Substitution at Saturated Carbon. Part XV.[1] The Effect of t-Butyl Alcohol–Methanol Mixtures on the Free Energy of Reactants and Transition States in the Substitution of Tetraethyltin by Mercury(II) Salts

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Standard free energies of transfer from methanol to t-butyl alcohol–methanol mixtures have been determined for tetraethyltin, mercury(II) chloride, mercury(II) iodide, mercury(II) acetate, and for the transition states in reaction (i; X = Cl, I, and OAc). It is shown that the increases in $\Delta G^\ddagger$ on change of solvent from methanol to t-butyl

$$Et_4Sn + HgX_2 \longrightarrow EtHgX + Et_3SnX \qquad (i)$$

alcohol–methanol mixtures observed for reaction (i; X = Cl, I, and OAc) are due largely to increases in the free energy of the transition states. An analysis of reaction (i; X = Cl) in terms of the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$ suggests that the $[Et_4Sn–HgCl_2]^\ddagger$ transition state possesses the very high dipole moment of *ca.* 14 D.

FREE energies of activation for reactions that involve only electrically neutral molecules as reactants usually decrease in value when the reaction medium is changed from an organic solvent to water or to an aqueous-organic mixture; in several cases it has been shown [2-7] that such decreases in $\Delta G^\ddagger$ are largely due to the effect of the more aqueous media in increasing the free energy of the initial state. For similar reactions that have been studied by use of non-aqueous solvents, initial-state effects are much smaller, and the major solvent effect is often on the transition state.[1,6,8] It has been shown [9] that values of $\Delta G^\ddagger$ for reaction (1; X = Cl, I, and OAc) are increased considerably as the reaction medium is changed from methanol to t-butyl alcohol–methanol mixtures, and we now report a dissection of this effect into initial-state and transition-state contributions.

$$Et_4Sn + HgX_2 \longrightarrow EtHgX + Et_3SnX \quad (1)$$

Theory of the Method.—As before,[3] we use equation (2) in which ΔG_t° represents the standard free energy of transfer of a given species from the reference solvent 1 (methanol) to another solvent 2. The transition state

$$\Delta G_t^\circ(Tr) = \Delta G_t^\circ(Et_4Sn) + \Delta G_t^\circ(HgX_2) + \delta\Delta G^\ddagger \quad (2)$$

is denoted by Tr, and $\delta\Delta G^\ddagger = \Delta G_2^\ddagger - \Delta G_1^\ddagger$; the latter quantities are the free energies of activation in solvents 2 and 1.

The most convenient method of determining $\Delta G_t^\circ(HgX_2)$ is through solubility measurements *via* equation (3). In this equation c_1 and c_2 are the molar solubilities

$$\Delta G_t^c = RT \ln (c_1/c_2) \qquad (3)$$

of the non-electrolyte in solvents 1 and 2, and ΔG_t^c is the standard free energy of transfer on the molar scale.

TABLE 1

Molar solubilities of mercury(II) salts in t-butyl alcohol–methanol mixtures at 25 °C

χ(MeOH)	$HgCl_2$	HgI_2	$Hg(OAc)_2$
1	1·768 [a]	0·0702 [b]	0·278 [c]
0·95	1·593	0·0674	
0·90	1·514	0·0582	
0·84			0·059
0·80	1·428	0·0424	
0·70	1·276	0·0312	
0·60	0·878	0·0229	
0·50	0·616	0·0161	
0·40	0·445	0·0109	0·026
0·30	0·326	0·0081	
0·20	0·248	0·0062	0·021
0·10	0·185	0·0048	
0·05	0·164	0·0043	
0·00	0·152	0·0039	0·014

[a] From ref. 10. [b] W. Herz and F. Kuhn, *Z. anorg. Chem.*, 1908, **60**, 152, give a value of 0·0696. [c] In the presence of 0·07M added acetic acid.

We denote quantities on the molar and mole fraction scales by the superscripts c and x respectively. Equa-

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[1] Part XIV, M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

[2] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 188.

[3] M. H. Abraham, *J. Chem. Soc.* (*A*), 1971, 1061.

[4] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[5] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 1610.

[6] M. H. Abraham, *Progr. Phys. Org. Chem.*, in the press.

[7] M. H. Abraham, *Chem. Comm.*, 1969, 1307.

[8] M. H. Abraham, *J. Chem. Soc.* (*B*), 1971, 299.

