Substitution at Saturated Carbon. Part 21.[1] Effect of Alcoholic Solvents on the Enthalpy and Entropy of the Tetraethyltin–Mercury(II) Chloride Transition State and of the t-Butyl Chloride Solvolysis Transition State; Comparison with 1 :1 Electrolytes

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Heats of solution are reported for tetraethyltin and mercury(II) chloride in methanol, methanol–t-butyl alcohol mixtures, and t-butyl alcohol. With previous data on free energies, these measurements lead to entropies of transfer as well as enthalpies of transfer from methanol to the other solvents of tetraethyltin, mercury(II) chloride, and the tetraethyltin–mercury(II) chloride transition state. It is shown that the very large variation in $\Delta S^‡$ for the reaction between tetraethyltin and mercury(II) chloride is almost entirely due to initial state effects. Heats of solution of t-butyl chloride in a number of pure alcohols have been determined and lead similarly to enthalpies and entropies of transfer of the solvolysis transition state from methanol to the other alcohols. Variations of the entropy of the $[Et_4Sn–HgCl_2]^‡$ and $[Bu^tCl]^‡$ transition states with change of alcoholic solvent are quite small, whereas the entropy of dissociated species such as $(Pr_4N^+ + I^-)$ or $(Me_4N^+ + Cl^-)$ is considerably lower in the less polar alcohols than in methanol. It is suggested that these dissociated species are poor models for the particular transition states discussed, and that in general thermodynamic properties of polar, electrically neutral, transition states are not comparable quantitatively with those of dissociated species, as far as variation with solvent is concerned.

A NUMBER of studies have been reported on the variation of enthalpy or of free energy of transition states with change of solvent (see ref. 2), but to date there have been few such studies on the entropy of transition states. This is not surprising, since in order to dissect solvent effects on values of $\Delta S^‡$ into initial-state and transition-state contributions, it is normally necessary first to carry out dissections in terms of both enthalpy and free energy. In this way, the effects of aqueous alcoholic solvents on $\Delta H^‡$, $\Delta G^‡$, and $\Delta S^‡$ have been analysed into initial-state and transition-state contributions both for the solvolysis of t-butyl chloride[3] and for the bimolecular reaction of tetraethyltin with mercury(II) chloride.[4] Few generalisations, however, are possible because of the large influence that the size of a species has on its entropy of transfer to and from aqueous media.[5] The effect of non-aqueous solvents on values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ has been analysed in terms of initial-state and transition-state contributions only for the Menschutkin reactions of pyridine with benzyl halides;[2,6] the marked decrease in $\Delta S^‡$ on transfer from methanol to dimethylformamide has been shown to arise largely from transition-state effects.*

Abraham and Behbahany[8] have determined activation parameters for reaction (1) using a number of methanol-t-butyl alcohol solvent mixtures ranging from pure methanol to pure t-butyl alcohol. Now since Abraham and Dorrell[9] have dissected the variation in $\Delta G^‡$ for reaction (1) into initial-state and transition-state contributions, it remains only to carry out a similar dissection of $\Delta H^‡$ in order also to separate $\Delta S^‡$ into initial-state and transition-state effects.

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

Solvent Effects on Reaction (1).—The effect of methanol–t-butyl alcohol mixtures on the enthalpy of the transition state (Tr) in reaction (1) can be analysed in terms of equation (2), where ΔH_t° is the standard enthalpy of transfer of a solute from the reference solvent 1 (methanol) to solvent 2, and $\Delta H_1^‡$ and $\Delta H_2^‡$ are the activation enthalpies in solvents 1 and 2; for brevity $\Delta H_2^‡ - \Delta H_1^‡$ will be referred to as $\delta\Delta H^‡$. Equation (2) assumes that the activation parameters for equation (1) refer exclusively to attack by $HgCl_2$ and not to attack by $HgCl_2$ plus $\overset{+}{Hg}Cl$. However, it has been shown[10] that in methanol $\overset{+}{Hg}Cl$ is kinetically not significant and therefore the activation parameters refer only to attack by $HgCl_2$. This should be the case also in the less polar alcoholic mixtures. The enthalpy of transfer of a solute, ΔH_t°, can be obtained from the heat of solution at infinite dilution of the given solute in solvents 1 and 2 [equation (3)].

