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The Mechanism of the Reactions of Alkoxy- and Aryloxytrimethylsilanes with Sulfinyl Chlorides. A Doubt about 4-Center Mechanism for the Bimolecular IVb-VIb Bond Cleavages[1)]

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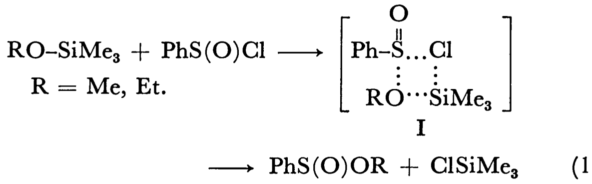
Kinetic studies have been conducted for the reactions of ethoxytrimethylsilane with benzenesulfinyl chloride and aryloxytrimethylsilane with methanesulfinyl chloride. Both the reactions were found to obey second order rate equation. A clear negative ρ value was observed for the reaction of aryloxytrimethylsilane. The solvent effects suggested that both the two reactions were quite similar in their mechanisms. Nucleophilic addition of silyl-oxygen atom to sulfinyl group has been suggested for these two reactions.

Recently, Harpp *et al.* conducted kinetic studies for the reaction of alkoxytrimethylsilanes with benzenesulfinyl chloride.[2)] They observed that the reaction was rather insensitive to the solvent polarity and sensitive to the steric effect of the alkoxyl group. A *four-centered nonionic transition state* (I) has been suggested for the reaction.



$$\mathrm{RO{-}SiMe_3 + PhS(O)Cl} \longrightarrow \left[\begin{matrix} \mathrm{Ph{-}\overset{O}{\overset{\|}{S}}\ldots Cl} \\ \vdots \quad \vdots \\ \mathrm{R\dot{O}\cdots SiMe_3} \end{matrix}\right] \qquad \mathrm{R = Me,\ Et.}$$

I

$$\longrightarrow \mathrm{PhS(O)OR + ClSiMe_3} \qquad (1)$$

The mechanism has widely been accepted to explain the course of the reaction involving the IVb element at the reaction center,[3)] however, only few were supported by kinetic and/or stereochemical evidences.[4,5)] Restricting to bimolecular IVb–VIb bond cleavage reactions as expressed by the following general formula (Eq. 2),[6)]

$$\equiv\mathrm{IVb{-}VIb{-}} + \mathrm{E{-}Nu} \longrightarrow \equiv\mathrm{IVb{-}Nu} + \mathrm{E{-}VIb{-}}$$

$$\mathrm{IVb = Si, Ge, Sn}\ \textit{etc.} \quad \mathrm{VIb = O, S, Se}\ \textit{etc.}$$

$$\mathrm{E{-}Nu = H_2O, ROH, RCO_2H, RX, RCOX, RS(O)X}\ \textit{etc.} \qquad (2)$$

the reaction of alkoxysilane reported by Harpp *et al.* is the only one reaction involving the mechanism supported by kinetic evidence.[2)]

We have reexamined the reaction of alkoxysilane with sulfinyl chloride in order to obtain additional kinetic aspects of the bimolecular *nonionic four-centered reaction*, or to take a new look at the mechanism and found that the reaction involved *ionic* nucleophilic attack of the silyl-oxygen atom.

Results and Discussion

Examination of the substituent effect of the *nonionic four-centered reaction* would be of interest or important to clarify the reaction mechanism. Thus, we tried to prepare substituted-benzenesulfinyl chlorides to examine the substituent effect of the reaction shown in Eq. 1. The substituted-sulfinyl chlorides can be prepared either from the corresponding disulfides[7a)] or from sodium sulfinates,[7b)] however, it was found to be difficult to prepare them in pure forms enough for kinetic experiments. Alternatively, the reaction of aryloxytrimethylsilane with methanesulfinyl chloride was chosen for our study. The reaction was found to give methanesulfinate and chlorotrimethylsilane in nearly quantitative yields.

$$p\text{-}\mathrm{X{-}C_6H_4OSiMe_3 + MeS(O)Cl} \longrightarrow p\text{-}\mathrm{X{-}C_6H_4OS(O)Me + Me_3SiCl} \qquad (3)$$

