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Multiphoton Chemistry of Perfluoropropene†

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The multiphoton decomposition of perfluoropropene (C_3F_6) has been studied with parallel and focused beams of selected radiation from a CO_2 laser. The predominant product for both geometries is C_2F_4, supporting the mechanism: $C_3F_6 + nh\nu \rightarrow C_2F_4 + CF_2$; $CF_2 + CF_2 \rightarrow C_2F_4$. NO, 2,3-dimethylbutene, and 2,3-dimethylbutane have little effect on the decomposition whereas O_2 changes both the yield and the nature of the products. Photolysis with parallel beams of 995- and 1004.3-cm^{-1} radiation gives highly selective decomposition of $CF_2{}^{13}CFCF_3$ over $CF_2{}^{12}CFCF_3$. The probabilities of decomposition, $^{13}P_d$ and $^{12}P_d$, for these two lines are reported as a function of initial C_3F_6 pressure from 0.2 to 10 torr.

Introduction

Work on the multiphoton chemistry of perfluoropropene, C_3F_6, was undertaken for a number of reasons. Although present understanding of infrared-induced multiphoton chemistry appears well-founded,[1] the underlying conclusions are drawn from only a few systems, and it is still important to expand the phenomenological base. Further, although simple molecules present reasonably tractable kinetic mechanisms with pure substrates, very little work has been done where additives are used to react with primary products or the precusors. Finally, although direct detection of CF_2 has proved useful in the understanding of the distribution of energy in infrared multiphoton dissociation,[2] the systems studied did not have CF_2 as a dominant primary product. The most probable decomposition channel in C_3F_6 does yield CF_2 and should, therefore, provide a CF_2 source which is representative of the dominant multiphoton decomposition channel.

The present paper reports a survey of the multiphoton chemistry of C_3F_6, giving the spectral dependence of multiphoton excitation, the kinetic mechanism from pure C_3F_6, the effect of additives such as O_2, NO, etc., and the isotopic selectivity of decomposition. We do not attempt a detailed study of any single facet, and those more complete studies will be reported later.

Experimental Section

Laser and Irradiations. All experiments were performed with radiation from a CO_2 TEA laser (Lumonics Model 101) modified to operate with sealed operation so that laser gas mixtures containing either $^{12}CO_2$ or $^{13}CO_2$ were possible.[3] This was necessary since, although the band center of the C_3F_6 spectrum was accessible to $^{12}CO_2$ radiation, photolysis on the red edge of that absorption band required $^{13}CO_2$ radiation.

Experiments with both focused and parallel beam geometries were carried out. In the focused beam experiments, the center of the laser beam (as defined by a 18-mm diameter aperture) was focused by a 10-cm focal length Ge lens placed about 1 cm in front of a 18 cm long × 5.2 cm diameter cylindrical Pyrex cell. The ends of the cell were sealed by NaCl windows.

TABLE I: Major Products in Decomposition of C_3F_6[a]

initial C_3F_6 pressure, torr	product[b]		
	$P_{C_2F_4}$, torr	$P_{C_2F_6}$, torr	% C_2F_6
0.26	0.085	0.0066	7.2
0.54	0.160	0.018	10.1
0.90	0.260	0.041	13.6
8.62	0.340	0.100	22.7

[a] Focused beam experiments at 1039 cm^{-1}. [b] Product pressure after a fixed number of pulses.

In parallel beam experiments, the laser beam was narrowed down by placing a long focal length (2-m) Ge lens in front of the laser. The front window of the cell was placed ~160 cm from the lens. The incident and transmitted beam diameter were both ~0.75 cm.

All experiments were conducted at ambient temperature, 295 ± 1 K. The CF_3CFCF_2, obtained from Peninsular Chemical Research, Inc., was thoroughly outgassed in a mercury-free vacuum system before use. The irradiated mixture was condensed into a cold finger at −160 °C (isopentane/liquid nitrogen slush), and the noncondensable products were vacuum distilled into a liquid nitrogen trap. Both condensable and noncondensable portions were analyzed by a Hitachi RMU-60 mass spectrometer. In experiments where the fractional decomposition was high, products were measured either by gas chromatography or by infrared absorption with a Perkin-Elmer 621 IR spectrometer.

