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SUBSTITUTION AT SATURATED CARBON

XXIII *. INITIAL-STATE AND TRANSITION-STATE SOLVENT EFFECTS OF METHANOL, ACETONITRILE AND DMSO ON SOME R_4Sn/HgX_2 REACTIONS

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Summary

The kinetics of the reaction of Me_4Sn with $HgCl_2$ in methanol have been reinvestigated; the activation parameters obtained are in good agreement with those previously reported by Abraham and Johnston. Activation parameters for a number of R_4Sn/HgX_2 reactions in methanol are compared with parameters in acetonitrile and DMSO; the latter two dipolar aprotic solvents lower the free energy and enthalpy of activation. By determining solvent effects on the free energy, enthalpy and entropy of the reactants it is shown that for the methanol → acetonitrile transfer the lowering of the $\Delta G^{\neq}$ and $\Delta H^{\neq}$ values is mostly due to an increase in the initial-state values. For the methanol → DMSO transfer, the decreases in $\Delta G^{\neq}$ are due to very large transition-state decreases combined with not-so-large initial-state decreases; this is also the case in terms of the enthalpy function.

It is shown that the solvation of the R_4Sn/HgX_2 transition state follows quite closely the solvation of the corresponding mercury(II) halide in methanol, acetonitrile and DMSO, so that the transition states to some extent resemble the reactants and can be described as "early" transition states.

Introduction

Rate constants have been reported for the reaction of a considerable number of tetraalkyltins with mercury(II) salts in polar solvents [1—9], so that Roberts [7], Reutov et al. [9], and also ourselves have been able to discuss the influence

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* For part XXII see ref. 26.

of various alkyl groups, R, on the reactivity of the R_4Sn compounds. Reutov et al. [9] have also drawn attention to the marked accelerating effect of dipolar aprotic solvents over hydroxylic solvents on these reactions, and have pointed out that a dissection of these solvent effects into initial-state and transition-state contributions is necessary for any understanding of the solvent effect. We set out to determine initial-state and transition-state effects for simple tetraalkyltin/mercury(II) halide reactions in the most studied hydroxylic solvent, methanol, and in typical dipolar aprotic solvents such as acetonitrile and dimethyl sulphoxide (DMSO). Unfortunately, any discussion is rendered very difficult because of a large discrepancy in the reported activation parameters for reaction of the first member of the series, tetramethyltin, with mercury(II) chloride in methanol. Abraham and Johnston [2] originally reported $\Delta H^{\neq}$ 10.6 kcal mol^{-1} and $\Delta S^{\neq}$ -22 cal K^{-1} mol^{-1}, but later work by Reutov et al. [9] resulted in values of $\Delta H^{\neq}$ 16.0 kcal mol^{-1} and $\Delta S^{\neq}$ -5 cal K^{-1} mol^{-1}. We therefore felt it necessary, before starting our solvent effect studies, to redetermine activation parameters for reaction 1 ($R = Me$, $X = Cl$) in methanol; at the same time we also checked results [7] for reaction 1 ($R = Me$, $X = I$) in methanol.

$$R_4Sn + HgX_2 \rightarrow RHgX + R_3SnX \qquad (1)$$

Kinetic studies in methanol

The only major difference in the experimental conditions used by Abraham and Johnston [2] and by Reutov et al. [9] is that the former experiments were carried out at zero ionic strength, and the latter in presence of 0.1 *M* sodium perchlorate. Although addition of salt might affect the rate constant, it is unlikely to produce very large changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$.Nevertheless, we felt it necessary to check this point and in Table 1 are given our newly-determined rate constants for reaction 1 ($R = Me$, $X = Cl$) both in the presence and absence of sodium perchlorate. The new results are in reasonable agreement with those of Abraham and Johnston [2], and show also that added sodium perchlorate considerably

TABLE 1

RATE CONSTANTS (l mol^{-1} s^{-1}) [a] FOR REACTION OF Me_4Sn WITH $HgCl_2$ AND HgI_2 IN METHANOL

T (K)	With $HgCl_2$				With HgI_2
	Zero ionic strength		With 0.1 *M* $NaClO_4$		This work
	Ref. 2	This work	Ref. 9	This work	
288.15				1.26	
298.15	1.55	1.40	0.97	2.54	0.310
303.15		2.00	1.44	3.56	
308.15					0.603
313.15	3.84	3.68	3.69	6.52	
318.15			5.56		1.064

[a] All rate constants in this work, or in ref. 2, are corrected for expansion or contraction of solvent from 298.15 K.