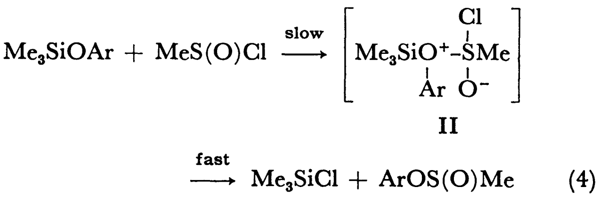
The rate of the reaction was measured by monitoring ^{1}H NMR trimethyl signals of the starting aryloxysilane and the formed chlorosilane at time. A good second order kinetic plot was obtained with satisfactory reproducibility. The results are given in Table 1.

Table 1. Rate of the reaction of $\mathrm{Me_3SiOC_6H_4X}$-p (0.19 mol/dm^3) with MeS(O)Cl (0.23 mol/dm^3) in PhCN

X	Temp/°C[a)]	k/dm^{3}mol^{-1} s^{-1}	Remarks
OMe	28	1.62×10^{-3}	
OMe	34	2.35×10^{-3}	$\Delta H^{\neq}=43.9$ kJ mol^{-1}
OMe	41	3.25×10^{-3}	$\Delta S^{\neq}=-151$ J K^{-1} mol^{-1}
OMe	47	5.06×10^{-3}	
OMe	—	2.96×10^{-3}	
Me	—	1.39×10^{-3}	Hammett plot
H	—	1.03×10^{-3}	$\rho(\sigma)=-1.44$
Cl	—	6.60×10^{-4}	$(\gamma=0.984)$
Br	—	6.30×10^{-4}	
$\mathrm{NO_2}$	—	7.04×10^{-5}	

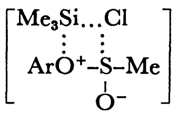
a) JEOL PS-100, VT Probe was used for measurement of activation parameters. Temperatures were calibrated. Substituent effect was measured on Hitachi R-20, at magnet temperature (36 °C); not calibrated.

The activation parameters appeared as normal magnitude for the reactions of this type shown in Eq. 2; not particular from the reactions involving either 5-coordination of the IVb element[8)] or nucleophilic attack of the VIb atom.[9)] More clear evidence in support of an *ionic mechanism* for the reaction is the substituent effect. A clearly negative ρ value was observed for the reaction in almost the same magnitude with those of the analogous reactions of (arylthio)trimethylstannanes with haloalkane (-1.40)[9a)] and with benzoyl chloride (-1.6)[9b)] in which nucleophilic attacks of the stannyl-sulfur atoms have been suggested for the reactions based on kinetic and stereochemical results. The value is also pretty close to that of sulfonium salt formation which undoubtedly involves nucleophilic attack (−1.2).10) In addition to these similarities, the magnitude of the entropy of activation is in accordance with that of the sulfonium salt formation (−138 J K^{-1} mol^{-1}).10) These results would suggest a rate-determining nucleophilic attack of the silyl-oxygen atom giving oxonium intermediate for the reaction of aryloxytrimethylsilane with sulfinyl chloride (Eq. 3). Thus, the mechanism shown below would be the most plausible for the reaction.



$$\mathrm{Me_3SiOAr} + \mathrm{MeS(O)Cl} \xrightarrow{\text{slow}} \left[\begin{array}{c} \qquad\ \ \mathrm{Cl} \\ \mathrm{Me_3SiO^+\text{-}SMe} \\ \mathrm{Ar}\ \ \mathrm{O^-} \end{array}\right]_{\mathrm{II}} \xrightarrow{\text{fast}} \mathrm{Me_3SiCl} + \mathrm{ArOS(O)Me} \qquad (4)$$

The detailed mechanism leading to the product from the onium intermediate (II) is not clear but *ionic four-centered transition state* (III) for the step is unlikely based on the similarities of the ρ and entropy values as discussed above.



