Infrared Laser Multiphoton Dissociation of CF₂ClCH₂Cl

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The infrared multiphoton decomposition (IRMPD) of CF₂ClCH₂Cl was studied with focusing geometry using the P(34) line of the 9.6- μ m CO₂ band (1033.6 cm⁻¹). The principal reaction product is CF₂CHCl. Other products of significance include CFClCHCl, CF₂CH₂, and CFCH. It is concluded that the primary processes of photodecomposition involve the molecular elimination of HCl and HF and, to a very minor extent, C-C bond rupture. The relative importance of the primary steps is approximately 1000:30:1, respectively. From a series of diagnostic experiments in the presence of hydrogen donors and D_2 , it is shown that CF_2CH_2 derives from the secondary photolysis of CF_2CHCl . The decomposition yield, the HF/HClratio, and the CF₂CH₂/CF₂CHCl ratio were investigated as a function of reactant and argon pressure, the latter serving as a buffer gas. From the dependence of the decomposition yield on pulse number at different pulse energies, E_0 , the specific rate of decomposition, b, was found to be proportional to $b \propto E_0^{1.8}$, the power dependence being somewhat higher than the standard $\frac{3}{2}$ power law for focusing geometry. These phenomena are interpreted in terms of a simple geometric fluence model which includes contributions from collisionally induced reactions in the outermost (lower fluence) irradiated region. The nonresonant photodecomposition of C_2H_6 and C_2H_4 at 1033.6 cm⁻¹ observed in auxiliary, diagnostic experiments is interpreted in terms of photosensitization processes.

Introduction

We have previously reported on the vacuum-ultraviolet (vacuum UV) photodecomposition of a series of chloro- and/or fluorosubstituted ethanes¹⁻⁴ including CF₂ClCH₂Cl.⁴ The interesting feature in these halo-substituted ethanes is that a number of competitive reaction channels seem possible. Hydrogen chloride, HF, and Cl₂ (or 2Cl) elimination, as well as C-Cl and C-C bond rupture may be plausible in CF_2ClCH_2Cl , for example. In the 147-nm photolysis of CF2ClCH2Cl, the detachment of two chlorine atoms was found to be the predominant process, while HCl elimination was also observed, the latter being the principal mode of decomposition in thermal activation. It is of interest to establish which reaction channels are accessible in IRMPD where the excitation energy of the photon is very small compared with the vacuum UV photolysis. Haloethanes are very suitable for infrared multiphoton decomposition (IRMPD) studies, since these compounds usually show strong absorption for CO_2 laser lines. It is well-known that, at the excitation wavelengths used in IRMPD studies, there is little selectivity due to rapid energy randomization³ in the molecule after optical excitation, and, as a result, the energetically lowest exit channel is realized predominantly. However, if the optical pumping rate exceeds the rate of decomposition at the lowest energy barrier, it may be possible to observe higher energy reaction channels.

In this kind of photochemical study it is desirable for the irradiation zone to be optically homogeneous. However, in practice, it is difficult to carry out such a study without focusing the laser beam into the reaction cell, since, in many cases, the unfocused intensity is insufficient and practically no products are observed. Therefore, as a result of adopting a focusing geometry, the irradiation zone becomes optically inhomogeneous. It is known that

with paraxial focusing geometry, in many instances, the decomposition yield has a laser fluence dependence of 3/2 order.^{6-8,16} This $\frac{3}{2}$ power dependence can be readily interpreted in terms of a simple threshold model⁸ which is based on the assumption that all molecules contained in a conical zone where the laser fluence is above some critical value decompose with unit probability and neglects any reactions outside this zone. Thus the decomposing volume per pulse is approximately equal to that of a truncated cone of circular cross section whose apex is the focal point of the laser beam. If it is assumed that diffusion in the reaction cell is completed within the time interval between pulses, the decomposition yield per pulse is the ratio of the conical volume to the total cell volume. Deviations from the 3/2 power law have been observed⁹⁻¹² and are not surprising since the simple threshold model ignores any contribution from the rest of the irradiated volume, where collision-induced reactions may occur.^{13,14} By investigating various effects on the product yields, such as reactant and buffer gas pressure, pulse number, pulse energy, and the influence of reactive additives $(H_2, C_2H_6, C_2H_4, NO, O_2)$ we have found that, for the system examined, reactions outside the critical fluence region provide a significant contribution to the product yield of the lower exit channel.

Experimental Section

A Lumonics 103-2 CO₂ TEA laser which could be tuned over the rotational lines of both vibrational bands of CO₂ was used as

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TABLE I: Relative Sensitivities^a of the Flame Ionization Detector in GC Analysis of Products

CH₄	0.49	CHF ₂ Cl	0.15	
C ₂ HF	0.73	C₂HČl	Ь	
C_2H_4	0.95	CH ₂ CFCl	b	
C_2F_4	Ь	CF ₂ CHCl	1.00	
CF ₂ CH ₂	1.06	CHFCFCI	b	
C_2H_2	1.00	CHFCHCl	Ь	
C ₂ HF ₃	0.94	$n-C_4H_{10}$	1.21	
C ₃ H ₈	1.64	C_2Cl_2	Ь	
C_2F_3Cl	ь	CFCICHCI	1.22	
CH₃Cl	0.44	CF ₂ ClCH ₂ Cl	1.20	

^a The flow rates of He, H₂, and air were 50, 30, and 420 mL/min, respectively. Relative sensitivity of FID toward CF₂CHCl is defined as 1.00. ^b Relative sensitivities were not determined and assumed to be unity.

a radiation source. Since the laser was operated with N_2 added to the laser gas mixture, the output pulse consisted of a sharp spike of about 100-ns fwhm, followed by low-intensity tail of about 1 μ s.¹⁵ The principal line used was the P(34) line of the 9.6- μ m CO_2 band (1033.6 cm⁻¹), but other lines were also used as needed. The pulse repetition rate was set at 1 Hz for all runs, and the pulse number was recorded by a counter using a signal from the laser. Since no products were observed without focusing geometry, a germanium lens with a focal length of 12.7 cm was used to focus the beam in the center of the reaction cell. The latter consisted of a cylindrical Pyrex tube of 20 cm length and 4 cm diameter, with both ends fitted with NaCl windows. Pulse energies were varied by attenuation with polyethylene sheets. The output energy of the pulse was monitored by a Joulemeter (Gentec ED-200) located just behind the exit window, due correction being made for window transmission (~ 0.92 at 1033.6 cm⁻¹).

In most experiments following irradiation, the gas mixture in the cell was condensed, using liquid N_2 , into a small sampling vessel and subjected to GC analysis. However, in those cases where condensation was impractical, as, for example, in experiments with added argon, the gas mixture was extracted by expansion into an evacuated vessel and analyzed directly, at the expense of omitting minor products.