Results and Discussion

Figure 1 gives the absorption band of C_3F_6 between 1020 and 1070 cm^{-1}. Included in this figure is the spectral dependence of multiphoton absorption; the average number of photons absorbed per molecule, $\langle n \rangle$, is displayed vs. the pumping frequency at constant energy density

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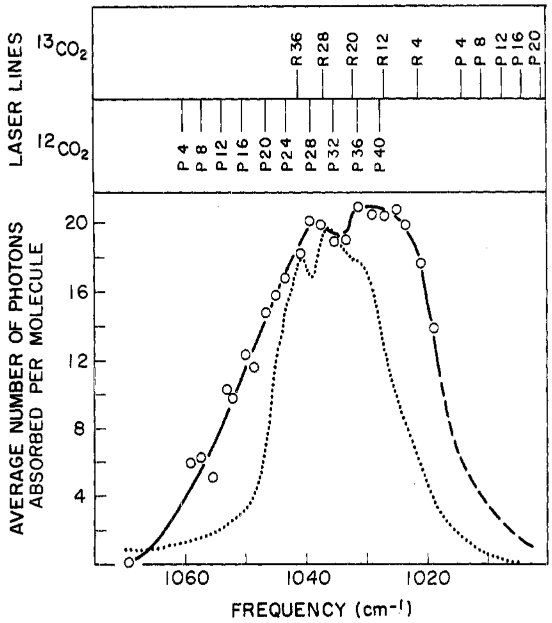

Figure 1. Multiphoton absorption curve of C_3F_6 between 1070 and 1020 cm^{-1}. Dotted line represents the corresponding linear absorption band at low intensity. Incident fluence = 1.4 J cm^{-2}; cell length = 18 cm; $P_{C_3F_6}$ = 3.3 torr.

(fluence). The linear absorption band has been assumed to be the C–F stretching vibration of the central carbon atom in the CF_3CFCF_2 molecule.[4,5] The features associated with the multiphoton spectrum, broadening of the band and the red shift (~7 cm^{-1}) of the band center, are typical of many previously studied systems, for example SF_6.[6] Inset in the figure are some of the lines obtained from carbon dioxide lasers using $^{12}CO_2$ and $^{13}CO_2$.

In all experiments on pure C_3F_6, the major decomposition product observed was C_2F_4.[18] Some C_2F_6 was produced, and its significance relative to C_2F_4 increases with increasing pressure as shown in Table I. The mass balance for carbon atoms in these experiments was typically better than 80%. The C_2F_4 is formed either directly as a major product (reaction 1) or by combination of CF_2 radicals (reaction 2). If the combination of CF_2 involves "hot" radicals, disproportionation becomes possible (reaction 3),

$$CF_3CFCF_2 + nh\nu \rightarrow C_2F_4 + CF_2 \qquad (1a)$$

$$E_a \approx 75 \text{ kcal mol}^{-1} \text{ (ref 7)}$$

$$CF_2 + CF_2 \rightarrow C_2F_4 \qquad (2)$$

$$CF_2 + CF_2 \rightarrow CF + CF_3 \qquad (3)$$

$$\Delta H = 24 \text{ kcal mol}^{-1} \text{ (ref 7)}$$

followed by dimerization of CF_3 radicals to form C_2F_6 (reaction 4). The fate of CF in this sequence is obscure.

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad (4)$$

The trend reported in Table I supports the general proposition. As the pressure increases, the confinement time of CF_2 radicals in the irradiated zone increases. Thus at low pressure, the CF_2 tends to diffuse out of the irradiated zone before combination and undergo reaction 2, whereas, at high pressure, CF_2 reacts within the "hot" irradiated zone undergoing reaction 3. If all CF_2 radicals undergo reaction 3, 20% of product would be C_2F_6, which is close to the high-pressure value shown. The alternative explanation for C_2F_6 formation involves increasing amounts of "pyrolysis" at higher pressures.[8] However, in simple pyrolysis studies of C_3F_6 in the temperature range 550–2300 K,[9-12] large amounts of butenes, cyclopropane, and cyclobutane are formed. In the present experiments all of these potential products are below limits of detection.

