

THERMAL DECOMPOSITION OF $(\text{CH}_3)_2\text{SnX}_2$ ($\text{X} = \text{F}, \text{SO}_3\text{F},$ OR SO_3CF_3)

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ABSTRACT

The TG and DTA of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$, $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{CF}_3)_2$, and $(\text{CH}_3)_2\text{SnF}_2$ were carried out under a dynamic nitrogen atmosphere. The decomposition of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ proceeds via $(\text{CH}_3)_2\text{SnF}(\text{SO}_3\text{F})$ ultimately giving SnO_2 . $(\text{CH}_3)_2\text{SnF}_2$, however, decomposes concurrently with sublimation near 360°C , whereas $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{CF}_3)_2$ first loses C_2F_4 , forming the transient species $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{CF}_3)(\text{SO}_3\text{F})$ between 120 and 310°C , after which the product appears to sublime in the range 310 – 450°C .

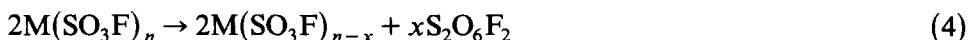
INTRODUCTION

Metal fluorosulfates decompose thermally by several routes such as those shown in the following reactions



Fluorosulfates in groups 2 and 12 usually thermally decompose by reaction (1) or (2). This fact has been attributed to a strong polarizing influence of the metal cation and to a tendency towards an increased coordination number [1–3]. In the presence of large amounts of SO_3 , Goubeau and Milne found that reaction (3) was favored [3]. Based on the amount of $\text{S}_2\text{O}_5\text{F}_2$ obtained during various decompositions, they concluded that strong covalent bonding between the metal cation and the fluorosulfate anion enhanced the proportion of $\text{S}_2\text{O}_5\text{F}_2$ produced.

A fourth thermal decomposition process involving d-block metal fluorosulfates is represented by the reaction



The only proven examples of fluorosulfates which yield bis(fluorosulfuryl)-peroxide ($\text{S}_2\text{O}_6\text{F}_2$) during pyrolysis are $\text{Ag}(\text{SO}_3\text{F})_2$ [4] and $\text{Pd(II)[Pd(IV)-}(\text{SO}_3\text{F})_6$ [5].

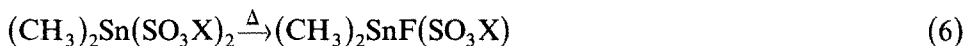
Trifluoromethane sulfonates characteristically decompose thermally to yield metal fluorides [6,7] according to the reaction



A recent study of the thermal decomposition of $\text{B}(\text{SO}_3\text{CF}_3)_3$ detected BF_3 , SO_2 , COF_2 , $(\text{CF}_3\text{SO}_2)_2\text{O}$, $\text{CF}_3\text{SO}_2\text{OCF}_3$ and B_2O_3 among the products [8].

Our interest in this paper was primarily focussed on the thermal decomposition of organotin fluorosulfates and trifluoromethane sulfates for two reasons: firstly, organometallic tin fluorosulfates have been the subject of considerable recent attention involving a variety of spectroscopic techniques [9–12]; and secondly, these organotin derivatives are readily prepared by simple solvolysis reactions [13,14] in the appropriate acids, usually at room temperature.

Two possible thermal decomposition processes may be anticipated for $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{X})_2$, where $\text{X} \equiv \text{F}$ or CF_3 . One is the stepwise cleavage of the tin–oxygen bond with concomitant elimination of either SO_3 or SO_2 and COF_2 , according to the reactions



Another process which might be expected is the simultaneous cleavage of the tin–carbon and tin–oxygen bonds accompanied by the formation of a variety of volatiles such as HF , COF_2 , $\text{S}_2\text{O}_5\text{F}_2$, SO_2F_2 , SO_3 , SO_2 and possibly C_2H_6 . Because $(\text{CH}_3)_2\text{SnF}_2$ is a possible intermediate in the thermal decomposition of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ and $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{CF}_3)_2$, studies of its thermal decomposition became an additional objective. We report here the results of our thermoanalytical study of the three $(\text{CH}_3)_2\text{SnX}_2$ compounds.

