent. In Table 14 are

$$I^- + I_2 \overset{K}{\rightleftharpoons} I_3^- \qquad (14)$$

details of the calculation of the second-order rate constant for reaction (13; R = Me) and also the corresponding values for reaction (13; R = Et) computed in exactly the same way. The final values of k_2 suffer, of course, from any inaccuracies in the determined values of K as well as experimental error in the observed values of k_2/K. With this proviso in mind, inspection of the data in Table 14 indicates that the effect of various aprotic solvents on the rate constant for reaction (13; R = Me and Et) is more pronounced than the effect of these solvents on the rates of Menschutkin reactions. Dimethyl sulphoxide behaves anomalously and leads to rate constants for reaction (13) that are much lower than expected; it has been suggested[40] that this effect is due to complex formation between iodine and dimethylsulphoxide.

In order to dissect solvent influences on reaction (13) into initial-state and transition-state contributions through equation (15), values of $\Delta G_t°(R_4Pb)$ and of $\Delta G_t°(I_2)$ are required. For consistency, all the terms in equation (15) must be expressed on the same concentration scale; the mol-fraction scale will here be used.

$$\Delta G_t°([R_4Pb\text{–}I_2]^‡) = \Delta G_t°(R_4Pb) + \Delta G_t°(I_2) + \delta\Delta G^‡ \qquad (15)$$

TABLE 15

Mol-fraction solubilities of iodine and free energies of transfer (on the mol-fraction scale) from methanol to other solvents of iodine, in kcal mol^{-1} at 298 K

Solvent	$N(I_2)$	ΔG_s^x	ΔG_t^x
Water	$2{\cdot}36 \times 10^{-5}$ [a]	6·31	+4·1
Methanol	$2{\cdot}56 \times 10^{-2}$ [b]	2·17	0
Ethanol	$4{\cdot}31 \times 10^{-2}$ [a]	1·87	−0·3
n-Propanol			−0·4 [c]
Dimethyl sulphoxide	0·571 [d]	0·33	−1·8
			−2·5 [e]
			−5·9 [f]
Acetonitrile	$1{\cdot}15 \times 10^{-2}$ [a]	2·64	+0·5
			+0·3 [e]
			−0·4 [f]
Acetone	$3{\cdot}33 \times 10^{-3}$ [c]	3·38	+1·2
Benzene	$4{\cdot}80 \times 10^{-2}$ [d]	1·80	−0·4
Chlorobenzene		2·07 [g]	−0·1
Carbon tetrachloride	$1{\cdot}42 \times 10^{-2}$ [d]	2·52	+0·3
		2·68 [g]	+0·5

[a] C. Barraque, J. Vedel, and B. Tremillon, *Analyt. Chim. Acta*, 1969, **46**, 263. [b] This work. [c] From data in ref. 45. [d] J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, ' Regular and Related Solutions,' Van Nostrand–Reinhold, New York, 1970. [e] From distribution data in ref. 43. [f] From data in refs. 29 and 41. [g] G. Junghahnel, *Wiss. Z. tech. Hochschule Karl-Marx-Stadt*, 1964, **6**, 1.

Values of $\Delta G_t^x(R_4Pb)$ are in Table 6, and values of $\Delta G_t^x(I_2)$ can be obtained from data on solubilities and distribution coefficients (see Table 15). Parker[29,41] gives the solubility of iodine in methanol at 25 °C as 0·24 molar. This value corresponds to a mol-fraction solubility of *ca.* $9{\cdot}8 \times 10^{-3}$ and is inconsistent with the mol-fraction solubility of $2{\cdot}86 \times 10^{-2}$ determined by Mahieu.[42] I find the solubility of iodine in methanol at 25 °C to be 0·632 molar and $2{\cdot}56 \times 10^{-2}$ in terms of mol-fraction, in reasonable agreement with Mahieu. The

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[37] L. Riccoboni, G. Pilloni, G. Plazzogna, and G. Tagliavini, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1966, **11**, 340.

[38] G. Pilloni and G. Tagliavini, *J. Organometallic Chem.*, 1968, **11**, 557.

[39] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1962, **71**, 32.

