to be inappropriate. Instead, we propose the plots of  $1/\Delta k_{\rm F}$ vs. 1/C, which should yield a straight line for a wide range of concentrations. The corresponding plots for the fluorescence quantum yield are possible on the basis of the following expression:

$$\frac{F}{F_{\rm O} - F} = \frac{k_{\rm M}}{k_{\rm E} - k_{\rm M}} + \frac{k_{\rm M}}{k_{\rm E} - k_{\rm M}} \frac{1}{KC}$$
(18)

where F and  $F_0$  denote the fluorescence quantum yields observed under the presence and the absence, respectively, of the heavy atom perturber.

In the kinetic scheme presented in this paper, no account is taken of the exciplex containing more than one heavy atom perturber. Consequently, the above treatment should be modified if one wants to work at much higher concentrations of the heavy atom perturber. We suspect that, if we keep increasing the concentration of ethyl iodide further, the Stern-Volmer plots begin to bend upward. Unfortunately, with the time resolution available to us at the moment, the measurements of decay data at such high concentrations are impossible. We hope to work along this line soon.

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# Infrared Laser Induced Decomposition of Tetrahydrofuran

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The pulsed CO<sub>2</sub> laser induced decomposition of tetrahydrofuran (THF) has been studied as a function of the THF pressure, focal length of lens, and added gases. The stable reaction products were analyzed by gas chromatography. Although  $C_2H_4$  and  $C_3H_6$  were the dominant hydrocarbon products under all experimental conditions, the distribution of  $C_2H_4$  and  $C_3H_6$ , as well as lesser products, was shown to be very dependent upon the experimental conditions. The laser induced reaction, studied in the pressure range 0.1-12 torr of THF, exhibited two different pressure regimes above and below  $\sim 2$  torr of THF. We propose a mechanism involving breakage of the C–O bond in THF to form an unstable 1,5 diradical which further decomposes via two different pathways. Each channel splits out a stable molecule and another diradical. One of the diradicals isomerizes and decomposes to radicals, while the other diradical closes or rearranges and is predominantly stabilized. Under the conditions of low THF pressure and a short focal length lens, the radicals produced react principally via radical-radical reactions. At higher THF pressures radical-THF reactions strongly perturb the product distribution. Evidence for collisional energy pooling reactions and rotational hole filling is presented.

#### Introduction

Multiphoton IR laser induced chemistry has been in an explosive mode for the past 5 years.<sup>1</sup> Much of the initial effort in this field has gone into demonstrating the nonthermal nature of the IR laser induced reactions. The successful demonstration of nonthermal chemistry has required chemical systems whose thermal kinetics and reaction pathways were well understood. In this paper we describe an attempt to use IR laser induced chemistry to provide information about a thermal reaction which is complex and poorly understood. The reaction that we have studied is the IR laser induced decomposition of tetrahydrofuran (THF). We have analyzed the stable reaction products from the pulsed IR laser induced decomposition of THF by gas chromatography. Variation of the reaction parameters altered the product distribution and yielded mechanistic information.

The thermal decomposition of THF, a five-membered cyclic ether, was studied by Klute and Walters in 1946.<sup>2</sup> At 550 °C, 200 torr of THF, and low conversions, the major

products of the reaction were hydrocarbon unsaturates, CO and CH<sub>4</sub>. The product analysis did not have the advantage of gas chromatography. Klute and Walters proposed that the main reactions occurring in the decomposition were

$$\begin{array}{c} CH_2 - CH_2 \\ I \\ CH_2 \\ CH_3 \\ CH_4 \\ CH_4$$

Ordinarily only the total unsaturate yield was measured, but in separate experiments the  $C_2H_4$  yield was shown to dominate the other unsaturates (presumed to be mostly  $C_3H_6$ ) by 3.75:1. Both aldehydes initially increased in yield and then decreased via decomposition as shown above.

The kinetics of the thermal decomposition of THF were followed by the change in total pressure. The pressuretime curve showed an induction period and did not reach a maximum until 40% of the reactant had been consumed. At the maximum rate of pressure change, the rate was dependent upon the THF pressure to the 3/2 power. Runs from 529 to 569 °C yielded an activation energy of 53 kcal/mol.

The addition of propylene and biacetyl increased the reaction rate dramatically while CH<sub>3</sub>CHO and NO had

<sup>(1)</sup> Examples of recent reviews include: W. C. Danen, Opt. Eng., 19, 21 (1980); 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); N.
 Bloembergen and E. Yablonovitch, Phys. Today, 31, 23 (1978).
 (2) C. H. Klute and W. D. Walters, J. Am. Chem. Soc., 68, 506 (1946).

little effect. A later study showed that other unsaturated hydrocarbons accelerated the decomposition of THF.<sup>3</sup> The authors were unable to determine whether the reaction proceeded via a nonchain decomposition (ring cleavage) or by a chain mechanism involving removal of a hydrogen from THF followed by decomposition of the  $C_4H_7O$ radical.

The UV photolysis of THF has been studied by Roquitte with a medium-pressure Hg arc.<sup>4,5</sup> The postulated decomposition mechanism involved the initial absorption of a UV photon, followed by breakage of the C-O bond and formation of a 1,5 diradical. Subsequent decomposition of this diradical led to H<sub>2</sub>CO and an excited ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>· diradical which rearranged to  $C_3H_6$  and "hot" c- $C_3H_6$ . Stabilization of the  $c-C_3H_6$  at the expense of  $C_3H_6$  was observed at higher pressures. Alternate suggested pathways from the 1,5 diradical led to  $C_3H_8$  plus CO, and  $C_2H_4$ plus CH<sub>3</sub> plus H plus CO. The major products of the reaction were CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, c-C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub>CO. At 10 torr of THF the ratio  $C_2H_4/C_3H_6$  was 2.2.

The photolysis of THF has also been studied in the vacuum-UV with rare-gas resonance lamps by Diaz and Doepker.<sup>6</sup> The major products of the reaction were  $C_2H_4$ ,  $C_3H_6$ , c- $C_3H_6$ , CO, and  $H_2$ . The ratio of quantum yields for  $C_2H_4$  and  $C_3H_6$  at 123.6 nm had a high-pressure limit of 1.2. Minor amounts of CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, allene, methylacetylene, and 1-butene were also observed, but no aldehydes were found. HI was used as a scavenger to identify  $CH_3$ ,  $C_3H_5$ , and  $C_2H_3$  as radicals. Abstraction of H by  $CH_3$  led to  $CH_4$ , and the dimerization of two  $CH_3$ radicals yielded  $C_2H_6$ . 1-Butene was formed by the reaction of  $CH_3$  plus  $C_3H_5$ . Seven primary reaction channels were identified and quantum yields assigned.