EXPERIMENTAL

The TG curves were obtained using a Perkin–Elmer TGS-2 thermobalance employing an *X–Y* plotter for data recording. A Deltatherm V Model D8100 DTA/DSC instrument was used to obtain the DTA curves. In a glovebox (Vacuum Atmospheres, Dri Lab, Model HE-493, filled with flowing dry nitrogen) samples of 2–3 mg size were loaded into either an aluminum capsule (cylindrical, 9 mm long $\times$ 3.5 mm diameter, from Lüdi Cie Metallwarenfabriken, CH-9230, Flawiu, Switzerland) or a silver capsule (cylindrical, 5 mm long $\times$ 3 mm diameter, from Sanda Incorporated, Philadelphia, PA). The open end of each capsule was crimped closed with pliers before removal from the glovebox in order to minimize contact of the samples with air. Immediately prior to pyrolysis of the sample capsules, a

pin-hole was introduced to permit volatile products to escape. Furnace heating rates of 5 and 10 °C min⁻¹ were employed and sample capsules were maintained under a dynamic, dry nitrogen atmosphere (ca. 40 ml min⁻¹) during both TG and DTA runs. A Perkin-Elmer Model 1330 IR spectrophotometer was used to obtain IR spectra with samples either pressed between AgBr windows (Harshaw Chemicals) or mulled with Nujol. Carbon and hydrogen analyses were carried out by Atlantic Microlab Inc., Norcross, GA.

The (CH₃)₂SnF₂ and (CH₃)₂Sn(SO₃CF₃)₂ samples were prepared according to the literature [13,14]. Purity was checked by IR spectroscopy and elemental analyses. A sample of (CH₃)₂Sn(SO₃F)₂ was kindly supplied by Professor F. Aubke of the University of British Columbia, Canada. The hygroscopic solids were handled in the glove box and volatiles produced during static pyrolysis reactions were manipulated using conventional vacuum line techniques. Static pyrolysis reactions were carried out in Pyrex reaction vessels of about 60 ml capacity fitted with a Teflon vacuum valve (Kontes). The valved end of the vessel was cooled with a stream of air during pyrolysis. Volatile products were collected periodically in the vacuum line during each pyrolysis to minimize undesirable side reactions of products formed in the pyrolysis.

RESULTS AND DISCUSSION

The thermoanalytical curves representing (CH₃)₂Sn(SO₃F)₂ are shown in Fig. 1. The TG curve is characterized by two major mass-loss regions. The first decomposition step, starting near 175 °C and extending to about 300 °C, involves a mass loss of about 24%, consistent with the release of one SO₃. The onset of the second decomposition is near 325 °C and appears to be complete at 480 °C. The total mass loss at that point (ca. 54%) indicates that conversion to SnO₂ has occurred.

Static pyrolyses of (CH₃)₂Sn(SO₃F)₂ samples were carried out in an attempt to verify indications concerning chemical processes suggested by the TG results. Pyrolysis of a sample (132.8 mg, 0.38 mM) at 220 ± 10 °C for 30 min gave 96.8 mg, 0.36 mM, of the intermediate (CH₃)₂SnF(SO₃F). Elemental analyses were in reasonable agreement with the formulation of the intermediate. The IR spectra of the volatiles produced during pyrolysis confirmed the presence of SO₃ (γ₁, 1070; γ₂, 1330 cm⁻¹) accompanied by a small amount of SO₂ (γ_s, 1150; γ_a, 1360 cm⁻¹). The IR spectrum of the product closely resembles that of (CH₃)₂SnCl(SO₃F) [13]. When the time of the pyrolysis was extended to 90 min at 220 ± 10 °C to determine if a second SO₃-loss step occurred, further mass loss resulted by analysis of the residue gave very low results for carbon and hydrogen. It thus appears that Sn-C bond cleavage, either directly or possibly through an SO₃ insertion

