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First Gas-Phase Detection of Dimethylstannylene and Time-Resolved Study of Some of Its Reactions

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Abstract: Using a laser flash photolysis/laser probe technique, we report the observation of strong absorption signals in the wavelength region 450−520 nm (highest intensity at 514.5 nm) from four potential precursors of dimethylstannylene, $SnMe_2$, subjected to 193 nm UV pulses. From GC analyses of the gaseous products, combined with quantum chemical excited state CIS and TD calculations, we can attribute these absorptions largely to $SnMe_2$, with $SnMe_4$ as the cleanest source of the species. Kinetic studies have been carried out by time-resolved monitoring of $SnMe_2$. Rate constants have been measured for its reactions with 1,3-C_4H_6, MeC≡CMe, MeOH, 1-C_4H_9Br, HCl, and SO_2. No evidence could be found for reaction of $SnMe_2$ with C_2H_4, C_3H_8, Me_3SiH, GeH_4, Me_2GeH_2, or N_2O. Limits of less than 10^{-13} cm^3 molecule^{-1} s^{-1} were set for the rate constants for these latter reactions. These measurements showed that $SnMe_2$ does not insert readily into C−H, Si−H, Ge−H, C−C, Si−C, or Ge−C bonds. It is also unreactive with alkenes although not with dienes or alkynes. It is selectively reactive with lone pair donor molecules. The possible mechanisms of these reactions are discussed. These results represent the first visible absorption spectrum and rate constants for any organo-stannylene in the gas phase.

Introduction

Despite the fact that stabilized dialkylstannylenes have been known for 25 years since the preparation of bis(bis(trimethylsilyl)methyl)tin(II), $Sn[CH(SiMe_3)_2]_2$, by Lappert's group in 1976,[1] rather little is known about the simpler organostannylenes such as $SnMe_2$. Certainly the existence of $Sn(CH_3)_2$ is in little doubt since the recording of its IR spectrum, together with that of its deuterio analogue, $Sn(CD_3)_2$, in an argon matrix by Neumann's group in 1982.[2] Neumann has indeed investigated and documented the known chemistry of $SnMe_2$.[3] It appears that although $SnMe_2$ is fairly easy to prepare, it is a reactive transient that does not insert into C−H or C−C bonds, and even its addition to C═C double bonds is unknown. In the presence of many potential reagents it simply polymerizes. Until now such conclusions have been based on inferences from end product analyses, i.e. lack of a specific product in reaction mixtures where $SnMe_2$ may plausibly be assumed to have been generated.

Since in recent years we have been able to generate and study the kinetics of reactions of other members of the heavy carbene family such as $SiMe_2$[4,5] and $GeMe_2$[6] by direct means using time-resolved methods in the gas phase, we decided to turn our attention to $SnMe_2$. The objective of the present study was to create $SnMe_2$ in the gas phase, characterize its visible/UV absorption spectrum, and study the kinetics of some of its characteristic reactions. Although the visible/UV spectrum of $SnMe_2$ is unknown, the low-lying $^1A_1 \rightarrow {}^1B_1$ transition may reasonably be expected to occur in the wavelength region 450−520 nm, by analogy with $GeMe_2$.[6] This argument depends on the similarity of energy spacings in the electronic states of SnH_2 and GeH_2.[7] To provide a more sound basis for this, we decided to calculate the energy of the lowest $S_0 \rightarrow S_1$ electronic transition for $SnMe_2$, using quantum chemical methods.[8,9] The spectrum

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is expected to be broad and featureless, and if it lies in this region, this makes $SnMe_2$ suitable for monitoring in absorption using an argon ion laser.

On the basis of the analogy with our earlier studies[4−6] of $SiMe_2$ and $GeMe_2$, the rational photoprecursors for $SnMe_2$ would be pentamethyldistannane and 1,1-dimethyl-1-stannacyclopent-3-ene. Lack of availability of these compounds led us to screen a number of other potential photoprecursors, viz. $SnMe_4$, Sn_2Me_6, Me_3SnH, and $PhSnMe_2H$. This paper describes our initial efforts, and the first gas-phase kinetic data generated for the species $SnMe_2$.

Experimental Section

The apparatus and equipment for these studies have been described in detail previously.[5a,6] Only essential and brief details are therefore included here. The target reactive transient was produced by flash photolysis of appropriate precursor molecules (see below) using a Coherent Compex 100 exciplex laser operating at 193 nm (ArF fill). Transient species absorptions were monitored in real time by means of a Coherent Innova 90-5 argon ion laser. For species characterization all nine available lines of the probe laser were employed, but for the kinetic studies the argon ion laser was generally only operated at 501.7 or 514.5 nm. Experiments were carried out in a spectrosil quartz cell with demountable windows. The photolysis beam (4 cm × 1 cm cross-section) entered the center of the cell laterally, while the probe beam was multipassed longitudinally along the axis of the cell up to 44 times, giving a maximum absorption path length of ca. 1.7 m. Photolysis laser pulse energies were typically 50−70 mJ with a variation of ±5%. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a BBC microcomputer. This was used to average the decays of typically five photolysis laser shots (at a repetition rate of 1 Hz or less).

Gas mixtures for photolysis were made up containing 10−30 mTorr of the transient precursor, variable pressures of reactive substrates with total pressures made up to 5 or 10 Torr with inert diluent (SF_6). Pressures were measured with capacitance manometers (MKS Baratron). Most measurements were made at room temperature or 296 ± 2 K.

