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CLEAVAGE OF ALKYLSILANES BY STRONG ACIDS II*. THE FORMATION OF METHANESULFONYL FLUORIDE**

CHARLES M. HARBORDT AND DANIEL H. O'BRIEN
Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)
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SUMMARY

The cleavage of methyl groups from trialkylsilyl fluorosulfonates by fluorosulfonic acid has been found to yield appreciable amounts of methanesulfonyl fluoride in addition to the formation of methane. Kinetic data show that this new mode of cleavage occurs after initial protonation of the silyl fluorosulfonate by the acid. A mechanism is proposed for methanesulfonyl fluoride formation in which nucleophilic attack by an acid molecule occurs at the silicon of the protonated silyl fluorosulfonate and is followed by rearrangement of a methyl group from silicon to sulfur.

INTRODUCTION

The cleavage of alkyl groups from silicon occurs with ease in the presence of strong proton acids[1]. The mechanism of this reaction has been disputed. Kinetic data for the reaction of 3-(trimethylsilyl)propionic acid with sulfuric acid were used to show that the reaction occurs by electrophilic attack at the methyl carbon[2] while other investigators indicated that nucleophilic attack at silicon by an acid molecule is important[3,4]. We have recently reported that the most important factor is the electron density at the methyl carbon in the acid cleavage of an alkyl group to form an alkane. These experiments were carried out on tetraalkylsilanes under homogeneous conditions using the stronger acid, fluorosulfonic acid[5].

RESULTS AND DISCUSSION

We now wish to report further studies of the cleavage of methyl groups from trialkylsilyl fluorosulfonates which show that a new mode of cleavage is possible for the reaction with fluorosulfonic acid. This new reaction is competitive with alkane formation and indeed may occur through nucleophilic attack by an acid molecule at the silicon of a *protonated* trialkylsilyl fluorosulfonate. Rearrangement of a methyl from silicon to sulfur results in the formation of methanesulfonyl fluoride.

Trimethylsilyl fluorosulfonate

As previously reported[5], the NMR spectrum of a homogeneous sample of

* For part I see ref. 5.
** Based on the Ph. D. dissertation of C. M. H., Texas A&M University, 1970.

tetramethylsilane (TMS) dissolved in an excess of fluorosulfonic acid at low temperature and allowed to warm slowly to room temperature shows rapid and quanttitative loss of one mole of methane and the formation of trimethylsilyl fluorosulfonate [(Ia), X=H; eqn. (1)]. This is followed by a much slower loss of a second methyl and the formation of three dimethylsilyl compounds [(II), (III) and (IV), X=H; eqn. (2)]. This second methyl cleavage results in the formation of appreciable amounts of

$$X\text{-}CH_2\text{-}Si(CH_3)_2\text{-}CH_3 + HSO_3F \rightarrow CH_4 + X\text{-}CH_2\text{-}Si(CH_3)_2\text{-}OSO_2F \quad (1)$$

(X=H or Cl) (I) [(IA), X=H; (IB), X=Cl]

$$(I) + HSO_3F \xrightarrow{+30^\circ}$$

$$X\text{-}CH_2\text{-}Si(CH_3)_2\text{-}F + X\text{-}CH_2\text{-}Si(CH_3)_2\text{-}OSO_2F + X\text{-}CH_2\text{-}Si(CH_3)(OSO_2F)_2 + CH_4 + CH_3SO_2F \quad (2)$$

(II) (III) (IV)

methanesulfonyl fluoride (60–70% of the cleaved methyls) in addition to methane. Methanesulfonyl fluoride formation was shown by the appearance of a downfield doublet in the proton spectrum at 3.51 ppm and a fluorine quartet at −69.0 [CCl_3F, internal; J(H–F) = 5.92 Hz.] The same coupling constant and proton and fluorine chemical shifts were found when a sample of methanesulfonyl fluoride was dissolved