III

The remaining question is whether the nucleophilic addition mechanism is applicable to the reaction of Harpp *et al.* shown in Eq. 1.2) Different mechanisms for the two reactions (Eqs. 1 and 3) are unlikely since the nucleophilic mechanism has been suggested even for the reaction of less nucleophilic aryloxy-oxygen atom. The more nucleophilic alkoxy-oxygen would attack the sulfinyl group in the same manner. Solvent effects on both the reactions were examined in order to prove the similarity of their mechanisms. The rates of the reactions were measured in various solvents including carbon tetrachloride and dichloromethane which have been employed by Harpp *et al.* The effect presently observed [k(CH$_2$Cl$_2$)/k(CCl$_4$)=3.8] is in accordance with that of them (5) as shown in Table 2.11)

Both the rates of the reactions were clearly accelerated in polar solvents. The observed solvent effect for the reaction of aryloxysilane [Eq. 3, X=MeO; k(Ph$_6$CN)/k(CCl$_4$)=70] is pretty close to that observed for the reaction of arylthiostannane with halo-alkane [k(PhCN)/k(C$_6$H$_6$)=*ca.* 100] in which nucleophilic attack was suggested as the mechanism.9a) The effect, however, appeared substantially smaller for the reaction of ethoxysilane (Eq. 1, R=Et). The difference in the magnitudes of the solvent effects is not clear; may perhaps due to difference in charge delocalization in the intermediates or in solvations, but both the rates in various solvents exhibit clearly linear correlation as shown in Fig. 1. The linear correlation (γ=0.998) would reveal that these two reactions proceed in a similar manner *i.e.*, the nucleophilic addition mechanism. The *nonionic four-center mechanism* suggested by Harpp *et al.*2) has thus been ruled out also for the reaction of alkoxysilane (Eq. 1).

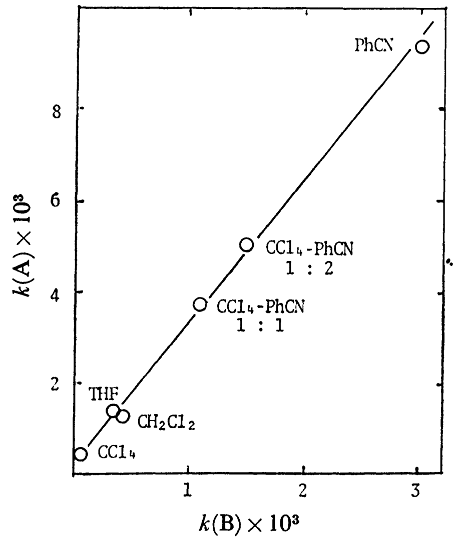


Fig. 1. Plot of the rates of the reaction A (Eq. 3, X=OMe) *vs.* reaction B (Eq. 1, R=Et) in various solvents.

The evidences cited by them in support of their mechanism were the solvent effect and the steric effect.2) They examined five different solvents but all nonpolar ones. They compared their result with that of cheleotropic denitrogenation reaction of a caged diazo compound12) in support of their *nonionic mechanism.* The auther claimed that the solvent effect of the reaction of alkoxysilane [k(CH$_2$Cl$_2$)/k(C$_6$D$_{12}$)=9] was pretty close

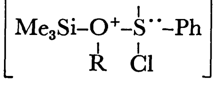
TABLE 2. RATES OF THE REACTIONS; Me$_3$SiOC$_6$H$_4$OMe-*p* (0.19 mol/dm^3)+MeS(O)Cl (0.23 mol/dm^3) [A] AND Me$_3$SiOEt (0.16 mol/dm^3)+PhS(O)Cl(0.20 mol/dm^3) [B] IN VARIOUS SOLVENTS AT 36 °C[a]

Solvent	Reaction [A][b]		Reaction [B]		
	k[d]	k_{rel}	k[d]	k_{rel}	k_{rel}[c]
CCl$_4$	4.34×10^{-5}	1.00	2.89×10^{-4}	1.00	1
Tetrahydrofuran	3.64×10^{-4}	8.4	1.23×10^{-3}	4.3	—
CH$_2$Cl$_2$	4.03×10^{-4}	9.3	1.11×10^{-3}	3.8	5
CCl$_4$-PhCN (1 : 1)[e]	1.03×10^{-3}	24	3.62×10^{-3}	12.5	—
CCl$_4$-PhCN (1 : 2)[a]	1.49×10^{-3}	34	4.93×10^{-3}	17	—
PhCN	2.96×10^{-3}	68	9.25×10^{-3}	32	—

a) Hitachi R-20 NMR magnet temperature; not calibrated. b) Reaction A and B are correspond to the reactions shown in Eqs. 3 and 1 in the text, respectively. c) Data from Ref. 2; initial concentrations were not recorded. d) Second order rate in dm^3 mol^{-1} s^{-1}. e) v/v Mixture.

