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# Infrared Multiphoton Decomposition of Pentafluoroethane. Comments on Multichannel **Dissociation**<sup>†</sup>

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HF elimination ( $E_A = 71.6 \text{ kcal/mol}$ ) and carbon-carbon bond scission ( $E_A = 93.5 \text{ kcal/mol}$ ) are observed in the multiphoton dissociation of pentafluoroethane. A simple model for the treatment of multichannel multiphoton dissociation in focused beams is presented.

## Introduction

In most systems, the primary dissociation process in infrared multiphoton chemistry occurs by a single pathway (the lowest-energy pathway).<sup>1</sup> However, multichannel dissociation is probable provided certain criteria are met. First, for the lower exit channel, with Arrhenius parameters  $A_1$  and  $E_1$ , to compete with a higher exit channel, with Arrhenius parameters  $A_2$  and  $E_2$ , it is necessary that  $A_2$  $\gg A_1$ . It is then possible, at some internal energy  $E_i > E_2$ , that the rate coefficient for spontaneous dissociation through the upper channel  $(k_2)$  is of the same order as that through the lower channel  $(k_1)$  and both channels will be observed. A second requirement is that the radiation field be able to pump molecules from internal energy  $E_1$  to the region of  $E_{\rm i}$  in competition with spontaneous dissociation.

Most usually, for relatively simple polyatomic systems, the lifetime of the dissociating state becomes short below the threshold energy for a second channel. Sudbø, Shulz, Grant, Shen, and Lee<sup>2</sup> have shown that many molecules dissociate in moderately intense infrared fields with mean lifetimes  $\approx 10^{-9}$  s (e.g., CFCl<sub>3</sub> (12 ns), CF<sub>2</sub>Cl<sub>2</sub> (5 ns), CF<sub>3</sub>Cl (5 ns), CF<sub>3</sub>Br (1 ns), CF<sub>3</sub>I (1 ns), CF<sub>2</sub>Br<sub>2</sub> (5 ns), and N<sub>2</sub>F<sub>4</sub> (1 ns) at internal energies lower than any second exit channel. Thus if a second channel is to be observable, either high laser flux (or fluence) must be used<sup>3</sup> or a molecular system must be chosen with sufficient accessible vibrational phase space so that high levels of excitation can be attained while the lifetime for dissociation remains relatively long.<sup>4</sup>

In partially fluorinated ethanes the lower channel, hydrogen fluoride elimination, has  $E_1$  in the range 58-71 kcal/mol and  $A_1$  in the range of  $10^{13}$  s<sup>-1</sup>. The carboncarbon bond scission has  $E_2$  values in the range 90-100 kcal/mol and large A factors, in the range of  $10^{17}$  s<sup>-1</sup>, characteristic of loose transition states. The reactions have been well studied both by chemical activation techniques<sup>5</sup> and by shock-tube pyrolysis studies.<sup>6,7</sup> Of these molecules only pentafluoroethane has been shown to undergo unambiguous multichannel decay in shock-tube studies,7 and this is almost certainly a consequence of particularly favorable Arrhenius parameters<sup>7</sup>  $E_1 = 71.6$  kcal/mol,  $A_1 = 10^{13.6}$  s<sup>-1</sup>,  $E_2 = 93.5$  kcal/mol,  $A_2 = 10^{16.6}$  s<sup>-1</sup>, whereas for ethanes with one, two, or three fluorine atoms  $E_2 - E_1 = 30 \pm 1 \text{ kcal/mol.}^5$  Thus, we have investigated the possibility of infrared multiphoton multichannel dissociation of pentafluoroethane.

Several examples of multichannel decomposition have been reported, and we quote, for example, the work of Brenner on the decomposition of ethyl vinyl ether.<sup>8</sup> It is not our intention in this paper simply to present yet another example. One of the important demonstrations yet to be made is where, at sufficiently high fluence, a clear switch is made from the low-threshold energy process to the higher-energy process. Ideally, this should be done

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with parallel beam geometry where the fluence and flux are steadily increased and a gradual transition is observed. In such a study, the system would be amenable to treatment in a fairly fundamental way with the level of excess internal energy obtained being compared in a detailed manner with predictions from RRKM. However, there are very significant experimental and instrumental constraints on carrying out such a study.