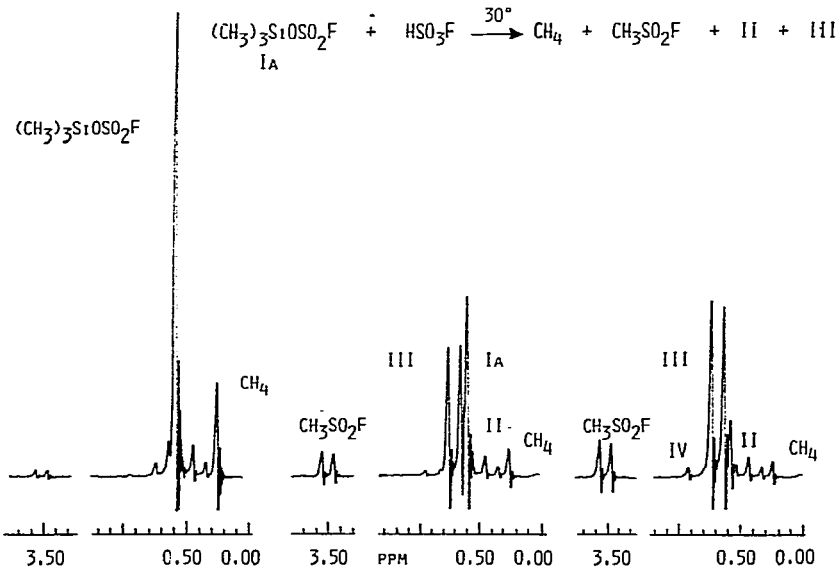


Fig. 1. Cleavage of trimethylsilyl fluorosulfonate by HSO_3F, 30°.

in fluorosulfonic acid. A proton spectrum showing the formation of methanesulfonyl fluoride during the course of the reaction is presented in Fig. 1.

(Chloromethyl)dimethylsilyl fluorosulfonate

The same reaction sequence is found for (chloromethyl)trimethylsilane except at a much reduced rate. The first cleavage reaction results in methane and (chloromethyl)dimethylsilyl fluorosulfonate as the only cleavage products. (Chloromethyl)-dimethylsilyl fluorosulfonate [(Ib), X = Cl; eqn. (1)] undergoes a slow second cleavage reaction to form both methane and methanesulfonyl fluoride. In this reaction, no evidence was found for the electrophilic cleavage of the chloromethyl nor for a cleavage product containing the chloromethylene carbon attached to sulfur.

It appears unlikely that the unexpected formation of methanesulfonyl fluoride in these two reactions occurs *after* the cleavage of a methyl group from silicon by a subsequent reaction of methane with fluorosulfonic acid. The reaction of alkanes with extremely strong acid systems has recently been reported[6,7]. However, the reaction of methane occurs at an appreciable rate only at higher temperatures (>80°) and with much stronger acid systems than fluorosulfonic acid. Further, in these systems the formation of stable carbonium ions is observed and *not* the formation of alkylsulfonyl fluorides.

Several attempts were made to see if dissolved methane would react with fluorosulfonic acid under the conditions of our experiments. All such attempts resulted in no detectable appearance of methanesulfonyl fluoride in the NMR spectrum. Obviously, such *negative* evidence can not conclusively prove that methanesulfonyl fluoride could not have been formed by the reaction of methane with fluorosulfonic acid. However, several pertinent observations make this possibility remote. In the low temperature cleavage of the first methyl, no formation of methanesulfonyl fluoride is observed even though appreciable amounts of methane can be directly observed in the NMR spectrum[5]. In the higher temperature second cleavages reported here, the yield of methanesulfonyl fluoride is high (60–70%) and shows a slight increase when the reaction temperature is raised (Tables 1 and 2, runs 8 and 4). It would be expected that the slight solubility of methane in fluorosulfonic acid would decrease with increasing temperature and that the opposite trend would be observed if methanesulfonyl fluoride formed as the result of the reaction of methane with fluorosulfonic acid. These observations and the consistency of the kinetic results to be discussed lead us to believe that the formation of methanesulfonyl fluoride is intimately involved in the cleavage process.

Kinetic measurements

In order to gain more insight into the mechanism of formation of methanesulfonyl fluoride, the kinetics of cleavage were studied under various conditions. Methyl cleavage from (Ia) and (Ib) gave good first-order kinetics in the presence of an excess of fluorosulfonic acid. These rates could be conveniently followed directly in the NMR probe by careful integration of the appropriate peaks. In all runs first-order plots were obtained over as many as three half-lives. Tables 1 and 2 present kinetic data for the methyl cleavage of (Ia) and (Ib) at various concentrations of fluorosulfonic acid. The range over which the concentration of fluorosulfonic acid could be varied was limited by the solubility of the silyl fluorosulfonates (~1/10,

TABLE 1

RATES OF CLEAVAGE OF TRIMETHYLSILYL FLUOROSULFONATE BY FLUOROSULFONIC ACID AT 30°

Run	HSO_3F (mole·l^{-1})	$k \times 10^6$ (sec^{-1})	$\frac{k}{[HSO_3F]}$	$\frac{k}{[HSO_3F]^2}$	CH_3SO_2F[a] (%)
1	12.5	5.68	0.454	0.364	72
2	13.3	6.30	0.474	0.356	71
3a	13.7	6.76	0.493	0.358	68
4	15.1	7.80	0.516	0.342	63
5	15.7	8.45	0.538	0.343	66
6a	16.0	8.77	0.550	0.343	64
7	16.3	9.83	0.602	0.369	65
8	14.2	965			75[b]
3b	13.7	5.24	(0.47 *M* KSO_3F added)		64
6b	16.0	6.65	(0.52 *M* KSO_3F added)		64

[a]Based on integration of CH_3SO_2F resonance to the integrals of (II), (III), and (IV). [b]At 57°.