Reaction mixtures were usually analyzed by gas chromatography (Shimadsu GC R1A) using a flame ionization detector (FID). Separation of products was mainly achieved with a Porapak N column of 3 m length. However, when placing emphasis on the quantitative analysis of products with very long retention times such as CFClCHCl, a n-octane/Porasil C column was used. In order to optimize peak area determinations, particularly for compounds with longer retention times, temperature programming was employed. In a typical GC analysis with a Porapak N column the flow rate of the carrier gas (helium) was 50 cm³/min and the temperature was programmed as follows: isothermal at 70 °C for 18 min, then raised at the rate of 10 °C/min to 120 °C and maintained for 50 min, followed by a final increase to 145 °C. However, for the identification of C_3H_8 produced in experiments with added C_2H_6 , isothermal analysis at 70 °C was adopted, since under the aforementioned conditions C_3H_8 and C_3H_6 could not be separated. Product identification was based on comparison of retention times of unknown peaks with those of authentic samples, which, with the exception of the haloacetylenes, were obtained commercially. The latter compounds were synthesized by vacuum UV or IRMP photolyses of appropriate starting materials. Quantitative product yields were obtained from peak areas corrected for the relative sensitivities of the flame ionization detector response, which were experimentally determined and are listed in Table I. The formation of hydrogen (H_2) in an experiment with added C₂H₆ was confirmed by GC analysis using a thermal conductivity detector in conjunction with a Molecular Sieve 5A column at 70 °C and argon as carrier gas.

The determination of the hydrogen isotopic distribution in 1,1-difluoroethylenes produced in the presence of added D_2 was



Figure 1. Dependence of the decomposition yield, X, on pulse number, N, and pulse energy, E_0 , at initial CF₂ClCH₂Cl pressure of $P_0 = 1$ torr.

carried out by mass spectrometric analysis (Hitachi RM 50 at 50-V ionizing voltage) of a purified product fraction isolated by preparative GC.

The reactant, CF₂ClCH₂Cl, and the principal product olefins, CF₂CHCl, CF₂CH₂, and CFClCHCl, were obtained from PCR Chemicals, Inc. CF₂ClCH₂Cl was purified by repeated bulbto-bulb distillations at ethanol slush temperature (ca. -100 °C). The haloethenes were purified by preparative gas chromatography. Ultrapure argon (99.999% stated purity) was obtained from Tomoe Co. Ltd. and was used without further purification. Deuterium (99.8 atom % D), H₂, C₂H₄, and C₂H₆ were obtained from the Takachiho Co. Ltd. and their purity was ascertained by GC.

Results

When gaseous CF₂ClCH₂Cl is irradiated with the 9.6- μ m P(34) CO₂ laser line (1033.6 cm⁻¹), 1,1-difluorochloroethylene (CF₂C-HCl) is produced as the dominant product. Three much lesser, yet relatively important, products listed in order of their significance are CF₂CH₂, CFClCHCl (both cis and trans isomers were separated by GC), and CHCF. Other minor products which were identified and quantitatively determined include C₂F₄, C₂HF₃, C₂F₃Cl, CHFCFCl, CH₂CFCl, CHFCHCl, C₂H₂, C₂HCl, and C₂Cl₂. In addition, several very minor unidentified peaks were also observed. The relative yields of these products, when the yield of CF₂CHCl is arbitrarily taken as 100, are shown in Table II in the sequence of their elution times, for the condition of 1-torr reactant pressure.

Data Evaluation. In order to establish the "rate law", the dependence of the total decomposition yield, X, on number of pulses was investigated. Here, X is defined as $X = (A_0 - A)/A_0$ where A_0 and A denote initial and final reactant concentration. An additional purpose in this determination was to examine any fluctuation in pulse energies within the preset conditions. Figure 1 shows a logarithmic plot of 1 - X vs. number of pulses for four different energies ranging from 0.21 to 0.53 J/pulse at a constant initial reactant pressure of 1 torr. The figure shows that a linear relationship holds up to about 30% decomposition at each selected pulse energy. The lack of scatter in the data, particularly at low total doses, also indicates that deviations in pulse-to-pulse energies from an average value are not significant. Further, the experiments confirm that at any selected pulse energy the *relative* product yields are invariant with total dose up to 30% decomposition.

The linear relationships in Figure 1 can be expressed by

$$1 - X = A/A_0 = (A_0 - \sum P_i)/A_0 = \exp(-bN)$$
 (I)

(15) Lumonics 103-2 CO₂ TEA laser manual.

where P_i denotes the concentration of the *i*th product, N is the

P _{CF₂CiCH₂Cl, torr}	P _{additive} , torr	E_{o} , J/pulse	H₂	CH₄	$C_2 HF^{a,b}$	$C_{2}H_{4}$	$C_2F_4^{a,b}$	CF ₂ CH ₂ ^a	$C_{2}H_{2}^{a,b}$	C ₂ HF ₃ ^a	
1.0		0.21	d	0	2.90	0	0.94	5.61	0.25	0.46	
1.0		0.37	d	0	2.52	0	0.98	4.96	0.27	0.49	
1.0		0.44	d	0	2.32	0	0.94	4.60	0.25	0.48	
1.0		0.53	d	0	2.26	0	1.02	4.42	0.26	0.50	
1.6	H ₂ , 2.5	0.20	d	0	3.51	0	0.77	26.2	11.6	0.75	
1.7	$C_{2}H_{6}, 2.4$	0.23	26.1	8.9	0. 9 0	28.3	е	13.6	5.30	0.08	
2.1	$C_{2}H_{4}, 1.0$	0.20	d	0.3	е	е	е	8.60	16.7	0.31	

TABLE II: Relative Product Yields in IRMPD of CF₂ClCH₂Cl

^a Product also observed in IRMPD of CF, CHCl. ^b Product also observed in IRMPD of CFClCHCl. ^c Reference product CF, CHCl = 100.



Figure 2. Dependence of the specific rate of decomposition, b, on pulse energy, E_0 , at initial reactant pressures of 0.3, 1.0, and 4.0 torr.

number of pulses, and the coefficient b is the decomposition yield per pulse or the ratio of the effective decomposition volume to the cell volume. Equation I bears a close resemblance to a first-order rate law, where the time variable, t, is replaced by N. Accordingly, b may be interpreted as a sort of dimensionless pseudo-first-order rate constant or as the specific rate of decomposition. For the evaluation of P_i/A_0 from the experimental data the following approximation was adopted. Since HCl elimination is by far the dominant reaction (vide infra)

$$CF_2CICH_2CI \rightarrow CF_2CHCI + HCI$$

$$A_0 - P_1 \rightarrow P_1 \qquad P_1$$

all of the other reactions can be ignored for the purpose of evaluating $P_1/A_0 \approx P_1/(A + P_1)$ directly from the GC analysis of the undecomposed reactant and the CF₂CHCl product. The contribution to the decomposition yield from the other products can then be calculated from

$$P_i/A_0 = (P_i/P_1)(P_1/A_0)$$
 (II)

where P_i/P_1 are the experimentally determined relative yields.

