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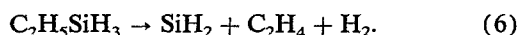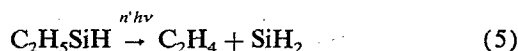J. S. Francisco,[a] J. L. Villanueva, and G. Reck

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Infrared multiple-photon dissociation (IRMPD) of ethylsilane has been found to lead to the formation of silylene radical.[1-3] It was suggested that the reaction can proceed along two kinetically indistinguishable pathways to produce SiH_2:[4] (a) by elimination of SiH_4 followed by subsequent dissociation of SiH_4 into SiH_2 viz.

$$\text{scheme I} \quad C_2H_5SiH_3 \xrightarrow{mh\nu} SiH_4 + C_2H_4 \quad (1)$$

$$SiH_4 \xrightarrow{m'h\nu} SiH_2 + H_2 \quad (2)$$

$$\overline{}$$

$$C_2H_5SiH_3 \rightarrow SiH_2 + C_2H_4 + H_2; \quad (3)$$

(b) by elimination of H_2 to form "hot" ethylsilylene, which fragments to form C_2H_4 and SiH_2 viz.

$$\text{scheme II} \quad C_2H_5SiH_3 \xrightarrow{nh\nu} C_2H_5SiH + H_2 \quad (4)$$

$$C_2H_5SiH \xrightarrow{n'h\nu} C_2H_4 + SiH_2 \quad (5)$$

$$\overline{}$$

$$C_2H_5SiH_3 \rightarrow SiH_2 + C_2H_4 + H_2. \quad (6)$$

SiH_4 is experimentally observed as a final product in both schemes, but in scheme II it is produced only by secondary collisional reactions. Scheme I seems to be supported by results from chemical activation studies[5,6] of ethylsilane and ethylsilane-d_3. Scheme II, on the other hand, is consistent with results from shock-tube studies of ethylsilane.[7,8] In both experiments the SiH_2 produced is detected by laser-induced fluorescence. These experiments do not provide any evidence about the source of SiH_2. In order to better understand the reaction mechanism and to elucidate the origin of SiH_2, we have performed IRMPD studies of ethylsilane in a molecular beam followed by mass spectrometric detection of the dissocation products.

Ethylsilane was introduced through a needle into a vacuum chamber, with a background pressure of 3.0×10^{-7} Torr, so that the pressure increased to 8.0×10^{-6} Torr. Under these conditions the experiment is carried out in the collision-free regime so as to minimize secondary collisional reactions of the fragments produced in the primary dissociation. A pulsed CO_2 laser, with a minimum pulse width of 200 ns, was tuned to the CO_2 line $10P(24)$. The frequency of this CO_2 line is 940.54 cm^{-1}. This frequency corresponds closely to the very strong absorption of the SiH_3 group for the in-plane and out-of-plane deformations.[9] This infrared beam was focused using a combination of germanium converging and diverging lenses forming a telescope. The CO_2 laser beam goes through these germanium lenses

and a NaCl window before being focused over the orifice of the needle from which an effusive beam of ethylsilane flows. At this focal point the beam was 2 mm in diameter. Two and one-half centimeters above this point is the first plate of the electron ionizer and quadrupole mass analysis system. The quadrupole mass analysis system was tuned manually to the masses of 43, 57, and 58. These m/e values correspond to the fragments $SiCH_3$, CH_3CH_2Si, and CH_3CH_2SiH. The fragments with an m/e ratio of 57 and 43 can originate from the electron impact fragmentation of both ethysilane and ethylsilylene radical (m/e 58).[10] By tuning to these mass fragments one can observe if there is a change in the ratio of the mass fragments with the infrared radiation. An increase in the m/e fragments of 58, 57, and 43 would indicate that ethylsilylene radical is being produced by IRMPD.