We present data derived by using focused beam geometry and show that, by use of the somewhat outmoded "threshold model" for focused beams with the usual conic relationships, a reasonable interpretation of the experimental results can be obtained. The yields from various processes become ratios of volumes defined by the threshold fluence contours which describe them. The two channel system can be interpreted in terms of a simple double threshold system with the transition region between the two being negligible within the limits of the model. It should be stated explicitly, however, that, by choosing a simple model and imposing threshold fluences, the concept of mean degree of excitation has no reality, and therefore we shall make no attempt to examine the results in terms of unimolecular theory.

#### **Experimental Section**

All irradiations were carried out in an 18-cm long  $\times$  5-cm diameter Pyrex cell equipped with sodium chloride windows. TEA-CO<sub>2</sub> lasers (Lumonics Model 101 and 103) equipped with high-efficiency gratings (P.T.R. Optical, 135 lines/mm master ruling) were used to irradiate the samples. The beam passed through a 1.44-cm aperture and was focused at the center of the cell by a 10-cm focal length germanium lens. The temporal profile of the excitation was monitored by a Rofin Model 7415 photon drag detector. Pulses consisted of an initial spike (fwhm 150 ns) followed by a slowly decaying tail ( $\tau_D = 1 \ \mu s$ ) with 80% of the energy contained in the initial spike. The incident fluence was measured by a calibrated pyroelectric detector.

Products were analyzed by GC (6-ft Porapak Q, 60-80 mesh; 6-ft silica gel; 90 °C, 0.25 in. o.d. copper tube) and by mass spectrometry. The GC response was calibrated with authentic aliquots of fluoroform, tetrafluoroethylene, pentafluoroethane, and hexafluoroethane.

Pentafluoroethane was obtained from PCR Inc. and purified by distillation at -160 and -78 °C. Gas chromatographic analysis failed to reveal impurities.

#### **Results and Discussion**

The infrared and Raman spectra of pentafluoroethane have previously been reported.<sup>9</sup> Only one transition overlaps the region of  $CO_2$  laser output. This is the strong band at 1111 cm<sup>-1</sup> assigned to an a' fundamental. Experiments were performed with the R(20) line of the 00°1–02°0 band of  ${}^{12}CO_2$  at 1078 cm<sup>-1</sup>.

No decomposition products were observed when 0.58 torr of pentafluoroethane was irradiated with 1000 pulses of a parallel beam of 0.22 J cm<sup>-2</sup> at R(20). However, copious decomposition was observed in focused beams.  $C_2F_6$ ,  $C_2F_4$ ,  $CF_3H$ , and  $C_2F_3H$  together with residual  $C_2F_5H$  were detected by gas chromatography. These products increased linearly with irradiation time at low conversions (up to 1000 pulses), and all other products comprised small fractions of the observed decomposition as the mass balance deficit for carbon atoms was always less than 5%. For a typical experiment, the production rates for the major products observed when 0.58 torr was photolyzed with the focused beam at 0.4 J cm<sup>-2</sup> incident fluence were as follows:  $C_2F_4$ ,  $1.5 \times 10^{-9}$  mol/pulse;  $C_2F_6$ ,  $2.7 \times 10^{-10}$  mol/pulse;

 $\rm C_2F_3H, \sim 2 \times 10^{-10}$  mol/pulse; and  $\rm CF_3H, 9 \times 10^{-11}$  mol/pulse.

This product array can be interpreted in terms of the mechanism forwarded by Tschuikow-Roux, Millward, and Quiring<sup>7</sup> to explain the single pulse shock wave pyrolysis of pentafluoroethane. Relevant steps are

$$C_2 F_5 H \xrightarrow{nn\nu} C_2 F_4 + HF \tag{1}$$

$$C_2F_5H \xrightarrow{nh\nu} CF_3 + CF_2H$$
 (2)

followed by the free radical combination reactions

$$CF_3 + CF_3 \rightarrow C_2F_6 \tag{3}$$

$$CF_3 + CF_2H \rightarrow CF_3H + CF_2 \tag{4}$$

$$\rightarrow C_2 F_5 H^* \xrightarrow{M} C_2 F_5 H \tag{5}$$

$$\rightarrow C_2 F_4 + HF \tag{6}$$

$$CF_2H + CF_2H \rightarrow CF_2H_2 + CF_2$$
(7)

$$\rightarrow C_2 F_4 H_2^* \rightarrow C_2 F_3 H + HF \tag{8}$$

Hydrogen abstraction reactions by the fluoromethyl radicals on the substrate have been omitted because an assumption of threshold decomposition in focused beams is that the radical concentrations are high and residual substrate concentrations are low. The validity of this assumption is attested to by the low value of  $[CF_3H]$  and by the constancy of the  $[C_2F_6]/[CF_3H]$  ratio with  $[C_2F_5H]$ .