Energy Dependence. The dependence of the yield, b, obtained from the slopes in Figure 1, upon pulse energy or fluence is shown in a log-log plot in Figure 2, together with analogous data at initial CF₂ClCH₂Cl pressures of 0.3 and 4.0 torr, respectively. The plots are linear and obey the relationship $b \propto E_0^{\beta}$. From the slopes in Figure 2 the value of the exponent is found to be $\beta = 1.8 \pm 0.2$ at 1 torr, and $\beta = 1.9 \pm 0.4$ at 4 torr reactant pressure (the larger uncertainty in the latter case reflects the smaller number of experiments). These two values are within experimental error and suggest that there is little, if any, pressure dependence of β . However, the exponent β is somewhat larger than the 3/2 power energy dependence which is usually observed for focussing geometry.^{8,16} We return to this point later in the discussion, but it may be noted here that the observed power dependence must



Figure 3. Dependence of the product yield (%) of CF₂CHCl on initial reactant pressure, P_0 . Experimental conditions: for $P_0 < 2$ torr, $E_0 = 0.21$ J/pulse, N = 200 pulses; for $P_0 \ge 2$ torr, $E_0 = 0.19$ J/pulse, N = 400 pulses. Dashed line: corrected for difference in E_0 and N.

be closely related to the HCl elimination process, in light of the fact that the major product is CF_2CHCl .

The effect of pulse energy on the product distribution is shown in Table II. From the viewpoint of relative yields those for C_2F_4 , C_2HF_3 , C_2F_3Cl , and C_2HCl show an increase with higher pulse energy, while the relative yields of CF_2CH_2 , CFClCHCl, and C_2HF show an opposite trend. In the case of C_2H_2 , C_2Cl_2 , and CHF_2Cl there appears to be no discernible energy dependence.

Effect of Pressure on Product Yields. The effects of reactant and argon pressure, the latter serving as an inert buffer gas, on the product distribution were investigated. Figure 3 shows that the yield of CF₂CHCl increases with CF₂ClCH₂Cl pressure to a maximum value at about 4 to 5 torr. Above this pressure the CF₂CHCl yield decreases monotonically. The results on the relative product yields as a function of reactant pressure (in the lower range of pressures) are tabulated in Table III. From an interpretive point of view, the decrease in the relative yield of CF₂CH₂ with increasing haloethane pressure is particularly worthy of note.

In the presence of argon the decomposition yield, X, as well as all individual product yields decrease with increasing Ar pressure. In this case particular attention was paid in searching for the "bottleneck" effect but no such effect was found. The relative yields of the significant products are summarized in Table IV. Here, it should be noted that the apparent increase in the relative yields of CF₂CH₂ and CFClCHCl with argon pressure is indicative that the yield of the principal (reference) product CF₂CHCl decreases more rapidly than the yields of CF₂CH₂ and CFClCHCl.

Effect of Additives. Hydrogen, ethane, and ethylene are considered to be H donors which hardly absorb at 1033.6 cm⁻¹. The addition of these compounds to the haloethane resulted in a remarkable increase in both the absolute yield (~6-fold) and relative yield of CF_2CH_2 , Table II.

Furthermore, the addition of C_2H_6 gives rise to a number of

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 TABLE II (Continued)

C ₃ H ₈	C ₂ F ₃ Cl ^{a, b}	CH ₃ Cl + CHF ₂ Cl	C ₂ HCl ^{a, b}	CH ₂ CFCl ^b	CF ₂ CHCl ^c	CHFCFC1 ^b	CHFCHCl ^{a, b}	<i>n</i> -C ₄ H ₁₀	$C_2 Cl_2^{a,b}$	CFCICHCI
0	0.12	0.02	0.36	0.01	100	0.88	0.02	0	0.43	3.47
0	0.16	0.02	0.39	0.02	100	0.80	0.02	0	0.46	3.26
0	0.16	0.02	0.39	0.04	100	0.70	0.02	0	0.46	3.04
0	0.17	0.02	0.42	0.04	100	0.60	0.03	0	0.46	2.42
0	3.42	0.12	0.77	0.49	100	0.44	0.34	0	0	4.07
3.66	0.55	0.88	0.78	0.42	100	0.42	0.07	5.01	0	3.62
(0.13) ^f	0.61	0.12	0.77	0.06	100	0.28	0.05	0	0	3.68

^d Product yield was not determined. ^e Product yield could not be determined due to analytical interference. $f C_3 H_8$ and/or $C_3 H_6$.

TABLE III: Relative Product Yields^{a,b} in IRMPD of CF₂ClCH₂Cl at Low Reactant Pressure

CF ₂ ClCH ₂ Cl, torr	Х,с %	C₂HF	C_2F_4	CF ₂ CH ₂	C_2H_2	C ₂ HF ₃	C ₂ F ₃ Cl	C ₂ HCl	CF ₂ CHCl	CHFCFCI	C_2Cl_2	CFCICHCI	
0.13	4.0	3.69	0.16	7.17	d	d	d	d	100	d	d	е	_
0.14	4.1	3.44	0.18	6.98	d	d	d	d	100	d	d	е	
0.24	4.0	4.16	0.41	7.06	d	d	d	d	100	d	d	е	
0.27	4.5	3.76	0.51	6.74	d	0.34	d	0.23	100	d	d	е	
0.56	4.9	3.62	0.70	6.21	0.21	0.39	0.12	0.30	100	0.42	d	е	
0.70	5.5	3.32	0.82	5.93	0.23	0.45	0.12	0.32	100	0.67	0.47	е	
1.0	6.5	2.90	0.94	5.61	0.25	0.46	0.12	0.36	100	0.73	0.43	е	
2.0	9.2	1.59	1.03	4.15	0.25	0.40	0.16	0.39	100	0.72	0.37	е	

^a Pulse energy, $E_0 = 0.21$ J/pulse. ^b Trace amounts of CH₃Cl, CH₂Cl, CH₂CFCl, and CHFCFCl were also detected. ^c Decomposition yield. ^d Product yield was too small to be determined. ^e In GC analysis with Porapak N column this product could not be quantitatively determined (see text).

TABLE IV: Relative Product Yields in IRMPD of CF2CICH2Cl in Presence of Argon

P _{CF2} CiCH torr	$P_{\rm Ar}$, torr	E_0 , J/pulse	X,ª %	C₂HF	C_2F_4	CF ₂ CH ₂	CF ₂ CHCl	CFCICHCI	
0.3	0.0	0.24	12.5	3.7	Ь	7.0	100	2.82	-
0.3	0.7	0.27	12.7	3.7	Ь	7.8	100	3.38	
0.3	2.0	0.26	10.1	3.7	Ь	8.3	100	4.34	
0.3	3.9	0.25	8.4	3.7	b	8.7	100	4.83	
0.3	10.5	0.28	4.6	3.7	b	12.7	100	5.10	
0.3	21.0	0.25	3.4	3.5	Ь	14.4	100	5.24	
0.3	26.6	0.24	2.9	3.0	b	16.2	100	5.63	
0.3	91.6	0.26	0.7	1.5	b	20.7	100	7.46	
1.0	0.0	0.55	38.5	2.85	1.11	5.24	100	3.42	
1.0	1.0	0.54	39.0	2.76	1.13	5.22	100	3.35	
1.0	2.6	0.56	37.3	2.79	1.30	5.74	100	3.66	
1.0	6.0	0.55	32.8	2.67	1.04	6.33	100	4.10	
1.0	10.5	0.55	24.4	2.64	1.10	7.27	100	4.94	
1.0	45.4	0.55	7.3	1.73	1.11	11.9	100	5.59	

