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Review

SOLVENT EFFECTS ON THE RATES AND MECHANISMS OF ORGANOTIN ALKYL EXCHANGE REACTIONS

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Introduction

The effects of solvent on the reactivity of organic derivatives of nontransition metals were first studied in 1929–1930, when Ziegler and his coworkers [1] showed, that organolithium compounds react substantially faster in ether than in hydrocarbons. Many examples demonstrating the dependence of the kinetics and mechanisms of reactions of nontransition organometallic compounds on the nature of solvent have been found since. These data show [2,3] that solvent effects in organometallic chemistry are very complicated and depend on several factors: the type of reaction under investigation, the nature of the organometallic compound and the substrate, their solvation, the solvation of the transition state and the polarity of the solvent. In Abraham's opinion [4], the principal difficulty in interpretation of the solvent effects on the kinetics and mechanisms of organometallic reactions lies in the separation of the reagents and the transition state free energies. The main model compounds in Abraham's studies [4] were organic derivatives of tin and mercury halides, for which he obtained the reaction activation parameters and the transfer enthalpies from one solvent to another. He used as solvents mixtures of hydroxyl-containing compounds.

In our studies, the attention has been concentrated on the solvent effects on the kinetics and mechanisms of organotin alkyl exchange reactions:

$$Me_4Sn + SnHal_4 \rightarrow Me_3SnHal + MeSnHal_3 \quad (1)$$

$$Me_3SnHal + SnHal_4 \rightarrow Me_2SnHal_2 + MeSnHal_3 \quad (2)$$

$$Me_4Sn + MeSnHal_3 \rightarrow Me_3SnHal + Me_2SnHal_2 \quad (3)$$

These reactions are preferred to other widely studied organometallic reactions (protolysis, halogen-demetallation, alkylation) not only because of the relative simplicity of their mechanisms, but also because the solvent effects on the reactivity of each pair of reagents, though different in magnitude, are in the same direction. Bearing in mind the presence of halogens in the model compounds used in our studies we tried to avoid the hydroxyl solvents, which could form complexes with the reagents, not only by solvation of tin atoms, but also by means of intermolecular

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hydrogen bonds. We tried also to use, as far as it was possible, a large number of solvents to have the possibility of changing the polar and solvating properties of the medium. High resolution NMR spectroscopy is a unique method to study the kinetics of this type of reactions and we used NMR also to obtain information about the structures and solvation of organotin molecules [5,6]. This was very helpful for better understanding of the solvation of the transition state in the reactions studied.

Reactions of tetramethyltin with tin tetrahalides

The type 1 reactions proceed practically immediately by mixing the reagents at room temperature, whereas to carry out the type 2 and 3 reactions under the same conditions takes about 2–3 hours. It is important to note, that the types 4–6 reactions, which could be considered as possible parallel processes, in fact proceed only on heating the reaction mixtures up to 150–200°C.

$$Me_4Sn + Me_2SnHal_2 \rightarrow 2Me_3SnHal \qquad (4)$$

$$Me_3SnHal + MeSnHal_3 \rightarrow 2Me_2SnHal_2 \qquad (5)$$

$$Me_2SnHal_2 + SnHal_4 \rightarrow 2MeSnHal_3 \qquad (6)$$

The types 2 and 3 reactions are related to those of type 1. Therefore, we studied, first of all, the half-lives of these reactions in various solvents. The data obtained are given in Table 1. These results show clearly that the rates of the types 1–3 reactions differ substantially from each other in CCl_4, benzene and nitrobenzene, while the type 1 reactions proceed in DMF only twice as fast as the type 3 reactions, which makes quantitative study of them in DMF rather difficult.

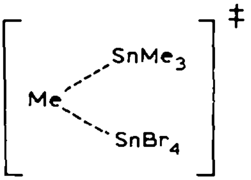
The dependence on time of the reagents concentration in CCl_4 and benzene shows that this type of reaction is substantially catalyzed by the products. The catalysis is more effective in CCl_4 than in benzene. Grant and Van Wazer [7] explained the analogous situation in terms of increasing medium polarity because

