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CLEAVAGE OF ALKYLSILANES BY STRONG ACIDS

IV *. THE REACTIONS OF ALKYLDIMETHYLFLUOROSILANES WITH FLUOROSULFONIC ACID

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Summary

The kinetics of cleavage of alkyl groups and fluorine from five alkyldimethylfluorosilanes by fluorosulfonic acid dissolved in methylene chloride has been studied with proton magnetic resonance. Competitive cleavage of alkyl, methyl and fluoro occurs to form three products. A mechanism is proposed based on the third order kinetics which involves the formation of a pentacoordinate intermediate through nucleophilic attack of fluorosulfonic acid at silicon followed by electrophilic attack α to silicon.

Introduction

Alkyl groups may be cleaved from silicon by proton acids [1]. Sulfuric acid reacts with tetraalkylsilanes to give alkanes and trialkylsilyl sulfonates at moderate temperatures (30 to 80°C) [2-5]. Stronger acids are necessary to cleave alkyl groups from organosilanes when one or more electronegative atoms are attached to silicon [3,4]. We have recently reported the reactions of tetramethylsilane and α-halomethyltrimethylsilanes with fluorosulfonic acid [6-8]. In these studies, nuclear magnetic resonance (NMR) was used to observe the stepwise cleavage of two alkyl groups from silicon.

The kinetics of cleavage of a series of alkyldimethylfluorosilanes (RMe_2SiF, R = Me, Et, n-Pr, i-Pr and t-Bu) with fluorosulfonic acid dissolved in methylene chloride have now been investigated. The alkyl groups were chosen to allow a study of the effect of increasing steric hindrance caused by branching at an α-carbon on the rate of the cleavage reactions. Alkyldimethylfluorosilanes were chosen because cleavage reactions occur at a convenient rate at about 30°C. Prod-

* For part III see ref. 24.

uct distributions and kinetics were determined with NMR by careful integration of the silicon-methyl resonances during the course of the reaction.

Results and discussion

The products of the cleavage reaction

All five alkyldimethylfluorosilanes reacted with fluorosulfonic acid in a similar manner. For trimethylfluorosilane (I), the NMR spectrum showed the appearance of two new silicon-methyl resonances, a silicon-methyl triplet at δ(ppm) 0.31 and a silicon-methyl singlet at δ 0.48. The triplet was identified as dimethyldifluorosilane. Addition of dimethyldifluorosilane to the reaction mixture caused the δ0.31 triplet to increase in intensity. The δ 0.48 singlet was due to trimethylsilyl fluorosulfonate formed through the replacement of fluorine on silicon by fluorosulfonate with no cleavage of silicon—carbon bonds. Integral totals determined during the reaction were consistent only if the δ 0.48 singlet was assigned to a compound containing three methyls. This chemical shift is close to that found previously for trimethylsilyl fluorosulfonate (δ 0.57) [6]. If methyl cleavage were occurring to give dimethylsilyl bis(fluorosulfonate), the methyl singlet would be expected to appear further downfield at δ0.86 [6]. The slight upfield shift found for trimethylsilyl fluorosulfonate in the present work (δ 0.48 vs. 0.56) probably indicates a smaller degree of protonation in dilute fluorosulfonic acid dissolved in methylene chloride compared to neat fluorosulfonic acid.

For the other four alkyldimethylfluorosilanes, three new silicon-methyl resonances appeared as the reactions progressed, two silicon-methyl triplets and a silicon-methyl singlet. The triplets, centered between 0.27 and 0.31 ppm, were easily assigned to dimethyldifluorosilane, the product of alkyl cleavage, and to alkylmethyldifluorosilane, the product of methyl cleavage. Careful integration of the silicon-methyl region compared to the alkyl region during and at the completion of the reaction led consistently to the assignment of the upfield triplet to

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF REACTANTS AND PRODUCTS [a]

