

CLEAVAGE OF ALKYLSILANES BY STRONG ACIDS

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SUMMARY

The stepwise cleavage of methyl groups from tetramethylsilane and (chloromethyl)trimethylsilane has been studied in strong acid systems. The number of methyl groups cleaved can be controlled by varying the temperature and the acid strength. The progress of the reactions and the products formed can be directly observed by nuclear magnetic resonance. Relative rate studies under homogeneous conditions indicate that the key step in the mechanism is electrophilic attack of the acid at the methyl carbon.

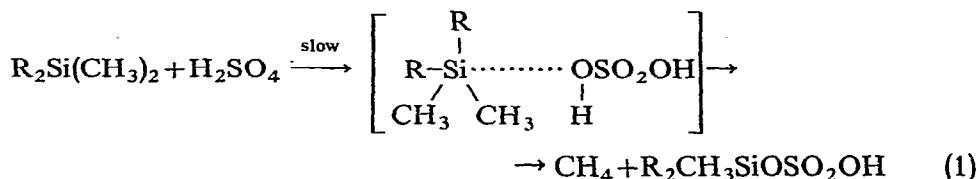
INTRODUCTION

Unsubstituted alkyl groups are easily cleaved from silicon by strong proton acids¹. In sulfuric acid, the acid most frequently used in previous studies, the first alkyl group is cleaved rapidly even at moderate temperatures (30° to 80°)². However, more vigorous conditions are usually necessary for the cleavage of a second alkyl group^{3,4}. Mechanistic studies of tetraalkylsilanes in sulfuric acid have been carried out under non-homogeneous conditions due to the low solubility of the silanes in sulfuric acid⁴. Under these conditions, reactivity variations cannot easily be distinguished from solubility effects. For these reasons, the initially formed products have often not been identified and mechanistic information is still lacking.

Kinetic investigations have also been made with organosilanes containing a functional group in the hydrocarbon chain. Two contrasting mechanisms have been proposed for the cleavage of one methyl from 3-(trimethylsilyl)propionic acid by sulfuric acid. One mechanism involved primarily electrophilic attack at the methyl carbon⁵ while the other required substantial nucleophilic attack at silicon^{4,6}. It is not clear whether further cleavage failed because of the deactivating influence caused by protonation of the carboxyl group or because of the lack of strength of the sulfuric acid system. These mechanistic conclusions have been criticized⁷. The presence of the carboxyl group makes these two studies rather specialized. It is not certain that mechanistic conclusions based on cleavage of organosilanes containing a carboxyl group would be generally applicable to acid cleavage of simple tetraalkylsilanes.

Recently, the sulfuric acid cleavage of several tetraalkylsilanes was studied under non-homogeneous conditions⁴. These workers concluded that the key step

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in the reaction mechanism was the nucleophilic attack of a sulfuric acid molecule at silicon [eqn. (1)].

RESULTS AND DISCUSSION

We wish to report the observation of the stepwise cleavage of methyl groups from silicon for tetramethylsilane and (chloromethyl)trimethylsilane. Acid systems stronger than sulfuric acid⁸, $HSO_3F/SbF_5/SO_2$, HSO_3F/SO_2 and HSO_3F , were used in the temperature range -80° to $+75^\circ$. It was possible to cleave either one or two methyl groups from silicon by controlling the temperature and acid strength of the system. These slow cleavage reactions and the several products formed could be directly observed by nuclear magnetic resonance.

Tetramethylsilane

The NMR spectrum of a homogeneous sample of tetramethylsilane (TMS) at -60° , dissolved in sulfur dioxide and containing an excess of fluorosulfonic acid ($\sim 1/25$, mole/mole), showed the slow disappearance of the TMS singlet and the appearance of a downfield singlet at 0.57 ppm (Fig. 1). Careful integration of the two singlets during the reaction and measurement of the amount of gas evolved from a known weight of TMS showed this new singlet to be due to a trimethylsilyl species. Slightly higher temperatures ($\sim -40^\circ$) resulted in the slow disappearance of the trimethylsilyl singlet and the appearance of an upfield proton doublet and a fluorine