$$\Delta H_t^\circ(\mathrm{Tr}) = \Delta H_t^\circ(Et_4Sn) + \Delta H_t^\circ(HgCl_2) + \Delta H_2^‡ - \Delta H_1^‡ \qquad (2)$$

$$\Delta H_t^\circ = \Delta H_s^\circ{}_{,2} - \Delta H_s^\circ{}_{,1} \qquad (3)$$

Determination of the heats of solution of tetraethyltin and mercury(II) chloride presented no difficulties except for mercury(II) chloride in mixtures containing large

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* Studies have been carried out on reactions of anions with uncharged solutes, but in these cases an extrathermodynamic assumption is always needed in order to deduce the effect of solvents on the anion and on the charged transition state (see *e.g.* ref. 7).

[1] Part 20, M. H. Abraham and P. L. Grellier, *J.C.S. Perkin II*, 1976, 1735.

[2] M. H. Abraham, *Prog. Phys. Org. Chem.*, 1974, **11**, 1.

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

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

[5] M. H. Abraham, *J.C.S. Faraday I*, 1973, **69**, 1375.

[6] R. W. Alder, R. Baker, and J. M. Brown, 'Mechanism in Organic Chemistry,' Wiley–Interscience, 1971, p. 50.

[7] B. G. Cox and A. J. Parker, *J. Amer. Chem. Soc.*, 1973, **95**, 408.

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

[9] M. H. Abraham and F. J. Dorrell, *J.C.S. Perkin II*, 1973, 444.

[10] M. H. Abraham, R. J. Irving, and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 199; M. H. Abraham and G. F. Johnston, *ibid.*, p. 188.

proportions of t-butyl alcohol. In these cases, the low solubility and consequent low rate of dissolution of the solute in the solvent resulted in less accurate determinations. Additionally, since t-butyl alcohol is a solid at 298 K, heats of solution in pure t-butyl alcohol were determined at 299 K. Results of the determinations are in Table 1; the new values for $\Delta H_s°$ in methanol agree well with the older values.[10,11] Values of $\Delta H_s°(Et_4Sn)$ are fairly constant over the solvent range covered, although it is interesting that a minimum value is reached at a molar fraction of methanol (x_{MeOH}) of 0.45. The $\Delta H_s°(HgCl_2)$ values, on the other hand, become increasingly more positive as x_{MeOH} becomes less, possibly because mercury(II) chloride is solvated by methanol much more strongly than by t-butyl alcohol.

TABLE 1

Heats of solution (cal mol^{-1}) of tetraethyltin and mercury(II) chloride in methanol–t-butyl alcohol mixtures, at 298 K

x_{MeOH} [a]	$\Delta H_s°(Et_4Sn)$	$\Delta H_s°(HgCl_2)$
1	1 840 [b]	−710 [c]
0.84	1 370	−310
0.70	1 160	+910
0.50	1 070	1 360
0.40	1 060	2 410
0.30	1 170	3 060
0.20	1 220	3 850
0.05	1 340	4 990
0 (299 K)	1 450	5 320

[a] Mol fraction methanol. [b] Ref. 10 gives 1 860. [c] Ref. 10 gives −690 and ref. 11 −710.

TABLE 2

Calculation of enthalpies of transfer from methanol to methanol–t-butyl alcohol mixtures of the transition state in reaction (1), at 298 K

x_{MeOH} [a]	$\delta\Delta H^‡$ [b]	$\Delta H_t°$/kcal mol^{-1} Et$_4$Sn	HgCl$_2$	Tr
1	0	0	0	0
0.84	0.50	−0.47	0.40	0.43
0.70	0.80	−0.68	0.90	1.02
0.50	0.05	−0.77	2.07	1.35
0.40	−0.80	−0.78	3.12	1.54
0.30	−1.95	−0.67	3.77	1.15
0.20	−2.40	−0.62	4.56	1.54
0.05	−3.95	−0.50	5.70	1.25
0	−4.05	−0.39	6.03	1.59

[a] Mol fraction methanol. [b] Ref. 8.

