A Kinetic Study of the Reaction of Arylthiotrimethylsilane with Carboxylic Acid Giving Acyloxytrimethylsilane and Arenethiol

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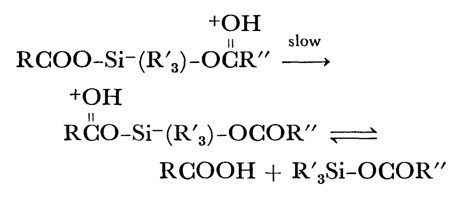
The mechanism of the reactions of arylthiotrimethylsilanes with carboxylic acids has been studied kinetically. The reaction was found to obey a second-order kinetic equation. The substituent effects of the aryl moiety ($\rho=-2.4$) and of the silicon atom, the hydrogen-deuterium kinetic isotope effect of the acid ($k_H/k_D=3$) were observed. A mechanism involving the 5-coordination of the silicon atom prior to the rate-determining protonation of the sulfur atom has been suggested for the reaction. A remarkable base catalysis was observed. The formation of the coordinated intermediate has been suggested to be the slow step in the presence of a bese.

The kinetic behavior of silicon–sulfur bond cleavage has scarcely been studied at all. Only one kinetic study, to the best of our knowledge, has been reported dealing with the hydrolysis of the Si–S bond in aqueous dioxane.[1)] On the other hand, we have ourselves

$$R_3Si\text{-}SAr + H^+ \rightleftharpoons R_3Si\text{-}S^+(H)Ar$$

$$R_3Si\text{-}S^+(H)Ar + nH_2O \xrightarrow{\text{slow}} R_3Si\text{-}OH + ArSH + H^+ + (n-1)H_2O$$

reported a kinetic aspects of the acyloxy-exchange reaction of acyloxysilane with carboxylic acid, which involves Si–O bond fission.[2)] In the mean time, an analogous reaction of carboxylic acid with thiosilane



$$RCOO\text{-}SiR'_3 + R''COOH \rightleftharpoons RCOO\text{-}Si^-(R'_3)\text{-}O\overset{\overset{+}{O}H}{\overset{\|}{C}}R'' \xrightarrow{\text{slow}} R\overset{\overset{+}{O}H}{\overset{\|}{C}}O\text{-}Si^-(R'_3)\text{-}OCOR'' \rightleftharpoons RCOOH + R'_3Si\text{-}OCOR''$$

has also been known to give the acyloxysilane in a Si-S bond cleavage reaction.[3)] We have now extended our kinetic study to this reaction: *i.e.*, the reaction of

$$RCOOH + (Me_3Si)_2S \longrightarrow H_2S + 2RCOO\text{-}SiMe_3$$

$$RCOOH + EtS\text{-}SiMe_3 \longrightarrow EtSH + RCOO\text{-}SiMe_3$$

arylthiotrimethylsilane with carboxylic acid in order to obtain more knowledge about the mechanism of the Si–S bond fission.

Results and Discussion

The reaction of arylthiosilane with carboxylic acid in chloroform was found to proceed smoothly at room temperature to give arenethiol and acyloxytrimethylsilane in high yields. The product was isolated and

$$Me_3Si\text{-}SAr + RCOOH \longrightarrow Me_3Si\text{-}OCOR + ArSH$$

characterized. The reverse reaction, *i.e.*, that giving the thiosilane from the acyloxysilane and arenethiol, was not found to proceed at all under the conditions used. Small amounts of hexamethyldisiloxane (8—10%) and trimethylsilanol (2%) were detected in the reaction mixture by NMR analysis, as in the acyloxy exchange reaction,[2)] but the amounts were found to be unchanged during the reaction. This suggests that these side products are independent of the reaction of thiosilane with acid. They may be formed by the interaction of the thiosilane with moisture, giving silanol, while the subsequent dehydration of the silanol results in the formation of the disiloxane.[4)]

