Thermal Decomposition of Distannane

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The kinetics of the thermal decomposition of Sn_2H_6 have been studied in the temperature range of −9 to 52 °C and found to be first order over the entire range. Above 15 °C gas-phase nucleation, similar to that observed in SiH_4 and Ge_2H_6 pyrolyses, leads to erroneously high mass spectrometrically measured concentrations of Sn_2H_6 which precludes obtaining specific reaction rates for the decomposition above this temperature. Arrhenius behavior in the range of −9 to 15 °C leads to an activation energy of $E_a = 1.28 \pm 0.14$ kcal/mol and a preexponential factor of $1.6 \pm 0.5\ s^{-1}$ for the decomposition. No higher tin hydrides were observed which, coupled with the original report of Sn_2H_6 synthesis, indicates that the products are simply Sn(s) and H_2.

Introduction

In his reports describing the preparation of SnH_4 by the reaction of stannite and hydroborate in aqueous acid, Jolly[1,2] observed the additional formation of small amounts of Sn_2H_6, the ratio of the yields being $[Sn_2H_6]/[SnH_4] \approx 0.05$. Jolly also noted the extreme thermal instability of Sn_2H_6 above −112 °C, the decomposition products being Sn and H_2.

During our studies[3] of the vacuum-ultraviolet photodecomposition of SnH_4, we have observed the formation of milliTorr quantities of Sn_2H_6 with a quantum yield of 0.06. When the photodecomposition of SnH_4 was stopped, it was possible to follow mass spectrometrically the thermal decomposition of Sn_2H_6 and examine the kinetics as a function of temperature. Herewith is a report of our results.

Experimental Section

The apparatus, which consists of a xenon resonance lamp and a photolysis cell coupled to a magnetic-sector mass spectrometer, has been described in detail in an earlier publication.[3]

Each experiment consisted of a photolysis of SnH_4 that was of sufficient duration to produce easily measurable quantities of Sn_2H_6. Then, on termination of the irradiation, the thermal decay of the concentration of Sn_2H_6 in the photolysis cell was monitored by following mass spectrometrically the ion current at $m/z = 240$ amu as a function of time.

The ion current at 240 amu is comprised of contributions (≥0.1%) from 18 isotopic species having the formula $Sn_2H_x^+$ ($x = 0-6$) with 71% of the total current being due to $^{118}Sn^{120}SnH_2^+$ (51.2%) and $^{120}Sn_2^+$ (19.7%). As we have found no indication of the presence of higher tin hydrides, we conclude that all of the ions at 240 amu are produced by electron impact on Sn_2H_6 and that, therefore, this ion-current is proportional to the concentration of Sn_2H_6 in the photolysis cell.

In view of the fact that both SnH_4 and H_2 are present in the photolysis cell in much larger amounts than could be expected from the decomposition of such small amounts of Sn_2H_6, it was impossible to determine whether these compounds were products of the thermal decomposition. On the basis of Jolly's work[1,2] and our failure to observe higher tin hydrides, however, we assume the sole products to be Sn and H_2.

All photolyses of SnH_4 to produce Sn_2H_6 were carried out by the 147 nm irradiation of a mixture of 1.0 Torr of SnH_4 in 14.0 Torr of He. The thermal decompositions were studied at 15 temperatures in the range of −8.7 to 51.6 °C. The reaction temperature was increased above ambient by means of an electrical heating tape wound around the reaction cell; the temperature was reduced below ambient by flowing cold air, produced by prior passage through a coil immersed in liquid N_2, around the cell. The temperature of the gas in the cell was measured immediately after the irradiation was stopped (i.e., at $t = 0$) using a Ni−Cr versus Ni−Al (chromel-alumel) thermocouple that was mounted through a stainless steel flange attached to the rear end of the cylindrical cell.