## **Experimental Section**

The radiation from a Tachisto 215G grating tuned TEA (transverse-excited atmospheric) pulsed CO<sub>2</sub> laser, operated multimode, was passed through a 5-mm aperture. After the aperture a NaCl beam splitter diverted  $\sim 1\%$  of the radiation through a 10-cm focal length BaF<sub>2</sub> lens into a Laser Precision R<sub>J</sub>P-735 pyroelectric probe and a second  $R_{J}P$ -735 probe monitored the radiation which passed through the cell. A Laser Precision R<sub>J</sub>7200 energy ratiometer simultaneously measured the energy from both probes, permitting absorption measurements to be made. The laser energy was calibrated with a Scientech 38-0102 volume absorbing disk calorimeter and energy indicator. The energy/pulse which passed through the aperture was typically about 0.12 J for the R16 line of the 9- $\mu$ m band at 1076 cm<sup>-1</sup> which was used to irradiate THF. The R16 line is  $\sim 6$  cm<sup>-1</sup> to the red of a strong THF absorption which has been ascribed to an asymmetric C–O stretch.<sup>7,8</sup> At 1076 cm<sup>-1</sup> we measured an extinction coefficient,  $\alpha$  (base e), of  $1.1 \times 10^{-2}$  cm<sup>-1</sup> torr<sup>-1</sup> with a Perkin-Elmer 299B infrared spectrometer. A 10-cm focal length NaCl lens was used to focus the laser radiation into the center of a Pyrex cell with NaCl windows. Other NaCl lenses had focal lengths of 30 and 50 cm.

The photolysis cells had windows  $\sim 45^{\circ}$  to the optical axis, rather than parallel, to limit absorption and focusing of the laser beam back into the lens by reflection. The diameters of the cells were 13.5- or 30.5-mm i.d. which accepted 25.4- or 50.8-mm NaCl windows at 45° cemented on with Varian Torr-Seal. The 13.5-mm i.d. cells were 76 mm long, and the 30.5-mm i.d. cells 76 or 127 mm long. The diameters of the cells were chosen to be much larger than the 5-mm beam diameter to eliminate wall effects.<sup>9</sup> No visible luminescence was observed with a dark adapted eye either from the laser beam hitting the cell wall or the cell volume itself. In single-shot experiments the laser energy was increased by removing the 5-mm aperture and only the large-diameter cells were used. Absorption experiments were carried out with the 30.5-mm i.d.  $\times$  76-mm long cell having a side arm for trapping out the THF with liquid  $N_2$ . The ratio of transmitted radiation through the cell containing THF to the radiation diverted by the beam splitter divided by the same ratio with THF trapped out determined  $I/I_0$ . Absorption measurements were also performed with unfocused radiation through a 1-m long cell. The photolysis cells and vacuum system had ground-glass stopcocks greased with Apiezon N. No differences in product ratios or yields were observed when a cell with Teflon stopcocks was used.

A conventional glass vacuum system with an oil diffusion pump was used for gas handling. Fisher-grade THF was used without further purification and degassed by a freeze-pump-thaw technique. Pressure in the photolysis cell was measured with an MKS Baratron 0-100-torr bakeable head. After irradiation of the THF with, typically, 100 laser pulses, reactants and products were distilled into a sample loop for introduction into the gas chromatograph. Freezing out the products with liquid N<sub>2</sub> increased the concentration of the products approximately by the ratio of the volume of the cell to the volume of the sample loop. However, small volatile products such as  $H_2$ , CO, and  $CH_4$  were not effectively trapped out. At low THF pressures and conversions less than 10% the  $C_2H_4$ vapor pressure at liquid-nitrogen temperature becomes comparable to the pressure of  $C_2H_4$  produced. For this reason the lowest THF pressure studied was 0.1 torr. Since the irradiated volume with a 10-cm lens was determind by the optics and all of the reaction products except  $H_2$ , CO, and  $CH_4$  were trapped out, the gas-chromatographic results were to a first approximation independent of the reaction cell.

The gaseous products were analyzed with a Varian 1520 C gas chromatograph using a flame ionization detector and a Carle 2014 sampling valve. The products were analyzed on 6 ft  $\times \frac{1}{8}$ -in. o.d. stainless-steel columns packed with Poropak Q or Carbopack C/0.19% picric acid (Supelco). The products of the reaction were initially identified by gas chromatography-mass spectroscopy. Some of the products were also verified by comparison of retention times with known samples on different columns. Peak height was used as a measure of product yield. The product yields have not been corrected for gas-chromatographic sensitivity, but with a Poropak Q column the relative sensitivities of the hydrocarbons differed from the average by <15%. The sensitivity of  $C_2H_4$  was 1.11 times that of  $C_3H_6$ , but  $C_2H_4$  had a sensitivity  $\sim 3.5$  times that of CH<sub>3</sub>CHO.

A 6 ft  $\times \frac{1}{8}$ -in. o.d. stainless-steel column packed with Carbosieve B (Supelco) was used with the thermal conductivity detector to detect  $H_2$ , CO,  $CH_4$ ,  $H_2CO$ , and  $C_2H_4$ . Products and reactants were expanded directly into an evacuated sample loop without using liquid nitrogen. In order to get sufficient product yield for analysis with the TC detector, 1000 or 2000 laser pulses were used to dis-

<sup>(3)</sup> G. McDonald, N. M. Lodge, and W. D. Walters, J. Am. Chem. Soc., (4) B. C. Roquitte, J. Phys. Chem., 70, 1334 (1966).
(5) B. C. Roquitte, J. Am. Chem. Soc., 91, 7664 (1969).
(6) Z. Diaz and R. D. Doepker, J. Phys. Chem., 82, 10 (1978).

<sup>(7)</sup> G. M. Barrow and S. Searles, J. Am. Chem. Soc., 75, 1175 (1953). (8) J. Eyster and E. W. Prohofsky, Spectrochim. Acta, Part A, 30, 2041 (1974).

<sup>(9)</sup> Z. Karny and R. N. Zare, Chem. Phys., 23, 321 (1977).

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sociate THF at a pressure of 5 or 10 torr.

The gas-chromatographic sensitivity factors for CO, CH<sub>4</sub>, and  $C_2H_4$  were determined by measuring the peak heights of pure samples at known pressure. The gas-chromatographic sensitivity factor for H<sub>2</sub>CO was obtained indirectly, because of the difficulty in working with H<sub>2</sub>CO. The thermal decomposition of oxetane (trimethylene oxide) is known to proceed by a nonradical mechanism to form ethylene and H<sub>2</sub>CO.<sup>10</sup>

$$\begin{array}{c|c} CH_2 - CH_2 \\ | & | \\ CH_2 - 0 \end{array} CH_2 = CH_2 + H_2 CO \quad (3)$$

Thus, under conditions identical with the THF experiments, oxetane was dissociated by the IR laser. The yield of  $C_2H_4$  was determined quantitatively and the assumption made that one molecule of  $H_2CO$  was formed for each molecule of  $C_2H_4$ . (Very small amounts of CO were formed and assumed to arise from decomposition of  $H_2CO$ .) Equating the yield of  $C_2H_4$  with the yield of  $H_2CO$  plus CO resulted in a sensitivity factor for  $H_2CO$ .

#### Results

The dominant laser induced decomposition products of THF are  $C_2H_4$ ,  $C_3H_6$ , and CO. The yield and the distribution of the C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> products were found to depend upon most of the parameters investigated, with the THF pressure and the focal length of the lens being most important. With a 10-cm lens at 0.3 torr of THF, the peak heights of  $C_2H_4$  and  $C_3H_6$  represent ~65% of the total hydrocarbon yield detected on a Carbopack C/0.19% picric acid column. At 3.0 torr of THF,  $C_2H_4$  and  $C_3H_6$ are  $\sim 75\%$  of the total hydrocarbon yield and the C<sub>2</sub>H<sub>4</sub> yield increses at the expense of  $C_3H_6$ . 1-Butene, cyclopropane (c- $C_3H_6$ ), and  $C_2H_6$  make up ~15% of the hydrocarbon yield at both pressures, and the balance is divided among 11 other hydrocarbons, mostly unsaturated  $C_3$  and  $C_4$  hydrocarbons, and minor oxygenated species. At higher pressures, CH<sub>4</sub> becomes an increasingly important product.