Reactants RMe_2SiF			Products					
R	δ(^{1}H)	J(H—F)	R δ(^{1}H)	Me_2SiF_2		$RMeSiF_2$		RMe_2SiOSO_2F δ(^{1}H)
				δ(^{1}H)	J(H—F)	δ(^{1}H)	J(H—F)	
Me	0.24(2)	8.0	—	0.31(3)	6.5	—	—	0.48(1)
Et	0.21(2)	8.0	1.12—0.53 [b]	0.31(3)	6.5	0.29(3)	6.5	0.46(1)
n-Pr	0.20(2)	8.0	1.79—0.58 [b]	0.31(3)	6.5	0.30(3)	6.5	0.47(1)
i-Pr	0.18(2)	8.0	1.11—0.84 [b]	0.31(3)	6.5	0.27(3)	6.5	0.44(1)
t-Bu	0.18(2)	8.2	F 0.85(2) [c]					
			F_2 0.96(3) [c]	0.31(3)	6.5	0.27(3)	6.3	0.45(1)
			X 0.97(1) [c]					

[a] Chemical shifts in ppm downfield from tetramethylsilane; figures in parentheses represent multiplicity of peaks. [b] Chemical shift range of overalpping R groups of reactants and products. [c] F = t-butyldimethylfluorosilane (J(H—F) 1.1 Hz.); F_2 = t-butylmethyldifluorosilane (J(H—F) 1.0 Hz.); X = t-butyldimethylsilyl fluorosulfonate.

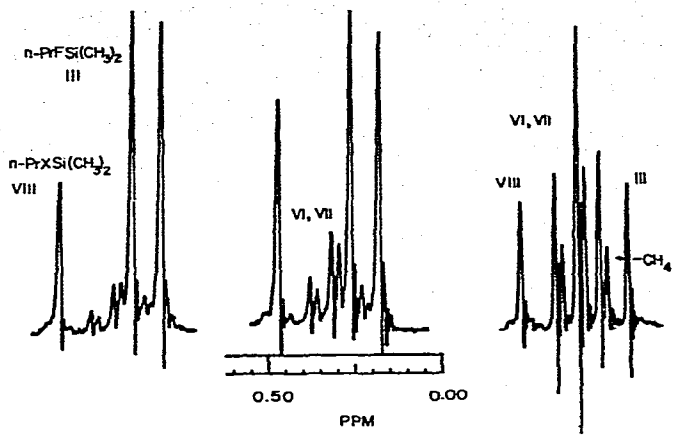


Fig. 1. The silicon-methyl resonances of n-propyldimethylfluorosilane (III) during the reaction with fluorosulfonic acid (X = OSO_2F).

alkylmethyldifluorosilane and the downfield triplet to dimethyldifluorosilane. Further, the addition of dimethyldifluorosilane to the reaction mixtures caused the downfield triplet to grow in intensity. Similar to the reaction of trimethylfluorosilane, the silicon-methyl singlet formed in the reaction of these four alkyldimethylfluorosilanes was due to alkyldimethylsilyl fluorosulfonates.

The NMR data for the reactants and products for the reactions of alkyldimethylfluorosilanes with fluorosulfonic acid are collected in Table 1. Typical spectra of the silicon-methyl region used to determine the rates of cleavage for n-propyldimethylfluorosilane (III) and t-butyldimethylfluorosilane (V) are shown in Figs. 1 and 2.

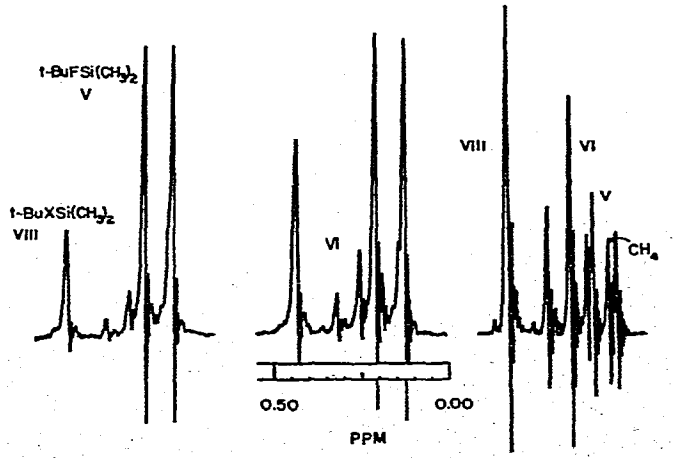


Fig. 2. The silicon-methyl resonances of t-butyldimethylfluorosilane (V) during the reaction with fluorosulfonic acid (X = OSO_2F).

