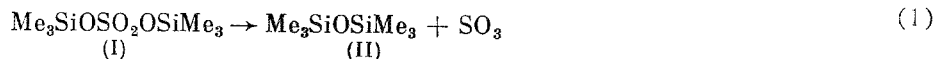


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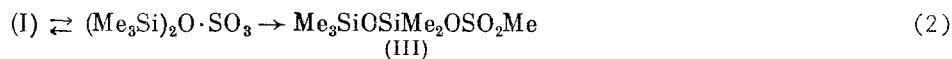
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It was previously reported [1] that bis(trimethylsilyl)sulfate (I) when heated at 150°C is cleaved by the scheme

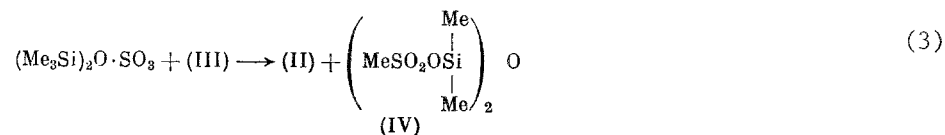


However, this reaction was not studied in detail and the decomposition products were not isolated.

It was shown by us that sulfate (I) is thermally quite stable and withstands long heating at 150° without change. It can even be distilled at atmospheric pressure (bp 217°) with only slight decomposition. We used the differential thermal analysis (DTA) method to study the thermolysis of (I). A substantial endothermic effect with a maximum at 58°, corresponding to the melting point of (I) (56-58°) [2], is clearly seen on the DTA curve (Fig. 1). Further heating leads to the appearance of a second endothermic effect on the DTA curve, which begins at 150° and has a maximum at 178°. The weight loss when the rate of heating is 4 and 6 deg/min is respectively 3 and 6%. The observed slow process is apparently caused by the isomerization of (I) to the more volatile (III) compound



The main process for the thermolysis of (I) begins at 192-195° and leads to the formation of hexamethyldisiloxane (II) (up to 20% yield) and the previously unknown tetramethyl-1,2-bis(mesyloxy)disiloxane (IV).



When (I) is heated for 1 h at 200° the signal of the protons of the CH₃SO₂O group appears in its PMR spectrum (δ 2.78 ppm) [3]. The thermolysis of (I) proceeds slowly. Thus, after heating for 30 h at 200° or for 2 h at 240° the PMR spectrum of the pyrolyzate retains the

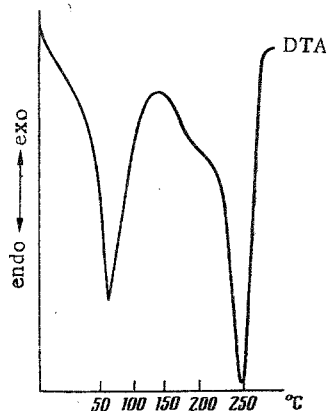


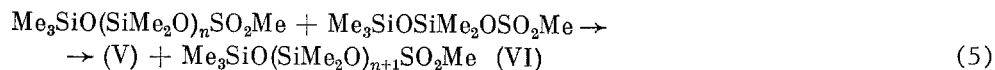
Fig. 1. DTA curve of bis(trimethylsilyl) sulfate (I).

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signal of the protons of the starting (I) (δ 0.35-0.37 ppm). Among the thermolysis products of (I) at 200-250° were identified (II) (20% yield) and (IV) (10%), and also trimethylsilyl methylsulfonate (V) (55%), which testifies to the competing progress of the thermolysis of (I) in two directions.

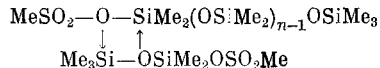


Sulfonate (V) is apparently formed along with oligomer (VI) via reactions of the type



$n = 1, 2, 3$, etc.

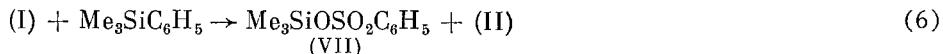
which proceed via the intermediate four-membered complex



The thermolysis of (I) is activated by either metallic Na or K, in whose presence it proceeds at a lower temperature, while the yield of hexamethyldisiloxane increases to 70%. Here the alkali metal is practically not consumed. The metals Mg, Al, Cu, Zn, and Hg, and also the nonmetals C, Si, P, and S, do not affect the thermolysis of (I) and do not react with it. Methane is evolved (20-30% yield) in the presence of 10 mole % of H_2SO_4 .

The possibility that the thermal decomposition of (I) proceeds by Eq. (1) is confirmed by the ability of (I) to be a donor of SO_3 in the sulfonation of aromatic and heterocyclic compounds [4], and also in the reactions with alkali metal sulfates [5].

Taking into consideration the ability of SO_3 to be inserted at the Si-C bond, including the Si-Ar bond [3, 6], we studied the reaction of (I) with trimethylphenylsilane, which enabled us to obtain trimethylsilyl phenylsulfonate (VII) in 42% yield.