TABLE 1

HALF-LIVES OF THE TYPES 1–3 REACTIONS WITH $c_0 = 0.5$ mol/l and $T = 20°C$

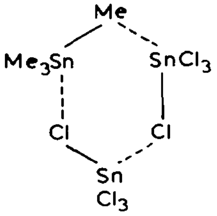
Reaction	Solvent			
	CCl_4	C_6H_6	$C_6H_5NO_2$	DMF
$Me_4Sn + SnCl_4$	20 min ($c_0 = 0.1$)	5 s	5 s	3.5 h
$Me_4Sn + SnBr_4$	6.0 h	20 min ($c_0 = 0.1$)	5 s	1.0 h
$Me_3SnCl + SnCl_4$	10 h ($T = 70°C$)	1.8 h ($T = 70°C$)	20 s	4% in 2.5 h ($T = 70°C$)
$Me_3SnBr + SnBr_4$	no reaction	4% in 6 h ($T = 70°C$)	3.7 h	10% in 2.5 h ($T = 70°C$)
$Me_4Sn + MeSnCl_3$	7.3 h ($T = 70°C$)	1.3 h ($T = 70°C$)	12 min	7.0 h
$Me_4Sn + MeSnBr_3$	no reaction	13.0 h ($T = 70°C$)	3.0 h	2.8 h

the accumulation of polar products. They proposed calculating the "normal" reaction rate constants at conversion degrees not higher than 50%. In our opinion such an approach is not the most fruitful, because the rate constants obtained in this way are rather complex and their physical sense is not clear. That is why we used in our studies the initial rates method [8] which although not very precise, does give information about the reaction kinetics which is not distorted by other factors. Using this method we obtained the partial orders of the reagents: for Me_4Sn and $SnBr_4$ both in CCl_4 and benzene close to 1.0, but for $SnCl_4$ in benzene equal to 1.7. These results are interpreted readily if we take into consideration the data from cryoscopic studies [9,10], which show that $SnCl_4$ in weakly solvating solvents has a higher tendency to self-association than $SnBr_4$. These self-associates are very weak and completely destroyed even by solution in benzene. Therefore, the reactions of Me_4Sn with $SnBr_4$ in CCl_4, as well as in benzene, proceed according to the simple S_E2 mechanism, i.e. through the open transition state (I):



(I)

At the same time the appropriate reaction with $SnCl_4$ in CCl_4 proceeds possibly through a mixed mechanism, which includes the simple bimolecular collision and trimolecular mechanisms with a transition state wherein two molecules of $SnCl_4$ participate as an associate (II), in which one of the tin atoms has larger positive



(II)

charge and therefore is more reactive than the tin atom in monomeric $SnCl_4$.

The kinetic data were treated by the integral method [8]. If we assume that

$$-\frac{dc}{dt}=k_0c^2+k_1c^2c_{cat} \tag{7}$$

i.e., the reaction is first order in the catalyst, then designating k_1/k_0 as r, we obtain

$$\frac{dc}{c^2[1+r(c_0-c)]}=-k_0dt \tag{8}$$

Integration of this equation gives

$$\frac{rc_0}{(rc_0+1)}\cdot\ln\frac{c_0[1+r(c_0-c)]^2}{c}+\frac{1}{rc_0+1}\cdot\frac{c_0}{c}=\frac{1}{rc_0+1}+k_0c_0t \tag{9}$$

TABLE 2

RATE CONSTANTS OF CATALYSED AND UNCATALYSED REACTION OF Me_4Sn WITH $SnBr_4$ IN BENZENE

T (°C)	k_0($\times 10^3$) (l mol^{-1} s^{-1})	k_1($\times 10^3$) (l^2 mol^{-2} s^{-1})	r
2	2.25	6.75	3.0
11	3.99	27.8	6.9
15	4.06	93.0	28.9
20	4.64	132.0	28.6

Taking the left part as Y and designating $1/rc_0 + 1$ as A and k_0c_0 as B we obtain the straight line equation $Y = A + Bt$. As A depends on r, we obtain a straight line only in that case, if r was selected correctly. If we choose r inaccurately then it is possible to show that the slope of the curve is equal to k_0c_0 if t values are small; if they are large then

$$\mathrm{tg}\alpha = k_0c_0\frac{r_t}{r_a} \tag{10}$$

where r_t is the true value of k_1/k_0 and r_a is the appropriate approximate value. Knowing the nature of the Y function one can select r values in such a way to obtain a straight line. But from the three cases studied we could realize a straightline only for the reaction of Me_4Sn with $SnBr_4$ in benzene. The k_1, k_0 and r values obtained are given in Table 2.