Using a delay generator, the CO_2 laser was triggered and 100 ms later the ion count signal from the channeltron electron multiplier was collected on an HP counter for the next 2.0 ms. The ion count signals were averaged over 50 shots. A similar experiment was performed with an inert gas, Ar, to estimate the contributions from the background gas. Argon was introduced into the chamber to the same pressure as the ethylsilane had been. In addition, counts were recorded for both cases without any CO_2 laser and were observed to be negligible. This procedure was repeated at three different laser fluences 0.95, 1.6, and 2.9 J/cm^2. The data presented in Fig. 1 are the difference between the ethylsilane signal and background. The uncertainty is quite large as can be seen in Table I but at these masses there is a clear enhancement over background during the period when the CO_2 laser is on. There appears to be a threshold for dissociation at a fluence of 0.95 J/cm^2 or less. The low threshold for dissociation is consistent with the "large molecule" behavior for such systems[11] and also with previous dissociation behavior for dis-
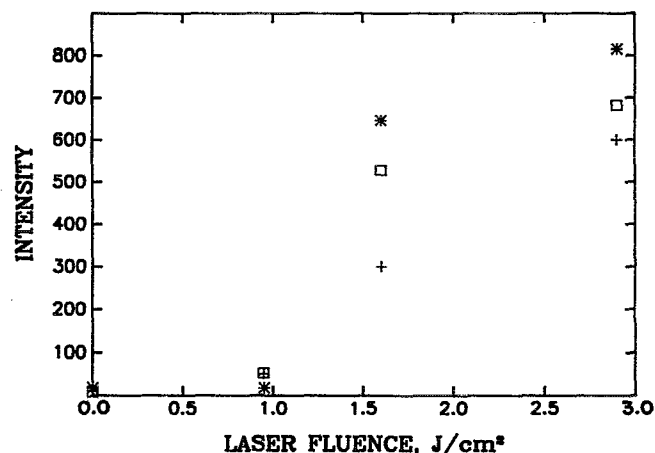

FIG. 1. Yield of ions per pulse for m/e (58, 57, and 43) as a function of CO_2 laser fluence. ($\square$) m/e 43 amu, ($+$) m/e 57 amu and ($*$) m/e 58 amu.

TABLE I. Number of ions per pulse at m/e for various fluences.

J/cm² mass	43	57	58
0	8	9	17
0.95	52 ± 23	50 ± 33	17 ± 3
1.6	528 ± 166	300 ± 110	646 ± 10
2.9	682 ± 237	600 ± 146	815 ± 255

sociation of ethylsilane in a static system.[1] Increased fluence produces more ions of m/e at 58, 57, and 43. This suggests that as more ethysilane is dissociated, the yields of these species increase. If scheme II prevails, the species resulting from ethylsilane dissociation, at m/e 58, 57, and 43 should mimic the fractional decomposition of ethylsilane with fluence. On the other hand, if scheme I were the case, the yield of all three ions should decrease as the ethylsilane is depleted. The trend of increasing yield of the fragments with increasing decomposition of ethylsilane suggests that they result from ethylsilane decomposition. It is therefore likely that under these collisionless dissociation conditions, ethylsilane dissociation yields ethylsilylene radical at m/e 58. Although the formation of ethylsilylene has been inferred in the past experimentally,[1,3,7,8] it is interesting to note that the formation of ethylsilylene has not been detected in gas phase experiments. The identification of ethylsilylene radical as one of the primary reaction products is consistent with theoretical studies of ethylsilane dissociation,[4] which predict that the H_2 elimination channel (reaction 4) should be the lowest energy channel with an activation energy of 66.6 kcal mol^{-1} while the SiH_4 elimination channel (reaction 1) would require an additional ca. 23 kcal mol^{-1} to proceed. The pathway leading to the carbon–silicon bond scission requires an energy of activation of ca. 75 kcal mol^{-1}. Other bond fission reactions such as the homolytic cleavage of the silicon–hydrogen and carbon–carbon bond require 80.5 and 79.7 kcal mol^{-1}, respectively, in order to proceed. These pathways are thermodynamcially unfavorable channels. The general observation in reactions induced by infrared multiphoton dissociation is that reactions proceed via the lowest thermal pathway.[11]

Consequently, the *ab initio* calculations suggest that the dominant primary dissociation channel for ethylsilane is decomposition to ethylsilylene and hydrogen.

Single rovibronic levels of silylene, produced by IRMPD of n-butylsilane,[12] were excited using a pulsed dye laser, and $Si(^3P)$ probed by atomic fluorescence using a time-delayed frequency-doubled, Raman-shifted dye laser pulse tuned to the $4s(^3P_1) \leftarrow 3p^2(^3P_0)$ transition at 39 760 cm^{-1}. The observed $Si(^3P)$ was suggested to have resulted not only from SiH_2 predissociation but also from n-butylsilylene produced in the primary IRMPD step followed by elimination of a silicon atom.[12] This observation is consistent with the present experimental result and *ab initio* calculation[4] on ethylsilane, and suggests that more generally the primary dissociation step in the dissociation of alkylsilanes is the elimination of H_2 with the formation alkylsilylene radicals.

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