The 193 nm Photodissociation of 1,1- and 1,2-Difluoroethylene

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The photodissociation of 1,1- and 1,2-difluoroethylene (DFE) at 193 nm was studied by measuring product translational energy distributions, $P(E_T)$, for the various product channels. The $P(E_T)$'s are used to obtain information on the exit barriers, product internal energy, transition states, and the stability of intermediates in many of these channels. Significant differences in the $P(E_T)$'s for three-centered elimination of HF to produce :C═CHF and four-centered elimination of HF to give HC≡CF were observed. These were attributed to differences in the exit barriers and transition states for the two types of elimination. This is the first reported study of the three- and four-centered H_2 elimination pathways producing :C═CF_2 and FC≡CF, respectively. Both reactions showed the presence of a small exit barrier. This work also gives the first detailed description of the H and F atomic elimination channels. The $P(E_T)$ for primary H atom elimination indicates a simple bond rupture mechanism; the $P(E_T)$ for secondary H atom elimination suggests that triplet product is formed. The $P(E_T)$'s for F atom elimination indicate that $^{\bullet}$CH═CHF is more stable than $^{\bullet}$CF═CH_2. Where appropriate, comparisons of the various DFE and ethylene photodissociation channels were made.

Introduction

The photodissociation studies of 1,1- and 1,2-difluoroethylene (DFE) were initially undertaken to better understand previous ethylene photodissociation experiments[1] as 1,1- and 1,2-DFE have larger absorption cross sections at 193 nm ($\sigma \sim 1-4 \times 10^{-18}$ cm^2 (ref 2) or 3×10^{-19} cm^2 (ref 3) versus 2×10^{-20} cm^2 for ethylene[4]). The results of these DFE studies, however, are more than an analogy to the ethylene work; they fill critical gaps in the understanding of molecular as well as of atomic elimination from halogenated olefins.

Interest in the DFEs was particularly high in the 1970s and 1980s primarily because vibrationally excited HF is the predominant photolysis product[5−8] and chemical lasers based on HF and HCl were being developed at that time.[9] As a result, these early studies concentrated on measuring the HF vibrational state distributions. In these experiments similar results were obtained whether infrared multiphoton excitation[8] or Hg photosensitization[6,7] was used, indicating that direct dissociation from the electronically excited state does not play a critical role in the photodissociation. It was found that ∼11% of the excess energy available to the products appeared in HF vibrational excitation for the 1,1-DFE but that this value was only ∼8% for the *cis*- and *trans*-1,2-DFE.[7] In addition, the HF vibrational distribution from the *cis*- and *trans*-1,2-DFE was nearly statistical, while that from the 1,1-DFE was not.[7] The differences in the HF product excitation between the 1,1- and 1,2-isomers were attributed to the elimination mechanism.[5,7] HF and fluoroacetylene (FA), HC≡CF, are expected to form from four-centered elimination in 1,1-DFE; three-centered or four-centered HF elimination can occur in 1,2-DFE producing fluorovinylidene (FV), :C═CHF, or FA, respectively. Since the heat of formation for FV is ∼40 kcal/mol greater than that for FA,[10,11] three-centered HF elimination to give FV should produce a colder HF vibrational distribution than four-centered HF elimination to give FA.[7,8] The three-centered HF elimination might also be expected to give a colder HF vibrational distribution because the three-centered exit barrier is lower so the forces acting on the separating photofragments are weaker. Forces associated with large exit barriers tend to put energy into vibrations nonstatistically.[7,10] More recently, Hall et al., measured the HF rotational and vibrational population distributions using time-resolved Fourier transform infrared spectroscopy following 193 nm excitation of 1,1-DFE.[3] Their results were consistent with the earlier studies. They found that approximately 15% of the excess energy available to products appeared in HF vibrational excitation and approximately 10% in HF rotational excitation. The authors then compared the results of their experiments with others in which different amounts of excess energy were available to the HF and HC≡CF products and showed that the HF product forms with more vibrational energy than expected statistically.

Recent experiments by Gordon's group have illuminated the mechanism for HCl elimination in the 193 nm photodissociation of vinyl chloride.[12] They used velocity-aligned Doppler spectroscopy to measure the translational energy distributions for individual rovibrational states of HCl. They found a preference for three-centered elimination, but their data suggested that this three-centered HCl elimination would occur in a concerted but nonsynchronous manner with H atom migration to give acetylene as the coproduct rather than vinylidene. Much of the isomerization energy release would go into acetylene, as well as HCl, vibrations.

Little work has been done on elimination channels other than HF in DFE dissociation. Figure 1[5,10,11,13−17] shows thermodynamically possible products and their energy levels with respect to the DFEs. The heat of formation ($\Delta H_f°$) of many of the products are quite uncertain (±5−15 kcal/mol) so all three DFE isomers have been grouped together since their $\Delta H_f°$'s differ by only ∼3−4 kcal/mol. An early shock tube study found that HF elimination was the predominant 1,1-DFE decomposition channel at low temperatures but that atomic elimination occurred at higher temperatures.[13] VUV photolysis of 1,1- and 1,2-DFE in a matrix showed no C_2H_2, C_2F_2, CF_2, or CHF products, indicating that F_2 and H_2 elimination as well as C−C bond

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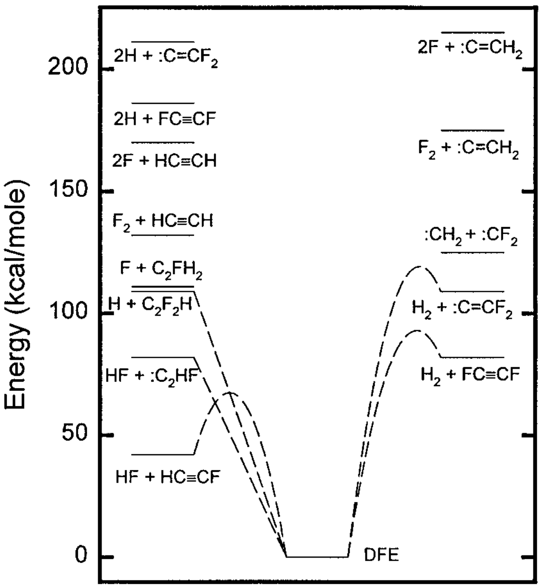