[40] M. Gielen and J. Nasielski, *J. Organometallic Chem.*, 1967, **7**, 273.

[41] R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, 1968, **90**, 5049.

[42] J. Mahieu, *Bull. Soc. chim. belges*, 1936, **45**, 667.

value of $\Delta G_t^x(I_2)$ for transfer from methanol to dimethyl sulphoxide calculated from data by Parker[29,41] is −5·9 kcal mol^{-1} whereas from results of distribution experiments carried out by Benoit[43] a value of −2·5 kcal mol^{-1} can be deduced. Solubility data are of limited use in this case because of the very high solubility of iodine[44] in dimethyl sulphoxide, but the value of −1·8 kcal mol^{-1} calculated from mol-fraction solubilities is as near the value of Benoit as could reasonably be expected.* One or two checks are possible on the $\Delta G_t^x(I_2)$ values obtained from solubility measurements. The molar distribution coefficient of iodine between benzene and water[45] is 364 (after extrapolation to zero concentration) which corresponds to standard free-energy changes of 3·49 kcal mol^{-1} (molar scale) and 4·49 kcal mol^{-1} (mol-fraction scale), as compared with a value of 4·5 kcal mol^{-1} (mol-fraction scale) from Table 16. Similarly, the molal distribution coefficient of iodine between carbon tetrachloride and water,[45] 52·44, corresponds to standard free energy changes of 2·35 kcal mol^{-1} (molal scale) and 3·62 kcal mol^{-1} (mol-fraction scale) as compared with values of 3·4 and 3·6 (both on the mol-fraction scale) from Table 15.

TABLE 16

Calculation of free energies of transfer (on the mol-fraction scale) from methanol to other solvents of transition states in the iododemetallation of tetra-alkyl-leads at 298 K

			ΔG_t^x/kcal mol^{-1}			
No.	Solvent	$\delta\Delta G^\ddagger$ [a]	Me_4Pb	I_2	$[Me_4Pb{-}I_2]^\ddagger$	Me_4NI [b]
11	Acetonitrile	−1·7	0	+0·4	−1·3	0·4
17	Acetone	−0·4	−0·8	+1·2	0	1·6
9	Dimethyl sulphoxide[b]	+0·3	+0·5	−2·9	−2·1	−0·8
2	Methanol	0	0	0	0	0
3	Ethanol	1·0	−0·5	−0·3	0·2	0·7
4	n-Propanol	1·5	−0·8	−0·4	0·3	1·1
31	Benzene	5·9	−1·8	−0·4	3·7	5·9
32	Carbon tetrachloride	8·1	−2·1	+0·5	6·5	10·5
		$\delta\Delta G^\ddagger$ [a]	Et_4Pb	I_2	$[Et_4Pb{-}I_2]^\ddagger$	Et_4NI [b]
11	Acetonitrile	−1·7	+0·2	+0·4	−1·1	1·2
17	Acetone	−0·4	−0·9	+1·2	−0·1	1·9
9	Dimethyl sulphoxide	+0·6	+0·6	−2·9	−1·7	0·3
2	Methanol	0	0	0	0	0
3	Ethanol	0·9	−0·8	−0·3	−0·2	1·1
4	n-Propanol	1·4	−1·1	−0·4	−0·1	1·4
31	Benzene	3·9	−2·4	−0·4	+1·1	6·4
32	Carbon tetrachloride	5·6	−2·6	+0·5	3·5	10·5

[a] From rate constants in Table 14 after conversion to units of mol-fraction^{-1} s^{-1}. [b] Values for ion pairs.

Results of the calculation of ΔG_t^x values for the transition states in reaction (13), denoted as $[R_4Pb{-}I_2]^\ddagger$, are in Table 16. For both reactions, initial-state effects are large enough to make $\delta\Delta G^\ddagger$ not a good approximation to $\Delta G_t^x([R_4Pb{-}I_2]^\ddagger)$. In particular, the relatively slow rate of reaction (13; R = Me and Et) in dimethyl sulphoxide is seen to be due entirely to initial-state effects. As suggested by Gielen and Nasielski[40] the effect of solvent dimethyl sulphoxide is to lower substantially the standard free energy of iodine and hence to increase the value of $\Delta G^\ddagger$.