^a Decomposition yield. ^b Product yield too small to be determined.

new compounds which are considered to be the products of the direct or indirect photolysis of C_2H_6 . These products include CH_4 , C_2H_2 , C_2H_4 , C_3H_8 , and n- C_4H_{10} . When pure C_2H_6 was pulse irradiated at 1033.6 cm⁻¹ small quantities of the same compounds were found, Table V. However, as may be seen from Table V, the yields of these hydrocarbon products are much enhanced when a mixture of C_2H_6 and CF_2CICH_2Cl is subjected to IRMPD. Similarly, the addition of C_2H_4 to the haloethane gives rise to a high yield of C_2H_2 , which is thought to be the product of the photolysis of C_2H_4 . Significantly, the addition of NO or O_2 to CF_2CICH_2Cl produced *no* noticeable effect on the product distribution.

Secondary Photolysis Products. Since the products listed in Table II are not necessarily primary products, it is relevant to investigate, at least for the more important products, what contribution to the observed product yields may be derived from some secondary photolysis processes. To this end, a number of auxiliary IRMPD experiments were carried out. It was noted that only 0.7% of CF₂CHCl was decomposed when irradiated with the 1033.6-cm⁻¹ line under the conditions of 1.1 torr of CF₂CHCl pressure, $E_0 = 0.23$ J/pulse, and 500 pulses, while in the case of CF₂ClCH₂Cl, under the same conditions, about 11% of the reactant was decomposed. Since these results would indicate that secondary photolysis of CF₂CHCl is not significant, further diagnostic experiments were performed. By adjusting the wavelength to the $R(14) CO_2$ line (972 cm⁻¹) the decomposition yield in pure CF₂CHCl at the same pulse energy and pulse number was increased to about 12% which indicates resonance absorption. The product yields of CF₂CHCl at 972 cm⁻¹ are listed in Table V. It is to be noted that the observed products are qualitatively the same as those in the IRMPD of CF₂ClCH₂Cl (Table II). Further, with reference to Table V, the addition of a hydrogen donor such as H₂ or C₂H₄ to CF₂CHCl results in a significant increase in the yield of CF₂ClCH₂Cl and suggests that CF₂CH₂ is not formed directly from CF₂ClCH₂Cl via the elimination of molecular Cl₂, but is derived from the secondary photolysis of the product, CF₂CHCl. Finally we note that, in the case of C₂H₄ as additive, a very large increase in the yield of C₂H₂ is also observed.

Also listed in Table V is the product distribution for the photodecomposition of CFClCHCl at 1089 cm⁻¹. In this case, the addition of H₂ gives rise to a large increase in the yield of CH₂CFCl which is significant for later interpretation.

Photolysis of CF_2ClCH_2Cl in Presence of D_2 . In order to clarify further the mechanism of formation of the second most important product CF_2CH_2 , an IRMPD study of CF_2ClCH_2Cl in the presence of deuterium was carried out at 1033.6 cm⁻¹. The 1,1-difluoroethylenes produced in this system were first separated

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reactant, torr	$P_{\mathbf{additive}}$, torr	$\overline{\nu}$, cm ⁻¹	J/pulse	CH₄	$C_2 HP$	C_2H_4	C_2F_4	CF_2CH_2	C_2H_2	C_2HF_3	C_3H_8	C_2F_3CI	C_2HCI	CH2 CFCI	CHFCFCI	CHFCHCI	n - C_4H_{10}	C_2CI_2
,H,, 2.6		1033.6	0.62	4	0	5	0	0	0.7	0	2	0	0	0	0	0	5	0
, Н., 2.6	CF, CICH, CI, 1.7	1033.6	0.47	270	q	250	q	q	42	q	41	q	q	p	q	q	30	q
JF, ČHCI, 1.0	4	972	0.23	0	35	0	15	ę	Ţ	21	0	1	2	0	0	0.4	0	7
F,CHCI, 1.0	Н., 1.3	972	0.23	0	48	0	9	42	20	٢	0	11	7	0	0	0	0	0
JF, CHCI, 3.6	C,H., 2.1	972	0.14	1.3	с	c	с	33	126	L	$(0.8)^{d}$	6	4	0	0	0	0	0
FCICHCI, 1.0	•	1089	0.18	0	4]	0	0	0	0.2	0	0	0	1	0.7	ę	0.4	0	40
FCICHCI, 1.0	H ₂ , 4.0	1089	0.18	0	32	0	0	0	21	0	0	0	11	81	1.5	7	0	13
^a Product yiel ermined due to	d is defined as the ra analytical interferen	utio (in %) c nce. ^d Proc	of product duct C ₃ H ₈	to initia	l reactan C ₃ H ₆ .	t. ^b Th	ese prod	ucts relate	to IRMP	D of CF ₂	cich₂ci	and not C	2H6, hen	se they are c	omitted. ^c P	roduct yield	could not b	c de-

TABLE V: Product Yields^a in IRMPD of C₂H₆, CF, CHCI, and CFCICHCI

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TABLE VI: Mass Spectrometric Analysis^a of 1,1-Difluoroethylenes in IRMPD of CF2ClCH2Cl in Presence of D2

PCFCCCHCh	<i>P</i> _D .,	<i>E</i> ₀ ,		m	/e		
torr	torr	J/pulse	63	64	65	66	
1.7	2.9	0.61	20	100	100	18	

^a Raw data uncorrected for m/e 64 overlap (see text).

from the other compounds by preparatory gas chromatography and subsequently analyzed by mass spectrometry. The mass spectra showed peaks corresponding to the parent peaks at m/e64, 65, and 66, Table VI. With the assumption that the cracking patterns for the D-labeled species are the same as for CF_2CH_2 , the following isotopic distribution was obtained, after correction for overlapping peaks at m/e 64:

$[CF_2CH_2]:[CF_2CHD]:[CF_2CD_2] = 0.9:1.0:0.2$

These results clearly indicate that most of the difluoroethylene is not formed directly from the parent molecule.

Wavelength Dependence. The R(20) line of the 9.6- μ m CO₂ band at 1078.6 cm⁻¹ was also used to explore any differences with the 1033.6-cm⁻¹ photolysis of CF_2ClCH_2Cl and to provide for comparison with data in the literature. Under the conditions of 1-torr reactant pressure, $E_0 = 0.336$ J/pulse, and N = 400, no appreciable change was found in the relative product yields. However, the decomposition yield was slightly higher at 1078.6 cm⁻¹, possibly reflecting a different mode of excitation.