In separate experiments at ~5 or 10 torr of THF, the decrease in THF after 1000 or 2000 laser shots was followed by IR spectroscopy and the products were analyzed for CO, H<sub>2</sub>CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> on a Carbosieve B column with a thermal conductivity detector. At 5 or 10 torr of THF, almost all of the oxygen from THF appears as CO or H<sub>2</sub>CO. The pressure of CO plus H<sub>2</sub>CO divided by the decrease in THF pressure was 0.98 at 5.1 torr and 0.94 at 10.6 torr. The result that most of the oxygen appears as CO or H<sub>2</sub>CO correlates with other results which showed that very little CH<sub>3</sub>CHO is formed at high THF pressures. The ratio of CO to H<sub>2</sub>CO was 2.3 at 5.1 torr and 2.1 at 10.6 torr. At 5.1 torr of THF, the pressure of C<sub>2</sub>H<sub>4</sub> plus H<sub>2</sub>CO divided by the decrease in THF pressure of C<sub>2</sub>H<sub>4</sub> plus H<sub>2</sub>CO divided by the decrease in THF pressure was 1.03, while at 10.6 torr of THF this ratio was 1.05.

Pressure Dependence. The pressure dependence of the IR laser induced decomposition of THF has been studied from 0.1 to 12 torr of THF. At each pressure 100 laser shots were focused with a 10-cm NaCl lens into the center of a 30.5-mm i.d.  $\times$  76-mm long cell containing a side arm for trapping out the THF with liquid N<sub>2</sub>. Absorption measurements were carried out simultaneously above 2.0 torr of THF where absorption was appreciable. The measurements from 0.1 to 1.0 torr of THF were taken one day and those from 2.0 to 12 torr were taken on the following day. At 12 torr we were below the THF pressure





**Figure 1.** Plot of the ratio of  $C_2H_4$  and  $C_3H_6$  peak heights vs. the THF pressure. Each point corresponds to irradiation of THF with 100 laser shots from the R16 line of the 9- $\mu$ m band focused with a 10-cm focal length lens.



**Figure 2.** log-log plots of the relative product yields of  $C_2H_4$  and  $CH_4$  vs. the THF pressure. Least-squares fits of the  $C_2H_4$  yield were calculated separately for the 0.1-1- and 2-12-torr regions because of the change in slope of the  $C_2H_4/C_3H_6$  ratio shown in Figure 1. The experimental conditions were the same as in Figure 1.

which resulted in dielectric breakdown.

In Figure 1 a plot of the THF pressure vs. the ratio of  $C_2H_4$  and  $C_3H_6$  peak heights is shown. Although there is considerable scatter in the data, two linear regions are apparent with a change in slope at ~2-torr THF pressure. From these data, and data taken at other times corroborating these results, we conclude that there are two different pressure regimes in the reaction. Therefore, all of the other parameters of the reaction were investigated at 0.3 torr of THF, which was representative of the low-pressure regime, and 3.0 torr of THF, which was associated with the high-pressure regime.

In Figure 2 a log-log plot of the relative product yields of  $C_2H_4$  and  $CH_4$  vs. THF pressure are shown, and in Figure 3 similar plots are shown for  $C_3H_6$  and  $C_2H_6$ . Least-squares fits of the power dependence of the product

<sup>(10)</sup> K. A. Holbrook and R. A. Scott, J. Chem. Soc., Faraday Trans. 1, 71, 1849 (1974).



**Figure 3.** log-log plots of the relative product yields of  $C_3H_6$  and  $C_2H_6$  vs. the THF pressure. Least-squares fits of the  $C_3H_6$  yield were calculated separately for the 0.1-1- and 2-12-torr regions because of the change in slope of the  $C_2H_4/C_3H_6$  ratio shown in Figure 1. The experimental conditions were the same as in Figure 1.

TABLE I: Power Dependence of the Product Yield on THF Pressure for Product Yield  $\propto$  (Pressure)<sup>n</sup>

product	n from 0.1 to 0.1 torr <sup><math>a</math></sup>	n from 2.0 to 12 torr <sup>a</sup>	
$\begin{array}{c} C_2H_4\\ CH_4\\ C_3H_6\\ C_2H_6\\ c-C_3H_6\end{array}$	1.3 (0.99) b 1.1 (0.99) 1.2 (0.99) 1.2 (0.99)	1.2 (0.95) 2.5 (0.97) 0.93 (0.95) c 1.3 (0.96)	

<sup>a</sup> Correlation coefficients are given in parentheses. <sup>b</sup> Not determined. <sup>c</sup>  $C_2H_6$  yield decreases above 4 torr.

yields on THF pressure from Figures 1 and 2 were calculated separately for the 0.1-1.0- and 2.0-12-torr regions because of the change in slope of the  $C_2H_4/C_3H_6$  ratio shown in Figure 1. The power dependencies are listed in Table I. Although CH<sub>4</sub> was not effectively trapped out with liquid N<sub>2</sub> into the sample loop, calibration experiments determined how much the concentration of a sample was increased by trapping out with liquid N<sub>2</sub>. From these measurements we estimate that the  $C_2H_4$  yield is ~10 times the CH<sub>4</sub> yield at 2.0 torr of THF, but by 12 torr of THF the two yields are comparable.

In Figure 4 the ratio of  $c-C_3H_6$  divided by the total yield having the  $C_3H_6$  molecular formula, i.e.,  $c-C_3H_6 + C_3H_6$ , is plotted vs. the THF pressure. The ratio increases almost linearly and starts to level off at ~8 torr of THF.

The yield of CH<sub>3</sub>CHO was very small in relation to  $C_2H_4$ . Even correcting for the fact that the gas-chromatographic sensitivity for  $C_2H_4$  is ~3.5 times that of CH<sub>3</sub>CHO, the yield of  $C_2H_4$  was still ~5 times greater than that of CH<sub>3</sub>CHO at the lowest pressures and increased to greater than 15 times at high pressure.

In contrast to the changes in the relative yields of  $C_2H_4$ 



**Figure 4.** Fractional yield of  $c-C_3H_6$ , defined as  $c-C_3H_6/(c-C_3H_6 + C_3H_6)$ , as a function of the THF pressure. The experimental conditions were the same as Figure 1.

and  $C_3H_6$  with THF pressure,  $1-C_4H_8$  was relatively constant. Over the pressure range 0.1-12 torr of THF the  $1-C_4H_8$  yield remained invariant in the range 9-11% of the total products detected on the Poropak Q column.

The absorption of focused laser radiation was linearly dependent upon the THF pressure from 2.0 to 12 torr. At 3.0 torr of THF, 6% of the radiation was absorbed and doubling the THF pressure doubled the amount of absorption. Because the radiation was focused, the path length was not defined.