The organotin compounds used in this work were obtained or prepared as follows. Tetramethyltin, $SnMe_4$, was obtained from Ventron at >99.5% purity. Hexamethyldistannane, Sn_2Me_6, was made (in 70% yield) by a coupling reaction of Me_3SnCl with Li metal in THF solution in an ultrasound bath similarly to the method of Mironov and Kravchenko.[10] It was purified by vacuum distillation to better than 95% (by GC analysis). Trimethylstannane, Me_3SnH, was made by the $LiAlH_4$ reduction of Me_3SnCl, in $^nBu_2O$ solution under N_2.[11] The product was collected and purified by low-temperature distillation to >94% purity (by GC analysis). Its identity was confirmed by ^1H and ^{13}C NMR.[12,13] Phenyldimethylstannane was made in a three-step synthesis using well-known procedures. The first step was the Grignard coupling of Me_2SnCl_2 and PhMgBr to give Me_2SnPh_2. This was followed by reaction of the latter with I_2 in CCl_4 to give Me_2SnPhI.[14] The last step was the reduction of the iodide by $LiAlH_4$ in ether solution.[11] Unfortunately the crude $PhSnMe_2H$ was contaminated with a not easily separated compound and could only be obtained in ca. 30% purity. Although this was disappointing, this compound was not crucial to the outcome of this work and we were able to obtain useful information from it despite the impurity. Because of the known hazards of organotin compounds, these were prepared, handled, and vented in fume cupboards.

All gases used in this work were degassed thoroughly prior to use. Commercial samples of reactive substrates used in this work were obtained as follows. Hydrocarbons (all >99%) were from Cambrian gases. HCl (99+%), N_2O (99.997%), MeOH (Gold label, 99+%), and ^nBuBr (99%) were from Aldrich. SO_2 (99.5%) was from BDH. Me_3SiH (99%) was from Fluorochem. GeH_4 (99%)[15] and Me_2GeH_2 (98%)[6b] were prepared by us previously. Gas chromatographic analyses of reactant and product mixtures were carried out on a Perkin-Elmer 8310 chromatograph equipped with a flame ionization detector. A 3 m silicone oil (OV101) column operated at 60 °C (or higher) was used to analyze most of the systems investigated, although other columns, such as Porapak Q, were also used when necessary (for light hydrocarbons). Retention times and peak sensitivities (GC response factors) were calibrated with authentic samples where possible.

Quantum-Chemical Calculations

Quantum-chemical calculations were carried out on $SiMe_2$ and $GeMe_2$ as well as $SnMe_2$ in order to see how the methods worked on similar species with known visible/UV spectra. Calculations were performed at two levels of theory. Geometry optimization and vibrational analyses of ZMe_2 (Z = Si, Ge, Sn) in the ground state were done using ab initio HF and DFT B3LYP[16] methods. The 6-31+G(d) basis set was used for H, C, Si, and Ge atoms. This basis set does not exist for Sn and therefore the quasirelativistic effective core potential (ECP) of Stevens et al.[17] combined with a split valence basis set supplemented by sets of d-functions ($\alpha_d = 0.183$) and diffuse sp-functions ($\alpha_{sp} = 0.0231$) was used instead. These basis sets are of a high enough quality for these calculations. Energies of the lowest vertical transitions in ZMe_2 were calculated with CIS[8] and TD DFT B3LYP[9] methods. The calculations were carried out with GAUSSIAN 98[18] at the computer center of N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow.

Results

$SnMe_2$ Precursors. Although the tin analogues to our $SiMe_2$ and $GeMe_2$ precursors were not available, we tested four compounds as sources for this transient, viz. $SnMe_4$, Sn_2Me_6, Me_3SnH, and $PhMe_2SnH$. All these compounds had strong UV absorptions at the 193 nm wavelength of photolysis. Laser photolysis gave rise to transient absorptions from all four compounds. Photodecomposition was accompanied in all cases by dust formation. Interference by dust was kept to a minimum, by keeping the exciplex laser energy low, waiting between shots (the dust is seen to settle out from the probe beam region), and frequent cleaning of the reaction vessel. The nature of the dust was not investigated. As well as recording transient absorption

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spectra, we also examined briefly the precursor photochemistry by end product analysis. This is described in a later section.

$SnMe_4$ has a UV spectrum with $\lambda_{max} = 189$ nm and $\epsilon = 1.6 \times 10^4$ dm^3 mol^{-1} cm^{-1}. End product analyses (see below) show C_2H_6 to be the major photoproduct formed via a molecular pathway. Under time-resolved conditions strong absorptions were obtained in the 450−520 nm region. Although the extinction coefficient of $SnMe_2$ is not known, transient decay traces exhibiting good signal-to-noise ratios could be obtained with 30 mTorr of $SnMe_4$ with averaging over 5 shots. It is possible that as much as 20% of the transient precursor in the irradiated volume may be decomposed per laser shot. However, since only ca. 5% of the total vessel volume was irradiated there is virtually no loss of precursor overall. The precursor in the photolyzed volume is replenished by diffusion between shots.

