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Laser-Induced Reactions of Hexafluorobenzene and Selected Hydride Compounds[1,2]

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Infrared-laser-induced reactions between C_6F_6 and general hydrides R–H (R = H, D, CH_3, $HC{\equiv}C$, $H_2C{=}CH$, and Cl) were studied by irradiating C_6F_6 at 1027 cm^{-1} in C_6F_6/R–H mixtures. In general, two competitive pathways involving C–F bond cleavage in C_6F_6 were observed as follows: (1) $C_6F_6 + R{-}H \rightarrow C_6F_5H + R{-}F$ and (2) $C_6F_6 + R{-}H \rightarrow C_6F_5R + HF$. C_6F_6 decomposition also took place to a minor extent depending on the mole fraction of C_6F_6 and gave rise to C_2F_4 and C_2H_2. From infrared and GC/MS analysis of the product mixtures after 20–200 pulses, C_6F_5H was observed in all reactions except that involving D_2. When D_2 was used C_6F_5D was the major product. C_6F_5H was the major product in the reactions involving H_2 and C_2H_2. In the reaction with C_2H_4, C_6F_5H was the major product derived from C_6F_6 though C_2H_2 was the major product of the reaction. The large amount of C_2H_2 seems to be derived from an additional sensitized decomposition of C_2H_4. C_6F_5H was present in minor amounts in the reaction with CH_4 and HCl. Besides C_6F_5H, other monosubstituted products derived from C_6F_6 were also formed, generally within 20–100 pulses. Thus, $C_6F_5CH_3$, $C_6F_5CH{=}CH_2$, $C_6F_5C{\equiv}CH$, and C_6F_5Cl were produced, respectively, in the reaction of C_6F_6 with CH_4, C_2H_4, C_2H_2, and HCl. In the first and last cases these products were the major ones observed. The results are discussed mechanistically in terms of the initial formation of the $C_6F_5^{\bullet}$ radical and synthetically in terms of the utility of obtaining selective laser-induced reduction of C_6F_6.

Introduction

In the preceding paper[1] the reaction of C_6F_6/SiH_4 mixtures was studied by single-pulse CO_2 laser irradiation. We observed that the decomposition of C_6F_6 was substantially increased by the addition of silane. One of the possibilities for the significant increment in the decomposition of C_6F_6 in the laser-induced reaction with SiH_4 could be related to the primary formation of pentafluorophenyl and fluorine radicals as follows:

$$C_6F_6 \rightarrow C_6F_6^{*} \rightarrow {}^{\bullet}C_6F_5 + {}^{\bullet}F \qquad (1)$$

The collisional reactions of fluorine atoms with various hydride molecules have been studied by Setser et al.[4] using infrared chemiluminescence techniques as well as by McDonald et al.[5] Setser et al.[4] have observed the partitioning of residual energy in HF after the reaction of fluorine atoms with various hydrides.

$${}^{\bullet}F + R{-}H \rightarrow HF + {}^{\bullet}R \qquad (2a)$$

McDonald et al.[5] found that the substitution reaction 3 was especially predominant in the reaction of fluorine atoms with olefins.

$$CH_2{=}CHX + {}^{\bullet}F \rightarrow CH_2{=}CHF + {}^{\bullet}X \qquad (3)$$

$$(X = H, Cl, Br, CH_3)$$

The pentafluorophenyl radical has not been studied as a reactive reagent, and its formation and stability have not been specifically confirmed spectroscopically or otherwise.

In this paper the results of a study of the laser-induced reaction of C_6F_6 with H_2, D_2, CH_4, $CH_2{=}CH_2$, $CH{\equiv}CH$, and HCl are reported. The products that are observed strongly suggest the presence of ${}^{\bullet}C_6F_5$ (and ${}^{\bullet}F$) radicals in the reactions and the results indicate that the laser method for reduction of the C–F bond in C_6F_6 is a useful one.

Experimental Section

A pulsed CO_2 TEA laser (Lumonics Research Ltd., Model K-203) was used in these experiments. The P(40) line at 1027.38 cm^{-1} was used and the laser beam size was 20 mm in diameter. No focusing techniques were utilized. The methods used for the measurement of the laser fluence (and E_{abs}) were the same as that described in the preceding paper.[1] Liquid C_6F_6 was purchased from Aldrich Chemical Co. and was purified by bulb to bulb distillation. H_2, CH_4, $CH_2{=}CH_2$, and HCl were purchased from Matheson Co. and D_2 and $CH{\equiv}CH$ from Airco Industrial Gases. All were used without further purification. Mole fractions of C_6F_6 (R) are given in terms of the following formula, $R = P_{C_6F_6}/P_{C_6F_6} + P_{R-H}$.

A cylindrical infrared cell, fabricated from stainless steel and equipped with KCl windows on both ends, was used as the reaction vessel. The optical path length was 2.54 cm.

The infrared spectra of C_6F_6 and hydride mixtures were measured before and after 20–200 pulses of laser irradiation. The reaction products were further analyzed by using GC–MS techniques (HP Model 5992). A Porapak Q column was used and the temperature of the column oven was increased from 90 to 200 °C linearly with an initial flow rate of 16 mL/min.

Results

$C_6F_6 + H_2$. The infrared spectra of a mixture of C_6F_6 (15.2 Torr) and H_2 (7.8 Torr) are shown in Figure 1a ($R = 0.66$) before and after laser irradiation (20 pulses). The fluence used was 0.7 J/cm^2. During the irradiation a bright emission was observed in the infrared cell which was observed even in the daylight. The infrared absorption frequencies observed after irradiation at 1648, 1512, 1182, 1142, 1079, 959, 837, and 719 cm^{-1} (Figure 1a) indicated the presence of pentafluorobenzene. The infrared absorption bands of C_2F_4 were also observed (1335 and 1185 cm^{-1}) together with those of $C_6F_5CF_3$ (1245 and 880 cm^{-1}). When the mole fraction of C_6F_6 was decreased to $R = 0.31$, the amount of C_2F_4 present after irradiation decreased as well (Figure 1b). In addition the infrared absorption bands at 730 and 630 cm^{-1}, respectively, indicated the presence of acetylene and 1,3-butadiyne.

