February, 1983] Bull. Chem. Soc. Jpn., 56, 573—576 (1983)

The Mechanism of the Reaction of (Aryloxy)trimethylstannane with Methanesulfonyl Chloride. Solvent and Substituent Effects on the Rate of the Reaction

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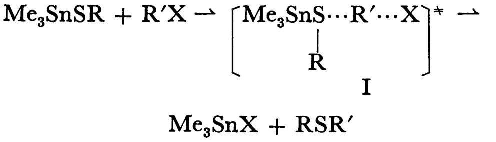
(Received September 10, 1982)

A kinetic study has been conducted on the reactions of (aryloxy)trimethylstannanes with methanesulfonyl chloride giving chlorotrimethylstannane and aryl methanesulfonates. The reaction was found to obey a second order kinetic equation. The solvent effect on the rate of the reaction appeared obscure although a small rate enhancement was observed in a polar solvent. Substituent effect of the aryloxyl group was found to be dependent on the solvent used while a clear isokinetic relationship was observed. A charge separated four-center transition state has been suggested for the reaction.

The mechanism of the bimolecular IVb–VIb bond cleavage reactions may be classified into three different types. The first one is a nucleophilic attack of the VIb atom (I). The reaction of (arylthio)trimethylstannane



$$\mathrm{Me_3SnSR + R'X} \rightarrow \left[\mathrm{Me_3Sn\underset{R}{\underset{|}{S}}\cdots R'\cdots X}\right]^{*} \rightarrow$$

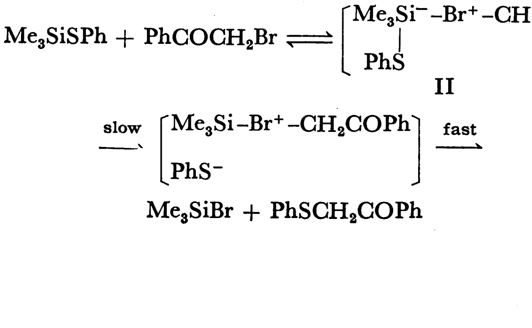
I

$$\mathrm{Me_3SnX + RSR'} \qquad (1)$$

R = alkyl, aryl; R′ = alkyl; X = halogen.

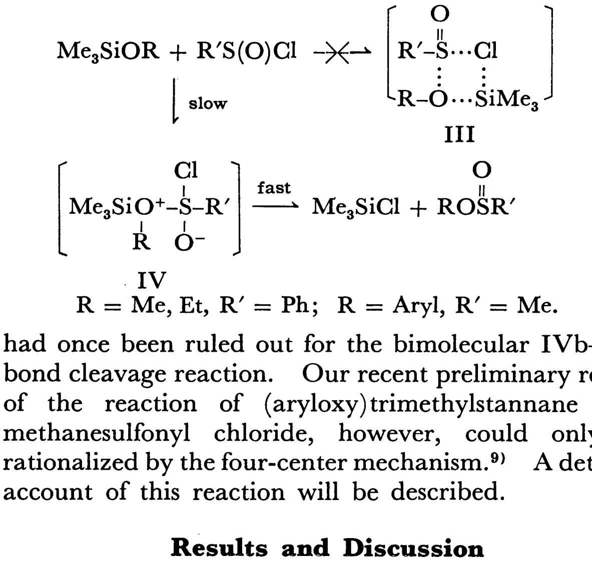
with haloalkanes has been considered to be the nucleophilic reaction based on the kinetic results (Eq. 1). Namely, the reaction obeyed a second order kinetic equation with apparently negative substituent effect of the arylthio moiety ($\rho=-1.4$). Other evidence observed in support of the mechanism were: the solvent effect on the rate of the reaction ($k_{\mathrm{PhCN}}/k_{\mathrm{C_6H_6}}=ca.\ 100$), relative reactivity of the haloalkanes which appeared in comparable to that of common S_N2 reactions, and inversion of configuration of the alkyl group of the haloalkane.[1] The reactions of (aryloxy)trimethylstannane with benzyl bromide[2] and (arylthio)trimethylstannane with benzoyl chloride[3] have also been suggested to proceed in similar manners.

