CH oscillator of  $C_6H_5CHBr_2$ ) are significantly higher than usual.<sup>1</sup> These greater uncertainties are undoubtedly due to the uncertainty in the peak positions of these low-intensity peaks, particularly at  $\Delta v_{\rm CH} = 5$  (both molecules). Therefore, the  $\omega$  and  $\omega x$  values for the alkyl CH oscillator of the orthogonal conformer of  $C_6H_5CHCl_2$ and the alkyl CH oscillator of  $C_6H_5CHBr_2$  should be regarded only as estimates. We also note that the values of  $\omega$  and  $\omega x$ associated with the two aryl peaks are averages in the sense that these peaks correspond to unresolved contributions from nonequivalent aryl CH bonds.

The transition frequencies (see Tables I and II) of the aryl CH oscillators of C<sub>6</sub>H<sub>5</sub>CHCl<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CHBr<sub>2</sub> are higher than the corresponding transition frequencies for the CH oscillator of benzene ( $\Delta E$ (benzene) = 8760, 11442, 14015, and 16467 cm<sup>-1</sup> for  $\Delta v_{CH} = 3, 4, 5, \text{ and } 6$ , respectively<sup>42</sup>). Both the -CHCl<sub>2</sub> and

(42) Patel, C. K. N.; Tam, A. C.; Kerl, R. J. J. Chem. Phys. 1979, 71, 1470.

-CHBr<sub>2</sub> groups are electron-attracting relative to hydrogen. Thus, they strengthen the aryl CH bonds of  $C_6H_5CHCl_2$  and  $C_6H_5C$ -HBr<sub>2</sub> and increase their vibrational frequencies relative to benzene.

It would be particularly useful to observe the CH-stretching overtone spectrum of  $C_6H_5CHCl_2$  in the gas phase. There is the possibility that peaks due to the nonequivalent aryl CH bonds would be resolved. Of even greater interest would be an indication of the role played by liquid-phase intermolecular interactions in stabilizing the orthogonal conformer. We are currently attempting to build a high-temperature facility for an intracavity dye laser photoacoustic spectrometer to investigate these possibilities.

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Registry No. C<sub>6</sub>H<sub>5</sub>CHCl<sub>2</sub>, 98-87-3; C<sub>6</sub>H<sub>5</sub>CHBr<sub>2</sub>, 618-31-5.

# Single Pulse Laser Induced Reactions of Hexafluorobenzene/Silane Mixtures at 1027 and 944 cm<sup>-1 1,2</sup>

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 $C_6F_6/SiH_4$  mixtures were irradiated with a single pulse of a megawatt  $CO_2$  infrared laser at 1027 and 944 cm<sup>-1</sup>, using fluences which ranged from 0.26 to 2.0 J/cm<sup>2</sup>. Neat  $C_6F_6$  (7.5 Torr, 1027 cm<sup>-1</sup>) underwent decomposition to  $C_2F_4$  at a fluence of 0.7 J/cm<sup>2</sup> with a conversion per flash (CPF) of 4.5%. At 0.3 J/cm<sup>2</sup> no reaction was observed, setting a fluence threshold for the laser-induced decomposition of  $C_6F_6$  between 0.3 and 0.7 J/cm<sup>2</sup>. In the presence of SiH<sub>4</sub> explosive reactions occurred with conversion of  $C_6F_6$  as high as 70%! Different decomposition products were observed depending upon the amount of SiH<sub>4</sub> present. At constant C<sub>6</sub>F<sub>6</sub> pressure (7.3 Torr) and at high C<sub>6</sub>F<sub>6</sub> mole fraction ( $R = P_{C_6F_6}/(P_{C_6F_6} + P_{SiH_4}) \ge 0.55$ ), fluorinated carbonaceous products were observed (C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>). At low C<sub>6</sub>F<sub>6</sub> mole fraction ( $R \le 0.55$ ), non-fluorinated carbonaceous products were observed ( $C_2H_2$ ,  $C_4H_2$ ). SiF<sub>4</sub> was the major gaseous product in both regions, while SiF<sub>3</sub>H was observed when R values were lower than 0.55. A polymeric black material was also deposited in the cell in both R zones. The highest CPF of  $C_6F_6$  was obtained when the mole fraction of  $C_6F_6$  was 0.55 and under these conditions only SiF<sub>4</sub>, SiF<sub>3</sub>H, and polymeric material were observed. Irradiation of  $C_6F_6/SiH_4$  mixtures (constant  $C_6F_6$  pressure, 7.5 Torr) at 944 cm<sup>-1</sup> using fluences below 1 J/cm<sup>2</sup> did not induce reaction. At 1.6 J/cm<sup>2</sup> no reaction was observed at C<sub>6</sub>F<sub>6</sub> mole fractions above 0.3. However, between 0.3 and 0.1 mole fraction values identical products as those obtained in this zone under 1027-cm<sup>-1</sup> irradiation were observed. Identical products were also obtained when the  $C_6F_6$  mole fraction was varied by adding  $C_6F_6$ to SiH<sub>4</sub> (constant SiH<sub>4</sub> pressure, 30 Torr). However, the threshold for reaction was observed at a  $C_6F_6$  mole fraction of R = 0.5 and no reaction was observed when R > 0.5. At higher overall pressure ( $P_{C_6F_6} = 72$  Torr;  $P_{SiH_4} = 37$  Torr, with R = 0.66) irradiation at 944 cm<sup>-1</sup> gave the same products as those observed in the high R zone of the 1027-cm<sup>-1</sup> irradiation. A higher fluence (2.05/cm<sup>2</sup>) was necessary, however, to induce the reaction at 944 cm<sup>-1</sup>. These results are discussed in terms of (a) the low fluence threshold observed for the laser-induced decomposition of  $C_6F_6$ , (b) the effects that added gases have on the decomposition of  $C_6F_6$ , (c) the use of  $C_6F_6$  as a sensitizer for laser-induced reactions, and (d) the potential for using SiH<sub>4</sub> for the laser-induced reduction of C-F bonds (C-F + Si-H  $\rightarrow$  C-H + Si-F).

## Introduction

Infrared-laser-induced bimolecular reactions have been given limited attention compared with their unimolecular counterparts. In 1981, Danen and Jang<sup>4</sup> suggested that products of bimolecular reactions might be generated by the simultaneous laser irradiation of both reactants. When infrared absorption bands of both

reactants coincide with one of the emission bands of the laser, the reaction may be influenced by a single laser irradiating wavelength. Bauer and Haberman<sup>5</sup> reported on an explosive reaction between silane  $(SiH_4)$  and sulfur hexafluoride  $(SF_6)$  initiated by CW CO<sub>2</sub> laser irradiation at 944 cm<sup>-1</sup>, in which both molecular species absorbed energy. Similarly, Haggerty and Cannon<sup>6</sup> succeeded in synthesizing  $Si_3N_4$  by irradiating mixtures of  $SiH_4$  and  $NH_3$ at 944 cm<sup>-1</sup> using focused and unfocused CW CO<sub>2</sub> techniques.

When the absorption bands of the reactant molecules are not coincident, the reaction might be induced by the simultaneous irradiation at two wavelengths by using two lasers. Alternatively,

<sup>(1)</sup> For previous paper in this series see: Madison, S. A.; Keehn, P. M. J. Anal. Appl. Pyrol. 1986, 9, 237-246.

<sup>(2)</sup> This work was presented at the 187th National Meeting of the American Chemical Society, April 1984. Abstract ORGN 43.
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<sup>(4)</sup> Danen, W. C.; Jang, J. C. In Laser Induced Chemical Processes; Steinfeld, J., Ed.; Plenum: New York, 1981; p 78.

<sup>(5)</sup> Bauer, S. H.; Haberman, J. A., IEEE J. Quantum Electron. 1978 QE-14, 233.

<sup>(6)</sup> Haggerty, J. S.; Cannon, W. R. In Laser Induced Chemical Processes; Steinfeld, J., Ed.; Plenum: New York, 1981; p 170.

