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CLEAVAGE OF ALKYLSILANES BY STRONG ACIDS

DANIEL H. O'BRIEN AND CHARLES M. HARBORDT*
Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)
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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 acids[1]. 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 acid[4]. 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 carbon[5] 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 criticized[7]. 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 conditions[4]. These workers concluded that the key step

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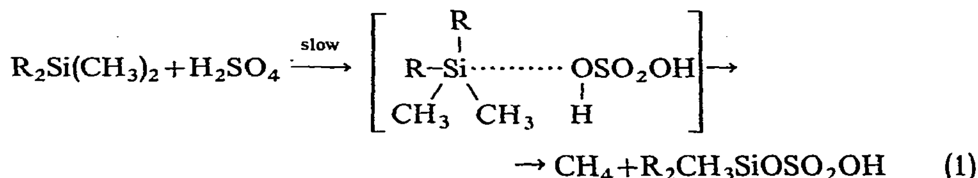


in the reaction mechanism was the nucleophilic attack of a sulfuric acid molecule at silicon [eqn. (1)].

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 acid[8], $HSO_3F/SbF_5/SO_2$, HSO_3F/SO_2 and HSO_3F, were used in the temperature range $-80°$ to $+75°$. 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°$) resulted in the slow disappearance of the trimethylsilyl singlet and the appearance of an upfield proton doublet and a fluorine

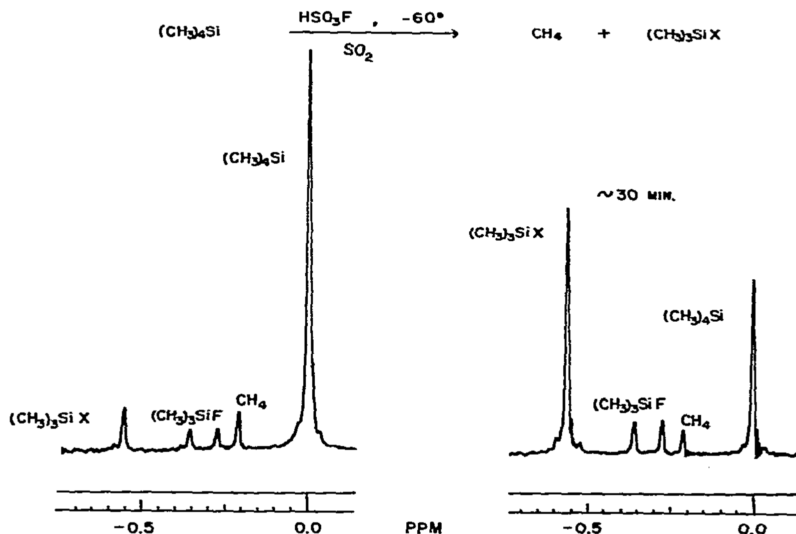


Fig. 1. Cleavage of tetramethylsilane in HSO_3F/SO_2, $-60°$ ($X=OSO_2F$).

Fig. 2. Rearrangement of trimethylsilyl fluorosulfonate in HSO_3F/SO_2, $-40°$ ($X = OSO_2F$).

decet (Fig. 2). In this reaction, integration showed no further loss of methyl hydrogens. A sample of trimethylfluorosilane dissolved in sulfur dioxide gave the same proton and fluorine chemical shifts and coupling constants. The chemical shift of the initially formed trimethylsilyl species (0.57 ppm) agrees well with the chemical shift previously reported for trimethylsilyl hydrogen sulfate dissolved in sulfuric acid (0.56 ppm)[2]. This evidence allows us to assign the initial singlet to trimethylsilyl fluorosulfonate (I).

$$(CH_3)_4Si + HSO_3F \xrightarrow[SO_2]{-60°} CH_4 + \underset{\text{(I)}}{(CH_3)_3SiOSO_2F} \xrightarrow{-40°} SO_3 + \underset{\text{(II)}}{(CH_3)_3SiF} \qquad (2)$$

The reaction sequence is shown in eqn. (2). The insertion of sulfur trioxide into trimethylfluorosilane in methylene chloride [(II) + SO_3 → (I)] has recently been reported[9].

The cleavage of the first methyl group is quantitative. Under these conditions (HSO_3F/SO_2, $-40°$), cleavage of a second methyl does not take place even after several hours. The small peak observed in these and subsequent spectra at 0.21 ppm is caused by a small amount of methane which remains dissolved in the acid system. This was shown by passing methane through the acid and observing a singlet with the same chemical shift. The slight solubility of methane in sulfuric acid has been noted previously[5].