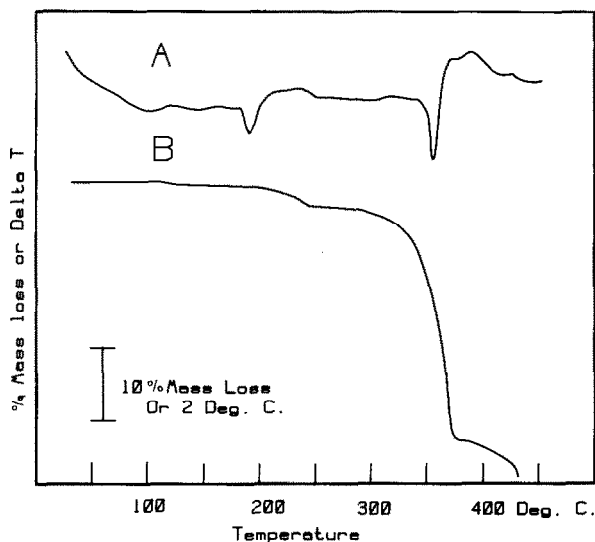
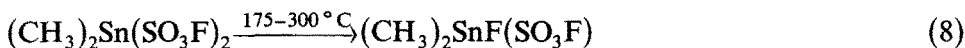


Fig. 1. Thermal decomposition of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$: A, DTA curve; B, TG curve.

step, becomes a dominant feature of the decomposition chemistry with prolonged heating. Unavoidable side reactions due to reactive volatile products which may include HF and $\text{S}_2\text{O}_5\text{F}_2$ could also play an important role in the loss of the methyl groups. We conclude that the major processes in the pyrolysis of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ are represented by the reactions



The strong similarity between the IR spectra of $(\text{CH}_3)_2\text{SnF}(\text{SO}_3\text{F})$ and $(\text{CH}_3)_2\text{SnCl}(\text{SO}_3\text{F})$ suggest that their structures are also similar. On the basis of IR, Raman and Mössbauer results, Aubke and coworkers [14] suggest a bent $(\text{CH}_3)_2\text{Sn}$ grouping and the presence of weak fluorine bridging in the structure of the chlorine derivative which they found to be thermally stable up to 108°C . The fact that the fluorine derivative appears to be stable to a considerably higher temperature suggests that the fluorine bridging is probably stronger in it.

The DTA curve for $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ (Fig. 1, curve A) also shows two clearly defined thermal processes in its decomposition. The first is an endothermic peak centered near 246°C which corresponds to the loss of SO_3 seen in the TG curve. The second, centered near 417°C , is exothermic and seems to be associated with the complete breakdown of the intermediate $(\text{CH}_3)_2\text{SnF}(\text{SO}_3\text{F})$ to SnO_2 .

The DTA and TG curves of $(\text{CH}_3)_2\text{SnF}_2$ are shown in Fig. 2, curves A and B respectively. Decomposition is evident in the TG curve beginning

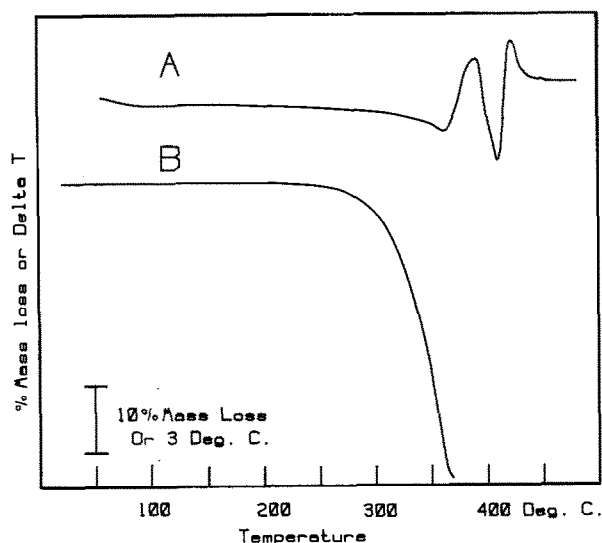


Fig. 2. Thermal decomposition of $(\text{CH}_3)_2\text{SnF}_2$: A, DTA curve; B, TG curve.

