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A Kinetic Study on the Reaction of (Arylthio)trimethylgermane with Benzoyl Chloride Giving *S*-Aryl Thiobenzoate and Chlorotrimethylgermane

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A kinetic study has been conducted on the reactions of (substituted arylthio)trimethylgermanes with aroyl chlorides giving *S*-aryl thioaroates and chlorotrimethylgermane. The rates of the reactions were distinctly accelerated in polar solvents. Both of the effects due to the substituents of the arylthio and the aroyl moieties gave positive ρ values especially in a polar solvent. A mechanism involving initial 5-coordination, ionic cleavage of the Ge–S bond giving arenethiolate ion, and followed by rate-determining addition of the thiolate to the carbonyl carbon, was suggested for the reaction.

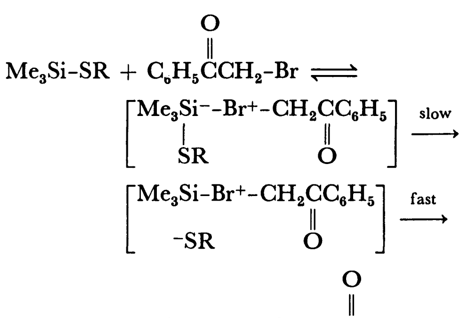
Previously, we have reported kinetic and stereochemical studies on the reactions of methylthio- and (substituted arylthio)trimethylstannanes with haloalkanes.[1] Nucleophilic attacks of the sulfur atom on the haloalkanes have been suggested for the reactions based on the negative ρ value together with other kinetic and stereochemical results.

$$\mathrm{Me_3Sn\text{-}SR + R'\text{-}X \longrightarrow [Me_3Sn\text{-}S^{+}RR'\,X^{-}]}$$
$$\mathrm{\longrightarrow R\text{-}S\text{-}R' + Me_3Sn\text{-}X}$$

R = substituted aryl ($\rho = -1.4$), Me
R′ = Me, Et, $C_6H_5CH_2$, 1-Me-heptyl (inversion)
X = I, Br, Cl.

Scheme 1.

On the other hand, quite different kinetic aspects were observed for the analogous reactions of arylthiosilanes. Namely, the reactions of (substituted arylthio)trimethylsilanes with a haloalkane were found to give the products in a similar way but with quite different kinetic results.[2] Phenacyl bromide was chosen as the haloalkane for the kinetic study because of the low reactivity of the arylthiosilanes towards common haloalkanes. A large positive ρ value (+2.2) was observed. The result was well recognized in terms of initial 5-coordination of the silicon atom and followed by the rate-determining Si–S bond cleavage (Scheme 2).

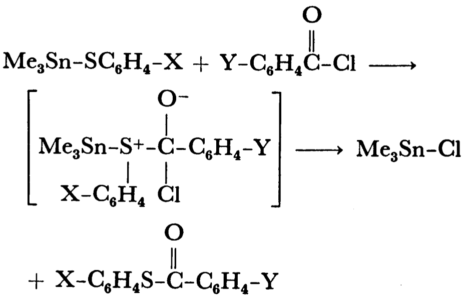


$$\mathrm{Me_3Si\text{-}SR + C_6H_5\overset{\overset{O}{\|}}{C}CH_2\text{-}Br \rightleftharpoons \left[\begin{matrix} Me_3Si^{-}\text{-}Br^{+}\text{-}CH_2\overset{}{C}C_6H_5 \\ \;|\qquad\qquad\qquad\;\, \| \\ SR\qquad\qquad\quad\;\; O \end{matrix}\right] \xrightarrow{\text{slow}} \left[\begin{matrix} Me_3Si\text{-}Br^{+}\text{-}CH_2CC_6H_5 \\ \qquad\qquad\qquad\;\| \\ {}^{-}SR\qquad\qquad\; O \end{matrix}\right] \xrightarrow{\text{fast}} Me_3Si\text{-}Br + RS\text{-}CH_2\overset{\overset{O}{\|}}{C}C_6H_5}$$

R = substituted aryl ($\rho = +2.2$)

Scheme 2.