Figure 1. Thermodynamic diagram showing the energy levels of possible products from the 193 nm (148 kcal/mol) photodissociation of DFE. For the most part, the values are quite uncertain (±5−15 kcal/mol), so the 1,1- and 1,2-DFE isomers have been grouped together. The exit barriers sketched are based on the results presented in the paper.

fission were not important dissociation pathways. Evidence of H atom elimination was seen, but there was no indication of F atom loss.[18]

Detailed studies by Gordon's group, however, have been done on elimination channels other than HCl for 193 nm photodissociation of chloroethylenes.[12,19−21] Gordon's group found that H atom, Cl atom, and H_2 elimination were all important pathways. No evidence was found for Cl_2 elimination. H atom elimination was found to involve simple bond rupture on the ground potential energy surface.[20,21] Bimodal translational energy distributions for both Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) spin−orbit states were found using magic angle Doppler spectroscopy; these distributions were explained in terms of photodissociation occurring on two potential energy surfaces, the ground surface and the (n,σ^*) excited surface.[12] Using resonance-enhanced multiphoton ionization, Gordon's group measured the rotational state distributions of H_2, and using magic angle Doppler spectroscopy they measured the translational energy distributions for some of the H_2 rovibrational states from the mono- and dichloroethylenes. This work showed that four-centered H_2 elimination, either directly or through three-centered elimination followed by H atom migration, was the dominant mechanism. The H_2 product translational energy distribution peaked away from zero, indicative of a substantial exit barrier.[19]

The experiments described here were carried out at 193 nm. The DFE 193 nm absorption involves the $\pi^* \leftarrow \pi$ transition, the same excitation as in 193 nm ethylene photodissociation;[1] the 193 nm DFE absorption, however, may also involve a transition to the Rydberg excited state.[2] The geometry of the DFE $\pi\pi^*$ excited state is thought to be less twisted than in ethylene, but the mercury triplet photosensitization work of Strausz et al. on the DFEs showed that free rotation about the C═C bond still occurred after excitation.[5] In this study, product translation energy distributions ($P(E_T)$) of the photoproducts of 1,1- and 1,2-DFE were obtained by measuring time-of-flight (TOF) spectra of the HF, H_2, H, and F photofragments. The HF elimination $P(E_T)$'s from the 1,1- and 1,2-DFE isomers were used to estimate the relative exit barrier heights for three- versus four-centered HF elimination, allowing us to determine the extent to which this difference in exit barrier heights is responsible for the reported differences in HF vibrational distributions for the two DFE isomers. The H_2 molecular elimination and atomic elimination channels, which have not been well studied in the past, were also examined.

Experiment

The apparatus used in these experiments is a modified fixed source/rotating detector molecular beam apparatus. The use of this machine in high-resolution photodissociation studies has been described previously in connection with the photodissociation of acetylene.[22] The 1,1- and 1,2- (cis, trans mixture) DFE used was from Matheson. The DFE lecture bottles were frozen in liquid nitrogen and pumped on to remove any noncondensable decomposition products before use. A 50 Hz pulsed DFE beam is produced by expanding neat DFE at a stagnation pressure of 50 Torr from a piezoelectric pulsed valve with a 1 mm diameter nozzle into a photolysis chamber (no skimmer is used). The DFE parent molecules will likely have some nonzero internal energy due to unrelaxed vibrational modes. Comparison to similar acetylene photodissociation studies[22,23] suggests that this energy will be on the order of 2 kcal/mol. This energy should be added to the total amount of energy available to the fragments. As the amount of internal energy present in the parent molecules is uncertain, this number is not included in the available energy values given in the text.

The focused output (~15 mm^2 spot at interaction region) of a Lambda Physik EMG 202MSC excimer laser operating at the 193 nm ArF transition enters the photolysis chamber and crosses the molecular beam perpendicularly, approximately 3 mm downstream from the nozzle tip. The quoted laser powers are those before the laser focusing lens; the actual power inside the chamber during the experiment will be somewhat lower because of the buildup of photolysis byproduct on the lens. The mass spectrometer detector is kept perpendicular to both the laser and molecular beams while measuring TOF spectra of the photofragments. To ensure that the slower HF and F products would be detected, no detector gating wheel was used.

Using an iterative process, the $P(E_T)$ is calculated from the measured TOF with a forward convolution data analysis procedure that averages over the apparatus function.[24] The detector parameters required in the calculation, including the flight path and the effective length of the ionizer, are established from the measurements of the H and D atoms $P(E_T)$'s in the photodissociation of HI and DI.

Table 1 shows the various products and their expected earliest arrival time under our experimental conditions assuming the ΔH values in Figure 1. The table shows that the H_2 and HF molecular elimination channels as well as the H atom elimination channel should be well separated from the slower thermalized background in the TOF spectra. In addition, H atoms from the atomic elimination channel should be easy to distinguish from the H^+ that results from dissociative ionization of other products in the electron impact ionizer. The F atoms from the atomic elimination, however, may be more difficult to separate from the F^+ that results from cracking of heavier products.

