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Citation: *The Journal of Chemical Physics* **107**, 7202 (1997); doi: 10.1063/1.474960

View online: <http://dx.doi.org/10.1063/1.474960>

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Infrared multiphoton dissociation of two perfluorobutenes

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(Received 1 May 1997; accepted 4 August 1997)

Photofragment translational spectroscopy was used to examine the infrared multiphoton dissociation of octafluoro-1-butene and octafluoro-2-butene. The predominant unimolecular reaction in octafluoro-1-butene at moderate laser fluences is cleavage of a carbon-carbon single bond to give the products CF_3 and C_3F_5 . The two other reactions that take place are CF_2 elimination and the formation of equal weight fragments with the chemical composition C_2F_4 ; both reactions take place via a diradical intermediate. Dissociation of octafluoro-1-butene to the resonance stabilized perfluoroallyl radical is suggested to account for the favoring of simple bond rupture. These three reaction pathways were also observed in octafluoro-2-butene dissociation, however, the branching fraction is different than from octafluoro-1-butene. In octafluoro-2-butene all three channels occur with roughly equal probability. The reactions involving CF_2 loss and C_2F_4 formation in octafluoro-2-butene are thought to proceed through the same diradical intermediate as in octafluoro-1-butene, necessitating a 1,2-fluorine migration. © 1997 American Institute of Physics. [S0021-9606(97)01042-8]

I. INTRODUCTION

The compounds in the fluorocarbon series of tetrafluoroethylene, hexafluoropropene, and octafluorobutene all have in common a single unsaturated site and complete fluorination. It is of fundamental chemical interest to examine whether these molecules exhibit similar chemical behavior when exposed to heat, light, or other perturbations. The focus of this research is on elucidating the possible chemical pathways in thermal-type dissociations under collisionless conditions. Multiple photons from an IR laser are used to create an isolated, highly vibrationally excited molecule that decomposes without complicating secondary reactions of the products. The primary products in an infrared multiphoton dissociation (IRMPD) experiment are identical to the products from thermal decomposition.¹ IRMPD experiments on hexafluoropropene have been described previously,² and the major primary decomposition products were CF_2 , CF_3 , C_2F_3 , and C_2F_4 .

Although tetrafluoroethylene has not been investigated using IRMPD, its thermal decomposition has generated a great deal of speculation as to the identity of the intermediate species involved. Combustion of tetrafluoroethylene without oxygen, produces solid carbon and carbon tetrafluoride.³ It is unlikely that the formation of carbon tetrafluoride can be attributed to a unimolecular dissociation, since this would involve two fluorine migrations before cleavage of the carbon-carbon (C-C) bond. One alternative explanation is that the C_2F_4 pyrolysis products could result from the decomposition of an intermediate species. C_2F_4 pyrolysis may produce the perfluorobutenes octafluoro-1-butene and octafluoro-2-butene among other products.⁴ CF_4 elimination

from the pyrolysis of one or both of these compounds could explain the C_2F_4 combustion products. The purpose of this study is to investigate these two perfluorobutenes by IRMPD coupled with photofragment translational spectroscopy to determine the primary reaction products.

An adiabatic compression study of tetrafluoroethylene and hexafluoropropene examined the formation and decomposition of some perfluorobutene compounds in detail.⁵ After compressing either tetrafluoroethylene or hexafluoropropene, the compounds containing four carbon atoms were identified as perfluoroisobutene, perfluorocyclobutane, octafluoro-1-butene, and octafluoro-2-butene. From the rate of formation at different compression values, activation energies for two decomposition reactions of octafluoro-2-butene were obtained. Buravtsev *et al.* found an activation energy of 100 ± 9 kcal/mol for reaction (1).



From the enthalpy values for these species a ΔH_{rxn} of ~ 65 kcal/mol at 298 K can be calculated, indicating that an exit barrier of ~ 35 kcal/mol exists for this channel.⁶ A second reaction (2), producing CF_2 and hexafluoropropene, was found to require an activation energy of 91 ± 1 kcal/mol.



This activation energy would leave ~ 24 kcal/mol available for translational energy as the ΔH_{rxn} is ~ 67 kcal/mol at 298 K.⁶

For this photofragmentation translational spectroscopy experiment, the octafluoro-2-butene used was a mixture of its *cis* and *trans* isomers. The activation energy for *trans-cis* isomerization of octafluoro-2-butene is 56.4 kcal/mol.⁷ The activation energies necessary for reactions (1) or (2) to take place are well above this isomerization barrier. This implies that the thermal decomposition of these species should be independent of which isomer is initially excited. Activation

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energies for these reactions initiated from octafluoro-1-butene were not determined in the adiabatic compression study.⁵ The barrier to isomerization from octafluoro-1-butene to octafluoro-2-butene is not known. If the dissociation pathways are similar in both octafluoro-1-butene and octafluoro-2-butene this would imply that the barrier to isomerization is less than the barrier for dissociation. Also, from the measured translational energy distributions, reaction mechanisms can be suggested. The isomerization of octafluoro-1-butene to octafluoro-2-butene or vice versa would confirm that fluorine migration takes place prior to dissociation in these large fluorocarbon systems. In addition, the elimination of CF_4 from either of these compounds would support the hypothesis that C_2F_4 polymerizes to a four carbon species before decomposing to produce CF_4 .

