Bull. Chem. Soc. Jpn., 63, 2843—2845 (1990)

The Reaction of (Arylthio)trimethylgermanes with Various Haloalkanes -Steric Effect on the Reaction Mechanism-

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(Received May 31, 1990)

A kinetic study has been conducted on the reactions of (arylthio)trimethylgermanes with various haloalkanes. Bimolecular nucleophilic attack of the sulfur atom has been found as the mechanisms for the reactions with normal haloalkanes while the mechanism was found to deviate from bimolecular attack to unimolecular ionization of the haloalkane, dependent on the structure of the alkyl groups with increasing of the steric hindrance. Reaction of a secondary haloalkane also proceeded by unimolecular ionization.

The length of the germaniume-sulfur bond in (arylthio)trimethylgermane has been appeared critical allowing the bimolecular attack of the sulfur atom on benzyl halides.[1] In fact, the sulfur atom in a shorter silicon-sulfur linkage has been found loosing nucleophilicity toward haloalkanes[2] and steric crowd around the sulfur atom was suggested controlling the reactivity.[1] Increment of steric hindrance had been expected to disturb the bimolecular nucleophilic attack of the sulfur atom for the reaction of the thiogermane with benzyl halides. Thus, the reaction of 1-aryl-1-bromoethanes with the arylthiogermanes was examined expecting deviation of the mechanism from the bimolecular nucleophilic attack to 5-coordination of the germanium atom as like as was observed in the reactions of the arylthiosilane analogues with phenacyl bromide.[2] Inhibition of the bimolecular nucleophlic attack was observed as expectation by introducing a methyl group into the α-position of the benzyl moiety. However, the mechanism, suggested based on the results, was not 5-coordination but unimolecular ionization (S_N1) of 1-aryl-1-bromoethane.[3]

The reaction would be an abnormal unimolecular nucleophilic substitution in view of the reaction conditions used. The reaction was carried out under typical bimolecular reaction conditions in nonpolar solvents with nearly equal amount of diluted (ca. 0.26 mol dm^{-3}) nucleophile of the arylthiogermanes. The particular mechanism would undoubtedly be due to the nature of the haloalkane generating much stabilized secondary benzylic cation on ionization.

A kinetic study will be reported here, on the reactions of (arylthio)trimethylgermanes with various haloalkanes. The subject of this work is examining a possible 5-coordination process for the reactions and also to examine unimolecular ionization of haloalkanes, other than 1-aryl-1-bromoethane, under typical second-order reaction conditions.[3]

Results and Discussion

Iodoalkanes, the most reactive haloalkanes, were chosen for the present study since haloalkanes have been known to be substantially less reactive than benzyl halides. The iodoalkanes are iodomethane and iodoethane as standard primary iodoalkanes, and stereochemically hindered primary iodoalkanes including 1-iodo-2-methylpropane and 1-iodo-2,2-dimethylpropane. 2-Iodopropane was also chosen as a typical secondary iodoalkane. All the reactions of those iodoalkanes with trimethyl(phenylthio)germane were found to give corresponding alkyl phenyl sulfides and iodotrimethylgermane (Eq. 1). No detectable amount of a side product was found. The reaction of the thiogermanes has thus been found to be

$$R\text{-}I + Me_3Ge\text{-}SC_6H_5 \longrightarrow R\text{-}SC_6H_5 + Me_3Ge\text{-}I \qquad (1)$$

similar to that of tin analogues[4] and different from that of the silicon compound in which side reactions of the thiosilane dominated rather than the reaction with most of the haloalkanes.[2]

Kinetic runs were done by ^{1}H NMR spectroscopy by following the relative ratio of the decreasing and increasing amounts of the starting and the product trimethylgermanes at time. A polar aprotic solvent, benzonitrile was used for the kinetic runs in order to observe the rates conveniently, because the reactions were found to proceed much slower than that of benzyl bromide.[1,3]

Rate constants for the reaction with iodomethane and iodoethane with (arylthio)trimethylgermanes are given in Table 1. The reactions apparently obeyed a second order kinetic equation, each first order in both the reactants. The relative reactivity of these iodoalkanes and the activation parameters were also quite reasonable for the difference in reactivities of those iodoalkanes toward bimolecular nucleophilic substitutions.[4,5] The observed substituent effects ($\rho_{(\sigma)}$= -1.25 and -1.00) were also quite reasonable for the suggested process. Thus, a bimolecular nucleophilic substitution has been confirmed for the reactions of the thiogermanes with these two iodoalkanes. The reactions of smaller primary iodoalkanes with the thiogermane were appeared to be quite resemble with that of the reaction of the tin analogues.[4]

