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Thermal decomposition of $(CH_3)_2SnSnF_6$ and $(CH_3)_2Sn(SbF_6)_2$

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Abstract

TG and DTA analyses of $(CH_3)_2SnSnF_6$ and $(CH_3)_2Sn(SbF_6)_2$ were carried out under a dry nitrogen atmosphere. The thermal decomposition of $(CH_3)_2SnSnF_6$ proceeds through a known intermediate, $(CH_3)_3SnF$, while that of $(CH_3)_2Sn(SbF_6)_2$ decomposes via complex volatile mixtures of antimony fluorides. The ultimate decomposition product in both cases is SnF_4.

INTRODUCTION

Our recent studies on $(CH_3)_2SnX_2$ (where X = F, SO_3F or SO_3CF_3) revealed interesting intermediates on pyrolysis [1]. While the fluorosulfate derivative decomposes via $(CH_3)_2SnF(SO_3F)$, a stable intermediate which was isolated and characterized, the trifluoromethylsulfate derivative decomposes through a transient intermediate, $(CH_3)_2Sn(SO_3CF_3)(SO_3F)$, which we were not able to isolate due to rapid mass loss in a narrow temperature range. The thermal decomposition of both derivatives was clearly defined as involving first the cleavage of a tin-oxygen bond followed by cleavage of a tin–carbon bond.

In the present work our interest was focussed on the thermal decomposition of dimethyltin derivatives containing strong Main-Group–fluorine bonds. We have selected dimethyltin(IV) hexafluorostannate(IV), $(CH_3)_2SnSnF_6$, and dimethyltin(IV) bis(hexafluoroantimonate(V)), $(CH_3)_2Sn(SbF_6)_2$, for pyrolysis studies. Our reasons for selecting these two derivatives are: (a) these two dimethyltin compounds have been studied extensively and are well-characterized by a variety of spectroscopic techniques [2–4]; (b) the SbF_6 derivative is considered to be a representative of a family of other derivatives involving singly negative anions such as TaF_6^-, NbF_6^- and CrF_6^-; and (c) the SnF_6 derivative, which is a structural isomer of CH_3SnF_3, has a dinegative anion.

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Several possible decomposition processes might be anticipated for $(CH_3)_2SnSnF_6$. The first is a simple decomposition back to its starting components

$$(CH_3)_2SnSnF_6 \xrightarrow{\Delta} (CH_3)_2SnF_2 + SnF_4 \tag{1}$$

A variation on eqn. (1) involves first a conversion to the isomeric intermediate CH_3SnF_3, followed by decomposition to the same final products

$$(CH_3)_2SnSnF_6 \xrightarrow{\Delta} 2[CH_3SnF_3] \rightarrow (CH_3)_2SnF_2 + SnF_4 \tag{2}$$

Alternatively, redistribution of CH_3 and F groups in the intermediate could also lead to $(CH_3)_3SnF$ and SnF_4

$$3(CH_3)_2SnSnF_6 \xrightarrow{\Delta} 2(CH_3)_3SnF + 4SnF_4 \tag{3}$$

As $(CH_3)_2SnF_2$ is known to undergo simultaneous sublimation and decomposition above 300 °C [1] and it is probable that $(CH_3)_3SnF$ behaves similarly (m.p. 375 °C (d) [2]), TG mass-loss curves may provide information on the decomposition reaction.

There are also several possible thermal decomposition processes which may be anticipated for $(CH_3)_2Sn(SbF_6)_2$

$$(CH_3)_2Sn(SbF_6)_2 \xrightarrow{\Delta} (CH_3)_2SnF_2 + 2SbF_5 \tag{4}$$

$$(CH_3)_2Sn(SbF_6)_2 \xrightarrow{\Delta} (CH_3)_2SnFSbF_6 + SbF_5 \tag{5}$$

$$(CH_3)_2Sn(SbF_6)_2 \xrightarrow{\Delta} SnF_4 + \text{volatile Sb-containing species} \tag{6}$$

Equation (4) represents decomposition to the starting materials (similar to that suggested for $(CH_3)_2SnSnF_6$), while the route in eqn. (5) proceeds through the intermediate $(CH_3)_2SnFSbF_6$, like that seen in the analogous fluoro fluorosulfate [1]. The third decomposition process (eqn. (6)) anticipates the formation of a mixture of volatile antimony fluorides, antimony methylfluorides and a residue of involatile SnF_4.

We report here the results of our thermal decomposition study of the dimethyl tin(IV) fluoro-compounds, $(CH_3)_2SnSnF_6$ and $(CH_3)_2Sn(SbF_6)_2$.