Calculation of the Knudsen number 4 for our experimental conditions indicates that the flow out of the photolysis chamber and into the ion source is in the intermediate region between molecular and viscous flow. Nevertheless, the leak rate of any species out of the photolysis cell is proportional to the concentration of that species in the cell and may therefore be represented by a first-order leak rate constant, λ. The leakage of Xe from the cell when it contains 15.0 Torr of a mixture of 1% Xe and 99% He may therefore be represented by the expression

$$[^{132}Xe] = [^{132}Xe]_0 e^{-\lambda t} = i_{132} = i^0_{132} e^{-\lambda t} \qquad (1)$$

where $[^{132}Xe]_0$ is the initial concentration of ^{132}Xe and i_{132} and i^0_{132} are the ion currents of $^{132}Xe^+$ at time t and at zero time, respectively. A logarithmic plot, according to (1), of Xe decay from a Xe−He mixture is shown in Figure 1, from which is derived the value $\lambda = (3.62 \pm 0.005) \times 10^{-4}\ s^{-1}$. Examination of the leakage rates of Ge_2H_6 ($M = 148$ amu) and C_4F_8 ($M = 200$ amu) from 15 Torr of the respective 1% mixtures in He shows that λ decreases slightly with increasing mass, extrapolating to a value of $\lambda = (3.5 \pm 0.5) \times 10^{-4}\ s^{-1}$ at $m/z = 240$ amu. We did not measure the temperature dependence of λ, but, on the basis of the flow characteristics, we do not expect it to be significant. In viscous flow, λ would vary with $T^{-1/2}$ and in molecular flow with $T^{1/2}$. Over our entire temperature range of 60 K the maximum variation of λ in either viscous flow or molecular flow due to temperature would be 10%; however, the actual variation obtained in our system for flow in the intermediate region should be much less since the temperature effects in viscous and molecular flow operate in opposite

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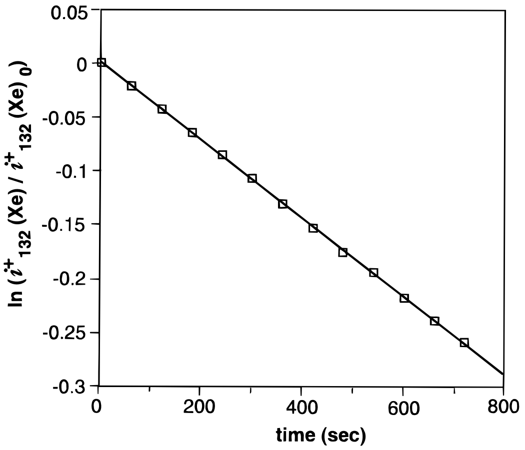

Figure 1. Decay of ion current of ^{132}Xe from 1% Xe in He at 15 Torr total pressure.

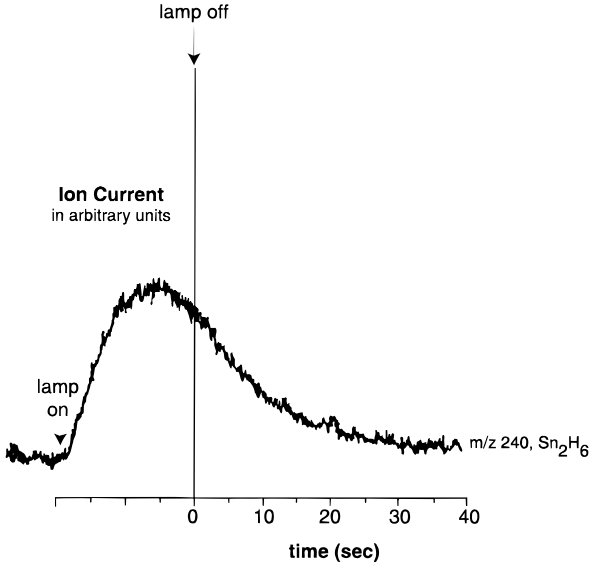

Figure 2. Recorder tracing of the growth and decay of ion current at $m/z = 240$ amu During and after photolysis of SnH_4.

directions. Moreover, as will be shown, the temperature range pertinent to the homogeneous gas-phase decomposition of Sn_2H_6 is −9 to 15 °C, for which a maximum possible variation of λ (either pure viscous or pure molecular flow) due to temperature is 4%; with flow in the intermediate region it is probably much less than this and is, hence, negligible.

SnH_4 was synthesized by the reduction of $SnCl_4$ with $LiAlH_4$ in $(C_2H_5)_2O$,[5,6] the details of which are described in our previous paper.[3]

Results and Discussion

A typical recorder tracing of the ion current at $m/z = 240$ amu versus time, depicted in Figure 2, shows the buildup of Sn_2H_6 during the photolysis of SnH_4 and the subsequent thermal decay after termination of the photolysis. The fact that the concentration of Sn_2H_6 reaches a maximum and subsequently decays prior to termination of the photolysis is due to the decomposition of Sn_2H_6 during the photolysis and the buildup of a tin film on the window of the reaction cell which significantly decreases the light intensity incident on the reaction mixture.[3]

In Figure 3 is shown a plot of $\ln(i_{240}/i^0_{240})$ as a function of time (at 1.5°) *after* the termination of the photolysis. The excellent linear behavior, over about 90% of the conversion of Sn_2H_6, demonstrates the first-order nature of the decomposition.