TABLE 2

ACTIVATION PARAMETERS [a] (MOLAR SCALE) FOR REACTION OF Me_4Sn WITH $HgCl_2$ AND HgI_2 IN METHANOL

	With $HgCl_2$				With HgI_2	
	Zero ionic strength		With 0.1 *M* $NaClO_4$		Zero ionic strength	
	Ref. 2	This work	Ref. 9	This work	Ref. 7 and 11	This work
$\Delta G^{\neq}$	17.19 ± 0.01	17.25 ± 0.01	17.47	16.90 ± 0.01	18.0	18.15 ± 0.02
$\Delta H^{\neq}$	10.6 ± 0.45	11.3 ± 0.35	16.0	11.2 ± 0.2	10.8 ± 0.5	11.0 ± 0.5
$\Delta S^{\neq}$	−22.1 ± 1.5	−19.9 ± 1.2	−5	−19.1 ± 0.7	−24.2 ± 1.7 [b]	−23.8 ± 1.7

[a] $\Delta G^{\neq}$ and $\Delta H^{\neq}$ in kcal mol^{-1}, $\Delta S^{\neq}$ in cal K^{-1} mol^{-1}, all calculated at 298.15 K. [b] The value of −26.9 given in ref. 7 was a statistically corrected value, the actual observed value was [11] −24.2 cal K^{-1} mol^{-1}.

accelerates reaction (by a factor of about 1.8). Calculated activation parameters are in Table 2, together with those of Abraham and Johnston [2] and of Reutov et al. [9], Added salt has but little effect on $\Delta H^{\neq}$ or $\Delta S^{\neq}$ (it should be noted that a rate enhancement by a factor of 1.8 corresponds only to a decrease of 0.35 kcal mol^{-1} in $\Delta H^{\neq}$ or to an increase of 1.2 cal K^{-1} mol^{-1} in $\Delta S^{\neq}$; these differences are of the order of our experimental errors). The new activation parameters are in substantial agreement with those originally reported by Abraham and Johnston [2], and we can offer no explanation for the very different values obtained by Reutov et al. [9].

We also studied reaction 1 (R = Me, X = I) and found, as for similar reactions, that a rate-determining step (1) is followed by the rapid equilibrium 2.

$$Me_3SnI + HgI_2 \overset{K}{\rightleftharpoons} Me_3Sn^+ + HgI_3^- \qquad (2)$$

Using our computer methods [10] to evaluate the kinetic data, we obtained the rate constants given in Table 1 and also the equilibrium constant for reaction 2. The latter was found to be 14 at all temperatures studied. Reaction 1, (R = Me, X = I) has also been studied by Roberts [7] who analysed the rate data by assuming $K = \infty$ in equation 2. Our mathematical analysis [10] suggests that the error in the rate constant introduced by this approximation is actually quite small, and in the event there is excellent agreement between the activation parameters found in this work and those obtained by Roberts [7,11], see Table 2.

Solvent effects on activation parameters

The activation parameters found by several workers [2,3,7,8,12] for reaction 1 (R = Me and Et, X = Cl and I) in methanol, acetonitrile and dimethyl sulphoxide (DMSO) are collected in Table 3. For any given reaction it is apparent that $\Delta G^{\neq}$ decreases (i.e. the rate constant increases) along the solvent series methanol > acetonitrile > DMSO, the dipolar aprotic solvents having a considerable rate-accelerating effect. In acetonitrile, the rate acceleration is entirely an enthalpic effect, $\Delta H^{\neq}(MeOH) > \Delta H^{\neq}(MeCN)$, because the activation entropies