Stereochemically hindered primary iodoalkanes, 1-

Table 1. Rate Constants for the Reactions of $Me_3Ge\text{-}SC_6H_4X$ with R-I in C_6H_5CN

Entry	R(mol dm^{-3})	X(mol dm^{-3})	Temp/°C	$k_2\times10^4$/dm^{3}mol^{-1}s^{-1}
1	CH_3(0.159)	H(0.131)	110	4.28±0.19
2	CH_3(0.159)	H(0.131)	120	7.81±0.31
3	CH_3(0.159)	H(0.131)	130	13.15±0.36
4	CH_3(0.159)	*p*-OCH_3(0.131)	120	12.21±0.32
5	CH_3(0.159)	*p*-CH_3(0.131)	120	11.02±0.34
6	CH_3(0.159)	*p*-Cl(0.131)	120	3.09±0.04
7	CH_3(0.159)	*m*-Cl(0.131)	120	2.16±0.05
8	CH_3CH_2(0.159)	H(0.131)	130	1.54±0.04
9	CH_3CH_2(0.159)	H(0.131)	140	2.08±0.05
10	CH_3CH_2(0.159)	H(0.131)	150	5.05±0.16
11	CH_3CH_2(0.159)	*p*-OCH_3(0.131)	150	7.74±0.07
12	CH_3CH_2(0.159)	*p*-CH_3(0.131)	150	6.81±0.07
13	CH_3CH_2(0.159)	*p*-Cl(0.131)	150	2.39±0.10
14	CH_3CH_2(0.159)	*m*-Cl(0.131)	150	1.97±0.03

$\Delta H^{\neq}_{400}=72$ kJ mol^{-1}; $\Delta S^{\neq}_{400}=-124$ J K^{-1}mol^{-1}, $\gamma=0.999$ for CH_3I. $\Delta H^{\neq}_{400}=84$ kJ mol^{-1}; $\Delta S^{\neq}_{400}=-114$ J K^{-1}mol^{-1}, $\gamma=0.957$ for CH_3CH_2I. $\rho(\sigma)=-1.25$, $\gamma=0.987$ for CH_3I and $\rho(\sigma)=-1.00$, $\gamma=0.989$ for CH_3CH_2I.