EXPERIMENTAL

The thermolysis of bis(trimethylsilyl) sulfate (I) was studied on a derivatograph manufactured by the MOM firm of the Paulik-Paulik-Erdey system (Hungary), with heating at a rate of 4 and 6 deg/min in a pure N_2 stream (300 ml/min). The PMR spectra were obtained on a Tesla BS-487B spectrometer (80 MHz) in CCl_4 solution and using TMS as the internal standard.

Thermolysis of (I). A charge of 20 g (0.08 mole) of (I) in a flask equipped with a Vigreux column was heated for 2-3 h at a bath temperature of 200-250°. Here 2.7 g (20%) of hexamethyldisiloxane (II) distilled, bp 98-99° (740 mm), n_D^{20} 1.3770, cf. [7]. Fractional distillation of the residue in vacuo gave 7.6 g (55%) of trimethylsilyl methylsulfonate (V), bp 56-58° (2 mm), n_D^{20} 1.4228, d_4^{20} 1.0945, cf. [8]. Found: C 28.40; H 7.22; S 18.89; Si 16.70%; mol. wt. (cryoscopically in benzene) 168; (acidimetrically [3]) 172. $\text{C}_4\text{H}_{12}\text{O}_3\text{SSi}$. Calculated: C 28.57; H 7.14; S 19.05; Si 16.66%; mol. wt. 168. The hydrolysis of (V) gave (II), bp 99° (740 mm), n_D^{20} 1.3763. Found: C 44.40; H 11.04; Si 34.46%. $\text{C}_6\text{H}_{18}\text{OSi}_2$. Calculated: C 44.44; H 11.11; Si 34.56%. In addition, we isolated 1.3 g (10%) of tetramethyl-1,2-bis(mesyloxy)disiloxane (IV), bp 170-172° (3 mm), n_D^{20} 1.4340, d_4^{20} 1.3508. Found: C 22.09; H 5.64; S 19.73; Si 17.27%, mol. wt. (cryoscopically in benzene) 312. $\text{C}_6\text{H}_{18}\text{O}_7\text{S}_2\text{Si}_2$. Calculated: C 22.36; H 5.59; S 19.87; Si 17.39%; mol. wt. 322.

Thermolysis of (I) in the Presence of an Alkali Metal. To 0.8 g (0.035 g-atom) of molten Na was added at 150°, in an N_2 atmosphere, 10 g (0.04 mole) of hot (I). Here 4.6 g (68%) of (II) distilled, bp 97°, n_D^{20} 1.3790.

Analogous results were obtained when metallic K was used.

Reaction of (I) with Trimethylphenylsilane. A mixture of 7.2 g (0.03 mole) of (I) and 5 g (0.033 mole) of $\text{Me}_3\text{SiC}_6\text{H}_5$ was heated in a flask, equipped with a Vigreux column, under reduced pressure (400 mm) at 175-210° (bath temperature) until (II) ceased to distill (3.3 g, 68%). Fractional distillation in vacuo gave 2.9 g (42%) of trimethylsilyl phenylsulfonate

(VII), bp 135° (3 mm), cf. [9]. Found: C 46.39; H 6.09; S 14.00; Si 12.16%. C₉H₁₄O₃SSi. Calculated: C 46.95; H 6.09; S 13.91; Si 12.17%. Infrared spectrum (ν , cm⁻¹): 770, 860, 1260 (SiMe₃); 1450, 2870 (CH₃); 950, 1105 (SiOS); 1190, 1350 (SO₂); 700, 750, 1485, 1590, 3075 (C₆H₅). PMR spectrum (δ , ppm): 0.44 s, 7.44-7.84 m.

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CONCLUSIONS

1. Based on the differential thermal analysis data, the chemical changes of bis(trimethylsilyl) sulfate begin at 150-170° and the formation of volatile thermolysis products at 192-200°. Among the thermolysis products were identified hexamethyldisiloxane, trimethylsilyl methylsulfonate, and tetramethyl-1,2-bis(mesyloxy)disiloxane.

2. In the presence of either metallic Na or K the thermolysis of bis(trimethylsilyl) sulfate leads only to the formation of hexamethyldisiloxane.

3. The reaction products of bis(trimethylsilyl) sulfate with trimethylphenylsilane are trimethylsilyl phenylsulfonate and hexamethyldisiloxane.

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REACTION OF FLUORINE GAS WITH IMINOESTERS OF PERFLUOROCARBOXYLIC ACIDS

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N-Fluoroiminoesters are usually obtained from other N-fluoroimino acid derivatives and primarily from their acid fluorides [1]. The synthesis of these compounds by the direct fluorination of the corresponding iminoesters is not known. Only the example of obtaining the ethyl ester of N-fluoroimino-p-fluorobenzoic acid by reacting trifluoromethyl hypofluorite with the iminoester of this acid is described [2].

We studied the possibility of converting the iminoesters of perfluorocarboxylic acids to the corresponding N-fluoroiminoesters.

The fluorination of the methyl ester of iminotrifluoroacetic acid, diluted with fluorine, at -15 to -10°C ended in the explosive decomposition of the reaction products. Evidently the iminoester, under the influence of the HF liberated under the experimental conditions, undergoes Pinner cleavage with the formation of the corresponding amide [3].

As is known, amides when fluorinated give N,N-difluoroamides, which in the presence of

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