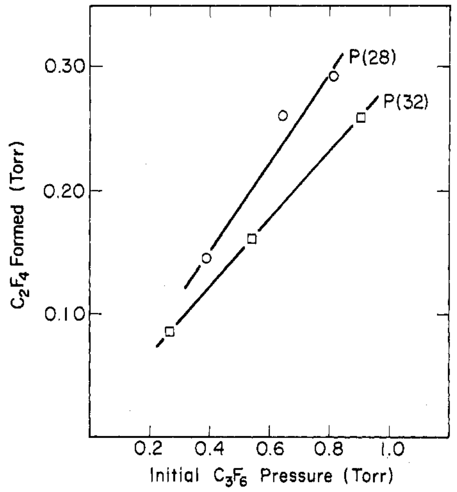

Figure 2. Product distribution vs. initial C_3F_6 pressure in the multiphoton decomposition of C_3F_6: (□) parallel beam experiments at 1035 cm^{-1} (P(32) line) with incident fluence = 1.4 J cm^{-2}; (○) focused beam experiments at 1039 cm^{-1} (P(28) line).

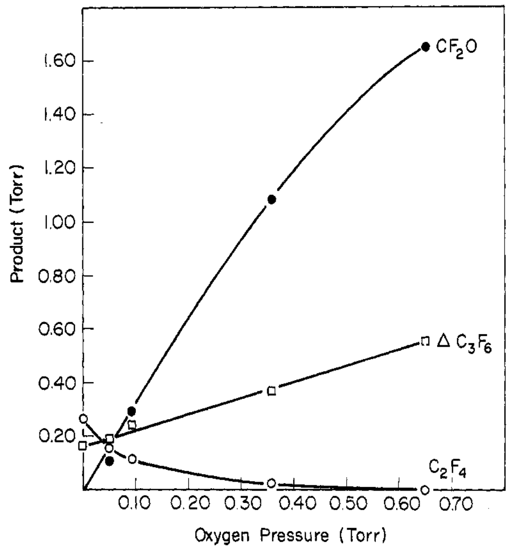

Figure 3. Product distribution in the multiphoton decomposition of C_3F_6 + O_2 with focused 1039 cm^{-1} radiation. Initial C_3F_6 pressure = 0.5 torr.

The amount of C_2F_4 produced increases linearly with the accumulated number of pulses, allowing for substrate depletion. Similarly, in the pressure range up to 1 torr, the amount of product formed increased linearly with pressure (see Figure 2).

Effect of Additives. Oxygen. Photolysis of C_3F_6 at 1039 cm^{-1} in the presence of molecular oxygen yields CF_2O and C_2F_4 as the only products.[19] We are aware of the presence of a CF_2O absorption band in this spectral region, but the observed yields show no dependence on the number of pulses. We conclude that the CF_2O produced does not undergo secondary photolysis on reaction. Figure 3 shows the effect of progressively larger amounts of added O_2 for one set of conditions in a focused beam. Within the precision of the calibration of the analytical methods, with excess C_3F_6 the added O_2 is totally consumed at all pressures shown. Thus, the data presented contain little kinetic information. Results of parallel beam experiments are presented in Table II and summarized below. (a) The multiphoton decomposition of C_3F_6 at ~0.2 torr shows