The infrared vibrational rotation lines of HF were also observed in the region of 3900 and 3800 cm^{-1} indicating its presence after irradiation. The observed vibrational rotation lines of HF molecule were assigned as $J = 1$ and $J = 4$ of the P(J) branch which corresponded with the values reported by Guelachvili.[6] In order

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(1) For previous paper in this series see: Koga, Y.; Serino, R. M.; Chen, R.; Keehn, P. M. *J. Phys. Chem. Soc.*, preceding paper in this issue.

(2) This work was presented in part at the Photochemical Conference at Okayama University, Oct. 6, 1984.

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(4) (a) Bogan, D. J.; Setser, D. W. In *Fluorine-Containing Free Radicals Kinetics* and *Dynamics of Reactions*; Root, J. W., Ed.; American Chemical Society: Washington, DC, 1978; pp 237–280. (b) Smith, D. J.; Setser, D. W.; Kim, K. C.; Bogan, D. J. *J. Phys. Chem.* **1977**, *81*, 898. (c) Bogan, D. J.; Setser, D. W.; Sung, J. P. *J. Phys. Chem.* **1977**, *81*, 888. (d) Sung, J. P.; Setser, D. W. *J. Chem. Phys.* **1978**, *69*, 3868. (e) Tamagake, K.; Setser, D. W. In *State-to-State Chemistry*; Brooks, P. R., Hayes, E. F., Eds.; American Chemical Society: Washington, DC, 1977; pp 124–126.

(5) (a) Moehlmann, J. G.; McDonald, J. D. *J. Chem. Phys.* **1975**, *62*, 3052; **1975**, *62*, 3061. (b) Moehlmann, J. G.; Gleaves, J. T.; Hudgens, J. W.; McDonald, J. D. *J. Chem. Phys.* **1974**, *60*, 4790.

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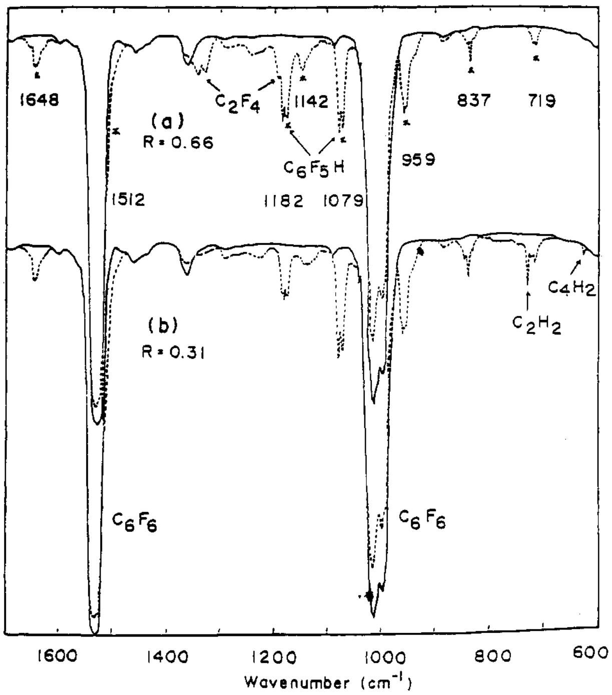

Figure 1. Infrared spectra of a mixture of C_6F_6 and H_2 before (—) and after (---) laser irradiation at 1027 cm^{-1} (20 pulses; fluence, 0.7 J/cm^2): (a) $R = 0.66$, (b) $R = 0.31$. * indicates the absorption bands of C_6F_5H.

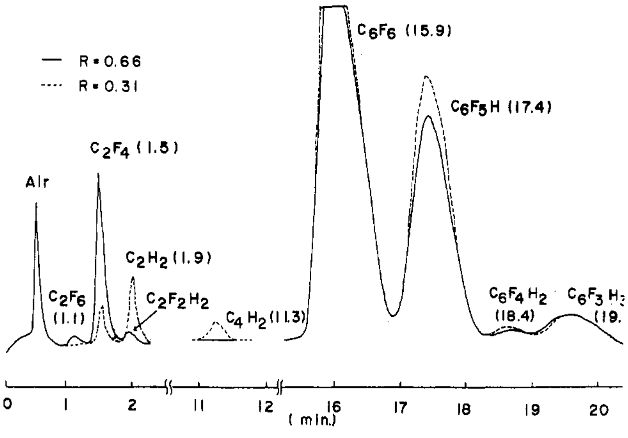

Figure 2. Gas chromatogram of the product mixture of C_6F_6 and H_2 after irradiation (20 pulses; fluence, 0.7 J/cm^2): $R = 0.66$ (—) and $R = 0.31$ (---). Retention times are given in parentheses (min) after each compound.

to observe the infrared spectrum of HF it was necessary to take the spectrum immediately after laser irradiation since the absorption lines of HF disappeared within 5 min.

GC–MS analysis of the product mixture in both cases ($R = 0.66$ and 0.31) demonstrated the presence of small amounts of $C_6F_4H_2$ and $C_6F_3H_3$ as well. Figure 2 shows the gas chromatogram of the products in the reaction of C_6F_6 and H_2. The peaks assigned to $C_6F_3H_3$ and $C_6F_5CF_3$ overlap. However, by mass spectral analysis, i.e., monitoring the M^+ ion signal for each compound, the two were distinguishable. C_2F_6 and $C_2F_2H_2$ were also present in trace amounts when the mole fraction was high ($R = 0.66$).

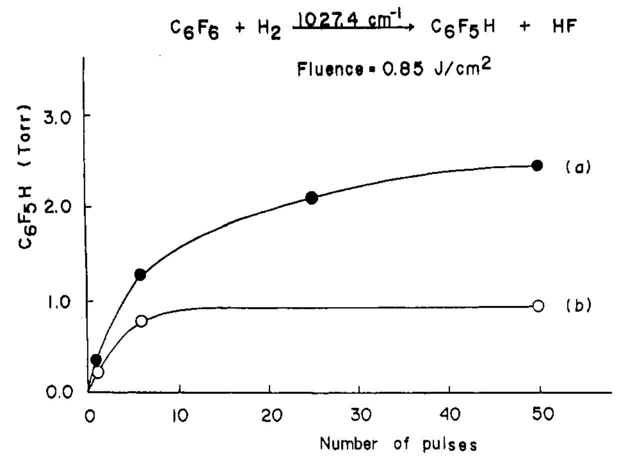

Figure 3. Dependence of the amount of C_6F_5H produced (Torr) on the number of laser pulses for the following mixtures: (a) $P_i(C_6F_6)$ = the initial pressure of C_6F_6 = 15.6 Torr, $P_i(H_2)$ = 19 Torr ($R = 0.45$); (b) $P_i(C_6F_6)$ = 8 Torr and $P_i(H_2)$ = 12 Torr ($R = 0.20$).