Focal Length of Lens. The product distribution and yield from the IR laser induced decomposition of THF was investigated for various focal length lenses at 0.3 and 3.0 torr of THF. At the higher pressures absorbance measurements were also made. At 0.3 torr of THF, the product distribution is a sensitive function of the focal length of the lens. With a 30-cm lens  $C_3H_6$ ,  $c-C_3H_6$ , and  $CH_3CHO$ increase in relative yield, while  $C_2H_4$ ,  $C_2H_6$ , and  $1-C_4H_8$ decrease when compared to the results with a 10-cm lens. Similar results were obtained at 3.0 torr for  $C_2H_4$ ,  $C_3H_6$ , and  $CH_3CHO$ , but the changes were much less dramatic. The percentage distribution of products for 10- and 30-cm lenses at 0.3 and 3.0 torr of THF are shown in Table II. The results for  $SiF_4$ -sensitized reactions are also shown in Table II for comparison. These results are for a Poropak Q column uncorrected for gas-chromatographic sensitivity.

The hydrocarbon product yield at 0.3 torr of THF with a 30-cm lens was  $\sim^{1}/_{3}$  the yield with a 10-cm lens. With a 50-cm lens the yield dropped to  $\sim^{1}/_{30}$  the yield with a 30-cm lens. In contrast, the product yield at 3.0 torr of THF was approximately the same for the 10- and 30-cm lenses and only decreased by a factor of  $\sim 2$  with the 50-cm lens. The absorbance at 3.0 torr of THF *increased* from 5.0% with the 10-cm lens, to 5.9% with the 30-cm lens, to 11.5% with the 50-cm lens.

When THF was irradiated with 10 000 unfocused laser pulses, corresponding to ~2300 J of energy, no reaction products were detected. Under focused conditions, fewer than 100 laser shots yield easily detectable products. Thus, we conclude that THF exhibits an energy-density threshold. Absorption measurements were also done with an unfocused laser beam through a 1-m cell equipped with two cold fingers for trapping out the THF. At an energy density of 0.5 J/cm<sup>2</sup> and 3.1 torr of THF, the average number of photons absorbed per molecule of THF,  $\langle n \rangle$ , was only 2.0.

Extent of Reaction. The disappearance of THF was followed by IR spectroscopy as a function of the number

TABLE II: Distribution of Products with Different Focal Length Lenses, Direct Excitation, and  $SiF_4$ -Sensitized Reactions of THF<sup>a</sup>

••••••••••••••••••••••••••••••••••••••	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	c-C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CHO	1-C4H8	CH <sub>4</sub>
······			0.3 torr of THF,	$v = 1076 \text{ em}^{-1}$			
10-cm lens	$40.4 \pm 1.8^{b}$	$6.4 \pm 0.4$	$35.1 \pm 1.0$	$5.6 \pm 0.2$	$2.8 \pm 0.2$	$9.1 \pm 0.3$	
30-cm lens	$32.9 \pm 1.7$	$3.4 \pm 0.9$	$42.5 \pm 1.9$	$10.1 \pm 0.3$	$5.7 \pm 0.7$	$4.5 \pm 0.3$	
			3.0 torr of THF.	$v = 1076 \text{ cm}^{-1}$			
10-cm lens	$60.0 \pm 3.0$	$4.3 \pm 0.8$	19.0 ± 1.2	$5.1 \pm 0.5$	$1.5 \pm 0.2$	$9.8 \pm 0.6$	$0.35 \pm 0.02$
30-cm lens	$56.0 \pm 2.1$	$4.2 \pm 0.4$	$22.6 \pm 0.2$	$5.1 \pm 0.4$	$2.1 \pm 0.3$	$9.7 \pm 0.9$	$0.31 \pm 0.02$
		0.3 torr	of THF + 5 torr	of $SiF_4$ , $\nu = 102$	5 cm <sup>-1</sup>		
10-cm lens	$69.9 \pm 1.3$	$2.8 \pm 0.4$	$14.8 \pm 1.2$	$5.8 \pm 0.2$	$1.1 \pm 0.2$	$5.0 \pm 0.6$	$0.73 \pm 0.04$
30-cm lens	$68.0 \pm 1.7$		$14.9 \pm 1.6$	$8.6 \pm 0.9$	$0.7 \pm 0.1$	$4.6 \pm 1.4$	$1.2 \pm 0.1$
		3.0 torr	of THF + 5 torr	of SiF <sub>4</sub> , $\nu = 102$	5 cm <sup>-1</sup>		
10-cm lens	$69.9 \pm 1.8$	$2.3 \pm 0.3$	$11.4 \pm 0.3$	$5.\tilde{6} \pm 0.4$	$0.7 \pm 0.1$	$7.4 \pm 0.9$	$2.8 \pm 0.1$
30-cm lens	$60.6 \pm 3.4$	$3.2 \pm 1.4$	$17.6 \pm 1.3$	$5.6 \pm 0.3$	$1.0 \pm 0.1$	$9.9 \pm 0.5$	$2.2 \pm 0.2$

<sup>a</sup> Product yields are expressed as a percentage of the total analyzed peak height on a Poropak Q column. No correction for gas-chromatographic sensitivity or product collection efficiency has been made. <sup>b</sup> Standard deviation.

of laser shots. Because of the low IR sensitivity, experiments were only carried out in the high-pressure regime at 2.9 and 8.1 torr of THF. In both cases the reaction was carried to >50% conversion (2400 laser shots). By way of comparison, the gas-chromatographic experiments were usually carried to 10% conversion or less at these pressures. A plot of ln  $(P_0/P)$  vs. the number of laser shots, where P is the THF pressure after s shots, was not a straight line. Hence, the theory which relates the reaction volume to the energy-density threshold is not applicable.<sup>11</sup>

The simple theory which relates the reaction volume to the energy-density threshold assumes that reactants disappear by a process which has the functional form of a first-order kinetic equation. In order to see whether the THF disappeared by a process functionally like an *n*thorder kinetic equation, we fit the data to an equation of the type

$$-d(THF)/ds \propto (THF)^n$$

This equation is analogous to an *n*th-order kinetic equation where the number of laser shots has been substituted for time.<sup>12</sup> Integration of this equation yields the following expression

$$1/(\text{THF})^{n-1} - 1/(\text{THF})_0^{n-1} \propto (n-1)s$$

and a plot of  $1/(\text{THF})^{n-1}$  vs. s should be a straight line for the correct value of n. In Figure 5 a plot of  $(\text{THF})^{-2}$  vs. s is shown to be linear, and hence the data fit a third-order reaction (n = 3). A third-order reaction should go to 50% completion in a time (number of laser shots) proportional to  $(\text{THF})_0^{-2}$ . However, the number of laser shots required for 50% conversion was the same, both at 2.9 and 8.1 torr of THF. Thus, analogies with standard kinetic theory do not explain the decrease in THF concentration with the number of laser shots.

From a measure of the absorption, the percent decomposition, and the laser energy, the efficiency of decomposition can be calculated. The decomposition efficiency decreases with the number of laser shots. At 100 laser shots and 2.9 torr of THF, ~140 photons are absorbed per molecule of THF decomposed. In the discussion section we calculate the bond dissociation energy of the C-O bond in THF to be ~75 kcal/mol. Thus, at 1076 cm<sup>-1</sup> a minimum of 25 photons must be accumulated in each molecule which dissociates. (This assumes that THF is not decom-



**Figure 5.** Pressure of THF remaining after *s* laser shots raised to the -2 power is plotted vs. the number of laser shots. The initial THF pressure was 8.1 torr and the THF was irradiated with the R16 line of the 9- $\mu$ m band focused with a 10-cm lens.

posed by radical attack.) The efficiency of the dissociation process, neglecting radical attack, is therefore  $\sim 18\%$ . Virtually identical results are obtained at 8.1 torr of THF.