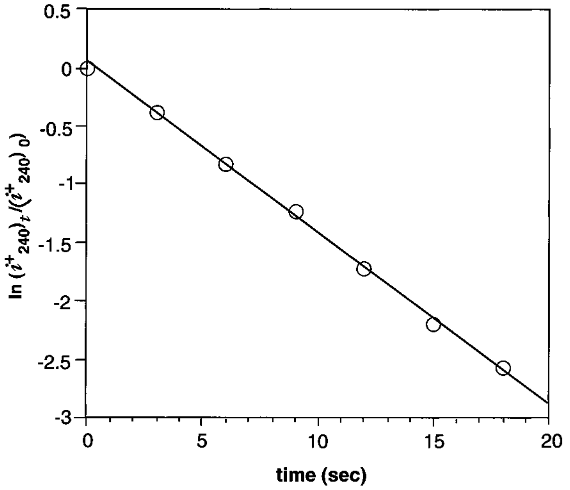

Figure 3. First-order plot of thermal decomposition of Sn_2H_6 at 1.5 °C.

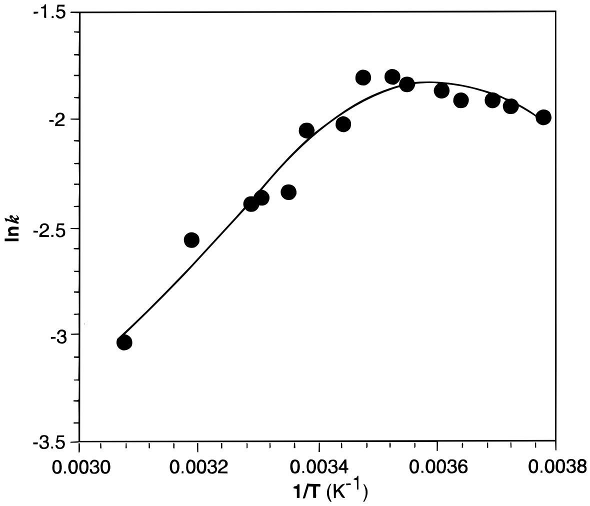

Figure 4. Arrhenius plot of observed first-order rate constants for Sn_2H_6 Decomposition in the range of −9 to 52 °C.

Therefore, we may describe the kinetics in the reaction chamber by the expression

$$\frac{1}{i^0_{240}}\frac{di_{240}}{dt} = \frac{1}{[Sn_2H_6]_0}\frac{d[Sn_2H_6]}{dt} = -(k+\lambda)\frac{[Sn_2H_6]}{[Sn_2H_6]_0} \quad (2)$$

or after integration

$$\ln\frac{i_{240}}{i^0_{240}} = \ln\frac{[Sn_2H_6]}{[Sn_2H_6]_0} = -(k+\lambda)t \quad (3)$$

where k is the first-order rate constant for the decomposition and λ is the leak rate constant which, as described earlier, has the value of $(3.5 \pm 0.5) \times 10^{-4}$ s^{-1}. From the slope in Figure 3, and the value of λ described earlier, we derive a value of 0.146 s^{-1} for the first-order rate constant of the thermal decomposition at 1.5 °C.

First-order rate constants for the decomposition were obtained from plots similar to that in Figure 3 at 15 different temperatures in the range of −9 to 52 °C. In all cases the value of the leak rate constant, λ, was significantly less than 1% of the value of the rate constant, k. An Arrhenius plot of ln k versus $1/T$ is shown in Figure 4 where it may be seen that the decomposition does not follow simple Arrhenius behavior over the entire temperature range studied. At the lower temperatures k

increases with temperature, as expected, but above 15 °C, *k* decreases as the temperature is increased.