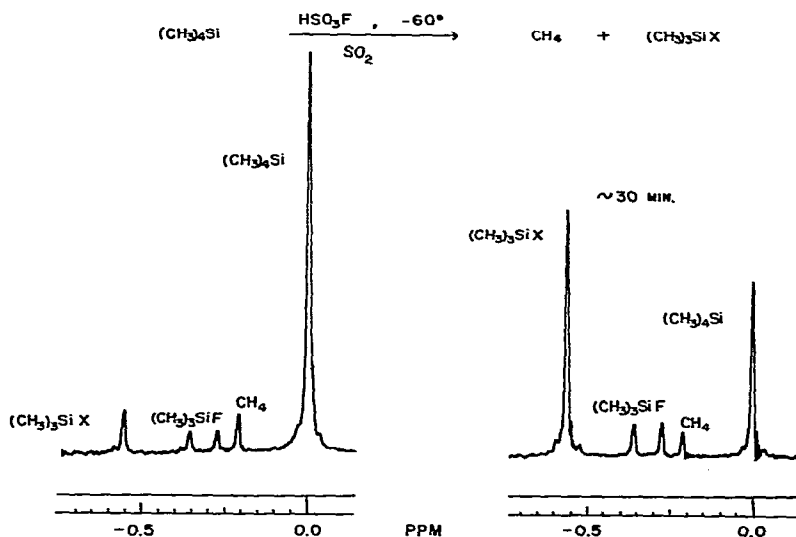
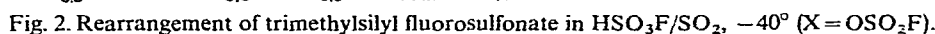


Fig. 1. Cleavage of tetramethylsilane in HSO_3F/SO_2 , -60° ($X = OSO_2F$).


$$(\text{CH}_3)_4\text{Si} + \text{HSO}_3\text{F} \xrightarrow[\text{SO}_2]{-60^\circ} \text{CH}_4 + (\text{CH}_3)_3\text{SiOSO}_2\text{F} \xrightarrow{-40^\circ} \text{SO}_3 + (\text{CH}_3)_3\text{SiF} \quad (2)$$

The reaction of TMS with a stronger acid system (10/1 $\text{HSO}_3\text{F}/\text{SbF}_5$ in SO_2 , -60°) resulted in the very rapid formation of (I). All attempts to observe any appreciable concentration of unreacted TMS failed even when the spectrum was taken less than one minute after sample preparation. At slightly higher temperatures ($\sim -40^\circ$) the trimethylsilyl fluorosulfonate reacts further as shown by the appearance

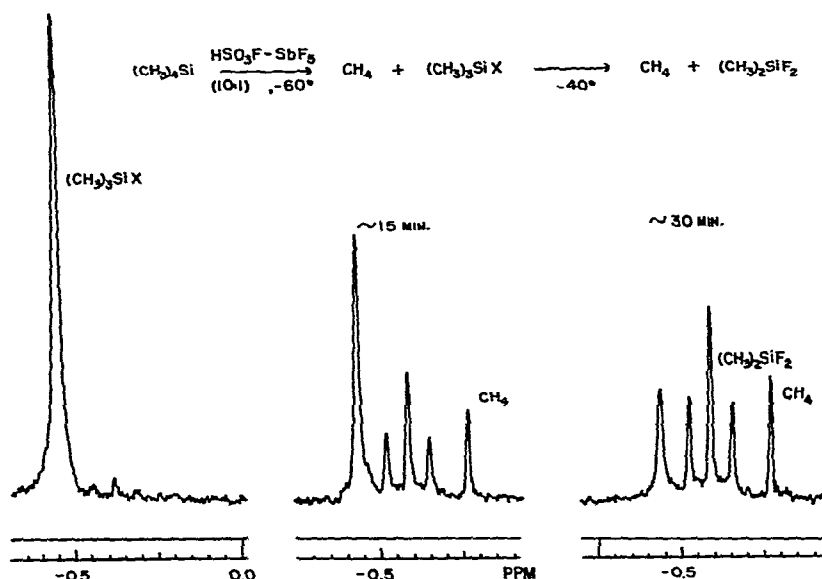
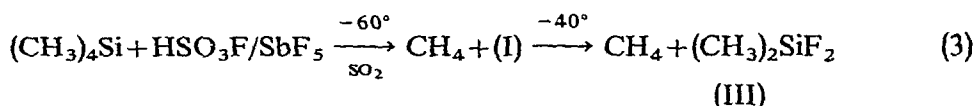


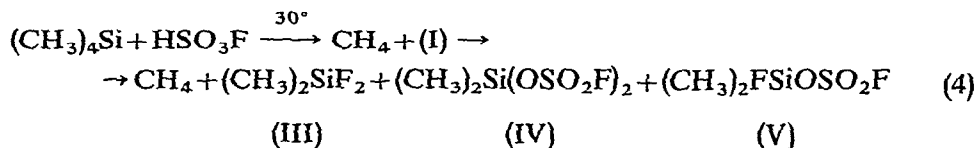
Fig. 3. Reaction of tetramethylsilane with $\text{HSO}_3\text{F}/\text{SbF}_5/\text{SO}_2$, -60° ($\text{X} = \text{OSO}_2\text{F}$).

of an upfield proton triplet and a fluorine septet (Fig. 3). Integration showed the loss of a second methyl group [eqn. (3)]. These new resonances are caused by dimethyl-



difluorosilane as shown by comparison with the chemical shifts and coupling constants of dimethyldifluorosilane dissolved in sulfur dioxide.