II. EXPERIMENTAL ARRANGEMENT

These experiments were performed on the Berkeley rotating source molecular beam apparatus that has been extensively described.⁸ A 5% mixture of the octafluorobutene⁹ of interest in He was passed through a Trickl type piezoelectric pulsed valve.¹⁰ A Lumonics TEA-820 or TEA-840 pulsed CO_2 laser was tuned to the $P(20)$ line of the $10.6\text{-}\mu\text{m}$ branch (944 cm^{-1}) and crossed the molecular beam at the interaction region. The laser was typically focused with a 25 cm focal length ZnSe lens to a $2 \times 1.5\text{ mm}^2$ spot with a laser fluence from 7 to 75 J/cm^2 . The fluence was varied by placing a copper screen in the laser path. The fragments created by IRMPD traveled 36.7 cm to the detector that consisted of an electron impact ionizer, quadrupole mass filter, and Daly type ion detector.¹¹ A multichannel scaler triggered by the laser collected the detector counts as a function of the time taken for the fragments to travel from the interaction region to the detector.

The formation of dimers at room temperature necessitated using a pulsed valve source with a heated copper extension that has been previously described.¹² Because of the lower throughput of this source, the distance between the pulsed valve and the laser was decreased by removing the first skimmer and moving the pulsed valve closer to the interaction region. This created a more intense beam at the interaction region but resulted in a broad angular spread ($\sim 4^\circ$). The source temperature was varied from 30 to 350°C . The velocity distribution of molecules in the beam was measured using standard time-of-flight (TOF) techniques with a spinning slotted wheel.¹³ A backing pressure of 600 Torr was commonly used and the mean velocity of the molecular beam ranged from 1000 to 1200 m/s with a full width at half-maximum (FWHM) of 7%–10%.

III. RESULTS AND ANALYSIS

Measurements were taken at detector to source angles of 15° , 20° , 30° , 40° , and 50° . Dissociation signal was observed at a large number of m/e ratios. The fragmentation of fluorocarbon species in the electron impact ionizer was significant. In a typical experiment, the TOF spectra of all fragments are measured and the requirement of the conservation

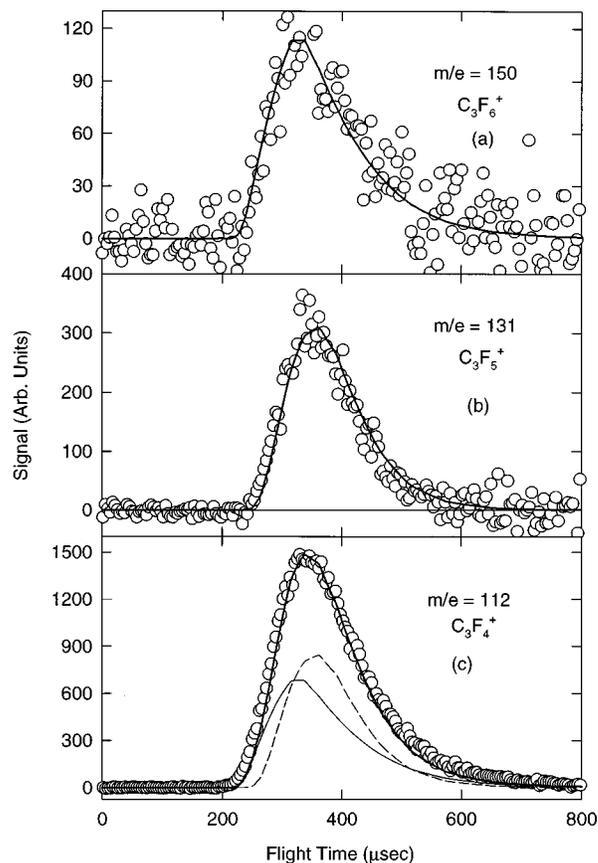


FIG. 1. TOF spectra from the dissociation of octafluoro-1-butene. In all the spectra the circles represent the experimental data points while the lines represent a fit assuming a specific translational energy distribution. The thick solid line represents the overall fit that is a sum of all the contributions. (a) The solid line represents the fit to the data at $m/e = 150$ from reaction (2). (b) The solid line represents $m/e = 131$ from reaction (3). (c) The signal at $m/e = 112$ can be explained as fragmentation of $m/e = 131$ (dashed line) and $m/e = 150$ (solid line).

of linear momentum for any pair of products in the center-of-mass (c.m.) coordinate system is used to identify which products belong to the same channel. This assignment becomes more difficult if each m/e ratio contains contributions from the dissociative ionization of numerous products. In addition, there are fluorocarbons that fragment so extensively in the electron impact ionization that no parent survives. CF_4 is one such example.¹⁴

A. Octafluoro-1-butene

The TOF spectra shown in Figs. 1–3 were taken at a fluence of $\sim 30\text{ J/cm}^2$, a source to detector angle of 20° , and a source temperature of 200°C . The TOF spectrum in Fig. 1(a) for $m/e = 150$ (C_3F_6^+) results from reaction (2), loss of CF_2 . Figure 1(b) illustrates that a second primary reaction channel (3) is present. At $m/e = 131$ (C_3F_5^+) the signal is from the heavy fragment produced in the cleavage of the C–C single bond; the peak position and rising edge of the signal for $m/e = 131$ are substantially slower than that of $m/e = 150$.