TABLE 2

RATES OF CLEAVAGE OF (CHLOROMETHYL)DIMETHYLSILYL FLUOROSULFONATE BY FLUOROSULFONIC ACID AT 30°

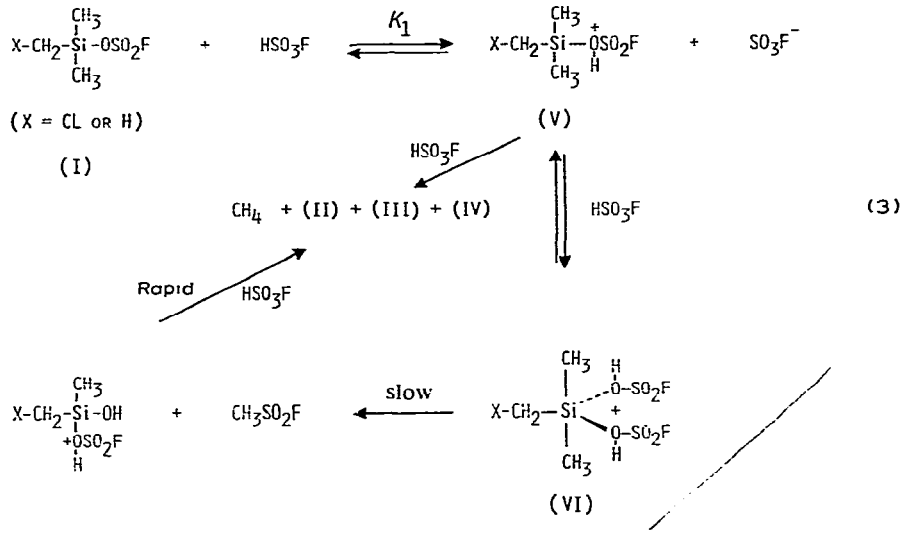
Run	HSO_3F (mole·l^{-1})	$k \times 10^6$ (sec^{-1})	$\frac{k}{[HSO_3F]}$	$\frac{k}{[HSO_3F]^2}$	CH_3SO_2F[a] (%)
1	13.3	0.660	0.0496	0.0373	68
2	14.6	0.835	0.0572	0.0392	[b]
3	16.2	1.040	0.0642	0.0396	[b]
4	13.3	19.0			71[c]

[a]Based on integration of CH_3SO_2F resonance to the integrals of (II), (III), and (IV). [b]Not determined. [c]At 57°.

mole/mole) and by the concentration of silyl fluorosulfonate necessary to obtain precise integrals (~1/80, mole/mole). No suitable diluent could be found which would allow the determination of the order of the reaction with respect to the acid other than by varying it over this rather narrow range.

These kinetics show that the reaction is first order in silyl fluorosulfonate and second order in fluorosulfonic acid. This can be accounted for by a reaction in which methane and methanesulfonyl fluoride are formed in a competitive manner. A reasonable mechanism for this competitive process is presented as eqn. (3). The silyl fluorosulfonates exist principally as the protonated species (V) in fluorosulfonic acid. Protonated intermediates have been proposed on the basis of kinetic evidence for the acid catalyzed cleavage of alkoxysilanes and for the rearrangement of cyclic and linear polysiloxanes[8-10]. Protonated alkoxysilanes have been observed by NMR at lower temperatures in strong acid systems[11].

The protonation of the silyl fluorosulfonates would account for the drastic decrease in the rate of methyl cleavage from (Ia) and (Ib) compared to methyl cleavage from TMS and (chloromethyl)trimethylsilane {k(TMS, −47°) = 43, k[(Ia), +30°] = 0.057; k(ClTMS, −47°) = 0.46, k[(Ib), +30°] = 0.0066 × 10^{-4} sec^{-1}}[5]. The presence of the protonated species as intermediate undergoing cleavage was also indicated by



(3)

a slight decrease in the rate upon the addition of potassium fluorosulfate (runs 3b and 6b). The protonated species (V) would be much less susceptible to electrophilic attack at the methyl carbon because of the presence of the positive charge. This decrease in the rate of electrophilic cleavage allows fluorosulfonic acid to display its weak nucleophilic character. The positively charged species (V) is attacked in a nucleophilic manner by a molecule of fluorosulfonic acid to form the pentavalent intermediate (VI). Rearrangement of a methyl from silicon to sulfur and cleavage of the sulfur–oxygen bond results in the formation of methanesulfonyl fluoride.