Sn_2Me_6 has a UV spectrum with $\lambda_{max} = 220$ nm and $\epsilon = 1.15 \times 10^4$ dm^3 mol^{-1} cm^{-1}. End product analyses (see below) show $SnMe_4$ to be a major photoproduct, mainly formed via a molecular pathway. Again strong absorptions were observed in the 450−520 nm region. Under the same experimental conditions (precursor concentration and total pressure) the transient signals were about 3 times stronger than those from $SnMe_4$.

Me_3SnH has a UV spectrum with $\lambda_{max} = 192$ nm and $\epsilon = 5.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}. End product analyses (see below) show CH_4 to be a major photoproduct, mainly formed via a molecular pathway. Again strong absorptions were observed in the 450−520 nm region. Under the same experimental conditions (precursor concentration and total pressure) the transient signals were about 65% of those obtained from $SnMe_4$.

Our sample (30% pure) of $PhSnMe_2H$ has a UV spectrum with $\lambda_{max} = 190$ nm and $\epsilon = 6.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}. End product analyses (see below) show benzene to be a major photoproduct, formed mainly in a molecular pathway. Again strong absorptions were observed in the 450−520 nm region. Under the same experimental conditions (precursor concentration and total pressure) the transient signals were about 3× those obtained from $SnMe_4$ (assuming the impurity plays no role in the photochemistry).

$SnMe_2$ Visible Absorption Spectrum. The transient absorption spectrum was obtained by monitoring the zero-time absorbance (obtained by fitting of exponential decay curves) at most of the nine available wavelengths of the argon ion probe laser for each of the precursors. In these experiments a suitable pressure of precursor in the range 10−30 mTorr was photolyzed in the presence of SF_6 at a total pressure of 5 Torr, at photolysis pulse energies of 65 ± 5 mJ/pulse. For each precursor the pressure chosen was as low as possible consistent with obtaining good signals [$SnMe_4$, 30 mTorr; Sn_2Me_6, 12 mTorr; Me_3SnH, 20 mTorr; $PhSnMe_2H$, 10 mTorr]. Because the quantum yields are not known, the absorptions were all scaled to a common value (100) at 514.5 nm. The results are shown in Figure 1, which also shows the $GeMe_2$ spectrum, obtained by us previously,[6a] for reference. The absorption signals from all precursors show, for the most part, a common trend of decreasing with decreasing wavelength. The solid line has been drawn through the data obtained with $SnMe_4$ as precursor, because it is the cleanest source (see later). The stronger absorptions at shorter wavelengths from Sn_2Me_6 and $PhSnMe_2H$ (in particular) suggest the presence of other absorbing intermediates. Another feature, not shown in the figure, is that the signal decays at 457.9 nm do not go to zero absorbance (even from $SnMe_4$), although the decay traces are very noisy because of dust formation. This suggests the presence of either an absorbing product or a nondecaying, absorbing reactant.

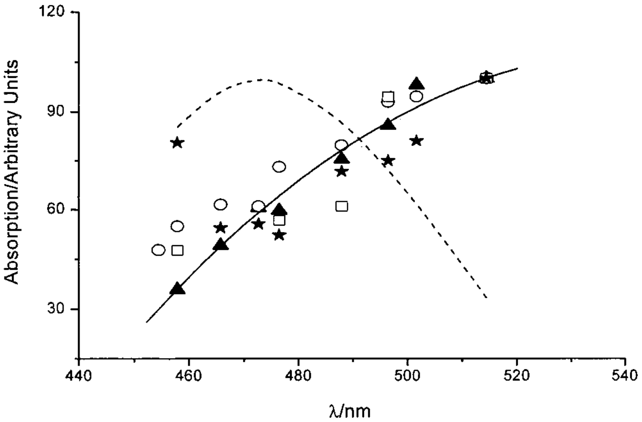

Figure 1. Spectra obtained from zero-time transient absorptions as a function of wavelength. Data points from different precursors are the following: (▲, $SnMe_4$; (○) Sn_2Me_6; (□) Me_3SnH; and (★) $PhSnMe_2H$. All spectra have been scaled to a common absorption at 514.5 nm. The solid line is the best fit gas-phase spectrum for $SnMe_2$ (see text). The dashed line is the gas-phase $GeMe_2$ absorption spectrum from ref 6a.

Table 1. Absorption Wavelengths (nm) for the $S_0 \rightarrow S_1$ Vertical Transitions in ZMe_2 (Z = Si, Ge, Sn) Calculated by CIS and TD Methods

method	$SiMe_2$	$GeMe_2$	$SnMe_2$
CIS	437	450	459
TD	483	495	511
exptl (λ_{max})	458[a]	480[b]	>514[c]

[a] Reference 5a. [b] Reference 6. [c] This work.

There is no previous report of this spectrum in the gas or other phase. The evidence supporting its assignment as the $S_0 \rightarrow S_1$ electronic absorption in $SnMe_2$ includes both comparison with the spectra of some other similar “alkyl” substituted stannylenes and the results of our calculations of the lowest vertical transitions in ZMe_2 (Z = Si, Ge, Sn).