The second is the reaction involving five-coordinated intermediate (II) as has been suggested for the reaction of (arylthio)trimethylsilane with phenacyl bromide based on the kinetic results. A large positive ρ value due to the arylthio moiety (+2.2) was observed with a large negative entropy of activation ($-156\ \mathrm{J\ K^{-1}\ mol^{-1}}$). As a result, five-coordinated silicon intermediate was suggested to be involved prior to the rate-determining heterolysis of the Si–S bond (Eq. 2).[4] Five-coordinated silicon intermediates have also been suggested for acyloxyl exchange reaction of acyloxysilane with carboxylic acid[5] and the reaction of arylthiosilane with carboxylic acid.[6]



$$\mathrm{Me_3SiSPh + PhCOCH_2Br} \rightleftharpoons \left[\begin{array}{l}\mathrm{Me_3Si^{-}\text{-}Br^{+}\text{-}CH_2COPh}\\ \quad | \\ \mathrm{PhS}\end{array}\right]_{\mathrm{II}} \xrightarrow{\text{slow}} \left[\begin{array}{l}\mathrm{Me_3Si\text{-}Br^{+}\text{-}CH_2COPh}\\ \mathrm{PhS^{-}}\end{array}\right] \xrightarrow{\text{fast}} \mathrm{Me_3SiBr + PhSCH_2COPh} \qquad (2)$$

The third possibility is a four-centered mechanism. The reaction of alkoxytrimethylsilanes with benzenesulfinyl chloride had once been suggested to involve nonionic four-centered transition state (III) based on the kinetic resuls that the rate of the reaction was little influenced by the solvent polarity but sensitive to the steric effect of the alkoxyl group.[7] This was the only one bimolecular IVb–VIb bond cleavage reaction involving this mechanism supported by kinetic evidences. The mechanism, however, was suspected and a nucleophilic attack of the oxygen atom (IV) has been suggested since the rate of the reaction was clearly accelerated in a more polar solvent and a negative ρ value (-1.44) was observed by the reaction of arylthiosilanes (Eq. 3).[8] Thus, the four-center mechanism



$$\mathrm{Me_3SiOR + R'S(O)Cl} \not\rightarrow \left[\begin{array}{ccc}\mathrm{R'\text{-}\overset{O}{\overset{\|}{S}}} & \cdots & \mathrm{Cl}\\ \vdots & & \vdots \\ \mathrm{R\text{-}O} & \cdots & \mathrm{SiMe_3}\end{array}\right]_{\mathrm{III}}$$

$$\downarrow \text{slow}$$

$$\left[\mathrm{Me_3Si\underset{R}{\overset{}{O^{+}}}\text{-}\overset{Cl}{\underset{O^{-}}{S}}\text{-}R'}\right]_{\mathrm{IV}} \xrightarrow{\text{fast}} \mathrm{Me_3SiCl + RO\overset{O}{\overset{\|}{S}}R'} \qquad (3)$$

R = Me, Et, R′ = Ph; R = Aryl, R′ = Me.

had once been ruled out for the bimolecular IVb–VIb bond cleavage reaction. Our recent preliminary results of the reaction of (aryloxy)trimethylstannane with methanesulfonyl chloride, however, could only be rationalized by the four-center mechanism.[9] A detailed account of this reaction will be described.

Results and Discussion

Product Analysis. Trimethylphenoxystannane was refluxed with an equimolar amount of methanesulfonyl chloride in carbon tetrachloride. The reaction was found to give chlorotrimethylstannane and phenyl methanesulfonate in nearly quantitative yield (Eq. 4).

$$\mathrm{Me_3SnOPh + MeSO_2Cl} \xrightarrow[\mathrm{CCl_4}]{\text{reflux 5 h}} \mathrm{Me_3SnCl + MeSO_2OPh} \qquad (4)$$

No other product was found in the reaction solution by NMR analysis. Phenyl methanesulfonate was isolated and characterized.