Rate constants for halogenodemetallation of tetra-alkyl-tins and -leads are (see *e.g.* refs. 37, 38, 40, and 46—48) always in the sequence $k(Me_4M) > k(Et_4M)$ when polar solvents such as methanol and acetonitrile are used, but follow the inverse order $k(Me_4M) < k(Et_4M)$ in non-polar solvents such as benzene and carbon tetrachloride. Tagliavini and his co-workers[38] have suggested that the sequence in polar solvents arises from co-ordination of the nucleophilic solvent to the metal atom; this co-ordination is inhibited by steric and inductive effects of alkyl groups attached to the metal so that a complex $Me_4M{\leftarrow}S$ is energetically favoured by comparison with the complex $Et_4M{\leftarrow}S$, where S is a solvent molecule. From Table 6 and 16, however, it is clear that such initial-state effects cannot account for the variation in rate constants (or, what is equivalent, $\delta\Delta G^\ddagger$ values) between iododemetallation of tetramethyl-lead and tetraethyl-lead. If the solvents methanol and carbon tetrachloride are compared, the two values of $\delta\Delta G^\ddagger$ (Table 16) differ by 2·5 kcal mol^{-1} whereas solvent effects on the tetra-alkyl-leads differ by only 0·5 kcal mol^{-1}. In any case, Tagliavini's theory suffers from a logical inconsistency, because any formation of sub-species (such as $R_4M{\leftarrow}S$) leads to a reduction in the standard free energy of the solute[49] and hence to an increase in $\Delta G^\ddagger$ [*cf.* the effect of dimethyl sulphoxide on values of $\Delta G_t^x(I_2)$ and $\delta\Delta G^\ddagger$ in Table 16] whereas Tagliavini's theory[38] requires the standard free energy

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* J. Courtot-Coupez and C. Madec (*Bull. Soc. chim. France*, 1971, 4626) give data from which a value for $\Delta G_t^x(I_2)$ of −3·2 kcal mol^{-1} can be calculated. The average of this value and that of Benoit[43] is −2·9 kcal mol^{-1}, and is used in Table 16.

[43] R. L. Benoit, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 723.

[44] T. Soda and J. H. Hildebrand, *J. Phys. Chem.*, 1967, **71**, 4561.

[45] 'Solubilities of Inorganic and Metal Organic Compounds,' (Seidell), ed. W. F. Linke, Van Nostrand, New York, 1958, 4th edn., vol. I, pp. 1265—1274.

[46] M. Gielen and J. Nasielski, *J. Organometallic Chem.*, 1963, **1**, 173.

[47] M. H. Abraham and J. A. Hill, *J. Organometallic Chem.*, 1967, **7**, 11.

[48] S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 443.

[49] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of organic Reactions,' Wiley, New York, 1963, p. 34, equation (44).

of a reactant to be increased by formation of such sub-species and hence the value of $\Delta G^{\ddagger}$ to be reduced.

Table 16 shows that the relative reactivities of tetramethyl-lead and tetraethyl-lead are due to transition-state solvent effects, as first suggested by Gielen and Nasielski[46] and later by others.[37,47] By comparison with non-polar solvents, the polar solvents such as methanol and acetonitrile stabilise the $[Me_4Pb-I_2]^{\ddagger}$ transition state more than the $[Et_4Pb-I_2]^{\ddagger}$ transition state. This could be due (*cf.* ref. 50) to steric inhibition of solvation in the $[Et_4Pb-I_2]^{\ddagger}$ transition state or to steric interactions in the $[Et_4Pb-I_2]^{\ddagger}$ transition state in polar solvents[46,47] leading to a higher free energy for the transition state.