The reaction of TMS with a stronger acid system (10/1 HSO_3F/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 ($\sim -40°$) the trimethylsilyl fluorosulfonate reacts further as shown by the appearance

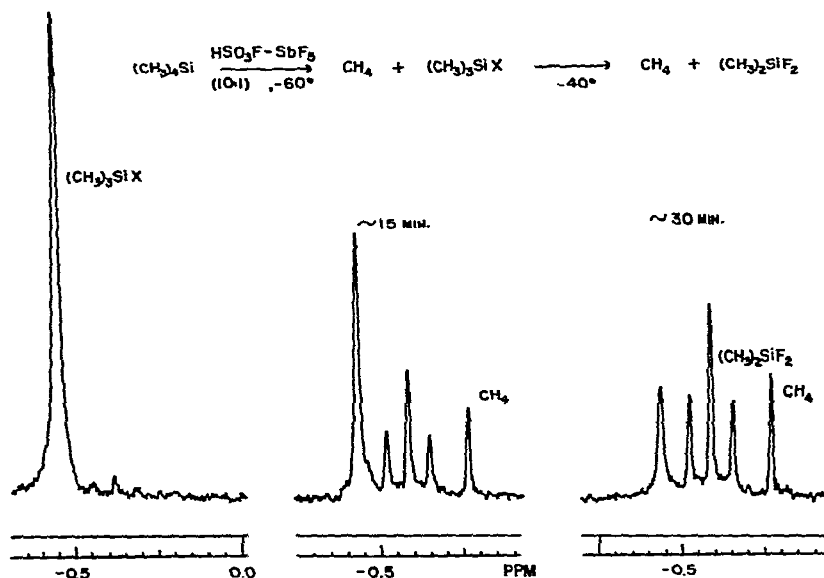
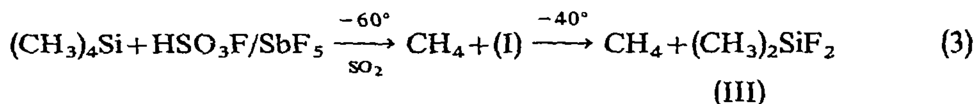


Fig. 3. Reaction of tetramethylsilane with $HSO_3F/SbF_5/SO_2$, $-60°$ ($X=OSO_2F$).

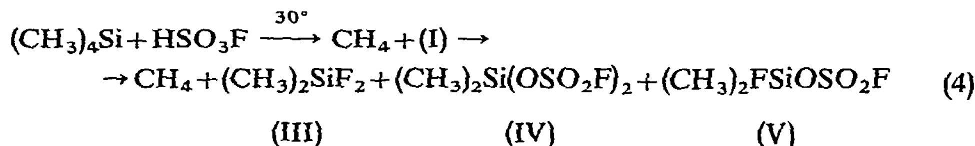
of an upfield proton triplet and a fluorine septet (Fig. 3). Integration showed the loss of a second methyl group [eqn. (3)]. These new resonances are caused by dimethyl-



$$(CH_3)_4Si+HSO_3F/SbF_5 \xrightarrow[SO_2]{-60°} CH_4+(I) \xrightarrow{-40°} CH_4+\underset{(III)}{(CH_3)_2SiF_2} \qquad (3)$$

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 $+30°$. 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 ($\sim$ 1 h) it was necessary to raise the temperature above $50°$ [eqn. (4)].



$$(CH_3)_4Si+HSO_3F \xrightarrow{30°} CH_4+(I) \rightarrow$$
$$\rightarrow CH_4+\underset{(III)}{(CH_3)_2SiF_2}+\underset{(IV)}{(CH_3)_2Si(OSO_2F)_2}+\underset{(V)}{(CH_3)_2FSiOSO_2F} \qquad (4)$$

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

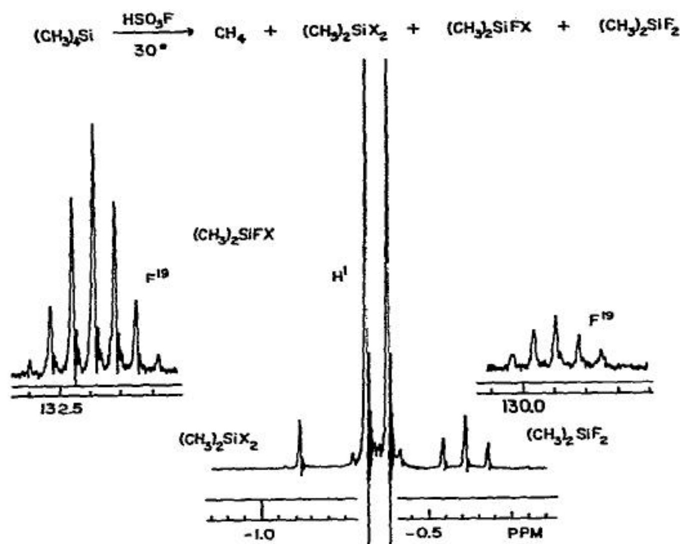


Fig. 4. Reaction of tetramethylsilane with HSO_2F, 30° ($X = OSO_2F$).