## IR-Laser-Induced Reactions of C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> Mixtures

one might take advantage of the different absorbing wavelengths of the reactants and specifically irradiate one or the other reactant. Under these circumstances different reaction channels might be expected to be dominant when the different species are irradiated.

Hexafluorobenzene ( $C_6F_6$ ) and SiH<sub>4</sub> possess molecular vibrational modes, at 1027 cm<sup>-1</sup> and 944 cm<sup>-1</sup>, respectively, which fall in the emission range of the CO<sub>2</sub> laser (900–1100 cm<sup>-1</sup>).  $C_6F_6$ has been considered to be relatively stable under laser irradiation and has been used as a sensitizer in laser-induced reactions.<sup>7</sup> Duignan, Grunwald, and Speiser<sup>8</sup> recently studied the decomposition of  $C_6F_6$  by time-resolved spectroscopy at fluences that ranged from 100 to 900 J/cm<sup>2</sup>. They demonstrated the intermediacy of C<sub>2</sub> and C<sub>3</sub> fragments, with C<sub>2</sub>F<sub>4</sub> and (C<sub>2</sub>F)<sub>n</sub> being formed as the major products. Minor amounts of C<sub>7</sub>F<sub>8</sub>, C<sub>3</sub>F<sub>6</sub>, and C<sub>4</sub>F<sub>8</sub>, and trace amounts of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> were also observed.

The infrared-laser-induced decomposition of SiH<sub>4</sub> has also been reported. Deutch<sup>9</sup> studied the decomposition of SiH<sub>4</sub> at a fluence of 140 J/cm<sup>2</sup> and at high conversions observed hydrogen and silylene polymer (SiH<sub>x</sub>)<sub>n</sub> as the major products. Longeway and Lampe<sup>10</sup> studied the decomposition of SiH<sub>4</sub> at low fluence (1 J/cm<sup>2</sup>) and low conversion levels (<1.5%) and observed Si<sub>2</sub>H<sub>6</sub> and Si<sub>3</sub>H<sub>8</sub> as major products along with hydrogen and minor amounts of Si<sub>4</sub>H<sub>10</sub> and Si<sub>5</sub>H<sub>12</sub>. At SiH<sub>4</sub> pressures of greater than 14 Torr (SiH<sub>x</sub>)<sub>n</sub> was the major product. When irradiated in the presence of HCl, chlorosilanes were observed along with H<sub>2</sub> and polysilanes.<sup>11</sup>

We have been studying the utility of  $SiH_4$  in laser-induced bimolecular reactions. Our interest stems from the potential use of SiH<sub>4</sub> not only as an energizer but also as a reactant and a reducing reagent since it is a convenient source of hydrogen. We have found that carbon halogen bonds can be reduced by SiH<sub>4</sub> when the latter is irradiated in the presence of simple halohydrocarbons.<sup>12</sup> Thus, as depicted in Scheme I a variety of halohydrocarbons afford the corresponding hydrocarbons after 10 pulses at low irradiation fluences with relatively high conversion of RX and SiH<sub>4</sub>. Since these reactions suggested the potential for selective deuteriation using SiD<sub>4</sub> and since SiD<sub>4</sub> does not have a strong absorption band in the 9-11- $\mu$ m emission region of the  $CO_2$  laser, it was important to determine if the above reaction could be induced by irradiation of the halohydrocarbon.  $C_6F_6$ was considered a good choice for the study because of its very strong C-F stretching mode at 1027 cm<sup>-1</sup> and because it seemed to be essentially inert at low fluence levels.<sup>7,8</sup>

In this paper we report the results of a study of the single pulse laser induced reactions of  $C_6F_6/SiH_4$  mixtures where the system is energized by selective excitation of either  $C_6F_6$  or SiH<sub>4</sub>. Single-pulse conditions were used so that the chemistry would not be complicated by the presence of product molecules. In the paper we describe the effects of the presence of a second gas on the decomposition of  $C_6F_6$ , and the effect of mole ratio, fluence, and wavelength of irradiation on the bimolecular and unimolecular reactions of these two molecules and suggest possibilities for mechanistic considerations.

## **Experimental Section**

The experiments were performed using a tunable pulsed  $CO_2$  laser (Lumonics Research, Ltd. Model K-203). Irradiation using



Figure 1. Optical configuration for laser-induced reactions: (1) laser beam; (2) beam splitter; (3) Cu mirror; (4) reaction cell; (5) lens (optional); (6) CaF<sub>2</sub> beam attenuator; (7) pyroelectric detector; (8) oscilloscope; (9) He-Ne alignment laser; (10) spectrum analyzer; (11) disk calorimeter; (12) laser power meter.

the P(40) line  $(1027.38 \text{ cm}^{-1})$  was carried out with an unfocused beam with fluences in the range of  $0.26-0.7 \text{ J/cm}^2$ . Irradiation using the P(20) line  $(944.18 \text{ cm}^{-1})$  was carried out with a beam condenser in order to obtain higher fluences of  $1.6-2.0 \text{ J/cm}^2$ . The incident beam energy was measured, after transmittance through a germanium beam splitter, with a Scientech disk calorimeter (Model 362). The laser beam entering the infrared cell was adjusted to 20 mm by using a variable aperture opening.

The optical bench used for the experiments is described in Figure 1. The laser beam, after passing through the 20-mm aperture, was reflected from the beam splitter (2) through the reaction cell (4). The amount of energy passing through the cell was measured after attenuation by a CaF<sub>2</sub> window (6) (transmittance, 37% at 1027 cm<sup>-1</sup>), using the pyroelectric detector (Lumonics Model 20D; 7). The average energy absorbed per mole in the irradiation volume ( $E_{abs}$ ) was then obtained from the difference between the incident energy and the amount passing through the empty and filled cells. The experimental error in the measurement of  $E_{abs}$  was about 15%.

The cell, fabricated from stainless steel, was cylindrical in shape and had polished KCl windows at either end. The volume of the cell was 22.7 cm<sup>3</sup> and the optical path length was 2.54 cm. A port with a stopcock was centrally located on the body of the cylinder and was used for filling and evacuating the cell.

Hexafluorobenzene was purchased from the Aldrich Chemical Co. (99%) and was degassed and purified by bulb to bulb distillation.  $SiH_4$  was obtained from the Matheson Gas Co. and was used without further purification.

An aluminum vacuum line was used in all gas manipulations since hexafluorobenzene attacks the grease of conventional glass systems. The pressures of the component gases were measured with an MKS Baratron manometer (Model 222B).  $C_6F_6$  and  $SiH_4$ gases were mixed in the infrared cell by thermal diffusion at room temperature. The concentration of the mixtures were defined by mole fraction (*R*) of  $C_6F_6$  which was obtained from the ratio of the partial pressure of  $C_6F_6$  to the total pressure of the mixture

$$R = \frac{P_{C_6F_6}}{P_{C_6F_6} + P_{SiH_4}}$$

The partial pressure of each of the gases in the mixture was verified by infrared spectroscopy before every experiment. Infrared spectra before and after a single pulse of laser irradiation were recorded with a Perkin-Elmer Model 683 infrared spectrophotometer. GC-MS spectrometric analysis was carried out after each reaction using a Hewlett Packard Model 5992 instrument. A Porapak N column was used with a flow rate of 16 mL/min and a temperature programming rate of 10 °C/min.

A single pulse of light at a specific wavelength was used to standardize all experiments and remove complications that would arise from chemistry that might take place when product molecules

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Figure 2. Infrared spectra before (---) and after (---) the irradiation of  $C_6F_6/SiH_4$  mixtures at 1027 cm<sup>-1</sup> (fluence 0.7 J/cm<sup>2</sup>;  $C_6F_6$  pressure constant, 7.3 Torr): (a) R = 1.0, (b) R = 0.7, (c) R = 0.3.

would be present after the first pulse.