Kinetic measurements

The kinetics of these reactions were studied at 30°C by careful integration of the silicon-methyl resonances as a function of time. Eq. 1 presents a reasonable scheme for the reactions of the alkyldimethylfluorosilanes with fluorosulfonic acid consistent with the NMR data. This sequence involves the competitive for-

$$\text{RMe}_2\text{SiF} + \text{HOSO}_2\text{F} \xrightarrow{k(\text{Me})} \text{CH}_4 + \text{RMeSiF}_2 + \text{SO}_3 \quad \text{(VI)} \qquad (1a)$$

$$\text{RMe}_2\text{SiF} + \text{HOSO}_2\text{F} \xrightarrow{k(\text{R})} \text{RH} + \text{Me}_2\text{SiF}_2 + \text{SO}_3 \quad \text{(VII)} \qquad (1b)$$

$$\text{RMe}_2\text{SiF} + \text{HOSO}_2\text{F} \xrightarrow{k(\text{F})} \text{HF} + \text{RMe}_2\text{SiOSO}_2\text{F} \quad \text{(VIII)} \qquad (1c)$$

$k(\text{X}) \uparrow \text{HOSO}_2\text{F}$

(I) R = Me
(II) R = Et
(III) R = n-Pr
(IV) R = i-Pr
(V) R = t-bu

mation of three products. Two of these reactions result in the cleavage of a carbon—silicon bond (eq. 1a and 1b). The dialkyldifluorosilanes (VI and VII) did not undergo further reaction at an appreciable rate at 30°C. Previously we found that dialkyldifluorosilanes were unreactive even toward neat fluorosulfonic acid at this temperature [7].

The third pathway is the formation of alkyldimethylsilyl fluorosulfonates (VIII) (eq. 1c). In order to study the kinetics of the competitive pathways, k(Me), k(R) and k(F), it was necessary to determine if VIII reacts further at a rate comparable to k(Me), k(R) and k(F). The percent VIII formed during the reactions was determined by integration through at least one half life. These data are presented in Table 2 and they show that this percent remains constant. The much slower reaction of VIII compared to the five alkyldimethylfluorosilanes probably reflects a greater degree of protonation of the fluorosulfonate. A greater degree of protonation would be expected to substantially decrease the rate of electrophilic attack at an α-carbon. We may therefore treat the reactions of the five alkyldimethylfluorosilanes as a competitive set leading primarily to three products, VI, VII and VIII.

The kinetics were measured at 30°C through at least one half life. The concentration of the organosilane was varied between 0.1 and 0.2 *M* and that of fluorosulfonic acid between 0.4 and 0.6 *M*. In these concentration ranges, the

TABLE 2

PERCENT ALKYLDIMETHYLSILYL FLUOROSULFONATE (VIII)

R	Percent reaction							
	25	30	35	40	45	50	60	70
Me	43	43	44	44	42	43	44	44
Et	32	31	32	32	33	33		
n-Pr	39	38	41	39	38	38		
i-Pr			18	19	18	21	18	
t-Bu		33	35	34	33	34	32	30

TABLE 3

RATE CONSTANTS AND PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF ALKYLDIMETHYLFLUOROSILANES WITH FLUOROSULFONIC ACID