Other Diagnostic Tests. Since it was anticipated that IRMPD may bear a resemblance to thermal decomposition, several diagnostic pyrolysis experiments were carried out with a single-pulse shock tube. A reaction mixture of 0.6% CF₂ClCH₂Cl diluted with argon was used. Reaction temperatures ranged from 1180 to 1325 K, and for all runs the dwell times were about 1 ms. Under these conditions the decomposition yield ranged from about 7% to 90%. At the lowest conversions, CF₂CHCl was the only product found. At higher temperatures, the formation of other products, including CF_2CH_2 , CFClCHCl, and C_2F_4 , was also observed; however, the yields of these compounds in relation to the main product, CF₂CHCl, were very small compared to the IR multiphoton dissociation. Thus, for example, the relative yields of CF_2CH_2 and CFClCHCl at conversions of 50 to 60% were 8 times smaller, and that of C_2F_4 some 20 times smaller, than those found in the IRMPD at 5% conversion.

Discussion

Primary Processes. It is well-known that partially substituted haloethanes in which the halogen substituents are F, Cl, or both decompose primarily by molecular elimination of hydrogen halide whether activated by thermal,¹⁷ chemical,¹⁸ or IR laser excitation.¹⁹⁻²¹ In those cases where both $\alpha\alpha$ and $\alpha\beta$ reaction channels are available, the $\alpha\beta$ elimination has been shown to be the kinetically preferred reaction path.^{22,23} Further, as shown in the present auxiliary shock tube experiments on CF₂ClCH₂Cl, the four-center HCl elimination is dominant over the corresponding HF elimination. These considerations, coupled with the fact that CF₂CHCl is by far the major photolysis product, strongly suggest that the principal mode of dissociation in IR multiphoton excitation is also the direct elimination of HCl. Similarly, the product CFClCHCl formed in lower, yet significant, yield can be ascribed

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to the molecular elimination of HF. Compelling evidence that CFClCHCl is not a secondary product is provided by the observation that it is not observed in the photolysis of CF₂CHCl, Table V. Further, the fact that CHF_2Cl and CH_3Cl are only found in trace amounts indicates that C-C bond cleavage occurs to a very small extent. Summing up the above considerations we find that the primary processes in the IR multiphoton dissociation of CF₂ClCH₂Cl under our experimental conditions may be represented by reactions 1-3, their relative importance being roughly

$$CF_2ClCH_2Cl \xrightarrow{nn\nu} CF_2CHCl + HCl$$
(1)

$$\xrightarrow{nn\nu} CFClCHCl + HF$$
(2)

$$\xrightarrow{nn\nu} CF_2Cl \cdot + CH_2Cl \cdot$$
(3)

in the ratio 1000:30:1. There is now sufficient evidence for the two-channel competitive dehydrohalogenation reaction induced by IR multiphoton absorption on this²⁰ and related systems.^{21,24,25} Ishikawa and Arai²⁰ investigated the IRMPD of CF₂ClCH₂Cl at 1078.6 cm⁻¹ by observing the infrared emission from HCl and HF and reported that under higher fluence the emission from HF exceeded that from HCl. This observation appears to be markedly different from our results based on halohydrocarbon product analysis. We also examined the IRMPD at 1078.6 cm⁻¹ but found no significant wavelength dependence in the product distribution. Plausible explanations for this apparent discrepancy may be sought in the experimental arrangements. While the reported product yields in the present study represent averages over all reactor zones corresponding to different fluence values, the observations conducted by Ishikawa and Arai were near the focal point. There was also a significant difference in the duration of the laser pulse between the two groups. The former study employed a sharp pulse $(\sim 80 \text{ ns})$ without added N₂, as distinct from the present arrangement where the output pulse consisted of a spike of ca. 100 ns followed by a low-intensity tail of about 1 μ s. A further possibility is that contributing to the HF-fluorescence signal observed at, or near, the focal point where the fluence is highest is some secondary photochemical process such as $CF_2CH_2 + nh\nu$ \rightarrow CFCH + HF, since CF₂CH₂ is a reaction product in the system. Such infrared emission has been observed for analogous reactions, for example, in CFClCH₂.²⁴

Secondary Photolysis Products. In terms of its yield, CF₂CH₂ is the second most important product. It is tempting to assign its mode of formation to the elimination of the elements of (Cl_2) , either directly, or by rapid, sequential C-Cl bond scission, in analogy to the vacuum UV photolysis of CF₂ClCH₂Cl where CF₂CH₂ was observed as the major product.⁴ However, the experimental evidence obtained (vide supra) strongly suggests that it is not produced in a primary process. In the first instance, the direct elimination of Cl₂ (or 2Cl) cannot explain the pronounced increase in the relative as well as a sixfold absolute yield of CF_2CH_2 when a hydrogen donor was added to the reactant. This observation points to hydrogen abstraction reactions. Moreover, the fact that more than half of the 1,1-difluoroethylene produced in the presence of D₂ is composed of CF₂CHD and CF₂CD₂ clearly indicates the occurrence of D-atom transfer reactions. It is therefore proposed that the observed CF_2CH_2 in the IRMPD of CF₂ClCH₂Cl is produced primarily via hydrogen atom abstraction by CF₂CH· radicals, which, in turn, originate from the secondary photolysis of the primary product CF2CHCl. It is clear that, for such abstraction reactions to be energetically feasible, the difluorovinyl radicals must be formed with sufficient excess energy. Our auxiliary, diagnostic experiments on the direct 972-cm⁻¹ laser photolysis of CF₂CHCl provide support for these reactions: the addition of hydrogen sources to CF2CHCl also results in a large increase in the observed yield of CF₂CH₂ (Table V). Furthermore, the formation of CF_2CD_2 in the presence of D_2 also indicates the existence of $F_2C = \ddot{C}$ radicals in the photolysis of CF_2CHCl . The

production of CF₂CH₂, CF₂CHD, and CF₂CD₂ can then be explained by the following secondary processes, where RH represents any hydrogen donor:

$$CF_2CHCl \xrightarrow{nh\nu} CF_2CH + Cl$$
 (4)

$$\xrightarrow{nh\nu} CF_2 = C: + HCl$$
(5)

$$CF_2CH \cdot + RH \rightarrow CF_2CH_2 + R$$
 (6)

$$CF_2CH + D_2 \rightarrow CF_2CHD + D$$
 (7)

$$CF_2 = C: + RH \rightarrow CF_2 CH + R$$
 (8)

$$CF_2 = C: + D_2 \rightarrow CF_2 CD + D$$
 (9)

$$CF_2CD + D_2 \rightarrow CF_2CD_2 + D$$
 (10)