## Results

Irradiation at 1027 cm<sup>-1</sup>: The C-F stretching mode of  $C_6F_6$ at 1027 cm<sup>-1</sup> is coincident with the P(40) line of the CO<sub>2</sub> laser, and in this series of experiments irradiation was carried out using this wavelength. Figure 2 shows the infrared specträ in the region between 1600 and 700 cm<sup>-1</sup>, before and after irradiation of different  $C_6F_6/SiH_4$  mixtures. The pressure of  $C_6F_6$  was held constant at 7.3 ± 0.2 Torr and the amount of SiH<sub>4</sub> was varied in order to obtain the different mole fraction (*R*) values. The fluence was constant at 0.7 J/cm<sup>2</sup>.

The  $E_{\rm abs}$  for C<sub>6</sub>F<sub>6</sub>, though containing a large experimental error, was relatively constant above R = 0.5, and averaged 218 kJ/mol. This represented the absorption of about 18 photons/molecule/pulse. The  $E_{\rm abs}$  was observed to increase with increasing SiH<sub>4</sub> pressure (decreasing R value) with the number of photons absorbed increasing to greater than 21/molecule/pulse (see Table I).

Figure 2a shows the results after one pulse were R = 1 (neat C<sub>6</sub>F<sub>6</sub>). The bands at 1340 and 1186 cm<sup>-1</sup>, indicative of C<sub>2</sub>F<sub>4</sub>, are easily observed. The reduction in optical density of the 1027-cm<sup>-1</sup> band of C<sub>6</sub>F<sub>6</sub> shows a conversion per flash (CPF) of 4.5%. Thus, even at low fluence levels<sup>13</sup> a substantial amount of decomposition

TABLE I: Fluence (f) of and Energy Absorbed  $(E_{abe})$  by the  $C_6F_6/SiH_4$  System at Various Mole Fractions (R) of  $C_6F_6$  for Irradiation at 1027 cm<sup>-1a</sup>

| <br>R | <i>f</i> , J/cm <sup>2</sup> | E <sub>abs</sub> ,<br>kJ/mol | R    | f, J/cm <sup>2</sup> | E <sub>abs</sub> ,<br>kJ/mol |
|-------|------------------------------|------------------------------|------|----------------------|------------------------------|
| 1.0   | 0.66                         | 212                          | 0.50 | 0.67                 | 220                          |
| 0.90  | 0.66                         | 214                          | 0.21 | 0.68                 | 247                          |
| 0.75  | 0.70                         | 221                          | 0.16 | 0.68                 | 255                          |
| 0.65  | 0.69                         | 219                          | 0.11 | 0.66                 | 273                          |
| 0.55  | 0.70                         | 220                          |      |                      |                              |

| <sup>a</sup> The    | pressure of | $C_6F_6$ was | s maintained | at 7.3 Torr | and the pressure   |
|---------------------|-------------|--------------|--------------|-------------|--------------------|
| of SiH <sub>4</sub> | was varied  | from 0 t     | o 61.5 Torr. | (Data rela  | ated to Figure 3). |



**Figure 3.** Variation of the absorbance ( $\alpha$ ) of the major products with the mole fraction of C<sub>6</sub>F<sub>6</sub> (*R*) in the irradiation of C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> mixtures at 1027 cm<sup>-1</sup> (fluence 0.7 J/cm<sup>2</sup>; C<sub>6</sub>F<sub>6</sub> pressure constant, 7.3 Torr).

of  $C_6F_6$  takes place after a single pulse.

Figure 2b shows the results after one pulse where R = 0.7. In this instance,  $C_2F_4$  was observed after an explosive reaction in substantially larger quantities than in the previous experiment. The CPF of  $C_6F_6$  was greater than 60%! Thus, the decomposition of  $C_6F_6$ , giving  $C_2F_4$ , is increased dramatically when irradiated in the presence of a reactant gas like SiH<sub>4</sub>. Along with  $C_2F_4$  and SiF<sub>4</sub>, CF<sub>4</sub> and  $C_2F_6$  were formed and a smaller amount of  $C_6F_5H$ . The inside of the cell was also coated with a grayish black material which is most likely mixtures of carbon, polymeric silanes, and fluorosilanes. (K<sub>2</sub>SiF<sub>6</sub> was observed spectrally as well and must be derived from a reaction involving the KCl windows, SiF<sub>4</sub>, and HF, see eq 2.)

Figure 2c shows the results after one pulse where R = 0.3. In this case no  $C_2F_4$  was observed at all though the reaction was explosive and the CPF of  $C_6F_6$  was greater than 50%. SiF<sub>4</sub> was the major product along with  $C_2H_2$ ,  $C_4H_2$ , SiHF<sub>3</sub>, and a lesser quantity of  $C_6F_5H$ . A light-brown material covered the inside of the cell and K<sub>2</sub>SiF<sub>6</sub> was observed spectrally but in a smaller amount than in the previous experiment (R = 0.7).

Figure 3 shows a distribution map of the major products observed in the reactions involving the irradiation of  $C_6F_6/SiH_4$ mixtures at 1027 cm<sup>-1</sup> with a fluence of 0.7 J/cm<sup>2</sup>. The infrared absorbances of the reaction products are plotted as a function of the mole fraction (*R*) of  $C_6F_6$ . A number of significant observations can be made by inspection of this plot. First, SiF<sub>4</sub> is produced over almost the entire range of *R* values (0.15 < *R* <

<sup>(13)</sup> Previous work on the laser-induced decomposition of  $C_6F_6$  was carried out using fluences of 100-900 J/cm<sup>2</sup>. See ref 8.

<sup>(14)</sup>  $K_2SiF_6$  was formed in a laser-induced reaction involving  $SiH_4$  and  $NF_3$  (see *Chem. Abstr. 93*, 228474P). In addition whenever we observed  $K_2SiF_6$  we always observed HCl by IR analysis. Finally, we have observed the H-F vibrational/rotational lines between 3900 and 3800 cm<sup>-1</sup> in the infrared spectrum when  $C_6F_6$  and  $H_2$  were irradiated. See following paper in this issue.



**Figure 4.** Variation of conversion per flash (CPF) of  $C_6F_6$  as a function of mole fraction (*R*) of  $C_6F_6$  in the irradiation of  $C_6F_6/SiH_4$  mixtures at 1027 cm<sup>-1</sup> ( $C_6F_6$  pressure constant, 7.3 Torr).

0.9). The production of SiF<sub>4</sub> is at a maximum when the mole fraction of the reagents are approximately equal ( $R \approx 0.55$ ) and two clearly defined regions of carbonaceous product materials are delineated at this point. For the most part, above R = 0.55, only fluorinated hydrocarbons are formed while below that point only non-fluorinated hydrocarbons are produced. At R = 0.55, only carbon, polymer, SiHF<sub>3</sub>, and SiF<sub>4</sub> seem to be formed. Second, below an approximate R value of 0.15 no reaction takes place at all. Third, the growth and decay of the fluorinated and non-fluorinated hydrocarbons do not overlap one another, indicating distinct pathways for their respective formations.

Figure 4 shows the variation of the CPF of  $C_6F_6$  as a function of mole fraction of  $C_6F_6(R)$  in  $C_6F_6/SiH_4$  mixtures at high (0.7  $J/cm^2$ ) and low (0.3  $J/cm^2$ ) fluences. The plot shows that the maximum CPF for  $C_6F_6$  is 70% after one flash and is observed at R = 0.55 and a fluence of 0.7 J/cm<sup>2</sup>. Even when the fluence is lowered to 0.3 J/cm<sup>2</sup> greater than 50% CPF can be obtained at this R value. The plot also shows that the threshold for neat  $C_6F_6$  decomposition is below 0.7 J/cm<sup>2</sup> but above 0.3 J/cm<sup>2</sup> and that the addition of even small amounts of  $SiH_4$  increases the conversion. The CPF is in fact substantial when the mole fractions of the components are approximately equivalent and under those circumstances even a drastic reduction in fluence below the normal threshold level for neat  $C_6F_6$  causes substantial  $C_6F_6$  conversion. The products observed in the experiment using a fluence level of  $0.3 \text{ J/cm}^2$  were the same and gave rise to a similar distribution map as that described in Figure 3 for a fluence of 0.7 J/cm<sup>2</sup> except the amounts were proportionally lower.

