2

$$X^* = (k_{-1} + k_2)^{-1} k_1 E^* S^*$$
(87)

There are two mass-conservation conditions, and, if we suppose only enzyme and substrate are present initially, they may be written

$$E + X = E_0$$
  $S + X + P = S_0$  (88)

Thus, there are two choices for L in the steady-state condition  $X^* \ll L$ , namely L = E, or L = S + P. Normally the concentration of substrate is larger than the enzyme concentration, so the steady-state condition that imposes the mildest restriction on the kinetic parameters is  $X^* \ll S + P \approx S_0$ , or

$$(k_{-1} + k_2)^{-1} k_1 E^* (S^* / S_0) \ll 1$$
(89)

We can, without further knowledge of  $E^*$  and  $S^*$ , make two simplifications, but each simplification yields an inequality that is somewhat more stringent than necessary. For the ratio  $S^*/S_0$ is between 0 and 1, so inequality 89 will certainly be satisfied if

$$(k_{-1} + k_2)^{-1} k_1 E^* \ll 1 \tag{90}$$

Furthermore, since  $E^* < E_0$ , the last inequality will be satisfied if

$$(k_{-1} + k_2)^{-1} k_1 E_0 \ll 1 \tag{91}$$

which asserts that the Michaelis constant

$$k_{\rm M} = (k_{-1} + k_2)/k_1 \tag{92}$$

must be very much greater than the initial enzyme concentration. Note that, had we chosen L = E, we would have obtained the more stringent condition that  $k_{\rm M} \gg S_0$ . When any of the preceding three inequalities are satisfied, the intermediate X has a stationary value for all values of t.

The maximum value of X and the time  $t^*$  at which the maximum  $X^*$  occurs are, in the second order of approximation, obtained from eq 54:

$$X^* = (k_1 E_0 S_0 / 2) [k_1 (E_0 + S_0) + k_{-1} + k_2]^{-1}$$
(93)

$$t^* = [k_1(E_0 + S_0) + k_{-1} + k_2]^{-1}$$
(94)

Using eq 93, we first write the steady-state condition  $X^* \ll S_0$ in the form

$$\frac{k_{\rm M}^{-1}E^*S^*/S_0}{2(E^*S^*/E_0S_0)[1+k_{\rm M}^{-1}(E_0+S_0)]} \ll 1$$
(95)

in which the numerator is identical with the left-hand member of expression 89. Now the product  $E^*S^*/E_0S_0$  is less than unity and tends to increase the numerator, but the factor of 2 and the quantity within the square brackets of the denominator offset this increase. Thus, the inequality 95 does attempt to maintain the condition imposed by inequality 89, which involves no approximation. By rearrangement, inequality 95 may be written

$$0.5 \ll 1 + k_{\rm M} + (S_0/E_0) \tag{96}$$

Finally, we note that nonsecular steady states for X occur for times much less or much greater than  $t^*$ .

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# Vacuum Ultraviolet Photochemistry of Fluoroethene and 1,1-Difluoroethene

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Products from the broad-band vacuum ultraviolet photolysis of CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub> were collected by using a novel gas collection technique and analyzed by using gas chromatography. The primary route of decay for both parents is through  $\alpha-\beta$  elimination of HF. Primary branching ratios for HF elimination, F atom ejection, and HH elimination from CH<sub>2</sub>CHF were determined: 0.82, 0.13, and 0.05, respectively. The technique does not permit detection of single H atom ejection. The ratio of  $(C_2F_2H_3)^{\dagger}$  stabilization by He vs. decomposition, formed by the addition of F to CH<sub>2</sub>CHF, is 0.029 ± 0.004 torr<sup>-1</sup>. The lifetime of the excited complex is approximately a factor of 5 longer relative to other related systems. A less detailed study of excited- $CH_2CF_2$  decay indicates similar trends.

#### Introduction

The decomposition of excited fluorinated ethenes has been studied by shock tube techniques,<sup>1</sup> photosensitization,<sup>2</sup> chemical activation,<sup>3</sup> vacuum ultraviolet photolysis,<sup>4</sup> matrix isolation,<sup>5</sup> and multiple-photon absorption.<sup>6</sup> These studies have shown that the main route of excited-fluoroethene decay is through HF molecular elimination. In general, it has been assumed that direct  $\alpha - \beta$ elimination predominates. However, chemical laser<sup>7</sup> and triplet photosensitization<sup>8</sup> experiments show that  $\alpha - \alpha$  elimination can occur in ethenes having both F and H on the same carbon atom.

HF elimination is not the only photochemical decay route of excited CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub>. Products, including CH<sub>2</sub>CF<sub>2</sub>, HCCF,  $CH_2CH_2$ ,  $CH_3CH_3$ , and  $CH_4$ , resulting from the steady-state 1470-Å gas-phase photolysis<sup>4</sup> of  $CH_2CHF$ , indicated to Kirk and Tschuikow-Roux that other processes such as si-

multaneous H + F atom ejection accompanied by subsequent bimolecular reactions also occur. Guillory and Andrews<sup>5</sup> concluded from their matrix isolation work that CH<sub>2</sub>CHF and

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 $CH_2CF_2$  eject H atoms via the parent triplet states when exposed to short-wavelength vacuum UV radiation.

Laser emission from HF in the near-IR resulting from the vacuum UV flash photolysis of fluorinated ethenes was first identified by Berry and Pimentel.<sup>9</sup> More recently Sirkin and Pimentel<sup>10</sup> observed laser emission from highly excited pure rotational HF transitions in the far-IR using a similar method. Identification of the primary routes of excited CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub> decay is fundamental to any discussion of these HF lasers. The motivation for the present work is derived from an interest in understanding the fluoroethene photochemistry as it relates to these laser systems.

#### **Experimental Section**

The apparatus consisted of three main components: the flash lamp and discharge circuitry, the sample collection apparatus, and the gas chromatograph. Details of the flash lamp and circuitry are given elsewhere.<sup>10</sup> The lamp was a coaxial design consisting of an inner Suprasil tube with 25-mm i.d. and 44 cm long. The ends of the tube were sealed with 25-mm O-ring quartz joints to which CsI windows were epoxied. Gas mixtures were introduced into the inner photolysis volume via a ground-glass ball joint on one of the O-ring assemblies. The flash discharge was restricted to the annular region defined by the outer surface of the photolysis volume (32.7-mm o.d.) and the inner surface of the outer Suprasil tube (29-mm i.d.). The outer surface of the outer Suprasil tube was coated with MgO so as to enhance the vacuum UV light intensity incident on the innermost sample region. The photolysis flash was generated when a spark gap shorted a high-voltage energy storage capacitor (Hi-Voltage 2.0 µF, 20 kV, 8 nH) to one of two Invar ring electrodes (separated by 38 cm) epoxied onto the ends of the annular discharge region. The other electrode was shorted to ground. Care was taken to minimize circuit inductance and to match the circuit impedance. The flash had a UV 0-100% rise time of 700 ns and a fwhm of 1.2  $\mu$ s.