Combination of the $\Delta H_s°$ values in Table 1 (as $\Delta H_t°$) with the corresponding enthalpies of activation yields the required values of $\Delta H_t°(Tr)$, in Table 2. We estimate the overall error in these values to be *ca.* ±0.3 kcal mol^{-1}. The reduction in $\delta\Delta H^‡$ when x_{MeOH} is less than *ca.* 0.4 is clearly due to an initial-state effect, since $\Delta H_t°(Tr)$ is always positive. An interesting feature of the $\delta\Delta H^‡$ values is the smooth maximum that occurs at x_{MeOH} *ca.* 0.7. Table 2 shows that the maximum arises from a combination of initial-state and transition-state effects.

The present enthalpy values may be combined with the free energy data of Abraham and Dorrell[4] to yield entropies of transfer through an equation similar to equation (2). Results are in Table 3, where all $\Delta S_t°$ values refer to the mol fraction scale.* The error in the final values of $\Delta S_t°(Tr)$ is mainly due to the error in $\delta\Delta S^‡$ and is *ca.* 2 cal K^{-1} mol^{-1}. Values of $\Delta S_t°(Et_4Sn)$ are not exceptional, but those of $\Delta S_t°(HgCl_2)$ are so large that they must reflect the solvation of mercury(II) chloride in the more methanolic media. The main feature of the $\delta\Delta S^‡$ values (Table 3) is the large reduction as the solvent becomes less polar; for the extreme solvents methanol and t-butyl alcohol, $\delta\Delta S^‡ = -22$ cal K^{-1} mol^{-1}. Now there is considerable evidence that the transition state for reaction (1) is similar in these two solvents, and in the various solvent mixtures. Reaction (1) exhibits positive kinetic salt effects in methanol, methanol–t-butyl alcohol mixtures, and t-butyl alcohol, with the polar term z^2d approximately constant over the entire range.[8] Constitutional effects of various alkyl groups in R_4Sn on rate constants for the R_4Sn–$HgCl_2$ reaction are very similar in methanol and t-butyl alcohol.[12] Hence the Et_4Sn–$HgCl_2$ transition state is likely to be geometrically similar, and of similar polarity in the methanol–t-butyl alcohol mixtures used. A conventional explanation of the variation in $\delta\Delta S^‡$ would attribute the variation to a transition state effect, with the polar transition state undergoing a decrease in entropy on transfer to the less polar media, perhaps due to ' freezing-out ' of solvent molecules. The present work shows that this explanation cannot be correct, since the decrease in $\delta\Delta S^‡$ is seen to be almost entirely the result of initial-state effects over the whole solvent range. For transfer from methanol to t-butyl alcohol, $\Delta S_t°(Tr)$ is only −3 cal K^{-1} mol^{-1}, whereas $\Delta S_t°$ (reactants) = +19 cal K^{-1} mol^{-1}, and for transfer to most of the solvent mixtures, $\Delta S_t°(Tr)$ is slightly positive. The maximum in $\delta\Delta S^‡$ at x_{MeOH} *ca.* 0.7 is due to a combination of initial-state and transition-state effects, but I wish to concentrate on the main features of the entropy

TABLE 3

Calculation of entropies of transfer, on the mol fraction scale, from methanol to methanol–t-butyl alcohol mixtures of the transition state in reaction (1), at 298 K

x_{MeOH} [a]	$\delta\Delta S^‡$ [b]	$\Delta S_t°$/cal K^{-1} mol^{-1} Et$_4$Sn	HgCl$_2$	Tr
1	0	0	0	0
0.84	0.4	−0.2	0.6	0.8
0.70	0.6	0.0	1.4	2.0
0.50	−2.8	0.7	4.2	2.1
0.40	−6.1	1.0	7.3	2.2
0.30	−10.3	1.7	9.0	0.4
0.20	−12.4	2.1	11.2	0.9
0.05	−19.6	3.1	14.4	−2.1
0	−22.0	3.9	15.3	−2.8

[a] Mol fraction methanol. [b] From ref. 8, after conversion to the mol fraction scale.