The experimental data show that r increases with increasing temperature, i.e. for the catalysed reaction the activation energy is higher than that for the appropriate uncatalysed reaction. The activation parameters obtained for the uncatalysed reactions on the basis of k_0 values are given in Table 3. Bearing in mind that we did not obtain a straight line for the reactions in CCl_4, we obtained the activation parameters for them from the initial rates. If V_0 is the initial rate and c_1 and c_2 the initial reagents concentrations, the following equation is valid [8]:

$$V_0 = kc_1^{\alpha}c_2^{\beta} \tag{11}$$

TABLE 3

KINETICAL PARAMETERS FOR THE REACTIONS OF Me_4Sn WITH $SnHal_4$ IN CCl_4 AND BENZENE AT 20°C

Solvent	Hal	k_2^0($\times 10^3$) (l mol^{-1} s^{-1})	k_2^{cat}/k_2^0	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (kcal mol^{-1})
CCl_4	Cl	34.6 [a]	40(−21°C)	6.1 ± 0.3	-44.4 ± 1.1	17.0
CCl_4	Br	0.007	45	8.1 ± 1.6	-54.8 ± 5.0	22.8
C_6H_6	Cl	700	–	–	–	15
C_6H_6	Br	3.47	29	4.1 ± 0.4	-55.9 ± 1.3	19.0

[a] The constant has partial order.

Taking logarithms of this equation one obtains:

$$\ln V_0 = \ln k + \alpha \ln c_1 + \beta \ln c_2 \qquad (12)$$

and then

$$\ln \frac{V_0}{T} = \ln \frac{k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H}{RT} + \alpha \ln c_1 + \beta \ln c_2 \qquad (13)$$

Measuring V_0 values at different T values and equal c_1 and c_2 values, one can obtain the dependence of $\ln V_0/T$ on $1/T$ and determine ΔH^* and ΔS^*. The results obtained are given in Table 3. The $\Delta G^{*(x)}$ values at 20°C, corresponding to the rate constants, expressed in terms of mole fractions, are given in the same Table. This kind of concentrations expression allows us to take into consideration the number of solvent molecules associated with the reagent molecules [4]. The k^x rate constant expressed in terms of mole fractions is given by the equation

$$k^x = \left(\frac{1000\rho}{M} \right)^{n-1} k^c \qquad (14)$$

where ρ and M are the density and molecular weight of the solvent and n is the total order of the reaction.

Taking into account that

$$-RT \ln k = \Delta G^* - RT \ln \frac{xT}{n} \qquad (15)$$

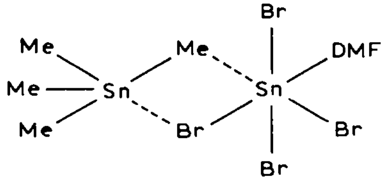
one obtains for the activation free energy

$$\Delta G^{*(x)} = \Delta G^{*(c)} - (n-1) RT \ln \frac{1000\rho}{M} \qquad (16)$$

The results obtained show that the reactions studied in nonpolar solvents are characterized by low values of activation enthalpies. In this case both activation parameters increase on going from chloride to bromide. The rates of both reactions are substantially higher in benzene than in CCl_4. At the same time the r values for bromide in benzene are lower than in CCl_4, i.e. catalysis by the products is not very substantial in benzene.

The acceleration of the reactions on going from CCl_4 to benzene, as one can see from Table 3, is due to an activation free energy decrease of 4 kcal/mole. This, in turn, is due to the ability of the benzene molecules to interact with tin tetrahalides via readily polarized π-electrons, which became evident from the appearance of small dipole moments (0.6–0.8 D) on going from cyclohexane to benzene solutions of $SnHal_4$ [10] and charge transfer bands at 300–360 nm in UV-spectra of $SnHal_4$ solutions in aromatic hydrocarbons [11,12].