The rate of the reaction of thiosilane with two equivalents of carboxylic acid was measured by monitoring the decrease in the ^1H NMR trimethyl signal of the starting thiosilane (δ 0.25—0.27 ppm) and the increase in that of acyloxysilane (δ 0.32—0.40 ppm). A good second-order rate constant was obtained with satisfactory reproducibility. The rate of the reaction with acetic acid could not be obtained by this kinetic procedure because the trimethyl signal of acetoxytrimethylsilane (δ *ca.* 0.3 ppm) appeared rather close to that of the starting material, therefore, the amounts of the two components could not be measured with a high accuracy. Accordingly, chloro-, dichloro-, and trichloroacetic acids were used in the present study. The results are given in Table 1. Good Hammett correlations were found for the reactions with each carboxylic acid with apparently negative ρ value ($\rho_{(\sigma)}=-2.4$, with $CHCl_2COOH$). The value thus obtained appeared quite similar in magnitude to those of the dissociation constants of arenethiols with the opposite sign ($\rho=+2.24$).[5)] This would suggest that the present reaction involves the formation of a sulfonium ion.

The effect of the acid strength of the attacking carboxylic acids was observed on the rate of the reaction. A plot of the results given in Table 1 against the σ^* constants gave a straight line with a ρ^* value of $+1.34$ ($X=OCH_3$; $\gamma=0.968$; similar ρ^* values were obtained

TABLE 1. RATE CONSTANTS FOR THE REACTIONS OF p-X-C_6H_4-S-$SiMe_3$ (0.60 mol/dm^3) WITH RCOOH (1.20 mol/dm^3) IN $CHCl_3$ AT 34 °C[a)]

	k_2/dm^3 mol^{-1} s^{-1}		
	R in RCOOH		
X	CH_2Cl ($\times 10^4$)	$CHCl_2$ ($\times 10^3$)	CCl_3 ($\times 10^2$)
OCH_3	2.58±0.07	1.47±0.14	4.70±0.80
CH_3	1.13±0.05	0.64±0.01	1.65±0.03
H	0.50±0.02	0.30±0.01	0.64±0.03
Cl	0.15±0.01	0.10±0.01	0.30±0.03
		$\rho_{(\sigma)}=-2.4$ $\gamma=0.993$	

a) NMR probe temperature, Hitachi-Perkin Elmer R-20 spectromerer.

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF Me_3SiSPh (0.60 mol/dm^3) WITH $CHCl_2COOH$ (1.20 mol/dm^3) IN $CHCl_3$

Temp/°C$^{a)}$	$k_2\times10^4$/dm^3 mol^{-1} s^{-1}	ΔH^* kcal/mol	ΔS^* e.u.
28	2.89 ± 0.21		
38	3.89 ± 0.16		
45	6.99 ± 0.27	8.8	-45.6
56	$10.9\ \pm1.1$		

a) JEOL PS-100 VT probe; the temperatures were calibrated by measuring the chemical shift of 1,2-ethanediol at the temperatures.

TABLE 3. RATES OF THE REACTIONS OF $Me_2RSiSPh$ (0.60 mol/dm^3) WITH $CHCl_2COOH$ AND $CHCl_2COOD$ (1.20 mol/dm^3) IN $CHCl_3$ AT 34 °C$^{a)}$

R	$k_2\times10^4$/dm^3 mol^{-1} s^{-1}	k_{rel}	k_{rel}, $Me_2RSiOAc^{b)}$
CH_3	2.96 ± 0.09 (H)	3.08	2.66
CH_3	1.08 ± 0.05 (D) $k_H/k_D=2.7$		($k_H/k_D=1.6$)
$PhCH_2$	1.15 ± 0.09 (H)	1.20	1.11 ($k_H/k_D=1.7$)
Ph	0.96 ± 0.04 (H)	1.00	1.00
Ph	0.29 ± 0.01 (D) $k_H/k_D=3.3$		

a) NMR probe temperature (Hitachi-Perkin Elmer, R-20). b) Rate of $Me_2RSiOAc + CHCl_2COOH \rightarrow Me_2RSiOCOCHCl_2 + AcOH$.[2)]

for each substituent, X). The ρ^* value appeared quite similar to that observed for the acyloxy exchange reaction of acyloxytrimethylsilane with various carboxylic acids.[2)]