[9] M. H. Abraham and F. Behbahany, *J. Chem. Soc.* (*A*), 1971, 1469.

tion (3) is only valid if the same solid phase is in equilibrium with the saturated solutions in solvents 1 and 2.

In Table 1 are the observed molar solubilities of the mercury(II) salts. Data for mercury(II) iodide are straightforward and values of $\Delta G_t^{c}(HgI_2)$ were calculated through equation (3). For mercury(II) chloride, a plot (not shown) of $c(HgCl_2)$ against the mole fraction of methanol in the solvent, χ(MeOH), yields a curve with a secondary maximum at $\chi(MeOH) = 0{\cdot}73$. We consider (*cf.* ref. 10) that methanol solvates of mercury(II) chloride are present in the solid phases in equilibrium with the solutions in the methanol-rich region, and consequently that equation (3) is valid for mercury(II) chloride only over the solvent range $\chi(MeOH) = 0{\cdot}7$ to $0{\cdot}0$. Fortunately, a value for $\Delta G_t^{c}(HgCl_2)$ for transfer from methanol to t-butyl alcohol can be calculated from the known[10] value for transfer from methanol to water together with a value for transfer from water to t-butyl alcohol obtained from the solubilities of mercury(II) chloride in these latter two solvents. We find that $\Delta G_t^{x}(HgCl_2)$ is 1458 cal mol^{-1} and $\Delta G_t^{c}(HgCl_2)$ is 1960 cal mol^{-1} for transfer from methanol to t-butyl alcohol at 298 K. Then over the range of t-butyl alcohol–methanol mixtures from $\chi(MeOH) = 1$ to $0{\cdot}7$, values of $\Delta G_t^{c}(HgCl_2)$ could be calculated by interpolation; they follow quite closely the directly determined values of $\Delta G_t^{c}(HgI_2)$. We also measured a few solubilities of mercury(II) acetate, although it was not so easy to obtain reproducible results with this salt.

Values of $\Delta G_t^{c}(Et_4Sn)$ were determined by the g.l.c. method exactly as described before.[3]

DISCUSSION

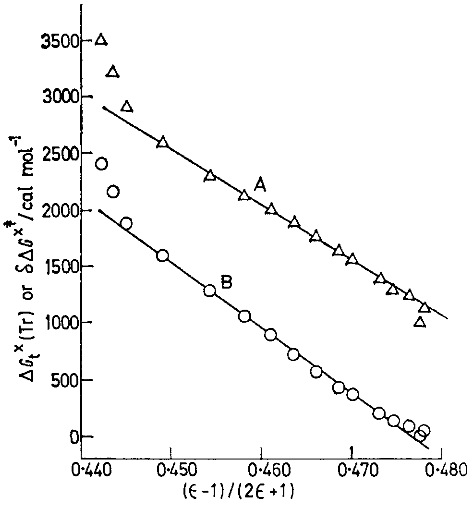
In Table 2 are values of $\Delta G_t^{x}(Et_4Sn)$, $\Delta G_t^{x}(HgCl_2)$, and the free energy of activation term $\delta\Delta G^{x\ddagger}$ for reaction (1; X = Cl); all quantities are thus expressed on the fundamental mole fraction scale. Although both $\Delta G_t^{x}(HgCl_2)$ and $\Delta G_t^{x}(Et_4Sn)$ each vary considerably with solvent composition, they do so in different directions so that the net solvent effect on the reactants is very small. [This is only true if the mole fraction scale is used. For example, for transfer from methanol to t-butyl alcohol, ΔG_t^{x}(Reactants) is -98 cal mol^{-1} but ΔG_t^{c}(Reactants) is no less than $+906$ cal mol^{-1}.] Thus the effect of t-butyl alcohol–methanol solvents on $\Delta G^{x\ddagger}$ values for reaction (1; X = Cl) is mostly due to the solvent effect on the transition state.