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* Strictly, the values of $\delta\Delta H^‡$ should also be recalculated on the mol fraction scale, whereas the values of Table 2 are the original molar values. However the difference between $\Delta H^{‡x}$ and $\Delta H^{‡c}$ is small, and the difference between $\delta\Delta H^{‡x}$ and $\delta H^{‡c}$ is quite negligible.

[11] C. T. Mortimer, H. O. Pritchard, and H. A. Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220.

[12] M. H. Abraham, F. Behbahany, and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 2566.

data: the decrease in $\delta\Delta S^\ddagger$ due to initial-state effects, and the apparent anomaly in that a polar transition state would be expected to give rise to negative values of $\Delta S_t^\circ(\mathrm{Tr})$ on transfer to a less polar solvent. Unfortunately, there are few data with which to compare the entropy values obtained in the present work, and so I thought it of interest to determine values of $\Delta S_t^\circ(\mathrm{Tr})$ for the solvolysis of the t-butyl halides, since these transition states in alcoholic solvents are known to be quite highly polar.

Solvent Effects on the Solvolysis of t-Butyl Halides.—The effect of alcoholic solvents on values of $\Delta G^\ddagger$ for the solvolysis of t-butyl chloride and bromide has already been dissected into initial-state and transition-state contributions. In addition, Rudakov and Tretyakov have carried out an analysis in terms of enthalpy and entropy, using data on heats of solution of t-butyl chloride derived from the variation of the Henry's law constant with temperature.[13] Since this method is not very reliable, it seemed better to determine the necessary $\Delta H_s^\circ(\mathrm{Bu^tX})$ values by direct calorimetry. Details of the measurements are in Table 4; the present value for $\Delta H_s^\circ(\mathrm{Bu^tCl})$ in ethanol, 339 cal mol^{-1}, compares well with that reported by Stoffer[14] (332 ± 8 cal mol^{-1}).* The thermodynamic parameters, ΔG_t°,[16] ΔH_t°, and ΔS_t°, for transfer of the t-butyl halides from methanol to various alcohols are also given in Table 4; as in the case of transfer of tetraethyltin from methanol to methanol–t-butyl alcohol mixtures, variations in ΔH_t° and ΔS_t° are small.

TABLE 4

Thermodynamics of transfer[a] of t-butyl halides from methanol to other alcohols, at 298 K

Solute	Solvent	ΔH_s°	ΔH_t°	ΔG_t°	ΔS_t°
$\mathrm{Bu^tCl}$	MeOH	360	0	0	0
	EtOH	339	−20	−260	0.8
	$\mathrm{Pr^nOH}$	427	+70	−340	1.4
	$\mathrm{Bu^nOH}$	530	+170	−460	2.1
	$\mathrm{Pr^iOH}$	836	+480	−300	2.6
$\mathrm{Bu^tBr}$	MeOH	475	0	0	0
	EtOH	401	−70	−390	1.1
	$\mathrm{Pr^nOH}$	451	−20	−500	1.6

[a] ΔH_s° (this work), ΔH_t°, and ΔG_t° in cal mol^{-1}; ΔS_t° in cal K^{-1} mol^{-1}. All on the mol fraction scale.