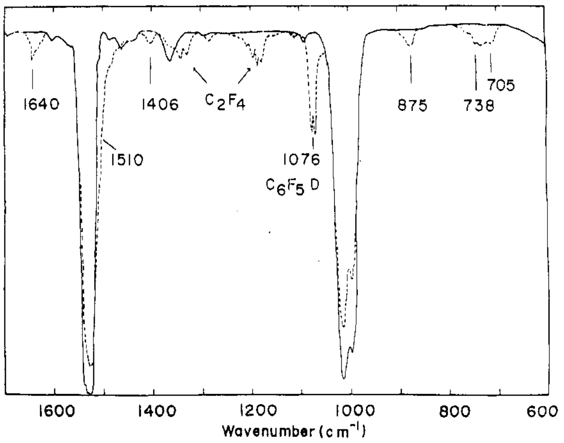

Figure 4. Infrared spectra of a mixture of C_6F_6 and D_2 before (—) and after (---) irradiation at 1027 cm^{-1} (20 pulses; fluence, 0.61 J/cm^2; $R = 0.51$).

TABLE I: Product Distribution on the C_6F_6/H_2 Reaction after a Single Pulse of Laser Irradiation (1027 cm^{-1}; Fluence, 0.7 J/cm^2)

initial press., Torr			CPF, %	product amounts, Torr			E_{abs},[a] kJ/mol
C_6F_6	H_2	R		C_6F_5H	C_2F_4	C_2H_2	
7.50	0	1.0	5		0.05		210
7.99	1.85	0.81	9	0.18	0.13		210
7.82	5.04	0.61	15	0.23	0.21		230
7.57	7.84	0.49	15	0.23	0.09	0.22	240
7.53	11.12	0.40	8	0.18	0.03	0.16	200
7.50	27.14	0.22	5	0.08			220

[a] E_{abs} is ±15%.

The dependence of the amount of C_6F_5H formed at a fluence of 0.85 J/cm^2 with the number of laser pulses is shown in Figure 3. The amount of C_6F_5H present was obtained from the infrared peak intensity of the 1079-cm^{-1} band. After 50 pulses a pressure of 2.4 Torr of C_6F_5H was produced from an initial pressure of 15.5 Torr of C_6F_6. This represents an overall yield of 15.5% of C_6F_5H with an average conversion per flash (CPF) of C_6F_6 of 1.4%. The curve for the production of C_6F_5H gradually approaches a plateau as the number of laser pulses increases.

The results of a single-pulse irradiation experiment are indicated in Table I. The fluence was 0.7 J/cm^2. Between $R = 0.4$ and $R = 0.8$ the CPF for C_6F_6 ranged between 8 and 15% while the amount of C_6F_5H increased to a maximum value and then decreased. At $R = 0.5$, when the CPF of C_6F_6 was 15%, the yield of C_6F_5H was 3%.

C_6F_6 + D_2. The infrared spectra of a mixture of C_6F_6 (15.6 Torr) and D_2 (15.1 Torr) are shown in Figure 4 before and after irradiation (20 pulses; fluence, 0.61 J/cm^2). Pentafluorodeuteriobenzene was observed as the main product and identified by its strong infrared bands at 1510 and 1076 cm^{-1} and its weaker bands at 1640, 1406, 875, 738, and 705 cm^{-1}. The infrared bands of C_6F_5D corresponded well with the wavenumbers observed by Eaton and Steele[7] for the in-plane modes, and by Pearce, Steele,

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(6) Guelachvili, G. *Opt. Commun.* **1976**, *19*, 150.

(7) Eaton, J. V.; Steele, D. *J. Mol. Spectrosc.* **1973**, *48*, 446.

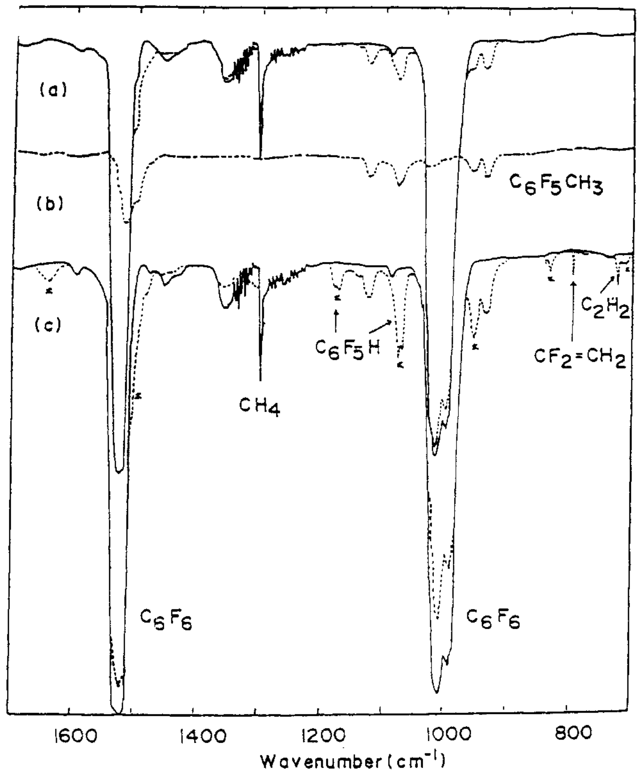

Figure 5. (a) Infrared spectra of a mixture of C_6F_6 and CH_4 before (—) and after (---) irradiation at 1027 cm^{-1} (100 pulses; fluence, 0.64 J/cm^2; R = 0.48). (b) Infrared spectrum of pure $C_6F_5CH_3$ (0.6 Torr). (c) Infrared spectra of a mixture of C_6F_6 and CH_4 before (—) and after (---) irradiation at 1027 cm^{-1} (100 pulses; fluence, 0.79 J/cm^2; R = 0.48).