EXPERIMENTAL

The $(CH_3)_2SnSnF_6$ and $(CH_3)_2Sn(SbF_6)_2$ starting compounds were prepared following the methods published in the literature [2]. All hygroscopic solids were handled in a glove box under dry nitrogen. Volatile materials produced during static pyrolysis reactions were manipulated using conventional vacuum-line techniques [5]. Static thermal decomposition reactions were carried out in Pyrex reaction vessels of about 60 ml capacity equipped with Kontes Teflon valves. The valved end of the vessel was cooled with a stream of air during thermolysis. During each pyrolysis, volatile products were transferred periodically into the vacuum line to minimize undesirable side reactions of the products formed during pyrolysis. Carbon and hydrogen analyses were performed by Atlantic Micro Labs.

TG (thermogravimetry) curves were obtained using a Perkin–Elmer TGS-2 thermobalance employing an *X–Y* plotter for data recording. A Deltatherm Model D 8100 DTA/DSC instrument was used to obtain the DTA (differential thermal analysis) curves. In a glove box (Vacuum Atmospheres, Dri Lab Model HE-493) filled with flowing dry nitrogen, samples of 4–5 mg were loaded into cylindrical silver capsules, 9 mm long and 3 mm in diameter, supplied by Refining System Co. (P.O. Box 72466, Las Vegas, NV 89170 U.S.A.). The open end of each capsule was crimped closed with pliers before removal from the glove box 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 (approximately 40 ml min^{-1}) during both TG and DTA runs. A Perkin–Elmer Model 1330 IR spectrometer was used to obtain IR spectra with samples either pressed between AgBr windows (Harshaw Chemical) or mulled with Nujol.

RESULTS AND DISCUSSION

The TG and DTA curves of $(CH_3)_2SnF_2$ [1] and $(CH_3)_2SnSnF_6$ are shown in Figs. 1 and 2, respectively. The TG curve of $(CH_3)_2SnSnF_6$ shows a continuous mass loss in the temperature range 100–450 °C. The initial mass loss is rather slow with a total loss of 32% registered up to 375 °C. The

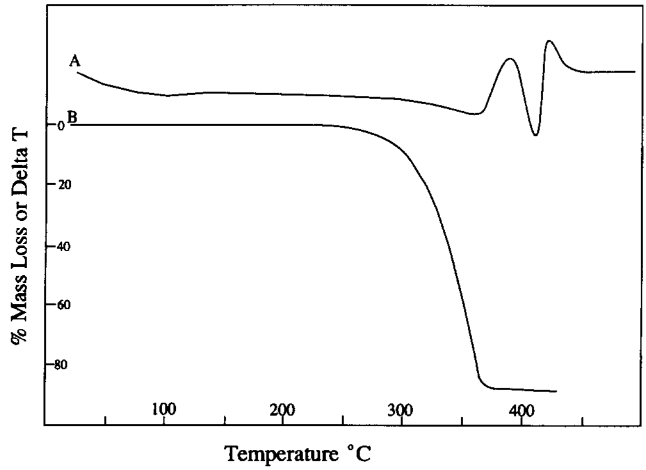

Fig. 1. Thermal decomposition of $(CH_3)_2SnF_2$: curve A, DTA curve, curve B, TG curve.

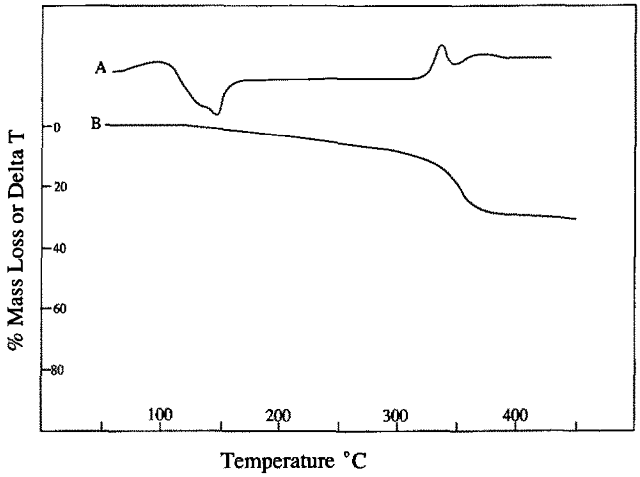

Fig. 2. Thermal decomposition of $(CH_3)_2SnSnF_6$: curve A, DTA curve; curve B, TG curve.

mass loss curve for $(CH_3)_2SnSnF_6$ is not consistent with a well-defined decomposition process leading to $(CH_3)_2SnF_2$ and SnF_4 as in eqn. (1). The calculated mass loss for that decomposition is 48.9%, assuming sublimation of $(CH_3)_2SnF_2$ which is known [1] to begin to sublime and decompose with a precipitous mass loss at around 300 °C (Fig. 1) and to exhibit exo- and endothermic peaks in the DTA from 300 to 425 °C. The absence of such features for this decomposition process rules out the route described by eqn. (1).