At a fluence level of  $0.2 \text{ J/cm}^2$  no reaction took place at all for C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> mixtures. Thus, the fluence threshold for the mixture where maximum reaction normally takes place (R = 0.5) lies between 0.2 and 0.3 J/cm<sup>2</sup> (see Figure 4).

Irradiation at 944 cm<sup>-1</sup>. The degenerate Si-H vibrational mode of SiH<sub>4</sub> is coincident with the P(20) emission line of the CO<sub>2</sub> laser. When silane was excited at 944 cm<sup>-1</sup> in a gas mixture of C<sub>6</sub>F<sub>6</sub> and SiH<sub>4</sub>, reaction did not occur at fluences lower than 0.9 J/cm<sup>2</sup>. However, when the fluence was increased to 1.6 J/cm<sup>2</sup> by using a beam condenser (where the size of the laser beam entering and leaving the cell was kept at 20 mm in diameter by changing the distance between two lenses of the beam condenser), the reaction occurred explosively.

Figure 5 shows the infrared spectra of different  $C_6F_6/SiH_4$ mixtures in the region between 1600 and 700 cm<sup>-1</sup> before and after a single pulse of radiation. The pressure of  $C_6F_6$  was held constant at 7.5 Torr and the amount of SiH<sub>4</sub> was varied in order to obtain the different mole fraction values (*R*). The fluence was also constant at 1.6 J/cm<sup>2</sup>.

The average  $E_{\rm abs}$  was 80 kJ/mol in the 0.075 < R < 0.24 region but was observed to increase as R decreased (see Table II). This represented the absorption of 6-8 photons/molecule/pulse.

As reflected in Figure 5a, the reaction did not occur when the mole fraction (R) was 0.3 or greater. This phenomenon will be



Figure 5. Infrared spectra before (—) and after (---) the irradiation of  $C_6F_6/SiH_4$  mixtures at 944 cm<sup>-1</sup> (fluence 1.6 J/cm<sup>2</sup>;  $C_6F_6$  pressure constant, 7.5 Torr): (a) R = 0.3, (b) R = 0.15, (c) R = 0.075.

TABLE II: Fluence (f) of and Energy Absorbed ( $E_{abs}$ ) by the  $C_6F_6/SiH_4$  System at Various Mole Fractions (R) of  $C_6F_6$  for Irradiation at 944 cm<sup>-1 a</sup>

| R    | f, J/cm <sup>2</sup> | E <sub>abs</sub> ,<br>kJ∕mol | R     | f, J/cm <sup>2</sup> | $E_{abs}, kJ/mol$ |  |
|------|----------------------|------------------------------|-------|----------------------|-------------------|--|
| 0.24 | 1.65                 | 68                           | 0.10  | 1.63                 | 88                |  |
| 0.21 | 1.64                 | 74                           | 0.075 | 1.56                 | 80                |  |
| 0.15 | 1.64                 | 85                           |       |                      |                   |  |

<sup>a</sup> The pressure of  $C_6F_6$  was maintained at 7.5 Torr and the pressure of SiH<sub>4</sub> was varied from 24 to 92 Torr. (Data related to Figure 6).

explained later and seems to be due to the low partial pressure of SiH<sub>4</sub> in the mixture. When the mole fraction was reduced however, reaction did take place. In Figure 5b where R = 0.15, a substantial reaction was observed (CPF of  $C_6F_6 > 60\%$ ) with SiF<sub>4</sub>, SiHF<sub>3</sub>,  $C_2H_2$ , and trace amounts of  $C_4H_2$  being formed. (These are the same products which are formed in the 0.1 < R< 0.5 region of the reaction initiated by iradiation at 1027 cm<sup>-1</sup>.) When R was lowered to 0.075 (Figure 5c) the conversion of  $C_6F_6$ was reduced as well (CPF  $\approx 43\%$ ), and no  $C_2H_2$  or  $C_4H_2$  was produced. SiF<sub>4</sub> and SiHF<sub>3</sub> were the only observable products.

Figure 6 shows the variation of the CPF of  $C_6F_6$  (a) and the variation of the absorbance of the reaction products (b) as a



Figure 6. Variation of conversion per flash (CPF) of  $C_6F_6$  (a) and absorbance ( $\alpha$ ) of the major products (b) with mole fraction (*R*) of  $C_6F_6$  in the irradiation of  $C_6F_6/SiH_4$  mixtures at 944 cm<sup>-1</sup> (fluence 1.6 J/cm<sup>2</sup>;  $C_6F_6$  pressure constant, 7.5 Torr).

TABLE III: Fluence (f) of and Energy Absorbed ( $E_{abb}$ ) by the  $C_6F_6/SiH_4$  System at Various Mole Fractions (R) of  $C_6F_6$  for Irradiation at 944 cm<sup>-1 a</sup>

| <br>R    | f, J/cm <sup>2</sup> | E <sub>abs</sub> ,<br>kJ∕mol | R    | f, J/cm <sup>2</sup> | E <sub>abs</sub> ,<br>kJ∕mol |  |
|----------|----------------------|------------------------------|------|----------------------|------------------------------|--|
| <br>0.59 | 1.59                 | 138                          | 0.30 | 1.62                 | 63                           |  |
| 0.56     | 1.65                 | 146                          | 0.20 | 1.58                 | 70                           |  |
| 0.52     | 1.65                 | 141                          | 0.11 | 1.57                 | 76                           |  |
| 0.50     | 1.62                 | -82                          | 0.0  | 1.58                 | 76                           |  |
| 0.40     | 1.61                 | -0.4                         |      |                      |                              |  |

<sup>a</sup> The pressure of SiH<sub>4</sub> was maintained at 30 Torr and the pressure of  $C_6F_6$  was varied from 0 to 43 Torr. The negative values indicate a net energy emission from the system as evidenced by a bright flash of light. (Data related to Figure 7).

function of mole fraction of  $C_6F_6(R)$  observed in the reactions involving the irradiation of  $C_6F_6/SiH_4$  mixtures at 944 cm<sup>-1</sup> with a fluence of 1.6 J/cm<sup>2</sup>. The maximum conversion of  $C_6F_6$  was observed at R = 0.15 and under these conditions SiF<sub>4</sub>,  $C_2H_2$ , SiHF<sub>3</sub> were produced in the greatest amount.

A slightly different profile was obtained when the SiH<sub>4</sub> pressure was held constant (30 Torr) and the C<sub>6</sub>F<sub>6</sub> pressure was varied. In these experiments a strong white/yellow emission was observed after the irradiation. Figure 7 shows the variation of the CPF of both C<sub>6</sub>F<sub>6</sub> and SiH<sub>4</sub> (a) and the variation of absorbance of the major reaction products (b) with mole fraction of C<sub>6</sub>F<sub>6</sub> (R) in the reactions involving the irradiation of C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> mixtures at 944 cm<sup>-1</sup> with a fluence of 1.6 J/cm<sup>2</sup>.

The  $E_{\rm abs}$  varied dramatically as the presence of  $C_6F_6$  was increased (see Table III). In the range 0.0 < R < 0.2 the  $E_{\rm abs}$  was relatively constant and averaged 74 kJ/mol. After that point there was a slow, than dramatic, decrease in  $E_{\rm abs}$  until at R = 0.5 the



Figure 7. Variation of conversion per flash (CPF) of SiH<sub>4</sub> and C<sub>6</sub>F<sub>6</sub> (a) and absorbance ( $\alpha$ ) of the major products (b) with mole fraction (R) of C<sub>6</sub>F<sub>6</sub> in the irradiation of C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> mixtures at 944 cm<sup>-1</sup> (fluence 1.6 J/cm<sup>2</sup>; SiH<sub>4</sub> pressure constant, 30 Torr).



