Kinetic Study on the Reaction of (Arylthio)trimethylsilanes with Phenacyl Bromide Giving Aryl Phenacyl Sulfides and Bromotrimethylsilane

Seizi KOZUKA,* Tetsuji HIGASHINO, and Takuro KITAMURA

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimotocho, Sumiyoshi-ku, Osaka 558

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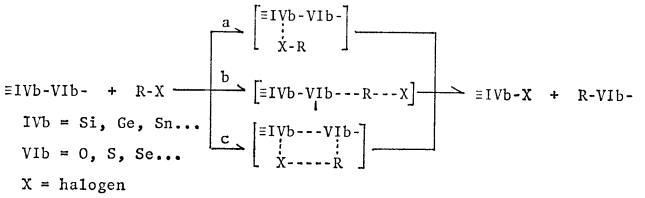
A kinetic study has been conducted on the reactions of (arylthio)trimethylsilanes with phenacyl bromide giving aryl phenacyl sulfides and bromotrimethylsilane. Remarkably large positive substituent effect ($\rho = +2.2$) and large negative entropy of activation were observed for the reaction. A mechanism involving 5-coordinated silicon intermediate prior to the rate-determining heterolysis of the Si–S bond has been suggested for the reaction based on the kinetic results.

Three different mechanisms are conceivable for the cleavage reaction of the group IVb–VIb bond by the reaction with haloalkane. Assuming the coordination ability of the IVb element, a 5-coordinated complex would be formed as an intermediate of the reaction (path a). On the other hand, a nucleophilic reaction by the attack of the VIb element is also a possible route for the reaction (path b). A mechanism involving four-centered transition state is the third possibility if the paths a and b occurred simultaneously (path c) although this mechanism for a bimolecular reaction of this type has recently been suspected by us.[1]



The reactions of (alkylthio and arylthio)trimethylstannanes with haloalkanes have been known to be the nucleophilic reaction (path b) based on detailed kinetic and stereochemical studies.[2] Namely the reaction obeys a second order rate equation, apparently negative ρ value (-1.40) of the substituent effect of the arylthio moiety, solvent effect on the rate of the reaction, relative reactivity of haloalkanes, and inversion of the alkyl group of the haloalkane by the reaction.

$$Me_3Sn\text{-}SPh + R\text{-}X \longrightarrow [Me_3Sn\text{-}S^{+}(Ph)\text{-}R\ X^{-}] \quad \text{(I)} \longrightarrow PhS\text{-}R + Me_3Sn\text{-}X$$

An analogous reaction of thiosilane with haloalkane has been known to give halosilane and sulfide which then further react with excess haloalkane giving trialkylsulfonium salt.[3,4] A silicon analogue of the sulfonium salt of the type I had once been reported as

$$R_3Si\text{-}SR' + R''\text{-}X \longrightarrow R_3Si\text{-}X + R'\text{-}S\text{-}R''$$
$$R'\text{-}S\text{-}R'' + R'' \longrightarrow R'R''_2S^{+}X^{-}$$

an isolable product in the reaction of (butylthio)-trimethylsilane with an equimolar amount of iodomethane.[3b] If the silylsulfonium salt was actually an isolable product, it would be a definite evidence in support of a nucleophilic reaction of the sulfur atom. It has been found, however, to be an erroneous result.[4]

Kinetic and stereochemical studies of this reaction would be of interest, since if the reaction proceeded by the same mechanism with that of the tin analogue,[2] stereochemistry of the silicon atom may clarify the final step of the reaction *i.e.*, the mechanism of the step leading to the product from the intermediate I. Thus, we have extended our study to the reaction of (arylthio)trimethylsilane with haloalkane in order to clarify the mechanism and to compare the aspects of the reaction with those of the reaction of the tin analogue.

