Tetrahedron Letters No.60,pp. 5233-5236, 1970. Pergamon Press. Printed in Great Britain.

SOLVENT EFFECTS ON THE FREE ENERGIES OF ION-PAIRS, AND OF TRANSITION STATES IN AN S_N1 AND AN S_N2 REACTION

M.H. Abraham

Department of Chemistry, University of Surrey, Guildford, Surrey

(Received in UK 2 November 1970; accepted for publication 25 November 1970)

The influence of solvents on the free energy of activation in the ionisation of t-butyl chloride may be dissected into initial-state and transition-state contributions through equation (1), where $\Delta G_t^o(Y)$

$$\Delta G_t^o([Bu^tCl]^*) = \Delta G_t^o(Bu^tCl) + \Delta G_2^* - \Delta G_1^* \qquad (1)$$

represents the standard free energy of transfer from solvent 1 to solvent 2 of species Y. In the Table are values of $\delta\Delta G^*$ ($\delta\Delta G^* = \Delta G_2^* - \Delta G_1^*$), together with values of the standard free energy of transfer (on the mole fraction scale) from the reference solvent methanol to other solvents of t-butyl chloride. These values of $\Delta G_t^o(Bu^tCl)$ are mostly either those I have obtained by gas-liquid chromatographic determinations of Henry's Law constants of t-butyl chloride, or are those of Rudakov and Tretyakov (who have already carried out a similar dissection for a number of solvents).[1] From the corresponding values of $\Delta G_t^o([Bu^tCl]^*)$, it can be seen that solvent influences on ΔG^* are largely the result of transition-state effects, with the exception of water as solvent.

I have also calculated values of ΔG_t^o for the dissociated species ($Me_4\overset{+}{N} + I^-$) and ($Et_4\overset{+}{N} + I^-$), and for the ion-pairs (Me_4NI) and (Et_4NI), from solubility data[2] and ion-pair association constants[3] (see ref. 4); values for the corresponding chlorides may then be obtained from solubilities of sparingly soluble chlorides and iodides, and from data in ref. 5. Values of ΔG_t^o (converted to the mole fraction scale) for a number of ion-pairs are in the Table. The $\Delta G_t^o([Bu^tCl]^*)$ values parallel closely those of $\Delta G_t^o(Me_4NCl)$, and a plot of $\Delta G_t^o([Bu^tCl]^*)$ against $\Delta G_t^o(Me_4NCl)$ yields a straight line of slope 0.7; the two additional estimated values of $\Delta G_t^o(Me_4NCl)$ fall also on the same straight line. The ion-pair (Me_4NCl) is clearly a good model for the $[Bu^tCl]^*$ transition state; the latter can be said to be "ion-pair-like" in character, and must carry a substantial separation of charge. Previous calculations[6] have yielded values of around 0.8 units of charge for the degree of charge separation, and the results of the present work are in accord with such a value.

ΔG_t^o values [4,7] for the S_N2 transition state in reaction (2) are

$$Me_3N + p\text{-}NO_2C_6H_4CH_2Cl \rightarrow p\text{-}NO_2C_6H_4CH_2\overset{+}{N}Me_3 + \overset{-}{Cl} \qquad (2)$$

also in the Table, and may be compared with the ΔG_t^o values for ion-pairs. The S_N2 transition state does not resemble any of the listed ion-pairs in behaviour, but rather more resembles the (non-polar) reactants. Charge separation in this Menschutkin reaction transition state must therefore be low, as has been suggested[4,7] recently (compare also ref. 8).

TABLE. Standard free energies of transfer (on the mole fraction scale) from methanol to other solvents, in kcal. mole^{-1} at 298° K

Solvent	-log k[a]	$\delta\Delta G^{*}$	ΔG_t^o					
			Bu^tCl	$[Bu^tCl]^{*}$	(Me_4NCl)[b]	$[Me_3NR/Cl]^{*}$[c]	(Et_4NI)[b]	(Et_4NCl)[b]
Water	1.54[d]	-6.22	4.57[d]	-1.65	-2.9	-	-0.3	-2.0
Methanol	6.10[e]	0	0	0	0	0	0	0
Acetic Acid	6.71[d]	0.83	-0.26[d]	0.57	-	-	-	-
Ethanol	7.07	1.32	-0.25[f]	1.07	0.9	0.5	1.2	1.8
n-Butanol	7.26	1.58	-0.46[g]	1.12	1.1	0.7	1.9	2.6
Nitromethane	8.12	2.76	-0.14[g]	2.62	1.8	-1.9	1.6	3.9
Dimethylformamide	8.48	3.25	-0.55[g]	2.70	-	-	-	-
Acetonitrile	8.49[h]	3.26	-0.39[i]	2.87	3.5	-1.6	1.3	5.1
Acetone	9.90[j]	5.18	-0.83[i]	4.35	6.1	-0.9	2.0	8.6
Benzene	12.16[h]	8.27	-1.06[i]	7.21	12.0[k]	1.0	6.6	14.0[k]
Pentane	16.0	13.5	-0.93[g]	12.6	20.0[k]	5.0[l]	14.0[k]	22.0[k]

[a] Rate coefficient for ionisation of t-butyl chloride in sec.$^{-1}$; values from ref. 1. [b] Ion-pairs. [c] R = p-nitrobenzyl; values from ref. 4. [d] Ref. 9. [e] Average value from refs. 1 and 9. [f] -0.24 (ref.10), -0.26 (this work). [g] Ref. 10. [h] Values estimated from high temperature data in ref. 11. [i] This work. [j] Ref. 12. [k] Estimated values. [l] Solvent hexane.

REFERENCES

1. E.S. Rudakov and V.P. Tretyakov, *Reakts. Spos. Organ. Soedin., Tartusk. Gos. Univ.*, **2** (Issue 4), 142 (1965).
2. P. Walden, *Z. Phys. Chem.*, **61**, 633 (1908); **55**, 698 (1906).
3. V.E. Bower and R.A. Robinson, *Trans. Faraday Soc.*, **59**, 1717 (1963); S. Lindenbaum and G.E. Boyd, *J. Phys. Chem.*, **68**, 911 (1964); D.F. Evans, C. Zawoyski, and R.L. Kay, *J. Phys. Chem.*, **69**, 3878 (1965); R.L. Kay, C. Zawoyski, and D.F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965); W.A. Adams and K.J. Laidler, *Can. J. Chem.*, **46**, 2005 (1968).
4. M.H. Abraham, *J. Chem. Soc.*, in the press.
5. A.J. Parker, *Chem. Rev.*, **69**, 1 (1969).
6. G.A. Clarke and R.W. Taft, *J. Amer. Chem. Soc.*, **84**, 2295 (1962); E.M. Kosower, *Reakts. Spos. Organ. Soedin., Tartusk. Gos. Univ.*, **1** (Issue 2), 238 (1964); M.H. Abraham and G.F. Johnston, *J.Chem.Soc.(A)*, 188 (1970).
7. M.H. Abraham, *Chem.Commun.*, 1307 (1969).
8. M.H. Abraham, *Chem.Commun.*, 293 (1970).
9. S. Winstein and A.H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 5937 (1957).
10. E.S. Rudakov and V.P. Tretyakov, *Reakts. Spos. Organ. Soedin., Tartusk. Gos. Univ.*, **2** (Issue 1), 135 (1965).
11. I.A. Koppel and V.A. Palm, *Reakts. Spos. Organ. Soedin., Tartusk. Gos. Univ.*, **4** (Issue 4), 862 (1967).
12. E.S. Rudakov, *Dokl. Akad. Nauk SSSR*, **127**, 1058 (1959).