A comparable difference was also observed between the analogous reactions of the arylthiostannanes and the arylthiosilanes with aroyl chlorides. The reactions of the (arylthio)trimethylstannanes with aroyl chlorides were found to give *S*-aryl thioaroates. The kinetic study on the reactions revealed opposite substituent effects due to the arylthio ($\rho_X = -1.6$) and the aroyl ($\rho_Y = +1.1$) moieties. Hereafter, the substituents on the arylthio and the aroyl groups are abbreviated as X and Y, respectively. Accordingly, the reaction was considered to involve a nucleophilic addition of the sulfur atom to the carbonyl carbon (Scheme 3).[3]



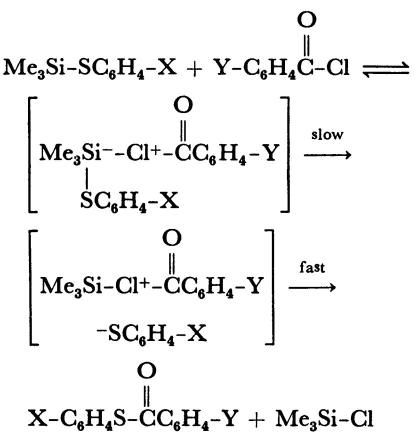
$$\mathrm{Me_3Sn\text{-}SC_6H_4\text{-}X + Y\text{-}C_6H_4\overset{\overset{O}{\|}}{C}\text{-}Cl \longrightarrow \left[\begin{matrix} \qquad\qquad O^{-} \\ \qquad\qquad | \\ Me_3Sn\text{-}S^{+}\text{-}C\text{-}C_6H_4\text{-}Y \\ \qquad\quad | \quad\;\, | \\ X\text{-}C_6H_4 \;\; Cl \end{matrix}\right] \longrightarrow Me_3Sn\text{-}Cl + X\text{-}C_6H_4S\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_4\text{-}Y}$$

$\rho_X = -1.6,\ \rho_Y = +1.1$

Scheme 3.

Contrary to these results, the reactions of the (arylthio)trimethylsilanes with aroyl chlorides were found to give the same thioaroates but with quite different kinetic aspects. A large positive ρ value due to X ($\rho_X = +2.50$) was observed while that of Y was small negative ($\rho_Y = -0.87$). These results suggested initial 5-coordination followed by rate-determining formation of arenethiolate ion for the reaction (Scheme 4).[4]

A kinetic study on the reactions of the arylthiogermane analogs would be of interest since quite different kinetic aspects were observed for the reactions of the arylthiosilanes and the arylthio-



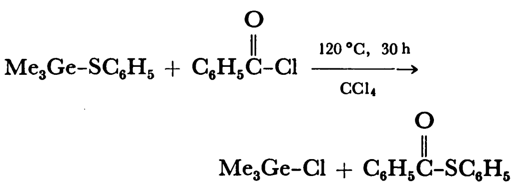
$\rho_X = +2.50$, $\rho_Y = -0.87$

Scheme 4.

stannanes as far described. Substituted aroyl chlorides were chosen as the reactants because the reactions of these reagents have well been studied kinetically.[3,4]

Results and Discussion

The reaction of trimethyl(phenylthio)germane with benzoyl chloride was found to give chlorotrimethylgermane and *S*-phenyl thiobenzoate. No other product was found in the reaction solution by ^{1}H NMR analysis. The chlorogermane and the thiobenzoate were isolated and characterized.



Scheme 5.

The rate of the reaction of the phenylthiogermane with a small excess of benzoyl chloride was measured by monitoring the decrease in the ^{1}H NMR trimethyl signal of the starting phenylthiogermane (δ=0.47) and the increase in that of the chlorogermane (δ=0.72). The reaction was found to obey a second order rate equation. The kinetic experiments were performed in various solvents at different temperatures. The results are given in Table 1 together with the activation parameters and the observed solvent effects. The possible reactions of the arylthiogermanes with the solvents were examined in control experiments. Small amounts of the solvolysis products were found on prolonged heating of the arylthiogermanes in some solvents. The rates (pseudo-first-order: k_1), however, were found much smaller and negligible comparing with those of the reactions with aroyl chlorides.