Added Gases. Various gases were added to THF at 0.3 and 3.0 torr of THF in order to determine more about the reaction mechanism.  $N_2$  and  $CH_4$  were added as inert gases;  $C_2H_4$ ,  $C_3H_6$ , and  $CH_3CHO$ , as products of the reaction, were added to influence secondary reactions; NO, HI, and  $H_2$  were investigated as radical traps, and SiF<sub>4</sub> was used as a sensitizer. In general, we tried to keep the added gas pressure comparable to the THF pressure in order not to perturb the system too much.  $N_2$  and SiF<sub>4</sub> were exceptions. The influence of  $N_2$  was studied as a function of  $N_2$  pressure up to 25 torr, and the pressure of SiF<sub>4</sub> was 5.0 torr independent of the THF pressure.

When gases were added to THF, the product distributions obtained in the laser induced decomposition were compared to control experiments without added gas run sequentially. The percentage change in these relative product distributions upon addition of foreign gases, as

 <sup>(11)</sup> D. R. Keefer, J. E. Allen, Jr., and W. B. Person, Chem. Phys. Lett., 43, 394 (1976).
 (12) S. W. Benson, "The Foundations of Chemical Kinetics",

<sup>(12)</sup> S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960.

TABLE III: Percentage Change in Relative Product Distribution with Added Gases for 0.3 torr of THF plus 0.3torr of Added Gasa

added gas	$C_{2}H_{4}$	$C_2H_6$	$C_3H_6$	c-C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CHO	$1-C_4H_8$	CH₄	dissociation yield <sup>b</sup>
N <sub>2</sub> <sup>c</sup>	+12		-4.7	+4.7	- 53	+1.5	-17	+74
$CH_4^c$	+2.4		+14	+13	- 94	+45		+35
$C_2 H_4^c$			-9.3	-16	+ 64	+15	-18	+ 59
$C_3H_6^c$	-1.4			-22	+ 20	+9.4	-21	+ 66
CH <sub>3</sub> CHO <sup>d</sup>	-22	+270	- 20	-30			+190	-37
NOd	+15	-61	- 6.6	+24	-24	-30	-3.6	+ 37
$HI^d$	+7.6	-5.1	-7.5	+11	+10	-35	+ 93	+43
$H_2^d$	-1.0	- 5.6	+3.8	+14	+ 5.7	+ 5.7	- 8.9	+1.4

<sup>a</sup> The products as a percentage of the total analyzed peak heights were compared with and without added gas. <sup>b</sup> The total analyzed peak heights were compared with and without added gas. <sup>c</sup> Products were analyzed with a Carbopack/0.19% picric acid column.  $C_2H_4$  values represent  $C_2H_4$  plus  $C_2H_6$  because these two products are not effectively separated on this column. <sup>d</sup> Products were analyzed with a Poropak Q column.

well as the percentage change in total reaction yield, were determined. In general, the added gases were most influential at 0.3 torr of THF, and the results for all added gases at 0.3 torr, except SiF<sub>4</sub>, are shown in Table III.

The product distribution from the laser induced decomposition of 0.3 torr of THF was studied with a Poropak Q column as a function of added N<sub>2</sub> from 0.3 to 25 torr of N<sub>2</sub>. The effect of added N<sub>2</sub> was to increase  $C_2H_4$  and  $C_2H_6$ at the expense of  $C_3H_6$  and c- $C_3H_6$ . The ratio  $C_2H_4/C_2H_6$ increased with added N<sub>2</sub> as did the  $C_3H_6/c$ - $C_3H_6$  ratio. The total yield initially increased and then decreased at high N<sub>2</sub> pressure.

The addition of up to 2.0 torr of  $N_2$  to 3.0 torr of THF led to an increase in  $C_2H_4$  and  $CH_4$  and a corresponding decrease in  $C_3H_6$  and  $C_2H_6$ . Above 5.0 torr of  $N_2$ , the product distribution remained unchanged except for the continued increase in  $CH_4$  production. The extent of absorption for 3.0 torr of THF with added  $N_2$  initially increased with 1.0 torr of  $N_2$  and then slowly decreased back to the value without  $N_2$  at 25 torr of  $N_2$ .

When the IR laser induced decomposition of THF was studied in the presence of  $C_2H_4$  and  $C_3H_6$ , a Carbopack C/0.19% picric acid column was used to analyze the products of the reaction. In the same series of experiments,  $N_2$  and  $CH_4$  were also investigated for their own intrinsic interest as well as to have a comparison for the same pressure of inert gas. In addition to determination of the percentage change in the principal reaction products shown in Table III, major changes (greater than factors of 2) in the amount of a given product formed were also used as a criterion for the added gas influencing the reaction. This scanning procedure emphasized changes in the minor products of the reaction.

The addition of 0.3 torr of N<sub>2</sub> to 0.3 torr of THF led to an absolute increase in all of the reaction products except CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>CHO, and C<sub>4</sub>H<sub>2</sub> (diacetylene). The corresponding amount of CH<sub>4</sub> led to even more severe decreases in these three products as well as CH<sub>3</sub>C=CH and C<sub>4</sub>H<sub>4</sub> (1-buten-3-yne). The addition of 0.3 torr of C<sub>2</sub>H<sub>4</sub> had an effect just the opposite of N<sub>2</sub>. Both CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>CHO as well as C<sub>4</sub>H<sub>4</sub> showed significant increases. C<sub>3</sub>H<sub>6</sub> had the same effect as C<sub>2</sub>H<sub>4</sub>, and in addition a dramatic increase in *i*-C<sub>4</sub>H<sub>10</sub> and 1,3-butadiene was observed.

The sensitized decomposition of THF has been studied at 0.3 and 3.0 torr of THF with SiF<sub>4</sub> as a sensitizer.<sup>13</sup> At both THF pressures 5.0 torr of SiF<sub>4</sub> was used and the laser tuned to the P42 line of the 9- $\mu$ m band at 1025 cm<sup>-1</sup>. The results for 100 laser shots depend somewhat upon the focal length of the lens at 3.0 torr of THF and are listed in Table II. For comparison, the unsensitized reaction product distributions are also given.

At 0.3 torr of THF, the SiF<sub>4</sub>-sensitized reaction produces considerably more  $C_2H_4$  and significantly less  $C_3H_6$  for both focal length lenses than the unsensitized reaction. More CH<sub>4</sub> is formed in the sensitized reaction and less  $C_2H_6$  and CH<sub>3</sub>CHO. A comparison of the results at 3.0 torr shows similar effects. In addition, the distribution of products is much less dependent upon the THF pressure in the sensitized reaction than in the direct reaction.

Sensitized reactions are indiscriminate. As products build up in concentration, the probability of sensitizing the products increaes. When the SiF<sub>4</sub>-sensitized reaction of THF was carried out with a single laser shot focused with a 10-cm lens, the ratio  $C_2H_4/C_3H_6$  was 5.8 at 3.0 torr and 6.0 at 0.3 torr of THF, essentially showing no pressure dependence. Conversely, when THF was irradiated directly by a single laser pulse focused with a 10-cm lens, the ratio  $C_2H_4/C_3H_6$  was 3.7 at 3.0 torr and 1.3 at 0.3 torr. Thus, the differences in product distribution between direct irradiation and sensitized reactions are most apparent at low THF pressures.