Abraham and Johnston[2,11] analysed the effect of methanol–water solvents on values of $\Delta G^{\ddagger}$ for reaction (1; X = Cl) in terms of the Kirkwood equation, and concluded that the dipole moment of the transition state was even higher than that in the solvolysis of t-butyl chloride. Unfortunately, an incorrect value was used for the conversion factor in the Kirkwood equation, so that their calculated dipole moments are in error; in any case, as has been pointed out,[6] the dielectric constants of the methanol–water mixtures are rather too high for the Kirkwood equation to apply. The t-butyl alcohol–methanol solvent system is a better choice of solvent, and the Figure shows a plot of $\delta\Delta G^{x\ddagger}$ for reaction (1; X = Cl) against the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$, where ε is the solvent dielectric constant. A good straight line of slope $-4{\cdot}98 \times 10^4$ cal mol^{-1} is obtained over most of the solvent range studied. The Stearn–Eyring[12] formula, $r = (V/8N)^{\frac{1}{3}}$ where V is the molar volume of a species and N is the Avogadro constant, can be used[6] to calculate radii, r, of solutes and transition states, and with[5] $V(HgCl_2) = 62$ ml mol^{-1} and $V(Tr) = 253$ ml mol^{-1} we obtain $r(HgCl_2) = 2{\cdot}34$ Å and $r(Tr) = 3{\cdot}74$ Å. Using also a value for $\mu(HgCl_2)$ of 1·47 D we calculate that μ(Tr) is no less than 13·8 D. Although the Kirkwood equation has often been applied to values

TABLE 2

Free energies of transfer from methanol to t-butyl alcohol–methanol mixtures of tetraethyltin, mercury(II) chloride, and the tetraethyltin–mercury(II) chloride transition state at 298 K

χ(MeOH) / mole fraction	$\delta\Delta G^{x\ddagger}$ / cal mol^{-1}	ΔG_t^{x}/cal mol^{-1} Et$_4$Sn	HgCl$_2$	Tr
1	0	0	0	0
0·950	124	−138	52	38
0·900	233	−269	121	85
0·875	290	−326	164	128
0·840	379	−409	226	196
0·750	557	−590	390	357
0·700	633	−684	481	430
0·600	760	−843	652	569
0·500	878	−972	813	719
0·400	1005	−1077	958	886
0·300	1119	−1164	1096	1051
0·200	1295	−1249	1231	1277
0·100	1590	−1361	1359	1588
0·050	1895	−1434	1411	1872
0·025	2210	−1482	1428	2156
0	2497	−1556	1458	2399



Plots of A, $\delta\Delta G^{x\ddagger}$ and B, $\Delta G_t^{x}(Tr)$ for reaction (1; X = Cl) in t-butyl alcohol–methanol mixtures against $(\varepsilon - 1)/(2\varepsilon + 1)$. Values of $\delta\Delta G^{x\ddagger}$ have been increased by 1000 cal mol^{-1} in the Figure

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[10] M. H. Abraham, J. F. C. Oliver, and J. A. Richards, *J. Chem. Soc.* (*A*), 1970, 203.

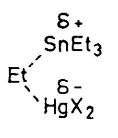
[11] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 193.

[12] A. E. Stearn and H. Eyring, *J. Chem. Phys.*, 1937, **5**, 113.

of $\Delta G^{\ddagger}$ (or of log k) for reactions proceeding in mixed solvents, it has not hitherto been used to correlate ΔG_t^{x}(Tr) values in such mixtures. As shown in the Figure, a good straight line of slope $-5{\cdot}78 \times 10^4$ cal mol^{-1} is obtained when ΔG_t^{x}(Tr) is plotted against $(\varepsilon - 1)/(2\varepsilon + 1)$.* For a single species, the Kirkwood equation can be stated as in equation (4) when ΔG_t^{x} is in cal mol^{-1}, r in Å, and μ in D. With r(Tr) as 3·74 Å,

$$\Delta G^{x}{}_{t} = -1{\cdot}44 \times 10^4 \left[\frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)\right] \qquad (4)$$

equation (4) leads to a value of 14·5 D for μ(Tr), very close to the value deduced from $\delta\Delta G^{x\ddagger}$. Since the dipole moment of the [Bu^{t}Cl]‡ transition state, calculated also from data in alcoholic solvents,[6] is 9·8—10·4 D we conclude that the dipole moment of the [Et$_4$Sn–HgCl$_2$]‡ transition state, 13·8—14·5 D, is higher than that of the S_N1 solvolysis transition state. Hence the conclusions of Abraham and Johnston [2,11] are (fortuitously) qualitatively and even quantitatively valid. The very high dipole moment suggests an 'open' transition state, *e.g.*, (I; X = Cl), for the S_E2 substitution. If a correction to μ(Tr) is made for the effect of the HgCl$_2$ group in the transition state (I), it can be calculated that with an Sn–Hg distance of 3·1 Å in (I; X = Cl), the charge separation is 0·86—0·91 unit. This value compares exceedingly well with that calculated from salt effects on reaction (1; X = Cl) in the same range of t-butyl alcohol–methanol solvents (average 0·88 unit),[9] and confirms the high polar character of the [Et$_4$Sn–HgCl$_2$]‡ transition state in hydroxylic solvents.