Lappert’s group[1a] reported the spectra of GeR_2 and SnR_2 [R = $CH(SiMe_3)_2$] in hexane solution. GeR_2 has an absorption maximum at 414 nm whereas SnR_2 has a maximum at 495 nm. Similarly, Kira et al.[19] reported the spectra of 1-E-2,2,5,5-tetra-(trimethylsilyl)cyclopentyl-idenes-1 (E = Ge,[19a]Sn[19b]) in hexane solution. Their absorption maxima are located at 450 and 484 nm, respectively.These are the only published “alkyl” substituted stannylene spectra, although there are plenty of reports of spectra of aryl and other stabilized stannylenes.[20] Given that the gas-phase spectrum of $GeMe_2$ is red shifted relative to solution,[6a] this should place the gas-phase absorption maximum for $SnMe_2$ somewhat to longer wavelengths than 514.5 nm, consistent with our findings.

The results of our CIS and TD B3LYP calculations on the lowest $S_0 \rightarrow S_1$ transition are shown in Table 1. Both methods give good agreement with experiment for $SiMe_2$ and $GeMe_2$.

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Of the three ZMe_2 species only $SiMe_2$ has had its UV spectrum studied before at a high theoretical level. The best previously calculated value[21] of the energy for the $S_0 \rightarrow S_1$ transition in $SiMe_2$, obtained at the CISD-Q/TZP level, corresponds to a wavelength of 456 nm and compares favorably with our results. The calculations give a singlet ground state for all three ZMe_2 species in agreement with their known multiplicities.[20] The $SnMe_2$ species has C_{2v} symmetry in the ground state although $SiMe_2$ and $GeMe_2$ have C_2 symmetry due to slight rotations of the methyl groups. However, the energy differences between C_2 and C_{2v} species (methyl hydrogens in the opposed position) for the $SiMe_2$ and $GeMe_2$ species are very small (less than 0.8 kJ mol^{-1}). For $SnMe_2$ the $S_0 \rightarrow S_1$ electronic transition can be denoted $^1A_1 \rightarrow {}^1B_1$. The calculations place the $S_0 \rightarrow S_1$ transition in $SnMe_2$ at 459 (CIS) and 511 nm (TD). Both values are reasonably close to the highest absorption obtained here of 514.5 nm, although the true band maximum may be at slightly longer wavelength. Of the two methods used TD DFT gives better agreement with experiment. Our calculations nicely reproduce the small shifts to longer wavelength experimentally observed for the ZMe_2 series. It is also interesting to note that the data show that the energy of the $S_0 \rightarrow S_1$ transition in all ZMe_2 species is amazingly insensitive to the nature of the central atom, Z.

In summary, both the wavelength location of this spectrum and the similarities between that from $SnMe_4$ and the other precursors provide strong evidence that this is indeed a part of the visible spectrum of $SnMe_2$. This is further supported by the photochemistry reported in a later section.

Gas-Phase Rate Constants for Reactions of $SnMe_2$. For kinetic studies, $SnMe_4$ was used as the $SnMe_2$ precursor. This was because the other precursors all showed some evidence of producing other transients additional to $SnMe_2$ (see the next section). The transient from $SnMe_4$ was monitored at both 501.7 and 514.5 nm, in the strongest absorption region. Decay traces (2 to 5 shot averages) were found to fit exponential forms consistent with first-order kinetics. Linear least-squares fitting up to 75% or greater for each decay trace was used to obtain the first-order decay constant, k_{obs}, for reactive substrates. For unreactive substrates decay traces were somewhat noisier, and fitting was only possible up to 60% in some cases. Rate constants were found to be independent of excimer laser energy (within a 40−80 mJ/pulse range) and also the number of laser shots (up to 20 shots). At a given substrate pressure the reproducibility of k_{obs} values was within ±10% of the mean, although often better than this. Substrates were chosen to cover a selection of potential reaction types. No reactions were found with C_3H_8 (10 Torr), Me_3SiH (10 Torr), GeH_4 (10 Torr), Me_2GeH_2 (10 Torr), C_2H_4 (30 Torr), and N_2O (10 Torr). Reactions were, however, found with 1,3-C_4H_6 (butadiene), $CH_3C{\equiv}CCH_3$, MeOH, HCl, 1-C_4H_9Br, and SO_2. In these studies, the partial pressure of reactive substrate was varied in a systematic way to test the dependence of k_{obs}. These experiments yielded reasonable linear plots as expected for second-order kinetics. Examples of such plots are shown in Figure 2 for the reactions with butyne-2, methanol, and HCl. The second-order rate constants found from the slopes of these plots are collected in Table 2. The uncertainties shown are single standard deviations. For the unreactive substrates, the lack of reaction was used to set upper limits for the rate constants. Apart from these, one other substrate, viz. O_2, was also studied, but a linear second-order plot was not obtained. If a second-order reaction does take place, it has a rate constant somewhere in the range 0.4−1.7 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. No attempt was made at this stage to investigate the overall pressure dependence of any of these reactions.

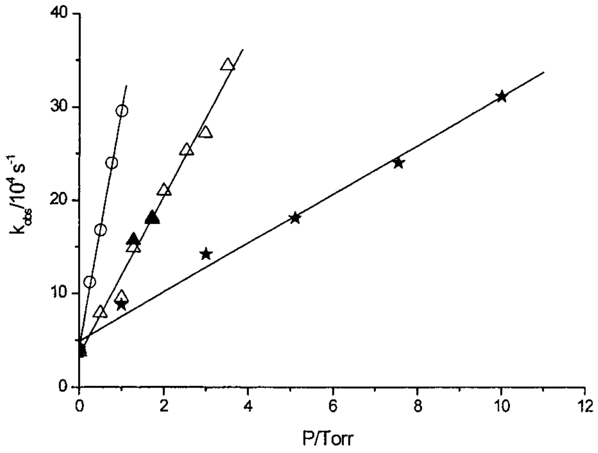

Figure 2. Second-order plots of the dependence of k_{obs} on reactive substrate pressures (monitoring wavelengths shown in parentheses): $MeC{\equiv}CMe$ (○, 501.7 nm); MeOH (△, 501.7 nm; ▲, 514.5 nm); and HCl (★, 514.5 nm).