Results and Analysis

A qualitative estimate of the importance of the various elimination pathways is possible from these experiments. The contribution to the $m/e = 1$ and 19 signals from HF dissociative ionization in the ionizer is greater than pure H or F elimination, suggesting that atomic elimination is less important than molecular. In fact, no F atom elimination was observed from the 1,1-DFE. It should be noted, however, that the importance

TABLE 1: Earliest Expected Photofragment Arrival Times for Energetically Accessible Channels

product	maximum translational energy (kcal/mol)	lab velocity (10^4 cm/s)	arrival time (μs)
H_2 (3-centered elimination)	40	127	34
H_2 (4-centered elimination)	66	164	27
$:C{=}CF_2$	40	[a]	[a]
$FC{\equiv}CF$	66	2	2335
F_2 (4-centered elimination)	16	11	374
$HC{\equiv}CH$	16	17	245
HF (3-centered elimination)	66	44	100
HF (4-centered elimination)	106	55	82
$:C{=}CHF$	66	19	219
$HC{\equiv}CF$	106	25	174
F	37	33	127
FC_2H_2	37	13	307
H	40	182	24
HC_2F_2	40	[a]	[a]
CH_2	24	33	127
CF_2	24	8	509

[a] Center-of-mass product velocity is less than the parent DFE velocity so no product can be detected perpendicular to the parent beam.

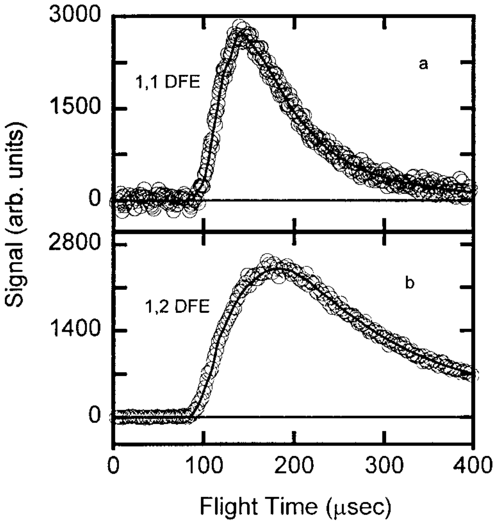

Figure 2. HF TOF spectra from the photolysis of (a) 1,1-DFE and (b) 1,2-DFE. The open circles show the data, and the solid line is the best fit obtained using the appropriate $P(E_T)$ shown in Figure 3. The scan in (a) represents 5.9×10^2 shots at an average laser power of 60 mJ/pulse. The scan in (b) represents 1.1×10^5 shots at an average laser power of 80 mJ/pulse.

of the H and F atom elimination is strongly dependent on the laser power. Of the two molecular elimination channels studied, the HF elimination channel is more important than the H_2 elimination for both the 1,1- and 1,2-DFE.

A. HF Molecular Elimination. The HF TOF spectra from the 1,1- and 1,2-DFEs are shown in Figure 2; Figure 3 shows the $P(E_T)$'s used to fit these data. Assuming that 1,2 migration of H and F atoms is not facile in the excited state (i.e., there is not complete randomization) as was found for ethylene photolysis,[1] it is expected that HF can be formed via both three- and four-centered elimination in 1,2-DFE but only through four-centered elimination in 1,1-DFE. The 1,1- and 1,2-DFE HF elimination $P(E_T)$'s both show a maximum product translational energy of ~80−90 kcal/mol which is greater than the expected maximum, 66 kcal/mol, for three-centered elimination to give FV. This shows that, as expected, photodissociation of both isomers produces some FA. For the 1,1-DFE, the FA will form via four-centered elimination; for the 1,2-DFE, the FA can form directly through four-centered elimination or possibly through three-centered elimination in concert with FV → FA isomerization. That the maximum is significantly less than what is predicted for four-centered elimination to give FA and HF (106 kcal/mol) suggests that the HF and $HC{\equiv}CF$ products are created with greater than ~16−26 kcal/mol internal energy (note that the uncertainty of the elimination reaction endothermicity is ±15 kcal/mol). In a previous studies of HF elimination from 1,2-DFE, Hall et al. found that approximately 15% of the available energy (16 kcal/mol) goes into HF vibrations and approximately 10% (11 kcal/mol) goes into HF rotations. The HF four-centered elimination is similar to the four-centered H_2 elimination in ethylene where the H_2 and $HC{\equiv}CH$ products were formed with greater than ~20 kcal/mol internal energy.[1] The lack of product with no vibrational excitation indicates that large structural changes from the transition state to product may be required.

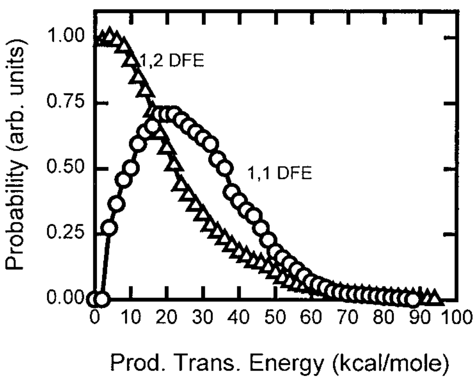

Figure 3. $P(E_T)$'s used to fit the DFE → HF + C_2HF channel. The circles show the distribution used to fit the 1,1-DFE photolysis (four-centered elimination). The triangles show the distribution used to fit the 1,2-DFE photolysis (three- and four-centered elimination).