The activation parameters appeared in similar magnitudes with those of the analogous reactions which proceed by ionic processes.[1-3] Distinct solvent effects were observed as shown in Table 1. The results also suggest an ionic process for the reaction.

The effect of the substituents of the arylthio group (ρ_X) was examined to clarify the reaction mechanism. The results are shown in Table 2.

Clearly positive ρ_X values were observed for both the reactions carried out in carbon tetrachloride and in benzonitrile as the solvents. The positive ρ_X values would suggest 5-coordination of the germanium atom as was suggested for the reactions of the

Table 1. Activation parameters and solvent effect on the rate of the reaction of $Me_4GeSC_6H_5$ [0.131 mol dm^{-3}] with C_6H_5COCl [0.159 mol dm^{-3}] in various solvents

Solvent(ε)[a]	Temp °C	$k_2 \times 10^4$ dm^3 mol^{-1}	$\Delta H^{\ddagger}_{400}$ kJ mol^{-1}	(γ)	$\Delta S^{\ddagger}_{400}$ J K^{-1} mol	k_{rel}[b]
CCl_4 (2.23)	110	1.85±0.31	37.0		−223	1.00
CCl_4	120	2.56±0.98		(0.999)		
CCl_4	130	3.45±0.28				
CH_2Br_2 (6.70)	110	5.78±0.33	45.6		−185	2.1
CH_2Br_2	120	8.76±0.09		(0.998)		
CH_2Br_2	130	19.8 ±0.20				
CH_2Cl_2 (8.90)	100	6.50±0.48	37.5		−208	4.9
CH_2Cl_2	110	9.18±0.87		(0.999)		
CH_2Cl_2	120	12.6 ±1.1				
C_6H_5CN (25.2)	40	7.83±0.42	63.0		−106	280
C_6H_5CN	50	15.2 ±1.1		(0.998)		
C_6H_5CN	60	34.6 ±3.0				
C_6H_5CN	70	62.9 ±3.9				

a) Dielectric constant. b) At 100 °C.

arylthiosilanes.[2,4,5] The enhanced ρ_X value observed in benzonitrile solution also suggests the rate-determining cleavage of the Ge–S linkage giving arenethiolate ion since the value is comparable with that of the dissociation of arenethiols.[6] The present reaction, thus once, appeared to be similar in the mechanism to that of the reactions of the arylthiosilanes with phenacyl bromide[2] and with aroyl chlorides[4] which involve initial 5-coordinations followed by rate-determining formations of arenethiolate ions. The effect of the substituent Y, (ρ_Y), however, strongly suggests that the rate-determining step of the present reaction is quite different from those of the reactions of the arylthiosilanes.[2,4]

As shown in Table 3, the effects of Y observed for the reactions in carbon tetrachloride were obscure, or rather U-shape plot was observed. On the other hand, the observed ρ_Y value is clearly positive for the reactions in benzonitrile as the solvent. The positive ρ_Y value strongly suggests an alternative mechanism for the reaction since a similar mechanism to that of the reactions of the arylthiosilanes demands a negative ρ_Y value (Scheme 4).[4]

Table 2. Rate constants for the reaction of $Me_3GeSC_6H_4$-X [0.131 mol dm^{-3}] with C_6H_5COCl [0.159 mol dm^{-3}]

X	Solvent	Temp	$k_2 \times 10^4$	
		°C	dm^3 mol^{-1} s^{-1}	Remarks
m-Br	CCl_4	130	13.3 ±1.2	$\rho_{X(\sigma)}=+1.46$
m-Cl	CCl_4	130	9.46±0.73	$\gamma=0.977$
p-Cl	CCl_4	130	4.59±0.51	
H	CCl_4	130	3.45±0.21	
p-Me	CCl_4	130	1.37±0.01	
p-OMe	CCl_4	130	1.26±0.06	
m-Cl	C_6H_5CN	50	64.3 ±4.2	$\rho_{X(\sigma)}=+2.32$
p-Cl	C_6H_5CN	50	59.6 ±5.5	$\gamma=0.982$
H	C_6H_5CN	50	15.2 ±1.1	
p-Me	C_6H_5CN	50	5.27±0.32	
p-OMe	C_6H_5CN	50	2.43±0.67	