Table 2. Gas-Phase Rate Constants for $SnMe_2$ at 296 ± 2 K

substrate	$k/cm^3\ molecule^{-1}\ s^{-1}$
1,3-C_4H_6	$(5.97 \pm 0.17) \times 10^{-11}$
$CH_3C{\equiv}CCH_3$	$(7.84 \pm 0.12) \times 10^{-12}$
CH_3OH	$(2.60 \pm 0.10) \times 10^{-12}$
HCl	$(8.08 \pm 0.35) \times 10^{-13}$
1-C_4H_9Br	$(2.88 \pm 0.28) \times 10^{-12}$
SO_2	$(3.35 \pm 0.12) \times 10^{-11}$
C_3H_8	$\leq 3.1 \times 10^{-14}$
Me_3SiH	$\leq 6.2 \times 10^{-14}$
GeH_4	$\leq 3.1 \times 10^{-14}$
Me_2GeH_2	$\leq 9.3 \times 10^{-14}$
C_2H_4	$\leq 1.0 \times 10^{-14}$
N_2O	$\leq 9.3 \times 10^{-14}$

The Search for End Products (Reaction Photochemistry). As a preliminary to these studies a brief investigation of the photolysis products of each precursor (at low conversions, ca. 10−25%) was undertaken with 25 to 100 photolysis laser shots of ca. 40−50 mJ/pulse. On the basis of GC analysis, the major product of photodecomposition of $SnMe_4$ (0.12 Torr in 100 Torr of N_2) was C_2H_6 (89%). Small amounts of CH_4 (1.5%), Me_3SnH (6%), and Sn_2Me_6 (3.5%) were also formed. Experiments with added oxygen had little effect on the C_2H_6 yield but reduced the Me_3SnH and Sn_2Me_6 yields to almost zero. The lack of effect on C_2H_6 shows that it cannot be produced via CH_3 radical recombination. These results strongly suggest the major primary process for $SnMe_2$ to be

$$SnMe_4 + h\nu\ (193\ nm) \rightarrow SnMe_2 + C_2H_6$$

with a minor contribution from

$$SnMe_4 + h\nu\ (193\ nm) \rightarrow SnMe_3 + Me$$

with Sn_2Me_6 coming from $SnMe_3$ recombination and Me_3SnH probably from $SnMe_3$ disproportionation.

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[21] Grev, R. S.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 5804.

The photodecomposition of Sn_2Me_6 (0.3 Torr in 100 Torr of N_2) yielded C_2H_6 and $SnMe_4$ in almost equal amounts with ca. 5% of Me_3SnH. Experiments with added oxygen approximately halved the yield of $SnMe_4$ while having little effect on the C_2H_6 yield. This suggests that a substantial proportion of the $SnMe_4$ comes via Me + $SnMe_3$ combination. Clearly the $SnMe_3$ radicals must be in excess or the C_2H_6 yield would also have been significantly affected. These results suggest that ≥50% of the primary process for Sn_2Me_6 comes via

$$Sn_2Me_6 + h\nu\ (193\ \mathrm{nm}) \rightarrow Sn_2Me_4 + C_2H_6$$

The nature of the Sn_2Me_4 product is unknown but the ease of 1,1-elimination of C_2H_6 from $SnMe_4$ suggests that it is more likely to be $Me_3SnSnMe$ than $Me_2SnSnMe_2$. Interestingly, published theoretical calculations indicate that H_3SnSnH is slightly more stable than H_2SnSnH_2.[22] The next most significant process (ca. 25%) is

$$Sn_2Me_6 + h\nu\ (193\ \mathrm{nm}) \rightarrow SnMe_2 + SnMe_4$$

with a further 15−20% contribution from

$$Sn_2Me_6 + h\nu\ (193\ \mathrm{nm}) \rightarrow 2SnMe_3$$

Methyl radicals must also be formed. They could arise either via a further minor primary process or via secondary decomposition of vibrationally excited $SnMe_3$.

The photodecomposition of Me_3SnH (0.29 Torr in 100 Torr of N_2) gave rise to CH_4 (45%) and C_2H_6 (50%) as the major products with ca. 1.5% of Sn_2Me_6 as a minor product and some 3.5% of unidentified peaks. Experiments with added oxygen reduced slightly the absolute yields of both CH_4 and C_2H_6 and largely eliminated the minor products. The relative yields of C_2H_6 and CH_4 were now 45% and 55%, respectively. This suggests a part of the C_2H_6 is coming via Me radical recombination. These results show that there are two major primary processes, viz.

$$Me_3SnH + h\nu\ (193\ \mathrm{nm}) \rightarrow SnMe_2 + CH_4$$

$$Me_3SnH + h\nu\ (193\ \mathrm{nm}) \rightarrow MeSnH + C_2H_6$$

with the first of these slightly predominating. Minor contributions probably come from

$$Me_3SnH + h\nu\ (193\ \mathrm{nm}) \rightarrow Me_2SnH + Me$$

$$Me_3SnH + h\nu\ (193\ \mathrm{nm}) \rightarrow SnMe_3 + H$$

It is also possible that the Me radicals are formed via secondary decomposition of vibrationally excited stannylenes.