Although the maximum translational energy of the HF products from the 1,1- and 1,2-DFEs are similar, the shapes of the $P(E_T)$'s are quite different. This can be seen directly in the HF TOF data where much of the 1,2-DFE HF signal occurs at slower times than for the 1,1-DFE. Since four-centered elimination, the less endothermic elimination channel, is the only way to produce HF from 1,1-DFE, it is expected that HF from 1,1-DFE will have more translational energy. The $P(E_T)$ for HF elimination in 1,1-DFE peaks away from zero (at ~22 kcal/mol) indicating the presence of a substantial exit barrier. This was also seen with the four-center elimination channel in $C_2H_2D_2$ photodissociation and is typical of concerted dissociations producing two stable molecules.[1]

The 1,2-DFE $P(E_T)$ suggests that three-centered elimination is preferred in this system. On the basis of structural probability alone, one would expect FV and FA to be produced in equal amounts from the HF elimination in 1,2-DFE. The $P(E_T)$ for 1,2-DFE, however, is significantly different from that of the 1,1-DFE where only four-centered elimination is expected to contribute. Similar behavior has been observed in ethylene photodissociation; three-centered elimination to produce H_2 was approximately three times as likely as four-centered.[1] Three-centered HCl elimination also appears to be favored in the photodissociation of vinyl chloride.[12,20]

The 1,2-DFE $P(E_T)$ peaks at or near 0 kcal/mol. This indicates that the exit barrier for three-centered elimination, if one even exists, must be much smaller than the exit barrier for four-centered elimination. Such a small exit barrier has been hypothesized to explain the more statistical HF vibrational distribution observed in the 1,2-DFE dissociation.[7] The peaking of the $P(E_T)$ for the HF and $:C{=}CHF$ products close to 0 kcal/mol is also evidence that the elimination is occurring from the ground electronic state. After the initial photon absorption, the

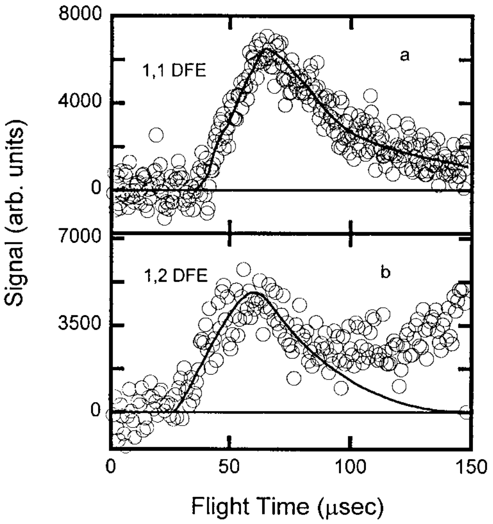

Figure 4. H_2 TOF spectra from the photolysis of (a) 1,1-DFE and (b) 1,2-DFE. The open circles show the data and the solid line is the fit calculated using the appropriate $P(E_T)$ in Figure 5. The scan in (a) represents 1.2×10^6 shots at an average laser power of 90 mJ/pulse. The scan in (b) represents 8.5×10^5 shots at an average laser power of 90 mJ/pulse.

electronically excited DFE must undergo internal conversion to the upper vibrational levels of the ground state.

The translational energy distribution for the HCl elimination channel in vinyl chloride photodissociation[12] shows a peak near 22 kcal/mol (averaged over the HCl $v = 0$, 1, and 2 states). The proposed mechanism for this system is three-centered elimination with concerted vinylindene–acetylene isomerization. The apparent exit barrier for this three-centered HCl elimination from vinyl chloride, due in part to the vinylidene–acetylene isomerization energy, is much greater than three-centered HF elimination from the 1,2-DFE. Perhaps this indicates that the H atom migration that would convert FV to FA does not occur in the three-centered elimination of HF from 1,2-DFE.

B. H_2 Molecular Elimination. H_2 product was seen in the photodissociation of both 1,1- and 1,2-DFE; the H_2 TOF spectra are shown in Figure 4. For both isomers, the H_2 product peak is fast enough that it is well separated from laser-correlated background which arrives later. There was more H_2 signal when photodissociating 1,1-DFE than 1,2-DFE. Assuming that the H and F atoms do not randomize in the excited state, H_2 can be produced only via three-centered elimination in the photolysis of the 1,1-DFE isomer and via four-centered elimination in the photolysis of the 1,2-DFE isomer. Thus, three-centered elimination is apparently preferred over four-centered as was found in the ethylene system,[1] HCl elimination in vinyl chloride,[12,20] and the HF elimination channel in the DFEs.

The H_2 TOF spectrum from the 1,2-DFE has a component that arrives after ~100 μs; it is unlikely that this could be H_2 from the direct photodissociation of the parent. On the basis of previous experience with the photolysis chamber,[1,22] the slow H_2 is probably the result of reactions of H atoms produced in the photodissociation. The interference of this slow H_2 background makes it impossible to accurately determine the shape of the very low transitional energy section of the $P(E_T)$.

The $P(E_T)$'s used to fit the TOF spectra are plotted in Figure 5. Photolysis of 1,2-DFE produces some H_2/C_2F_2 that are faster than those from the 1,1-DFE. This is expected since three-centered H_2 elimination in 1,1-DFE to give $:C{=}CF_2$ is more endothermic than four-centered H_2 elimination to give $FC{\equiv}CF$ in the 1,2-DFE system. In three-centered H_2 elimination in ethylene, some products were detected with a faster translational energy than the total available energy. This was attributed to contamination of our parent beam, uncertainty in fitting the data, and possible acetylene formation due to simultaneous H atom migration during the H_2 elimination.[1] Gordon's group's studies of HCl elimination in the photodissociation of vinyl chloride showed that three-centered elimination occurred in concert with vinylidene–acetylene isomerization.[12] That we are not seeing H_2/C_2F_2 product from the 1,1-DFE photodissociation that have translational energy as fast as the four-centered elimination product from the 1,2-DFE photodissociation suggests that $:C{=}CF_2 \rightarrow FC{\equiv}CF$ isomerization does not occur. Similarly, in Huang and Gordon's study of three-centered HCl elimination produced in the 193 nm photodissociation of 2-chloro-1,1-difluoroethylene, they found no evidence of concerted $:C{=}CF_2 \rightarrow FC{\equiv}CF$ isomerization.[25] This result is not surprising. Reiser et al. found in their infrared multiphoton excitation study of $F_2C{=}CHCl$ that $:C{=}CF_2$ is long-lived and does not undergo rearrangement to form $FC{\equiv}CF$.[26] Also, calculations show that the activation barrier for $:C{=}CF_2 \rightarrow FC{\equiv}CF$ isomerization is approximately 60 kcal/mol greater than that for vinylidene–acetylene isomerization.[27]