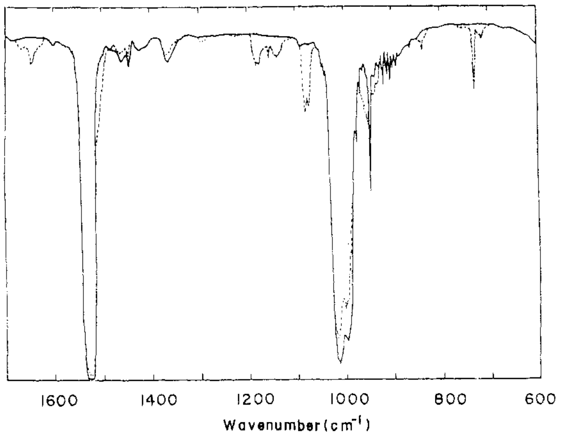

Figure 6. Infrared spectra of a mixture of C_6F_6 and C_2H_4 before (—) and after (---) irradiation at 1027 cm^{-1} (50 pulses; fluence, 0.64 J/cm^2; R = 0.49).

and Radcliffe[8] for the out-of-plane modes. DF and $CF_2{=}CF_2$ were also observed in the infrared spectrum after irradiation. The infrared absorption lines of DF, observed in the region of 2906 cm^{-1} were in good agreement with those observed by Rao et al.[9] GC-MS analysis indicated the presence of $C_6F_4D_2$ and $C_6F_3D_3$ as well as $C_6F_5CF_3$.

C_6F_6 + CH_4. The infrared spectra of a mixture of C_6F_6 (15.5 Torr) and CH_4 (17 Torr) are shown in parts a and c of Figure 5 before and after the irradiation (100 pulses) at fluences of 0.64 and 0.79 J/cm^2, respectively. As seen in Figure 5a the four infrared absorption bands (1130, 1082, 960, and 938 cm^{-1}) associated with $C_6F_5CH_3$ (Figure 5b) were present after irradiation and indicated that $C_6F_5CH_3$ was the major product. A trace amount of C_6F_5H was also observed. The GC-MS data confirmed this and indicated the presence of $C_6F_5CH_3$ and C_6F_5H only. In this laser-induced reaction a pressure of 0.6 Torr of $C_6F_5CH_3$ was produced after 100 pulses which represented a yield of 4% of this compound.

TABLE II: GC-MS Analysis of the Reaction Mixture Produced after Irradiation of a Mixture of C_6F_6/C_2H_4 at 1027 cm^{-1} (50 pulses; Fluence, 0.64 J/cm^2; R = 0.49)

products	amount, Torr	retention time,[a] min
$CH{\equiv}CH$	3.0	1.7
$CH_2{=}CHF$	1.2	2.4
$CH_2{=}CH{-}CH{=}CH_2$	0.55	11.6
$CH_2{=}CF{-}CH{=}CH_2$	trace	13.3
C_6F_5H	1.8	19.3
$C_6F_4H_2$	trace	20.2
$C_6F_3H_3$	trace	21.2
$C_6F_5CH{=}CH_2$	0.37	36.2

[a] Porapak Q column was used at 90–200 °C.

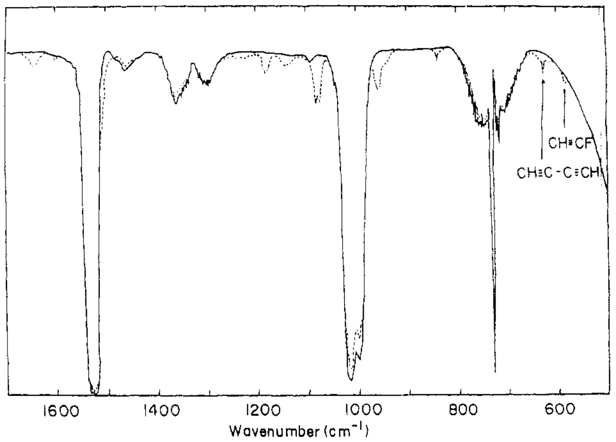

Figure 7. Infrared spectra of a mixture of C_6F_6 and C_2H_2 before (—) and after (---) irradiation at 1027 cm^{-1} (200 pulses; fluence, 0.59 J/cm^2; R = 0.26).

The amount of C_6F_5H increased substantially when a higher fluence (0.79 J/cm^2) was used as shown in Figure 5c. The infrared absorption bands of $CF_2{=}CF_2$ (1335 and 1185 cm^{-1}), $CF_2{=}CH_2$ (806 cm^{-1}), and $CH{\equiv}CH$ (730 cm^{-1}) were also observed. These were absent in the reaction at lower fluence.

C_6F_6 + $CH_2{=}CH_2$. The infrared spectra of a mixture of C_6F_6 (15 Torr) and $CH_2{=}CH_2$ (15.6 Torr) are shown in Figure 6 before and after laser irradiation (50 pulses; fluence 0.64 J/cm^2). Infrared absorption bands of C_6F_5H, $CH_2{=}CHF$, and $CH{\equiv}CH$ were observed with the latter being the major product of the reaction but the former being the major product derived from C_6F_6 reduction. The mixture was further analyzed by GC-MS (see Table II). In addition to the compounds identified by IR analysis (C_2H_2, 19%; C_2H_3F, 8%; C_6F_5H, 12%), butadiene (7%), fluorobutadiene, tetrafluorobenzenes, trifluorobenzenes, and $C_6F_5CH{=}CH_2$ (0.37 Torr) were observed by GC-MS analysis. The latter compound (2.4% yield) could not be detected by IR analysis because its IR bands overlapped with those of C_6F_6.

C_6F_6 + $CH{\equiv}CH$. The infrared spectra of a mixture of C_6F_6 (16.3 Torr) and $CH{\equiv}CH$ (45 Torr) are shown in Figure 7 before and after laser irradiation (200 pulses; fluence, 0.59 J/cm^2). Infrared bands associated with C_6F_5H (1648, 1182, 1079, 959, 837 cm^{-1}), $CH{\equiv}CF$ (580 cm^{-1}), and $CH{\equiv}C{-}C{\equiv}CH$ (630 cm^{-1}) were observed. The product mixture was also analyzed by GC-MS. In addition to the products observed by IR analysis trace amounts of $CH{\equiv}C{-}CF_3$, $C_6F_3H_3$, and $C_6F_5CF_3$ were observed. Furthermore, an ion peak at m/e 192 was detected (retention time, 38 min) which corresponded to the molecular ion of $C_6F_5C{\equiv}CH$.