The photodecomposition of $PhSnMe_2H$ (60 mTorr in 100 Torr of N_2) produced CH_4, C_2H_6 ,and C_6H_6 (benzene) as well as small amounts of other products. Because of the presence of the impurity it was impossible to provide a quantitative description. However, it was verified that none of these products was substantially suppressed in the presence of added oxygen. This suggests that all of the following primary processes are occurring to some extent:

$$PhSnMe_2H + h\nu\ (193\ \mathrm{nm}) \rightarrow PhSnMe + CH_4$$

$$PhSnMe_2H + h\nu\ (193\ \mathrm{nm}) \rightarrow PhSnH + C_2H_6$$

$$PhSnMe_2H + h\nu\ (193\ \mathrm{nm}) \rightarrow SnMe_2 + C_6H_6$$

These analytical studies strongly indicate the formation of $SnMe_2$ as a primary product of photodissociation of all four precursors, broadly consistent with spectral evidence. They also suggest the formation of other transient stannylenes from Sn_2Me_6 ($Me_3SnSnMe$), Me_3SnH (MeSnH), and $PhSnMe_2H$ (PhSnH, PhSnMe). The spectra found from each precursor show some differences, suggestive that there may be species other than $SnMe_2$ present. This evidence led us to believe that the photodecomposition of $SnMe_4$ was likely to be the cleanest source of $SnMe_2$.

The main objective of the analytical studies was to characterize the precursor photochemistry. Additionally a brief search by GC of the products in the reaction systems of $SnMe_2$ with 1,3-C_4H_6 and butyne-2 indicated the clear presence of a product in the former case and a possible product in the latter. However, the small size of the gas sample and the lack of any synthetic samples of potential products left us unable to characterize these new GC peaks. Since this was not the main objective of this work, product studies were not further pursued here.

Discussion

Although photochemical decomposition of organostannanes has often been used as a source of tin-centered free radicals in solution,[23] there seem to have been no previous gas-phase photochemical studies of the stannanes used in this work. In low-temperature matrices[24] it has been reported that $SnMe_4$ photolysis[24a] gives rise to $Me_2Sn{=}CH_2$ and Me_3SnH photolysis[24b] produces $SnMe_2$, identified by Mössbauer spectroscopy (also Me_2SnH_2 forms MeSnH[24b]). The measurements reported here are strongly indicative of the formation of $SnMe_2$ in the gas phase and the kinetic studies represent the first experimental determination of gas-phase rate constants for this species (and indeed any stannylene). The results show that $SnMe_2$ does not insert into C−H, Si−H, or Ge−H bonds (nor, indeed, into C−C, Si−C, and Ge−C bonds) at room temperature on the time scale of these experiments. It also does not readily add to simple C═C double bonds (insofar as C_2H_4 is representative) although it appears to react with the C≡C triple bond (but see later). It reacts rapidly with 1,3-butadiene. It does not react with N_2O, one potential n-type lone pair donor, although it does react with MeOH, another lone pair donor. Reactions with halides are observed. These findings are, in general terms, consistent with what is already known from solution and end product studies.[3]

The observed lack of reactivity with many of the substrates previously found reactive toward silylenes and germylenes is not too surprising. As far as bond insertion is concerned, $SiMe_2$ and $GeMe_2$ insert fairly slowly into Si−H[5c] and Ge−H[6b] bonds, respectively. From studies with SiH_2 and GeH_2 (which are more reactive than $SiMe_2$ and $GeMe_2$, respectively) it seems that the

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Table 3. Comparison of Addition Rate Constants of the Dimethyl Heavy Carbenes to Unsaturates at Room Temperature

substrate	$SiMe_2$	$GeMe_2$	$SnMe_2$
C_2H_4	$2.2 \times 10^{-11\,a,b}$	$2.0 \times 10^{-11\,c}$	$<1.0 \times 10^{-14\,d}$
$1,3\text{-}C_4H_6$	$7.5 \times 10^{-11\,a}$	$1.2 \times 10^{-11\,c}$	$6.0 \times 10^{-11\,d}$
$CH_3C{\equiv}CCH_3$	$1.7 \times 10^{-10\,a}$	$3.4 \times 10^{-11\,e}$	$7.8 \times 10^{-12\,d}$

[a] Reference 5b. [b] Reference 5e. [c] Reference 6a. [d] This work. [e] Reference 30.

heavy methylenes get less reactive with increasing size, i.e. GeH_2 has lower rate constants than SiH_2.[25] Moreover, reactivity is affected by the strength of the substrate bond for insertion. Thus GeH_2 insertion into Si−H bonds[25] is considerably slower than SiH_2 insertion into Ge−H bonds.[26] Thus from these considerations $SnMe_2$ is unlikely to insert easily into any M−H bond stronger than Sn−H, and given the sluggishness of $GeMe_2$ insertion into Ge−H,[6b] even this is likely to be very slow.