near 250°C accompanied by a precipitous mass loss reaching nearly 88% at 375°C . The DTA curve shows two overlapping exo- and endothermic peaks from about 300 to 425°C . The only reasonable explanation is that a thermally induced decomposition is accompanied by sublimation of $(\text{CH}_3)_2\text{SnF}_2$ leaving a small nonvolatile residue from the decomposed part of the sample.

The TG curve of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{CF}_3)_2$ (Fig. 3, curve B) shows mass loss in three steps. The first step (ca. 10% mass loss), occurring over the tempera-

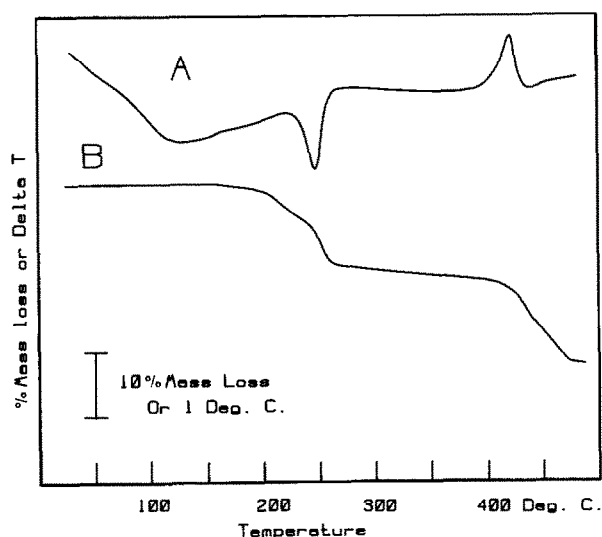
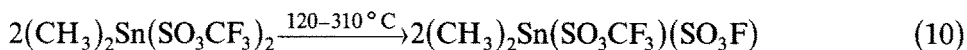


Fig. 3. Thermal decomposition of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{CF}_3)_2$: A, DTA curve; B, TG curve.

ture range 120–310 °C, seems to correspond to the loss of C₂F₄ according to eqn. (10), but a static pyrolysis



at 270 °C in an attempt to prepare (CH₃)₂Sn(SO₃CF₃)(SO₃F) was not successful: a slow continuous mass loss was observed. The second mass-loss step (ca. 69%) occurred from 310 to 375 °C and a third step (ca. 13%) followed from 375 to 435 °C. The DTA curve (Fig. 3, curve A) shows an endothermic feature centered at 195 °C associated with the proposed C₂F₄ elimination and a larger endothermic feature at 353 °C apparently overlapping a broad exothermic peak near 380 °C. Again, this suggests that a combination of decomposition chemistry and sublimation takes place in this temperature range, making further analysis of mass-loss values difficult. In any case the identification of intermediates, such as (CH₃)₂SnF(SO₃CF₃) and (CH₃)₂SnF₂, anticipated in the introduction was not realized.

CONCLUSIONS

Dimethyltinfluoro fluorosulfate was obtained by the pyrolysis of (CH₃)₂Sn(SO₃F)₂ at 220 °C; at higher temperatures it decomposes directly to SnO₂. The thermal decomposition of (CH₃)₂Sn(SO₃CF₃)₂ appears to proceed through transient formation of (CH₃)₂Sn(SO₃CF₃)(SO₃F), but this could not be isolated by static pyrolysis. Dimethyltin difluoride thermally decomposes concurrently with sublimation at 360 °C.

ACKNOWLEDGMENTS

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