C_6F_6 + HCl. The infrared spectra of a mixture of C_6F_6 (16.7 Torr) and HCl (16.1 Torr) are shown in Figure 8 before and after laser irradiation (100 pulses; fluence, 0.59 J/cm^2). The infrared bands of C_6F_5Cl were clearly visible at 1508, 1102, and 882 cm^{-1}. Other products observed in the infrared spectrum were C_6F_5H, $C_6F_5CF_3$, $CF_2{=}CF_2$, CF_3CF_3, and HF. GC-MS analysis of this

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[8] Pearce, R. A. R.; Steele, D.; Radcliffe, K. *J. Mol. Struct.* **1973**, *15*, 409.

[9] Spanbauer, R. N.; Rao, K. N. *J. Mol. Spectrosc.* **1965**, *16*, 100.

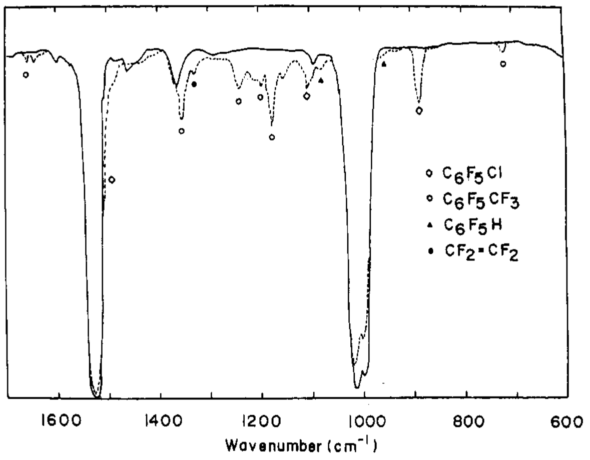

Figure 8. Infrared spectra of a mixture of C_6F_6 and HCl before (—) and after (- - -) irradiation at 1027 cm^{-1} (100 pulses; fluence, 0.59 J/cm^2; R = 0.51).

reaction mixture corroborated the infrared analysis but also indicated the presence of a trace amount of $CClF_3$.

Discussion

The results of the laser-induced reactions of C_6F_6 with various hydride reagents indicate that the C–F bond in C_6F_6 can be reduced rather efficiently by the laser method. In addition, the data strongly supports the presence of the pentafluorphenyl radical and suggests that homolytic C–F bond cleavage in C_6F_6 is an important primary reaction after C_6F_6 excitation. One of the possible decomposition channels suggested by Grunwald et al. in the laser-induced decomposition of C_6F_6 involves the homolytic cleavage of the C–F bond as noted in eq 1.[10] In the presence of hydride reagents R–H (where R = H, D, CH_3, C_2H_3, C_2H, and Cl) these radicals should abstract a hydrogen and/or an R unit giving C_6F_5H, C_6F_5R, HF, and RF as follows:

$$^{\bullet}C_6F_5 + RH \rightarrow C_6F_5H + {}^{\bullet}R \qquad (4a)$$

and/or

$$^{\bullet}C_6F_5 + RH \rightarrow C_6F_5R + {}^{\bullet}H \qquad (4b)$$

$$^{\bullet}F + RH \rightarrow HF + {}^{\bullet}R \qquad (2a)$$

and/or

$$^{\bullet}F + RH \rightarrow RF + {}^{\bullet}H \qquad (2b)$$

The overall reactions, therefore, can be expressed by eq 5 and 6.

$$C_6F_6 + R\text{–}H \rightarrow C_6F_5H + RF \qquad (5)$$

$$C_6F_6 + R\text{–}H \rightarrow C_6F_5R + HF \qquad (6)$$

Since each should have different enthalpies (as explained later) the processes should compete more or less with one another. This is generally what we observed.

C_6F_6 + H_2. The primary chemical reaction for the C_6F_6/H_2 system is given in eq 7 (underlined compounds indicate an observed product). A mechanism by which this reaction may take place

$$C_6F_6 + H_2 \rightarrow \underline{C_6F_5H} + \underline{HF} \qquad (7)$$

is suggested as follows:

Initiation

$$C_6F_6 \rightarrow C_6F_6{}^{*} \rightarrow {}^{\bullet}C_6F_5 + {}^{\bullet}F \qquad (1)$$

Propagation

$$^{\bullet}F + H_2 \rightarrow HF + {}^{\bullet}H \qquad (8)$$

$$^{\bullet}C_6F_5 + H_2 \rightarrow C_6F_5H + {}^{\bullet}H \qquad (9)$$

$$^{\bullet}H + C_6F_6 \rightarrow {}^{\bullet}C_6F_5 + HF \qquad (10)$$

Termination

$$^{\bullet}C_6F_5 + {}^{\bullet}H \rightarrow C_6F_5H \qquad (11)$$

$$^{\bullet}H + {}^{\bullet}F \rightarrow HF \qquad (12)$$

$$2{}^{\bullet}H \rightarrow H_2 \qquad (13)$$

$$2{}^{\bullet}F \rightarrow F_2 \qquad (14)$$

$$2{}^{\bullet}C_6F_5 \rightarrow C_6F_5\text{–}C_6F_5 \qquad (15)$$

C_6F_5H was produced over a wide range of R values as denoted in Table I. This implies that the decomposition of C_6F_6 expressed in eq 1 occurs uniformly in these regions such that C_6F_5H can be formed by hydrogen abstraction or scavening by $C_6F_5{}^{\bullet}$ radical. The amount of C_2F_4 and C_2H_2 on the other hand seems to depend more on the mole fraction of C_6F_6 (R). In a fashion similar to that observed in the C_6F_6/SiH_4 system,[1] as the amount of C_2F_4 decreased, C_2H_2 increased in the $R \leq 0.5$ region. This implies that competitive decomposition of C_6F_6 (eq 16) occurs simultaneously with the reaction described in eq 1. Thus, as C–F bond breaking takes place leading to $C_6F_5{}^{\bullet}$ with ultimate formation of C_6F_5H and HF, C–C bond breaking takes place leading to fragmentation of C_6F_6 (C_2F_4 and C_2H_2) albeit in a more selective R range and to a lesser extent.

$$C_6F_6 \rightarrow C_6F_6{}^{*} \rightarrow {}^{\bullet}CFCFCFCFCFCF^{\bullet} \qquad (16)$$

The energy requirements for these two decomposition pathways were estimated by Grunwald et al.[10] to be similar. It seems reasonable therefore that both C_6F_5H and C_2F_4 should be observed under similar conditions (Figure 1, Table I). However, the amount of C_2F_4 decreases faster than C_6F_5H in the $0.6 < R < 0.2$ zone. This suggests that the energy requirement for the reaction leading to C_2F_4 is slightly greater than that leading to C_6F_5H. That is, since the average energy per molecule decreases (due to collisional deactivation) as the H_2 pressure increases and since C_6F_5H continues to be formed in substantial quantities, the energy requirement for C–C bond cleavage should be greater than that for C–F bond cleavage.[11]

During the propagation steps, H_2 can act as a radical scavenger. This would generate C_6F_5H and HF along with the $H^{\bullet}$ radical. $C_6F_5{}^{\bullet}$ radical might be expected to continue the process (eq 8–10) despite the expected endothermicity of reaction 10 because of the excess energy generated in reactions 8 and 9.