Although there is general agreement between various workers as to values of the rate constant for solvolyses of t-butyl chloride at 298 K, there is not such agreement concerning the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for solvolyses in pure alcohols. Only for solvolyses in methanol[17-19] and perhaps ethanol[17] can the quoted activation parameters be considered reliable, and for the other alcoholic solvents, I have calculated the values of $\Delta H^\ddagger$ from various recorded rate constants at different temperatures.[16,20-22] The activation parameters for solvolysis of t-butyl chloride are in Table 5, together with values for the t-butyl bromide solvolysis from the work of Virtanen.[23] Combination of these $\Delta H^\ddagger$ values with data on $\Delta H_t^\circ(\mathrm{Bu^tX})$ yields the values of ΔH_t° for the transition states, Table 6. As suggested by Rudakov and Tretyakov,[21] initial-state effects are small. Since all the ΔG_t° values are known for these transfers,[2,16] the corresponding ΔS_t° values may be calculated (Table 7). It is surprising that the entropies of transfer of the polar solvolysis transition states are numerically small. Arnett,[24] in his analysis of the effect of ethanol–water mixtures on $\Delta H^\ddagger$ for solvolysis of t-butyl chloride, showed that salts such as ($\mathrm{Me_4N^+ + Cl^-}$) and ($\mathrm{Me_3S^+ + Cl^-}$) were reasonable models for the solvolysis transition state. Since then, it has been shown that, in terms of free energy, salts of type ($\mathrm{Me_4N^+ + X^-}$) were not very good models, but that ion pairs ($\mathrm{Me_4NX}$) were much better transition-state models.[16] There seems little possibility of obtaining accurate entropies of transfer of such ion pairs, but it is clearly of interest to see if ΔS_t°

TABLE 5

Activation parameters[a] for the solvolysis of t-butyl halides at 298 K

Halide	Solvent	$-\log k$[b]	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Ref.
$\mathrm{Bu^tCl}$	MeOH	6.10	25.77	25.10	−2.2	*c*
	EtOH	7.07	27.10	26.10	−3.4	17
	$\mathrm{Pr^nOH}$	7.33	27.45	26.0	−5	*d*
	$\mathrm{Bu^nOH}$	7.39	27.53	23.6	−13	*d*
	$\mathrm{Pr^iOH}$	7.74	28.01	24.5	−12	*d*
$\mathrm{Bu^tBr}$	MeOH	4.46	23.54	23.00	−1.8	23
	EtOH	5.35	24.75	24.40	−1.2	23

[a] $\Delta G^\ddagger$ and $\Delta H^\ddagger$ in kcal mol^{-1}; $\Delta S^\ddagger$ in cal K^{-1} mol^{-1}. [b] Values from refs. 2 and 16. [c] $\Delta H^\ddagger$ taken as the average of values calculated from data in refs. 17—19. [d] $\Delta H^\ddagger$ calculated from rate constants given in refs. 16 and 20—22.

TABLE 6

Calculations of enthalpies of transfer from methanol to alcohols of transition states in the solvolysis of t-butyl halides, at 298 K

			ΔH_t°/kcal mol^{-1}	
Halide	Solvent	$\delta\Delta H^\ddagger$	$\mathrm{Bu^tX}$	Tr
$\mathrm{Bu^tCl}$	MeOH	0	0	0
	EtOH	1.0	0.0	1.0
	$\mathrm{Pr^nOH}$	0.9	0.1	1.0
	$\mathrm{Bu^nOH}$	−1.5	0.2	−1.3
	$\mathrm{Pr^iOH}$	−0.6	+0.5	−0.1
$\mathrm{Bu^tBr}$	MeOH	0	0	0
	EtOH	1.4	−0.1	1.3

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* A value of 361 cal mol^{-1} was obtained earlier by Arnett.[15]

[13] E. S. Rudakov and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1965, 2(4), 142.

[14] J. O. Stoffer, W. C. Duer, and G. L. Bertrand, *Chem. Comm.*, 1969, 1188.

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[16] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

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[18] J. Biordi and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1962, 4291; values of $\Delta H^\ddagger$ recalculated in the present work.

[19] C. R. Turnquist, J. W. Taylor, E. P. Grimsrud, and R. C. Williams, *J. Amer. Chem. Soc.*, 1973, **95**, 4133; values of $\Delta H^\ddagger$ recalculated in the present work.