TABLE 1. RATE CONSTANTS FOR THE REACTION OF $Me_3SnOC_6H_5$ (0.242 mol dm^{-3}) WITH $MeSO_2Cl$ (0.175 mol dm^{-3}) IN VARIOUS SOLVENTS

Solvent	$(\varepsilon)^{a)}$	Temp °C	$k_2\times10^4$ $dm^3\ mol^{-1}\ s^{-1}$	k_{rel}	$\Delta H^{\neq}_{400}$ kJ mol^{-1}	$\Delta S^{\neq}_{400}$ J $K^{-1} mol^{-1}$
CCl_4	(2.23)	120	2.50 ± 0.21		44.5	−204
CCl_4		130	3.74 ± 0.12	1.00	$\gamma=0.998^{b)}$	
CCl_4		150	6.94 ± 0.50			
CH_2Br_2	(6.7)	120	1.04 ± 0.037		41.2	−221
CH_2Br_2		130	1.41 ± 0.06	0.38	$\gamma=0.999$	
CH_2Br_2		140	1.98 ± 0.11			
CH_2Cl_2	(8.9)	130	1.20 ± 0.06	0.32	38.6	−228
CH_2Cl_2		150	2.39 ± 0.16		$\gamma=0.997$	
CH_2Cl_2		160	2.82 ± 0.23			
C_6H_5CN	(25.2)	120	5.11 ± 0.17		47.0	−192
C_6H_5CN		130	7.56 ± 0.91	2.0	$\gamma=0.999$	
C_6H_5CN		140	10.7 ± 1.1			
CH_3CN	(36.2)	100	8.58 ± 0.79		59.2	−148
CH_3CN		110	13.0 ± 1.1		$\gamma=0.997$	
CH_3CN		130	37.8 ± 2.3	10		

a) Dielectric constant. b) Correlation coefficiency of the Arrhenius plot.

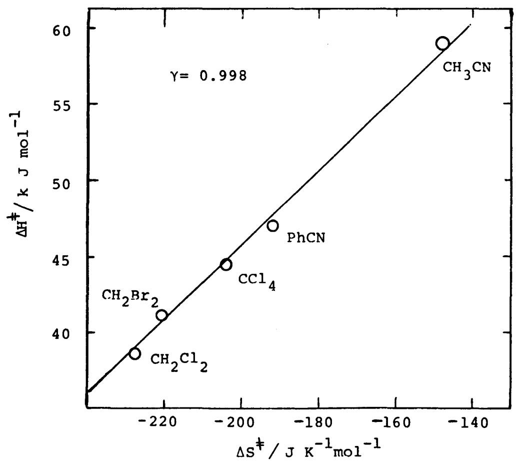


Fig. 1. Plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ in various solvents.

Kinetics and Mechanism. The rate of the reaction of trimethylphenoxystannane (0.242 mol dm^{-3}) with methanesulfonyl chloride (0.175 mol dm^{-3}) was measured by following the decrease and rise of the ^1H NMR methyl signal of the starting chloride ($MeSO_2Cl$, δ 3.58 ppm) and of the sulfonate (δ 3.03 ppm). A good second order kinetic plot ($\gamma=0.998$) was obtained for more than 80% completion with tolerable reproducibility (±8%). The rates of the reactions at various temperatures were measured in five different solvents including carbon tetrachloride as a nonpolar solvent and acetonitrile as the most polar one. The results are summerized in Table 1.

The solvent effect shown in Table 1 is quite smaller than that observed for the nucleophilic reaction of arylthiostannane with haloalkane[1] and abnormal. No dependency of the rates on the solvent polarities was observed although it was slightly accelerated in polar solvents except for that in carbon tetrachloride. The result may suggest different mechanism for the reaction in carbon tetrachloride from that in polar solvents.