## Discussion

Similarities between the distribution of hydrocarbon products produced in the vacuum-UV photolysis and IR laser induced decomposition of THF at 0.3 torr suggest that many of the mechanistic features in the vacuum-UV photolysis can be applied to the IR laser induced decomposition of THF. Although UV excitation into an excited electronic state and IR multiphoton excitation via vibrational levels of the ground electronic state are uniquely different processes, the initial bond-breaking step in both cases is consistent with breakage of the C-O bond in THF. Differences with the vacuum-UV results arise from the much higher concentrations of radicals produced by the focused IR laser beam. The higher level of excitation with vacuum-UV photons produces more fragmentation of the THF molecule. However, in the IR laser experiments the formation of vibrationally excited species which can decompose directly or absorb subsequent IR photons and decompose leads to further decomposition of THF product molecules. Following the IR laser pulse,  $V \rightarrow T/R$  relaxation may result in thermal decomposition of reactant as well as product molecules. At higher THF pressures  $C_2H_4$ dominates over  $C_3H_6$ . This result is more compatible with the thermal chemistry and, hence, at higher THF pressures features of the thermal reaction should be incorporated into the mechanism for the IR laser induced decomposition.

Mechanism. The weakest bond in the THF molecule should determine the initial bond breakage. Using a

<sup>(13)</sup> K. J. Olszyna, E. Grunwald, P. M. Keehn, and S. P. Anderson, Tetrahedron Lett., 19, 1609 (1977).

thermochemical cycle which starts with 1-butanol, breaks the O-H bond and a terminal C-H bond, and then reforms  $H_2$  leads to an estimate of 31.5 kcal/mol for the heat of formation of •CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O•.<sup>14,15</sup> When combined with  $\Delta H_{\rm f}^{\circ}$  for THF, the C–O bond strength is calculated to be 74.6 kcal/mol. The C-H bond strength in THF is estimated to be 90.7 kcal/mol. This value is obtained from the calculated  $\Delta H_{\rm f}^{\circ}$  of the oxacyclopentyl-1 radical (loss of the  $\alpha$  H in THF) of -4.5 kcal/mol.<sup>16</sup> Thus, the C-O bond in THF is the weakest bond in the molecule. Although both molecular channels proposed in the thermal decomposition of THF, i.e., formation of  $C_2H_4$  and  $CH_3$ . CHO or  $C_3H_6$  and  $H_2CO$ , have lower heats of reaction than breakage of the C-O bond, the experimental results are not compatible with such a mechanism. In addition, formation of either molecular channel involves breakage of a C-O and C-C bond with a 1,2 H shift all occurring simultaneously.

At THF pressures below  $\sim 2$  torr, we propose that breakage of the C-O bond occurs following absorption of a sufficiently large number of IR photons.

$$\begin{array}{c} CH_2 - CH_2 \\ \downarrow \\ CH_2 \\ O \end{array} \xrightarrow{CH_2} CH_2 \xrightarrow{CH_2 - CH_2} CH_2 \\ CH_2 \\ CH_2 \\ O \end{array} \Delta H = 74.6 \text{ kcal/mol} \quad (4)$$

We expect, on the basis of the IR multiphoton dissociation of other molecules, that at or above the dissociation limit the energy is statistically distributed among the THF vibrational levels and that RRKM theory will be valid.<sup>17</sup> If we further assume that most of the THF molecules decompose during the laser pulse, then RRKM theory predicts that the THF molecule, with 33 vibrational degrees of freedom, must have internal energy significantly in excess of the bond energy. Following breakage of the C-O bond, any excess internal energy will reside in the diradical leading to further decomposition.

The transient ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O· diradical can further decompose via two different pathways by breakage of different C-C bonds.

$$CH_2 = CH_2 + CH_2CH_2O \cdot \Delta H = 22.8 \text{ kcal/mol} (5)$$

$$CH_2 = CH_2 + CH_2CH_2O \cdot \Delta H = 22.8 \text{ kcal/mol} (5)$$

$$H_2C = O + CH_2CH_2CH_2 \cdot \Delta H = 9.3 \text{ kcal/mol} (6)$$

In reaction 5 the transient diradical splits into ethylene  $(C_2H_4)$  and another transient diradical,  $\cdot CH_2CH_2O_2$ , while reaction 6 proceeds to form formaldehyde ( $H_2CO$ ) and a transient trimethylene diradical,  $\cdot CH_2CH_2CH_2$ , which will be shown to rearrange to propylene or cyclopropane. Thus, reaction 5 is the ethylene channel and requires 94.4 kcal/mol of energy and reaction 6 is the propylene/cyclopropane channel and requires 83.9 kcal/mol of energy.<sup>14,15</sup> Hence, propylene/cyclopropane is the thermodynamically favored product rather than ethylene. Reactions 5 and 6 are analogous to free radicals splitting off  $C_2H_4$  in a Rice-Hertzfeld mechanism.<sup>12</sup>

We now consider the fate of the transient diradicals in reactions 5 and 6.

$$\cdot CH_2CH_2O \cdot \underbrace{CH_2 - CH_2^* - M_2 - CH_2}_{CH_3CHO^* - M_2 - CH_3CHO} (8)$$

- CH3 + CHO (9)

The transient ·CH<sub>2</sub>CH<sub>2</sub>O· diradical can close to form ethylene oxide or rearrange to form acetaldehyde (CH<sub>3</sub>C-HO).<sup>18</sup> Both reactions are highly exothermic. Unless collisions (denoted by M) are effective in removing energy from the excited ethylene oxide molecules, they will revert back to the original diradical. Under the conditions of our experiments, collisions are not very effective in stabilizing either ethylene oxide or acetaldehyde. In fact, ethylene oxide is not observed as a product. On the basis of the exothermicity of reaction 8, CH<sub>3</sub>CHO\* has  $\geq$  81.5 kcal/mol of energy whereas the activation energy for decomposition to  $CH_3 + CHO$  (reaction 9) is only 79 kcal/mol.<sup>18</sup> Hence, most of the  $\cdot$ CH<sub>2</sub>CH<sub>2</sub>O  $\cdot$  diradicals end up as CH<sub>3</sub> radicals and HCO radicals. Thus, the net reaction for the ethylene channel is the formation of  $C_2H_4 + CH_3 + CHO$  as products, just as in the vacuum-UV photolysis of THF.

In the thermal reaction significant quantities of CH<sub>3</sub>C-HO were observed initially with subsequent decomposition into  $CH_4 + CO$ . The pressure of THF in the thermal experiments was 200 torr, and at those pressures collisional stabilization of excited CH<sub>3</sub>CHO\* by THF should be competitive with decomposition to  $CH_3$  and HCO.