Reactions 4-10 are consistent with the laser photolysis results on CF₂CHCl reported in the literature.^{5,26} Sudbo et al.⁵ investigated the IRMPD of CF₂CHCl in transverse molecular beam experiments in conjunction with mass spectrometric product analyses and concluded that C-Cl bond cleavage and the threecenter HCl elimination compete with comparable probabilities. Reiser and Steinfeld²⁶ also studied the IR multiphoton dissociation of CF_2CHCl in the absence and presence of H/D donors. In the absence of additives the principal carbon-containing products were C_2F_4 (67%) and C_2F_3H (37%). Significantly, no C_2F_2 or CFCCl was observed. In the presence of labile hydrogens, the reported product distribution was $C_2F_2H_2$ (82%), C_2F_3H (12%), and C_2F_4 (6%). When the photolysis was carried out in the presence of D_2S the principal product found was C₂F₂HD, with a lesser amount of $C_2F_2D_2$, and small amounts of the above non-deuterated compounds. While the formation of $C_2F_2D_2$ was interpreted as confirmation of the existence of the difluorovinylidenecarbene CF_2 =C:, the large amount of C_2F_2HD was cited as evidence for the importance of the C-Cl homolysis channel, reaction 4. Further, from the observation that C_2F_2 was not a photolysis product in pure CF₂CHCl, Reiser and Steinfeld concluded that in their system the CF_2 =C: species is long lived and proposed as a possible mechanism for C₂F₄ formation its secondary photolysis to yield free carbon plus CF₂:

$$CF_2 = C: \xrightarrow{nh\nu} CF_2: + C$$
(11)

$$2CF_2: \rightarrow C_2F_4 \tag{12}$$

Our observed product distribution in the photolysis of CF₂CHCl at 972 cm⁻¹ is in good qualitative agreement with the results of Reiser and Steinfeld. Indeed, reactions 11 and 12 may well account for the formation of C_2F_4 in both the CF_2CHCl and CF₂ClCH₂Cl systems.

Finally, we note that the much lower yield of CF_2CH_2 in the absence of added hydrogen donors may reflect a higher activation energy for hydrogen abstraction by CF₂CH· radicals from the highly halogen-substituted parent molecule, in analogy to the trends observed for hydrogen abstraction by Cl atoms from fluoroethanes^{27,28} and chloroethanes.^{29,30} Thus a larger fraction of the difluorovinyl radicals produced in reaction 4 may be consumed by some other reactions, e.g., disproportionation/combination or addition to an olefin:

$$2CF_2CH \rightarrow CF_2CHF + CFCH$$
(13)

$$\rightarrow C_4 F_4 H_2 \tag{14}$$

⁽²⁶⁾ C. Reiser and J. I. Steinfeld, J. Phys. Chem., 84, 680 (1980).
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$$CF_2CH + CF_2CHCl \rightarrow polymer$$
 (15)

Though, owing to analytical difficulties the formation of $C_4F_4H_2$ and/or higher halohydrocarbons could not be established; as noted earlier, some minor unidentified peaks with elution times longer than the parent compound were observed. These peaks could be the products of radical combination reactions.

One final observation in connection with the formation of CF_2CH_2 deserves comment here. Thus, while the proposed mechanism for CH_2CF_2 production appears to be substantiated at 972 cm⁻¹, the baffling question which arises is why significant amounts of the product CF_2CHCl can decompose in the photolysis of CF_2ClCH_2Cl at 1033.6 cm⁻¹ where absorption by CF_2CHCl has been shown to be rather weak. One explanation proffered here is that the CF_2CHCl molecule produced at high fluence in the primary process 1 may have sufficient residual energy to be in a quasi-continuum and, as such, readily absorb any light; such a molecule has been termed "colorblind".²⁴

The formation of the minor products CH_2CFCl and CHFCHCl can be attributed to the secondary photolysis of CFClCHCl formed in reaction 2. This is supported by the data in Table V on the auxiliary 1089-cm⁻¹ photolysis of CFClCHCl. The enhanced yields of CH_2CFCl and CHFCHCl in the presence of H_2 also suggest C–Cl bond rupture followed by hydrogen atom transfer.

$$CFClCHCl \longrightarrow CFClCH + Cl$$
(16)

$$\xrightarrow{\text{arr}} \text{CHClCF} + \text{Cl} \tag{17}$$

$$CFClCH + RH \rightarrow CFClCH_2 + R.$$
(18)

$$CHClCF + RH \rightarrow CHClCHF + R.$$
(19)

Assuming that the rate constants for hydrogen abstraction for chlorofluorovinyl radicals are similar, our results would indicate that reaction 16 is about 10 times faster than reaction 17, in agreement with the notion that geminal fluorine substitution strengthens the C–Cl bond.^{31,32}

As noted earlier, fluoroacetylene is a product of some importance (Table II) and a possible contribution to its formation may be the disproportionation reaction 13. However, since the yield of C₂HF₃ is much lower than that of C₂HF, other sources for the formation of the latter must be sought. C₂HF is a product in the photolyses of pure CF2CHCl and CFClCHCl, but a comparison of the relative yields (%) at the same pulse energy and pulse number (see Results section and Tables II and V) shows that secondary photolysis of CF₂CHCl and/or CFClCHCl in the CF2ClCH2Cl system could not provide a significant contribution to the C₂HF yield. On the other hand, from the observation that there is a close correlation between the yields of C₂HF and CF₂CH₂ under different reaction conditions (Tables II and III) and the fact that HF elimination is the lowest energy channel in the thermolysis of CF2CH2,33 we propose the secondary photolysis CF_2CH_2 as the main source of the observed C_2HF

$$CF_2CH_2 \xrightarrow{nh\nu} CFCH + HF$$
 (20)

The formation of the other minor products (C_2H_2 , CHCCl, C_2Cl_2 , CHFCFCl, C_2F_3 Cl) points to more complex secondary processes. If we note that C_2Cl_2 is a significant product in the photolysis of pure CFClCHCl, the elimination of HF by secondary photolysis in the CF_2ClCH_2Cl system may account for some of its yield. However, a more detailed discussion of possible reaction schemes for the formations of this and the other minor products would be purely speculative and hence not warranted.

Pressure Dependence of the Product Yields. The effects of substrate and buffer gas pressure on the product distribution frequently serve as a diagnostic to decipher reaction mechanisms in reaction kinetics. In the case of IRMPD studies these effects can relate to the geometry and fluence of the laser beam. Geo-



(HCI Elimination)

Figure 4. Extended fluence model for focused beam geometry.

metrical effects on IRMPD results have been discussed by a number of authors.^{6-11,13,16,34,35} Here we consider the simple extended threshold model presented by Hackett et al.13 to interpret the pressure dependence of the branching ratio and the product yields in the IRMPD of C_2F_5H . As has been shown in an earlier shock tube pyrolysis study,³⁶ the decomposition of C_2F_5H proceeds by two competitive pathways: molecular HF elimination and C-C bond cleavage, the latter corresponding to the higher energy channel. Briefly, in the extended model which is based on the usual conic relationships, the relative yields from various processes become ratios of volumes defined by the threshold fluence contours which describe them. To facilitate discussion a schematic representation for a two-channel system is shown in Figure 4. In this diagram the conical beam is divided into three volume elements, between the incident fluence F_0 and the focal point. F_1 and F_2 denote some critical or threshold fluence values for the lower and higher exit channels, respectively. The model postulates that all molecules contained in the irradiated volume between F_1 and F_2 dissociate via the lower energy channel with unit efficiency. At the fluence value of F_2 and above, the radiation field is sufficiently intense to pump molecules to internal energies above the higher threshold for decomposition. The upper exit channel may thus become competitive or dominant. The irradiated volume which is subjected to fluence values between F_0 and F_1 is inhomogeneously excited (to below the lower threshold) by the photon flux, and the vibrationally excited molecules are thermalized by collision or removed by diffusion into the surrounding unirradiated space. During the stochastic process of thermalization collision-induced decomposition can occur as a result of energy pooling.^{10,13,37} By use of this geometrical model Hackett et al.¹³ were able to explain the absolute and relative increase in the yield of the lower exit channel with increasing substrate pressure over the pressure range ~ 0.5 to 1.5 torr. Reactions induced by intermolecular energy transfer in IRMPD studies have also been invoked by Choo et al.14 to interpret the formation and pressure dependence of C_2Cl_2 in the photolysis of C_2HCl_3 and by Sugita et al.¹² to explain the isotopic scrambling in the 944-cm⁻¹ IRMPD of mixtures of CHCl₂F and CDCl₂F.