Results and Discussion

Iodomethane was chosen as a typical haloalkane for the kinetic study of the reaction with (arylthio)-trimethylsilane. Although this reaction without the use of a solvent gave aryl methyl sulfide and iodotrimethylsilane on heating as analogously to the reaction of (alkylthio)silanes,[3,4] the reaction in a solvent was found to be sluggish even at high temperature and gave mainly unexpected product. Namely, hydrolysis by moisture or decomposition of the substrate giving hexamethyldisiloxane took place faster than the reaction with iodomethane when the reaction was carried out in such a nonpolar solvent as carbon tetrachloride at 120 °C. In a polar solvent, acetonitrile, the consumption of the thiosilane was found to be much faster than that in nonpolar solvent, the reaction gave a similar complex products. The reaction of the thiosilane with benzyl bromide was tried since this compound is more reactive than iodomethane toward tin analogue of the thiosilane *i.e.*, trimethyl-(phenylthio)stannane.[2] The main product derived from the reaction of benzyl bromide was bromotrimethylsilane but still accompanied with substantial amounts of the disiloxane although milder reaction conditions gave a better result.

$$Me_3SiSPh \xrightarrow{RX} Me_3SiX + RSPh$$
$$Me_3SiSPh \xrightarrow{\text{hyd. or decompn.}} Me_3SiOSiMe_3$$

Kinetic study of the reaction was thus found to be difficult due to instability of the thiosilane and our attempts were failed to compare the kinetic and stereochemical results of the reaction with those of

the tin analogue by using the same haloalkanes. These results, however, reveal that the possibility of a kinetic study on the reaction of the thiosilane with more reactive haloalkane in a polar solvent under mild reaction conditions.

Phenacyl bromide was chosen as one of the most reactive haloalkane. The reaction of phenacyl bromide with an equivalent of trimethyl(phenylthio)silane was carried out at 60 °C in acetonitrile solution. Although the formation of the disiloxane was detected, even at the beginning of the reaction, the amount was found to increase little during the reaction until all the starting thiosilane was converted to the bromosilane (5h). The products of the reaction were bromotrimethylsilane, phenacyl phenyl sulfide, and small amounts of hexamethyldisiloxane and diphenyl disulfide. The volatile products were identified by GLC and NMR analyses and sulfides were characterized by isolation.

$$PhSSiMe_3 + PhCOCH_2Br \xrightarrow[\text{in } CH_3CN]{60\,^\circ C,\ 5\,h}$$

$$Me_3SiBr + PhCOCH_2SPH + (Me_3Si)_2O + Ph_2S_2$$
$$75\% \qquad 82\% \qquad 10\% \qquad 8\%$$

The rate of the reaction of trimethyl(phenylthio)-silane with two equivalents of phenacyl bromide in acetonitrile was measured by monitoring ^1H NMR trimethyl signals of the thiosilane (δ 0.26 ppm) and bromotrimethylsilane (δ 0.57 ppm) at time intervals. A good second order rate constant was obtained with tolerable reproducibility ($\approx\pm10\%$). In order to confirm the first order dependency of the rate on the concentration of phenacyl bromide, the rate of the reaction was measured with different concentrations of phenacyl bromide. A clear first order dependency was observed. Thus, the reaction was found to be second order. Rates of the reactions of several (arylthio)trimethylsilanes were measured similarly. Rates were also measured at various temperatures to obtain activation parameters. These results are given in Table 1.

An unexpectedly large negative entropy of activation was observed for the reaction. A similar large negative value was observed for the reaction of thiostannane with haloalkane in a nonpolar solvent ($CHCl_3$) but it was shown to fall in a smaller negative value when the reaction was carried out in a polar solvent (PhCN).[2] By an analogy, a smaller negative entropy value was expected in the present study since a much polar solvent (CH_3CN) was used. Therefore, the value may suggest that the reaction of (arylthio)trimethylstannane with haloalkane differs from that of (arylthio)-trimethylsilane with phenacyl bromide in the mechanism.

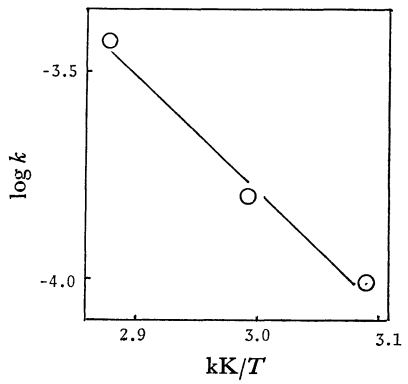


Fig. 1. Arrhenius plot of the rates of the reaction, $C_6H_5SSiMe_3 + C_6H_5COCH_2Br$ ($\gamma=0.984$).