Table 3. Rate constants for the reaction of $Me_3GeSC_6H_5$ [0.131 mol dm^{-3}] with Y-C_6H_4COCl [0.159 mol dm^{-3}]

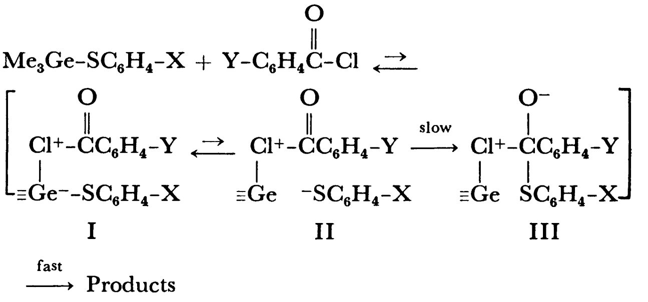
X	Solvent	Temp	$k_2 \times 10^4$	
		°C	dm^3 mol^{-1} s^{-1}	Remarks
p-NO_2	CCl_4	130	26.8 ± 3.3	
m-Cl	CCl_4	130	7.03± 0.43	No linear
p-Br	CCl_4	130	4.75± 0.36	correlation
p-Cl	CCl_4	130	4.52± 0.33	in CCl_4.
H	CCl_4	130	3.45± 0.21	
p-Me	CCl_4	130	5.95± 0.54	
p-OMe	CCl_4	130	7.00± 0.27	
p-NO_2	C_6H_5CN	50	294 ±83	
m-Cl	C_6H_5CN	50	70.1 ± 1.1	$\rho_{Y(\sigma)}=+1.90$
p-Br	C_6H_5CN	50	38.3 ± 2.3	$\gamma=0.990$
p-Cl	C_6H_5CN	50	38.5 ± 0.8	
H	C_6H_5CN	50	15.2 ± 1.1	
p-Me	C_6H_5CN	50	6.05± 0.30	
p-OMe	C_6H_5CN	50	2.59± 0.32	

The most appropriate mechanism for the reaction based on the kinetic results can be depicted as follows (Scheme 6).

The positive ρ_Y value observed in benzonitrile can be rationalized in terms of a rate-determining addition of the thiolate ion to carbonyl carbon giving the intermediate III. The positive ρ_X value would be originated from the both steps, the initial 5-coordination giving the intermediate I and the ionic fission of the Ge–S bond giving the ion pair II. Energetically disfavored equilibrium giving I and II might well account for the observed positive ρ_X values since favorable formations of I and II would disappear the effect of X or bring small negative ρ_X values.

It is uncertain, why the effects of Y in carbon tetrachloride gave a U-shaped Hammett plot. The electron-donating substituents Y may stabilize both the intermediates I and II. The stabilizations may slightly accelerate the reactions. Another process to rationalize the abnormal effects of Y is a charge-separated 4-center transition state which has been suggested for the reactions of the (aryloxy)trimethylstannanes with methanesulfonyl chloride.[7] The 4-center process may be favorable for the ionic reactions forced to proceed in nonpolar solvents. However, the observed solvent effects ($k_{C_6H_5CN}/k_{CCl_4}$= 280) are too large in comparison with that of the 4-center reaction which showed small and abnormal solvent effects.[8] Different mechanisms in individual solvents are not plausible in view of a clear isokinetic relationship in all the solvents examined as shown in Fig. 1.

The mechanism of the reactions of (substituted arylthio)trimethylgermanes with the aroyl chlorides has thus been found to be similar to that of the analogous reactions of the arylthiosilanes at the initial step and the following heterolysis of the metal-sulfur bond, but differ in the rate-determining step. The reactions of the arylthiosilanes involve rate-



Scheme 6.