When 0.3 torr of THF was irradiated with a single laser pulse, the  $C_2H_4$  yield was still greater than 5 times the CH<sub>3</sub>CHO yield. This result rules out laser induced decomposition of  $CH_3CHO$  in subsequent laser pulses. Alternate possibilities include decomposition of CH<sub>3</sub>CHO in the same laser pulse or thermal decomposition following  $V \rightarrow T/R$  relaxation. However, in separate experiments, the laser induced decomposition of 2-methyloxetane at 1076 cm<sup>-1</sup> was shown to yield  $C_2H_4$  and  $CH_3CHO$  in approximately equal amounts. (2-methyloxetane is an isomer of THF and decomposes principally by molecular channels to  $C_2H_4$  plus  $CH_3CHO$  or  $C_3H_6$  plus  $H_2CO.^{19}$ )

$$\begin{array}{c} \mathsf{CH}_2 \notin \mathsf{CH}_{---}\mathsf{CH}_3 \\ | & | & --- \mathsf{C}_2\mathsf{H}_4 + \mathsf{CH}_3\mathsf{CHO} \\ \mathsf{CH}_2 \notin \mathsf{O} \end{array}$$
(10)

This result suggests that at low conversions CH<sub>3</sub>CHO is not destroyed by the laser pulse at 1076 cm<sup>-1</sup> or by the thermal pulse following the laser pulse.

Finally, we note that the reaction of ethylene plus oxygen atoms produces an excited C<sub>2</sub>H<sub>4</sub>O\* species.<sup>20</sup> The reaction products of the ethylene plus O atom reaction are CO, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>CHO, C<sub>3</sub>H<sub>7</sub>CHO, C<sub>2</sub>H<sub>4</sub>O (ethylene oxide),  $CH_2CO$ ,  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$ . All of these products were observed in the IR laser induced decomposition of THF except  $C_2H_4O$  and  $CH_2CO$ . At best very small amounts of  $C_2H_4O$  were observed in the ethylene plus O reaction and ketene was only tentatively identified.  $C_{3}H_{7}CHO$  has the same retention time as THF, and its presence would be obscured by THF in our experiments.

The transient  $\cdot CH_2CH_2CH_2$  diradical can react in much the same way as the ·CH<sub>2</sub>CH<sub>2</sub>O· diradical, but the ener-

<sup>(14)</sup> A similar type calculation has been used to calculate  $\Delta H_f^{\rm o}$  for the trimethylene diradical. See S. W. Benson, J. Chem. Phys., 34, 521 (1961). (15) Thermochemical data were taken from S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976. The C-H

bond strength was estimated from propane and the O-H bond strength from ethanol.

 <sup>(16)</sup> Reference 15, p 77.
 (17) Aa. S. Sudbo, P. A. Schulz, E. R. Grant, Y. R. Shen, and Y. T. Lee, J. Chem. Phys., 70, 912 (1979).

<sup>(18)</sup> S. W. Benson, J. Chem. Phys., 40, 105 (1964).

<sup>(19)</sup> G. F. Cohoe and W. D. Walters, J. Phys. Chem., 71, 2326 (1967); G. F. Cohoe, Ph.D. dissertation, The University of Rochester, Rochester, NY, 1965.

<sup>(20)</sup> R. J. Cvetanovic, J. Chem. Phys., 23, 1375 (1955).

getics are different.<sup>14,21</sup> The ·CH<sub>2</sub>CH<sub>2</sub>·CH<sub>2</sub>· diradical can close to form cyclopropane or rearrange to propylene. On the basis of the exothermicity of these reactions, both cyclopropane and propylene are formed with excess energy,  $\geq$ 54.1 and  $\geq$ 61.9 kcal/mol, respectively. Decomposition of vibrationally excited  $C_3H_6$  can occur by breakage of a C-H bond to form an allyl radical plus a H atom which requires  $\sim 88$  kcal/mol or by breakage of a C-C bond to form  $C_2H_3$  and  $CH_3$  radicals which requires ~98 kcal/mol. Thus, propylene and cyclopropane are much more stable with respect to fragmentation than CH<sub>3</sub>CHO.<sup>22</sup> Under intense focused conditions vibrationally excited propylene can be formed with more than 88 kcal/mol or absorb additional photons leading to production of an allyl radical and an H atom. The decreased C<sub>3</sub>H<sub>6</sub> yields, relative to  $C_2H_4$  at high energy density, could also be explained by the increasing importance of the higher-energy dissociation channel to form  $C_2H_4$ .

The primary radicals formed in the IR laser induced decomposition of THF at pressures below  $\sim 2$  torr should be  $CH_3$  and CHO, with smaller yields of  $C_3H_5$  and H. The formation of  $C_2H_6$  can be explained principally by the dimerization of  $CH_3$  radicals and the formation of  $1-C_4H_8$ , in the absence of other  $C_4$  alkenes, by the reaction of  $CH_3$ and  $C_3H_5$  radicals. The presence of  $C_3H_5$  was confirmed by the detection of 1,5-hexadiene which is formed by the dimerization of C<sub>3</sub>H<sub>5</sub>.<sup>23</sup> As pointed out by Diaz and Doepker, most of the conceived reactions of the HCO radical, e.g., unimolecular decomposition,<sup>24</sup> bimolecular reactions with other radicals including HCO itself,25-27 and decomposition at a wall<sup>28</sup> lead to the formation of CO. Since we have not analyzed the reaction products for  $H_2$ . it is difficult to determine the fate of H atoms. Conceived reactions include abstraction and addition to the olefins formed in the reaction.

At pressures above  $\sim 2$  torr of THF, there is a change in slope of the dependence of the  $C_2H_4/C_3H_6$  ratio on the pressure. Large amounts of  $CH_4$  are formed in a process which has a power dependency on the THF pressure twice that of  $C_2H_4$ , implying that secondary radical attack on THF by  $CH_3$  is important. Furthermore, a falloff in the absolute yield of  $C_2H_6$  and a flattening out of the 1- $C_4H_8$ yield above 4 torr of THF are both consistent with removal of CH<sub>3</sub> radicals by an additional channel. Methyl radicals can attack THF and abstract an H atom to form two different radicals.



The abstraction of both the  $\alpha$  and  $\beta$  hydrogens in THF has been observed by ESR studies in solution.<sup>29</sup> Formation of radical I (loss of the  $\alpha$  hydrogen) was favored over radical II. The observation of both 2- and 3methyltetrahydrofuran as minor products of the reaction implies that both radicals are formed in our work and that the rate of reaction between radicals I and II and CH<sub>3</sub> must be competitive with the decomposition rate for each radical. It is difficult to exclude the possibility that some fraction of radicals I and II originate in a primary process via breakage of a C-H bond in THF.

Radical I can either rearrange to CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHO by breaking the C-O bond followed by the splitting out of  $C_2H_4$  or proceed directly to  $C_2H_4$  and  $CH_2CHO$  by breakage of two bonds simultaneously. Similarly, radical II can either rearrange to  $CH_2$ =CHCH<sub>2</sub>CH<sub>2</sub>O or  $CH_2$ = CHCH<sub>2</sub>OCH<sub>2</sub> by breaking a C-O or C-C bond, respectively, followed by the splitting out of H<sub>2</sub>CO or proceed directly to  $C_3H_5$  and  $H_2CO$  by breakage of two bonds simultaneously.

Thus, at higher pressures methyl attack on THF will lead to increased  $C_2H_4$  yields via decomposition of radical I at the expense of  $C_3H_6$  and substantial quantities of  $1-C_4H_8$  will be formed from the  $C_3H_5$  formed in the decomposition of radical II. The large amount of C<sub>2</sub>H<sub>4</sub> formed in the thermal decomposition of THF is consistent with  $C_2H_4$  being generated in part by  $CH_3$  attack on THF. The observation of an induction period in the thermal reaction can be correlated with the buildup of the CH<sub>3</sub> concentration. In addition, CH<sub>3</sub> precursors, such as a biacetyl and other radical sources, were shown to accelerate the THF decomposition.