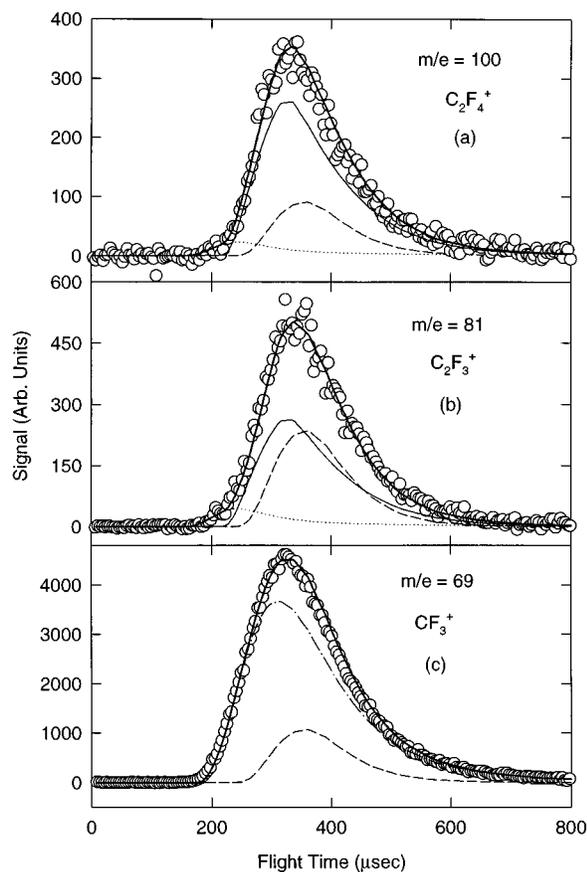


FIG. 2. TOF spectra of the dissociation products of octafluoro-1-butene. (a) The solid line in the $m/e=100$ spectrum results from fragmentation of $m/e=150$ while the dashed line is from $m/e=131$. The dotted line represents the contribution from reaction (1). (b) The TOF spectrum for $m/e=81$ contains the same three components, fragmentation from $m/e=150$ (solid line), $m/e=131$ (dashed line), and $m/e=100$ (dotted line). (c) At $m/e=69$ the dash-dot-dash line represents the dissociation partner, CF_3 , to $m/e=131$. Some fragmentation from $m/e=131$ is also observed (dashed line).



The TOF spectrum for $m/e=112$ (C_3F_4^+) in Fig. 1(c) can be completely explained as resulting from dissociative ionization of both $m/e=131$ and 150 .

At $m/e=100$ (C_2F_4^+) in Fig. 2(a) a small contribution from an additional fast component is observed, in addition to signal from the daughter ions of C_3F_6^+ and C_3F_5^+ . This is attributed to reaction (1), which produces two C_2F_4 fragments. The signal at $m/e=81$ (C_2F_3^+), shown in Fig. 2(b), contains the same contributions as $m/e=100$ and no new channels are evident. The primary component at $m/e=69$ (CF_3^+) in Fig. 2(c) is the dissociation partner of C_3F_5 in the simple bond rupture reaction. A significant contribution from reaction (1) is necessary to explain the dissociation signal observed in Fig. 3(a) at $m/e=62$ (CF_2CF^+). The TOF spectra at $m/e=50$ (CF_2^+) and 19 (F^+), shown in Figs. 3(b) and 3(c), contain contributions from reactions (1), (2), and (3). The translational energy distributions for these three reactions are displayed in Fig. 4(a). The average translational energy release for reaction (1), production of two C_2F_4 prod-