Two methyl groups are also lost when TMS is reacted with fluorosulfonic acid at $+30^\circ$. However, two additional dimethylsilyl species were detected which were not observed in the low temperature reaction (Fig. 4). These new resonances were assigned to dimethylsilyl bis(fluorosulfonate) (IV) and dimethylfluorosilyl fluorosulfonate (V). Cleavage of a third methyl group does not take place under these conditions. In fact, in order to complete the cleavage of the second methyl group in a reasonable time (~ 1 h) it was necessary to raise the temperature above 50° [eqn. (4)].



The chemical shifts and coupling constants for the cleavage products of TMS and (chloromethyl)trimethylsilane are summarized in Table 1. The cleavage reactions were studied in the presence of a large excess of acid in order to insure homogeneity. For this reason, isolation of the products without further reaction with the acid proved quite difficult. Identification of the products is more conveniently carried out by

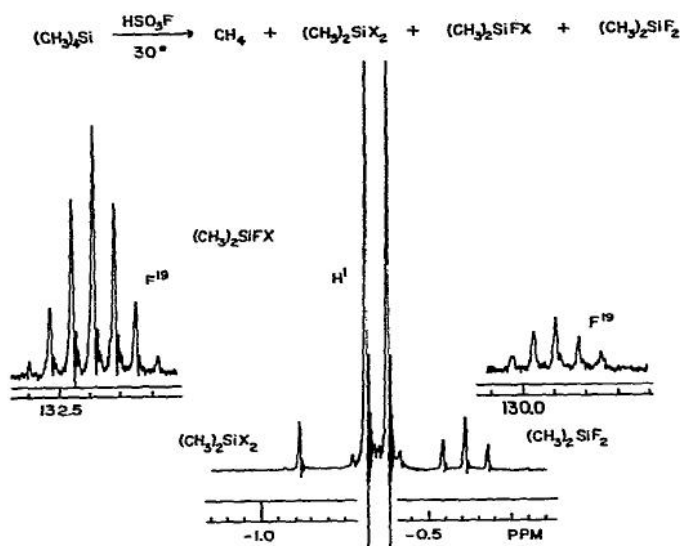


Fig. 4. Reaction of tetramethylsilane with HSO_3F , 30° ($\text{X} = \text{OSO}_2\text{F}$).

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF CLEAVAGE PRODUCTS OF TETRAMETHYLSILANE AND CHLORO-METHYLTRIMETHYLSILANE^{a,b}

Compound ($\text{R} = \text{CH}_3$; $\text{X} = \text{OSO}_2\text{F}$)	$\delta^1\text{H}$	$J(\text{H}-\text{F})$	$\phi^{19}\text{F}$	$J(^{29}\text{Si}-\text{CH}_3)$
R_3SiX (I)	0.57 (1)			7.0
R_3SiF (II)	0.32 (2)	7.4	155.1 (10)	6.9
R_2SiF_2 (III)	0.39 (3)	6.7	130.1 (7)	c
R_2SiX_2 (IV)	0.89 (1)			7.8
R_2FSiX (V)	0.68 (2)	6.6	132.6 (7)	7.8
$\text{R}_3\text{SiCH}_2\text{Cl}$	CH_3 : 0.15 (1)			6.6
	CH_2 : 2.94 (1)			3.7
$\text{R}_2\text{XSiCH}_2\text{Cl}$ (VI)	CH_3 : 0.68 (1)			7.1
	CH_2 : 3.11 (1)			c
$\text{R}_2\text{FSiCH}_2\text{Cl}$ (VII)	CH_3 : 0.45 (2)	8.0		7.0
	CH_2 : 3.02 (2)	3.1		c
$\text{RF}_2\text{SiCH}_2\text{Cl}$ (VIII)	CH_3 : 0.56 (3)	6.1	137.9 (3×4)	c
	CH_2 : 2.96 (3)	3.8		c
$\text{RFXSiCH}_2\text{Cl}$ (IX)	CH_3 : 0.82 (2)	6.4	139.4 (3×4)	c
	CH_2 : 3.15 (2)	3.2		c

^a ^1H shifts in ppm downfield from TMS (internal); ^{19}F shifts in ppm upfield from CCl_2F (internal); figures in parentheses represent multiplicity of peaks; coupling constants in Hz. ^b Fluorine in fluorosulfonyl group not observed due to large excess of HSO_3F . ^c Not observed due to overlap with other peaks or because of low concentration.

comparison of the NMR spectra with those for the known compounds in the absence of acid.