TABLE 2. RATE CONSTANTS FOR THE REACTIONS OF $Me_3SnOC_6H_4X$-*p* (0.242 mol dm^{-3}) WITH $MeSO_2Cl$ (0.175 mol dm^{-3})

Solvent	Temp/°C	Substituent X	k_2/$dm^3\ mol^{-1}\ s^{-1}$
CCl_4	130	OCH_3	$5.37\pm0.51\times10^{-4}$
CCl_4	130	CH_3	$3.99\pm0\ 29\times10^{-4}$
CCl_4	130	H	$3.74\pm0.12\times10^{-4}$
CCl_4	130	Cl	$2.81\pm0.15\times10^{-4}$
CCl_4	130	NO_2	$4.17\pm0.90\times10^{-5}$
CH_2Cl_2	130	OCH_3	$5.13\pm0.20\times10^{-4}$
CH_2Cl_2	130	CH_3	$3.23\pm0.19\times10^{-4}$
CH_2Cl_2	130	H	$1.20\pm0.06\times10^{-4}$
CH_2Cl_2	130	Cl	$4.66\pm0.37\times10^{-5}$
CH_2Cl_2	130	NO_2	$1.74\pm0.29\times10^{-5}$
C_6H_5CN	130	OCH_3	$1.73\pm0.29\times10^{-3}$
C_6H_5CN	130	CH_3	$9.67\pm0.59\times10^{-4}$
C_6H_5CN	130	H	$7.56\pm0.91\times10^{-4}$
C_6H_5CN	130	Cl	$6.18\pm0.23\times10^{-4}$
C_6H_5CN	130	NO_2	$7.58\pm0.91\times10^{-4}$
CH_3CN	100	OCH_3	$5.04\pm0.51\times10^{-4}$
CH_3CN	100	CH_3	$6.28\pm0\ 38\times10^{-4}$
CH_3CN	100	H	$8.58\pm0.79\times10^{-4}$
CH_3CN	100	Cl	$1.34\pm0.29\times10^{-3}$
CH_3CN	100	NO_2	$5.68\pm0.52\times10^{-3}$

The hypothesis, however, conflicts with the isokinetic relationship. Plots of the activation parameters observed in all the solvents examined, gave a clear straight line as shown in Fig. 1, which strongly rules out the possibility of the different mechanism in polar and nonpolar solvents.

Substituent effects of the aryloxyl groups were examined in these solvents in order to obtain more evidence about the reaction mechanism. The reactions were carried out at 130 °C except for the reactions in acetonitrile which were conducted at 100 °C since some reactions in this solvent were too fast to be measured at the higher temperatures. The results are given in Table 2 and Hammett plots are shown in Figs. 2—5.

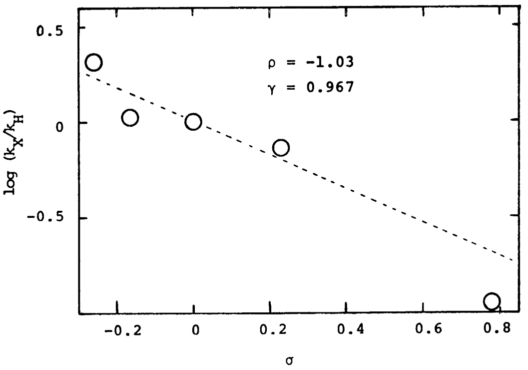


Fig. 2. Hammett plot of the rates in CCl_4 at 130 °C.