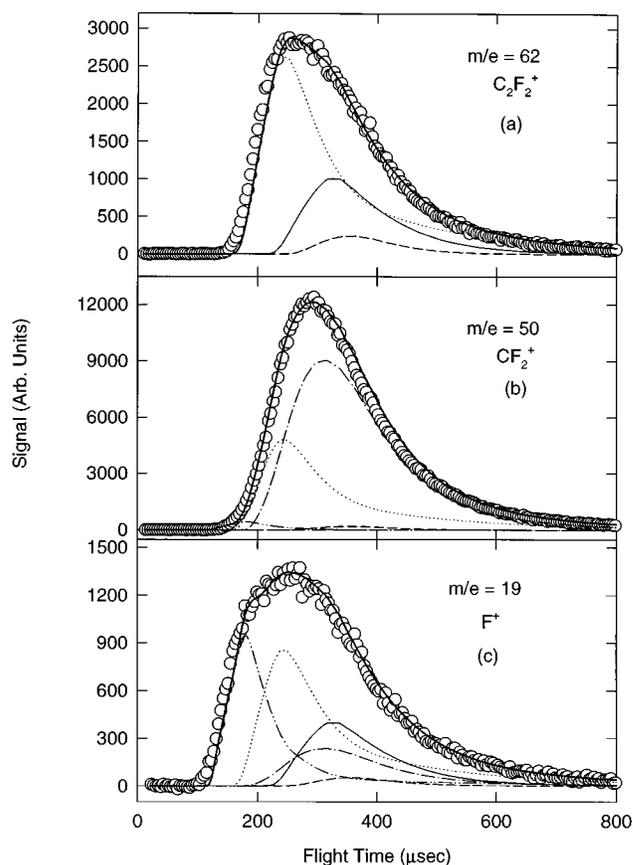


FIG. 3. TOF spectra for the lower weight fragments in the IRMPD of octafluoro-1-butene. (a) At $m/e=62$ the dotted line represents the contribution from $m/e=100$. Dissociative ionization from $m/e=150$ (solid line) and $m/e=131$ (dashed line) is also observed. (b) Fragmentation from $m/e=69$ (dash-dot-dash line) and $m/e=100$ (dotted line) dominate the TOF spectrum. A contribution from the dissociation partner, CF_2 , to $m/e=150$ is also present (dash-dot-dot line). (c) The fluorine atom TOF spectrum has a number of contributions that are all attributed to dissociative ionization. The most significant are $m/e=50$ (dash-dot-dot line), $m/e=100$ (dotted line), $m/e=150$ (solid line), and $m/e=69$ (dash-dot-dash line).

ucts, is 12.6 kcal/mol while for reaction (2), CF_2 loss, a value of 12.3 kcal/mol is obtained. For reaction (3), a simple C–C bond rupture, the distribution peaks near zero and averages 2.8 kcal/mol.

There is a second C–C single bond in octafluoro-1-butene that, if broken, would give the products C_2F_3 and C_2F_5 . There is no evidence at $m/e=119$ (C_2F_5^+) for this channel and the signal at $m/e=81$ (C_2F_3^+) can be explained by the above mentioned channels.

B. Octafluoro-2-butene

The TOF spectra shown in Figs. 5–7 were taken at a fluence of ~ 30 J/cm², a source to detector angle of 20° , and a source temperature of 200°C ; these conditions are identical to those in the octafluoro-1-butene experiments. The signal from octafluoro-2-butene dissociation is typically weaker than that from octafluoro-1-butene and the TOF spectra shown were collected over a longer time period. The disso-

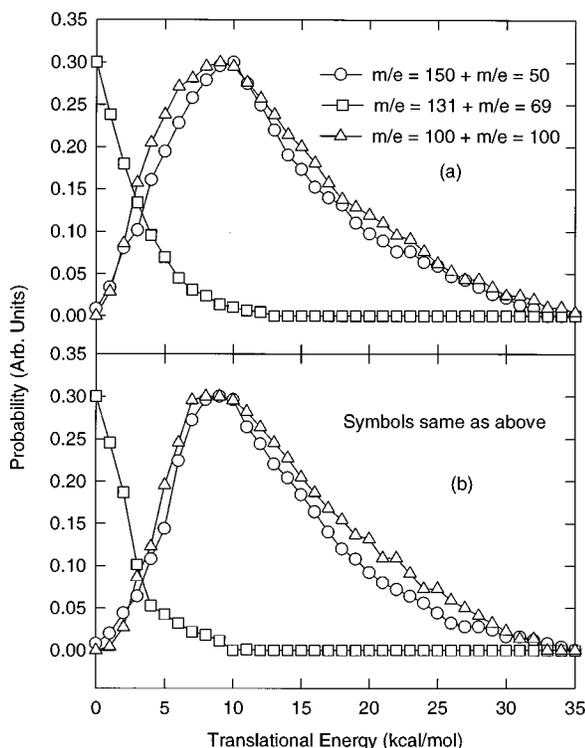


FIG. 4. The c.m. translational energy distributions for reactions (1), (2), and (3). The distributions shown in the top panel are from octafluoro-1-butene dissociation, while the bottom panel illustrates product translational energy distributions from the IRMPD of octafluoro-2-butene.

ciation product formed at $m/e = 150$ ($C_3F_6^+$) from reaction (2) [Fig. 5(a)] contributes to the signal at $m/e = 131$ ($C_3F_5^+$), however, it cannot completely explain the $m/e = 131$ TOF spectrum [Fig. 5(b)]; a contribution from reaction (3) is necessary. A similar TOF distribution is observed for $m/e = 112$ ($C_3F_4^+$) and is shown in Fig. 5(c). In Fig. 6 the TOF spectra for $m/e = 100, 81,$ and 69 show similar contributions as in octafluoro-1-butene. The contributions at $m/e = 62, 50,$ and 19 (Fig. 7) are all from the dissociative ionization of products mentioned before and do not require any reactions other than (1), (2), and (3) to explain the signal observed.