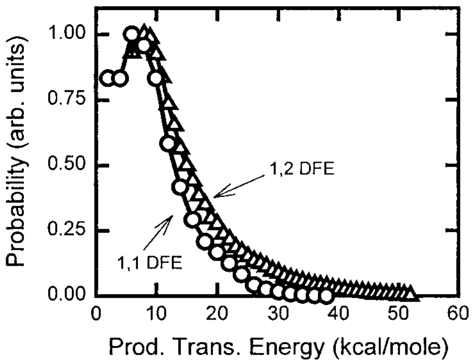

Figure 5. $P(E_T)$'s for the DFE → $H_2 + C_2F_2$ channel. The circles show the distribution used to fit the H_2 TOF spectrum from the 1,1-DFE photolysis (Figure 4a) which is expected to be a three-centered elimination of H_2 to give $:C{=}CF_2$. The triangles show the distribution used to fit the 1,2-DFE photolysis to give H_2 and $FC{\equiv}CF$ (Figure 4b) which should be a four-centered elimination.

Comparison of the maximum translational energy release for the 1,2-DFE, 50 kcal/mol, to that predicted from the enthalpy of four-centered elimination, $C_2H_2F_2 \rightarrow H_2 + FC{\equiv}CF$, 66 kcal/mol, suggests that the products are formed with greater than ~16 kcal/mol internal energy. This amount of product internal energy is similar to that observed in four-centered HF elimination in the 1,2-DFE and in the ethylene system.[1] The three-centered H_2 elimination products from the 1,1-DFE have a maximum translational energy of ~32 kcal/mol. This is slightly less than the value predicted from the enthalpy of the $C_2H_2F_2 \rightarrow H_2 + :C{=}CF_2$ reaction (40 kcal/mol) and suggests that the products are formed with greater than ~8 kcal/mol internal energy. The minimum product internal energy could not be calculated for three-centered HF elimination in the 1,2-DFE since four-centered elimination also occurred.

The peak of the $P(E_T)$ for three-centered elimination in 1,1-DFE (1,1-DFE $\rightarrow H_2 + :C{=}CF_2$) is ~8 kcal/mol. That the $P(E_T)$ peaks away from zero indicates the presence of a small exit barrier. Three-centered H_2 elimination in 1,1-DFE is different from three-centered H_2 elimination in the deuterated ethylenes[1] and from three-centered HCl elimination in vinyl chloride[12,20] where larger exit barriers (~22 kcal/mol) were found. This difference may be because there is no $:C{=}CF_2 \rightarrow FC{\equiv}CF$ isomerization in the three-centered H_2 elimination in 1,1-DFE, while there is likely vinylidene–acetylene isomerization with an associated barrier in three-centered H_2 elimina-

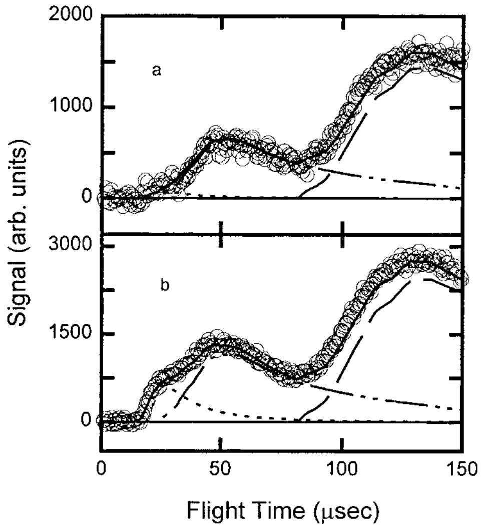

Figure 6. $m/e = 1$ TOF spectra from the photolysis of 1,1-DFE at two different laser powers. The spectrum in (a) shows the lower power scan accumulated for 2.2×10^5 shots at an average laser power of 25 mJ/pulse. The spectrum in (b) is the high-power scan which represents 1.1×10^5 shots at an average laser power of 70 mJ/pulse. The open circles show the data. The solid line shows the total fit. The dashed line represents the contribution from the dissociative ionization of HF, calculated using the $P(E_T)$ in Figure 3 (circles). The —••— line shows the primary H atom TOF spectrum (1,1-DFE → H + $HCCF_2$) calculated using the $P(E_T)$ in Figure 8. The dotted line shows the secondary H atom TOF spectrum ($HCCF_2$ → H + C_2F_2) calculated using the $P(E_T)$ in Figure 9 and assuming that all the C_2F_2H has an equal probability of absorbing a photon and dissociating.

tion from ethylene and three-centered HCl elimination from vinyl chloride.

The $P(E_T)$ for the 1,2-DFE → H_2 + FC≡CF four-centered elimination has a peak at ~9 kcal/mol, indicating the presence of a small exit barrier. A larger exit barrier (~22 kcal/mol) was found in four-centered HF elimination from 1,1-DFE as well as four-centered H_2 elimination from C_2H_4.[1] Although the details of the four-centered eliminations are undoubtedly different, they all appear typical of concerted reactions producing two stable molecules.