Figure 8. Infrared spectrum of the product mixture after irradiation of 72 Torr of  $C_6F_6/37$  Torr of SiH<sub>4</sub> (R = 0.66) at 944 cm<sup>-1</sup> (fluence 2.0 J/cm<sup>2</sup>).

 $E_{abs}$  was negative! At this R value an extremely bright white light was emitted from the cell and the  $E_{abs}$  reflected the emitted energy. At higher R values (0.52 < R < 0.59) the  $E_{abs}$  was relatively constant again and averaged 141 kJ/mol. This higher  $E_{abs}$ , relative to that at low R values, is assumed to be due to additional absorption by  $C_6F_6$  at these high  $C_6F_6$  pressures. Though the products for the constant SiH<sub>4</sub> pressure experiment were the same as those obtained in the reaction described in Figure 6 the threshold for reaction appears at R = 0.52 rather than R = 0.3. Using this fluence no chemistry takes place at all above an R value of 0.52. In addition, the maximum conversion for both  $C_6F_6$  and SiH<sub>4</sub> is observed at higher R value (R = 0.5) and the maximum formation of SiF<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> is greater under these conditions albeit at a value of R(0.4) different than the previous runs (where the pressure of  $C_6F_6$  was constant).

At fluences greater than 1.6  $J/cm^2$  reaction does take place in the *R* region greater than 0.52. This can be observed in Figure 8 which shows the infrared spectrum of the product mixture after

### IR-Laser-Induced Reactions of C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> Mixtures

a single pulse of irradiation (944  $\text{cm}^{-1}$ ) at a fluence of 2 J/cm<sup>2</sup>. In this case when the mole fraction was 0.66 ( $C_6F_6$  pressure 72 Torr, SiH<sub>4</sub> pressure 37 Torr) a substantial reaction was observed. The products formed under these conditions are the same as those generated when  $C_6F_6$  was irradiated (1027 cm<sup>-1</sup>, Figure 2b) except that CHF<sub>3</sub> was also observed under these conditions and the relative amounts of the products differed.

#### Discussion

Duignan, Grunwald, and Speiser<sup>8</sup> have identified the gas products from the multipulsed-laser-induced decomposition of C<sub>6</sub>F<sub>6</sub> at high fluence (>100 J/cm<sup>2</sup>). They found the major product to be  $C_2F_4$ . Smaller amounts of  $C_6F_5CF_3$ ,  $C_3F_6$ , and  $C_4F_8$  and trace amounts of  $CF_4$  and  $C_2F_6$  were also present. Despite the absence of these minor products, our results indicate that neat  $C_6F_6$  can be decomposed by using fluences as low as 0.7 J/cm<sup>2</sup> and that substantial decomposition takes place even in a single pulse. At this fluence a 4.5% CPF of  $C_6F_6$  was observed (see Figure 4). The symmetric (1186 cm<sup>-1</sup>) and antisymmetric (1340 cm<sup>-1</sup>) stretching bands, indicative of  $C_2F_4$ , were clearly visible in the infrared spectrum (see Figure 2a). The absence of the minor products is perhaps due to the insensitivity of the IR spectrophotometer to the small concentrations of these products which may have been generated, but is more likely due to the lower fluence or single-pulse nature of our experiments. If these latter variables are significant the implication is that products other than  $C_2F_4$  are derived from secondary reactions and that the likelihood of observing them would increase with fluence and number of pulses as was observed by Duignan et al. The actual fluence threshold for neat  $C_6F_6$  decomposition is probably slightly less than  $0.7 \text{ J/cm}^2$  as indicated in the graph of Figure 4 but somewhat greater than  $0.3 \text{ J/cm}^2$ .

Though the minor products (observed by Duignan et al.) were absent in our irradiation of neat  $C_6F_6$ , most of them were observed when SiH<sub>4</sub> was present during irradiation. Thus, while  $C_2F_4$  and SiF<sub>4</sub> were the major products observed in the single-pulse irradiation of  $C_6F_6/SiH_4$  mixtures (R = 0.7), CF<sub>4</sub>,  $C_2F_6$ , and  $C_6F_5H$ were also observed by IR analysis (see Figure 2b), and C<sub>3</sub>F<sub>6</sub> was detected by GC/MS analysis. The significance of this result is that, in the presence of 30 mol % of  $SiH_4$ , the CPF of  $C_6F_6$  was more than 10 times greater, and the peak intensity of  $C_2F_4$  was 20 times greater than that observed in the decomposition of neat  $C_6F_6$ . In fact, even when the mole fraction of SiH<sub>4</sub> was as low as 10%, the CPF of  $C_6F_6$  was 3 times greater than that observed in the neat decomposition. Thus, the presence of  $SiH_4$  during the irradiation of  $C_6F_6$  has the effect of decreasing the threshold of the decomposition reaction of  $C_6F_6$  and suggests that a similar decrease in the decomposition threshold might also occur in the presence of other added reagent gases. We have demonstrated that this is true for a wide variety of other molecular systems and we discuss the potential of the chemistry derived from the irradiation of some simple  $C_6F_6$  mixtures in the following paper.

The above represents an important observation since  $C_6F_6$  is used as a sensitizer in infrared-laser-induced chemistry and is generally considered to be inert in the presence of other molecular systems. Based on our results,  $C_6F_6$  can participate as a reactant if the mole fraction and fluence levels are correct. Care should therefore be exercised in its use as a sensitizer.<sup>12</sup>

In order to define the energy threshold for the reaction involving  $C_6F_6/SiH_4$  mixtures the fluence was varied. When a mixture of  $C_6F_6/SiH_4$  (7 Torr/3 Torr; R = 0.7) was irradiated at 1027 cm<sup>-1</sup> at a fluence of 0.3  $J/cm^2$ , an explosive reaction occurred and  $C_2F_4$ was observed (Figure 4). When an identical mixture was irradiated by using a fluence of  $0.26 \text{ J/cm}^2$  no reaction occurred. Thus, the energy threshold for inducing reaction at R = 0.7appears to lie in the 0.3-0.26 J/cm<sup>2</sup> fluence region. Since CPF maxima are observed at R = 0.55 when either 0.7 and 0.3 J/cm<sup>2</sup> fluences are used (see Figure 4) it seems reasonable that reaction could also take place at even lower fluences when R = 0.5. That is, based on the data shown in Figure 4, the fluence threshold for reaction at R = 0.5 should be less than 0.3 J/cm<sup>2</sup>.

It seems reasonable that among the numerous decomposition channels available to  $C_6F_6$  those that involve direct degradation should not be affected by the presence of SiH<sub>4</sub>. On the other hand, the ones which involve the formation of intermediates, especially radicals, should be effected by SiH<sub>4</sub>. One such reaction involves the formation of  $C_6F_5^{\bullet}$  and  $F^{\bullet}$  radicals ( $C_6F_6 \rightarrow C_6F_5^{\bullet} + F^{\bullet}$ ,  $\Delta H = 644 \text{ kJ/mol}$ ).<sup>8,16,19</sup> If this is an important primary reaction,  $SiH_4$  could easily cause increased decomposition by exploiting its strong affinity (silicon and/or hydrogen atoms) for fluorine radicals. Under a given set of energy input conditions, when SiH<sub>4</sub> is absent, there may be enough energy to dissociate the C-F bond in  $C_6F_6$  but subsequent decomposition may be energetically disfavored with recombination taking place. However, in the presence of  $SiH_4$  a cascade effect could be realized since quite a bit of energy would be released when HF and SiF<sub>4</sub> are formed.<sup>20</sup> Since the concentration of the F<sup>•</sup> radicals would be depleted rather rapidly the  $C_6F_5$  radicals could react rapidly with SiH<sub>4</sub> to give  $C_6F_5H$  which may be the first product in a series of reactions which leads to full reduction and ring degradation.