Radical combination, as described in eq 11–15, may lead to the following possibilities. These reactions may generate a significant amount of C_6F_5H and HF due to the probability of there being high concentrations of radicals during the laser reaction. Decafluorobiphenyl (C_6F_5–C_6F_5), however, was not detected either by IR or GC–MS analysis.[12] This may be due to the nonvolatile nature of the compound, to the amount formed being below detection sensitivity or to the possibility that the compound would not survive the laser reaction conditions.

The most abundant product in the C_6F_6/H_2 reaction was C_6F_5H (Figures 1 and 2 and Table I). Its yield increases with the number of pulses as shown in Figure 3 and corresponds to as much as 0.5 mg of C_6F_5H (from 3.5 mg of C_6F_6) after 50 pulses at a fluence of 0.85 J/cm^2. When considering that the reaction takes place during the laser flash and immediately thereafter (1 μs) this implies that the material was produced conservatively in no more than 50 μs. Extrapolated, this would give 10 g of product in 1 s of real laser irradiation, an amount which is significant for large scale production.

The formation of $C_6F_4H_2$ and $C_6F_3H_3$ (Figure 2) may be considered in terms of successive exchange reactions identical to that found for C_6F_6. Thus, as depicted in eq 17 and 18, reduction

$$C_6F_5H + H_2 \rightarrow C_6F_4H_2 + HF \qquad (17)$$

$$C_6F_4H_2 + H_2 \rightarrow C_6F_3H_3 + HF \qquad (18)$$

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(10) Duignan, M.; Grunwald, E.; Speiser, S. *J. Phys. Chem.* **1983**, *87*, 4387.

(11) This assumes that $C_6F_5{}^{\bullet}$ is not the precursor of C_2F_4 though this is by no means assured.

(12) Bryce-Smith, D.; Connett, B. E.; Gilvert, A. *Chem. Ind.* **1966**, 855.

of C_6F_5H should give $C_6F_4H_2$ and reduction of $C_6F_4H_2$ should give $C_6F_3H_3$. To support the suggestion and to demonstrate the generality of the laser-induced C–F bond reduction, we irradiated C_6F_5H (15 Torr) at 1080 cm^{-1} in the presence of H_2 (11.9 Torr). After 300 flashes at a fluence of 1.4 J/cm^2 a 41% conversion of C_6F_5H was realized and all three tetrafluorobenzene isomers were observed by GC–MS analysis (Chromosorb column). Since C_6F_5H does not absorb at 1027 cm^{-1} (the wavelength used to initiate reduction in the C_6F_6/H_2 system) the likely mechanism for its activation in the C_6F_6/H_2 system is via sensitization by C_6F_6 as depicted in eq 19. This might be followed by dissociation of

$$C_6F_6{}^* + C_6F_5H \rightarrow C_6F_5{}^*H + C_6F_6 \qquad (19)$$

$$C_6F_5{}^*H \rightarrow {}^\bullet C_6F_4H + {}^\bullet F \qquad (20)$$

$C_6F_5{}^*H$ to ${}^\bullet C_6F_4H$ and ${}^\bullet F$ radicals and successive reduction by H_2 to give $C_6F_4H_2$ in a manner similar to that described for the reduction of C_6F_6 (eq 8–11). Though $C_6F_3H_3$ was not observed in the irradiation of the C_6F_5H/H_2 system, its formation from $C_6F_4H_2{}^*$ in the C_6F_6/H_2 system is more likely since C_6F_6 is probably a better sensitizer than C_6F_5H.

C_6F_6 + D_2. In a fashion similar to that described for the C_6F_6/H_2 system (eq 7–15) the reaction of C_6F_6 and D_2 afforded C_6F_5D. This reaction may be written as in eq 20a with the primary

$$C_6F_6 + D_2 \rightarrow \underline{C_6F_5D} + \underline{DF} \qquad (20a)$$

step again being the formation of ${}^\bullet C_6F_5$ and ${}^\bullet F$ radicals. Though the amount of $C_6F_4D_2$ and $C_6F_3D_3$ was relatively small it was detected by GC–MS analysis. The replacement of fluorine by deuterium is synthetically useful and this new method of synthesis of C_6F_5D suggests the utility of the laser-induced process for the preparation of similar deuteriated aromatics from their fluorinated analogues.

C_6F_6 + CH_4. From the results described in Figure 5a,c the product of the laser-induced reaction of C_6F_6/CH_4 mixtures depends on the laser fluence. The primary product of the reaction at a fluence of 0.64 J/cm^2 was $C_6F_5CH_3$ (Figure 5a). C_6F_5H was hardly observed under these conditions. (Compare part a of Figure 5 with part b, the infrared spectrum of neat $C_6F_5CH_3$.) On the other hand, at higher fluence (0.79 J/cm^2) the amount of C_6F_5H is increased substantially (Figure 5c).

