Free Energies and Entropies of Transfer from Methanol to Aqueous Methanol of the Reactants and the Transition State in the Bimolecular Substitution of Tetraethyltin by Mercuric Chloride

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Summary Variations in the free energy and entropy of tetraethyltin and mercuric chloride with solvent composition, in methanol–water mixtures, are of comparable magnitude to corresponding variations in the free energy and entropy of the tetraethyltin–mercuric chloride transition state.

THE free energy of activation of the bimolecular substitution (1) decreases with decreasing mole fraction of methanol in methanol–water mixtures. A separation of this solvent effect into ground-state and transition-state contributions

$$Et_4Sn + HgCl_2 \rightarrow EtHgCl + Et_3SnCl \qquad (1)$$

may be established through equation (2), where $\Delta G^\circ_t(X)$ represents the standard free energy of transfer from methanol (solvent 1) to some other solvent (solvent 2) of species X. We have determined values of $\Delta G^\circ_t(Et_4Sn)$ from Henry's Law constants, and values of $\Delta G^\circ_t(HgCl_2)$ through

$$\Delta G^\circ_t(Tr) = \Delta G^\circ_t(Et_4Sn) + \Delta G^\circ_t(HgCl_2) + \Delta G^\ddagger_2 - \Delta G^\ddagger_1 \qquad (2)$$

solubility measurements; combination of these with values of $\Delta G^\ddagger$ yields values of $\Delta G^\circ_t(Tr)$, the standard free energy of transfer of the transition state. Corresponding values of ΔS°_t may be calculated from the values of ΔG°_t, together with our previously determined[1] values of ΔH°_t. Details are given in the Table.

Free energies and entropies of activation for reaction (1), *and free energies and entropies of transfer* (*on the molar scale*) *from methanol to aqueous methanol of the reactants and the transition state, at* 298° K

		ΔG°_t				ΔS°_t		
χ(MeOH)	$\Delta G^\ddagger$	Et_4Sn	$HgCl_2$	Tr	$\Delta S^\ddagger$	Et_4Sn	$HgCl_2$	Tr
1	20832	0	0	0	−21·8	0	0	0
0·96	20648	130	34	−20	−22·4	0·2	1·3	0·9
0·91	20455	270	73	−34	−24·5	0·3	2·6	0·2
0·87	20286	450	110	14	−25·4	0·6	3·6	0·6
0·80	19987	725	187	67	−25·6	1·0	5·3	2·5
0·72	19653	970	294	85	−24·1	1·5	7·2	6·4
0·64	19368	1220	412	168	−23·7	1·8	8·0	7·9
0·51	18859	1800	619	446	−22·2	1·3	9·5	10·4
0	16300[a]	6660[b]	1623	3750	—	—	—	—

[a] Extrapolated value; [b] From ref. 4; free energies in cal. mole.$^{-1}$, and entropies in cal. deg.$^{-1}$ mole.$^{-1}$

The decrease in $\Delta G^\ddagger$ with decreasing mole fraction of methanol is almost entirely due to increases in the free energy of the reactants; $\Delta G^\circ_t(Tr)$ is slightly negative over part of the solvent range, but becomes increasingly large and positive towards the more aqueous region. From the observed values of $\Delta G^\circ_t(Tr)$, it seems most probable that the transition state for reaction (1) is of the S_E2(open) type, since very much larger positive values would be expected for $\Delta G^\circ_t(Tr)$ if a relatively nonpolar cyclic transition state obtained. Fluctuations in $\Delta S^\ddagger$ result from quite large variations in values of ΔS°_t for the reactants and the transition state. It is apparent that solvent effects on the reactants [in equation (1)] are of the same order of magnitude as solvent effects on the transition state, and hence it seems clear that any theories of chemical reactivity that do not take into account possible solvent effects on reactants cannot be expected to describe adequately the influence of solvents on the rates of chemical reactions.

The present work, together with our data[1] on the corresponding enthalpies of transfer, represents the first recorded dissection of solvent effects on a bimolecular reaction into ground-state and transition-state contributions in terms of all three parameters, *G*, *H*, and *S*. There is only one example of a unimolecular reaction, the solvolysis of t-butyl chloride in ethanol–water mixtures[2] and methanol–water[3] mixtures, that has been thus examined. Here again, ground-state solvent effects are just as important as transition-state solvent effects.

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[1] M. H. Abraham, F. Behbahany, M. J. Hogarth, R. J. Irving, and G. F. Johnston, *Chem. Comm.*, 1969, 117.

[2] E. M. Arnett, W. G. Bentrude, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 2048.

[3] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937; E. M. Arnett, P. McC. Duggleby, and J. J. Burke, *ibid.*, 1963, **85**, 1350.

[4] M. Alfenaar and C. L. de Ligny, *Rec. Trav. chim.*, 1967, **86**, 929.