Table 2. Rate Constants for the Reactions of $Me_3Ge\text{-}SC_6H_4X$ with R-I

Entry	R(mol dm^{-3})	X(mol dm^{-3})	Solvent	Temp/°C	k/dm^3 mol^{-1} s^{-1} (or s^{-1} for k_1)
15	$CH_3CH(CH_3)CH_2$(0.159)	H(0.066)	C_6H_5CN	150	k_1 $(2.51\pm0.10)\times10^{-6}$
16	$CH_3CH(CH_3)CH_2$(0.159)	H(0.131)	C_6H_5CN	150	k_1 $(3.13\pm0.24)\times10^{-6}$
17	$CH_3CH(CH_3)CH_2$(0.159)	H(0.197)	C_6H_5CN	150	k_1 $(5.20\pm0.16)\times10^{-6}$
18	$CH_3CH(CH_3)CH_2$(0.159)	H(0.131)	C_6H_5CN	130	k_2 $(1.01\pm0.05)\times10^{-5}$
19	$CH_3CH(CH_3)CH_2$(0.159)	H(0.131)	C_6H_5CN	140	k_2 $(2.04\pm0.09)\times10^{-5}$
20	$CH_3CH(CH_3)CH_2$(0.159)	H(0.131)	C_6H_5CN	150	k_2 $(4.21\pm0.29)\times10^{-5}$
21	$CH_3CH(CH_3)CH_2$(0.159)	*p*-OCH_3(0.131)	C_6H_5CN	150	k_2 $(5.02\pm0.17)\times10^{-5}$
22	$CH_3CH(CH_3)CH_2$(0.159)	*p*-CH_3(0.131)	C_6H_5CN	150	k_2 $(4.47\pm0.13)\times10^{-5}$
23	$CH_3CH(CH_3)CH_2$(0.159)	*p*-Cl(0.131)	C_6H_5CN	150	k_2 $(2.43\pm0.34)\times10^{-5}$
24	$CH_3CH(CH_3)CH_2$(0.159)	*m*-Cl(0.131)	C_6H_5CN	150	k_2 $(2.04\pm0.19)\times10^{-5}$
25	$CH_3C(CH_3)_2CH_2$(0.477)	H(0.197)	CH_3CN	160	k_1 $(1.69\pm0.30)\times10^{-6}$
26	$CH_3C(CH_3)_2CH_2$(0.477)	H(0.393)	CH_3CN	160	k_1 $(1.80\pm0.05)\times10^{-6}$
27	$CH_3C(CH_3)_2CH_2$(0.477)	H(0.591)	CH_3CN	160	k_1 $(1.98\pm0.05)\times10^{-6}$
28	$CH_3C(CH_3)_2CH_2$(0.477)	H(0.393)	CH_3CN	140	k_1 $(0.36\pm0.01)\times10^{-6}$
29	$CH_3C(CH_3)_2CH_2$(0.477)	H(0.393)	CH_3CN	150	k_1 $(0.82\pm0.05)\times10^{-6}$
30	$CH_3C(CH_3)_2CH_2$(0.477)	*p*-OCH_3(0.393)	CH_3CN	160	k_1 $(1.33\pm0.09)\times10^{-6}$
31	$CH_3C(CH_3)_2CH_2$(0.477)	*p*-CH_3(0.393)	CH_3CN	160	k_1 $(1.46\pm0.03)\times10^{-6}$
32	$CH_3C(CH_3)_2CH_2$(0.477)	*p*-Cl(0.393)	CH_3CN	160	k_1 $(1.27\pm0.10)\times10^{-6}$
33	$CH_3C(CH_3)_2CH_2$(0.477)	*m*-Cl(0.393)	CH_3CN	160	k_1 $(1.07\pm0.03)\times10^{-6}$
34	$CH_3CH(CH_3)$(0.159)	H(0.131)	C_6H_5CN	130	k_1 $(3.23\pm0.07)\times10^{-4}$
35	$CH_3CH(CH_3)$(0.159)	H(0.131)	C_6H_5CN	140	k_1 $(6.82\pm0.31)\times10^{-4}$
36	$CH_3CH(CH_3)$(0.159)	H(0.131)	C_6H_5CN	150	$k_1$$(14.53\pm0.55)\times10^{-4}$

$\Delta H^{\neq}_{400}=101$ kJ mol^{-1}; $\Delta S^{\neq}_{400}=-92$ J K^{-1}mol^{-1}, $\gamma=0.999$ for R=$CH_3CH(CH_3)CH_2$. $\Delta H^{\neq}_{400}=120$ kJ mol^{-1}; $\Delta S^{\neq}_{400}=-81$ J K^{-1}mol^{-1}, $\gamma=0.999$ for R=$CH_3C(CH_3)_2CH_2$. $\Delta H^{\neq}_{400}=104$ kJ mol^{-1}; $\Delta S^{\neq}_{400}=-95$ J K^{-1}mol^{-1}, $\gamma=0.999$ for R=$CH_3CH(CH_3)$. $\rho(\sigma)=-0.63$, $\gamma=0.974$ for R=$CH_3CH(CH_3)CH_2$. Little effect of X on the rates of the reactions of R=$CH_3C(CH_3)_2CH_2$.

iodo-2-methyl and 1-iodo-2,2-dimethylpropanes, gave somewhat complicated results. The rate of the reaction with 1-iodo-2-methylpropane could be measured in a similar manner at slightly elevated temperatures. Both first-order and second-order kinetic plots gave slightly curved correlations. The rate constants with various concentrations of the haloalkane were calculated by a first-order kinetic equation in order to observe the rate dependency clearly. The results are given in Table 2. As seen in the Table, the rates of the reaction of 1-iodo-2-methylpropane were apparently dependent on the concentrations of the haloalkane (Entries 15 to 17). The dependency, however, was appeared not in first-order but substantially less than unit. Triple concentration of the haloalkane accelerated the reaction only about twice. The substituent effect due to substituents on the arylthio group of the thiogermane (Entries 20 to 24) appeared negative ($\rho(\sigma)=-0.63$), but too small to be considered that the reaction involved a bimolecular nucleophilic attack of the sulfur atom. These results may suggest a borderline mechanism which consists of both S$_N$1