TABLE II: Summary of Experiments Performed To Study the Effect of O_2 on the Multiphoton Decomposition of C_3F_6 by Parallel Beams of 1039-cm^{-1} Radiation

expt	fluence, J cm^{-2}	no. of pulses	$P_{C_3F_6}$, torr	P_{O_2}, torr	P_d	$[CF_2O]/[C_2F_4]$	$[C_2F_6]/[C_2F_4]$
1	2.30	10	0.204		1.15×10^{-1}		0.024
2	1.46	10	0.204		7.9×10^{-3}		0.021
3	1.40	20	0.202		7.9×10^{-3}		0.021
4	1.60	21	0.200	0.016	1.4×10^{-2}	1.25	0
5	1.48	20	0.199	0.038	6.6×10^{-3}	0.89	0
6	1.40	20	0.199	0.063	5.1×10^{-3}	0.65	0
7	1.44	20	0.204	0.061	5.6×10^{-3}	0.60	0
8	1.49	20	0.202	0.115	6.6×10^{-3}	0.73	0
9	1.51	20	0.205	0.301	6.7×10^{-3}	0.81	0
10	1.55	20	0.201	0.503	2.9×10^{-3}	0.80	0
11	1.50	20	0.202	0.867	9.1×10^{-4}	0.96	0
12	1.43	40	0.206	0.807	1.3×10^{-3}	2.11	0
13	1.51	20	0.199	0.183	3.5×10^{-3}	1.29	0
14	1.70	10	0.199	0.183	7.0×10^{-2}	1.46	0
15	2.22	10	0.200	0.186	5.3×10^{-2}	3.36	0
16	2.10	15	0.500		1.3×10^{-2}		0.09
17	2.10	15	0.502	0.610	2.8×10^{-2}	8.23	0
18	2.00	15	0.494	1.856	5.9×10^{-3}	15.31	0

similar fluence dependence (P_d, the probability of dissociation per pulse per irradiated molecule, $\propto[F]^6$) in the presence (experiments 13, 14, and 15) and absence (experiments 1, 2, and 3) of O_2, and the probability of dissociation is not significantly changed by addition of small amounts of O_2. However, addition of large quantities of O_2 reduces P_d drastically (experiments 5–11). (b) With the same initial C_3F_6 and O_2 pressures (experiments 13, 14, and 15), $[CF_2O]/[C_2F_4]$ increases with increase in fluence. (c) With the same C_3F_6 pressure and fluence (experiments 6–12, 16–18), $[CF_2O]/[C_2F_4]$ increases slightly with increase in added O_2 at $P_{O_2} > 0.05$ torr.

The focused and parallel beam experiments can be rationalized by the following mechanism, where $C_3F_6^{\dagger}$ denotes a highly vibrationally excited C_3F_6 molecule:

$$C_3F_6 + nh\nu \rightarrow C_3F_6^{\dagger} \rightarrow C_2F_4 + CF_2 \tag{1a}$$

$$\xrightarrow{+O_2} 2CF_2O + CF_2 \tag{1b}$$

$$\xrightarrow{+O_2} C_2F_4 + CF_2O + O \tag{1c}$$

$$CF_2 + CF_2 \rightarrow C_2F_4 \tag{2}$$

$$CF_2 + O_2 \rightarrow CF_2O + O \tag{5}$$

$$O + C_2F_4 \rightarrow CF_2O + CF_2 \tag{6}$$

$$O + C_3F_6 \rightarrow C_2F_4 + CF_2O \tag{7}$$

$$O + CF_2 \rightarrow CF_2O \tag{8}$$

At low conversions (i.e., $\Delta[C_3F_6]/[C_3F_6] < 0.01$) and low fluence as in the parallel beam experiments, reactions 1, 5, and 7 dominate. Both sequences 1c, 7 and 1a, 5, 7 predict $[CF_2O]/[C_2F_4] \approx 1$ at high O_2, which is in fair agreement with our experimental results. However, the sequence 1b, 5, 7, which predicts $[CF_2O]/[C_2F_4] = 4$ at high O_2, cannot be excluded at this stage. All three sequences predict $P_d(O_2)/P_d = 2$, but this ignores the degree of nonreactive quenching by O_2, so that comparison to experimental data is not very useful.

As the degree of conversion increases, reactions 6 and 8 will compete with reaction 7, and $[CF_2O]/[C_2F_4]$ in the final product will increase. At 298 K, $k_6/k_7 \approx 33$,[14] and reaction 8 probably proceeds at near gas collisional rates so both reactions 6 and 8 will become significant at relatively low conversions. Reactions 2, 5, and 6 constitute a chain sequence converting C_2F_4 into CF_2O and account for $[CF_2O]/[C_2F_4]$ approaching infinity in the focused beam experiments.