Thermal decomposition according to eqn. (2) also seems unlikely because the observed mass loss (approx. 32%) is considerably less than that expected for eqn. (2) (around 49.2%). In addition, the DTA curve clearly indicates an exothermic peak at around 350 °C which is close to the reported [6] decomposition temperature for $(CH_3)_3SnF$ of around 360 °C. As CH_3SnF_3, the covalent isomer of $(CH_3)_2SnSnF_6$, decomposes at 321°C [6] and no decomposition processes appear around that temperature in the DTA curve (Fig. 2), we conclude that CH_3SnF_3 is not one of the products of pyrolysis. From the above discussion, the only remaining decomposition route for $(CH_3)_2SnSnF_6$ is that according to eqn. (3), leading to $(CH_3)_3SnF$ and SnF_4. The two features in the DTA curve near 135 °C and near 350 °C seem to represent, first the decomposition of $(CH_3)_2SnSnF_6$, probably to $(CH_3)_3SnF$ and SnF_4, and then decomposition of the intermediate $(CH_3)_3SnF$ at around 350 °C. Although the mass loss profile in the TG curve is not clear cut, it does show an overall mass loss of about 36% which is close to the calculated value of 32.3% expected from eqn. (3). Our attempt to isolate and characterize the intermediate product was not successful due to the absence of clearly defined stages in the mass loss curve. However, an IR spectrum of the residue obtained after pyrolysis confirmed the presence of SnF_4.

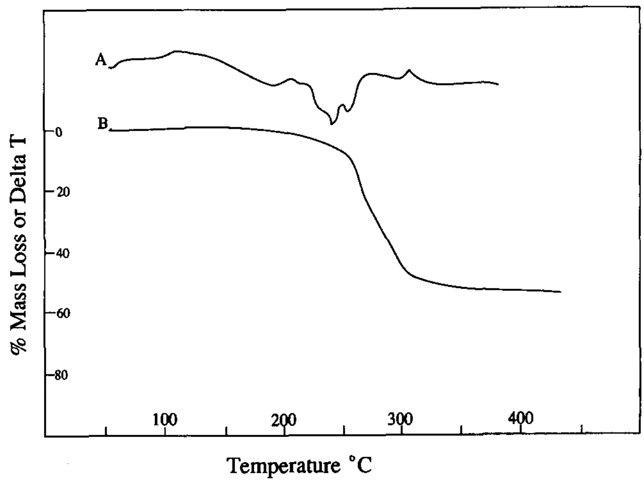

Fig. 3. Thermal decomposition of $(CH_3)_2Sn(SbF_6)_2$: curve A, DTA curve; curve B, TG curve.

The TG and DTA curves of $(CH_3)_2Sn(SbF_6)_2$ are shown in Fig. 3. Thermal decomposition is first evident near 180 °C, and an almost continuous mass loss up to about 300 °C is seen in the TG curve; the curve clearly does not resemble that of $(CH_3)_2SnF_2$. As SbF_5 has a boiling point of 142.6 °C [5], if formed in the decomposition it would be volatile in this temperature range, resulting in a mass loss larger than the one observed. This suggests that the decomposition does not follow eqn. (4). The smooth, continuous mass loss in the TG curve seems inconsistent with a possible step-wise loss of SbF_5 via $(CH_3)_2SnFSbF_6$, as in eqn. (5), followed by loss of another SbF_5 eventually giving SnF_4. The DTA curve of $(CH_3)_2Sn(SbF_6)_2$ shows a number of endothermic peaks near 250 °C and an exothermic peak near 315 °C. This suggests that the decomposition process produces a complex mixture of intermediates, perhaps containing complex species such as $Sb_2F_9^-$, $Sb_2F_{11}^-$, etc., along with other volatile intermediates. The formation of species containing $Sb_2F_{11}^-$ has been proposed to accompany the thermal decomposition of $O_2^+SbF_6^-$ [7]. Thus, the most satisfactory decomposition pathway is that according to eqn. (6). An infrared spectrum of the residue confirms the presence of SnF_4. Though the calculated mass loss (approx. 68.6%) did not exactly match that observed (around 60%), it is possible that reactive antimony fluorides formed during decomposition attack the sample capsule forming involatile silver fluoride (b.p. > 1100 °C), thereby causing some error in the observed mass loss.

CONCLUSIONS

Dimethyltin(IV) hexafluorostannate(IV) decomposes through an intermediate believed to be $(CH_3)_3SnF$ which could not be isolated by static pyrolysis due to continuous mass loss. Pyrolysis of dimethyltin(IV) bis(hexafluoroantimonate(V)) causes a complex decomposition process, leading to SnF_4 and unidentified antimony fluorides.

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