The data in Table 1 show that the type 1 reactions accelerate much more on going to the highly polar nitrobenzene ($\mu = 4.23$; $\varepsilon = 34.8$), the solvating ability of which is rather low [6]. Hence this acceleration can be rationalized in terms of the Hughes-Ingold concept [13], which presumes a shift of the equilibrium in the more polar solvents to the more polar products. In this case one has to admit that in the transition state (I) a certain separation of charges arises, analogous to that in the interaction of tetraalkylstannanes with mercury halides. On going to the strongly solvating DMF one observes (Table 1) a sharp decrease of the rates of the reactions studied, in spite of the high polarity of the solvent ($\mu = 3.95$; $\varepsilon = 37.7$). It follows that in this case one observes once more the competitive influences of the polarity and solvating properties of the medium, leading to a substantial deceleration of reactions due to formation of $SnHal_4 \cdot 2DMF$ complexes. The reactivity of these complexes is substantially lower than that of free $SnHal_4$ molecules, because of the strong decrease of the electrophilicity of the tin atom in these complexes [14] and due to occupation of tin orbitals, which are important for the transition state (I) formation. It is interesting that $SnBr_4$ reacts with Me_4Sn in DMF faster than does $SnCl_4$, while the order is reverse in weakly solvating media. The data in Table 1 show that this phenomenon is general for the organotin alkyl exchange reaction. Bearing in mind that $SnHal_4 \cdot 2DMF$ complexes have *cis*-structures [15], but could be isomerized to *trans*-octahedrons with the intermediate formation of $SnHal_4 \cdot DMF$ complexes [16], and taking into consideration the low reactivity of the 1 : 2 complexes (see above) one can conclude that the 1 : 1 complexes enter into reactions. On the other hand it is known [17] that $SnBr_4$ interacts with hard Lewis bases, such as DMF, more weakly than $SnCl_4$ [15]. In our opinion all these facts explain the higher reactivity of $SnBr_4$ in DMF in comparison with $SnCl_4$. One can assume, that in this case the reaction proceeds through a closed transition state in which nucleophylic assistance can play an important role due to the substantial increase of the nucleophilicity of bromine [14].



(III)

Thus, the kinetics of the dismutation of tetramethyltin with tin tetrahalides in weakly solvating media is specified mainly by the polarity of the solvent, while in strongly solvating media the overall effects are mainly due to complexation of tin tetrahalides.

Reactions of trimethyltin halides with tin tetrahalides

The data in Table 1 show that this type of reaction proceeds much slower than the tetramethyltin dismutation reactions described in the previous section. The results are in accordance with the data given in ref. 6, which gave rise to the assumption that the Sn–C bond covalencies in trimethyltin halides are higher than in tetramethyltin. Such a passivity of trimethyltin halides, especially in nonpolar weakly-solvating media (CCl_4, benzene) does not allow to carry out the complete kinetical investigation. Nevertheless, even the data we could obtain show rather well the regularities of solvent effects on the rates and mechanisms of these reactions.

It is noteworthy that the kinetical curves for reactions of Me_3SnCl with $SnCl_4$ in CCl_4 and benzene do not show anomalies, analogous to those observed for the reactions of Me_4Sn with $SnHal_4$ (see above). In our opinion, this fact is due to lower catalytic activity by the products in these reactions in comparison with that in the type 1 reactions. Besides, it is very interesting to compare the total and partial orders for reactions of types 1 and 2 in nonpolar and weakly-solvating media. Comparison

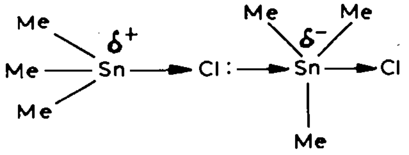
TABLE 4

PARTIAL ORDERS OF REAGENTS FOR REACTIONS OF Me_3SnCl WITH $SnCl_4$ IN CCl_4 AND BENZENE

Reagents	Solvent	
	CCl_4 (70°C)	Benzene (28°C)
Me_3SnCl	2.48 ± 0.15	1.93 ± 0.03
$SnCl_4$	1.06 ± 0.08	0.80 ± 0.20

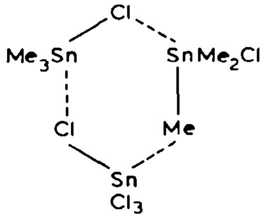
of the data in Table 4 with the partial orders for reactions of Me_4Sn with $SnHal_4$ (see above) shows, that there is a principal difference in the results obtained.

First of all, it is necessary to stress that $SnCl_4$ reacts in accordance with type 2 reactions in CCl_4 as well as in benzene as a monomer, while for Me_3SnCl in benzene the partial order is equal to 2.0 and in CCl_4 even to 2.5. It is unlikely that Me_3SnCl can exist in CCl_4 at 70°C as a trimer. Even more difficult is it to assume that the transition state can be formed as a result of tetramolecular collision. In our opinion, the partial orders observed are due to increasing medium polarity with increasing Me_3SnCl concentration in the appropriate kinetic experiments. However, one cannot exclude the possibility of formation of the dimer IV.