(I)

Less complete data on reaction (1; X = I) are in Table 3. The general trends shown in Table 3 are similar to those in Table 2, and we conclude that the nature of the [Et$_4$Sn–HgCl$_2$]‡ and [Et$_4$Sn–HgI$_2$]‡ transition states must be very close. Hence transition state (I; X = I) can also be held to obtain in the various solvents studied (Table 3), the charge separation in (I; X = I) being about the same as that in (I; X = Cl).

TABLE 3

Free energies of transfer from methanol to t-butyl alcohol–methanol mixtures of tetraethyltin, mercury(II) iodide, and the tetraethyltin–mercury(II) iodide transition state at 298 K

χ(MeOH)/mole fraction	$\delta\Delta G^{x\ddagger}$/cal mol^{-1}	ΔG_t^{x}/cal mol^{-1}		
		Et$_4$Sn	HgI$_2$	Tr
1	0	0	0	0
0·840	374	−409	93	58
0·400	1095	−1077	739	757
0·200	1602	−1249	1014	1367
0	3098	−1556	1210	2752

Data on the mercury(II) acetate reaction are in Table 4, the most noteworthy feature being the large increase in value of ΔG_t^{x}(Tr) over the solvent range χ(MeOH) = 1 to 0·84. A possible source of error, however, is that the rate constant for reaction (1; X = OAc) in the most polar solvent methanol might include a contribution from the electrophile HgOAc$^+$. Any correction for such a contribution would decrease the values of $\delta\Delta G^{\ddagger}$ and ΔG_{xt}(Tr) by a constant amount throughout, thus bringing the latter values more into line with those observed for the chloride and iodide reactions.

TABLE 4

Free energies of transfer from methanol to t-butyl alcohol–methanol mixtures of tetraethyltin, mercury(II) acetate, and the tetraethyltin–mercury(II) acetate transition state at 298 K

χ(MeOH)/mole fraction	$\delta\Delta G^{x\ddagger}$/cal mol^{-1}	ΔG_t^{x}/cal mol^{-1}		
		Et$_4$Sn	Hg(OAc)$_2$	Tr
1	0	0	0	0
0·840	740	−410	800	1130
0·400	1630	−1080	1060	1610
0·200	2160	−1250	1100	2010
0	3290	−1560	1270	3000

EXPERIMENTAL

The solvents and the mercury(II) salts were exactly as described.[9] Saturated solutions of the salts were obtained by shaking an excess of the mercury(II) salt with a given solvent for not less than 72 h at 25·0 ± 0·1 °C. It was not found necessary to filter the saturated solutions, and aliquot portions were withdrawn and analysed as follows. Solutions of mercury(II) chloride were suitably diluted with water and the mercury(II) content determined by titration with use of ethylenediaminetetra-acetic acid (edta). The mercury(II) acetate aliquot portions were added directly to an excess of edta, then buffered to pH 9 and back-titrated against zinc sulphate as usual; this procedure avoids the necessity of acidifying the quenched solution in order to stop precipitation of mercury(II) oxide. End points in the edta titration with mercury(II) iodide were very indistinct, and the mercury(II) iodide solutions were therefore analysed spectrophotometrically. Aliquot portions of the mercury(II) iodide saturated solutions were diluted with methanol and the absorbance of the diluted portion determined at 335 nm by use of an SP 500 spectrophotometer. The molar absorptivity of mercury(II) in methanol solution in the presence of t-butyl alcohol was found in separate calibration experiments to be given by equation (5) in which the term b denotes the molar concentration of t-butyl alcohol in the solvent. This calibration was necessary because the low

$$A(\mathrm{HgI_2})^{335} = (0{\cdot}127b + 1{\cdot}69) \times 10^2 \qquad (5)$$

solubility of mercury(II) iodide in the t-butyl alcohol-rich region resulted in solutions for analysis containing large quantities of t-butyl alcohol.

Values of ΔG_t^{x}(Et$_4$Sn) were determined by the g.l.c. method [1,3] and are in Table 2.

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* The linear relations shown in the Figure do not hold for solvent mixtures with $\varepsilon < 13$; it is interesting that this limit corresponds closely with that calculated using the equation of Bell[13] with μ(Tr) = 14 D and r(Tr) = 3·74 Å, namely $\varepsilon = 11$.

[13] R. P. Bell, *Trans. Faraday Soc.*, 1935, **31**, 1557.