[20] E. S. Rudakov and Y. A. Kivalin, *Reakts. spos. org. Soedinenii*, 1964, 1(2), 114.

[21] E. S. Rudakov and V. P. Tretyakov, *Reakts spos. org. Soedinenii*, 1965, 2(1), 135.

[22] A. O. Körgesaar, V. H. Timotheus, and V. A. Palm, *Tr. Konf. po Probl. Primeneniya Korrelyatsion Uravneniiv Organ. Khim. Tartusk Gos. Univ. Tartu*, 1962, **1**, 265.

[23] P. O. I. Virtanen, *Suomen Kem.*, 1967, **40B**, 179.

[24] E. M. Arnett, in 'Physico-chemical Processes in Mixed Aqueous Solvents,' ed. F. Franks, Heinemann, London, 1967.

values for dissociated pairs of ions are in any way comparable with values for the solvolysis transition state.

Comparisons of Solvent Effects on 1 : 1 *Electrolytes with Transition States.*—Tetra-n-propylammonium iodide was chosen as a suitable electrolyte. Heats of solution were determined at various final concentrations, and extrapolation to zero concentration by methods outlined before [25-27] yielded the $\Delta H_s°$ values in Table 8. As a check on the purity of the salt, its heat of solution in water was also determined. Combination of the derived $\Delta H_t°(\mathrm{Pr_4N^+ + I^-})$ values with corresponding $\Delta G_t°$ values yields the entropy of transfer of the dissociated pair of ions, Table 9. Use of Abraham's method [5] then enables $\Delta S_t°$ values to be deduced for the pair of ions $(\mathrm{Me_4N^+ + X^-})$, where X = Cl or Br, Table 9.

TABLE 7

Calculation of entropies of transfer, on the mol fraction scale, from methanol to alcohols of transition states in the solvolysis of t-butyl halides, at 298 K

Halide	Solvent	$\Delta S^‡$	$\Delta S_t°$/cal K^{-1} mol^{-1}	
			$\mathrm{Bu^tX}$	Tr
$\mathrm{Bu^tCl}$	MeOH	0	0	0
	EtOH	−1.2	0.8	−0.4
	$\mathrm{Pr^nOH}$	−3	1	−2
	$\mathrm{Bu^nOH}$	−11	2	−9
	$\mathrm{Pr^iOH}$	−10	3	−7
$\mathrm{Bu^tBr}$	MeOH	0	0	0
	EtOH	0.6	1.1	1.7

TABLE 8

Heats of solution (cal mol^{-1}) of tetra-n-propylammonium iodide, at 298 K

Solvent	$\Delta H_s°$
H_2O	2 770,[a] 2 740 [b]
MeOH	6 110 [c]
EtOH	6 280 [b]
$\mathrm{Pr^nOH}$	6 830 [b]
$\mathrm{Bu^nOH}$	5 100 [b]
$\mathrm{Pr^iOH}$	6 200 [b]

[a] C. M. Criss and O. N. Bhatnagar, *J. Phys. Chem.*, 1969, **73**, 174; T. S. Sarma, R. K. Mohanty, and J. C. Ahluwalia, *Trans. Faraday Soc.*, 1969, **65**, 2333. [b] This work, extrapolated to infinite dilution and corrected for ion association. [c] Calculated from the value of 2 770 in water, and the single-ion transfer values given in ref. 5.

TABLE 9

Entropies of transfer,[a] on the mol fraction scale, from methanol to alcohols, at 298 K

	$\mathrm{Pr_4N^+ + I^-}$			$\mathrm{Me_4N^+ + X^-}$
	$\Delta G_t°$ [b]	$\Delta H_t°$ [c]	$\Delta S_t°$	$\Delta S_t°$ [d]
MeOH	0	0	0	0
EtOH	2.0	0.2	−6	−12
$\mathrm{Pr^nOH}$	3.2 [e]	0.7	−9	−16
$\mathrm{Bu^nOH}$	3.8	−1.0	−15	−22
$\mathrm{Pr^iOH}$	4.1	0.1	−13	−20

[a] $\Delta G_t°$ and $\Delta H_t°$ in kcal mol^{-1}; $\Delta S_t°$ in cal K^{-1} mol^{-1}. [b] Refs. 2 and 16. [c] This work. [d] Calculated by the method in ref. 5. [e] M. H. Abraham and A. F. Danil de Namor, unpublished work.