Substituent effect also suggests that these two analogous reactions are quite different in their mechanisms. The results given in Table 1 are best correlated with σ constants giving a large positive ρ value (+2.2) with tolerable linearity as shown in Fig. 2. The deviation may be due to the instability of the thiosilanes.[5] The positive ρ value is consistent with a 5-coordination process and rules out the nucleophilic attack of the sulfur atom since the process would demand a negative ρ value as was observed for the reaction of the thiostannane with haloalkane.[2] The magnitude of the ρ value, however, appeared too large to be rationalized only by the formation of the 5-coordinated silicon intermediate.[6] A rate determining heterolysis of the Si–S bond of the coordinated intermediate would be involved in the reaction since

Table 1. Rate constant for the reaction of $X\text{-}C_6H_4SSiMe_3$ (0.56 mol dm^{-3}) with $PhCOCH_2Br$ in CH_3CN

Substituent X	Mol ratio $-CH_2Br/-SSi\equiv$	Temp °C	$10^5\,k$/dm^3 mol^{-1} s^{-1}	$\equiv SiOSi\equiv$[a] (%)	Remarks
H	1.20	51.5	6.09±0.37	—	
H	1.70	51.5	8.90±0.72	—	
H	2.16	51.5	9.68±0.10	3.5	54.0, −156[b]
H	3.72	51.5	16.7±1.1	—	
H	2.16	61.5	15.6±0.8	—	
H	2.16	75.0	37.2±3.7	6.8	
p-OCH_3	2.16	51.5	2.66±0.44	5.0	+2.2[c]
p-CH_3	2.16	51.5	9.23±0.60	13	
p-Cl	2.16	51.5	46.1±2.6	10	
p-Br	2.16	51.5	28.1±4.3	20	
m-Br	2.16	51.5	117±10	10	

a) The amount of hexamethyldisiloxane. b) ΔH^* and ΔS^* values in kJ mol^{-1} and J K mol^{-1}, respectively. c) ρ value against σ constant ($\gamma=0.966$).

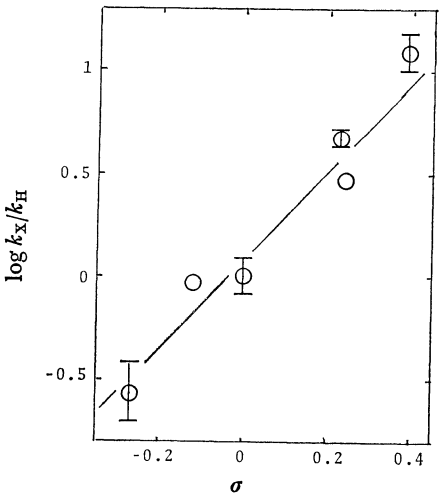


Fig. 2. Hammett plot of the rates of the reaction, $XC_6H_4SSiMe_3+C_6H_5COCH_2Br$ in CH_3CN at 51.5 °C.

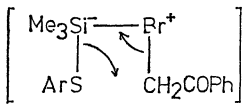
the value appeared in almost comparable magnitude to that of dissociation constants of arenethiols (+2.58).[7] Thus, the most plausible mechanism for the reaction can be formulated as follows:

$$Me_3SiSAr + PhCOCH_2Br \rightleftharpoons \underset{\text{II}}{\left[\begin{array}{l} Me_3Si^{-}\text{--}Br^{+}\text{-}CH_2CPh \\ \quad | \qquad\qquad \| \\ \quad ArS \qquad\quad O \end{array}\right]}$$

$$\xrightarrow{\text{slow}} \underset{\text{III}}{\left[\begin{array}{l} Me_3Si\text{-}Br^{+}\text{-}CH_2CPh \\ \qquad\qquad \| \\ ArS^{-} \qquad\quad O \end{array}\right]} \xrightarrow{\text{fast}}$$

$$Me_3SiBr + ArSCH_2\underset{\|}{C}Ph.$$
$$O$$

The large positive ρ value observed in the present study would be rationalized in terms of the sum of those of the first and the second steps *i.e.*, the formation of II and the heterolysis of II giving III. The intermediate III would be a short lived tight ion pair which collapsed rapidly into the product since a large negative entropy of activation was observed in the present study even the reaction was carried out in a polar solvent. An ionic four-centered transition state (IV) leading to the product from II is an attractive alter-



IV

native choice to account for the large negative entropy value since it has often been considered to suggest a cyclic transition state.[8] The large negative entropy value, however, could not be a definite evidence in support of a cyclic transition state since all the bimolecular reactions of this type which have been studied in detail, were found to proceed by non-cyclic process regardless of the large negative entropy values.[9]