TABLE 3

ACTIVATION PARAMETERS, MOLAR SCALE, AT 298 K

Reactants	Solvent	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\delta\Delta G^{\neq}$	$\delta\Delta H^{\neq}$	$\delta\Delta S^{\neq}$	Ref.
$Me_4Sn + HgCl_2$	Methanol	17.25	11.3	−19.9	0	0	0	This work
$Me_4Sn + HgCl_2$	Acetonitrile	16.84	8.0	−29.6	−0.41	−3.3	−9.7	3
$Me_4Sn + HgCl_2$	DMSO	16.56			−0.69			8
$Me_4Sn + HgI_2$	Methanol	18.15	11.0	−23.8	0	0	0	This work
$Me_4Sn + HgI_2$	Acetonitrile	17.10	9.6	−25.0	−1.05	−1.4	−1.2	7, 11
$Me_4Sn + HgI_2$	DMSO	16.26	10.0	−21.1	−1.89	−1.0	+2.7	7, 11
$Et_4Sn + HgCl_2$	Methanol	20.83	14.3	−21.7	0	0	0	2
$Et_4Sn + HgCl_2$	Acetonitrile	19.81	11.3	−28.5	−1.02	−3.0	−6.8	12
$Et_4Sn + HgI_2$	Methanol	21.00	13.0	−26.7	0	0	0	12
$Et_4Sn + HgI_2$	Acetonitrile	19.46	10.2	−31.0	−1.54	−2.8	−4.3	12

are all more negative in acetonitrile. For the single reaction for which $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in DMSO are available, both of these parameters contribute to the lowering of $\Delta G^{\neq}$ in DMSO.

In order to discuss more deeply these solvent effects, it is necessary to determine whether they are the result of initial-state effects or transition-state effects. As shown before [13–16], equation 3 where P = G, H, or S, may be used. In eq. 3, Tr referes to the transition state, ΔP_t^0 is the difference in the free energy,

$$\Delta P_t^0(\text{Tr}) = \Delta P_t^0(\text{R}_4\text{Sn}) + \Delta P_t^0(\text{HgCl}_2) + \delta\Delta P^{\neq} \qquad (3)$$

enthalpy, or entropy of a given species in acetonitrile or DMSO as compared with methanol, and $\delta\Delta P^{\neq}$ is the difference in the activation parameter, see Table 2. Values of ΔG_t^0 for the R_4Sn compounds are known from vapour-liquid equilibria, and ΔG_t^0 values for $HgCl_2$ and HgI_2 were determined through solubility measurements in methanol and acetonitrile, care being taken to avoid difficulties over solvate formation. Balyatinskaya [17] has given values for the transfer of numerous mercury(II) species from water to DMSO, and combination with known values for the water to methanol transfer yields the required ΔG_t^0 values for transfer of $HgCl_2$ and HgI_2 from methanol to DMSO; all these values are in Table 4, together with a few heats of solution taken from the literature [18,19].

The results for the various reactants, Table 4, may be compared with solvent effects on a number of non-electrolytes and electrolytes, listed in Table 5; the ΔH_t^0 and ΔG_t^0 values are from various literature sources [20–24] and where necessary the ΔG_t^0 values have been recalculated to the molar scale. The R_4Sn reactants behave as simple nonelectrolytes; the ΔH_t^0, ΔG_t^0 and ΔS_t^0 values are not exceptional, and the latter is a small positive quantity as expected. However,

TABLE 4

SOLVENT EFFECTS ON REACTANTS, MOLAR SCALE, AT 298 K

Reactant	ΔH_s^0 in MeOH [a]	ΔH_s^0 in MeCN [a]	MeOH → MeCN		
			ΔH_t^0	ΔG_t^0 [b]	ΔS_t^0 [c]
Me_4Sn	0.89	2.15	1.26	0.08 [d]	4.0
Et_4Sn	1.84	2.52	0.66	0.33 [d]	1.1
$n\text{-}Pr_4Sn$	2.06	2.85	0.79	0.49 [d]	1.0
$HgCl_2$	−0.71	1.00	1.71	0.42 [e]	5.3
HgI_2	1.85 [f]	6.34 [g]	4.49	1.36 [e]	10.5
	ΔH_s^0 in MeOH	ΔH_s^0 in DMSO	MeOH → DMSO		
			ΔH_t^0	ΔG_t^0	ΔS_t^0
Me_4Sn	0.89	2.50	1.61	0.74 [d]	2.9
$HgCl_2$	−0.71	−5.07 [h]	−4.36	−4.5 [i]	0.5
HgI_2	1.85 [f]	−1.03 [g]	−2.88	−4.7 [i]	6.1

[a] In kcal mol^{-1}, by direct calorimetry (this work) unless shown otherwise. [b] In kcal mol^{-1}. [c] In cal K^{-1} mol^{-1}. [d] From vapour-liquid equilibrium data (see ref. 14). [e] From solubility data (this work). [f] Ref. 18. [g] From the temperature variation of solubility (this work). [h] Ref. 19. [i] Using values from ref. 17 for transfer from water to DMSO, together with known values for the water → MeOH transfer.