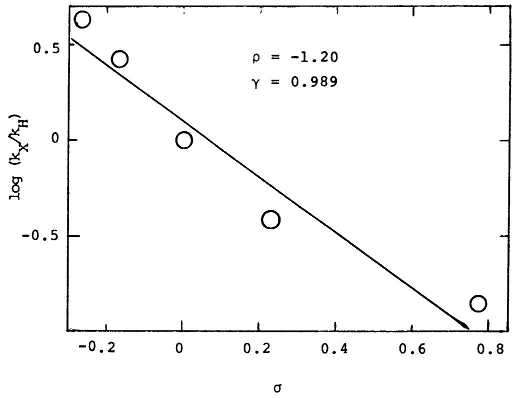


Fig. 3. Hammett plot of the rates in CH_2Cl_2 at 130 °C.

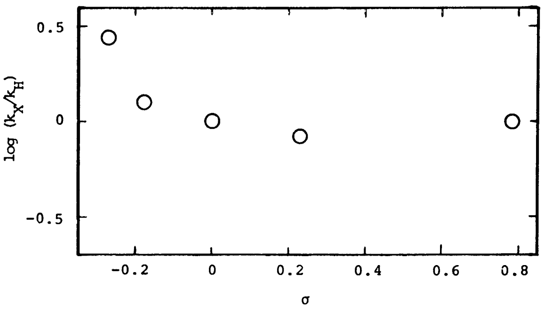


Fig. 4. Hammett plot of the rates in C_6H_5CN at 130 °C.

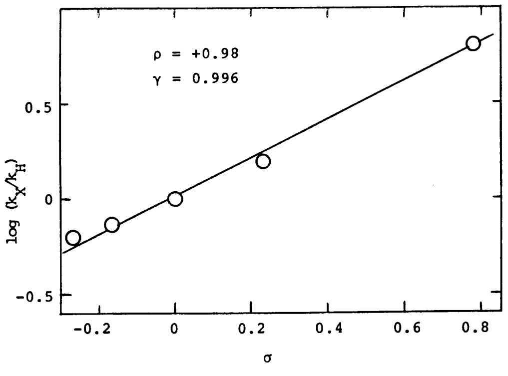


Fig. 5. Hammett plot of the rates in CH_3CN at 100 °C.

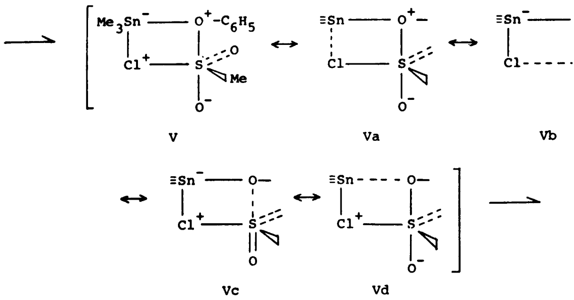
As shown in Figs. 2—5, the substituent effects are markedly dependent on the solvent used. Negative ρ values were observed for the reactions in carbon tetrachloride and dichloromethane though the magnitudes are somewhat smaller than most of that of the IVb–VIb bond cleavage reactions involving nucleophilic attacks of the VIb atom.[1–3] On the contrary, almost no substituent effect and a small positive ρ value were observed in benzonitrile and in acetonitrile, respectively.

The negative ρ values observed in carbon tetrachloride and in dichloromethane may postulate an ionic process for the reaction *i.e.*, a nucleophilic attack of the oxygen atom on the sulfonyl sulfur. The mechanism, however, is inconsistent with the substituent effects observed in benzonitrile and in acetonitrile and also conflicts with the small and obscure solvent effect. If such ionic process was operative even in the nonpolar solvent, it should be facilitated more in the polar solvents. The ρ values observed in the polar solvents have to appear clearly negative and more enhanced solvent effect would be expected as were observed for the analogous reactions.[1,3,8] The ρ values presently observed in the polar solvents together with the solvent effect are inconsistent with these considerations. Furthermore, the positive ρ value observed in acetonitrile could not be explained by postulation of a five-coordination process in the solvent. Different mechanisms in individual solvents are hardly acceptable for the reaction in view of the isokinetic relationship as discussed above.