Within 1 min of a single flash exposure the photolyzed gas sample was collected for analysis. Gases were collected by expanding them from the 0.258-L photolysis volume into a 3-L pistonlike compressor. A subsequent compression cycle of the compressor forced the gas into a 30-mL coiled  $1/_4$ -in. stainless steel tube. In this fashion 85% of the original gases were collected into a sample chamber and immediately injected into a gas chromatograph. Hence, except for free radicals, higher polymers, and HF, all the products could be collected. Accurate measurements of all relevant volumes (photolysis region, connecting tubing, expansion volume, and sample chamber) enabled absolute product yield measurements. A more detailed description of the gas collection apparatus is given elsewhere.<sup>10b,11</sup>

Photolysis products were identified and their concentrations measured by an Aerograph Model 202 gas chromatograph equipped with a conventional thermal conductivity (TC) detector. A 5 ft  $\times 1/8$  in. stainless steel column packed with Porapak N (100-120 mesh, Waters Associates Inc., Milford MA) and operated at room temperature was well suited for quick, efficient separation of the HCCH and CH<sub>2</sub>CHF peaks. The He carrier gas was adjusted to 40 mL/min at an 80 psi head pressure. Typically the TC detector current was set to 150-200 mA. Its response was amplified by a 1000× dc amplifier, sent through a low pass RC filter ( $t_{1/2} = 1.3$  s), and recorded on a dual-channel strip chart recorder. For the experiments described in this work, the TC detector signal was processed by digital filtering equipment including an Intel 8080 microprocessor and a Microdata 32/s minicomputer. This enables us to increase the S/N by a factor of 50, store the spectra on magnetic tape in digital form, and digitally integrate each peak. In this way the TC detector could sense 0.5 nmol of HCCH corresponding to an initial 0.03 mtorr in the photolysis region.

TABLE I: Retention Times of Major Gases Identified as Products of the Vacuum UV Photolysis of CH,CHF/He and CH,CF,/He

	retention	product retention time, s	
gas	time, s	CH <sub>2</sub> CHF	CH <sub>2</sub> CF <sub>2</sub>
H,	<150		
trans-CHFCHF	$160 \pm 15$	180	180
CH <sub>2</sub> CH <sub>2</sub>	$200 \pm 15$	205	
CO,	$215 \pm 10$		
HCČF	а	215	220
CF,CF,	$220 \pm 20$	· · ·	
CH, CF,	$265 \pm 20$	270	270
HCCH	$340 \pm 25$	345	
CH <sub>2</sub> CHF	$380 \pm 25$	375	370
CF, CHF	$485 \pm 35$		440
cis-CHFCHF	$620 \pm 50$		700

<sup>a</sup> HCCF's retention time was not measured directly.

He carrier gas was obtained from the University of California College of Chemistry with a stated purity of 99.99+%. Ne (99.99%), Kr (99.995%), CO (99.0%), NO (99.0%), CH<sub>2</sub>CHF (99.9%), CH<sub>2</sub>CF<sub>2</sub> (99.0%), HCCH (99.6%), and CH<sub>2</sub>CH<sub>2</sub> (99.5%) were purchased from Matheson Gas Products. Ar (99.995%) was purchased from Liquid Carbonics. Ne, Kr, Ar, CO, and NO were used directly from their cylinders and the rest subjected to at least two freeze-thaw cycles prior to use. Gases were handled in a conventional glass vacuum line, with Apiezon N greased stopcocks. Samples were prepared at least 24 h in advance of experiments and stored in 1-L blackened gas bulbs. All piping associated with the gas compressor consisted of 1/4-in. 316 stainless tubing and manual Whitey valves. Pressures were measured with either Hg manometers or a Hg McLeod gauge.

#### Results

Product Identification. Products from the vacuum ultraviolet photolysis of CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub> were identified primarily by their GC retention times. Measured retention times for gases relevant to the ethene decomposition are listed in Table I along with the uncertainty in the measurements. The HCCF retention time was not measured but was identified by mass-spectral measurements (see following discussion). The retention time measurements were taken by injecting each gas at a known sample chamber pressure (0.3-2 torr in 30-mL sample chamber) into the GC and noting the time after injection at which the tip of the peak appeared. Depending on the initial gas pressure the retention times could vary by as much as 30 s. The observed trend indicated that lower pressures caused longer retention times. For example, when the HCCH pressure was decreased from 4 to 0.28 torr, the retention time was delayed by approximately 10% (or 30 s). Typical nondigitized gas chromatographs obtained by collecting the products of the CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub> photolyses are shown in Figure 1. The unlabeled peaks were observed in spectra even when no gas was present in the sample chamber. Their intensities varied depending on the precise timing of the valving sequence on sample introduction. They are therefore attributed to interruptions in the carrier gas flow. Peaks 1 and 2 in the CH<sub>2</sub>CHF/He spectrum are identified as CH<sub>2</sub>CH<sub>2</sub> and HCCF, respectively. The 205-s retention time of peak 1 coincides closely with the 200-s  $CH_2CH_2$  peak. Peak 2, which had a retention time of 215 s, matches that of  $CF_2CF_2$ ; however, assigning it to the perfluorinated ethene was eliminated on the basis of mass spectra of collected samples (see following discussion). The mass-spectral data do suggest, instead, that HCCF is a likely assignment of peak 2. It was also the most prominent peak, after the parent peak, in the CH<sub>2</sub>CF<sub>2</sub> GC spectrum which, by analogy with the CH<sub>2</sub>CHF system, is expected to be HCCF. Peaks 3-5 were readily identified as CH<sub>2</sub>CF<sub>2</sub>. HCCH, and CH<sub>2</sub>CHF, which had 265, 340, and 380-s retention times, respectively. Although not indicated in Figure 1, a sixth peak was observed occasionally in the CH<sub>2</sub>CHF/He spectra at approximately 180 s, slightly before peak 1. A reasonable assignment would be trans-CHFCHF, which had a 160-s retention time.

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Figure 1. Gas chromatographs of products collected from the vacuum UV photolysis of (A)  $CH_2CHF/He$  and (B)  $CH_2CF_2/He$  samples; 5.5-torr photolysis volume pressure, 1:10 mixtures.

Peak 1 of the  $CH_2CF_2/He$  gas chromatograph is attributed to *trans*-CHFCHF. Its slightly delayed appearance relative to the *trans*-CHFCHF retention time of 160 s could be due to a lower sample pressure (see previous discussion). Peak 2 can be associated with HCCF. Although its retention time was not measured, HCCF is expected to be a major product of the  $CH_2CF_2$  photolysis as HCCH is for  $CH_2CHF$ . Peak 3 with a retention time of 270 s is readily identified with  $CH_2CF_2$ . The retention time of peaks 4 and 5 are 370 and 440 s. Peak 4 has a retention time near that of  $CH_2CHF$  and is so assigned. The most reasonable assignment for peak 5, even though its appearance time is 45 s earlier than expected, is  $CHFCF_2$ .

Exposing both  $CH_2CHF/He$  and  $CH_2CF_2/He$  mixtures to more than three flashes produced only one additional peak at roughly 700 s. It corresponded best with *cis*-CHFCHF, which had a 620-s retention time. Except for the parent molecule peaks all the peaks grew in intensity as the same sample would be exposed to more flashes. The *trans*-CHFCHF peak in the CH<sub>2</sub>CHF/He chromatograph grew more in relation to the others. Hence, with the exceptions of *cis*- and *trans*-CHFCHF any contributions from secondary photolysis were minor.