In order to obtain the activation parameters, the rate of the reaction of trimethyl(phenylthio)silane with dichloroacetic acid in chloroform was measured at various temperatures. The results are shown in Table 2. An Arrehnius plot of the data gave 8.8 kcal/mol (4.184 J) and −45.6 e.u. for the enthalpy and entropy values respectively. Here again, the values appeared to be quite similar to those observed for the acyloxy exchange reaction.[2)] The large negative entropy value suggests a tight transition state for the reaction, but it does not suggest a 4-centered reaction, since a remarkably negative ρ value was observed in the present study, as has been mentioned above. The tight transition state may be explained in terms of an ionic reaction which is forced to proceed in a nonpolar solvent, as was suggested for the reaction of thiostannane with haloalkane, in which a large negative entropy value was observed when the reaction was carried out in a nonpolar solvent, while the value fell to a normal magnitude in a polar solvent.[6)]

TABLE 4. EFFECT OF BASE ON THE RATE OF THE REACTION OF Me_3SiSPh (0.60 mol/dm) with $CHCl_2COOH$ (1.20 mol/dm^3) IN $CHCl_3$ AT 34 °C$^{a)}$

Base	Mole ratio Base/Sulfide	k_2 dm^3 mol^{-1} s^{-1}	k_{rel}
None	0	$3.0\pm0.1\times10^{-4}$	1.0
Et_3N	0.1	$1.3\pm0.1\times10^{-2}$	43
C_5H_5N	0.1	$7.6\pm0.8\times10^{-3}$	25

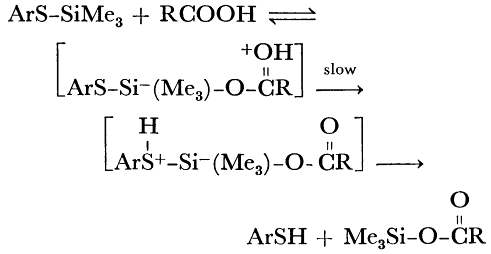
a) NMR probe temperature (Hitachi-Perkin Elmer R-20).

TABLE 5. RATES OF THE REACTIONS OF p-X-$C_6H_4SSiMe_3$ (0.31 mol/dm^3) WITE $CHCl_2COOH$ (0.65 mol/dm^3) IN $CHCl_3$ AT 34 °C$^{a)}$ IN THE PRESENCE OF C_5H_5N (0.03 mol/dm^3)

X	$k_2\times10^3$/dm^3 mol^{-1} s^{-1}	
OCH_3	2.05 ± 0.13	
CH_3	2.53 ± 0.11	
H	2.86 ± 0.27	$\rho_{(\sigma)}=+0.74$
Cl	4.61 ± 0.15	$\gamma=0.983$

a) NMR probe temperature (Hitachi-Perkin Elmer R-20).

The steric and electronic effects of the silicon substituent were examined by carrying out the reaction of dichloroacetic acid with alkyl (or aryl)dimethyl(phenylthio)silanes. The results obtained can be explained in terms of the steric effect rather than the electronic effect of the substituent. The hydrogen-deuterium kinetic isotope effect was also examined, and a positive isotope effect was observed. The results are summarized in Table 3. The positive kinetic isotope effect and the negative ρ value suggest a rate-determining protonation of the sulfur atom. In the meantime, the steric effect of the bulky substituent on the silicon atom appeared almost the same as those observed in the acyloxy exchange reactions of the corresponding acyloxysilanes, as is shown in Table 3. These results, together with the similarity of the ρ^* value, the activation parameters, and the positive kinetic isotope effect to those of the acyloxy exchange reaction,[2)] strongly suggest that these two reactions are similar in their mechanisms; *i.e.*, the reaction involves the 5-coordination of the silicon atom prior to the rate-determining proton transfer. Thus, the most plausible mechanism for the reaction can be formulated as follows. The first step of the reaction would be the formation of a 5-coordinated intermediate by a reversible reaction. Thus, the bulky substituent on the silicon atom disfavors the formation of the intermediate. The second step is the rate-determining proton migration from the carbonyl oxygen to the sulfur atom. An electron-withdrawing substituent on the aryl moiety would destabilize the second intermediate of the sulfonium ion, resulting in a deceleration of the reaction and bringing forth a negative ρ value. The sulfonium intermediate would rapidly col-



$$ArS\text{-}SiMe_3 + RCOOH \rightleftharpoons \left[ArS\text{-}Si^-(Me_3)\text{-}O\text{-}\overset{+OH}{\overset{\|}{C}}R\right] \xrightarrow{\text{slow}} \left[Ar\overset{H}{\overset{|}{S}}{}^+\text{-}Si^-(Me_3)\text{-}O\text{-}\overset{O}{\overset{\|}{C}}R\right] \longrightarrow ArSH + Me_3Si\text{-}O\text{-}\overset{O}{\overset{\|}{C}}R$$

lapse into the products.