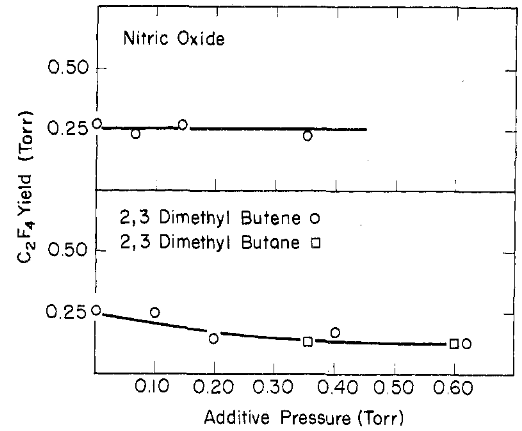

Figure 4. Product distribution in the multiphoton decomposition of C_3F_6 + NO, 2,3-dimethylbutene, and 2,3-dimethylbutane with focused 1039-cm^{-1} radiation. Initial C_3F_6 pressure = 0.5 torr.

It is interesting to speculate further on the initial reaction. As noted above, on the basis of yield ratios we are unable to distinguish among initiation reactions 1a, 1b, and 1c because of the complicated reaction kinetics. However, C_3F_6 does not enter into any secondary reactions in the focused beam experiments, and so the amount of C_3F_6 consumed should be independent of the presence of oxygen with reactions 1a plus 6–8. However, if reaction 1b or 1c does play a significant role, vibrationally excited C_3F_6 in the prefocal region which for pure C_3F_6 simply relaxed could react with oxygen, giving enhanced C_3F_6 disappearance. As shown in Figure 3, the decomposition yield of C_3F_6 is significantly higher with oxygen present, suggesting participation of one or both of these two reactions, 1b and 1c. Without a fully detailed mechanism, including possible back reaction of the type of reaction 9, this conclusion must remain speculative.

$$C_2F_4 + CF_2 \rightarrow C_3F_6 \tag{9}$$

Other Additives. The effect of additions of NO, 2,3-dimethylbutane, and 2,3-dimethylbut-2-ene are shown in Figure 4. Nitric oxide has no perceptible effect. The butane and the butene, however, do reduce the observed yield of C_2F_4. The decrease in C_2F_4 is not accompanied by formation of new products; thus the most reasonable effect of these additives is simply quenching of vibrational

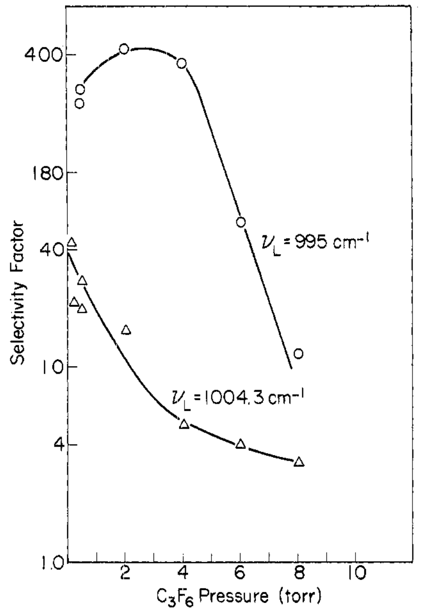

Figure 5. Selectivity factor α (= probability of decomposition of $CF_2{}^{13}CFCF_3$/probability of decomposition of $CF_2{}^{12}CFCF_3$) vs. initial C_3F_6 pressure. Experiments performed with parallel beams of (O) 995 and (Δ) 1004.3 cm^{-1} radiation. Incident fluence ≈ 2 J cm^{-2}.