It is rather surprising that although the rate of methyl cleavage from fluorosulfonates (Ia) and (Ib) differ by a factor of ten, the yield of methanesulfonyl fluoride remains about the same (Tables 1 and 2). The rate decrease in going from (Ia) to (Ib) cannot be explained by a difference in the extent of protonation (*i.e.* the size of K_1). One would predict that the inductive effect of the chloromethyl would lead to an *increase* in the concentration of (V) and a corresponding increase in the rate of methyl cleavage. Just the opposite is observed.

This rate decrease is consistent with the proposed mechanism if the extent of protonation is large for both (*i.e.* K_1 is large) and the decrease in rate is explained by differences in electrophilic and nucleophilic attack by the acid on the protonated species (V). The rate of electrophilic attack at the methyl carbon to form methane would be expected to be smaller for protonated (chloromethyl)dimethylsilyl fluorosulfonate than for protonated trimethylsilyl fluorosulfonate. On the other hand, nucleophilic attack at the silicon of (V) would be expected to be enhanced by the inductive effect of the chloromethyl leading to an increased yield of methanesulfonyl fluoride. However, steric hinderance to the formation of the pentavalent intermediate (VI) might well compensate for this effect and lead to comparable yields of methanesulfonyl fluoride for both (Ia) and (Ib). A more detailed separation of steric and inductive effects on the formation of methanesulfonyl fluoride and methane is not possible with the present data. Work is now underway on the cleavage pathways for compounds not containing electronegative α-substituents in order to determine if the formation of methanesulfonyl fluoride is indeed sterically dependent.

A mechanism like the one described may help explain the conflict concerning the relative importance of electrophilic and nucleophilic attack in the cleavage of alkyl groups from silicon[2,3]. This work dealt with the first methyl cleavage reactions of organosilanes containing a remote functional group capable of protonation. It is important to note that following the reaction by observing only the dissappearance of the starting silane and the appearance of *silicon-containing* products will not uniquely determine the pathway of cleavage [eqn. (3)].

The formation of methanesulfonyl fluoride from silyl fluorosulfonates bears a striking resemblance to several reactions of silicon–carbon bonds with sulfur trioxide or alkylsulfonates[12–14]. In these reactions, sulfur trioxide is 'inserted' into both aryl and alkyl silicon–carbon bonds but mechanistic details have not been presented [eqn. (4)]. It seems probable that the mechanism for such reactions is similar to the

$$R_3SiR + SO_3 \rightarrow R_3Si-O-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}-R \qquad (4)$$

one described here, nucleophilic attack at silicon followed by rearrangement of the aryl or alkyl group from silicon to sulfur. The only difference lies in the nature of the attacking group (HSO_3F *vs.* SO_3).

EXPERIMENTAL

Materials

Tetramethylsilane, (chloromethyl)trimethylsilane and methanesulfonyl fluoride were commercially available materials and were used without further purification. Technical grade fluorosulfonic acid was refluxed under an atmosphere of dry nitrogen for several hours and then distilled just prior to use.

Kinetic measurements

Varian Associates Models A-60 and HA-100-NMR spectrometers equipped with variable temperature probes were used for all kinetic measurements. Samples for rate measurements were prepared by adding TMS or (chloromethyl)trimethylsilane to freshly distilled fluorosulfonic acid at $-76°$ and warming to about $-35°$ to allow the first cleavage reaction to go to completion[5]. Homogeneous samples of the silyl fluorosulfonates, (Ia) and (Ib), were obtained if the ratio of the acid to the silane was greater than about 10/1 (mole/mole). Samples prepared in this manner were then diluted to the desired concentration with fluorosulfonic acid and kept in a constant temperature bath ($30.0 \pm 0.1°$).

The rates of cleavage were followed by careful integration of the silicon–methyl resonances during the course of the reaction (Fig. 1). The integrals were found to have an average deviation of about 1% at fifty per cent reaction. This precision probably decreased at the beginning and the end of the reaction when the percentage of either reactant or products was small (5%). Since the kinetic runs were quite slow [$t_{\frac{1}{2}}$ (Ia) = 35 h; $t_{\frac{1}{2}}$ (Ib) = 292 h) the silicon–methyl integral of (I) divided by the total

silicon–methyl integral (product integrals corrected for the loss of one methyl) was used to determine the amount of reactant present as a function of time and to allow for any differences in spectrometer tuning.

Psuedo-first-order plots were obtained in this manner through as many as three half-lives. A slight increase in the ratio of methanesulfonyl fluoride to methane was noted during the course of several of the runs. For this reason, reliable values for the individual rates of formation of methane and methanesulfonyl fluoride were not obtained. This slight increase was insufficient to influence the first-order plots and was perhaps due to the increase in sulfur trioxide present in equilibrium with products (II), (III) and (IV). The reaction of sulfur trioxide with the silyl fluorosulfonates in a manner similar to the mechanism for methanesulfonyl fluoride formation might well cause this small increase.

ACKNOWLEDGEMENT

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