C. H Atom Elimination. The $m/e = 1$ TOF spectra from the 1,1- and 1,2-DFEs are shown in Figures 6 and 7. The spectra consist of a slow and fast peak. The HF $P(E_T)$ in Figure 3 gives a good fit to the slow peak, suggesting that this peak corresponds to H^+ ions formed when the HF photofragment cracks in the ionizer. On the basis of the estimates in Table 1, the fast peak, assuming it is a primary product, can come only from H atom elimination: DFE → H + HC_2F_2. The fast edge of the spectra shows a strong dependence on laser power, suggesting that some H atoms are formed from secondary dissociation, most likely of HC_2F_2. This is not surprising; in ethylene experiments, the vinyl radical (C_2H_3) readily absorbed a photon and lost an H atom.[1]

The 1,1-DFE spectra were fit first since they had the least interference from secondary dissociation. In the fitting, it was assumed that the maximum translational energy would be ~40 kcal/mol (i.e., that the C−H bond energy is ~108 kcal/mol, approximately the C−H bond energy in ethylene[13]). The primary $P(E_T)$ obtained is shown in Figure 8. The $P(E_T)$ peaks close to 0 kcal/mol and is typical of a simple bond rupture. This would suggest, as did the molecular elimination results, that after the DFE absorbs the photon, it internally converts to the ground electronic state before dissociating. Similarly, H atom elimination in ethylene[1] and in the chloroethylenes[21] occurs via the same mechanism.

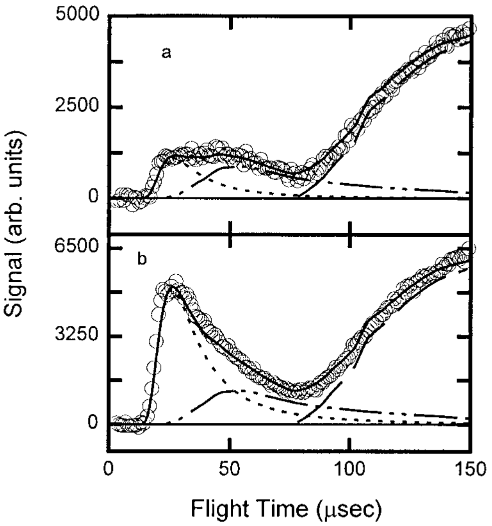

Figure 7. 1,2-DFE high- and low-power $m/e = 1$ TOF spectra. The spectrum in (a) was accumulated over 1.5×10^5 shots at an average laser power of 45 mJ/pulse. The spectrum in (b) was acquired over 5.4 $\times 10^5$ shots at an average laser power of 130 mJ/pulse. The open circles show the data and the solid line is the total fit. The dashed line shows the $m/e = 1$ contribution from the dissociative ionization of HF calculated using the 1,2-DFE → C_2HF $P(E_T)$ in Figure 3. The primary (—••—) and secondary (dotted line) H atom contributions have been calculated using the same $P(E_T)$'s used to fit the 1,1-DFE $m/e = 1$ TOF spectra in Figure 6 (see Figures 8 and 9).

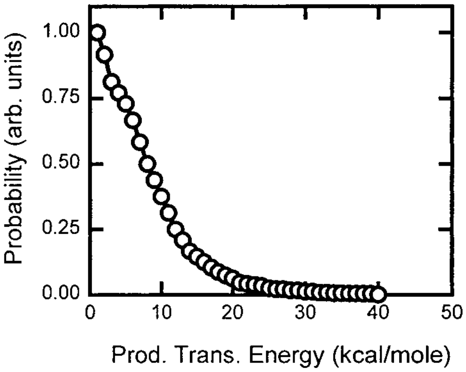

Figure 8. $P(E_T)$ for the primary H atom elimination (DFE → H + C_2F_2H) used to fit both the 1,1- and 1,2-DFE H atom TOF spectra in Figures 6 and 7.

The H atom TOF spectrum for 1,1-DFE taken at the higher laser power was used to get some idea of the secondary dissociation $P(E_T)$. The secondary dissociation was assumed to be sequential as in the ethylene,[1] and it was further assumed that all of the C_2HF_2 formed had an equal chance of absorbing a second photon. The secondary $P(E_T)$ is shown in Figure 9. In the secondary dissociation of the 1,1-DFE, unless the F atom migrates, only the :C=CF_2 will be produced. Therefore, the maximum possible secondary product translation energy would be ~(84 kcal/mol − E_{Int}). As was found in the ethylene secondary photodissociation, the secondary product is much slower than expected; the peak is at ~20 kcal/mol. In the ethylene case, this was attributed to formation of triplet product.[1] Perhaps the same is true here. In the only other study of H atom elimination in DFEs, the triplet quenching studies of Guillory and Andrews,[18] it was inferred that the DFE triplet state was somehow involved.

It should be noted that there are other possible sources for the secondary H atoms observed, for example, 1,1-DFE → HC≡CF + HF followed by secondary photodissociation of the HC≡CF to give $^{\bullet}$C≡CF + H. In fact, because atomic

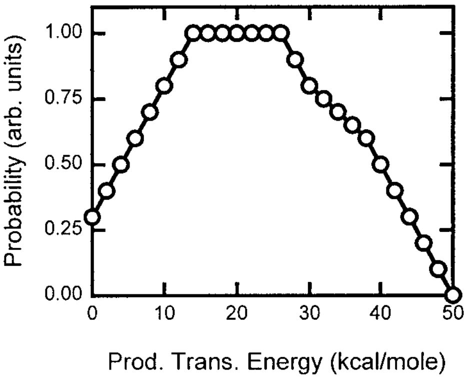

Figure 9. $P(E_T)$ for the secondary H atom elimination, $C_2F_2H \rightarrow H + C_2F_2$, used to fit the 1,1- and 1,2-DFE H atom TOF spectra in Figures 6 and 7. It was calculated assuming that all the C_2F_2H created have an equal probability of absorbing a second photon.

elimination is less important than molecular, there will be more HC≡CF produced. Unraveling the secondary dissociation mechanisms is difficult in these experiments.