It is not easy to assess the extent of charge separation in the $[R_4Pb-I_2]^{\ddagger}$ transition states, because it is difficult to distinguish between a very polarisable transition state carrying a low charge separation and a moderately polarisable transition state carrying a charge separation of, say, 0·3 unit. In both cases, values of $\Delta G_t^{\circ}(Tr)$ will increase with decreasing solvent polarity. Table 17 gives data on four polarisable, but electrically neutral, transition states; the term $[D-A]^{\ddagger}$ refers to the transition state in the Diels–Alder reaction of maleic anhydride and 1,3-butadiene. Wong and Eckert[51] showed that solvent effects on the transition state $[D-A]^{\ddagger}$ were very similar to solvent effects on maleic anhydride, so that this transition state can be considered as an example of a highly polarisable transition state which carries but a low separation of charge. There is a gradual increase in the response of transition state to change of solvent along the series $[D-A]^{\ddagger} < [Et_4Pb-I_2]^{\ddagger} \simeq [Me_3N-ArCH_2Cl]^{\ddagger} < [Me_4Pb-I_2]^{\ddagger}$ and this series can be taken as one of increasing charge separation in the transition states. Values of $\Delta G_t^{x}([Me_4Pb-I_2]^{\ddagger})$ vary with change of solvent much more in polar solvents than in non-polar solvents; this behaviour might be due to change in mechanism from S_E2(open) to S_E2(cyclic), but further work is needed to confirm or deny such an hypothesis.

Conclusions.—For electrically neutral transition states that carry a moderate or high charge separation, the extent of charge separation can be estimated by a comparison of values of $\Delta G_t^{\circ}(Tr)$ with ΔG_t° values for a suitable model ion pair. If the electrically neutral transition states carries a low separation of charge, ion pairs are no longer suitable models, and values of $\Delta G_t^{\circ}(Tr)$ are more usefully compared either with observed values of ΔG_t° for polarisable and non-polarisable non-electrolytes or with values of ΔG_t° for non-electrolytes calculated from regular-solution theory (*cf.* ref. 51).

In certain cases, solvent influences on reactants are small enough in comparison with solvent influences on $\Delta G^{\ddagger}$ to allow values of $\delta\Delta G^{\ddagger}$ to be taken as approximately equal to corresponding values of $\Delta G_t^{\circ}(Tr)$. Such cases include the decompositions of t-butyl chloride and t-butyl bromide in non-aqueous solvents, and Menschutkin reactions in aprotic solvents. For these cases, comparison of values of $\delta\Delta G^{\ddagger}$ with values of ΔG_t° for a model ion pair also will yield an estimate of the extent of charge separation in the transition state. On the other hand, solvent influences on the reactants in the iododemetallation of tetra-alkyl-leads are large enough in comparison with values of $\delta\Delta G^{\ddagger}$ to preclude the use of $\delta\Delta G^{\ddagger}$ as an estimate of $\Delta G_t^{\circ}(Tr)$. In addition, solvent influences on non-electrolytes are generally very large whenever aqueous solvent mixtures are employed, and for such aqueous mixtures it is necessary to carry out a dissection of solvent effects into initial-state and transition-state contributions, since $\delta\Delta G^{\ddagger}$ again cannot be used instead of $\Delta G_t^{\circ}(Tr)$.

TABLE 17

Free energies of transfer (on the mol-fraction scale) from benzene to other solvents of some polarisable, neutral transition states at 298 K

	ΔG_t^{x}/kcal mol^{-1}			
Solvent	$[D-A]^{\ddagger}$ [a]	$[Et_4Pb-I_2]^{\ddagger}$	$[Me_3N-ArCH_2Cl]^{\ddagger}$ [b]	$[Me_4Pb-I_2]^{\ddagger}$
Nitromethane	−1·2		−3·3	
Acetonitrile		−2·2	−2·6	−5·0
Acetone		−1·2	−1·8	−3·7
Ethyl acetate	−0·3		−0·8	
Benzene	0	0	0	0
Ether	0·9		2·3	
Carbon tetrachloride	1·6	2·4	3·0 [c]	2·8

[a] Transition state in the Diels–Alder reaction of maleic anhydride with buta-1,4-diene. Values from data given in ref. 51. [b] Ar = p-$NO_2 \cdot C_6H_4$. [c] Estimated value.