The translational energy distributions derived from the TOF spectra are shown in Fig. 4(b). These distributions are strikingly similar to those found in the IRMPD of octafluoro-1-butene. For reaction (1) an average translational energy of 13.1 kcal/mol is found and for CF_2 loss a value of 12.5 kcal/mol is obtained. For the simple bond rupture reaction (3) the distribution peaks at zero and slowly decays with an average translational energy release of 2.5 kcal/mol. Within the experimental uncertainty of these measurements, the translational energy distributions for octafluoro-1-butene and octafluoro-2-butene dissociation do not differ.

C. Branching fractions

In the dissociation of octafluoro-1-butene at 30 J/cm² the predominant channel is CF_3 loss, reaction (3). Considering the signal observed at all masses, the branching fraction of reactions 3:2:1 is 3:1:1. Approximately 60% of the reaction

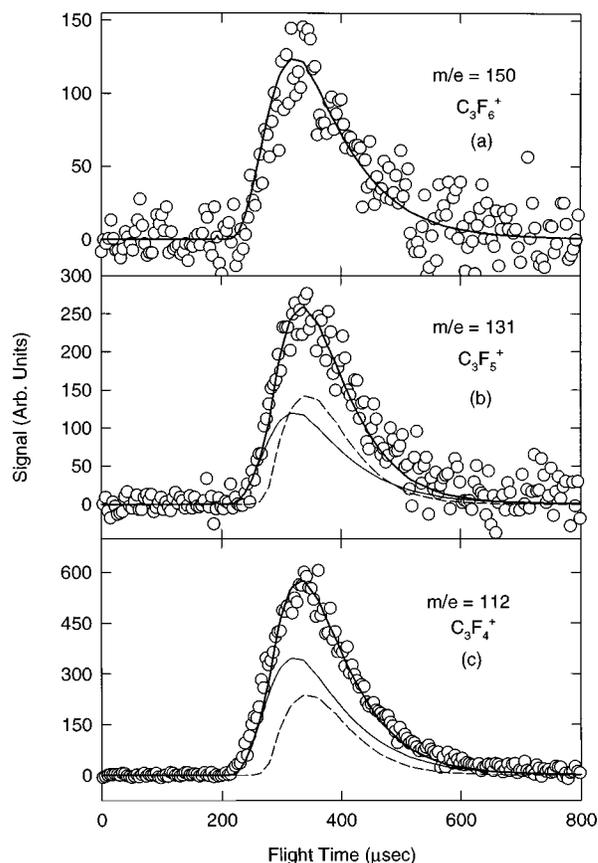


FIG. 5. TOF spectra from the dissociation of octafluoro-2-butene. (a) The solid line represents the fit to the data at $m/e = 150$ from reaction (2). (b) The signal at $m/e = 131$ results from fragmentation of $m/e = 150$ (solid line) and from reaction (3) (dashed line). (c) The signal at $m/e = 112$ is due to the fragmentation of $m/e = 150$ (solid line) and $m/e = 131$ (dashed line).

products are from C–C single bond cleavage. This fraction increases as the fluence is lowered. At a fluence of 7 J/cm² there is only evidence for reaction (3) in the IRMPD of octafluoro-1-butene. In the dissociation of octafluoro-2-butene, approximately equal amounts of products are formed for all three channels at 30 J/cm² and no signal is observed from any channel at a fluence of 7 J/cm². The uncertainties in these branching fractions are about 30% of the value given. This large uncertainty results from the difficulty in assigning parent ion fragmentation. The signal at certain m/e ratios, that is $m/e = 50, 62,$ and 69 , is very intense and modifying the fragmentation patterns at these masses can alter the branching fraction significantly. Nevertheless, the differences in the branching fractions between the two compounds are significant.

IV. DISCUSSION

In the IRMPD of octafluoro-1-butene, reaction (3) is the only channel observed at low fluences (7 J/cm²), and continues to be the predominant channel at higher fluences. This is markedly different from the IRMPD of octafluoro-2-butene,