(IV)

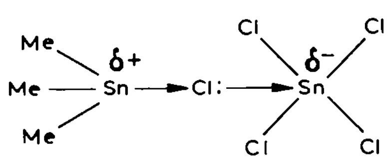
The interaction of this type of dimer with $SnCl_4$ can proceed through the closed transition state:



(V)

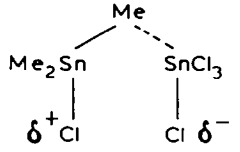
Such an activated complex, generally speaking, can be formed through the interaction of Me_3SnCl with a mixed associate of type VI, the formation of which in this reaction is quite probable because of the greater accepting properties of $SnCl_4$ in comparison with Me_3SnCl.

It is important to note, that in the mixed associate VI both reagents have lower reactivity because of the decrease of the tin atoms electrophilicity in $SnCl_4$ and the



(VI)

carbon atoms nucleophilicity in Me_3SnCl. However, it is quite possible that the formation of such an associate will facilitate formation of the transition state V by the collision of the associate with a second Me_3SnCl molecule, due to a local increase in the dielectric permeability because of the higher dipole moment of VI. The formation of a transition state of the type V is perferred in CCl_4 and benzene in comparison with the highly polar transition state VII, which can be formed by bimolecular collision.



(VII)

Earlier, transition states of type VII had been proposed to explain the kinetic anomalies in the anion exchange reactions of trimethyl derivatives of tin.

To obtain additional information about the mechanisms of the type 2 reactions in various solvents we have studied the activation parameters for the reactions of Me_3SnCl with $SnCl_4$ in benzene and Me_3SnBr with $SnBr_4$ in nitrobenzene. The data obtained, with estimated values of $\Delta G^{\neq(x)}$ and k^c (see above) are given in Table 5. The analysis of these results shows, that they obey the same regularities, which have

TABLE 5

KINETICAL PARAMETERS FOR REACTIONS OF Me_3SnHal WITH $SnHal_4$ IN VARIOUS SOLVENTS

Solvent	Hal	$k_2(\times 10^3)$ (l mol^{-1} s^{-1})	$\Delta G^{\neq(x)a}$, (kcal mole^{-1})	$\Delta H^{\neq b}$ (kcal mol^{-1})	$\Delta S^{\neq c}$ (e.u.)
CCl_4	Cl	0.113(70°C)[d]	22.4(70°C)	–	–
CCl_4	Br	no reaction	–	–	–
Benzene	Cl	0.075(20°C)[d]	19.9(20°C)	7.6	–51.5
		0.586(70°C)	21.1(70°C)		
Benzene	Br	0.007(70°C)[e]	24.9(70°C)	–	–
$C_6H_5NO_2$	Cl	100(20°C)	17.0(20°C)	–	–
$C_6H_5NO_2$	Br	0.205(20°C)[f]	20.8(20°C)	11.6	–35.8
$C_6H_5NO_2$	Br	4.373(70°C)	22.3(70°C)		
DMF	Cl	0.009(70°C)	26.4(70°C)	–	–
DMF	Br	0.022(70°C)	25.8(70°C)	–	–

[a] ±0.15. [b] ±0.3; [c] ±1.0. [d] The constant has partial order. [e] Accepting $V = k^c c^2$ (Me_3SnBr) $c(SnBr_4)$. [f] Second order reaction.

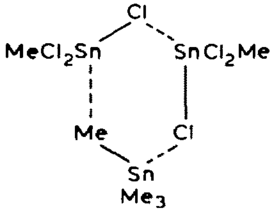
been in the case of reactions of Me_4Sn with $SnHal_4$. Indeed, the reactions somewhat accelerate on going from CCl_4 to benzene, proceed much faster in nitrobenzene and sharply decelerate in DMF.

Thus, the concept of competitive influence of the polar and solvating properties of solvents on the kinetics and mechanisms of reactions, formulated in the previous section, is valid also for the type 2 reactions.

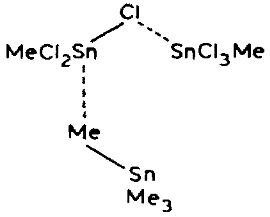
Reactions of tetramethyltin with methyltin trihalides

First of all, we have to note that the kinetic properties of the reaction of Me_4Sn with $MeSnCl_3$ in CCl_4, similarly to the appropriate reaction with $SnCl_4$ (see above), demonstrate the catalysis by the products. The "autocatalytical" character of the kinetic curves is less noticeable in benzene and was not observed in polar and highly solvating media. Furthermore, the kinetic curves were linear with $1/c_1 t$ coordinates in polar and solvating media, which indicates total second order for the reaction studied.