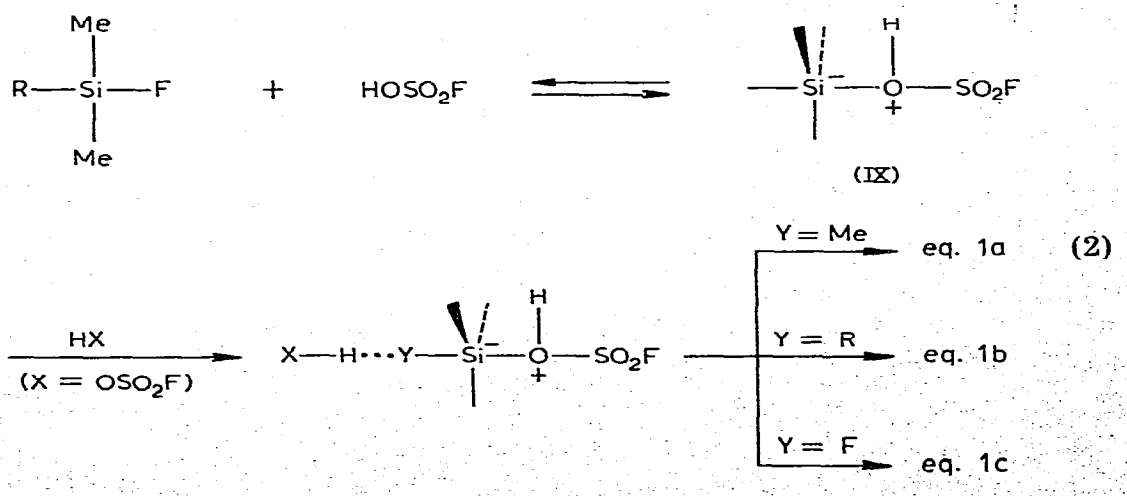
Compound	R	$k_3 \times 10^3$ l^2 mol^{-2} min^{-1}	Product distributions		
			% Methyl cleavage	% Alkyl cleavage	% Fluoro cleavage
I	Me	1.58 ± 0.09	57.0		43.0
II	Et	2.93 ± 0.09	43.9	23.4	32.7
III	n-Pr	2.31 ± 0.11	38.0	21.5	40.5
IV	i-Pr	1.17 ± 0.09	79.4	~1.7	18.9
V	t-Bu	1.09 ± 0.05	62.6	~4.2	33.2
Me_3SiOSO_2F		0.02 [a]	68.0	CH_3SO_2F:	32.0

[a] Rate constant for reaction in neat fluorosulfonic acid [7].

reaction gave good third-order kinetics, first-order in organosilane and second-order in fluorosulfonic acid. The third order rate constants and product distributions for the five alkyldimethylfluorosilanes are collected in Table 3. Also included in this table is the third-order rate constant for the reaction of trimethylsilyl fluorosulfonate in neat fluorosulfonic acid reported previously [7]. The size of this constant compared to those for the alkyldimethylfluorosilanes in dilute fluorosulfonic acid confirms that the rate of alkyl cleavage for VIII does not compete effectively with the three pathways of eq. 1.

Discussion of the mechanism of the reaction

A reasonable mechanism for these cleavage reactions consistent with the kinetics is presented in eq. 2. The order with respect to fluorosulfonic acid requires that two molecules are involved before the rate-determining step. The mechanism shows fluorosulfonic acid attacking in a nucleophilic manner to



(2)

form a pentacoordinate species IX followed by electrophilic attack at an α-carbon or at fluorine to produce the three cleavage products. The important fea-

ture of this mechanism is that both nucleophilic and electrophilic attack are required. The rate constants presented in Table 3 reach a maximum when the alkyl group is ethyl and then decrease as the alkyl group becomes larger. It should be noted that the rates change only by a factor of three throughout the series.

If nucleophilic attack at silicon were the only important factor, we might expect similarities to carbon S_N2 reactivity. However, relative rates for S_N2 reactions at carbons in which bulk is increased by β-branching show a much larger change and decrease throughout the series (e.g., relative rates for $RCH_2I + Cl^-$: R = CH_3, 1.00; R = CH_3CH_2, 0.60; R = $(CH_3)_2CH$, 0.04; R = $(CH_3)_3C$, 10^{-5}) [9,10].

This leveling effect seen in the relative rates for alkyldimethylfluorosilanes is due to two features which make reactions at silicon very different from S_N2 reactions at carbon. First, silicon is larger than carbon, making the reactions less sensitive to steric influences. Secondly, branching α to silicon affects the two steps of the mechanism in opposite directions. Thus, in going from I to II to III, α-methyl substitution causes a decrease in the rate of nucleophilic attack to form the pentacoordinate intermediate IX but this is compensated for by an increase in the ease of electrophilic attack at the α-carbon. In the series studied, a balance is reached between II and III. With substitution of two methyls (IV) and three methyls (V), it appears that the bulk of the alkyl substituent controls the relative rates.