The reaction of thiosilane with phenacyl bromide has thus appeared quite different in mechanism from that of thiostannane with haloalkane.[2] The reason for the difference is obscure at present but higher energy release by forming Si–X bond from Si–S bond (*ca.* 35 kcal/mol, X=Cl) than that of tin (23 kcal/mol, X=Cl)[10] may be one of the important factors to control the course of the reaction. The high reactivity of phenacyl bromide seems to play no important role to control the course of the reaction since the opposite substituent effects were also found for the reactions of benzoyl chloride with (arylthio)trimethylstannanes ($\rho=-1.6$)[11] and with (arylthio)trimethylsilanes ($\rho=+2.50$).[12]

Experimental

Materials. The (arylthio)trimethylsilanes were prepared by the same procedure described previously.[6] Phenacyl bromide was recrystallized from hexane–chloroform before use. Solvents were dried and distilled.

The Reaction of Trimethyl(phenylthio)silane with Iodomethane or Benzyl Bromide. The thiosilane (55 mg, 0.30 mmol) and iodomethane (426 mg, 3.0 mmol) were dissolved in carbon tetrachloride (total 5 cm³). The solution was divided and sealed in glass tubes each containing *ca.* 0.5 cm³. The tubes were heated in a constant temperature bath (120 °C) and subjected to NMR analysis at time intervals. After heating for 1 h, only a small amount of hexamethyldisiloxane (δ 0.07 ppm, 8%) was detected as the product. The formation of iodotrimethylsilane (δ 0.55 ppm) was detected after heating for 17 h (5%) accompanied with a large amount of the disiloxane (35%). The disiloxane would be formed by hydrolysis of the starting thiosilane and the product,

$$MeSiSAr \text{ and } Me_3SiI \xrightarrow{\text{moisture}} Me_3SiOH$$
$$2\,Me_3SiOH \longrightarrow Me_3SiOSiMe_3 + H_2O$$

iodotrimethylsilane or oxidation of them. All the materials and the apparatus were dried carefully but the results were not improved significantly. A similar result was also found by the reaction carried out in a polar solvent of acetonitrile. The consumption of the thiosilane was found to be faster in this solvent (within 1 h) but the detected product was manily the disiloxane. In separate experiments, both trimethyl(phenylthio)silane and iodotrimethylsilane were found to give substantial amounts of hexamethyldisiloxane by heating at 120 °C in these solvents.

The reaction of trimethyl(phenylthio)silane (0.06 mol dm^{-3}) with benzyl bromide (0.6 mol dm^{-3}) in acetonitrile was carried out similarly. The solution was heated at 80 °C until the thiosilane was consumed giving a mixture of bromotrimethylsilane (60%) and hexamethyldisiloxane (40%).

The Reaction of Trimethyl(phenylthio)silane with Phenacyl Bromide. The thiosilane (1 g, 5.5 mmol) and phenacyl bromide (1.1 g, 5.5 mmol) in acetonitrile (10 cm³) were heated at 60 °C for 5 h. Solvent and volatile components were distilled off. Bromotrimethylsilane (75%) and hexamethyldisiloxane (10%) were identified by GLC and NMR analyses of the distillate. Identifications were done by comparing the NMR spectra and the GLC retention times with those of the authentic samples. The residue was separated by chromatography (silica gel, hexane–chloroform). Phenacyl phenyl sulfide (82%) and diphenyl disulfide (8%) were isolated and characterized. Phenacyl phenyl sulfide; Found: C, 73.42, H. 5.30%. Calcd for $C_{14}H_{12}OS$: C, 73.65, H, 5.30%.

Kinetics. The procedure is essentially the same with

that employed for the reaction of (arylthio)trimethylsilanes with carboxylic acids.[5] Concentrations of the substrates are recorded in Table 1. Temperatures were calibrated by measuring chemical shift of 1,2-ethanediol.

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12) The reaction of $Me_3SiSC_6H_4X$ with YC_6H_4COCl in tetrachloroethane at 34 °C giving Me_3SiCl and $YC_6H_4COSC_6H_4X$ was found to be second order with ρ values of $+2.50$ (for X, $\gamma=0.984$) and -0.87 (for Y, $\gamma=0.994$) which may suggest 5-coordination of silicon atom prior to the rate determining cleavage of the Si–S bond. S. Kozuka and I. Naribayashi, Unpublished.