The lack of reaction of $SnMe_2$ with simple C═C bonds is almost certainly connected with the weakness of the interaction, or to put it another way, the strain involved in forming the stannirane ring. Studies of GeH_2 with C_2H_4[27] and C_3H_6[28] show that germirane rings are highly strained (more so than siliranes), and therefore stanniranes can be expected to be even more strained. There are no published theoretical calculations on stanniranes. There are, however, calculations by Boatz, Gordon, and Sita[29] on stannirene, which show that this ring, although highly strained, is weakly bound by some 52 kJ mol^{-1} relative to $SnH_2 + C_2H_2$ (calculation at the MP2/3-21G(d)//RHF/3-21G(d) level). This weak binding suggests that the potential tetramethylstannirene product of the reaction

$$SnMe_2 + MeC{\equiv}CMe \rightarrow c\text{-}Me_2SnC_2Me_2$$

should redissociate very readily. This makes it questionable whether such a product could be stabilized at room temperature. The measured rate constant for this reaction is surprisingly high (although not as high as those of $SiMe_2$[5b] and $GeMe_2$[30] with MeC≡CMe; Table 3) and the decay traces show no obvious signs of reversibility. However, the reaction may be less efficient at low pressures, where stabilization of the product should be less effective. We plan to investigate the pressure dependence of this reaction. If there is another pathway for this reaction it is not obvious what it might be. It is worth pointing out, however, that a stannirene has previously been prepared, albeit from a strained cycloalkyne and a highly stabilized stannylene.[31]

The reaction of $SnMe_2$ with butadiene again comes as no surprise. Lappert's stannylene could be trapped with 2,3-dimethylbuta-1,3-diene[1b] and Neumann's group have shown that Lappert's stannylene adds to a number of other dienes to give a set of 1-stannacyclopent-3-enes,[32] although they were unable to trap $SnMe_2$ itself with dienes.[2] Theoretical calculations at the MNDO level suggest a synchronous 1,4 cycloaddition mechanism[33] and indeed Neumann's group found evidence for this by reacting Lappert's stannylene with a stereolabeled diallenyl compound.[34] We would, however, reserve judgment on this until more definitive experiments have been done using $SnMe_2$ itself with simpler dienes (without steric encumbrance). The evidence for $SiMe_2$ and $GeMe_2$ cycloadditions to dienes favors 1,2 addition followed by ring expansion.[35,36] The observation of a high rate constant in this work is of itself not definitive as to the mechanism. Table 3 compares the gas-phase rate constants of addition reactions of the dimethyl heavy carbenes, under the conditions of measurement. The pattern for butadiene seems erratic, although since the pressure dependences of these reactions have not been studied it is premature to draw any hard conclusions. It seems to us not impossible that $SnMe_2$ could initially form a vinylstannirane followed by rapid ring expansion to the stannacyclopentene.

Table 4. Some Bond Dissociation Energies (kJ mol^{-1})

bond	radical, R	
	C_2H_5[a]	Me_3Sn[b]
R−H[c]	423 ± 2	322 ± 17
R−Cl[c]	351 ± 2	425 ± 17[d]
R−Br[c]	296 ± 2	381 ± 17
R−I[c]	236 ± 2	320 ± 17
R−OH[c]	395 ± 2	488 ± 17
R−CH$_3$[c]	370 ± 2	295 ± 17

[a] $\Delta H_f^o(C_2H_5)$ = 121 kJ mol^{-1} from ref 38. [b] ΔH_f^o for Me_3SnX compounds, including $\Delta H_f^o(Me_3Sn)$ = 130 kJ mol^{-1} from ref 39. [c] ΔH_f^o for other compounds from ref 40. [d] Estimated using ΔH_{vap} = 40 kJ mol^{-1}.

The reactions of $SnMe_2$ with HCl and 1-BuBr are consistent with the known affinity of Lappert's stannylene with halides.[1b] The solution studies by Neumann et al.[37] of $SnMe_2$ and $SnBu_2$ could not establish conclusively that the observed bond insertion products were necessarily those of a free stannylene. There is also the issue of whether this insertion reaction proceeds directly or via halogen abstraction, illustrated, for the current case, as follows:

$$BuBr + SnMe_2 \rightarrow Bu..Br..SnMe_2 \rightarrow BuSnMe_2Br$$

$$BuBr + SnMe_2 \rightarrow Bu + BrSnMe_2 \rightarrow BuSnMe_2Br$$

This question is open to further investigation by product analysis, which we plan to undertake in a more detailed study. However, it is possible to comment on the likelihood of abstraction from the thermochemical viewpoint, since the overall abstraction reaction involves breaking a primary C−Br bond and making a trialkyltin−Br bond. The relevant bond dissociation energies for this and related cases are shown in Table 4. The data are

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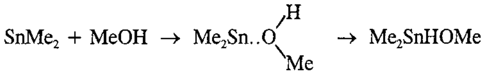
taken from the best sources we are aware of.[38-40] It can be clearly seen that the Sn−hal bonds are considerable stronger that their C−hal counterparts. The situation is slightly more complicated, however, because the overall energy gain is reduced by the contribution of the divalent state stabilization energy (DSSE)[41] of $SnMe_2$. The value of this quantity is not known with certainty, but is estimated as 100 ± 20 kJ mol^{-1}.[42] This makes the abstraction reactions at best marginal, although the MNDO calculations[33] favored it in the case of MeI + $SnMe_2$. It should be pointed out, however, that the evidence from the solution studies of Lappert's stannylene[43] with alkyl halides favors the abstraction mechanism.