This dual requirement for both nucleophilic and electrophilic attack in reactions of organosilanes has been recognized for some time through both kinetic and stereochemical studies [11]. In early kinetic studies by Swain [12] and in more recent work [13,14] hydrolysis of triphenylfluorosilane and of triphenylaryloxysilanes was found to follow a mechanism similar to the one proposed in eq. 2. These studies show that silicon becomes less positive in the transition state and this argues against the possibility of an intermediate siliconium ion [15]. However, one might expect a change to a siliconium ion mechanism in reactions with exceptionally electrophilic reagents such as fluorosulfonic acid or aluminum halides. The present kinetic study shows this not to be the case. Similar conclusions have been reached for the reaction of alkoxysilanes with antimony pentafluoride/fluorosulfonic acid [16], for the exchange of fluoride between methylfluorosilanes and antimony pentafluoride [17], and for the intramolecular rearrangement of α-chloroalkyltrialkylsilanes with Lewis acids [18].

A closer look at the reaction of alkyldimethylfluorosilanes is obtained if the individual rates of methyl, alkyl and fluoro cleavage are compared (Table 4). These relative rates were obtained by multiplying the product distributions by the total rate (k_3, Table 3) and comparing these partial rates to the rate of cleavage of one methyl group for trimethylfluorosilane (I). The relative rates of cleavage of methyl and fluoro rise and fall in a similar manner, reflecting the balance between formation of the pentacoordinate intermediate IX and electrophilic attack α to silicon (eq. 2). The striking feature of this Table is the drastic decrease in the rate of i-propyl and t-butyl cleavage. The changes in the relative rates of alkyl cleavage (k(R)) are remarkably similar to the migratory aptitudes found for the intramolecular analog of the cleavage reactions presented here. For the rearrangement of (chloromethyl)alkyldimethylsilanes with aluminum chloride the following relative rates were found: R = Me, 1.00; R = Et, 2.07; R = n-Pr,

TABLE 4
RELATIVE RATES OF CLEAVAGE [a]

R	k(Me)	k(R)	k(F)
Me	1.00	1.00	2.26
Et	2.14	2.29	3.19
n-Pr	1.46	1.66	3.12
i-Pr	1.55	0.07	0.74
t-Bu	1.14	0.15	1.20

[a] Relative rates statistically corrected and compared to the rate of cleavage of one methyl group.

2.97; R = i-Pr, << 1.00; R = t-Bu, << 1.00 [19].

The large relative rate decrease for the cleavage of i-propyl and t-butyl strongly implies that reaction occurs through stereospecific electrophilic attack upon the pentacoordinate intermediate (IX) and that the stereochemistry of this intermediate is different for IV and V than for I, II, and III. However, present data do not allow a detailed description of the structure of this intermediate.

Experimental

General

Dimethyldichlorosilane, trimethylfluorosilane (I), bromoethane, 1- and 2-bromopropane, and t-butyllithium were commercially available and were used without further purification. Technical grade fluorosulfonic acid was refluxed under a nitrogen atmosphere and then distilled. The acid was stored in Teflon bottles.

Varian Associates Models A-60 and HA-100 spectrometers equipped with variable temperature probes were used for all proton spectra. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (internal).

Syntheses

Ethyldimethylfluorosilane (II). Ethylmagnesium bromide was prepared by the reaction of bromoethane (55.0 g, 0.50 mol) with magnesium turnings (12.0 g, 0.50 g-atom) in 150 ml of ether. The ethylmagnesium bromide solution was added slowly to a solution of dimethyldichlorosilane (64.0 g, 0.50 mol) in 100 ml of ether. After the addition was complete, the reaction mixture was stirred for 14 h. Fractional distillation gave ethyldimethylchlorosilane (30.5 g, 0.25 mol, 50% yield, b.p. 87—88°C/755 mmHg, lit. [20]: 88—88.5°C). The ethyldimethylchlorosilane (30.5 g, 0.25 mol) was added slowly to 49% hydrofluoric acid (366 g, 9.0 mol) cooled to 5°C and stirred for 5 h. After separation of the organic layer and drying over magnesium sulfate, distillation gave ethyldimethylfluorosilane (II) (18.9 g, 0.18 mol, 71% yield, b.p. 50—52°C/755 mmHg, lit. [20]: 50—50.5°C.)