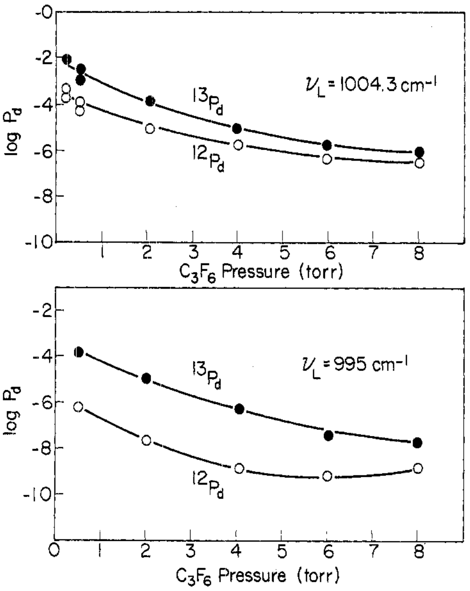

Figure 6. Probability of decomposition P_d vs. initial C_3F_6 pressure. Experiments performed with parallel beams of 995- and 1004.3-cm^{-1} radiation. Incident fluence ≈ 2 J cm^{-2}.

excited precusors to decomposition.

Isotopic Selectivity. As discussed above, the vibration excited in the present experiment is probably associated with the central carbon atom. As a direct consequence of this, photolysis on the red edge of the absorption band will favor C_3F_6 molecules of the composition $^{12}CF_3{}^{13}CF^{12}CF_2$. We define the selectivity factor, α, in terms of the ratio of the rates of decomposition of $^{12}CF_3{}^{13}CF^{12}CF_3$ molecules compared to that of other isotopic variants without a central ^{13}C atom. Plots of selectivity factors and the equivalent dissociation probabilities for two laser frequencies ν_L as a function of substrate pressure are shown in Figures 5 and 6, respectively. Going further to the red of the absorption band leads to an increase in selectivity and a decrease in yield (reflected in relatively low P_d values). With ν_L = 1004.3 cm^{-1} the selectivity of the photolysis decreases with increasing pressure over the entire range studied. With ν_L = 995 cm^{-1}, however, there is an initial increase in selectivity with pressure. As shown in Figure 6, $^{12}P_d$ decreases more rapidly with pressure than does $^{13}P_d$ up to 4 torr when $^{12}P_d$ tends to flatten off or even increase as the pressure is raised further (at 6 torr $^{12}P_d$ = 6.8 × 10^{-10} and at 8 torr $^{12}P_d \approx$ 1.5 × 10^{-9}). This behavior (increase in selectivity with pressure followed by a decrease) has been observed in other systems[15,16] and is in fact becoming characteristic of photolysis far to the red of absorption. The phenomenon can adequately be explained by the competition between the collisionless optical pumping process and the various types of collision-induced energy-transfer processes.[16]

Although the isotopic selectivity of the primary process can be quite high at low pressures, the ratio ^{13}C:^{12}C in the C_2F_4 product, *m*, is limited because of the symmetry of the molecule. Hence an α of 300 corresponds to a value of 0.35 in *m*. In fact, *m* can never be higher than 0.5. Since the decomposition of C_3F_6 goes through a cyclic intermediate,[17] suppression of the CF_2 recombination reaction 2 by scavengers cannot enhance *m*. This limiting value of *m* will no doubt restrict the potential of using C_3F_6 in laser-enrichment processes.

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(18) It is important that none of the potential products absorb at the same wavelength as C_3F_6 so that secondary photolysis does not modify the product array (perfluoromethylcyclopropane, ν_{max} = 840 cm^{-1}; perfluorocyclopropane, ν_{max} = 1272, 865 cm^{-1}; *trans*-perfluorobut-2-ene, ν_{max} = 882 cm^{-1}, *cis*-perfluorobut-2-ene, ν_{max} = 952 cm^{-1}; perfluorocyclobutane, ν_{max} = 1292, 963 cm^{-1}).

(19) CF_2O hydrolyzes slowly (with traces of H_2O present in the system) to give $CO_2{}^{13}$ during our analysis, but the sum CF_2O + CO_2 remains constant and $[CO_2]/[CF_2O] < 0.2$. We report $[CF_2O] + [CO_2]$ as $[CF_2O]$.