Large negative entropy of activations were observed for the present reaction in all the solvents as shown in Table 1. These paramters would be an evidence in support of a four-centered mechanism although they could not be a definite evidence. Namely, large negative entropy of activation values were observed for the nucleophilic[1,8] and five-coordination[4] reactions involving cleavages of IVb–VIb bonds, regardless of their mechanisms. Most of the values presently observed, however, are substantially more negative than those observed previously. Consequently, the activation parameters could be considered to be an evidence suggesting a four-center process for the reaction and this is the only remaining possible mechanism.

It is difficult, however, to rationalize the solvent and the substituent effects by a fully concerted nonionic four-center transition state like III. An alternative four-center transition state is a charge separated one, similar to the associative mechanism which has been suggested for the unimolecular rearrangement of β-keto silanes.[10] In the rearrangement of β-keto silanes, little[11] or noticeable solvent effect was observed[10] although a wide variety of solvents has not yet been examined for the rearrangement. Moreover, small substituent effects were also observed for the rearrangements.[11,12] These observations quite resemble to those of the present study although the effect of the solvent on the substituent effect has not been reported yet for the rearrangement. As an analogy, a charge separated associative four-center transition state (V) would be the most suitable process for the present reaction.

Some modifications of the transition state, as shown in Va—d, may profit to account for the present observa-



tions. In the nonpolar solvents, the transition state is characterized by the O–S bond forming. The nucleophilic character of the oxygen atom, as depicted in Va as an extreme, would account for the negative substituent effect. Another way to rationalize the negative ρ value in nonpolar solvent is considering the Cl–S bond cleavage at the transition state (Vb). On the other hand, the positive substituent effect observed in acetonitrile may due to the Sn–Cl bond formation (Vc) or to the Sn–O bond fission (Vd) at the transition state. The reaction in benzonitrile may involve nearly ideal four-center transition state, V. All these transition states involve charge separations despite of the small deviations in their characters dependent on the solvents used. Thus, the small but noticeable solvent effect would be expected as was observed except for that in carbon tetrachloride. The small rate enhancement in carbon tetrachloride than in dibromo- and dichloro-methanes is difficult to explain, however, a similar slight rate enhancement in carbon tetrachloride was also observed for the reaction of ketenimine with thioketone.[13] The solvent may be too poor to solvate and to stabilize the reactants and may allow them to cohere and facilitate the bimolecular reactions in some extents.

Experimental

Materials. Preparations of (aryloxy)trimethylstannanes were carried out according to the literature.[2] Solvents for the kinetic runs were dried and distilled before use.

Product Analysis. Trimethylphenoxystannane (0.92 g) was refluxed for 5 h with methanesulfonyl chloride (0.40 g) in carbon tetrachloride (20 ml). The reaction solution was subjected to NMR analysis before work up. Only chlorotrimethylstannane and phenyl methanesulfonate were detected in the solution. The mixture was washed with water and extracted with chloroform. Phenyl methanesulfonate was isolated from the extract by evaporation of the solvent followed by recrystallization from hexane–chloroform (0.55 g, 91%) and identified by comparing with an authentic sample.

Kinetics. A typical procedure is described. (Aryloxy)-trimethylstannane (0.242 mol dm^{-3}) and methanesulfonyl chloride (0.175 mol dm^{-3}) were dissolved in a solvent using 5 ml volumetric flask. The sotution was devided into 10 portions and sealed in glass tubes of *ca.* 0.7 ml volume. The tubes were heated in a constant temperature bath (130 °C) and samples were taken out at time intervals. Each solutions were subjected to ^{1}H NMR analysis with 7—8 repeated recording of methyl signals of methanesulfonyl chloride (δ 3.58 ppm) and of the sulfonate (δ 3.03 ppm). The second order rate constant, k_2 was obtained by least square calculation of the averaged peak intensities of the methyl signals at time t.

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