Comparison of data in Tables 7 and 9 shows at once that the pair of ions $(\mathrm{Me_4N^+ + Cl^-})$ is not at all a suitable model for the t-butyl chloride solvolysis transition state, at least in terms of entropy. Especially in the more polar alcohols ethanol and propan-1-ol, $\Delta S_t°$ for $(\mathrm{Me_4N^+ + Cl^-})$ is far more negative than that for $[\mathrm{Bu^tCl}]^‡$. The same also is true for $(\mathrm{Me_4N^+ + Br^-})$ as compared with $[\mathrm{Bu^tBr}]^‡$ for transfer from methanol to ethanol.

It is now possible to review the data on the $[\mathrm{Et_4Sn{-}HgCl_2}]^‡$ transition state, Table 3, in the light of the above results. Of course, transfers of the bimolecular reaction transition state are from methanol to mixed solvents and not to pure alcohols, but the mixed solvents (Table 3) are all alcoholic in type. If transfers from methanol to an alcoholic solvent of $\varepsilon = 20$ are considered (*e.g.* to propan-1-ol and to $\mathrm{MeOH{-}Bu^tOH}$ of x_{MeOH} 0.5) and if we compare species of about the same molar volume, then we have for $\Delta S_t°$ in cal K^{-1} mol^{-1}:

$$[\mathrm{Et_4Sn{-}HgCl}]^‡ + 2 \text{ and } (\mathrm{Pr_4N^+ + I^-}) - 9$$
$$[\mathrm{Bu^tCl}]^‡ - 2 \text{ and } (\mathrm{Me_4N^+ + Cl^-}) - 16$$

It seems as though quite polar transition states such as $[\mathrm{Bu^tCl}]^‡$ give rise to $\Delta S_t°$ values that are not highly negative. Since charge separation in the $[\mathrm{Et_4Sn{-}HgCl_2}]^‡$ transition state is considered to be less than in the $[\mathrm{Bu^tCl}]^‡$ transition state, it is not surprising that its entropy of transfer is less negative. The data in Table **3** are thus not incompatible with a transition state that carries a moderate charge separation, and the present results do not conflict with previous conclusions that the transition state is quite polar in character.

At the present state of knowledge, it seems difficult to draw rigorous conclusions as to the nature of transition states from just a knowledge of entropies of transfer. For the methanol–alcohol systems discussed in the present work, much more entropy data are required in order to reach definite conclusions.

EXPERIMENTAL

The solvents, and the various solutes used, were exactly as described previously.[5,8] Heats of solution of $\mathrm{Et_4Sn}$ and $\mathrm{HgCl_2}$ in the $\mathrm{MeOH{-}Bu^tOH}$ mixtures were obtained by using the apparatus described before.[10] Heats of solution of $\mathrm{Pr_4NI}$, $\mathrm{Bu^tCl}$, and $\mathrm{Bu^tBr}$ in the alcohols were determined by using an LKB solution calorimeter; some of these measurements were carried out in the usual manual way, but others were performed by using a flat-bed recorder coupled to the LKB calorimeter in order to provide a continuous read-out of the calorimetric run. In all cases, corrections were made for the heat of breaking of the ampoule. For the volatile solutes $\mathrm{Bu^tBr}$ and (especially) $\mathrm{Bu^tCl}$ there is also a correction to be made for condensation of the solute vapour in the vapour space of the ampoule. In order to reduce the size of such corrections heats of solution of these two solutes were determined with much larger quantities of solute (and hence less vapour space) than usual, the final solutions being about 3×10^{-2}M. Thermochemical functions refer to the isothermal process at 298 K and are expressed in terms of the defined calorie (4.184 0 J).

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