Arrhenius plots similar in shape to that in Figure 4 have been observed in the decomposition of other group IV hydrides. Scott et al.[7] report a similar Arrhenius behavior in a study of film growth in the chemical vapor deposition of SiH_4 at a gas temperature of 650 °C when there is cooling of the solid substrate. Eres et al.[8] report a similar form of Arrhenius plots in a study of film growth in the pyrolysis of Ge_2H_6 in the temperature range 380−600 °C. The most likely explanation for this complex Arrhenius behavior in film formation from gas-phase pyrolysis has been suggested by Sladek,[9] who pointed out that, as the frequency of gas-phase collisions increases with temperature, nucleation leading to powder formation in the gas phase begins to predominate over diffusion of reaction products to the walls, thus slowing formation of the film.

While the similarity of the Arrhenius plots strongly suggests that a phenomenon similar to that observed in the chemical vapor deposition of SiH_4 and Ge_2H_6 occurs also in the thermal decomposition of Sn_2H_6, the experiments are not analogous. In the chemical vapor deposition experiments the growth rate of the solid film was measured while in the thermal decomposition of Sn_2H_6 we have measured the rate of change in the concentration of Sn_2H_6. In the chemical vapor deposition experiments gas-phase nucleation results in slower buildup of film. In our system, nucleation leads to formation of clusters in the gas phase, some of which will be transmitted into the mass spectrometer ionization chamber. The resulting ionization would presumably create a number of ion fragments containing two Sn atoms. Over 90% of the ion current at $m/z = 240$ amu, which we use to monitor Sn_2H_6, is comprised of Sn_2^+, Sn_2H^+, and $Sn_2H_2^+$ ions, and these are fragments to be expected from the ionization of clusters formed in the gas-phase nucleation. The ionized cluster fragments would contribute to the ion current at $m/z = 240$ amu, and this effect would be manifested in our system as an apparent slowdown of the decomposition and a decrease in the rate constant with increasing temperature.

On the basis of the above discussion, we believe that gas-phase nucleation is not significant below 15 °C and therefore that below this temperature our data reflect accurately the thermal decomposition of Sn_2H_6. Accordingly, in Figure 5 is shown an Arrhenius plot of ln *k* versus 1/*T* over the range of −9 to 15 °C. From this plot we derive the following values for the activation energy and preexponential factor.

$$E_a = 1.28 \pm 0.14 \text{ kcal/mol} \qquad A = 1.6 \pm 0.5 \text{ s}^{-1}$$

The kinetic parameters shown above lead to a half-life of Sn_2H_6 at room temperature of about 4 s, which accords with Jolly's[1,2] observation of the extreme thermal instability of this compound.

The observed activation energy is very low, and the preexponential factor is many orders of magnitude smaller than those typical of homogeneous gas-phase decompositions.[10] This suggests strongly that the observed decomposition of Sn_2H_6 is not occurring homogeneously in the gas phase but rather on the surfaces of the reaction chamber. As pointed out many years ago by Hinshelwood,[11] an observed first-order rate constant is based on the fraction of the total number of molecules in the reaction chamber that react per unit time. However, if the reaction is occurring on the chamber surfaces, only those molecules adsorbed, which comprise only a very small fraction of the total present, have a chance to react. This results in a very low observed (or apparent) rate constant and correspondingly low values of the observed Arrhenius parameters. Hinshelwood[11] showed that the true activation energy, E_T, is related to the observed activation energy, E_a, and the energy of desorption, E_D, by the relationship

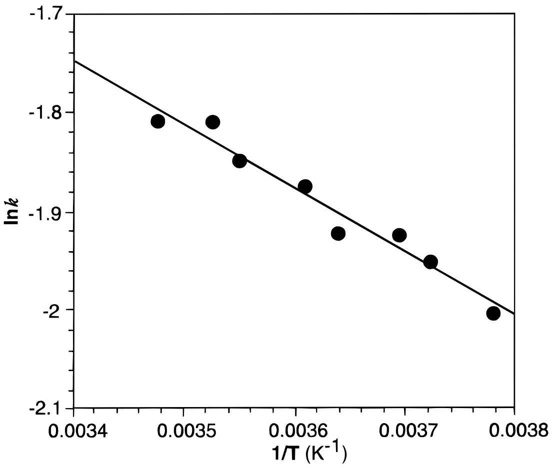

Figure 5. Arrhenius plot of first-order rate constants for Sn_2H_6 decomposition in the range of −9 to 15 °C.

$$E_T = E_a + E_D$$

Hence, our observed value of E_a must be considered only as a lower limit to the true energy of activation.

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