TABLE 5

SOLVENT EFFECTS ON VARIOUS SOLUTES, MOLAR SCALE, AT 298 K

Solute	MeOH → MeCN			MeOH → DMSO		
	ΔH_t^0 [a]	ΔG_t^0 [b]	ΔS_t^0 [c]	ΔH_t^0 [a]	ΔG_t^0 [b]	ΔS_t^0 [c]
n-Pentane	1.11	−0.02	3.8	1.84	0.83	3.4
n-Hexane	1.27	0.11	3.9	2.06	1.00	3.6
n-Heptane	1.46	0.26	4.0	2.30	1.20	3.7
Benzene	0.25	−0.45 [d]	2.3	0.26	−0.12 [d]	1.3
Toluene	0.33	−0.35 [e]	2.3	0.45	−0.10 [e]	1.8
$Me_4N^+ + Cl^-$ [f]	−0.8	5.0	−19	−1.5	3.0	−15
$Me_4N^+ + I^-$ [f]	−5.1	0.5	−19	−6.5	−1.8	−16

[a] In kcal mol^{-1}, from ref. 20 unless shown otherwise. [b] In kcal mol^{-1} from ref. 21 unless shown otherwise. [c] In cal K^{-1} mol^{-1}. [d] From ref. 22. [e] From ref. 23. [f] Ref. 24.

the transfer parameters for mercury(II) iodide are quite different from those for simple non-electrolytes, and also quite different for the two transfers studied. It seems as though mercury(II) iodide is much less solvated in acetonitrile than it is in methanol, whereas mercury(II) chloride is slightly less solvated in acetonitrile, and both mercury(II) salts are very highly solvated in DMSO. Of course, the thermodynamic parameters for the transfers of the mercury(II) halides are quite different from those for transfer of the dissociated electrolytes, because the mercury(II) halides are essentially unionised.

Now that the solvent effect on the initial reactants in eq. 1 are known, eq. 3 may be used to obtain these effects on the transition states. Calculations of ΔG_t^0(Tr) values are in Table 6. For transfer from methanol to acetonitrile, it seems as though the decrease in $\Delta G^{\neq}$ (i.e. increase in rate constant) is due mostly to initial-state effects, since the solvent effect on the transition states is not large and in any case is usually positive. For transfer to DMSO, the situation is quite different; the negative $\delta\Delta G^{\neq}$ values arise because although the initial states are much lower in free energy in DMSO, the transition states are even lower still. It seems clear (see Tables 4 and 5) that the very large reductions in free energy of the transition states in DMSO arise in the same way as do those for the mercury(II) halides, namely that the transition states in DMSO are highly solvated. We can conclude that in forming the transition states from the

TABLE 6

CALCULATION OF ΔG_t^0(Tr), IN kcal mol^{-1}, MOLAR SCALE, AT 298 K

Reactants	Transfer	$\Delta G_t^0(R_4Sn)$	$\Delta G_t^0(HgX_2)$	$\delta\Delta G^{\neq}$	ΔG_t^0(Tr)
$Me_4Sn + HgCl_2$	MeOH → MeCN	0.1	0.4	−0.4	0.1
$Me_4Sn + HgI_2$		0.1	1.4	−1.1	0.4
$Et_4Sn + HgCl_2$		0.3	0.4	−1.0	−0.3
$Et_4Sn + HgI_2$		0.3	1.4	−1.5	0.2
$Me_4Sn + HgCl_2$	MeOH → DMSO	0.7	−4.5	−0.7	−4.5
$Me_4Sn + HgI_2$		0.7	−4.7	−1.9	−5.9

TABLE 7

CALCULATION OF ΔH^0_t(Tr) IN kcal mol^{-1} AT 298 K

Reactants	Transfer	$\Delta H^0_t(\mathrm{R_4Sn})$	$\Delta H^0_t(\mathrm{HgX_2})$	$\delta \Delta H^{\neq}$	ΔH^0_t(Tr)
$Me_4Sn + HgCl_2$	MeOH → MeCN	1.3	1.7	−3.3	−0.3
$Me_4Sn + HgI_2$		1.3	4.5	−1.4	4.4
$Et_4Sn + HgCl_2$		0.7	1.7	−3.0	−0.6
$Et_4Sn + HgI_2$		0.7	4.5	−2.8	2.4
$Me_4Sn + HgI_2$	MeOH → DMSO	1.6	−2.9	−1.0	−2.3

reactants, the DMSO molecules that strongly interact with the mercury(II) halides are still retained in the transition states.