The infrared multiphoton decomposition of  $C_2F_5H$  obviously gives products which are derived from CF<sub>3</sub> and CF<sub>2</sub>H radicals. The observation that the production rate of  $C_2F_4$  is more than *five times* that for  $C_2F_6$  clearly demonstrates the involvement of the competitive molecular channel. The multiphoton decomposition of CF<sub>3</sub>COCF<sub>2</sub>H gives only a radical channel, and studies carried out under conditions very similar to the present work give equal production rates for  $C_2F_4$  and  $C_2F_6$ .<sup>10</sup> This is in line with the results from chemical activation studies<sup>11</sup> which predict a relatively minor role for reaction 6,  $k_6/k_5 \sim 1.3 \times 10^{-3}$  torr, at room temperature.

Accepting the above mechanism and the observation that in the multiphoton decomposition of  $CF_3COCF_2H$  the yields of  $C_2F_6$  and  $C_2F_4$  are equal, it is reasonable to use  $[C_2F_4-C_2F_6]$  as a surrogate for the yield of the molecular channel (channel 1). Defining the yield of channel 2 in equivalent terms is not quite as clear, but, if it is assumed that half of the  $CF_3$  radicals react to form  $C_2F_6$ , then the amount of  $C_2F_5H$  decomposing via channel 2 is  $2[C_2F_6]$ .

The pressure dependence of the yields of the two channels is shown in Figure 1. At low pressures both channels increase linearly with pressure up to about 0.6 torr, above which the molecular channel shows a supralinear behavior while the radical channel continues to increase linearly. This behavior is entirely consistent with a threshold fluence model of multiphoton induced multichannel decay (Figure 2). In this model the lower decomposition channel is induced for all molecules with unit efficiency at some threshold fluence  $F_1$ . At some higher fluence,  $F_2$ , the radiation field is sufficiently intense to drive all molecules to internal energies where the upper decomposition channel dominates. The irradiated volume which is subjected to fluence between  $F_0$ , the incident fluence, and  $F_1$  is inhomogeneously excited by the field. The resultant vibrationally excited molecules are then thermalized by collisions within the irradiated volume and cooled by diffusion into the surrounding cold unirradiated volume. During the thermalization process collision-induced decomposition can occur as a result of energy

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Figure 1. Yields from the two decomposition channels as a function of pressure. As discussed in the text, the yield of the molecular channel is taken as  $[C_2F_4-C_2F_6]$ /pulse and that for the radical channel as 2[C2F6]/pulse. Experimental conditions: ca. 400 pulses of 1078-cm<sup>-1</sup> radiation at 0.4 J cm<sup>-2</sup> incident fluence ( $F_0$ ) focused with f = 10-cm lens, temperature 22 °C.



Figure 2. Schematic for multichannel multiphoton dissociation in focused beam geometry.

pooling reactions.<sup>12,13</sup> The yield of the collision-induced channel increases with pressure as (i) the channel is collisionally induced and (ii) the rate constant for cooling to the surrounding volume has an inverse pressure dependence as does the diffusion coefficient. Furthermore, it is not unreasonable that the collisional-induced dissociation exits preferentially by the lower channel as the vibrational temperature of the volume undergoing these reactions is necessarily less than that of other reacting volumes.

The agreement between the results and the predictions of the simple geometrical model is more clearly demonstrated in experiments where the energy per pulse is varied. It is very simple to predict that the ratio of channels should be *invariant* with pulse energy, whereas in a homogeneous branching model there should be a strong dependence on incident fluence. We have varied  $F_0$  for two pressures, and the relevant ratios are reported in Table I. For each pressure a fivefold variation in pulse energy has no effect on the ratio of yields while the yields of individual channels show the standard  $^{3}/_{2}$ -power dependence (product  $\propto$ 