EXPERIMENTAL

t-Butyl chloride (B.D.H.) was shaken with a mixture of anhydrous sodium carbonate and anhydrous sodium sulphate and distilled just before use. t-Butyl bromide (B.D.H.) was similarly treated. The tetra-alkyltins were prepared and purified as described.[52] Tetraethyl-lead was a gift. Tetramethylammonium iodide (B.D.H.) was recrystallised twice from water and dried at 60 °C and 2 mmHg for several days. Tetraethylammonium iodide (B.D.H.) was recrystallised twice from aqueous acetone and dried similarly. The tetra-alkylammonium perchlorates were prepared by the addition of aqueous perchloric acid to aqueous solutions of the corresponding hydroxides; the precipitated perchlorates were filtered off, washed with cold distilled water,

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[50] V. Bade and F. Huber, *J. Organometallic Chem.*, 1970, **24**, 387.

[51] K. F. Wong and C. A. Eckert, *Trans. Faraday Soc.*, 1970, **66**, 2313.

[52] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 193; M. H. Abraham and T. R. Spalding, *ibid.*, 1968, 2530; 1969, 399.

and twice recrystallised: Me_4NClO_4 (from water), Et_4NClO_4 (from water, and also from aqueous acetone), $Pr^n{}_4NClO_4$ (from water). The recrystallised perchlorates were dried at 60 °C and 2 mmHg for several days. Alcohols were dried over calcium oxide, aprotic solvents over an appropriate agent, and all solvents were distilled just before use. Dimethyl sulphoxide, purified by recrystallisation, was a gift from Mr. Derek Earls.

Solubilities of the tetra-alkylammonium iodides were determined by agitating an excess of the iodide with the appropriate solvent at 25·0 °C for 1—3 weeks. If the solubility of the iodide was greater than 10^{-4}M, aliquot portions of the supernatant liquid were withdrawn, added to either water or methanol, and titrated against aqueous 1×10^{-2}M-silver nitrate. The silver nitrate solution was added from a microburette and the end point determined conductometrically; care was taken to ensure that the iodide solution remained homogeneous throughout the titration. Duplicate analyses usually agreed to within 0·5%, and the solubility determined after 1 week was invariably identical with that determined after 2—3 weeks. In some cases, aliquot portions were removed after the iodide–solvent mixture had been filtered, but results were identical with those obtained without the filtration step. When the solubility of the iodide was less than 10^{-4}M, a known volume (up to 1 l) of the solution was either decanted from the residual iodide or was filtered off (again results were the same by the two methods), and was then extracted several times with water. The iodide content of the combined aqueous extracts was then determined as above. For all analyses, both direct and by extraction, blank determinations with use of the appropriate quantity of solvent were carried out. Results are in Table 1.

Solubilities of the tetra-alkylammonium perchlorates were determined by withdrawing aliquot portions of the saturated solutions (prepared as above), carefully evaporating the solvent, and drying the residual solid to constant weight (at 60 °C and 2 mmHg).

Relative Henry's law constants $(P_2/N_2) : (P_1/N_1)$ were determined by the g.l.c. method.[3] Solutions of a given solute in various solvents were made up by weight and samples of the vapour above the solutions analysed for the solute in order to obtain P_2/P_1, where the subscripts denote solvents 1 and 2. The concentration of the solute in the various solvents was arranged so that P_2/P_1 was close to unity. The apparatus and conditions for analysis of vapour samples containing tetramethyltin, tetraethyltin, tetraethyl-lead, t-butyl chloride, and t-butyl bromide were the same as described before [3] for the analysis of vapour samples containing tetramethyltin· and tetraethyltin, with the exception that the diglycerol column was operated at 40 °C for analyses involving the two alkyl halides.

Values of γ^∞ for solutes in solvent methanol were determined as before [3] by comparison of vapour samples from solutions of a given solute in methanol with vapour samples from the pure liquid solute. The determined values of γ^∞ are in Table 6. These absolute values cannot be determined as accurately as can the ratios $(P_2/N_2) : (P_1/N_1)$, especially when γ^∞ is rather small. Hence values of γ^∞ in methanol for solutes t-butyl chloride ($\gamma^\infty = 10$) and t-butyl bromide ($\gamma^\infty = 13$) are subject to a much greater error than values of γ^∞ for the tetra-alkyls of tin and lead ($\gamma^\infty = 31$ for Me_4Sn).

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