At lower fluence (0.64 J/cm^2) the reaction between C_6F_6 and CH_4 may be written as in eq 21. At higher fluence (0.79 J/cm^2)

$$C_6F_6 + CH_4 \rightarrow \underline{C_6F_5CH_3} + \underline{HF} \qquad (21)$$

reactions 22–24 seem to be occurring along with (21) with the formation of C_6F_5H and $CH_2{=}CF_2$.

$${}^\bullet C_6F_5 + CH_4 \rightarrow \underline{C_6F_5H} + {}^\bullet CH_3 \qquad (22)$$

$${}^\bullet F + CH_4 \rightarrow {}^\bullet CH_3 + \underline{HF} \qquad (23)$$

$${}^\bullet CH_3 + {:}CF_2 \rightarrow \underline{CH_2{=}CF_2} + {}^\bullet H \qquad (24)$$

Difluorocarbene $:CF_2$ (eq 24) is no doubt formed by the laser-induced decomposition of C_6F_6[10] and its reaction with ${}^\bullet CH_3$ to form $CF_2{=}CH_2$ has already been reported.[13]

C_6F_6 + $CH_2{=}CH_2$. Based on the IR and GC–MS analyses a suggestion for the mechanism of the $C_6F_6/CH_2{=}CH_2$ reaction is diagrammed in Figure 9. The formation of vinyl fluoride can be viewed as the addition of the fluorine radical to ethylene followed by elimination of the $H^\bullet$ radical, a reaction studied by Kato and Morokuma using ab initio methods.[14] Similarly the addition of pentafluorophenyl radical to ethylene followed by loss of ${}^\bullet H$ would give $C_6F_5CH{=}CH_2$.

It should be noted that similar to the C_6F_6/CH_4 system both types of reactions (eq 5 and 6) occurred similtaneously in the C_6F_6/C_2H_4 system at a fluence of 0.64 J/cm^2 (Figure 9). The formation of the vinyl radical $CH_2{=}\dot{C}H$ is supported by the production of 1,3-butadiene and fluoro-1,3-butadiene.

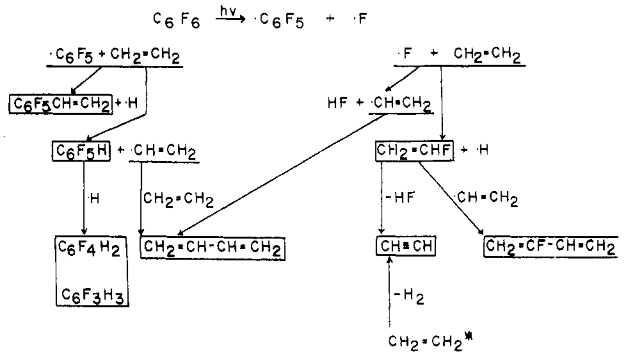

Figure 9. Diagram of product formation in the laser-induced reaction of C_6F_6 and $CH_2{=}CH_2$.

The formation of acetylene is possible by at least two different pathways as shown in eq 25 and 26 in addition to those originating directly from C_6F_6 and the hydride source. When C_2H_2 is derived

$$CH_2{=}CH_2{}^* \rightarrow CH{\equiv}CH + H_2 \qquad (25)$$

$$CH_2{=}CHF^* \rightarrow CH{\equiv}CH + HF \qquad (26)$$

solely from C_6F_6 the amount of C_2H_2 formed was observed to be small (see Table I). The formation of C_2H_2 by the reactions described in eq 25 and 26 is supported by previous studies on the laser-induced decomposition of C_2H_4 (949 cm^{-1}) and C_2H_3F (944 cm^{-1}) by Nagai[15] and Quick,[16] respectively and the processes are quite efficient. Since C_6F_6 has been used as a sensitizer,[17] excitation of C_2H_4 and C_2H_3F under the reaction conditions is reasonable. Thus, the greater part of C_2H_2 production is likely derived from sensitized decomposition of C_2H_4 which occurs simultaneously with, but separate from, C_6F_6 reduction which produces C_6F_5H as the major product.

C_6F_6 + $CH{\equiv}CH$. The products observed in the C_6F_6/C_2H_2 system (fluence (0.59 J/cm^2)) were C_6F_5H, $HC{\equiv}CF$, and diacetylene as shown in Figure 7. The major reaction is summarized in eq 27. With pentafluorobenzene as the most abundant product

$$C_6F_6 + CH{\equiv}CH \rightarrow \underline{C_6F_5H} + \underline{CH{\equiv}CF} \qquad (27)$$

the C–F → C–H exchange reaction (eq 5) represents the major channel. However a trace of pentafluorophenylacetylene ($C_6F_5C{\equiv}CH$) was detected by GC–MS analysis (m/e 192) indicating that the other exchange reaction (eq 6) also occurs, albeit, to a lesser extent.

C_6F_6 + HCl. The reactions for the C_6F_6/HCl system are given by eq 28 and 29. At 0.59 J/cm^2 the formation of C_6F_5Cl was

$$C_6F_6 + HCl \rightarrow \underline{C_6F_5Cl} + \underline{HF} \qquad (28)$$

$$C_6F_6 + HCl \rightarrow \underline{C_6F_5H} + FCl \qquad (29)$$

favored over C_6F_5H. It should be noted that the formation of C_6F_5Cl was also observed in the laser-induced reactions of C_6F_6 with Cl_2, CCl_4, $SiCl_4$, and BCl_3 at 1027 cm^{-1}.[18] It seems therefore that the fluorine atom of hexafluorobenzene can be easily substituted by a chlorine atom, as well as a hydrogen atom, in the laser-induced process.

The formation of $C_6F_5CF_3$ (Figure 8) is indicative of $:CF_2$ formation as suggested by Duignan et al.[10] and implies the simultaneous direct decomposition of C_6F_6 in this system.

Enthalpies of Reaction for the Various C_6F_6/RH Systems. Using the general reactions described in eq 5 and 6 and neglecting the minor side and secondary processes (i.e., formation of C_2F_4, C_2H_2, $C_6F_5CF_3$, $C_6F_4H_2$, $C_6F_3H_3$, etc.) the enthalpies of the two exchange processes can be estimated roughly from bond dissociation energies. The reactions, their calculated enthalpies and various bond dissociation energies[19,20] are given in Table III. From

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(13) Ritter, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 2441.

(14) Kato, S.; Morokuma, K. *J. Chem. Phys.* **1980**, *72*, 206.

(15) Nagai, K.; Katayama, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1269.

(16) Quick, C. R., Jr.; Wittig, C. *J. Chem. Phys.* **1978**, *69*, 4201.

(17) Selamoglu, N.; Steel, C. *J. Phys. Chem.* **1983**, *87*, 1133.

(18) To be published.