The data obtained with the initial rates method show that in nonpolar solvents (CCl_4, benzene) the partial orders in $MeSnHal_3$ exceed 1.0 and even approach 2.0. To explain these results one has to assume, as was done above, the possibility of the formation of transition states of the types VIII and IX.



(VIII)



(IX)

Formation of these transition states together with an increase of the medium dielectric permeability when increasing the concentration of $MeSnHal_3$ leads to a substantial acceleration of the reactions. NMR spectroscopy [5,6] does not prove the existence of dimers of the type $(MeSnHal_3)_2$ in CCl_4 and benzene, but we cannot deny completely the possibility of formation in this kind of solvents of small quantities of these dimers, the reactivity of which could be higher than for monomeric $MeSnHal_3$, due to the enhanced reactivity of tin atom in one of the molecules as is shown in VIII and IX. Since the dimer–monomer equilibrium can be shifted substantially at lower temperature to the associate, we have studied the temperature dependences of partial orders for these reactions. The results obtained are given in Table 6. Analysis of these data shows that the partial order in $MeSnHal_3$ is almost independent of the temperature for the reactions with Me_4Sn in nonpolar solvents. This situation can be realized only if

$$\delta(\Delta H^{\neq}) = \Delta H^{\neq}_{BMR} - \Delta H^{\neq}_{TMR} \approx \Delta H_{as} \qquad (17)$$

where BMR and TMR represent the bi- and tri-molecular reactions.

Equation 17 may be interpreted in such a way that with changing temperature the ratio of the bi- and tri-molecular reactions rates remains constant. This means that

TABLE 6

TEMPERATURE DEPENDENCE OF THE PARTIAL ORDER OF $MeSnHal_3$ FOR REACTIONS WITH Me_4Sn IN CCl_4 AND BENZENE

Solvent	Hal	T(°C)					
		40	50	55	60	65	70
CCl_4 [a]	Cl	–	–	2.05	2.03	2.40	2.07
CCl_4	Br	–	–	–	–	–	–
Benzene [b]	Cl	1.35	1.36	–	1.37	–	1.29
Benzene	Br	–	1.50	–	–	–	1.57

[a] Accuracy of determination ±0.1 to ±0.3. [b] Accuracy of determination ±0.04 to ±0.08.

the standard heats of formation of the bi- and tri-molecular transition states must be almost equal, what is unlikely for two such different activated complexes. Therefore, we believe that in this case the partial orders higher than 1.0 are also mainly due to electrostatic effects.

The activation parameters for reactions of Me_4Sn with $MeSnHal_3$ are given in Table 7. Analysis of these data shows in particular that $\Delta G^{\neq}$ for reaction of Me_4Sn with $MeSnCl_3$ decreases in the series.

$$CCl_4 > C_6H_6 > \text{acetone} > C_6H_5NO_2 > CD_3CN \tag{18}$$

This indicates that the reaction rates increase in weakly solvating media with increasing polarity. The free activation energy increases substantially in DMF and DMSO, reflecting the appropriate decrease in reactions rates.

In the case of $MeSnBr_3$ there is no increase in $\Delta G^{\neq}$, which is rationalized in accordance with the model considered below in terms of lower sensitivity of bromides to the decelerating effect of specific solvation. The results in Table 7 show also that the activation enthalpies and entropies do not change corresponding to the free activation energies changes but in a more complicated way. To understand

TABLE 7

RATE CONSTANTS ($l\ mol^{-1}\ s^{-1}$) AND ACTIVATION PARAMETERS ($kcal\ mol^{-1}$) FOR REACTIONS OF Me_4Sn WITH $MeSnHal_3$ (Hal = Cl, Br) IN VARIOUS SOLVENTS AT 20°C

Solvent	$k_2(\times 10^3)$		$\Delta G^{\neq (x) a}$		$\Delta H^{\neq b}$		$\Delta S^{\neq}$ (e.u.)[c]	
	Cl	Br	Cl	Br	Cl	Br	Cl	Br
1 CCl_4	0.019 [d]	–	22.0	–	14.2	–	36.2	–
2 C_6H_6	0.04 [d]	0.0007 [d]	21.3	23.3	9.4	14.9	46.9	35.9
3 $PhNO_2$	3.23	0.189	19.2	20.8	13.7	15.9	23.1	21.3
4 MeCN	17.9	–	17.8	–	11.1	–	28.9	–
5 Me_2CO	1.69	–	19.4	–	12.6	–	28.2	–
6 DMF	0.072	0.233	21.2	20.5	18.3	16.4	15.2	19.3
7 DMSO	0.04	–	21.5	–	16.7	–	21.7	–