In order to verify the assignments of peaks 1-3 in the CH<sub>2</sub>CHF/He chromatograph some of the GC effluents were collected and analyzed via mass spectrometry. This was accomplished by attaching a coiled 1/8 in. stainless steel tube, valved off at both ends, to the exit port of the GC. The coil was immersed in a liquid-N<sub>2</sub>-cooled trap and the valves opened only during the time period that peaks 1-3 emerged from the TC detector. In order to ensure maximum sensitivity a 2.5-torr sample of CH<sub>2</sub>CHF was exposed to six 400-J flashes. The mass peaks resulting from an analysis of this sample are listed in Table II. The three most intense peaks at m/e 44, 28, and 64 are indicative of the parent ions,  $C_2FH^+$ ,  $C_2H_4^+$ , and  $C_2F_2H_2^+$ , respectively. The breaking patterns associated with the parent peaks are also consistent with the published spectra<sup>12</sup> (see Table II) of HCCF, CH<sub>2</sub>CHF, and CH<sub>2</sub>CH<sub>2</sub>, verifying the gas-chromatograph assignments. For example, peak intensities at m/e 28, 27, 26, and 25 resemble those for pure CH<sub>2</sub>CH<sub>2</sub>, thus eliminating N<sub>2</sub> at m/e 28 as a possible

TABLE II:	Mass-Spectral Assignments for Peal	ks 1-3	in
CH <sub>2</sub> CHF/He	e Photolysis		

		mass peak intensity			
mle	assignment	peaks 1-3	CH <sub>2</sub> - CH <sup>a</sup>	HCCF <sup>a</sup>	CH <sub>2</sub> - CF <sup>a</sup>
				0.06	
24	C <sub>2</sub> <sup>+</sup>	0.016	0.1.7	0.06	
25	C <sub>2</sub> H <sup>+</sup>	0.071	0.12	0.17	
26	$C_2H_2^+$	0.33	0.62		
27	$C_2H_3^{+}$	0.33	0.65		
28	$C_2H_4^+$	0.64	1.0		
29	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	0.011			
31	CF*	0.24		0.24	0.51
32	$CHF^{+}(C_{2}F_{2}H_{2}^{2+})$	0.017			
33	CH <sub>2</sub> F <sup>+</sup>	0.11			0.42
43	$C_2F^+$	0.075		0.13	
44	$C_{2}FH^{+}(CO_{2}^{+})$	1.00		1.0	0.39
45	$C_2 FH_2^+$	0.21			0.67
50	CF <sub>2</sub> <sup>+</sup>	0.11			
63	$C_2F_2H^*$	0.038			
64	$C_{2}F_{2}H_{2}^{+}$	0.41			1.0
66	$C_{2}F_{4}H_{4}^{+}(C_{5}H_{6}^{+})$	0.025			
85	C,FH,+	0.075			
87	$C_{5}FH_{8}^{+}(C_{4}F,H^{+})$	0.023			
101	$C_{1}F_{1}H_{1}^{+}(C_{2}F_{4}H^{+})$	0.18			
103	$C_{s}F_{1}H_{1}^{+}(C_{s}FH_{1}^{+})$	0.11			
105	$C_{s}F_{H_{7}}^{+}(C_{a}F_{3}^{+})$	0.018			
116	$C_{F}H_{+}^{+}(C_{F}H_{+}^{+})$	0.020			
151	$C_{4}F_{4}H_{4}^{+}(C_{3}F_{6}H^{+})$	0.14			
153	$C_{F}H_{+}^{+}(C_{F}H_{+}^{+})$	0.086			
155	$C_{6}^{\circ}F_{4}H_{7}^{+}(C_{3}F_{6}^{\circ}H_{5}^{+})$	0.014			
<sup>a</sup> From	ref 12.				

TABLE III: CH,CHF/He Product Yields vs. He Pressure

He	yield, <sup>a</sup> %			
press., torr	$\frac{\mathrm{CH_2CH_2}}{\mathrm{HCCF}} +$	CH <sub>2</sub> CF <sub>2</sub>	НССН	CH₂CHF
$\begin{array}{c} 0.0\\ 0.0\\ 2.56\\ 2.50\\ 5.15\\ 5.12\\ 10.0\\ 20.0\\ 30.0\\ 40.0\\ 50.0\\ 50.0\\ \end{array}$	$\begin{array}{c} 0.9 \pm 0.2 \\ 1.4 \pm 0.3 \\ 1.0 \pm 0.2 \\ 1.3 \pm 0.3 \\ 1.0 \pm 0.2 \\ 1.1 \pm 0.2 \\ 1.1 \pm 0.2 \\ 1.1 \pm 0.2 \\ 1.3 \pm 0.3 \\ 1.1 \pm 0.2 \\ 0.9 \pm 0.2 \\ 0.8 \pm 0.2 \\ 0.5 \pm 0.1 \\ 1.0 \pm 0.3 \end{array}$	$\begin{array}{c} 1.53 \pm 0.09 \\ 1.37 \pm 0.09 \\ 1.06 \pm 0.07 \\ 1.20 \pm 0.08 \\ 0.98 \pm 0.06 \\ 0.87 \pm 0.07 \\ 0.71 \pm 0.04 \\ 0.65 \pm 0.05 \\ 0.57 \pm 0.09 \\ 0.43 \pm 0.03 \\ 0.45 \pm 0.04 \\ 0.31 \pm 0.02 \end{array}$	$\begin{array}{c} 9.3 \pm 0.3 \\ 10.2 \pm 0.3 \\ 7.4 \pm 0.3 \\ 7.4 \pm 0.3 \\ 7.5 \pm 0.3 \\ 7.5 \pm 0.3 \\ 7.5 \pm 0.3 \\ 7.1 \pm 0.3 \\ 6.1 \pm 0.3 \\ 6.1 \pm 0.3 \\ 6.5 \pm 0.3 \\ 6.5 \pm 0.3 \end{array}$	$88 \pm 587 \pm 590 \pm 591 \pm 591 \pm 591 \pm 591 \pm 592 \pm 593 \pm 593 \pm 592 \pm 5$
75.0 75.0 100.0 100.0	$\begin{array}{c} 0.7 \pm 0.2 \\ 0.6 \pm 0.1 \\ 0.9 \pm 0.2 \\ 0.6 \pm 0.1 \end{array}$	$\begin{array}{l} 0.28 \pm 0.09 \\ 0.41 \pm 0.03 \\ 0.26 \pm 0.06 \\ 0.25 \pm 0.04 \end{array}$	$\begin{array}{l} 6.7 \pm 0.3 \\ 6.8 \pm 0.3 \\ 7.0 \pm 0.3 \\ 7.1 \pm 0.3 \end{array}$	$\begin{array}{r} 92 \pm 5 \\ 92 \pm 5 \\ 92 \pm 5 \\ 92 \pm 5 \\ 92 \pm 5 \end{array}$

<sup>a</sup> Yield of molecular gases as percent of total collected gases.

assignment. No peaks at m/e 100 or 81 (C<sub>2</sub>F<sub>4</sub><sup>+</sup> and C<sub>2</sub>F<sub>3</sub><sup>+</sup>) were observed, indicating that C<sub>2</sub>F<sub>4</sub> was not present and therefore could not be assigned to peak 2.