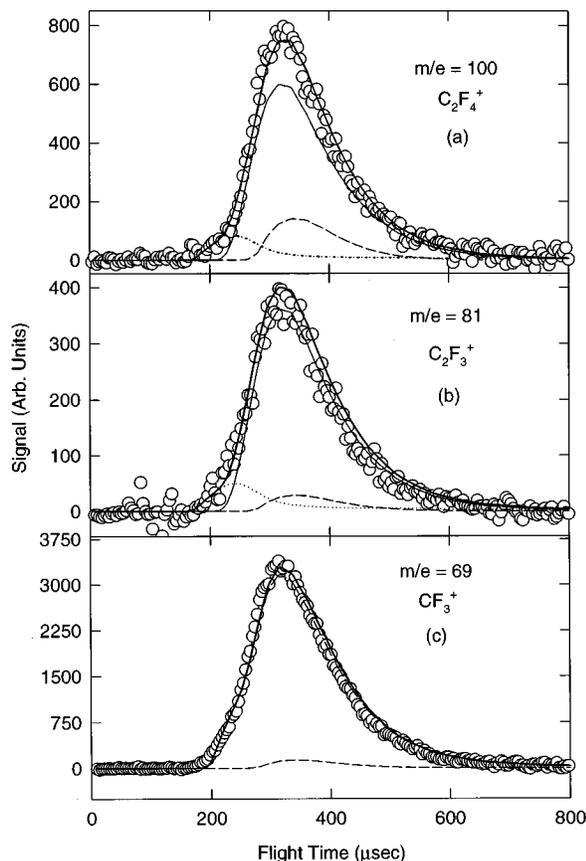


FIG. 6. TOF spectra from octafluoro-2-butene dissociation products. (a) A new feature at $m/e=100$ is attributed to reaction (1) (dotted line), while fragmentation from $m/e=150$ and $m/e=131$ (dashed line) is also evident. (b) As in octafluoro-1-butene the contributions at $m/e=81$ are similar to those in the $m/e=100$ spectrum. (c) CF_3 , from reaction (3), dominates the TOF spectrum at $m/e=69$, with a slight contribution from fragmentation of $m/e=131$ (dashed line) possible.

where reaction (3) accounts for only $\sim 1/3$ of the observed signal at 30 J/cm^2 . In the following sections the reasons for these differences will be discussed.

A. Resonance stabilization

The loss of CF_3 from octafluoro-1-butene results in the formation of the fluorinated allyl radical. The fluorinated allyl radical is formed in a single step by simple bond rupture, as evidenced by the slow translational energy distribution [Fig. 4(a)]. The π molecular orbitals overlap in this allyl-like radical, resulting in stronger bonds and greater stabilization than in a system without such overlap. In octafluoro-2-butene the direct loss of CF_3 forms a fluorinated propene radical. A 1,3-fluorine migration in this radical would be necessary to form the presumably more stable fluorinated allyl radical. An explanation for the signal observed at such low fluences in the dissociation of octafluoro-1-butene, is that it requires much less energy to directly form the resonance stabilized radical than it does to form the fluorinated propene radical from octafluoro-2-butene.¹⁵ It also seems to be clear that the

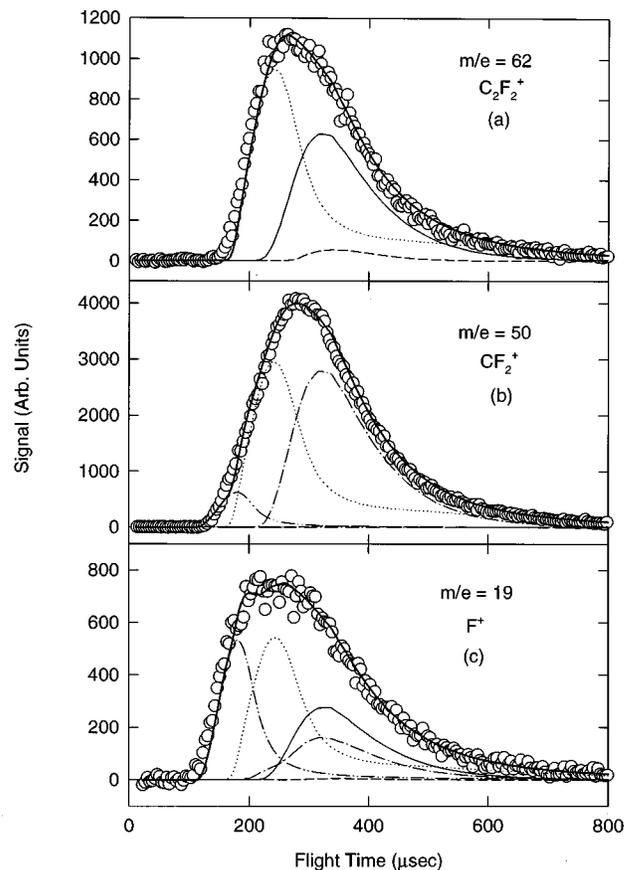


FIG. 7. More TOF spectra from the dissociation of octafluoro-2-butene. (a) The signal at $m/e=62$ is attributed to fragmentation from $m/e=150$ (solid line), $m/e=131$ (dashed line), and $m/e=100$ (dotted line). (b) At $m/e=50$, the fast edge has a contribution from CF_2 , the momentum matched partner to $m/e=150$ (dash-dot-dash line). Other contributions include fragmentation from $m/e=100$ (dotted line) and $m/e=69$ (dash-dot-dot line). (c) TOF spectrum of $m/e=19$. Contributions include fragmentation from $m/e=50$ (dash-dot-dash line), $m/e=100$ (dotted line), $m/e=69$ (dash-dot-dot line), and $m/e=150$ (solid line).

1,3-fluorine migration rate which converts octafluoro-2-butene into octafluoro-1-butene is slower than the rate of CF_3 elimination in octafluoro-1-butene.