There is less H atom elimination in the 1,2-DFE isomer relative to the amount of $m/e = 1$ from HF than in the 1,1-DFE. Huang et al. looked at H atom elimination from deuterated vinyl chloride and found that there is a greater tendency to remove H atoms from the β carbon (i.e., from $-CH_2$ rather than $-CHCl$)[20] because of the greater stability of the $^{\bullet}CH{=}CHCl$ radical versus the $^{\bullet}CCl{=}CH_2$. Comparison with this work, then, would suggest that the $^{\bullet}CH{=}CF_2$ radical is more stable than the $^{\bullet}CF{=}CFH$. Another explanation, however, is that there is more HF elimination in the 1,2-DFE due to the preferred three-centered elimination and, thus, less H atom elimination in 1,2-DFE.

A qualitative comparison of the data shows that secondary dissociation is much more predominant in the 1,2-DFE isomer. This can be partly attributed to the average laser power being approximately twice as great in the 1,2-DFE experiments than in the 1,1-DFE experiments. More likely, however, the greater power dependence is because in the secondary photodissociation, the major primary products in 1,2-DFE photodissociation, :C=CHF or $^{\bullet}CF{=}CHF$, have a stronger 193 nm absorption than the major primary products in 1,1-DFE photodissociation, HC≡CF or $^{\bullet}CH{=}CF_2$. (After absorption of a second photon, H elimination should be the major dissociation channel for all these species.)

The greater power dependence for the 1,2-DFE made it much more difficult to derive the product energy distribution for primary H atom elimination. As a first approximation, it was assumed that the primary and secondary $P(E_T)$'s used in the 1,1-DFE fitting would also apply to the 1,2-DFE. Figure 7 shows that this method results in a reasonable fit. That the same primary $P(E_T)$ can be used to describe the H atom elimination from the 1,1- and 1,2-DFEs suggests that this elimination is not strongly affected by the presence of a F atom on the same carbon atom as the departing H. Comparison with the work of Gordon's group shows that this result is not surprising. In their study of H atom elimination in the chloroethylene, Mo et al. found that only atoms bounded to the carbon from which the H atom is detaching will share energy with the dissociating H atom. In some cases (e.g., CH_2CHCl and CHClCHCl), however, they found that even the atoms bonded to the same carbon from which the H atom detaches will not affect the energy distribution for the H atom elimination.[21]

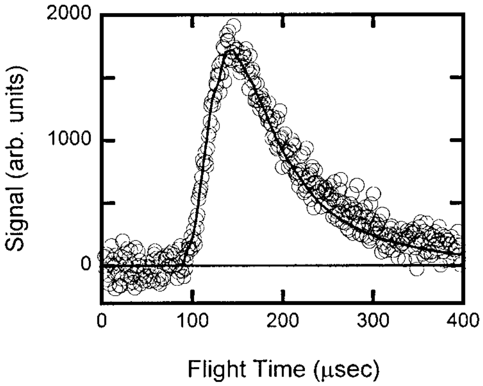

Figure 10. $m/e = 19$ TOF spectrum from the photolysis of 1,1-DFE. The scan was accumulated for 4.0×10^5 shots at an average laser power of 80 mJ/pulse. The open circles show the data and the solid line is the calculated spectrum using the 1,1-DFE → HF + C_2HF $P(E_T)$ shown in Figure 3 (circles).

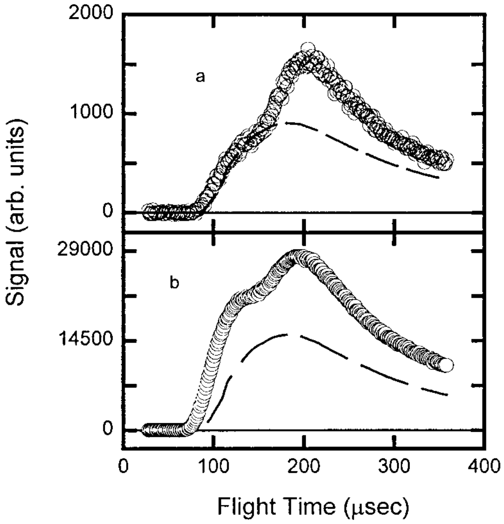

Figure 11. $m/e = 19$ TOF spectra from the photolysis of 1,2-DFE at two laser powers. The spectrum in (a) shows the low power scan which was accumulated for 1.1×10^5 shots at an average laser power of 40 mJ/pulse. The spectrum in (b) shows a high-power scan which represents 5.4×10^4 shots at an average laser power of 120 mJ/pulse. The open circles in both spectra are the data. The dashed lines show the $m/e = 19$ TOF spectra expected from the dissociative ionization of HF (1,2-DFE → HF + C_2HF) calculated using the $P(E_T)$ in Figure 3 (triangles).

D. F Atom Elimination. The TOF spectrum monitored at $m/e = 19$ from the photolysis of the 1,1-DFE isomer is shown in Figure 10. Since the $P(E_T)$ for 1,1-DFE → HF + :C=CHF gives an excellent fit to this spectrum, the F^+ ions observed must be from HF undergoing dissociative ionization in the detector. There is no evidence for any primary F atom elimination from 1,1-DFE.

The $m/e = 19$ TOF spectra from the 1,2-DFE photolysis at two different laser powers are shown in Figure 11. The spectra are similar to the HF $m/e = 20$ spectrum, but there is also a new, slower component suggesting that another channel is involved. The dashed line shows the expected contribution to the signal from dissociative ionization of HF, calculated using the $P(E_T)$ in Figure 3. The new F atom component starts to arrive at ~100−150 μs. Consulting Table 1, the most likely candidates are F atoms from 1,2-DFE → F + FC_2H_2 or F^+ from a crack of HC≡CF formed from 1,2-DFE → HF + FC≡CH. The lack of a similar slow signal from 1,1-DFE photodissociation, which should also give FC≡CH, and the fact that the arrival time of the F atom component is appreciably faster than what is expected for FC≡CH, make the F + C_2H_2F channel the obvious first choice. It is clear, however, that there are many other possible sources of F^+ signal.