Several peaks at higher m/e also had significant intensities. In particular m/e 101, 103, and 105 and m/e 151, 153, and 155 stood out because of their nearly identical relative intensity patterns. The  $\Delta(m/e)$  of 2 within each series results from a loss of H<sub>2</sub> and the subsequent formation of a higher order C-C bond. The cleavage of a CF<sub>2</sub> group (m/e 50) accounts for the m/edifference between the 101-105 and 151-155 series. Hence, a reasonable structure for the ion appearing at m/e 155 is one containing a CF<sub>2</sub> terminal group such as [CHF=CH-CHF-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>]<sup>+</sup>. Since GC peaks 1-3 are expected to contain only low molecular weight gases, the most likely source of these trimers would be due to reactions within the ion source of the mass-spectral analyzer.

Pressure Dependence. The effect of He pressure on the product yields (Q's) resulting from the flash photolysis of CH<sub>2</sub>CHF/He mixtures is shown in Table III. Measurements were made on samples containing 0.50 torr of CH<sub>2</sub>CHF exposed to a single 400-J



Figure 2.  $Q_{\text{HCCH}}$  resulting from photolysis of CH<sub>2</sub>CHF/He vs. He pressure.



Figure 3.  $Q_{CH_2CF_2}$  resulting from photolysis of  $CH_2CHF/He$  vs. He pressure.

flash. Results from multiple-flash experiments exhibited the same trends as the single-flash experiments. Peaks identified as CH<sub>2</sub>CHF, HCCH, CH<sub>2</sub>CF<sub>2</sub>, and CH<sub>2</sub>CH<sub>2</sub> were digitally integrated and sample chamber pressures determined from calibration curves. Due to their close proximity the CH<sub>2</sub>CH<sub>2</sub> and HCCF peak areas were combined and the detector sensitivity assumed to be that of CH<sub>2</sub>CH<sub>2</sub>. This introduced a slight error in the measurements of  $Q_{CH_2CH_2}$  and  $Q_{HCCF}$  but a negligible effect on the remaining peaks. Due to a slight overlap between the HCCH and CH<sub>2</sub>CHF peaks ( $\sim 5\%$  of the HCCH area) they were deconvoluted (see ref 10b). The percent yields were calculated by dividing the partial pressure of each product (as determined from the GC peak area and calibrated GC sensitivity for each product) by the sum of the partial pressures. In this way errors caused by incomplete sample collection from the flash lamp, which were not insignificant near 100-torr He pressures, were eliminated. By carefully measuring the relevant volumes within the flash photolysis and gas collection apparatus one can extrapolate the product partial pressures as measured by the GC to those in the initial photolysis zone. The sum of partial pressures determined in this fashion was consistently 17% higher than the initial CH<sub>2</sub>CHF partial pressure in the flash lamp prior to photolysis. This is probably due to either incomplete sample mixing after photolysis and before gas collection and/or errors in pressure measurement, both of which enter the yield calculations as systematic errors. Product yield measurements listed in Table III were made in random order and repetition of the measurements at random intervals gave consistent results. Uncertainties for each product yield are due to a combination of the calibration and area measurement accuracies. Unusually large uncertainties indicate a peak with a sloping base line.

Two major trends can be derived from Table III. First, except for 0 torr of He,  $Q_{\rm HCCH}$  remained constant. This is seen more clearly in Figure 2, where  $Q_{\rm HCCH}$  is plotted as a function of He



Time

Figure 4. Gas chromatographs of the  $CH_2CH_2$ , HCCH, and  $CH_2CF_2$  peaks vs. He pressure.

 TABLE IV:
 Percent Product Yields from Photolysis of

 1:10 CH<sub>2</sub>CHF/M<sup>a</sup>
 1

	yield, <sup>b</sup> %			
М	$\overline{ \begin{array}{c} \mathrm{CH_2CH_2} \\ \mathrm{HCCF} \end{array} } + \\ \mathrm{HCCF} \end{array} \\$	CH <sub>2</sub> CF <sub>2</sub>	нссн	CH <sub>2</sub> CHF
He	$1.1 \pm 0.2$	$0.87 \pm 0.07$	7.3 ± 0.3	91 ± 5
Ne	$1.1 \pm 0.4$	$1.0 \pm 0.1$	$7.4 \pm 0.3$	91 ± 5
Ar	С	$0.86 \pm 0.09$	$7.1 \pm 0.3$	92 ± 5
Kr	С	$1.0 \pm 0.1$	$6.7 \pm 0.3$	92 ± 5
CO	С	$0.7 \pm 0.1$	$6.5 \pm 0.3$	$93 \pm 5$
NO	d	$1.0 \pm 0.1$	$5.5 \pm 0.3$	93 ± 5

<sup>a</sup> M = He, Ne, Ar, Kr, CO, and NO;  $P_{total} = 5.5$  torr. <sup>b</sup> Yield of molecular gases as percent of total collected gases. <sup>c</sup> Peak area integration was unreliable due to a steeply sloped base line. <sup>d</sup> The CH<sub>2</sub>CH<sub>2</sub> peak was not present in the samples containing NO but was present when CH<sub>2</sub>CH<sub>2</sub> was deliberately added indicating that CH<sub>2</sub>CH<sub>2</sub> was not a product of CH<sub>2</sub>CHF photolysis in the presence of NO. A peak did appear at the time HCCF would be expected to appear but its area could not be determined due to a steeply sloped base line.

pressure. It remained at 7% up to He pressures of 100 torr in the photolysis volume. In contrast, the amount of  $CH_2CF_2$  decreased with added He pressures as shown in Figure 3. Signal-averaged  $CH_2CH_2$ , HCCF, and  $CH_2CF_2$  peaks are shown in Figure 4 on a more sensitive scale. On close examination it becomes clear that the  $CH_2CH_2$  also decreased with added He but to a lesser extent than  $CH_2CF_2$ . The HCCF peak, on the other hand, remained constant until 40–50 torr of He. An additional peak appearing before  $CH_2CH_2$ , probably due to *trans*-CHFCHF, is observed in some GC spectra at low He pressures. The spike on top of the  $CH_2CF_2$  peak in the 20-torr He run, resulting from electrical noise induced by a nearby high-voltage discharge, was subtracted from the peak area.

Bath Gas Effects on Product Yields. In another set of experiments the He was replaced with Ne, Ar, and Kr under sample conditions identical with the CH<sub>2</sub>CHF/He 1:10 run. Table IV lists the percent product yields and the  $Q_{\rm HCCH}/Q_{\rm CH_2CF_2}$ 's. Due to slowly recovering base lines  $Q_{\rm CH_2CH_2}$  and  $Q_{\rm HCCF}$  for the Ar and Kr samples could not be reliably determined. Table IV suggests that the rare gas type has no significant effect on  $Q_{\rm HCCH}$  or  $Q_{\rm CH_2CF_2}$ .

In addition to the rare gases, He was also replaced by CO and NO under identical conditions. The results are given in Table IV. Five torr of NO reduced  $Q_{HCCH}$  by approximately 20% and eliminated the CH<sub>2</sub>CH<sub>2</sub> peak entirely. Deliberate addition of



Figure 5. Photochemical reaction energetics of the vacuum UV photolysis of (A) CH<sub>2</sub>CHF and (B) CH<sub>2</sub>CF<sub>2</sub>.

