skilled assistance in the preparation of the compounds and in the DSC studies.

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Evidence for Photoinduced Heterolytic Bond Cleavage in Iodotrimethylstannane

In contrast to the extensive literature on the photochemistry of transition-metal compounds, relatively little attention has been given the photochemistry of main-group-metal compounds, particularly those of tin. In a recent summary of selected examples, Vogler and co-workers have shown that the observed reactivity correlates with the orbital nature of the excited state,[1] although in some cases charge transfer is accompanied by reductive elimination.[2] Similar correlations have yet to be developed for organotin compounds, but scattered observations have led to the generally accepted idea that UV excitation of R_3SnX (R = alkyl, X = halogen) leads to homolytic cleavage of the Sn–X bond.[3-9] Our interest has focused on volatile organotin compounds, since these reagents offer a means of using standard photolithographic techniques to change the refractive index and, in some cases, the structure of glass and glass gels.[10-12] Utilizing these techniques as routes to integrated optics[12] and nonlinear photonic materials,[13] however, requires a detailed understanding of the photochemistry. Here, we describe a series of experiments which show that, under certain conditions, $(CH_3)_3SnI$ exhibits a different mode of photoreactivity.

In the 200–800-nm range, the electronic spectrum of $(CH_3)_3SnI$ in *n*-hexane consists of a single absorption with maximum at 234 nm ($\epsilon = 3.45 \times 10^3$ M^{-1} cm^{-1}). A 254-nm photolysis of a 7.37 × 10^{-4} M *n*-hexane solution of $(CH_3)_3SnI$ causes a decline in the 234-nm band and concurrent appearance of an intense band at 211 nm and weaker bands at 290, 365, and 520 nm (Figure 1A). The 211-nm band agrees with that of $((CH_3)_3Sn)_2$, while the 520-nm band indicates I_2 formation. The bands at 290 and 365 nm are due to the formation of I_3^-. Although the larger absorbance gives the impression that I_3^- is a major photoproduct, the amount formed is always less that 2% of the amount of I_2 formed, and extrapolations to zero irradiation time indicate that I_3^- is a secondary photoproduct. The spectral changes exhibit isosbestic points at 224 and 252 nm, which are maintained through 50 and 100% of the reaction, respectively. Consequently, all photolyses were limited to ≤50% conversion. Under these conditions, the quantum yield of $(CH_3)_3SnI$ dissappearance is 0.32 ± 0.01 with 254-nm excitation and declines to 0.060 ± 0.006 with 310-nm excitation and ≤0.01 with 350-nm excitation. Stoichiometric measurements yield 0.50 ± 0.05 mol of $((CH_3)_3Sn)_2$ formed/mol of $(CH_3)_3SnI$ consumed and 0.50 ± 0.05 mol of I_2 formed/mol of $(CH_3)_3SnI$ consumed. In short, the results are in exact agreement with previous observations which suggest that the primary photochemical event is homolytic cleavage of the Sn–I bond.

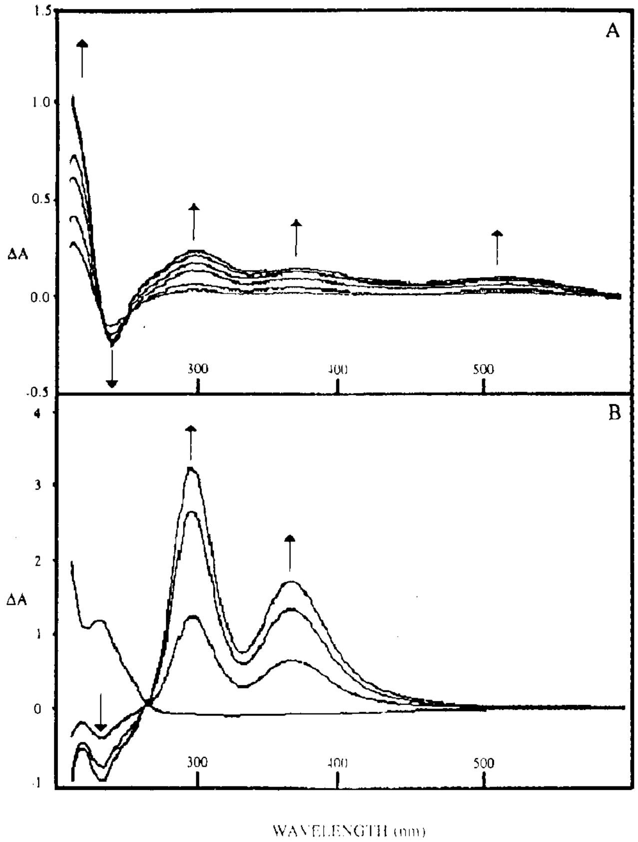

Figure 1. Difference spectra recorded during 254-nm photolysis of 7.37 × 10^{-4} M $(CH_3)_3SnI$ in (A) *n*-hexane and (B) ethanol.