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF CLEAVAGE PRODUCTS OF TETRAMETHYLSILANE AND CHLOROMETHYLTRIMETHYLSILANE[a,b]

Compound ($R = CH_3$; $X = OSO_2F$)	δ^1H	J(H–F)	$\phi^{19}F$	$J(^{29}Si–CH_3)$
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
R_3SiCH_2Cl	CH_3: 0.15 (1)			6.6
	CH_2: 2.94 (1)			3.7
R_2XSiCH_2Cl (VI)	CH_3: 0.68 (1)			7.1
	CH_2: 3.11 (1)			[c]
R_2FSiCH_2Cl (VII)	CH_3: 0.45 (2)	8.0		7.0
	CH_2: 3.02 (2)	3.1		[c]
RF_2SiCH_2Cl (VIII)	CH_3: 0.56 (3)	6.1	137.9 (3 × 4)	[c]
	CH_2: 2.96 (3)	3.8		[c]
$RFXSiCH_2Cl$ (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_3F (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.

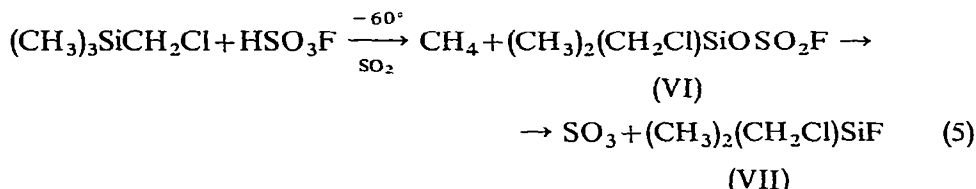
comparison of the NMR spectra with those for the known compounds in the absence of acid.

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

methyl groups are replaced by more electronegative groups. Similar chemical shift trends have been reported for methylalkoxysilanes[10], methylfluorosilanes[11], and methyl(fluorosulfonyl)silanes[9]. The products most easily identified are obviously those which contain a fluorine on silicon since they gave a recognizable coupling pattern with the remaining methyl group(s). When the product gave only an NMR singlet, integration during its formation, its chemical shift and the presence of ^{29}Si–CH_3 coupling allowed definite structural assignment.

(Chloromethyl)trimethylsilane

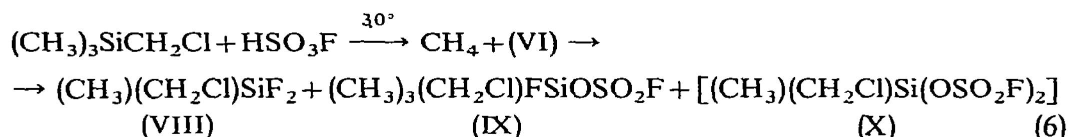
The cleavage of (chloromethyl)trimethylsilane by the acid systems followed a reaction sequence similar to the cleavage of TMS but at a greatly reduced rate. The NMR identification of the cleavage products was considerably easier than for TMS because of the well-separated resonance of the chloromethylene group. Reaction with HSO_3F in SO_2 at $-60°$ resulted in the exclusive cleavage of one methyl group. This was shown by the appearance of new doublets in the silicon methyl region and the chloromethylene region [eqn. (5)]. In this low temperature reaction, formation of the



$$(CH_3)_3SiCH_2Cl + HSO_3F \xrightarrow[SO_2]{-60°} CH_4 + \underset{(VI)}{(CH_3)_2(CH_2Cl)SiOSO_2F} \rightarrow SO_3 + \underset{(VII)}{(CH_3)_2(CH_2Cl)SiF} \quad (5)$$

fluoride from the fluorosulfonate [(VI) → (VII)] was rapid compared to the very slow cleavage of the methyl from (chloromethyl)trimethylsilane. This is in contrast to the formation of (II) from (I) [eqn. (2)] where the rate of cleavage of methyl from TMS was comparable to the rate of loss of sulfur trioxide from fluorosulfonate (I) and each reaction could be observed separately (Figs. 1 and 2).

The reaction of (chloromethyl)trimethylsilane with HSO_3F at 30° also paralleled the reaction of TMS under the same conditions but at a greatly reduced rate [eqn. (6)]. An appreciable concentration of the bis(fluorosulfonate) (X), analogous to (IV), was not observed.



$$(CH_3)_3SiCH_2Cl + HSO_3F \xrightarrow{30°} CH_4 + (VI) \rightarrow \underset{(VIII)}{(CH_3)(CH_2Cl)SiF_2} + \underset{(IX)}{(CH_3)_3(CH_2Cl)FSiOSO_2F} + \underset{(X)}{[(CH_3)(CH_2Cl)Si(OSO_2F)_2]} \quad (6)$$

In order to gain some insight into the mechanism of these cleavage reactions, relative rate measurements were made on homogeneous samples for the first and second reactions (Table 2). Both TMS and (chloromethyl)trimethylsilane require more vigorous conditions to effect cleavage of the second methyl compared to the first. Cleavage of a third methyl does not take place even under these strong acid conditions. For the weaker sulfuric acid system, previous work has shown that the reaction stops after only one cleavage below about $+50°$ [4,6]. These general trends reflect a large rate decrease as methyls are replaced by more electronegative groups.

For the first cleavage, (chloromethyl)trimethylsilane reacts at a greatly reduced rate compared to TMS. This rate comparison is not complicated by 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 $+30°$.

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 dissappearance 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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