 $CH_2CH_2$  to a second sample containing NO demonstrated that, if  $CH_2CH_2$  had been present, it would have appeared on the returning slope of the unidentified peak. Therefore,  $CH_2CH_2$  was not a product in the samples containing NO. CO may have reduced the yields somewhat but not definitively outside the uncertainty limits.

#### Discussion

Figure 5, A and B, illustrates the reactant and product energetics in the vacuum UV photolysis of CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub>. The vacuum UV spectra shown in the upper left were taken from Belanger and Sandorfy.<sup>13</sup> Typical of olefins, the absorption coefficients are very high. The overlapping dashed curve shows the Suprasil quartz (2 mm thick) transmission vs.  $\lambda$  as measured by Berry.<sup>14</sup> The product of the two curves yields a crude approximation of the initial CH<sub>2</sub>CHF\* and CH<sub>2</sub>CF<sub>2</sub>\* excitation level. A description of how the energies and assignments were derived is given elsewhere.<sup>10b</sup> Briefly, all the product energies are reliable with the exception of the carbenes (i.e., CHFC:, CH<sub>2</sub>C:, etc.). The Rydberg 0-0 levels were determined by Belanger and Sandorfy from the origin of their vibronic progressions. The valence state (V and T) energy levels should be regarded as upper limits. For example, a comparison with the CH<sub>2</sub>CH<sub>2</sub> vacuum UV spectrum and its band origin suggests that the CH<sub>2</sub>CHF and  $\dot{C}H_2CF_2~^{1}V$  states should lie in the vicinity of 120 kcal/mol (42000 cm^{-1}).^{10b}

Photochemical Source of HF and HCCH(HCCF). The source of excited HF is of primary interest due to the activity of both the vibrotational and rotational chemical lasers.<sup>9,10</sup> Neither the H abstraction of F nor the F abstraction of H can account for the amount of vibrational and rotational excitation of HF as observed in these chemical lasers. Although both are exothermic (17 and 24 kcal/mol, respectively) at most they are able to produce HF in states as high as v = 2, J = 5. Vibrational and pure rotational laser emissions are, however, observed from many transitions involving levels at much higher energies. "Hot" F atom chemistry is an unlikely explanation for this higher level of excitation since He was found to be much less effective than Ne in producing HF rotational laser emission. HF-HF collisional up-pumping cannot account for the large HF energy due to early laser times-to-threshold and low concentrations.

Whereas abstraction reactions are unable to provide enough energy to pump highly excited states of HF, the molecular elimination of HF from excited  $CH_2CHF$  and  $CH_2CF_2$  is more than sufficient (see Figure 5, A and B). Moreover, the large concentrations of HCCH and HCCF present as products in the photolysis of  $CH_2CHF$  and  $CH_2CF_2$  strongly suggest that photoelimination is the primary route of HF production:

$$CH_2CHF^* \rightarrow HF^\dagger + HCCH$$
 (1)

$$CH_2CF_2^* \rightarrow HF^\dagger + HCCF$$
 (2)

The similarity in rotational HF lasing patterns resulting from CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub> vacuum UV photolysis indicates the dominance of  $\alpha - \beta$  elimination.<sup>10</sup> By association of the HCCH with the production of HF, a branching ratio of 0.82 is suggested for reaction 1 (for 0 torr of He, assuming [HCCF]  $\simeq$  [CH<sub>2</sub>CH<sub>2</sub>] and branching ratio =  $[HCCH]/[HCCH] + [CH_2CH_2] +$ [HCCF]). In addition to  $\alpha$ - $\beta$  photoelimination CH<sub>2</sub>CHF can also exhibit  $\alpha - \alpha$  elimination as suggested previously in light of lasing patterns perculiar to CH<sub>2</sub>CHF but absent in CH<sub>2</sub>CF<sub>2</sub>.<sup>10</sup> In the present work evidence for  $\alpha - \alpha$  elimination may be implied by the 23% (see Table IV) reduction in HCCH yield when NO replaced He as a bath gas, attributed to a reaction between  $CH_2$ =C: and NO. A similar reaction between  $CH_2$  + NO and  ${}^{3}CH_{2} + NO$  was reported by Laufer and Bass.<sup>15</sup> For this type of reaction to be active in the present study, the H<sub>2</sub>C=C:  $\rightarrow$ HCCH rearrangement must have a rate comparable to or slower than the H<sub>2</sub>C=C: + NO collision frequency,  $\sim 2.5 \times 10^5 \text{ s}^{-1}$ . Theoretical estimates of the vinylidine rearrangement barrier height range from 0.9 to 8.6 kcal/mol.<sup>16</sup> At the lower end of this range, vinylidine rearrangement would be much faster than NO collisions. Nevertheless, the newly formed acetylene would be very highly excited and its reaction with NO might still compete with its deactivation. If the rearrangement barrier is near the 8.6 kcal/mol range, the NO scavenger reaction with vinylidine would probably compete. In either case, if NO scavenging of HC=C: (or the hot HCCH<sup> $\dagger$ </sup> produced from it) accounts for the 23% reduction in HCCH yield, then it provides an estimate of the fraction of the HF photoelimination that proceeds via  $\alpha - \alpha$ 

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elimination. If the overall HF photoelimination branching ratio is 0.82, then the fraction of  $\alpha - \alpha$  (0.23)(0.82) = 0.19 and the remainder, 0.63, would be the fraction of  $\alpha - \beta$  elimination.

Although photoelimination accounts for the bulk of HF, F atom abstraction may still contribute to the population of lasing HF. It is a well-established fact that atomic addition to ethylene is favored over abstraction; <sup>17</sup> the rate for  $H + CH_2CH_2 \rightarrow CH_2CH$ + H<sub>2</sub> has been measured to be 1/15 that for H + CH<sub>2</sub>CH<sub>2</sub>  $\rightarrow$ CH<sub>3</sub>CH<sub>2</sub>. Although analogous results are not available for fluorinated ethenes, Teng and Jones<sup>18</sup> estimate a rate constant of  $1.8 \times 10^4$  torr<sup>-1</sup> s<sup>-1</sup> for the H+ CH<sub>2</sub>CF<sub>2</sub>  $\rightarrow$  HF + CH<sub>2</sub>CF reaction based on a computer model of their flow experiments. This is too slow to be of any significance in the present work. Despite the absence of a detailed analysis on the subject it has been estimated by Smith et al.<sup>19</sup> that the addition of F to ethene is favored over the abstraction reaction to form HF by a factor of 3. Assuming that the HCCH concentration corresponds 1:1 with the HF concentration resulting from HF photoelimination and the CH<sub>2</sub>CF<sub>2</sub> 1:1 with the F addition product (see following discussion) the Smith et al. estimate indicates that 5% of the overall HF concentration can arise from the F abstraction reaction.