The data obtained at lower laser power was fit by scaling the HF contribution, for which the $P(E_T)$ is known, to the fast shoulder; the rest of the signal was assumed to be from F elimination. The $P(E_T)$ obtained peaks at 10−12 kcal/mol. A nonzero peak for what should be a simple bond rupture is surprising. The observation of C−F bond rupture in 1,2-DFE, but not in 1,1-DFE, however, might suggest that fluorovinyl radical with F in the β position, $^{\bullet}$CH=CHF, is much more stable than that with F in the α position, $^{\bullet}CF{=}CH_2$. The H atom elimination results similarly suggested that the $^{\bullet}CH{=}CF_2$ radical might be more stable than the $^{\bullet}$CF=CFH. The additional stability of the $^{\bullet}$CH=CHF would also explain why an exit barrier for C−F bond rupture in the 1,2-DFE is observed. Another explanation is that F atom elimination occurs from the (n,σ*) potential energy surface. Huang et al. found that some of the Cl atom elimination from vinyl chloride and dichloroethylene isomers occurred from this (n,σ*) potential energy surface.[12]

Increasing the laser power (Figure 11b) seemed to add some faster product from secondary photodissociation of primary product. The most likely source of this fast component is the secondary photodissociation of :C=CFH to form $^{\bullet}$CH≡CH + F.

Conclusions

The 193 nm photodissociation of DFE is similar to that of ethylene. In both molecules, molecular elimination is preferred over atomic elimination. Also, molecular and H atom elimination appear to go through the vibrationally excited ground electronic state. There are, however, some differences in the details of the molecular and atomic elimination channels that result from the unique nature of the transition states, as well as the stabilities of the various intermediates in the reactions.

Three-centered elimination was found to depend on what photofragments were formed as well as the parent molecule. Three-centered elimination of H_2 in ethylene ($C_2H_4 \rightarrow H_2 + {:}C{=}CH_2$) had a substantial exit barrier (~22 kcal/mol). Three-centered HF elimination in 1,2-DFE to produce :C=CHF was quite different; the $P(E_T)$ peaked close to 0 kcal/mol, indicating a very small exit barrier. This result may be because three-centered HF elimination in 1,2-DFE occurs from a looser critical complex than three-centered H_2 elimination in ethylene. Another possibility is that H atom migration (:C=CHF → HC≡CF isomerization) is not as important in this system or has different energetics. Three-centered H_2 elimination producing $:C{=}CF_2$ in 1,1-DFE had a small exit barrier, ~8 kcal/mol. Again, the size of this barrier relative to that found for three-centered H_2 elimination from ethylene suggests that $:C{=}CF_2 \rightarrow FC{\equiv}CF$ isomerization is not important.

Four-centered elimination was observed in the DFEs (DFE → H_2 + FC≡CF, DFE → HF + HC≡CF) and in ethylene ($C_2H_4 \rightarrow H_2 + HC{\equiv}CH$). In all cases, the $P(E_T)$ peaked away from 0 (~9, 22, and 22 kcal/mol respectively). The presence of an exit barrier suggests that four-centered elimination is a concerted reaction in which two stable molecules are produced. In all three reactions, the products are formed with a substantial amount of internal energy indicating that these four-centered eliminations also involve large structural changes.

H atom elimination in the DFE's was very much like that in ethylene in that secondary photodissociation was significant and the secondary photofragments have only a very small percentage of their energy in translation. This suggests that an electronically excited state, most likely the lowest triplet of FC≡CF or $:C{=}CF_2$, might be formed. The involvement of a triplet is expected based on Guillory and Andrews triplet quenching studies.[18]

No F atom elimination was detected from 1,1-DFE. F^+ that could not be attributed to the cracking of HF in the ionizer was detected in the 1,2-DFE photodissociation. The F^+ is thought to come from atomic elimination: 1,2-DFE → F + $^{\bullet}$CH=CHF. The $P(E_T)$ obtained for this atomic elimination, however, did not seem consistent with simple bond rupture. The presence of an exit barrier may be explained by the unusual stability of $^{\bullet}$CH=CHF. The stability of the $^{\bullet}$CH=CHF could also explain why no 1,1-DFE → F + $^{\bullet}CF{=}CH_2$ was observed. The exit barrier may also be due to dissociation on the (n,σ*) potential energy surface.

The 193 nm photodissociation of 1,1- and 1,2-DFE was found to be quite similar to 193 nm photodissociation of the chloroethylenes.[12,19−21] Three-centered elimination of HX is the favored molecular elimination pathway in both systems. H atom elimination occurs after internal conversion to the ground state, and there is a greater tendency to remove H atoms from the carbon not bonded to a halogen atom. Halogen atom elimination is also observed; in both systems, the product translational energy distributions observed are consistent with some elimination occurring from the (n,σ*) potential energy surface.

There were, however, some differences found in photodissociation of the DFEs and the chloroethylenes.[12,19−21] In three-centered HF elimination from 1,2-DFE, :C=CHF → HC≡CF isomerization did not appear to occur or did not occur with the same barrier as the vinylidene−acetylene isomerization in three-centered HCl elimination from vinyl chloride. Three-centered H_2 elimination in 1,1-DFE with no $:C{=}CF_2 \rightarrow FC{\equiv}CF$ isomerization was the preferred channel while four-centered H_2 elimination (or three-centered elimination in concert with H atom migration) in the mono- and dichloroethylenes dominated. These differences likely result from the different transition states and intermediates involved in the photodissociations.

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