to that of the cheleotropic reaction which was studied over a wide variety of solvents and a small solvent effect ($\simeq$15-fold) was noted.2) The effects, however, appeared opposite. The rates of the cheleotropic reaction appeared no correlation to the solvent polarity; rather accelerated in nonpolar solvent (2-Me-heptane) and depressed in polar solvent (96% EtOH).12) On the other hand, the rates of the reaction of alkoxysilane were apparently accelerated in a polar solvent (CH_2Cl_2).2) In the present study, it was shown to be accelerated more in more polar solvent.

The steric effect of the alkoxy moiety [k(EtO)/k(MeO)$=$10] indicates that the reaction is sensitive to the steric hindrance as they claimed.2) The sensitivity to the steric hindrance, however, is also acceptable to the steric crowd in the onium intermediate (IV), bearing bulky trimethylsilyl group and trigonal bipyramid sulfur functionality.



$$\left[\mathrm{Me_3Si{-}\underset{R}{O^+}{-}\overset{O^-}{\underset{Cl}{S^{\cdot\cdot}}}{-}Ph}\right] \quad \mathrm{R = Me, Et,}$$

IV

The *nonionic four-centered mechanism* has been ruled out for the reactions of (arylalkoxy)silanes with sulfinyl chlorides. None of the bimolecular reactions of this type shown in Eq. 2, has been known to proceed *via* either *ionic* or *nonionic four-center transition state* which has been supported by any evidence.

Experimental

Materials. Trimethylphenoxysilane was prepared from hexamethyldisilazane (5.0 g) and phenol (4.7 g) in the presence of imidazole,2) bp 41 °C/2 mmHg (1 mmHg$=$133.332 Pa), 88% yield. Other aryloxytrimethylsilanes were prepared similarly. Methanesulfinyl chloride was prepared by chlorination of dimethyl disulfide in acetic anhydride,7a) bp 38—41 °C/14 mmHg, 84% yield. Benzenesulfinyl chloride was prepared from sodium benzenesulfinate and thionyl chloride,7b) 77 °C/1 mmHg, 95% yield.

Product Analysis. An equimolar mixture of methanesulfinyl chloride and trimethylphenoxysilane (10 mmol) in dichloromethane (4 ml) was heated at 45 °C for 20 h in a sealed tube. The solvent and volatile product were distilled off. Only chlorotrimethylsilane was detected in the distillate. ^{1}H NMR spectrum of the residue was consisted of the signals due to the remaining trimethylphenoxysilane and phenyl methanesulfinate with trace amounts of impurities which probably derived from thermal decomposition of the sulfinate ester. Signals were identified by comparing with those of the authentic phenyl methanesulfinate prepared from methanesulfinyl chloride and phenol in the presence of pyridine.13) Attempts to isolate the sulfinate from the remaining trimethylphenoxysilane were failed due to its thermal instability. Accordingly, the conversion was obtained by integration of the NMR signals of the reaction mixture, 70%. Other aryloxytrimethylsilanes gave similar results. Substituent, reaction conditions, and conversion were: p-OMe, 45 °C 5 h, 80%; p-NO_2, 45 °C 24 h, 50%.

Kinetics. The procedure is essentially the same as that employed for the acyloxyl exchange reaction of acetoxysilane.8a) Trimethylphenoxysilane (21 mm^3, 0.121 mmol) and methanesulfinyl chloride (10 mm^3, 0.143 mmol) were dissolved in the solvent (600 mm^3) and the reaction was monitored by following ^{1}H NMR trimethyl signals of the starting trimethylphenoxysilane (δ 0.27 ppm) and the product, chlorotrimethylsilane (δ 0.40 ppm) with time.

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