F Addition Reactions. The presence of two F atoms on a single ethene indicates a bimolecular reaction between two monofluorinated reactants. The following reactions represent possible mechanisms:

HF + HCCF →  $CH_2CF_2$  ( $E_a = 43.3 \text{ kcal/mol}$ ) -26.7 kcal/mol (3)  $CH_2CF + CH_2CHF \rightarrow CH_2CF_2 + CH_2CH \sim 0 \text{ kcal/mol}$ (4)

$$CH_{2}CHF + CH_{2}CHF \rightarrow CH_{2}CF_{2} + CH_{2}CH_{2} - 5 \text{ kcal/mol} (5)$$

$$\mathbf{F} + \mathbf{CH}_2 \mathbf{CHF} \rightarrow [\mathbf{C}_2 \mathbf{H}_3 \mathbf{F}_2]^{\dagger} \tag{6}$$

$$[C_2H_3F_2]^{\dagger} \rightarrow CH_2CF_2 + H \qquad -16.3 \text{ kcal/mol} \qquad (7)$$

Reaction 3 can be ruled out on the basis of the HCCF partial pressure which is found to be much less then either the  $CH_2CF_2$ or CH<sub>2</sub>CHF pressures and on the basis of the high activation barrier which would require vibrationally excited HF, in  $v \ge 4$ , addition to the ethyne triple bond. In a bath of CO, hot HF should be rapidly quenched and result in virtually no CH<sub>2</sub>CF<sub>2</sub> if reaction were active. Since both  $CH_2CF_2$  and HCCH were equivalently reduced by the addition of CO, this hot channel appears unlikely.

On the basis of both statistical and thermodynamic arguments the abstraction of F by CH<sub>2</sub>CF from CH<sub>2</sub>CHF is unlikely. There are three H's per CH<sub>2</sub>CHF to one F and C-H bonds are weaker than the C-F bond by an average of 3.0 kcal/mol. The addition of NO to the sample had no effect on  $Q_{CH_2CF_2}$  but reduced  $Q_{CH_2CH_2}$ to nil. This suggests that  $CH_2CH_2$  is formed in a radical reaction but  $CH_2CF_2$  is not. Thus, this evidence disfavors both reactions 4 and 5.

Hence, reactions 6 and 7 are suggested as the most likely route for producing  $CH_2CF_2$ . Unlike the reaction between  $CH_2CH +$ NO, F + NO is termolecular. In pure NO the rate constant is  $1.7 \times 10^2$  torr<sup>-1</sup> s<sup>-1</sup> for F + NO + NO.<sup>20</sup> Assuming a rate constant of  $4 \times 10^6$  torr<sup>-1</sup> s<sup>-1</sup> for F + CH<sub>2</sub>CHF the olefin removes F 600 times faster than NO (in 5.5-torr CH<sub>2</sub>CHF/NO 1:10 samples). Therefore, as observed, the NO is not expected to affect  $Q_{CH_2CF_2}$  under the present sample conditions. Kirk and Tschiukow-Roux<sup>4</sup> also attributed the formation of CH<sub>2</sub>CF<sub>2</sub> to the addition of F to CH<sub>2</sub>CHF and subsequent ejection of H.

Figure 6 illustrates the reaction between F and CH<sub>2</sub>CHF along two possible reaction coordinates. The abstraction reaction, which



Figure 6.  $F + CH_2CHF$  reaction pathways.



Figure 7.  $Q_{\rm HCCH}/Q_{\rm CH_2CF_2}$  vs. He pressure.

is shown by the lighter arrow to be crudely 1/3 as fast as the addition, can produce HF only up to low rotational levels of v =2. Two decay pathways are possible for the addition complex  $[C_2H_3F_2]^{\dagger}$ , either H ejection (reaction 7) or radical stabilization:

$$[C_2H_3F_2]^{\dagger} + He \rightarrow [C_2H_3F_2] + He$$
(8)

The stabilized ethyl radical can then react with other CH<sub>2</sub>CHF's and polymerize. That 5 torr of NO was unable to remove the fluoroethyl radical suggests either that its lifetime is shorter than the NO collision frequency or that its reaction rate is slower than gas kinetic. Pratt and Veltman<sup>21</sup> measured the bimolecular rate constant for  $C_2H_5$  + NO at 325 K at a pressure of 7 torr of NO as  $7.2 \times 10^3$  torr<sup>-1</sup> s<sup>-1</sup>. Assuming the same rate constant for  $C_2H_3F_2$  the lifetime of the excited complex is less than 27 ms or  $k_8 > 3.7 \times 10^4 \text{ s}^{-1}$ .

Branching ratios for reactions 7 and 8 are dependent on He pressure. Assuming that the concentration of the excited fluoroethyl radical  $[C_2H_3F_2]^{\dagger}$  remains in a steady state it can be shown that

$$[\text{HCCH}]/[\text{CH}_2\text{CF}_2] = \\ \{[\text{HCCH}]/K\} + [\text{He}]\{[\text{HCCH}]/K\}k_8/k_7$$

where K is a constant depending on the rate of reaction 6, [F], and [CH<sub>2</sub>CHF]. Thus, a plot of  $Q_{\text{HCCH}}/Q_{\text{CH}_2\text{CF}_2}$  vs. He pressure, (see Figure 7) should yield a straight line having the relationship

$$k_8/k_7 = \{\text{slope}\}/\{\text{intercept}\}$$

$$k_8/k_7 = \{0.20 \pm 0.01\}/\{6.8 \pm 0.4\} = 0.029 \pm 0.004 \text{ torr}^{-1}$$

By including [HCCH] in the analysis one can eliminate errors caused by changes in gas collection efficiency. If the deactivation of  $[C_2H_3F_2]^{\dagger}$  is gas kinetic, then  $g_8 = 3.9 \times 10^6$  torr<sup>-1</sup> s<sup>-1</sup> and  $k_7$ 

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Photochemistry of Fluoroethene and 1,1-Difluoroethene

=  $1.36 \times 10^8$  s<sup>-1</sup>, or the excited fluoroethyl radical lifetime is at least 7.4 ns.

Independent measurements of  $k_7$  and  $k_8$  have not been reported. RRKM calculations by Farrar and Lee<sup>22</sup> predict that for the F + CH<sub>2</sub>CH<sub>2</sub> reaction  $[C_2H_4F]^{\dagger}$  has a lifetime near 0.8 ns. This is a factor of 9 below the shortest lifetime consistent with our experiments. Williams and Rowland<sup>23</sup> examined the stabilization vs. decomposition of  $[C_2H_4^{18}F]^{\dagger}$  formed in the  ${}^{18}F + CH_2CH_2$ reaction. They determined that 80 torr of SF<sub>6</sub> reduced the decomposition product CH<sub>2</sub>CH<sup>18</sup>F to half its maximum. Assuming a  $SF_6 + [C_2H_4^{18}F]^{\dagger}$  hard-sphere collision rate constant of 8  $\times$ 10<sup>6</sup> torr<sup>-1</sup> s<sup>-1</sup> this suggests a radical half-life of 1.5 ns or twice the Farrar and Lee number, but one-fifth times the minimum  $[C_2H_3F_2]^{\dagger}$  lifetime observed in this work.