B. Reaction mechanisms

Besides CF_3 loss two other reactions occur to a significant extent in octafluoro-2-butene and octafluoro-1-butene dissociation. The translational energy distributions obtained from the products from reaction (1), shown in Fig. 4, are peaked away from zero at $\sim 9 \text{ kcal/mol}$. It is possible to form either the carbene, $CFCF_3$, or the closed shell species tetrafluoroethylene. As discussed in the IRMPD experiments on hexafluoropropene,² the energy gained from electron pairing upon formation of 1CFCF_3 can result in a translational energy distribution peaked away from zero. The singlet-triplet splitting for $CFCF_3$ has been calculated to be 9.2 kcal/mol with the singlet lying lower in energy.¹⁶ If two 1CFCF_3 species are formed when the double bond is broken, a translational energy distribution peaked at 10 kcal/mol might be

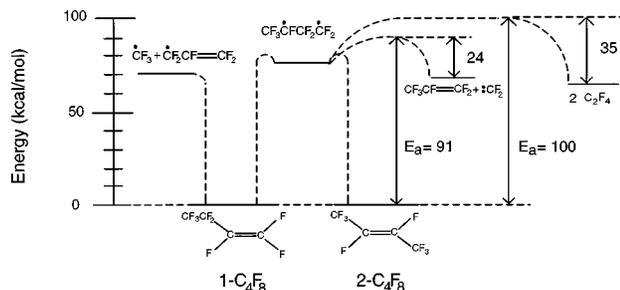


FIG. 8. Energy level diagram for octafluoro-1-butene and octafluoro-2-butene. The heats of formation for the perfluorobutenes are assumed to be similar. The lowest accessible reaction is the formation of CF_3 and the perfluoroallyl radical. A diradical species reached by a 1,3-fluorine migration in octafluoro-2-butene and a 3,2-fluorine migration in octafluoro-1-butene is suggested as a key intermediate. This diradical intermediate allows both octafluoro-1-butene and octafluoro-2-butene to access pathways to all three dissociation channels.

reasonable. If two tetrafluoroethylene molecules are formed, the repulsion between two closed-shell species would presumably result in a translational energy distribution peaked further away from zero. In addition, this channel involves simultaneous migration of two fluorine atoms and is probably unlikely. The most likely reaction mechanism for reaction (1) is formation of one C_2F_4 molecule and one CF_3CF_2 carbene. A 1,2-fluorine migration in octafluoro-2-butene and a 3,2-fluorine migration in octafluoro-1-butene can produce the $\text{CF}_3\text{CFCF}_2\text{CF}_2$ diradical, which would be a common intermediate in the production of the C_2F_4 and CF_3CF pair. The similarity in the translational energy distributions suggests that the intermediate is the same in both molecules. This indicates that although migration of a fluorine atom to the diradical intermediate followed by dissociation takes more energy than CF_3 elimination from octafluoro-1-butene, it takes less energy than cleavage of the double bond in octafluoro-2-butene.

The third channel present in the IRMPD of octafluoro-2-butene and octafluoro-1-butene is reaction (2), which results in the loss of CF_2 . Again, the translational energy distributions are similar and both are peaked away from zero at ~ 9 kcal/mol. In the case of octafluoro-2-butene a 1,2-fluorine migration, which produces the $\text{CF}_3\text{CFCF}_2\text{CF}_2$ diradical mentioned above, could also eliminate CF_2 competitively. The similarity of the translational energy distributions suggests that a 3,2-fluorine migration in octafluoro-1-butene takes place rather than direct cleavage of the C–C double bond. The repulsion between the closed-shell species, hexafluoropropene, and $^1\text{CF}_2$ explains the observed translational energy distribution, which is peaked away from zero.

C. Overall energetics

From the reactions observed at the varying fluences in octafluoro-1-butene and octafluoro-2-butene, a rough energy level diagram can be sketched (Fig. 8). From the extensive signal at low fluence, the simple bond rupture reaction of octafluoro-1-butene must have a lower activation energy than any of the other reaction pathways. It is not possible to esti-

mate the ΔH_{rxn} for CF_3 loss from octafluoro-1-butene as the ΔH_f of the perfluoroallyl radical is unknown. Because the two other reaction pathways, (1) and (2), give similar translational energy distributions, the fluorine migration to form the $\text{CF}_3\text{CFCF}_2\text{CF}_2$ diradical in both compounds may be an important process at higher laser fluences. The differences in the branching ratios for the simple bond rupture reaction indicate isomerization between octafluoro-1-butene and octafluoro-2-butene, requiring a 1,3-fluorine migration, is not as competitive as a 1,2-fluorine migration in octafluoro-2-butene, otherwise the branching ratios would be identical.