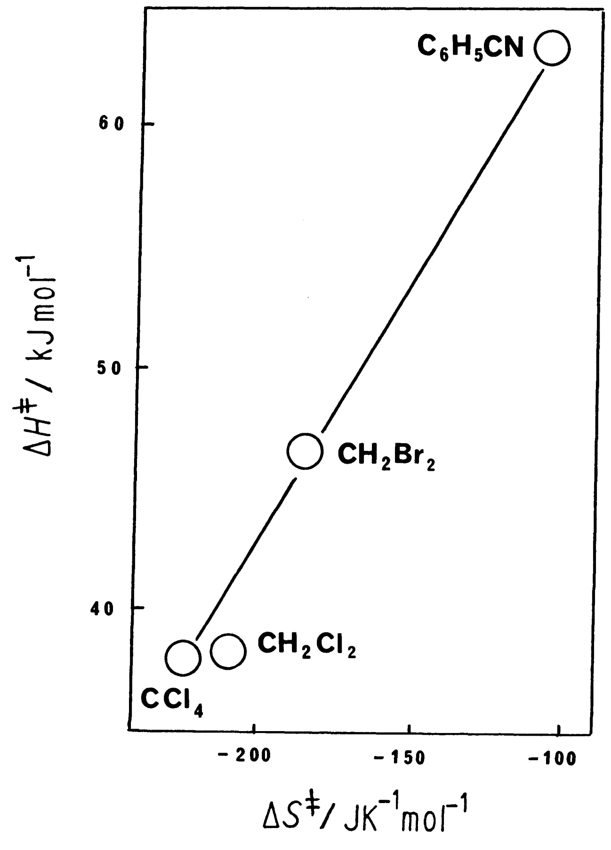


Fig. 1. Plot of ΔH^* *vs.* ΔS^* in various solvents.

determining heterolyses of the metal–sulfur bonds while the heterolysis is the second equilibrium step in the present reaction as shown in Scheme 6. The mechanism presently suggested is also different from that of the analogous reactions of the arylthiostannanes.[3] Thus, the reactions of the arylthiosilanes, -germanes, and -stannanes with aroyl chlorides have been found to proceed by individually different mechanisms.

Experimental

Materials. Solvents were dried and distilled. Substituted aroyl chlorides were purified by distillation or recrystallization before use.

Preparation of Tetramethylgermane. The germane was prepared by modified procedure of the literature.[9] In a 3-necked flask equipped with a stirrer, a refluxing condenser, and dropping funnel, 20 g of magnesium was placed and dry nitrogen gas was passed for 30 min. Dibutyl ether (300 cm^3) was added. Methyl iodide (114 g) diluted with dibutyl ether (*ca.* 70 cm^3) was added dropwise with cooling (ice bath) and stirring. After the addition, the Grignard solution was allowed to stand for 30 min with stirring. Tetrachlorogermane (25 g) dissolved in dibutyl ether (*ca.* 20 cm^3) was added dropwise with cooling (ice-salt bath, −15 °C) and vigorous stirring. The solution was gently heated up to 70 °C after the addition. Water was carefully added dropwise with cooling (ice bath) to consume the remaining Grignard reagent. The resulting mixture was distilled and low-boiling fraction containing tetramethylgermane, water, and dibutyl ether was collected (bp 42—89 °C). Water was separated from the distillate and the organic layer was dried (Na_2SO_4). Centrifugation of the reaction mixture to separate the precipitated magnesium salt and water, and followed by rough distillation was also effective to obtain crude tetramethylgermane. Fractional distillation gave tetramethylgermane, 4.92 g, bp 42—43 °C, ^{1}H NMR δ=0.15.

Preparation of Bromotrimethylgermane. Bromine (5.94 g) was added to tetramethylgermane (4.92 g) containing catalytic amount of aluminium trichloride (*ca.* 30 mg) with stirring. The mixture was allowed to stand overnight with stirring. Excess bromine was decolorized by addition of small amount of mercury. Bromotrimethylgermane was obtained by distillation, bp 113—114 °C, 5.94 g (81%), ^{1}H NMR δ=0.85.