In the irradiation of  $C_6F_6/SiH_4$  mixtures the products and product ratios were found to be dependent on the mole fraction (R) of  $C_6F_6$ . As can be seen in Figure 3, SiF<sub>4</sub> was produced throughout the entire mole fraction region (where R varies from 0.9 to 0.2). The yield of SiF<sub>4</sub> was however greatest when R =0.55. At this point the CPF of  $C_6F_6$  was the highest observed and no (or below detectable limits of) fluorinated and nonfluorinated hydrocarbons were produced. During the irradiation the inside of the cell became black by an explosive reaction and the greatest amount of solid K<sub>2</sub>SiF<sub>6</sub> was formed.<sup>21</sup> It seems reasonable therefore that in the region where 0.9 > R > 0.2 an important reaction could be the one expressed in eq 1 with the largest conversion taking place at R = 0.55 (i.e., when the mole fractions of  $C_6F_6$  and  $SiH_4$  are about equal). Though HF is indicated in eq 1 it was not observed spectrally. However, this

$$C_6F_6 + SiH_4 \rightarrow SiF_4 + 6C + 2HF + H_2 \tag{1}$$

species almost certainly exchanges with chlorine of the window material (present as KCl) to give K<sub>2</sub>SiF<sub>6</sub> (observed) as denoted in eq  $2.^{14}$ 

$$SiF_4 + 2HF + 2KCl \rightarrow K_2SiF_6(s) + 2HCl + 2H_2 \quad (2)$$

In addition to the chemistry suggested in eq 1 and 2 other reactions also seem to be occurring when the mole fraction of  $C_6F_6$ and SiH<sub>4</sub> are not equal ( $R \neq 0.5$ ). When R > 0.5 only fluorinated hydrocarbons are produced ( $C_2F_4$ ,  $C_2F_6$ ,  $CF_4$ ). Since the products in this region are almost the same as those obtained in the irradiation of neat C<sub>6</sub>F<sub>6</sub> described by Grunwald,<sup>8</sup> the chemistry in this zone seems to be represented mainly by  $C_6F_6$  degradation either directly or via the  $C_6F_5$  radical. Some decomposition channels, similar to those reported by Duignan et al.<sup>8</sup> are likely taking place, albeit with increased conversion, due to the presence of SiH<sub>4</sub>. The primary bond-breaking reactions may be those described in eq 3 and 4 as previously reported by Grunwald,<sup>8</sup> but

$$C_6F_6 \xrightarrow{n\nu} CF = CF - CF = CF - CF = CF$$
 (3)

$$C_6F_6 \xrightarrow{n\nu} C_6F_5 + F^{\bullet}$$
 (4)

<sup>(15)</sup> Selamoglu and Steel<sup>7</sup> have successfully used  $C_6F_6$  as a sensitizer without decomposition in the degradation of cyclobutanone. In their studies the fluence range used was below  $0.35 \text{ J/cm}^2$  and mole fraction of  $C_6F_6$  was 0.95. Based on the data in Figure 4,  $C_6F_6$  should not decompose under these conditions. The fact that no  $C_6F_6$  decomposition occurred suggests that a similar CPF/R curve is true for the  $C_6F_6/C_4H_6O$  system.

<sup>(16)</sup> The C-F bond energy for  $C_6F_6$  has been estimated to be as low as 477 kJ/mol<sup>17</sup> and as high as 644 kJ/mol.<sup>18,19</sup> (17) Okafo, E. N.; Whittle, E. Int. J. Chem. Kinet. **1978**, 10, 591.

<sup>(18)</sup> Gilbert, R.; Theoret, A. J. Phys. Chem. 1976, 80, 1017.
(19) (a) Kroch, M. J.; Price, S. J. W.; Yared, W. F. Can. J. Chem. 1974, 52, 2673–2678. (b) Price, S. J. W.; Sapiano, H. J. Can. J. Chem. 1974, 52, 2673–2678. 4109-4111.

<sup>(20)</sup>  $H^{\bullet} + F^{\bullet} \rightarrow HF$ ,  $\Delta H = -564 \text{ kJ/mol}$ ;  $F_3 \text{Si}^{\bullet} + F^{\bullet} \rightarrow \text{Si}F_4$ ,  $\Delta H = -606$ kJ/mol.

<sup>(21)</sup> In general a substantial explosion was observed in the R = 0.75-0.25region when the CPF of  $C_6F_6$  was greater than 50%. When the CPF of  $C_6F_6$ was lower than 50% the explosion was not substantial.

at least two other decomposition channels depicted by eq 5 and 6 may also be occurring in this region. Since we were able to

$$C_6F_6 \xrightarrow{n\nu} FC \equiv C - C \equiv CF + CF_2 = CF_2$$
 (5)

$$C_6F_6 \xrightarrow{n\nu} 3:CF_2 + 3C$$
 (6)

detect  $C_6F_5H$  when irradiating  $C_6F_6$  in the presence of SiH<sub>4</sub> we believe that formation of  $C_6F_5^{\bullet}$  (eq 4) represents an important primary reaction channel for  $C_6F_6$  decomposition. (This seems general for a variety of other hydrogen-containing addends as well; see following article in this issue.) The formation of  $C_2F_4$ ,  $C_2F_6$ ,  $C_3F_6$ , and  $CF_4$  can be explained by the reactions of : $CF_2$  and  $F^{\bullet}$ with each other and with  $C_2F_4$  as depicted in eq 7-10.  $C_6F_5H$ 

$$:CF_2 + :CF_2 \rightarrow CF_2 = CF_2$$
(7)

$$CF_2 = CF_2 + :CF_2 \rightarrow CF_2 = CF - CF_3$$
 (8)

$$CF_2 = CF_2 + 2F^* \rightarrow CF_3 - CF_3 \tag{9}$$

$$: CF_2 + 2F^{\bullet} \to CF_4 \tag{10}$$

is most likely derived from the abstraction of hydrogen in  $SiH_4$  by  $C_6F_5^*$  (eq 11) with  $SiH_3^*$  and  $F^*$  radicals likely being the

$$C_6F_5 + SiH_4 \rightarrow C_6F_5H + SiH_3$$
(11)

precursors for SiHF<sub>3</sub> and HF.

In the region where 0.5 > R > 0.1 the main carbonaceous product is  $C_2H_2$  with a smaller amount of  $C_4H_2$  and  $C_6F_5H$  being observed as well. No  $C_2F_4$  or any other fluorinated hydrocarbon was detected. Along with a substantial quantity of SiF<sub>4</sub>, SiHF<sub>3</sub> was also found but no other fluorinated silanes (see Figures 2 and 3). In addition, when R < 0.2, a yellow-brown solid was observed in the cell which almost certainly is  $(SiH_x)_n$ , and/or  $(SiF_x)_n$ ,  $(SiH_xF_y)_n$ .<sup>10,11</sup>

Since no  $C_2F_4$  or other simple fluorinated hydrocarbons are observed in this R zone, decomposition of  $C_6F_6$  by reactions like those described in eq 5 and 6 do not seem to be taking place. Reduction of the simple fluorinated hydrocarbons by SiH<sub>4</sub>, depicted in these equations, is, however, possible (e.g.,  $C_4H_2$  can be considered to be formed from  $C_4F_2$  after its generation from  $C_6F_6$ ; see eq 5). However, if this were general, one might expect to observe at least some  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $CH_4$  or similar simple partially or fully reduced hydrocarbons. This is not the case.

