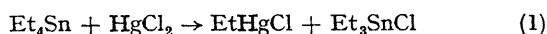


Free Energies and Entropies of Transfer from Methanol to Aqueous Methanol of the Reactants and the Transition State in the Bimolecular Substitution of Tetraethyltin by Mercuric Chloride

By M. H. ABRAHAM,* G. F. JOHNSTON, J. F. C. OLIVER, and JOHN A. RICHARDS
(Department of Chemistry, University of Surrey, Guildford, Surrey)

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



may be established through equation (2), where $\Delta G_i^\circ(\text{X})$ represents the standard free energy of transfer from methanol (solvent 1) to some other solvent (solvent 2) of species

transfer of the transition state. Corresponding values of ΔS_i° may be calculated from the values of ΔG_i° , together with our previously determined¹ values of ΔH_i° . Details are given in the Table.

The decrease in ΔG^\ddagger with decreasing mole fraction of methanol is almost entirely due to increases in the free energy of the reactants; $\Delta G_i^\circ(\text{Tr})$ 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 $\Delta G_i^\circ(\text{Tr})$, it seems most probable that the transition state for reaction (1) is of the $S_E2(\text{open})$ type, since very much larger positive values would be expected for $\Delta G_i^\circ(\text{Tr})$ if a relatively nonpolar cyclic transition state obtained. Fluctuations in ΔS^\ddagger result from quite large variations in values of ΔS_i° for the reactants and the transition state. It is apparent that solvent effects on the

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

$\chi(\text{MeOH})$	ΔG^\ddagger	ΔG_i°			ΔS^\ddagger	ΔS_i°		
		Et_4Sn	HgCl_2	Tr		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

X. We have determined values of $\Delta G_i^\circ(\text{Et}_4\text{Sn})$ from Henry's Law constants, and values of $\Delta G_i^\circ(\text{HgCl}_2)$ through

$$\Delta G_i^\circ(\text{Tr}) = \Delta G_i^\circ(\text{Et}_4\text{Sn}) + \Delta G_i^\circ(\text{HgCl}_2) + \Delta G_2^\ddagger - \Delta G_1^\ddagger \quad (2)$$

solubility measurements; combination of these with values of ΔG^\ddagger yields values of $\Delta G_i^\circ(\text{Tr})$, the standard free energy of

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 data¹ 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 mixtures² and methanol-water³ 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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