One unusual feature of the  $F + CH_2CHF$  addition (reaction 6) is the fact that the predominant difluoro product  $CH_2CF_2$  places both F atoms on the same carbon. Free-radical addition to CH<sub>2</sub>CHF has been found to occur preferentially on the  $\beta$ -carbon, as in the case of methyl radicals,<sup>24</sup> which favor the  $\beta$ -carbon by a factor of 5:1 and perfluoromethyl radicals<sup>25</sup> 8:1. Thus, the present work suggests either an opposite trend or that the F atom adds initially to the  $\beta$ -carbon, forming FCH<sub>2</sub>CHF, and then migrates prior to or in the course of H ejection (reaction 7). Small amounts of trans-CHFCHF were observed in the multiple-flash experiments on CH<sub>2</sub>CHF. The time required for the migration may account for the longer fluoroethyl radical lifetimes observed.

Radical Abstraction Reactions. Evidence for abstraction reactions is suggested by the formation of CH<sub>2</sub>CH<sub>2</sub>:

 $H_2 + HCCH \rightarrow CH_2CH_2 (E_a = ?)$ -41.6 kcal/mol (9) 

$$H + CH_2CHF \rightarrow C_2H_4F) \rightarrow CH_2CH_2 + F + 11 \text{ kcal/mol (10)}$$

$$CH_2CH + CH_2CH \rightarrow HCCH + CH_2CH_2$$
 -64 kcal/mol (11)

$$CH_2CH + CH_2CHF \rightarrow CH_2CH_2 + CH_2CF \quad 0 \text{ to } +10 \text{ kcal/mol} (12)$$

On the basis of known<sup>1</sup> activation energies for HF + HCCF and HF + HCCH the  $E_a$  for reaction 9 is expected to be on the order of 11 kcal/mol. Although hot  $H_2$  may be present as a result of CH<sub>2</sub>CHF elimination of H<sub>2</sub>, the low  $Q_{\text{HCCF}}$  suggests that the direct formation of  $H_2$  is not a significant  $CH_2CHF$  decay route. Moreover, the addition of NO eliminated  $Q_{CH_2CH_2}$  entirely, which suggests the importance of free-radical reactants in its formation,

The effect of NO on  $Q_{CH_2CH_2}$  can also be used to rule out reaction 10 since H + 2NO is termolecular and under the present experimental conditions would not be expected to affect the rate of the addition reaction. In addition, reaction 10 requires a hot H atom which certainly would have cooled at different rates when He was replaced with Ne, Ar, or Kr.

Reactions 11 and 12 are left as possible sources of the ethylene product. Reaction 11, the radical-radical recombination, would not be important in the low-intensity photolysis<sup>4</sup> but might become a factor in flash photolysis if F atom ejection produces enough vinyl radical. The competition between these two reactions would also be affected by the activation energies which, for reaction 12, would be at least as large as the endothermicity. The uncertainties do not permit a choice on the basis. Either reaction would account for the loss of ethylene product in the presence of NO since NO scavenging of  $CH_2CH$  has been reported earlier.<sup>26,27</sup> There is, however, one piece of evidence that favors reaction 12, the effect of helium pressure on the CH<sub>2</sub>CH<sub>2</sub> and HCCH yields. Table III shows that the HCCH product yield changes very little at helium

pressures above 2.5 torr, whereas the  $CH_2CH_2 + HCCF$  yield continues to decrease up to helium pressures of 100 torr. Since we attribute this decrease to the ethylene component (see Figure 4), the evidence is not compatible with reaction 11 as the only source of ethylene.

Thus, reaction 12, which requires a hot CH<sub>2</sub>CH radical, is the more probable route for ethene formation. The source of hot  $CH_2CH$  (>40 kcal/mol) could be the photoejection of F from excited CH<sub>2</sub>CHF which is amply exothermic in the vacuum UV. Like  $Q_{CH_2CF_2}$ ,  $Q_{CH_2CH_2}$  has a He pressure dependence due to a competition between decomposition and stabilization of the hot CH<sub>2</sub>CH radical. The chemistry of hot CH<sub>2</sub>CH was also observed in the vacuum UV photolysis of CH<sub>2</sub>CH<sub>2</sub> by Tanaka and coworkers.<sup>26,28</sup> The presence of  $CH_2CH_2$  as a product in the present work contradicts that of Wijnen and co-workers,<sup>29</sup> who observed no CH<sub>2</sub>CH<sub>2</sub> resulting from the photolysis of CH<sub>2</sub>CHF at 1470 Å. The cause of this difference may be a result of the shorter wavelengths in their study causing a shift toward H and/or 2H ejection at the expense of F atom ejection.

Reaction 5 may be a potential source of  $CH_2CH_2$ ; however, it would require the four-center reaction between an excited metastable CH<sub>2</sub>CHF and ground-state CH<sub>2</sub>CHF. Moreover, the reaction must be specific in that the exchanged atoms reorient themselves so that two F's are on the same carbon atom of one of the ethene products. In this case the absence of  $CH_2CH_2$ product in the NO samples may be a result of the NO-induced deactivation of the excited CH2CHF metastable. However, under the same conditions no NO effect on the CH<sub>2</sub>CF<sub>2</sub> product was observed. Since the values in Table III have been corrected for detector sensitivities to different gases, a detectable change in the CH<sub>2</sub>CF<sub>2</sub> product yield should have resulted. Thus, contributions to the  $CH_2CH_2$  product resulting from reaction 5 may be present but are most probably small in relation to reaction 12.

Direct Photoelimination of  $H_2(2H)$ .  $Q_{\text{HCCF}}$  was not noticeably affected by NO, He pressure, or substitution of He by other rare gases. Thus, the most reasonable cause for its presence would be a result of direct photoelimination of  $H_2$  or 2H from excited CH<sub>2</sub>CHF:

$$CH_2CHF^* \rightarrow H_2 \text{ (or } 2H) + HCCF$$
 (13)

Either molecular or diatom elimination is energetically possible (see Figure 5A) and the present work is unable to distinguish which occurs.

Primary Branching Ratios for CH<sub>2</sub>CHF Photoelimination. Assuming that all the F atoms are scavenged by 0.5 torr of  $CH_2CHF$  to form  $CH_2CF_2$  (reactions 6 and 7) and that every  $CH_2CH$  yields a molecule of  $CH_2CH_2$  (reaction 11) it is possible to determine the branching ratios for the following three decay routes of vacuum UV photolyzed CH<sub>2</sub>CHF:

 $CH_2CHF^* \rightarrow HF^\dagger + HCCH$  $\beta_{\rm HF} = 0.82 \pm 0.05$  $CH_2CHF^* \rightarrow F + CH_2CH^{\dagger}$  $\beta_{\rm F} = 0.13 \pm 0.04$  $CH_2CHF^* \rightarrow H_2$  (or 2H) + HCCF  $\beta_{2H} = 0.05 \pm 0.04.$ 

The branching ratios were determined from the relevant O's at 0 torr of He where minimal stabilization of the fluoroethyl radical is expected (see reaction 7 and 8). The integrated area under the HCCF peak is roughly half that listed in Table III since those numbers are the sum of both the HCCF and CH<sub>2</sub>CH<sub>2</sub> peaks. This rough approximation is the cause of the large uncertainty in the last branching ratio. Because the most likely reaction products of  $H + CH_2CHF$  are the regeneration of the parent or polymerization, the present experiments are not capable of detecting H atom ejection, which is expected to be an important photoexicted  $CH_2CHF$  decay process. The sum of  $\beta_{HF}$  and  $\beta_{2H}$  compares very well with results observed by Tanaka and co-workers<sup>26</sup> on the

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vacuum UV photolysis of  $CH_2CH_2$  at 1849 Å. The ratio between molecular and diatom elimination of H2 vs. H ejections was reported as 0.86:0.14, whereas in the present work the corresponding ratio is 0.87:0.13.