The proton chemical shifts for methyl groups on silicon do not differ by more than 0.9 p.p.m. However, small but definite downfield trends can be noted as the

TABLE 2

RATES OF CLEAVAGE OF METHYL GROUPS FROM TETRAMETHYLSILANE AND (CHLOROMETHYL)TRIMETHYLSILANE

Run	$R_1R_2Si(CH_3)_2$		Temp. (°C)	$HSO_3F/Silane$ (mole/mole)	$k \times 10^{-4}$ (sec^{-1})	k_{TMS}/k_{Chloro}
	R_1	R_2				
1	CH_3	CH_3	-47.0	~30/1	43	94
2	CH_2Cl	CH_3	-47.0	~30/1	0.46	
3	CH_3	OSO_2F	+57.5	10.1/1	0.192	10.1
4	CH_2Cl	OSO_2F	+57.5	10.1/1	0.0190	

presence of a functional group which can be protonated. Since the chlorine is separated from the silicon, this rate decrease is clearly due to the inductive influence of the chlorine. If nucleophilic attack by the acid were rate determining [eqn. (1)], one would predict a rate increase for (chloromethyl)trimethylsilane. Therefore, the most important factor in determining the rate of the first methyl cleavage is the electron density at the methyl carbon. Exclusive methyl cleavage from (chloromethyl)trimethylsilane is consistent with this view. Electrophilic attack at the electron deficient chloromethyl carbon would not be expected and is not observed.

In the second cleavage reaction [(I)→(III)+(IV)+(V); (VI)→(VIII)+(IX)+(X)], compounds (I) and (VI) both contain fluorosulfonate groups. These groups may be protonated in the strong acid medium and this may be primarily responsible for the greatly reduced reactivity compared to the first cleavage. In compound (VI) the fluorosulfonate is one bond closer to the leaving methyl group than the chlorine. For this reason, the inductive effect of the chlorine does not primarily determine the electron density at the methyl carbon in the second cleavage reaction as it does in the first. This is shown by the observed decrease in the *relative* rates of the first and second cleavage reactions (94 vs. 10).

EXPERIMENTAL

Materials

Tetramethylsilane and (chloromethyl)trimethylsilane were commercially available materials and were used without further purification. Fluorosulfonic acid and antimony pentafluoride were purified by passing a stream of dry nitrogen through them at reflux to remove any entrapped hydrogen fluoride. They were then distilled and stored in teflon bottles.

NMR measurements

Varian Associates Models A-60 and HA-100 NMR spectrometers equipped with variable temperature probes were used for all proton spectra. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (internal). Fluorine spectra were obtained using a Varian Associates Model HA-100 spectrometer equipped with a V-4311 radio frequency unit operating at 94.1 MHz. Fluorine chemical shifts were measured using sidebands generated from a Hewlett-Packard Model 200 CD audio oscillator and are reported in ppm upfield from trichlorofluoromethane. Fluorine shifts are believed precise within ± 0.1 ppm (Table 1).

Sample preparation

Samples investigated at low temperatures were prepared by dissolving approximately 1 ml of fluorosulfonic acid or fluorosulfonic acid/antimony pentafluoride (10/1 mole/mole) in an equal volume of sulfur dioxide and cooling to -76° . Approximately 0.2 ml of the silane was dissolved in 1 ml of sulfur dioxide, cooled to -76° and slowly added to the acid solution with vigorous agitation. Samples investigated in fluorosulfonic acid only were prepared by carefully adding the silane to the fluorosulfonic acid at -76° and allowing the solution to slowly warm to $+30^{\circ}$.

Kinetic measurements

Samples for rate measurements of the second cleavage (runs 3 and 4, Table 2) were prepared by adding TMS or (chloromethyl)trimethylsilane to fluorosulfonic acid at -76° and allowing the samples to warm to 57.5° in the NMR probe. By this time, the very rapid cleavage of the first methyl was complete. Homogeneous samples of the silyl fluorosulfonates, (I) and (VI), were obtained if the ratio of the acid to the silane was greater than about 9/1 (mole/mole). The rates of methyl cleavage were determined by following the disappearance of the silicon methyl resonance in the proton spectrum.

As would be expected, the solubility of TMS and (chloromethyl)trimethylsilane was much less than the fluorosulfonates. For the low temperature rate measurements (runs 1 and 2, Table 2) it was necessary to use sulfur dioxide as a diluent in order to insure homogeneity and to keep the samples non-viscous. Homogeneous solutions were obtained if the ratio of acid to silane was greater than about 25/1 (mole/mole) and the samples were diluted with an equal volume of sulfur dioxide. Because of the lower solubility, the low temperature runs were subject to larger errors than the high temperature ones.

ACKNOWLEDGEMENT

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