n-Propyldimethylfluorosilane(III). n-Propyldimethylchlorosilane was prepared in a similar manner to the preparation of ethyldimethylchlorosilane from 1-bromopropane (123 g, 1.0 mol), magnesium turnings (24.0 g, 1.0 g-atom), and dimethyl-

dichlorosilane (128 g, 1.0 mol). Distillation gave n-propyldimethylchlorosilane (60 g, 0.44 mol, 44% yield, b.p. 114—116° C, lit. [21]: 113.8° C/736 mmHg). Reaction of n-propyldimethylchlorosilane (36 g, 0.26 mol) with 49% hydrofluoric acid gave n-propyldimethylfluorosilane (III) (18.5 g, 0.15 mol, 59% yield, b.p. 73—74° C/755 mmHg).

i-Propyldimethylfluorosilane (IV). n-Propyldimethylchlorosilane was prepared in a similar manner to the preparation of ethyldimethylchlorosilane from 2-bromopropane (123 g, 1.0 mol), magnesium turnings (24.0 g, 1.0 g-atom), and dimethyldichlorosilane (128 g, 1.0 mol). After long reflux (45 h), distillation gave i-propyldimethylchlorosilane in low yield (4.7 g, 0.03 mol, 4% yield, b.p. 108—109° C/754 mmHg, lit. [22]: 109.8—110° C/738 mmHg). Reaction of i-propyldimethylchlorosilane (4.7 g, 0.03 mol) with 49% hydrofluoric acid gave i-propyldimethylfluorosilane (IV) (1.8 g, 0.015 mol, 50% yield, b.p. 70—71° C/755 mmHg).

t-Butyldimethylfluorosilane (V). t-Butyldimethylchlorosilane was prepared by the reaction of t-butyllithium (2 *M*, 125 ml, 0.25 mol) in hexane with dimethyldichlorosilane (32.0 g, 0.25 mol). Distillation gave t-butyldimethylchlorosilane (24.2 g, 0.16 mol, 64% yield, b.p. 124—125° C/753 mmHg, lit. [23]: 125° C/733 mmHg). Reaction of t-butyldimethylchlorosilane (12.0 g, 0.08 mol) with 49% hydrofluoric acid gave t-butyldimethylfluorosilane (V) (8.3 g, 0.06 mol, 75% yield, b.p. 75—76° C/755 mmHg).

Kinetic studies

Standard solutions of fluorosulfonic acid were prepared by diluting a weighed amount of freshly distilled fluorosulfonic acid with carefully dried and distilled methylene chloride in a volumetric flask. The acid concentration was varied between 0.4 and 0.6 *M*. These limits were dictated by the solubility of fluorosulfonic acid in methylene chloride at the upper limit and by the concentration needed to obtain reasonable half-lives and reasonable signal-to-noise at the lower limit. The concentration of the silanes was varied between 0.1 and 0.2 *M*. Samples were prepared by cooling known volumes of the silane and acid solutions in a dry ice/acetone bath. After cooling, the silane was slowly added to the acid. If this precaution was not taken, a significant amount of the reaction occurred due to the heat of mixing. After mixing the samples were transferred to an NMR tube and warmed to 30° C in a constant temperature bath. The bath was maintained at 30.0 ± 0.1° C by a Sargent Company Thermo-Controller. The samples were removed from the bath and spectra recorded at various time intervals. The temperature of the NMR probe was 30 ± 1° C. Because the half-lives were very long, the time the tubes were out of the thermostatted bath or the spectrometer had a negligible effect on the rates.

The rates were determined by careful integration of the silicon-methyl region during the course of the reaction (Figs. 1 and 2). Where overlap of starting material and product resonances occurred, concentrations could be determined by using only one of the resonances of a multiplet and multiplying its integral by the appropriate factor because the silicon-methyl doublets and triplets are perfectly first-order (Me—Si—F and Me—Si—F_2 coupling). The measurement of error presented in Table 3 is the average root mean square deviation for at least three kinetic runs for each compound. The largest contributing factor to this error

was probably caused by the difficulty in precisely integrating two close resonances. This was particularly difficult for the alkylmethyldifluorosilanes of II and III and dimethyldifluorosilane (Table 1).

Acknowledgement

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