The pressure dependence of the product distribution observed in the present study can also be rationalized, at least in the lower pressure region, by the simple model of Hackett et al.¹³ We therefore consider those CF₂ClCH₂Cl molecules in the region between F_0 and F_1 which have been vibrationally excited by multiphoton absorption to some unspecified level of excitation, but below the critical threshold for spontaneous decomposition. With such molecules denoted by A* the following collisional processes may lead to further excitation or stabilization³⁷

$$A^* + A^* \to A^{**} + A \tag{21}$$

⁽³¹⁾ R. Foon and K. B. Tait, J. Chem. Soc., Faraday Trans. 1, 68, 1121 (1972).

 ⁽³²⁾ J. M. Pickard and A. S. Rodgers, *Int. J. Chem. Kinet.*, **15**, 569 (1983).
 (33) J. M. Simmie and E. Tschuikow-Roux, *J. Phys. Chem.*, **74**, 4075 (1970).

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⁽³⁷⁾ P. A. Hackett, C. Willis, and M. Gauthier, J. Chem. Phys., 71, 2682 (1979).

Infrared Laser Multiphoton Dissociation of CF2ClCH2Cl

$$A^* + A \to A + A \tag{22}$$

$$A^{**} \rightarrow \text{products}$$
 (23)

where A** denotes activated molecules with an internal energy content augmented by V-V energy transfer to above the critical energy. For reaction 21 to be feasible requires a high population of A* molecules, which is not unreasonable at the photon densities in the laser beam. Because of rapid energy randomization the collisionally induced processes proposed here resemble intrinsically a thermal activation system. Therefore, it is to be anticipated that contributions to the product yield derived from this reactor region will reflect the lower energy exit channel. As shown in our shock tube experiments the latter corresponds to HCl elimination. Moreover, based on these and thermochemical considerations, one would predict that the HCl produced in reaction 23 is in its ground state. With reference to Figure 3, the increase in the yield of CF₂CHCl with substrate pressure in the range of low pressures (up to about 5 torr) can then be attributed to an increased probability for reaction 21. The observed turning point in the dissociation yield at higher pressures may be rationalized in terms of two factors: a decrease in fluence in the inner irradiated volume due to optical thickness resulting in a reduction of the effective reaction zone volume, and/or collisional quenching of vibrational excited molecules. A similar pressure dependence of the decomposition yield with reactant pressure has been observed in the IRMPD of CHCl₂F and CDCl₂F at 942.2 cm⁻¹, 12 and CH₂ClCHFCl at 1033.6 cm⁻¹.25

In the presence of argon as a buffer gas, the V-V energy transfer process 21 is suppressed by collisional deactivation of A* with argon and, as a result, the dissociation yield decreases monotonically, Table IV. It is further considered that under much higher argon pressure collisional deactivation of excited molecules and even deexcitation in the optical pumping process⁹ may become important. The observed increase in the HF/HCl elimination branching ratio with argon pressure (Table IV) is consistent with this interpretation. Similarly, one can explain the increase in the relative yield of CF₂CH₂ with argon pressure, provided the critical fluence for the secondary photolysis of CF₂CHCl is higher than that for HCl elimination from CF_2ClCH_2Cl , as corroborated by thermochemical considerations. In fact, since different threshold fluence values are to be anticipated for various secondary photolysis processes, those with higher threshold values will be less sensitive to the buffer gas pressure.

Finally, as noted earlier, our experimental value of $\beta \sim 1.8$ obtained from the plot of $\ln b$ vs. $\ln E_0$ in the range of 0.3-4.0 torr reactant pressure is somewhat larger than the standard $\frac{3}{2}$ power dependence. Similar larger β values have been found by Takeuchi et al.^{11,38} in their study of hydrogen isotope separation in the IRMPD of trifluoromethanes. This higher-order power dependence was explained by Takeuchi et al.¹¹ in terms of a more rigorous fluence model. This model, which also takes cognizance of contributions from reactions in the outer irradiation zone, predicts that, at relatively low pulse energy and local fluence below the critical fluence, the power dependence of b is higher than the "standard" value, and approaches the 3/2 power law as E_0 increases. Therefore, in the light of this modified model, the higher power dependence determined in this study lends further support to the significant role of collisionally induced reactions in the subcritical fluence zone.

Photosensitized Decomposition of C_2H_6 . As mentioned earlier, the addition of C_2H_6 as a hydrogen donor to CF_2ClCH_2Cl gives rise to hydrocarbon products which can only be attributed to the decomposition of C_2H_6 itself. Since pure C_2H_6 shows only a very weak absorption at 1033.6 cm⁻¹ (Table V), the answer as to the mode of hydrocarbon formation must be sought in secondary processes. This conclusion is based on the comparison of the product yields in the IRMPD of pure C_2H_6 and a mixture of CF_2ClCH_2Cl in C_2H_6 , Table V. Significant here is the dramatic increase in the yields of CH_4 , C_2H_4 , C_2H_2 , C_3H_8 , and n- C_4H_{10} in the presence of the haloethane. There is no doubt that the chlorine atoms and difluorovinyl radicals produced in the secondary photolysis of CF₂CHCl will preferentially abstract hydrogen from $C_2H_6^{28,30}$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5$$
 (24)

$$CF_2CH + C_2H_6 \rightarrow CF_2CH_2 + C_2H_5$$
(25)

leading to ethyl radical reactions. However, as seen from Table II, the sum of the relative yields of the hydrocarbon products is much larger than that of CF_2CH_2 . Furthermore, the production of CH_4 and C_3H_8 indicates the presence of CH_3 radicals in the system, which are not likely to be produced by any other process than C-C bond rupture in ethane: $C_2H_6 \rightarrow 2CH_3$. The direct IRMPD can account only to a negligible extent for the CH₃ radical formation, since C_2H_6 is off-resonant at 1033.6 cm⁻¹. What then is the mechanism for C₂H₆ decomposition? In two studies of laser isotope separation in mixtures of CHCl₂F/CDCl₂F¹² and CHCl₃/CDCl₃,³⁹ Ishikawa and co-workers reported that, even though the laser line was tuned to the respective absorption bands of CDCl₂F or CDCl₃, in each case a considerable amount of nonresonant CHCl₂F or CHCl₃ was decomposed. This observation was interpreted as being the result of V-V energy transfer processes. A similar explanation is also plausible in the present system where C_2H_6 may be activated by collisions with energized CF_2 -ClCH₂Cl molecules, (A*). However, since the C-C bond dissociation energy in C_2H_6 (85.8 kcal mol⁻¹)⁴⁰ is higher than the threshold energy for HCl elimination from CF2ClCH2Cl, some additional energy injection must be postulated. The possibility of thermal processes at higher substrate pressure has been mentioned by Sugita et al.¹² An alternative possibility and one preferred here is that the collisional process with A* molecules propels the C_2H_6 to an energy niveau where it can absorb the 1033.6-cm⁻¹ radiation. It seems reasonable that such energy pooling could occur particularly in the long tail (~1 μ s) of the laser pulse. On this basis, and for lack of better alternatives, we propose photosensitization and multiphoton absorption, reactions 26 and 27,