Acetylene is a major product and may be the result of the reduction of all the simple fluorinated hydrocarbons derived from  $C_6F_6$  decomposition (eq 3-6). However, since SiF<sub>3</sub>H is a major product as well in this zone,  $C_2H_2$  and SiF<sub>3</sub>H may be generated as depicted in eq 12, either directly or through some partially or

$$C_6F_6 + 2SiH_4 \rightarrow \rightarrow 2SiHF_3 + 3C_2H_2$$
(12)

fully reduced form of  $C_6F_6$ . The presence of  $C_6F_5H$  argues for the possibility of a stepwise reduction to tetra, tri, di, mono, and unfluorinated benzenes with subsequent decomposition to  $C_2H_2$ .<sup>22</sup> The formation of  $C_4H_2$  can be rationalized by dimerization of acetylene as shown in eq 13 and 14.<sup>23</sup>

$$C_{2}H_{2} \rightarrow CH \equiv C^{*} + H^{*}$$
 (13)

$$2CH \equiv C^{\bullet} \rightarrow C_4 H_2 \tag{14}$$

In general, it seems that the major reactions in this region (R < 0.5) do not involve direct C<sub>6</sub>F<sub>6</sub> decomposition (i.e., eq 5 and 6) though it seems that reactions described by eq 3, 4, and 11 may be taking place. Rather, this zone seems to be defined more by the decomposition of SiH<sub>4</sub> and reduction of radical fragments derived from C<sub>6</sub>F<sub>6</sub>. That is, SiH<sub>4</sub>, when present in relatively large

amounts, easily reduces the  $C_6F_6$ -derived radicals and is energized by the  $C_6F_6$  absorber. This suggests sensitized decomposition of SiH<sub>4</sub> as described in eq 15–17. By referring to eq 15 and 16 the

$$C_6F_6 \xrightarrow{n\nu} C_6F_6^*$$
 (15)

$$C_6F_6^* + SiH_4 \to C_6F_6 + SiH_4^*$$
 (16)

$$\operatorname{SiH}_4^* \rightarrow :\operatorname{SiH}_2 + \operatorname{H}_2 \text{ or } ^{\circ}\operatorname{SiH}_3 + \operatorname{H}^{\circ}$$
(17)

absence of reaction products similar to those observed in the R > 0.5 region ( $C_2F_4$ ,  $C_2F_6$  etc.) may be explained in the following manner. When R < 0.5, deactivation of  $C_6F_6^*$  by SiH<sub>4</sub> plays an important role. Thus, as R is decreased,  $C_6F_6^*$  is quenched by SiH<sub>4</sub> and the latter is activated by sensitization. Below an approximate R value of 0.15 deactivation of  $C_6F_6$  is complete. Since the relative amount of SiH<sub>4</sub> increases as R decreases the average energy per SiH<sub>4</sub> molecule is reduced at constant energy absorption. Below R = 0.15 the fraction of SiH<sub>4</sub> molecules decomposing falls below our detection sensitivity.

When  $C_6F_6/SiH_4$  mixtures were irradiated at 944 cm<sup>-1</sup>, coincident with SiH<sub>4</sub> absorption, the products observed in the R >0.5 and R < 0.5 zones are similar to those found in the 1027-cm<sup>-1</sup> irradiation (see Figures 5-8 and compare with Figures 2-4). Thus, examining Figures 2-8 and especially comparing Figures 2c with 5b, 2b with 8, and 3 with 6 and 7 one notes that in the 0.1 < R< 0.5 zone SiF<sub>4</sub>, SiHF<sub>3</sub>,  $C_2H_2$ , and  $C_4H_2$  are all present while in the 1.0 > R > 0.5 zone SiF<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and CF<sub>4</sub> are present. The fluence requirement needed to induce reaction at 944 cm<sup>-1</sup>, however was greater. At this wavelength no reaction was observed in any region at fluences less than 0.9 J/cm<sup>2</sup>. At 1.6 J/cm<sup>2</sup>, when the  $C_6F_6$  pressure is held constant at 7.5 Torr (see Figure 6), the point at which one observes maximum absorption for the products occurred at R = 0.15, an R value lower than that observed for the irradiation at 1027 cm<sup>-1</sup> (see Figure 3,  $R \approx 0.25$ ). In addition, the threshold for reaction under these conditions (944 cm<sup>-1</sup>, 1.6  $J/cm^2$ ,  $C_6F_6$  pressure constant) appears at a lower value of R (R < 0.3), since the CPF is zero at R = 0.3. From previous studies on silane decomposition<sup>10</sup> it has been demonstrated that SiH<sub>4</sub> decomposes by molecular collisions after laser excitation. If the pressure of SiH<sub>4</sub> were decreased, the threshold energy of the decomposition would be expected to increase. At a fluence 1.6  $J/cm^2$  neat SiH<sub>4</sub> begins to decompose at a pressure higher than 20 Torr. In our experiments when the value of R is 0.3 (Figure 6) the pressure of  $SiH_4$  is 17.4 Torr and this pressure is lower than that of the threshold pressure required for the decomposition. (No reaction occurs lower than  $R \approx 0.075$  because the average energy per molecule is too low.)

When R is varied by adding  $C_6F_6$  to a constant pressure of SiH<sub>4</sub> (30 Torr, Figure 7) the threshold for reaction increases and is observed at  $R \simeq 0.52$ . The point at which maximum absorption occurs for the two major products (SiF<sub>4</sub> and  $C_2H_2$ ) also increases and is observed at  $R \approx 0.4$ . When  $R \simeq 0.4-0.5$  a very strong emission was observed after the single laser pulse and the measured  $E_{abs}$  was negative (i.e., more energy released by the reactions than absorbed by the reactants). Under these conditions SiH<sub>4</sub> appears to be decomposing and reacting after initial excitation at 944 cm<sup>-1</sup> by the reactions suggested in eq 18, 17, and 19. As the  $C_6F_6$ 

$$\operatorname{SiH}_4 \xrightarrow{n\nu} \operatorname{SiH}_4^*$$
 (18)

 $5SiH_3$  +  $3C_6F_6 \rightarrow \rightarrow$ 

$$2SiF_4 + 3SiHF_3 + 3C_2H_2 + 3C_4H_2 + F^{\bullet}$$
 (19)

$$SiH_4^* + C_6F_6 \to C_6F_6^* + SiH_4$$
 (20)

pressure is increased the reaction becomes very exothermic due to the formation of an increased number of Si-F bonds (SiF<sub>4</sub>). In addition, as the amount of  $C_6F_6$  increases, deactivation of SiH<sub>4</sub>\* by  $C_6F_6$  (eq 20) becomes increasingly important. This can be seen from Figure 7. At R = 0.52 (pressure of SiH<sub>4</sub> 30 Torr) despite the presence of greater than 20 Torr of SiH<sub>4</sub> the reaction is totally quenched by  $C_6F_6$  (33 Torr). Thus, while chemistry derived from SiH<sub>4</sub>\* takes place preferentially up to about  $R \approx 0.5$ , quenching

<sup>(22)</sup> Isomeric tetra- and trifluorinated benzenes have been observed when  $C_6F_6$  was irradiated in the presence of other reducing agents. See following article in this issue.

<sup>(23)</sup> From an enthalpic point of view acetylene radicals could be scavenged with SiH<sub>4</sub> by the following exothermic reaction: CH==C<sup>+</sup> + SiH<sub>4</sub>  $\rightarrow$  CH== CH + 'SiH<sub>3</sub>. But since CH==C<sup>+</sup> is most likely formed in a secondary process the presumed lower internal energy of the radical may not be as efficient as the primarily formed C<sub>6</sub>F<sub>5</sub><sup>+</sup> and F<sup>+</sup> radicals in abstracting hydrogen from SiH<sub>4</sub>.

by  $C_6F_6$  seems to be the exclusive reaction above this R value and suggests that at these reactant concentrations the rate of quenching is greater than the rate of SiH<sub>4</sub>\* decomposition. The reason that no  $C_6F_6$  decomposition occurs above this point, despite the absorption of greater than 80 kJ/mol (fluence 1.6 J/cm<sup>2</sup>), is because at this total pressure (63 Torr) the average energy per  $C_6F_6^*$ molecule is too low for decomposition.