Experiments were also carried out in polar solvents, principally ethanol, as a way to mimic in fluid solution the behavior that might occur on the polar, hydroxylated surface of porous glass or glass gels. The electronic spectrum of $(CH_3)_3SnI$ in ethanol is similar to that in *n*-hexane except that the band maximum shifts to 218 nm ($\epsilon = 1.54 \times 10^4$ M^{-1} cm^{-1}). This was initially thought to be a solvent shift, but the photochemical behavior is quite different. A 254-nm photolysis of an ethanol solution 7.37 × 10^{-4} M in $(CH_3)_3SnI$ causes a decline in the 218-nm absorbance (Figure 1B) and a concurrent growth of peaks at 290 and 360 nm. There is no indication of the higher energy absorption attributable to $((CH_3)_3Sn)_2$ or a lower energy absorption, ca. 450 nm, attributable to I_2. Raman spectra recorded periodically during photolysis yield similar results. A progressive decline in the intensity of the 167-cm^{-1} Sn–I vibration occurs without any indication of the appearance of the 186-cm^{-1} Sn–Sn vibration of $((CH_3)_3Sn)_2$. Rather, the 290- and 360-nm absorptions agree precisely with the

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spectrum of HI. The spectral data yield 0.97 ± 0.07 mol of HI formed/mol of $(CH_3)_3SnI$ consumed, and treating the photolyte with excess $AgNO_3$ yields AgI in the same stoichiometric ratio. In ethanol, the quantum yield of $(CH_3)_3SnI$ dissappearance and HI appearance is 0.65 ± 0.05 with 254-nm excitation and declines to 0.01 and ≤0.001 with 310- and 350-nm excitation, respectively.

Although I_2 absorbs in the UV region ($\epsilon = 2.75 \times 10^3$ M^{-1} cm^{-1} at 254 nm), HI does not derive from secondary photolysis of I_2. There is no indication of an induction period preceding HI formation. Instead, the 290- and 360-nm bands characteristic of HI appear immediately and increase in intensity with the maintainance of an isosbestic point at 260 nm through 100% conversion. Furthermore, the quantum yield is independent of added I_2. In the presence of 10^{-5} to 5×10^{-5} M I_2, the quantum yield of HI appearance during 254-nm photolyses, 0.65 ± 0.09, is within experimental error of that measured in the absence of I_2.

In both polar (ethanol, acetonitrile) and nonpolar (hexane) solvents, the quantum yield of $(CH_3)_3SnI$ dissappearance is independent of the presence of O_2, and no emission occurs in the 260–850-nm region when room- and low-temperature (77 K) solutions of $(CH_3)_3SnI$ are excited with 254-nm light. These results, as well as the wavelength dependence of the quantum yield, suggest that reaction initiates in the high-energy state populated on absorption. Nevertheless, in hexane, the primary photochemical event is homolytic cleavage, whereas, in ethanol, the data indicate that the primary photochemical event is heterolytic cleavage of the Sn–I bond.

The change in behavior is attributed to the formation of a solvent adduct. Titrating an *n*-hexane solution 7.37×10^{-4} M in $(CH_3)_3SnI$ with 1-hexanol causes a decline in the initial absorbance at 234 nm and the growth of a band at 221 nm. The spectral changes occur with an isosbestic point at 237 nm, and the final spectrum, a band at 221 nm, is equivalent to that obtained on dissolving $(CH_3)_3SnI$ in 1-hexanol. Job's plots of the data indicate the formation of a 1:1 $(CH_3)_3(I)Sn{\cdot}OHC_6H_{13}$ adduct. Although the limited solubility of ethanol in *n*-hexane precluded equivalent experiments with ethanol, the spectral changes found on addition of 1-hexanol closely resemble the hypsochromic shift from 234 nm in *n*-hexane to 218 nm in ethanol. Although the band maxima differ slightly, similar spectral changes occur when the compound is dissolved in acetonitrile, and the photochemical behavior resembles that found in ethanol.

R_3SnX compounds are known to form 1:1 and 1:2 adducts with Lewis bases.[14-18] The data gathered here indicate that $(CH_3)_3SnI$ reacts with ethanol to form a $(CH_3)_3(I)Sn{\cdot}OHC_2H_5$ adduct. The ability to readily increase their coordination numbers differentiates these main-group compounds from transition-metal complexes. In solvents capable of acting as Lewis bases, formation of an adduct increases the coordination number and, as indicated by the hypsochromic shift of the absorption, changes the electronic structure of the compound.[19,20] The absorptions of halotrimethylstannanes have not been assigned, and the nature of the excited states is clouded by extensive electron delocalization and covalent bonding.[1] Even if one assumes some charge-transfer character, the increase in transition energy with increasing ionization potential of the halogen suggests LMCT character.[21] Clearly, further work is necessary to determine the nature of the excited states and the electronic changes concurrent with forming a solvent adduct. Nevertheless, the change that does occur appears to be sufficient to switch the photochemical reaction from homolytic to heterolytic cleavage of the Sn–I bond. Photolysis releases I^-, which then abstracts a proton to form HI and $(CH_3)_3Sn{\cdot}OC_2H_5$.

Conclusion. The photochemical reactivity of $(CH_3)_3SnI$ initiates in the high-energy singlet state populated on absorption. However, the observed reaction pathway depends on the solvent medium. In nonpolar solvents, excitation leads to homolytic cleavage, while, in solvent capable of acting as Lewis bases, formation of a solvent adduct switches the reactivity to heterolytic cleavage of the Sn–X bond.

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