On the other hand, Wijnen and co-workers<sup>30</sup> observed in their studies on CH<sub>2</sub>CHCl photolysis that at  $\lambda > 2000$  Å the main route of CH<sub>2</sub>CHCl\* decay was via Cl ejection rather than HCl molecular elimination. Most probably this preference of atom ejection is due to the much weaker C-Cl bond. However, at shorter wavelengths  $\lambda \sim 1470$  Å, the molecular elimination began to be favored as observed in the present study.

Vacuum UV Photochemistry of  $CH_2CF_2$ . By analogy with the previous discussion on CH<sub>2</sub>CHF photochemistry, the decay of  $CH_2CF_2$  can be expected to follow the sequence:

$$CH_2CF_2^* \rightarrow HF^\dagger + HCCF$$
 (2)

$$CH_2CF_2^* \rightarrow F + CH_2CF^{\dagger}$$
 (14)

$$\mathbf{F} + \mathbf{C}\mathbf{H}_2\mathbf{C}\mathbf{F}_2 \rightarrow [\mathbf{C}_2\mathbf{H}_2\mathbf{F}_3]^{\dagger} \tag{15}$$

 $[C_2H_2F_3]^{\dagger} \rightarrow CHFCF_2 + H$ (16)

$$[C_{2}H_{2}F_{3}]^{\dagger} + He \rightarrow [C_{2}H_{2}F_{3}] + He \qquad (17)$$

- $[C_2H_2F_3] + CH_2CF_2 \rightarrow CH_2FCF_2CH_2CF_2$ , etc. (18)
- $CH_2CF^{\dagger} + CH_2CF_2 \rightarrow CH_2CHF + CF_2CH$ (19)
- $[C_2H_2F_3]^{\dagger} \rightarrow trans-CHFCHF (cis-CHFCHF) + F$ (20)
  - $CH_2CF_2^* \rightarrow trans-CHFCHF$  (cis-CHFCHF). (21)

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All stable products from these reactions were observed in the GC. Like  $[C_2H_3F_2]^{\dagger}$ ,  $[C_2H_2F_3]^{\dagger}$  is expected to exhibit a He stabilization vs. decomposition (reactions 16 and 17). Although trans-CHFCHF was also observed in the CH2CHF photodecomposition, it was a minor product relative to its concentration in the CH<sub>2</sub>CF<sub>2</sub> photodecomposition. Quantitative studies like those for CH<sub>2</sub>CHF were not conducted on CH<sub>2</sub>CF<sub>2</sub> samples, preventing one from estimating primary branching ratios.

#### Conclusions

The primary route of CH<sub>2</sub>CHF and CH<sub>2</sub>CF<sub>2</sub> decay upon exposure to broad-band vacuum UV radiation above 1550 Å is direct  $\alpha - \beta$  photoelimination of molecular HF. The photoelimination is sufficiently exothermic to produce rotationally excited HF up to v = 1, J = 31 as observed in the rotational laser experiments. At most, the F abstraction of H could result in 5% of the observed HF. Excluding single H atom ejection, which could not be identified in the present experimental design, the primary branching ratios for the decay of the photoexcited CH<sub>2</sub>CHF are as follows: HF molecular elimination,  $0.82 \pm 0.05$ ; F atom ejection,  $0.13 \pm 0.04$ ; HH molecular or diatom elimination, 0.05  $\pm$  0.04. Pressure studies of the CH<sub>2</sub>CHF decay indicate that a difluoroethyl radical ejects an H atom and forms the 1,1-difluoroethene.

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Registry No. CH<sub>2</sub>CHF, 75-02-5; CH<sub>2</sub>CF<sub>2</sub>, 75-37-6; CH<sub>2</sub>CH<sub>2</sub>, 74-85-1; HCCF, 2713-09-9; HCCH, 74-86-2; trans-CHFCHF, 1630-78-0; CF2CHF, 359-11-5; cis-CHFCHF, 1630-77-9; CF2CF2, 116-14-3; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; CO, 630-08-0; NO, 10102-43-9.

# Photochemistry of the Tris(2,2'-bipyridine)ruthenium(II)–Peroxydisulfate System in Aqueous and Mixed Acetonitrile–Water Solutions. Evidence for a Long-Lived **Photoexcited Ion Pair**

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The photooxidation of  $Ru(bpy)_{3}^{2+}$  (bpy = 2,2'-bipyridine) by peroxydisulfate,  $S_2O_8^{2-}$ , was investigated by steady-state luminescence quenching and emission lifetime techniques in aqueous and mixed CH<sub>3</sub>CN-H<sub>2</sub>O solutions. The resulting Stern-Volmer plots showed downward curvature for data obtained from solutions of increasing ionic strength, S-shaped curves for data obtained in solutions of low but constant ionic strength, and linear plots from solutions of high ionic strength. The results are consistent with the formation of a ground-state ion pair [Ru(bpy)<sub>3</sub><sup>2+</sup>·S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]. The lifetime of the photoexcited ion pair-ion pair association constant and oxidative rate constant are reported for aqueous and several CH<sub>3</sub>CN-H<sub>2</sub>O solutions (up to 50% CH<sub>3</sub>CN v/v). The lifetime of the photoexcited ion pair  $[Ru(bpy)_3^{2+}S_2O_8^{2-}]^*$  is unusually long, ranging from 0.11  $\mu$ s in H<sub>2</sub>O to 0.53  $\mu$ s in 50% CH<sub>3</sub>CN.

### Introduction

The reaction of the excited state of  $Ru(bpy)_3^{2+}$  (bpy = bipyridine) with peroxydisulfate,  $S_2O_8^{2-}$ , to produce the Ru(III) species, has been investigated recently in connection with the design of photoelectrochemical cells1 and electrogenerated chemiluminescent systems.<sup>2,3</sup> Although Irvine first noted the catalytic effect

of sunlight upon the  $Ru(bpy)_3^{2+}-S_2O_8^{2-}$  reaction,<sup>4</sup> the mechanism and quantum efficiency were only recently established by Bolletta and co-workers.5

 $2Ru(bpy)_{3}^{2+} + S_{2}O_{8}^{2-} \xrightarrow{h_{\nu}} 2Ru(bpy)_{3}^{3+} + 2SO_{4}^{2-}$ (1)

Because the overall quantum efficiency (i.e., Ru(bpy)<sub>3</sub><sup>3+</sup> produced/photon absorbed) as shown in eq 1 is 2, the following photoinduced oxidation scheme has been proposed:

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 (3) Bolletta, F.; Ciano, M.; Balzani, V.; Serpone, N. Inorg. Chim. Acta

<sup>1982, 62, 207.</sup> 

<sup>(4)</sup> Irvine, D. H. J. Am. Chem. Soc. 1959, 81, 2977.

<sup>(5)</sup> Bolletta, F.; Juris, A.; Maestri, M.; Sandrini, D. Inorg. Chim. Acta 1980, 44, L175.