[a] ±0.2. [b] ±0.7. [c] ±1.5. [d] The constant has partial order.

better the nature of these changes we attempted a series of thermochemical experiments studying the solvation of the reagents in the solvents we were interested in. In so doing we proceeded from the possibility to divide ΔH^{*} into the contributions due to the initial and transition states solvation. If we express the solvation enthalpy by the following equation [18]

$$\Delta H_{\mathrm{solv}} = \Delta H_{\mathrm{sol}} - \Delta H_{\mathrm{vap}} \tag{19}$$

where ΔH_{sol} is the heat of solution and ΔH_{vap} the heat of vaporisation, and if one of the series of solvents used is taken as a standard, then the transfer enthalpy from the standard solvent to the solvent D is:

$$\delta(\Delta H_{\mathrm{solv}}) = \Delta \mathrm{H}^{\mathrm{D}}_{\mathrm{solv}} - \Delta H^{0}_{\mathrm{solv}} = \Delta H^{\mathrm{D}}_{\mathrm{sol}} - \Delta H^{0}_{\mathrm{sol}} = \delta(\Delta H_{\mathrm{sol}}) \tag{20}$$

The standard heat of formation for the transition state in solvent D can be written in the form:

$$\Delta H^{\mathrm{D}}_{\mathrm{TS}} = \Delta H^{\mathrm{D}}_{\mathrm{solv}} + \Delta H^{*(\mathrm{D})} \tag{21}$$

Hence one can calculate the heat of formation for the transition state in solvent D relative to the heats of solvation of the reagents in the standard solvent:

$$\delta(\Delta H^{\mathrm{D}}_{\mathrm{TS}}) = \Delta H^{\mathrm{D}}_{\mathrm{solv}} + \Delta H^{*(\mathrm{D})} - \Delta H^{0}_{\mathrm{solv}} = \delta(\Delta H_{\mathrm{sol}}) + \Delta H^{*(\mathrm{D})} \tag{22}$$

The values of the heats of solution of $\mathrm{Me_4Sn}$ and $\mathrm{MeSnHal_3}$ in different solvents obtained calorimetrically and calculated values of the heats of transfer of the reagents and transition states are given in Table 8.

Nitrobenzene was selected as the standard solvent because it has the lowest solvating ability in the isokinetic series of solvents in which the reactions of $\mathrm{Me_4Sn}$ with $\mathrm{MeSnHal_3}$ have bimolecular mechanisms. The experimental results obtained show that the enthalpies of formation of the transition states change as a whole analogously to the solvation enthalpies of the reagents. This fact indicates that the nature of the transition state solvation in reactions of $\mathrm{Me_4Sn}$ with $\mathrm{MeSnHal_3}$ is analogous to the solvation of the reagents.

It must be mentioned that the enthalpies of formation of transition states formation have been used successfully in the case of organic reactions [19–21] to elucidate the structures of the transition states. In so doing it was shown that this success was notably due to the availability of adequate models for the transition states, i.e. stable compounds resembling in structures and properties the apparent transition states. For the reactions studied in this part of our work the most suitable model compounds for the transition states are methyltin trihalides. Analysis of NMR parameters [5,6], kinetic results (Tables 6 and 7) and thermochemical data (Table 8) suggests that, in contrast to $\mathrm{CCl_4}$ and benzene, in which these reactions proceed with the formation of transition states VIII and IX, in polar weakly and highly solvating media the transition states X and XI are formed. The first of these is likely to be preferred in the case of acetone and acetonitrile, while the second in DMF and DMSO. This type of reaction fits well the scheme proposed [18]:

$$\begin{array}{ccccc} (\mathrm{AB})_n & \overset{k_a}{\leftrightarrows} & n\mathrm{AB} + \mathrm{D} & \overset{k_{\mathrm{D}}}{\rightleftarrows} & \mathrm{ABD} \\ +\mathrm{C}\downarrow k_a & & +\mathrm{C}\downarrow k_{\mathrm{M}} & & +\mathrm{C}\downarrow k_{\mathrm{D}} \\ \mathrm{ABC} & & \mathrm{ABC} & & \mathrm{ABC} \end{array}$$

if we designate $\mathrm{MeSnHal_3}$ as AB, $\mathrm{Me_4Sn}$ as C and solvent as D.