D. Question concerning CF_4 and solid carbon formation

As discussed earlier, one goal in these fluorocarbon experiments was to explain the explosive decomposition of C_2F_4 to the products CF_4 and solid carbon. From the IRMPD experiments, no evidence of the direct elimination of CF_4 was observed. Rather, the predominant reaction process in these compounds is CF_3 loss. It is possible that CF_4 can be formed if CF_3 abstracts a fluorine atom from another species such as the fluorinated allyl radical. If the reaction of two C_2F_4 molecules can produce CF_4 and CF_2CCF_2 the subsequent reaction of C_2F_4 and CF_2CCF_2 could produce CF_4 and $\text{CF}_2\text{CCCFCF}_2$. In this manner a carbon chain or network could be produced. In these IRMPD experiments direct evidence for a fluorine migration was observed in the loss of CF_2 from octafluoro-2-butene. In addition, at high fluences the TOF spectra for these two molecules begin to share similar characteristics, indicating that the activation barrier for isomerization from octafluoro-1-butene to octafluoro-2-butene is greater than the activation energy for CF_3 loss, but close to the activation energy for CF_2 loss.

V. CONCLUSIONS

The predominant reaction in octafluoro-1-butene at moderate laser fluences is cleavage of a C–C single bond to give the products CF_3 and C_3F_5 . These products were observed at very low fluences owing to allylic resonance stabilization of the C_3F_5 fragment. In octafluoro-2-butene and octafluoro-1-butene at high fluences CF_2 loss and formation of two equal mass products, C_2F_4 , from a diradical intermediate compete with CF_3 loss. No evidence for the loss of CF_4 was observed in either perfluorobutene.

ACKNOWLEDGMENTS

The octafluoro-1-butene was kindly supplied by Dr. M. H. Hung at DuPont. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional funding for this project was provided by DuPont.

¹ P. A. Schulz, Aa. S. Sudbo, D. J. Krajnovich, H. S. Kwok, Y. R. Shen, and Y. T. Lee, *Annu. Rev. Phys. Chem.* **30**, 379 (1979).

² C. A. Longfellow, L. A. Smoliar, Y. T. Lee, Y. R. Lee, C. Y. Yeh, and S. M. Lin, *J. Phys. Chem.* **101**, 338 (1997).

- ³Y. I. Babenko, Y. A. Lisochkin, and U. I. Poznyak, *Combust. Explos. Shock Waves* **29**, 603 (1993).
- ⁴B. Atkinson and A. B. Trenwith, *J. Chem. Soc.* **1953**, 2082; B. Atkinson and V. A. Atkinson, *ibid.* **1957**, 2086.
- ⁵N. N. Buravtsev, A. S. Grigor'ev, and Y. A. Kolbanovskii, *Kinet. Catal.* **30**, 386 (1989).
- ⁶The heats of formation at 298 K were obtained from the following sources: C_2F_4 , -157.4 ± 0.7 kcal/mol, *J. Phys. Chem. Ref. Data Suppl.* **14**, 655 (1985); C_3F_6 , -268.9 ± 2 kcal/mol and 1CF_2 , -44.2 ± 2 kcal/mol, D. S. Bomse, D. W. Berman and J. L. Beauchamp, *J. Am. Chem. Soc.* **103**, 3967 (1981). The value for octafluoro-2-butene of -380 ± 6 kcal/mol is from Ref. 5.
- ⁷E. W. Schlag and E. W. Kaiser, *J. Am. Chem. Soc.* **87**, 1171 (1965).
- ⁸A. M. Wodtke and Y. T. Lee, *J. Phys. Chem.* **89**, 4744 (1985).
- ⁹The octafluoro-2-butene purchased from PCR Inc. contained a 50–50 mixture of *cis* and *trans* octafluoro-2-butene. Twenty-five grams of octafluoro-1-butene were supplied by Dr. M. H. Hung of DuPont.
- ¹⁰D. Proch and T. Trickl, *Rev. Sci. Instrum.* **60**, 713 (1989).
- ¹¹Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, *Rev. Sci. Instrum.* **40**, 1402 (1969).
- ¹²C. A. Longfellow and Y. T. Lee, *J. Phys. Chem.* **99**, 15 532 (1995).
- ¹³See, e.g., B. A. Balko, Ph.D. thesis, University of California, Berkeley, 1991.
- ¹⁴*Atlas of Mass Spectral Data, Vol. 1*, edited by E. Stenhagen, S. Abrahamsson, and F. W. McLafferty (Wiley, New York, 1969).
- ¹⁵From F atom loss in the UV dissociation of hexafluoropropene [C. A. Longfellow, L. A. Smoliar, Y. T. Lee, Y. R. Lee, C. Y. Yeh, and S. M. Lin, *Chem. Phys. Lett.* **271**, 33 (1997)] a bond dissociation energy of 121 ± 2 kcal/mol was found. Using a ΔH_f for F atom of 19 ± 0.1 kcal/mol at 298 K this leads to a ΔH_f of -167 ± 3 kcal/mol for C_3F_5 . The uncertainties in these values are large, but for the simple bond rupture reaction $2-C_4F_8 \rightarrow CF_3 + C_3F_5$ a ΔH_{rxn} of 101 ± 5 kcal/mol is estimated. The ΔH_f values for CF_3 (-112.4 ± 1 kcal/mol) and F are from *J. Phys. Chem. Ref. Data Suppl.* **14**, 570, 1011 (1985).
- ¹⁶D. A. Dixon, *J. Phys. Chem.* **90**, 54 (1986).