TABLE III: Heats of Reaction (ΔH in kJ/mol) Obtained from Bond Dissociation Energies[19,20] in the Reactions of C_6F_6 with Various Hydrides

$\underset{644}{C_6F_5\text{-}F} + \underset{435}{H\text{-}H} \rightarrow \underset{636}{C_6F_5\text{-}H} + \underset{565}{H\text{-}F}$	$\Delta H = -122$
$\underset{644}{C_6F_5\text{-}F} + \underset{444}{D\text{-}D} \rightarrow \underset{(\sim 644)}{C_6F_5\text{-}D} + \underset{578}{D\text{-}F}$	$\Delta H \approx -134$
$\underset{644}{C_6F_5\text{-}F} + \underset{435}{CH_3\text{-}H} \xrightarrow{1} \underset{439}{C_6F_5\text{-}CH_3} + \underset{565}{H\text{-}F}$	$\Delta H_1 = -75$
$\xrightarrow{2} \underset{636}{C_6F_5\text{-}H} + \underset{452}{CH_3\text{-}F}$	$\Delta H_2 = -9$
$\underset{644}{C_6F_5\text{-}F} + \underset{431}{H\text{-}Cl} \xrightarrow{1} \underset{544}{C_6F_5\text{-}Cl} + \underset{565}{H\text{-}F}$	$\Delta H_1 = -34$
$\xrightarrow{2} \underset{636}{C_6F_5\text{-}H} + \underset{255}{F\text{-}Cl}$	$\Delta H_2 = +184$
$\underset{644}{C_6F_5\text{-}F} + \underset{460}{CH_2{=}CH\text{-}H} \xrightarrow{1} \underset{636}{C_6F_5\text{-}H} + \underset{(>460)}{CH_2{=}CH\text{-}F}$	$\Delta H_1 = (-)$
$\xrightarrow{2} \underset{(>419)}{C_6F_5\text{-}CH{=}CH_2} + \underset{565}{H\text{-}F}$	$\Delta H_2 = (+)$
$\underset{644}{C_6F_5\text{-}F} + \underset{523}{CH{\equiv}C\text{-}H} \xrightarrow{1} \underset{636}{C_6F_5\text{-}H} + \underset{(>523)}{CH{\equiv}C\text{-}F}$	$\Delta H_1 = (-)$
$\xrightarrow{2} \underset{(?)}{C_6F_5\text{-}C{\equiv}CH} + \underset{565}{H\text{-}F}$	$\Delta H_2 = (?)$

these calculations it is predicted that the reactions of C_6F_6 with H_2 and D_2 should be exothermic and the formation of C_6F_5H and C_6F_5D, respectively, should be favored. On the other hand, in the reaction of C_6F_6 with CH_4 or HCl the favored pathway should be that described by eq 6, i.e., C_6F_5H should not be favored. These calculations are supported by our experiments. In the C_6F_6/CH_4 system, specifically, the results at different fluences can be understood as well. At low fluence (0.64 J/cm^2) $C_6F_5CH_3$ is the major product as predicted. At higher fluence (0.79 J/cm^2) the production of C_6F_5H competes more favorably due to the increased energy imparted to the system.

Since the above calculations compare well with observed experimental results and since bond dissociation data for C_6F_5–C_2H_3 and C_6F_5–C_2H could not be obtained the favored pathway for the reactions of C_6F_6 with C_2H_4 and C_2H_2 may be inferred from the more abundant product in each reaction. In both systems C_6F_5H is the major observed product from C_6F_6 and therefore the exchange reaction as given in general eq 5 should be the more favored process in these cases. That is, the pathways for the formation of C_6F_5H should be more exothermic than those forming C_6F_5-C_2H_3 and perhaps $C_6F_5C_2H$.

It should be noted however that C_2H_2 is present in rather substantial quantities in the C_6F_6/C_2H_4 system and though it could easily be derived from the direct sensitized degradation of C_2H_4 it is potentially also available, along with C_6F_5H, from the degradation of C_6F_5—CH═CH_2. If the latter were actually the major primary product in the C_6F_6/C_2H_4 system but did not survive the reaction due to sensitized or direct degradation, then C_6F_5H would be the result of a secondary reaction and the above conclusion concerning its favored formation in a primary process is weakened. A similar argument can be made for the possibility of C_6F_5–C_2H being the major product in the C_6F_6/C_2H_2 system since C_4H_2 was observed. However, in view of our results involving C_6F_6 and other hydride reagents, we believe that at least some C_6F_5H found in the C_6F_6/C_2H_4 and C_2H_2 system is derived via the general reaction described in eq 5.

Conclusion

At high mole fractions (R) of C_6F_6, in a manner similar to that observed in the reaction of SiH_4 with C_6F_6,[1] the decomposition of C_6F_6 to C_2F_4 was observed. In the broader R range however, another decomposition pathway for C_6F_6 was observed. Our data suggest that this involves the primary cleavage of the C–F bond in C_6F_6 with the formation of $^\bullet C_6F_5$ and $^\bullet F$ radicals. Though not observed directly this process was strongly indicated by analysis of the products derived from the reactions of the $C_6F_5^\bullet$ and $^\bullet F$ radicals with the added hydride reagents.

In general, except for the reactions involving CH_4 and HCl, the major product was C_6F_5H (D) derived from the reaction of $^\bullet C_6F_5$ with the hydride sources (H_2, D_2, C_2H_4, C_2H_2). The best yield of C_6F_5H was produced by using H_2 as a "H" source with C_6F_5H being produced in 15% yield after 15 laser pulses. This reaction is synthetically useful for selective C–F bond reduction especially if deuterium is to replace the fluorine atom.

Because the pathway leading to the formation of C_6F_5H in the reactions involving CH_4 and HCl are not favored, at low fluences, exchange of the fluorine atom in C_6F_6 for a methyl group or chlorine atom was realized (formation of $C_6F_5CH_3$ and C_6F_5Cl, respectively). Thus, exchange involving other groups also seem possible. At high fluence, however, the formation of C_6F_5H is competitive with these other exchange processes and mixtures are obtained.

We are continuing our studies in this area in attempts to substitute the fluorine atom of C_6F_6 with other useful functionality and to define more clearly the effects of reagent pressure and fluence on the reaction.

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Registry No. C_6F_6, 392-56-3; H_2, 1333-74-0; D_2, 7782-39-0; CH_3, 74-82-8; CH≡CH, 74-86-2; CH_2═CH_2, 74-85-1; HCl, 7647-01-0.

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[19] Krech, M. J.; Price, S. J. W.; Yared, W. F. *Can. J. Chem.* **1974**, *52*, 2673.

[20] *CRC Handbook of Chemistry and Physics*, 65th ed.; The Chemical Rubber Co.: Cleveland, OH, 1984.