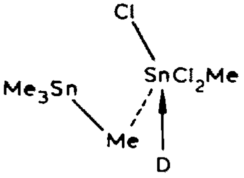
To better understand the nature of the interactions which influence the kinetics

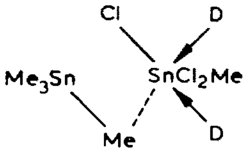
TABLE 8

RESULTS OF THERMOCHEMICAL STUDIES OF SOLVATION OF REAGENTS AND TRANSITION STATES IN REACTIONS OF Me_4Sn WITH $MeSnHal_3$ IN VARIOUS SOLVENTS

Solvent	ΔH_{sol}			$\delta(\Delta H_{sol})$		
	Me_4Sn [a]	$MeSnCl_3$ [b]	$MeSnBr_3$ [b]	Me_4Sn	$MeSnCl_3$	MeSn Br_3
CCl_4	0.28	5.54	4.69	−0.95	3.59	1.96
C_6H_6	0.97	3.78	3.70	−0.26	1.85	0.97
$C_6H_5NO_2$	1.23	1.95	2.73	0	0	0
CH_3CN	2.10	−3.63	–	0.87	−5.68	–
Acetone	1.44	−3.54	–	0.21	−5.49	–
DMF	1.65	−19.54	−18.40	0.43	−21.45	−21.00

[a] Accuracy of determination ±0.03 kcal mol^{-1}. [b] Accuracy of determination ±0.35 kcal mol^{-1}. [c] Assuming the order in $MeSnCl_3 = 2$. [d] Assuming the order in $MeSnCl_3 = 1.34$. [e] Assuming the order in $MeSnBr_3 = 1.54$.


(X)


(XI)

and mechanisms of the reactions studied, we attempted a correlation of the free energies of activation for reactions of Me_4Sn with $MeSnCl_3$ with the Kirkwood function, $\varepsilon - 1/2\varepsilon - 1$, and with the "electrostatic factor" $EF = \varepsilon\mu$ [22], which allows us to make corrections for the difference in microscopic dipole–dipole interactions and to take into account the dielectric permeability of the medium. However, the dependencies are obviously unsatisfactory in both cases, as could be expected because both parameters take into account only the polar properties of the solvents.

Bearing in mind that for some reactions which proceed through comparatively nonpolar transition states the correlations of lg k^x values with the Hildebrand solubility parameter "δ" were observed, we attempted to correlate $\Delta G^{*(x)}$ values with "δ" values and obtained somewhat better results. However, the points for acetone, DMF and DMSO deviate substantially from this dependence by an amount proportional to the solvating ability of the solvents.

The correlation of the free energy activation to the E_T parameter was of special interest, because this parameter is determined for a large number of solvents [23] and represents currently the most adequate measure of solvent polarity, accounting for the microscopic interactions of solvent molecules with dissolved polar substances. In our case the $\Delta G^{*(x)}$ values are on a straight line with slope −0.3 and correlation coefficient 0.994, except for DMF and DMSO, for which strong specific interactions with the reagents account for the deviation of the points for all the correlations. Thus, the data obtained show that the rates of the reactions studied depend in weakly solvating media mainly on the polar properties of the solvents, while strongly

$\delta(\Delta H_{reag})$		ΔH^{0}_{TS}		$\delta(\Delta H^{D}_{TS})$	
$MeSnCl_3$	$MeSnBr_3$	$MeSnCl_3$	$MeSnBr_3$	$MeSnCl_3$	$MeSnBr_3$
6.15[c]	–	20.34[c]	–	6.64[c]	–
2.22[d]	1.28[e]	11.60[d]	16.20[e]	−2.10[d]	0.30[e]
0	0	13.70	15.90	0	0
−4.71	–	6.35	–	−7.35	–
−5.28	–	7.31	–	−6.39	–
−21.02	−20.67	−2.70	−4.27	−16.40	−20.17

solvating solvents, in spite of their high polarities, decrease substantially the rates of the reactions due to formation of $MeSnHal_3 \cdot D$ or $MeSnHal_3 \cdot 2D$ complexes, the reactivities of which are much lower than those of the free methyltin trihalides.

The results obtained in this study show that rates of alkyl exchange for organotin compounds increase with increasing medium polarity and decrease as the solvating ability of the solvent increases. The mechanisms of the reactions also change substantially on going from weakly solvating media to strongly solvating ones.

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