

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

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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 $\Delta G_t^0(Y)$

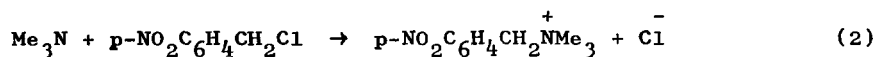
$$\Delta G_t^0([Bu^tCl]^*) = \Delta G_t^0(Bu^tCl) + \Delta G_2^* - \Delta G_1^* \quad (1)$$

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 $\Delta G_t^0(Bu^tCl)$ 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 $\Delta G_t^0([Bu^tCl]^*)$, 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^0 for the dissociated species ($Me_4N^+ + I^-$) and ($Et_4N^+ + I^-$), and for the ion-pairs (Me_4NI) and (Et_4NI), from solubility data² and ion-pair association constants³ (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^0 (converted to the mole fraction scale) for a number of ion-pairs are in the Table. The $\Delta G_t^0([Bu^tCl]^+)$ values parallel closely those of $\Delta G_t^0(Me_4NCl)$, and a plot of $\Delta G_t^0([Bu^tCl]^+)$ against $\Delta G_t^0(Me_4NCl)$ yields a straight line of slope 0.7; the two additional estimated values of $\Delta G_t^0(Me_4NCl)$ 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 calculations⁶ 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^0 values^{4,7} for the S_N2 transition state in reaction (2) are



also in the Table, and may be compared with the ΔG_t^0 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 Menshutkin 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^0					
			Bu ^t Cl	[Bu ^t Cl] ⁺	(Me ₄ NCl) ^b	[Me ₃ NR/Cl] ⁺ c	(Et ₄ NI) ^b	(Et ₄ NCl) ^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

^aRate coefficient for ionisation of t-butyl chloride in sec.⁻¹; values from ref. 1. ^bIon-pairs.

^cR = p-nitrobenzyl; values from ref. 4. ^dRef. 9. ^eAverage value from refs. 1 and 9. ^f-0.24 (ref. 10), -0.26 (this work). ^gRef. 10. ^hValues estimated from high temperature data in ref. 11.

ⁱThis work. ^jRef. 12. ^kEstimated values. ^lSolvent hexane.

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