TABLE I: Effect of Pulse Energy<sup>a</sup>

| initial<br>press | energy<br>per     | channel<br>yields, (mol/<br>pulse × 10 <sup>-9</sup> ) |      | ratio<br>of<br>chan-<br>nels | threshold<br>fluence,<br>J/cm <sup>2</sup> |         |
|------------------|-------------------|--|------|------------------------------|--|---------|
| torr             | pulse, J          | 1  | 2    | 2/1                          | $F_{1}$                                    | $F_{2}$ |
| 0.30             | $0.40^{b}$        | 0.61   | 0.26 | 2.3                          | 7.9  | 17.8    |
|                  | $0.54^{c}$        | 0.48   | 0.32 | 1.5                          | 11.2                                       | 20.6    |
|                  | 0.93 <sup>c</sup> | 1.14   | 0.72 | 1.6                          | 10.6                                       | 20.7    |
|                  | $1.80^{c}$        | 3.47   | 1.97 | 1.8                          | 10.4                                       | 20.5    |
|                  | $1.95^{c}$        | 3.14   | 2.00 | 1.6                          | 11.7                                       | 21.9    |
| 1.30             | $0.40^{b}$        | 3.86   | 1.16 | 3.3                          | 6.5  | 17.2    |
|                  | $0.58^{c}$        | 4.89   | 1.42 | 3,4                          | 8.1  | 20.5    |
|                  | $0.97^{c}$        | 11.0   | 3.62 | 3.0                          | 7.7  | 19.6    |
|                  | $1.90^{c}$        | 30.2   | 9.64 | 3.1                          | 7.8  | 20.0    |

<sup>a</sup> 50-400 pulses per experiment, 22 °C. <sup>b</sup> Lumonics Model 101 laser. <sup>c</sup> Lumonics Model 103 Laser. Pulse energy varied by germanium beam splitters and polyethylene absorbers.

 $F_0^{1.5\pm0.04}$ ). These strongly support the geometrical arguments presented. Included in Table I are the threshold fluences implied by the model comparison.

Given the approximate nature of both the model and the threshold interpretation, it is unwise to speculate on the actual values derived. By analogy with RRKM cal-culations on very similar molecules,<sup>14,15</sup> we would expect the two channels to have approximately equal rates for an intermediate lifetime of between 0.3 and 3 ns. It is not unreasonable, therefore, that the excited molecule would remain undecomposed long enough to decompose predominantly by the higher-energy channel at quite moderate fluences.

There is consistent agreement of values across the spectrum of pressure and pulse energies used which is persuasive that the observation of mixed products in a focused beam is consistent with interpreting them in terms of two reaction channels from the main excitation manifold.

## **References and Notes**

- (1) D. Gutman, W. Brown, and W. Tsang, J. Chem. Phys., 67, 4291 (1977).
- Aa. Sudbø, P. A. Shulz, E. R. Grant, Y. R. Shen, and Y. T. Lee, J. Chem. Phys., 70, 912 (1978).
  J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, *Phys.* (2)
- Rev. Lett., 38, 1131 (1977).
- L. D. Spicer and B. S. Rabinovitch, Annu. Rev. Phys. Chem., 21, (4) 349 (1970). (5)
- (6)
- 349 (1970).
  See, for example, D. W. Setser, *MTP Int. Rev. Sci.: Phys. Chem.*, *Ser. One*, *1972-1973*, 9, 1–42 (1972).
  J. M. Simmie and E. Tschuikow-Roux, *J. Phys. Chem.*, 74, 4075 (1970); E. Tschuikow-Roux and W. J. Quiring, *ibid.*, 75, 295 (1971);
  G. E. Millward, R. Hartig, and E. Tschuikow-Roux, *ibid.*, 76, 3195 (1971);
  G. E. Millward and E. Tschuikow-Roux, *ibid.*, 76, 292 (1972).
  E. Tschuikow-Roux, G. E. Millward, and W. J. Quiring, *J. Phys. Chem.*, 75, 2492 (1971).
- (7)75, 3493 (1971).
- D. M. Brenner, Chem. Phys. Lett., 57, 357 (1978).
- J. R. Nielsen, H. H. Claasen, and N. B. Moran, J. Chem. Phys., 23, (9)329 (1955).
  (10) M. Drouin, P. A. Hackett, C. Willis, and M. Gauthier, *Can. J. Chem.*,
- 57, 3053 (1979).
- G. O. Pritchard and M. J. Perona, Int. J. Chem. Kinet., 1, 413 (1969). (12) P. A. Hackett, M. Gauthier, and C. Willis, J. Chem. Phys., 69, 2924
- (1978) (13) P. A. Hackett, C. Willis, and M. Gauthier, J. Chem. Phys., 71, 2682
- (1979).
- (14) H. W. Chang, N. L. Craig, and D. W. Setser, J. Phys. Chem., 76, 954 (1972).
  (15) K. C. Kim, D. W. Setser, and B. E. Holmes, J. Phys. Chem., 77, 725 (1973).