In the SiH<sub>4</sub> irradiation experiments (944 cm<sup>-1</sup>) the reaction products were the same in the 0.1 < R < 0.5 region as those found in the C<sub>6</sub>F<sub>6</sub> irradiation (1027 cm<sup>-1</sup>). When the pressures of SiH<sub>4</sub> and C<sub>6</sub>F<sub>6</sub> were increased, and the fluence was increased the reactions in the 1.0 > R > 0.5 zone could be examined. However, since the maximum vapor pressure of C<sub>6</sub>F<sub>6</sub> is about 72 Torr at ambient temperature a complete study could not be carried out and only a few experiments were done to determine the products. Thus, when SiH<sub>4</sub> (37 Torr) was irradiated at 944 cm<sup>-1</sup> in the presence of C<sub>6</sub>F<sub>6</sub> (72 Torr; R = 0.66) at a fluence of 2.0 J/cm<sup>2</sup> a reaction occurred explosively in a single laser pulse. The IR spectrum of this reaction mixture is shown in Figure 8. As can be seen from the figure the conversion is rather large and SiF<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>, CF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub> are present in addition to CHF<sub>3</sub>. Except for CHF<sub>3</sub>, these products are the same as those found in the 1027-cm<sup>-1</sup> irradiation of C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> at R = 0.7.

#### Conclusions

The above study points out a few significant aspects related to the infrared-laser-induced chemistry of  $C_6F_6$  and  $C_6F_6/SiH_4$ mixtures. First, the fluence threshold for the laser-induced decomposition of neat  $C_6F_6$  at 1027 cm<sup>-1</sup> is lower than originally thought and lies in the 0.3-0.7 J/cm<sup>2</sup> range for  $C_6F_6$  pressures of about 7 Torr. Second, and most important, the presence of  $SiH_4$  significantly enhances  $C_6F_6$  decomposition. Using 50 mol % of SiH<sub>4</sub> in the mixture, the CPF of  $C_6F_6$  after a single pulse  $(\sim 70\%)$  is at least 15 times greater than for the decomposition of neat C<sub>6</sub>F<sub>6</sub> (~4.5%). The presence of even 10 mol % of SiH<sub>4</sub> increases the CPF threefold over the neat decomposition. These results are especially important in light of the use that  $C_6F_6$  gets as a sensitizer, since the presence of other reactants might also enhance the decomposition of  $C_6F_6$ . Indeed, we have found that a large variety of organic molecules, including H<sub>2</sub>, D<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>5</sub>H<sub>8</sub>, CHF<sub>3</sub>, C<sub>6</sub>H<sub>12</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>O, MeOH, MeOMe, H<sub>2</sub>S, and CH<sub>3</sub>Cl, cause similar increased decomposition of  $C_6F_6$  when present during its irradiation. This is explored in more detail in the following publication for a series of hydride compounds.

Third, two sets of carbonaceous products are found during the  $C_6F_6/SiH_4$  irradiation which are dependent upon the fractional pressure of the two gases and which are found in two distinct mole fraction zones straddling the R = 0.55 region. One set, which contains fluorine ( $C_2F_4$ ,  $C_2F_6$ ), is found only in the 0.55 < R < 1 zone, while the other, which contains no fluorine  $(C_2H_2, C_4H_2)$ , is found only in the 0.1 < R < 0.55 zone. At R = 0.55 C<sub>6</sub>F<sub>6</sub> decomposition takes place with the greatest efficiency and only SiF<sub>3</sub>H, SiF<sub>4</sub>, and Si and C polymers are formed. At low SiH<sub>4</sub> pressure enhanced  $C_6F_6$  decomposition is observed selectively while at high SiH<sub>4</sub> pressure the decomposition is accompanied by reduction of the carbon-fluorine bonds (C-F  $\rightarrow$  C-H). At high  $C_6F_6$  mole fractions,  $C_6F_6$  decomposition leading to  $C_2F_4$  seems to be dominant while at low  $C_6F_6$  mole fraction  $C_6F_6$  decomposition leading to  $C_2H_2$  seems to be significant along with SiH<sub>4</sub> decomposition. As SiH<sub>4</sub> pressure is increased quenching of  $C_6F_6^*$ by SiH<sub>4</sub> plays an increasingly important role and allows for SiH<sub>4</sub> chemistry to develop.

Though the mechanisms of these transformations are not fully understood and further experimentation is required to define them, it seems likely that more than one reaction channel is operable and that : $CF_2$ , :SiH<sub>2</sub>,  $C_6F_5^*$ ,  $F^*$ , SiH<sub>3</sub>\*, and H\* radicals are formed early in the reaction and play significant roles in the overall processes. Since  $C_6F_5H$  was observed in minor amount in almost the entire R range (R = 0.9-0.25) we believe that it is an important primary product which is derived from the reduction of  $C_6F_5^*$  by SiH<sub>4</sub> (or some other reducing species present), and generally does not survive the reaction conditions.<sup>24</sup>

Finally, the reactions can be initiated by irradiating either  $C_6F_6$ at 1027 cm<sup>-1</sup> or SiH<sub>4</sub> at 944 cm<sup>-1</sup>. The products are the same irrespective of the wavelength used. Higher fluences, however, are required to drive the reaction at 944 cm<sup>-1.25</sup> In general,  $C_6F_6$ seems to be a better energizer (sensitizer) and quencher than SiH<sub>4</sub> for the mixed system. As SiH<sub>4</sub> is added to  $C_6F_6$ , the latter's decomposition (1027 cm<sup>-1</sup>; 0.7 J/cm<sup>2</sup>) is enhanced even with small mole fractions of SiH<sub>4</sub> present (<5%) while quenching of  $C_6F_6$ by SiH<sub>4</sub> does not take place until after greater than 85 mol % of SiH<sub>4</sub> is present. As  $C_6F_6$  is required to influence SiH<sub>4</sub> chemistry or initiate  $C_6F_6$  decomposition (944 cm<sup>-1</sup>, 1.6 J/cm<sup>2</sup>; Figure 7), but quenching of SiH<sub>4</sub> by  $C_6F_6$  seems to take place efficiently when even as little as 30 mol % of  $C_6F_6$  is present.

Though specific reductive chemistry of  $C_6F_6$  leading to  $C_6F_5H$ was only minimally observed in our C<sub>6</sub>F<sub>6</sub>/SiH<sub>4</sub> study, reduction of C-F bonds on a more efficient scale may be possible by infrared laser irradiation of  $C_6F_6$ . If the process could be controlled whereby explosive reactions could be minimized (e.g., with the use of other H containing species like R-H) it might well be possible to observe the  $C_6F_6 + RH \rightarrow C_6F_5H + RF$  reaction as the major process and it could be of preparative and commercial use. In the above study however since Si-H (370 kJ/mol) and C-F (644 kJ/mol) bonds were being broken, and Si-F (606 kJ/mol) and HF (564 kJ/mol) bonds were being formed, the excess energy released during the process gave rise to uncontrolled decompositions. With the use of other hydride reagents, where the difference in energy of the bonds broken to bonds formed would be smaller, one should have a better opportunity of controlling the reaction and obtaining selective reduction of C-F bonds. If this could be demonstrated it would also generate strong support for the intermediacy of the  $C_6F_5$  radical. Such a study is presented in the following article.

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Registry No. C<sub>6</sub>F<sub>6</sub>, 392-56-3; SiH<sub>4</sub>, 7803-62-5; K<sub>2</sub>SiF<sub>6</sub>, 16871-90-2.

<sup>(24)</sup> We have irradiated  $C_6F_5H$  (15 Torr) in the presence of  $H_2$  (12 Torr) (1.4 J/cm<sup>2</sup>, 300 pulses, 1080 cm<sup>-1</sup>) and have observed, after a 41% conversion of  $C_6F_5H$ , all three tetrafluorobenzenes. Though we irradiated the  $C_6F_6/SiH_4$  system at 1027 cm<sup>-1</sup> we believe that the  $C_6F_3H$  produced could be energized by  $C_6F_6$  and afford the tetrafluorobenzenes via a sensitized pathway.

<sup>(25)</sup> It is possible that the energy requirement differences for the reactions at 1027 and 944 cm<sup>-1</sup> are due to the different absorption cross section for the two cases. The average absorption cross section for the 994-cm<sup>-1</sup> excited reaction ( $0.83 \times 10^{-19}$  cm<sup>2</sup>/molecule) is lower than that for the 1027-cm<sup>-1</sup> excited reaction ( $5.2 \times 10^{-19}$  cm<sup>2</sup>/molecule).