Trimethyl(phenylthio)germane. The phenylthiogermane was prepared as follows: To chloroform (50 ml) solution of bromotrimethylgermane (1.0 g) and triethylamine (0.77 g), benzenethiol (0.56 g) was added and the mixture was refluxed for 2 h. The solvent was evaporated and hexane (30 ml) was added to precipitate the amine salt. Trimethyl(phenylthio)germane was obtained by distillation after evaporation of hexane, bp 62 °C/1 mmHg (133.332 Pa.), ^{1}H NMR δ=0.47. Other (arylthio)trimethylgermanes were prepared similarly. Substituents, bp at 1 mmHg, and ^{1}H NMR signals other than aryl protons are as follows: *p*-Methoxy-, 85 °C, δ=0.48 and 3.83; *p*-Methyl-, 83 °C, δ=0.47 and 2.37; *p*-Chloro-, 76 °C, δ=0.44; *m*-Chloro-, 87 °C, δ=0.42; *m*-Bromo-, 106 °C, δ=0.42.

Product Analysis. Trimethyl(phenylthio)germane (1.00 g, 5.1×10^{-3} mol) was heated with an equimolar amount of benzoyl chloride (0.71 g) in carbon tetrachloride (10 cm^3) in a sealed tube at 120 °C for 30 h. ^{1}H NMR Analysis of the solution showed signals only due to chlorotrimethylgermane and *S*-phenyl thiobenzoate. Chlorotrimethylgermane was isolated by distillation (bp 108—110 °C, 68%). *S*-Phenyl thiobenzoate was obtained from the residue and purified by recrystallization, mp 55 °C (from chloroform–hexane, 70%, lit,[10] 56 °C).

Kinetics. (Arylthio)trimethylgermanes (6.55×10^{-4} mol) and aroyl chlorides (7.55×10^{-4} mol) were dissolved in the solvent using 5 ml volumetric flask. The solutions were devided into 10 portions and sealed in glass tubes of *ca.* 0.7 cm^3 volume. The tubes were heated in a constant temperature bath (±0.1 °C) and samples were taken at appropriate time intervals and cooled (ice bath). Each sample of the solution was subjected to NMR analysis. Conversion at the time was measured by the relative intensities of the starting trimethyl (δ=0.42—0.48) and that of the product (chlorotrimethylgermane: δ=0.72) which were determined by 8 to 10 repeated scannings. The rate constant k was obtained by least squares calculation of second order rate equation.

The Reactions of the Arylthiogermanes with the Solvents Used for the Kinetics. Carbon tetrachloride solution of (*m*-chlolophenylthio)trimethylgermane (0.13 mol dm^{-3}) was heated at 130 °C for 22 h. The reaction conditions correspond to more than 80% completion of the reaction of the germane with the least reactive *p*-methoxybenzoyl chloride. The amount of chlorotrimethylgermane (δ=0.72) was measured by ^{1}H NMR analysis. Pseudo-first-order rate constant (k_1) was estimated from the conversion. Similarly, other arylthiogermanes were heated in carbon tetrachloride or in dibromomethane and the amounts of the chlorogermane (in CCl_4) and the bromogermane (in CH_2Br_2) were measured. The arylthiogermanes, solvent, and k_1 at 130 °C were as follows: $Me_3GeSC_6H_4Cl$-*m*, CCl_4, $7\times10^{-7}\,s^{-1}$; $Me_3GeSC_6H_4OMe$-*p*, CCl_4, $1\times10^{-6}\,s^{-1}$; $Me_3GeSC_6H_5$, CH_2Br_2, $3\times10^{-5}\,s^{-1}$. No reaction was found with benzonitrile under the kinetic conditions (50 °C, 24 h). The solvolyses rates were thus found much smaller than those of the reactions with aroyl chlorides and can be neglected for the kinetic studies with aroyl chlorides.

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8) Abnormal solvent effect was observed for the reaction of trimethyl(phenoxy)stannane with methanesulfonyl chloride: k_{rel} in CCl_4, CH_2Br_2, CH_2Cl_2, C_6H_5CN, and CH_3CN were 1.00, 0.38, 0.32, 2.0, and 10, respectively.(7)

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