According to the mechanism, one can expect the base catalysis of the reaction, since the carboxylate ion would be a better reagent than the conjugate acid for the formation of a 5-coordinated silicon atom. Furthermore, an opposite substituent effect of the aryl ring, that is, a positive ρ value, would be expected for the base-catalyzed reaction because of the lack of the protonation step. The rate of the reaction was found to be markedly accelerated by the addition of a base, as is shown in Table 4. The rates of the reactions of arylthiotrimethylsilanes with dichloroacetic acid in the presence of pyridine as the base are given in Table 5. As expected, a small but clearly positive substituent effect ($\rho = +0.74$) was observed. The reaction scheme in the presence of a base is formulated below:

$$\mathrm{RCOOH} + :\mathrm{B} \rightleftharpoons \mathrm{RCOO}^- + \mathrm{BH}^+$$

$$\mathrm{RCOO}^- + \mathrm{Me_3Si\text{-}SAr} \rightleftharpoons \mathrm{RCOO\text{-}Si^-(Me_3)\text{-}SAr}$$

$$\mathrm{RCOO\text{-}Si^-(Me_3)\text{-}SAr} \longrightarrow \mathrm{RCOO\text{-}SiMe_3} + \mathrm{ArS}^-$$

The substituent on the aryl ring affects the stability of the coordinated silicon atom with a formal anionic character through the sulfur linkage. As a result, a positive ρ value would result in a moderate magnitude.

Experimental

Materials. The arylthiotrimethylsilanes were prepared from chlorotrimethylsilane and lead arenethiolates.[7] Benzyl (or phenyl)dimethyl(phenylthio)silane was prepared similarly from the corresponding chlorodimethylsilane; bp 142—146°C/1 mmHg (133.332 Pa), NMR ($CDCl_3$) δ(ppm), 0.46 s(6H), 2.36 s(2H), and 7.00—7.23 m(10H). The carboxylic acids were purified by distillation. Dichloroacetic acid-*d* was obtained by the hydrolysis of the corresponding anhydride with D_2O. The deuterium content was measured by the integration of the NMR signals (90%).

Product Analysis. Trimethyl(phenylthio)silane (48 mg, 0.26 mmol) and dichloroacetic acid (70 mg, 0.56 mmol) were dissolved in chloroform-*d* (0.37 cm^3), and then the mixture was allowed to stand for 5 h at room temperature. Trimethyl(dichloroacetoxy)silane (75%), benzenethiol(81%), haxamethyldisiloxane ($\simeq$10%), and trimethylsilanol (2%) wew detected in the reaction mixture by NMR analysis. No other compound was detected. The assignmemt of these signals was performed by comparing them to those of the authentic samples. The latter two compounds were found in almost the same amounts even at the beginning of the reaction and in the absence of the acid. Thus, these two compounds were concluded to be formed by the hydrolysis of the thiosilane during work-up. Trimethyl(dichloroacetoxy)silane was isolated by GLC separation (SE-30, 2 m, 150°C), and the structure was characterized by comparison with an authentic sample.[8]

Kinetics. Trimethyl(phenylthio)silane (48 mg, 50 mm^3, 0.26 mmol) was dissolved in chloroform (0.37 cm^3), after which the solution, in a sample tube was placed in a NMR probe. Dichloroacetic acid (70 mg, 46 mm^3, 0.56 mmol) was then added to the solution. Immediately after the addition, trimethyl signals of the starting thiosilane (δ 0.25 ppm) and the product (δ 0.36 ppm) were recorded repeatedly at short time intervals. Twenty to thirty measurements were done for each run until the completed conversion exceeded a half. After the reaction, the total volume of the solution was measured, and the concentrations of each component were calculated. The second-order rate constant, k, was obtained by means of the following equation, where a and b are the initial concentrations of the thiosilane and the acid respectively, and where x is the amount of the acetoxysilane formed at time t.

$$kt = \frac{l}{b-a} \ln \frac{a(b-x)}{b(a-x)}$$

A good reproducibility was obtained ($\pm$10% error established by a duplicate run). The kinetics of the base-catalyzed reactions were done by using half concentrations of the starting materials.

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