$$A^* + C_2 H_6 \rightarrow C_2 H_6^{\dagger} + A \tag{26}$$

$$C_2 H_6^{\dagger} \xrightarrow{nh\nu} 2CH_3^{\bullet}$$
 (27)

for the formation of CH_3 radicals in the system. The formation of the observed hydrocarbon products can then be explained, in part, by the following disproportionation/combination (D/C) reactions

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6 \tag{28}$$

$$\rightarrow C_4 H_{10} \tag{29}$$

$$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4 \tag{30}$$

$$\rightarrow C_3 H_8$$
 (31)

where the C_2H_5 radicals are derived from reactions 24 and 25 and, possibly, reaction 32

$$CH_3 \cdot + C_2 H_6 \rightarrow CH_4 + C_2 H_5 \cdot \tag{32}$$

The D/C ratios for the radical pairs C_2H_5/C_2H_5 and CH_3/C_2H_5 are about 0.13 and 0.04,⁴¹ respectively. Since the yield of C_2H_4 is much larger than that of $n-C_4H_{10}$ (Table II), it is clear that an additional source of C_2H_4 must be found. The well-established chain propagation reactions in the pyrolysis of $C_2H_6^{42}$

$$C_2H_5 \rightarrow C_2H_4 + H_{-} \tag{33}$$

$$H \cdot + C_2 H_6 \rightarrow C_2 H_5 \cdot + H_2 \tag{34}$$

⁽³⁹⁾ Y. Ishikawa, T. Yamazaki, Y. Hama, and S. Arai, *Appl. Phys. B*, 32, 85 (1983).

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are untenable on thermochemical grounds since reaction 33 is endothermic by about 39 kcal mol^{-1.43} Searching for alternatives we propose here a branching reaction in the decomposition of C₂H₆[†]

$$C_2 H_6^{\dagger} \xrightarrow{nn\nu} C_2 H_4 + H_2 \tag{35}$$

Reaction 35 is analogous to the vacuum UV photolysis of ethane, where molecular H_2 elimination has been shown to be the principal reaction channel.⁴⁴ Processes similar to reactions 26 and 35 may

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(44) H. Okabe and J. R. McNesby, J. Chem. Phys., 34, 668 (1961).

also be postulated for the production of C_2H_2 from C_2H_4 , where H_2 elimination has also been shown to occur.⁴⁵ In fact, as noted earlier, hydrogen formation in the presence of hydrocarbon additives was observed in the present system, Table II.

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Registry No. CF2ClCH2Cl, 1649-08-7; CF2CHCl, 359-10-4; C2H6, 74-84-0; C₂H₄, 74-85-1; H₂, 1333-74-0; D₂, 7782-39-0.

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Evidence for Charge Trapping at the Gold/Chlorogallium Phthalocyanine Interface Using Photocurrent Spectroscopy with One or Two Illumination Sources

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Photocurrent vs. wavelength spectra were reported for thin films of chlorogallium phthalocyanine (GaPc-Cl) on optically transparent gold substrates in contact with aqueous hydroquinone solutions. Charge carriers were produced which, depending upon the absorptivity of the film and direction of illumination, were localized near either the Au interface or the solution interface. Under positive bias (hole harvesting at the solution interface), with illumination of the Au/Pc interface first, photons near the absorbance maximum in the visible range (600-750 nm) produced charge which was trapped at the Au/Pc interface. This trapping arose because of the formation of a potential well brought about by a mismatch in the Fermi levels of bare gold and the Pc film. The Fermi level of the Pc layer before contact with either phase is ca. 0.5 eV above the valence band edges, thus allowing the formation of space charge layers at both interfaces. The potential well at the Au/Pc interface extends ca. 250 nm into the 1-µm-thickness films for bias potentials 200-300-mV positive of the flat-band potential (e.g., the equilibrium potential for H_2Q/BQ couple). Carriers generated by the addition of a second CW light source attenuated the effects of the potential well at the Au/Pc interface and thus enhanced the photocurrent yields from the primary, modulated light source.

Introduction

Thin films of chlorogallium phthallocyanine (GaPc-Cl) vacuum deposited onto optically transparent metallized polymer gold electrodes (MPOTE) have been shown to be highly active photoconductors capable of positive or negative photopotentials with facile charge-transfer kinetics when contacting various aqueous redox couples.¹ The absorbed light photocurrent quantum efficiency for these photoconductors was 2-10%, indicating considerable trapping and recombination of charge occurred within the Pc film. We have shown that the photocurrent action spectrum for the Au/GaPc-Cl electrodes in excess of 0.3 μ m thickness displayed different photocurrent spectral behavior when illuminated through the backside (BS, i.e., illumination at the metal/dye interface first) relative to frontside (FS, i.e., illumination at the dye/electrolyte interface first).² For GaPc-Cl films of sufficient thickness (ca. 1 μ m), frontside illumination resulted in an action spectrum possessing a broad featureless current response from about 550 to 850 nm which closely resembles the absorption spectrum. Backside illumination resulted in a diminished response in the same wavelength region and displayed two maxima in the photocurrent response curve. Weakly absorbed light associated with the wings of the absorption spectra at ca. 550 and 820 nm was most efficient in generating photocurrent with BS illumination. These results have been documented previously for other Pc systems as well and were rationalized in terms of holes being the

most mobile photogenerated charge carrier.^{2,3} In order for the holes to be harvested by the redox active species in solution, they must be generated within the effective collection length (l) of the front surface. For frontside illumination, strongly absorbed light was most efficient in generating harvestable holes within a distance *l* of the front surface. In contrast, for backside illumination, only light which had a penetration depth on the order of the film thickness generated harvestable carriers. If a *uniform electric* field is assumed across the electrode, a quantitative expression can be derived which demonstrated that the maximal photocurrent for backside illumination should occur when the penetration depth of the light $(1/\beta, \text{ where } \beta \text{ is the absorption coefficient})$ was equal to the thickness of the film (d), less one collection length $(1/\beta)$ = d - l). Results shown here and in the following paper indicate that a uniform electric field cannot always be presumed in these Pc films.

Recently we reported on a series of experiments in which the photocurrent yield from a modulated light source (probe) was significantly increased by using an auxillary, constant intensity illumination source (pump),⁴ an experimental technique first

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