The enthalpy data (Table 7) show again, that initial-state effects on the methanol→acetonitrile transfer are very large, and that the reduction in $\Delta H^{\neq}$ are mostly due to an increase in the enthalpy of the initial states. The methanol→DMSO transfer is again different, the reduction in $\Delta H^{\neq}$ now being due to a large reduction in the transition state enthlapy overcoming a reduction in the enthalpy of the reactants.

More informative is the entropy function, because as seen from Tables 4 and 5, species of different type yield quite different ΔS^0_t values. For the methanol→acetonitrile transfer, the ΔS^0_t(Tr) values are quite similar to those for the corresponding mercury(II) halide, suggesting once again that solvation of the transition states follows closely that of the mercury(II) halides. Thus the transition state probably resembles the reactants more than the products, and can be described as an "early" transition state.

For both transfers, the ΔS^0_t(Tr) values in Table 8 are quite different from the very large negative values which arise in the transfer of dissociated ions, see values for ($Me_4N^+ + X^-$) in Table 5. It is therefore rather unlikely that a halide ion is displaced from the HgX_2 reagent in the transition state.

Experimental

Kinetic measurements were carried out exactly as described before [1,3,10,12]. For reactions using $HgCl_2$, initial concentrations were 3×10^{-4} *M* in Me_4Sn and 2×10^{-4} *M* in $HgCl_2$, and for reactions with HgI_2, initial concentrations were 1.4×10^{-3} *M* in Me_4Sn and 0.75×10^{-3} *M* in HgI_2. Several runs were carried out at each temperature, and the average values of the rate constants are in Table 1. The standard deviation in the rate constants is about 2% for the $HgCl_2$ reactions

TABLE 8

CALCULATION OF ΔS^0_t(Tr), IN cal K^{-1} mol^{-1}, MOLAR SCALE, AT 298 K

Reactants	Transfer	$\Delta S^0_t(\mathrm{R_4Sn})$	$\Delta S^0_t(\mathrm{HgX})_2$	$\delta \Delta S^{\neq}$	ΔS^0_t(Tr)
$Me_4Sn + HgCl_2$	MeOH → MeCN	4	4	−10	−2
$Me_4Sn + HgI_2$		4	10	−1	13
$Et_4Sn + HgCl_2$		1	4	−7	−2
$Et_4Sn + HgI_2$		1	10	−4	7
$Me_4Sn + HgI_2$	MeOH → DMSO	3	6	3	12

and 4% for the HgI_2 reactions, and the quoted errors in the activation parameters (Table 2) are based on these standard deviations.

The ΔG_t^0 values for Me_4Sn and Et_4Sn were taken from ref. 14, after conversion to the molar scale, and the value for Pr_4Sn was obtained as described before [14]. For the methanol→acetonitrile transfer, ΔG_t^0 values for the mercury(II) halides were obtained through solubility measurements. The theoretical solubility of $HgCl_2$ in methanol at 318.15 K is [25] 3.697 *M*, and combination with the solubility in acetonitrile found in this work, 2.170 *M* at 318.15 *K* yields $\Delta G_t^0(HgCl_2)$ 0.34 kcal mol^{-1} at 318.15 K; using the known ΔH_t^0 values in Table 4, the corresponding value at 298.15 K was calculated to be 0.42 kcal mol^{-1}. The $\Delta G_t^0(HgI_2)$ value was obtained directly from the solubilities at 298.15 K, 7.02×10^{-2} *M* in methanol [15] and 7.10×10^{-3} *M* in acetonitrile, this work. For the methanol→DMSO transfer, the $\Delta G_t^0(HgX_2)$ values were taken from ref. 17, see Table 4.

Direct calorimetric measurements, carried out as described recently [16], yielded ΔH_s^0 values for the R_4Sn compounds and for $HgCl_2$ in methanol and acetonitrile. The ΔH_s^0 values for $HgCl_2$ in DMSO [19] and for HgI_2 in methanol [18] and DMSO [19] were literature values, and ΔH_s^0 for HgI_2 in acetonitrile was determined through the temperature variation of the solubility.

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