Enthalpies of Transfer from Methanol to Acetonitrile, t-Butyl Alcohol, and Aqueous Methanol of the Reactants and the Transition State in the Bimolecular Substitution of Tetraethyltin by Mercuric Chloride

By M. H. ABRAHAM,* F. BEHBAHANY, M. J. HOGARTH, R. J. IRVING, and G. F. JOHNSTON
(*Department of Chemistry, University of Surrey, Battersea Park Road, London, S.W.*11)

THE enthalpy of activation of the bimolecular electrophilic substitution (1) is considerably higher in solvent methanol than in solvents acetonitrile, t-butyl alcohol, and aqueous methanol (Table). Whether this is due to solvent effects on the reactants or on the transition state (or on both) may be established through equation (2), where $\Delta H_t^\circ(X)$ represents the enthalpy of transfer from methanol (solvent 1) to some other solvent (solvent 2) of species X. We have determined values of $\Delta H_t^\circ(Et_4Sn)$ and $\Delta H_t^\circ(HgCl_2)$ calorimetrically, and have combined these with values of $\Delta H^\ddagger$ to yield values of $\Delta H_t^\circ(Tr)$, the corresponding enthalpy of transfer of the transition state. Details are given in the Table, and it is clear that the reduction in ΔH from methanol to aqueous methanol is due to a large solvent effect on the reactants. The transition state is little affected in the methanol-rich region, but is progressively destabilised in the more aqueous region. This behaviour is in line with that in the solvolysis of t-butyl chloride,[1] where $\Delta H_t^\circ(Bu^tCl) \simeq +4$ kcal. mole^{-1} and $\Delta H_t^\circ(Tr) \simeq +1$ kcal. mole^{-1} on transfer from methanol to aqueous methanol ($\chi_{MeOH} = 0·51$).

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

$$\Delta H_t^\circ(Tr) = \Delta H_t^\circ(Et_4Sn) + \Delta H_t^\circ(HgCl_2) + \Delta H_2^\ddagger - \Delta H_1^\ddagger \qquad (2)$$

Replacement of methanol by t-butyl alcohol is characterised by a very large value of $\Delta H_t^\circ(HgCl_2)$, and again the transition state is destabilised by comparison to its state in solvent methanol. The dipolar aprotic solvent acetonitrile also leads to an increase in the enthalpy of the reactants, but in this case the transition state is of about the same enthalpy as it is in solvent methanol.

Enthalpies of activation for reaction (1), *and enthalpies of transfer from methanol to other solvents of the reactants and the transition state, in kcal. mole*$^{-1}$ *at* 298° K

MeOH: H_2O		ΔH_t^0		
χ_{MeOH}	$\Delta H^\ddagger$	Et_4Sn	$HgCl_2$	Tr
1	14·35	0	0	0
0·96	13·95	0·20	0·40	0·20
0·91	13·15	0·35	0·85	0
0·87	12·40	0·65	1·15	−0·15
0·80	12·35	1·00	1·75	0·75
0·72	12·45	1·40	2·45	1·95
0·64	12·30	1·75	2·80	2·50
0·51	12·25	2·20	3·25	3·35
MeCN	11·30	1·15	1·65	−0·25
Bu^{t}OH	10·25	−0·40	6·20	1·70

No other electrophilic substitution has been examined by this method, and in the only study of an S_N2 reaction so far reported, values of −3·7 to −7·8 kcal. mole^{-1} for $\Delta H_t^\circ(Tr)$ were found for transfer of transition states in Menschutkin reactions from methanol to DMF.[2] Our result of $\Delta H_t^\circ(Tr) = -0·25$ kcal. mole^{-1} for the similar solvent pair methanol–acetonitrile contrasts with that for the Menschutkin reaction.

In all cases we have studied, the major factor in the reduction in activation enthalpy of reaction (1) on proceeding from methanol to the other solvents used is an increase in the enthalpy of the reactants. Values of $\Delta H_t^\circ(Tr)$ are never more negative than −0·3 kcal. mole^{-1} and, indeed, rise to as much as +3·3 kcal. mole^{-1}

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[1] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.
[2] P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginsberg, and P. Steinherz, *Chem. Comm.*, 1968, 194.