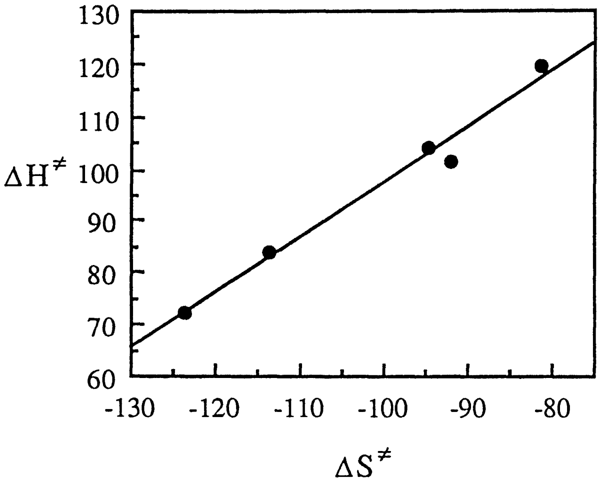

Fig. 1. Plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ values of the reactions.

and S_N2 characters. The carbon-iodine bond would be much stretched at the transition state than that of a typical bimolecular nucleophilic substitution.

The rate of the reaction of 1-iodo-2,2-dimethylpropane, on the other hand, appeared too slow to be measured under the same reaction conditions. Acetonitrile, a much polar solvent was used for this reaction, instead of benzonitrile, and higher concentrations of the starting materials were employed to observe faster conversion of the reactions. Here again, slightly curved kinetic plots were obtained by both first-order and second-order kinetic equations although the former gave a much better plot, as summarized in Table 2. The dependency of the rates on the concentration of the haloalkane was observed almost negligible (Entries 25 to 27), which supports first-order reaction of the haloalkane. The substituents on the arylthio moiety had little effect on the rates of the reactions (Entries 26 and 30 to 33). The result does not conflict with the mechanism involving unimolecular ionization of 1-iodo-2,2-dimethylpropane. Thus, the mechanism of the reaction would involve unimolecular ionization of the haloalkane at the rate-determining step almost exclusively, although minor contribution of bimolecular reaction cannot be ruled out.

The reaction of 2-iodopropane with the thiogermane clearly obeyed a first-order kinetic equation. The results are given in Table 2. A unimolecular ionization of 2-iodopropane would be suggested as the mechanism for the reaction.

The activation parameters for the present reactions resulted a linear correlation as shown in Fig. 1. The isokinetic relationship suggests a gradual change of the kinetic characteristics of the reactions from S_N2 for the simple iodoalkanes to S_N1 for the stereochemically hindered primary iodoalkanes and secondary iodoalkanes.

The particular mechanism i.e., S_N1 reaction under second order reaction conditions has thus been found being not limited to the reaction of 1-aryl-1-bromoethanes,[3] but common to the reactions of secondary and stereochemically hindered primary iodoalkanes. The reactions of tertiary iodoalkanes would proceed by the same manner. Thus, the present study revealed universality of the unimolecular ionization mechanism. Steric hindrance of iodoalkanes and iodoalkanes generating stabilized cation on ionization, promote the particular process even under typical bimolecular reaction conditions in aprotic solvents with small amounts of nucleophiles. The expected 5-coordination process was not found in the reactions presently examined.

Experimental

Materials. The preparations of (arylthio)trimethylgermanes were reported previously.[6] Commercial haloalkanes and solvents were distilled before use.

Product Analysis. Trimethyl(phenylthio)germane (0.5 g, 2.2 mmol) was heated in a sealed tube in the presence of an equal amount of iodomethane (0.31 g, 2.2 mmol) at 100 °C for 16 h. The resulting mixture was distilled under reduced pressure connecting with a cold trap. Methyl phenyl sulfide was obtained as the distillate (bp 160 °C/30 mmHg, 0.45 g, 83%, mmHg=133.322 Pa) and iodotrimethylgermane was obtained in the trap (0.14 g, 52%). The products were identified by their spectra and by comparison with the authentic samples. Product analysis of the reactions of other haloalkanes were performed by ^{1}H NMR spectra. Dilution by solvents did not change the product distributions. Possible rearranged products were not detected.

Kinetics. The procedure was essentially the same to that previously reported.[6] Concentrations of the reactants and temperatures are recorded in Tables 1 and 2.

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