The reaction of $SnMe_2$ with n-type lone pair donors such as CH_3OH comes as no surprise, given the facility with which silylenes[5d,44] and germylenes[45,46] react with this type of molecule. Thus we should expect the following mechanism for this reaction:



$$SnMe_2 + MeOH \rightarrow Me_2Sn..O\overset{H}{\underset{Me}{}} \rightarrow Me_2SnHOMe$$

An interesting question here is whether the initial formation of the donor−acceptor (zwitterion) complex from $SnMe_2$ + MeOH is reversible. The evidence from $SiMe_2$ studies[5d] is that, at room temperature, the reaction of $SiMe_2$ + MeOH is not reversible although $SiMe_2 + Me_2O$ is. The analogous reactions of $GeMe_2$[45] do not show reversibility at room temperature. The reactions of SiH_2 + MeOH[44c] and Me_2O[44a,b] are both reversible at higher temperatures and unpublished investigations[46] suggest similar results for GeH_2 + MeOH and $GeH_2 + Me_2O$. There is no evidence of reversibility in our present room temperature study but we may expect that at higher temperatures this may well occur, since there is no reason to believe that the Sn···O bond in the intermediate complex should be any stronger than the Si···O bond in the analogous complex.

Regarding the potential reactions of $SnMe_2$ with SO_2 and N_2O, we may consider the likelihood of the O-atom transfer steps

$$SnMe_2 + SO_2 \rightarrow Me_2SnO + SO$$

$$SnMe_2 + N_2O \rightarrow Me_2SnO + N_2$$

Clearly from our results only the first of these is a possibility, and even then the reaction may be indirect or have other pathways (unpublished calculations and experiments in our labs[47] suggest that the analogous reaction of $SiH_2 + CO_2 \rightarrow H_2SiO + CO$ is anything but direct). It is premature, without further experiments, to discuss these reactions in detail. We consider here only their thermochemical feasibility. The key quantity will be the stability of Me_2SnO about which little seems to be known. Provided the Sn═O double bond[48-50] is as strong or stronger than D(OS═O) and likewise D(NN═O), then these reactions are feasible. The values for D(OS═O) and D(NN═O) are easily calculated from well-established thermochemistry[51] at 552 and 167 kJ mol^{-1}. Since the Sn−O single bond in Me_3-Sn−OH has a strength of ca. 488 kJ mol^{-1} (see Table 4) this seems to imply that reaction of Me_2Sn with SO_2 (by this route) should at best be marginal,[52,53] whereas with N_2O it is a reasonable possibility. Because this argument appears contrary to our findings, clearly there are other considerations involved here. It should be added that there are no studies of $SiMe_2$ or $GeMe_2$ with these molecules although SiH_2 is known to react with N_2O[54] and recent studies have shown that both SiH_2[55] and GeH_2[56] react with SO_2.

Since $SnMe_2$ is rather unreactive toward several of the potential substrate molecules investigated here, it is legitimate to enquire what its fate is in these systems. The decays under these conditions are usually noisy and not very well characterized. When fitted in the usual way to exponentials, k_{obs} values of $(2-5) \times 10^4$ s^{-1} are obtained. The question that arises is whether these traces might be mistaken for second order, i.e. hyperbolic, decays, corresponding to the reaction

$$2SnMe_2 \rightarrow Sn_2Me_4$$

From the experimental conditions (percent absorption, path length) and an assumed extinction coefficient of 10^3 dm^3 mol^{-1} cm^{-1} (cf. that for $SiMe_2$[57]), a maximum concentration of $SnMe_2$ of 5.8×10^{13} molecule cm^{-3} (=1.8 mTorr) can be estimated. If the recombination reaction occurred at the collision rate (ca. 3×10^{-10} cm^3 molecule^{-1} s^{-1}) then this would correspond to a half-life of 5.8×10^{-5} s, corresponding to a k_{obs} value of 1.2×10^4 s^{-1}. Thus at the maximum rate this reaction is just too slow to occur under the conditions of this study. Given the uncertainty in the extinction coefficient it is possible that it may contribute to the $SnMe_2$ decay. In his review[3] Neumann states that "simple stannylenes like $SnMe_2$, ... polymerise very rapidly,

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$k = 10^8$ M^{-1} s^{-1}...". However, to be rapid in the gas phase the rate constant has to be more than 10^3 faster still. We suspect that in the absence of reactive substrates or in the presence of unreactive ones the slow decays are caused by a mixture of self-reaction and reaction with other intermediates produced simultaneously in the photodecomposition of $SnMe_4$ (e.g. Me radicals). Although slow these decays are still too fast to be attributable to diffusion or reaction with dust. The decay constants do not appear to be dependent on $SnMe_4$ precursor pressure, which allows us to set an upper limit of 3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the rate constant of the reaction

$$SnMe_2 + SnMe_4 \rightarrow products$$

This upper limit is still quite high and not very restricting. However, we suspect that the rate constant for this reaction is much lower than this, since otherwise large amounts of the likely product, Sn_2Me_6, would have been seen in the GC product analyses.

We plan to extend these studies and hope to throw further light on the kinetic behavior of $SnMe_2$ in future work.

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