The mechanism presented above proposes that THF decomposes via two channels. One channel leads to  $C_2H_4$ and a •CH<sub>2</sub>CH<sub>2</sub>O• diradical and the second channel leads to H<sub>2</sub>CO and a ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>· diradical. Thus, at low pressure the yield of  $C_2H_4$  plus  $H_2CO$  should equal the decrease in THF pressure. The assumptions in this argument are that  $\cdot CH_2CH_2O$  and  $\cdot CH_2CH_2CH_2$  do not lead to  $C_2H_4$  or  $H_2CO$  as stable products and that  $C_2H_4$  and H<sub>2</sub>CO are not removed by any reaction. At higher THF pressures the reaction is complicated by the secondary reactions of CH<sub>3</sub> radicals with THF to abstract a H atom from THF forming either of two radicals (reactions 11 and 12). Decomposition of radical I was predicted to yield  $C_2H_4$ and a CH<sub>2</sub>CHO radical while radical II was predicted to decompose to a  $C_3H_5$  radical and  $H_2CO$ . Thus, any THF molecule decomposed by radical attack should also yield a molecule of  $C_2H_4$  or a molecule of  $H_2CO$ . In support of this mechanism the pressure of  $C_2H_4$  plus  $H_2CO$  divided by the decrease in THF pressure was 1.03 at 5.1 torr of THF and 1.05 at 10.6 torr of THF.

Focal Length of Lens. The enrichment factor per pulse in the isotopically selective photodissociation of  $SF_6$  de-

<sup>(21)</sup> S. W. Benson and P. S. Nangia, J. Chem. Phys., 38, 18 (1963). (22) Both 1,3 diradical intermediates can either close or isomerize, yet  $c-C_3H_6$  was observed as a product, but ethylene oxide was not. The exothermicity for closure of the two diradicals is virtually the same and the activation energies for closure are estimated to be similar.<sup>14,15,18</sup> Assuming that an equal fraction of the oscillators are active in c-C<sub>3</sub>H<sub>6</sub> and ethylene oxide and that both molecules have comparable internal energies, the lifetime with respect to ring opening of  $c-C_3H_6$ , with six more vibrational modes, could be  $\sim 10^4$  times longer than ethylene oxide. This factor could be very important in collisional stabilization of c-C<sub>3</sub>H<sub>8</sub>. In

addition, the ratio of closure to isomerization for  $-CH_2CH_2O$  is not known. (23) Although  $C_3H_5$  could be formed by  $CH_3$  abstraction of an H atom from propylene, this would appear to be a minor path at best. CH<sub>3</sub> addition to propylene is much faster than abstraction (R. J. Cvetanovic and R. S. Irwin, J. Chem. Phys., 46, 1694 (1967)). Addition and aband R. S. Hwill, J. Chem. Phys., 46, 1054 (1954). Addition and addition and addition and addition have comparable activation energies, 7.4 and 7.2 kcal/mol, respectively, but the A factor for addition is 16.5 times larger than for abstraction. The small yield of n-C<sub>4</sub>H<sub>10</sub> formed relative to 1-C<sub>4</sub>H<sub>8</sub> and the absence of increased 1-C<sub>4</sub>H<sub>8</sub> yield with the addition of C<sub>3</sub>H<sub>6</sub> both argue against C<sub>3</sub>H<sub>5</sub> formation by CH<sub>3</sub> abstraction of H from C<sub>3</sub>H<sub>6</sub>. (24) F. E. Blacet and J. N. Pitts, Jr., J. Am. Chem. Soc., 74, 3382 (1959)

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pended linearly on the focal length of lens,  $f^{.30}$  This result was explained by assuming that reaction occurred within a volume whose boundary was determined by an energydensity threshold, and this volume scaled as f. This result implies that the photodissociation rate per unit volume is a constant and, hence, that the range of energy densities seen by reactant molecules is independent of f. (Although the peak energy density will be higher for shorter focal length lenses, the volume at the beam waist will be much less than the total reaction volume.)

In contrast to the SF<sub>6</sub> experiments, photodissociation yields from vinyl-*trans-d* chloride and formaldehyde both increased with shorter focal length lenses.<sup>31,32</sup> With long focal length lenses, isomerization of vinyl-*trans-d* chloride takes place, but very little dissociation occurs. With successively shorter focal length lenses, the cis/trans ratio increases as does the percentage dissociation, even though the reaction volume gets smaller. Calculations based upon a kinetic model and RRRM theory indicate that the average vibrational excitation increases with shorter focal length lenses.

A theoretical model of the mulitphoton dissociation process in formaldehyde was developed to analyze the focal length data.<sup>32</sup> The shape of the illuminated volume was approximated by a "dog bone" consisting of a double cone joined at the tops by a cylinder. One of the conclusions of this model was that for short focal length lenses the main contribution to the dissociation yield comes from the cylindrical section of the dog bone.

Using the dog bone geometry above, we can calculate the dimensions of the central cylinder for the 10-, 30-, and 50-cm lenses used in the THF experiments. The radius of the cylinder, which is estimated from the calculated spot size of a focused Gaussian beam, is  $1.2 \times 10^{-2}$  cm for a 10-cm lens and results in a peak energy density of 274  $J/cm^2$  for a pulse energy of 0.12 J. For a 10-cm lens the calculated length of the cylinder is 0.94 cm and the volume  $4.1 \times 10^{-4}$  cm<sup>3</sup>. The values for the 30- and 50-cm lens can be easily calculated by noting that the radius scales as f, the length as  $f^2$ , the peak fluence as  $f^{-2}$ , and the cylinder volume as  $f^4$ . To determine the volume of the two cones which are effective in promoting dissociation, an energydensity threshold for reaction must be estimated. The length of the central cylinder with a 50-cm lens is approximately twice the length of the cell; hence, we can assume that the energy density inside the cell is approximately constant. At 0.3 torr of THF, the dissociation yield with the 50-cm lens is only  $1/_{30}$  the yield with a 30-cm lens. Therefore, as an approximation we equate the threshold energy density with the energy density attained with the 50-cm lens  $(10.9 \text{ J/cm}^2)$ . The energy density at the cell window in a 12.7-cm long cell with a 30-cm lens is above the threshold, while the length of the dog bone with the 10-cm lens is 4.7 cm. The total volume of the dog bone is  $1.75 \times 10^{-2}$  cm<sup>3</sup> for the 10-cm lens and 3.4 times larger for the 30-cm lens.

The experimental results on THF with different focal length lenses are compatible with the results on vinyltrans-d chloride and formaldehyde. There is no evidence for a constant photodissociation rate per unit volume as with SF<sub>6</sub>. For 0.3 torr of THF, the reaction yield per unit volume with a 10-cm lens is ~10 times the value with a 30-cm lens and ~700 times the value with a 50-cm lens. As with vinyl-trans-d chloride, this result implies higher average excitation levels with the shorter focal length lens. Evidence for the higher average levels of excitation are reflected in the decreased fractional yield of  $c-C_3H_6$  with a 10-cm lens. In addition, the higher peak energy density and smaller reaction volume attained with a 10-cm lens produces higher radical concentrations. Thus, more radical-radical reaction products such as  $C_2H_6$  and  $1-C_4H_8$ should be and are formed with a shorter focal length lens.

Role of Collisions. Above 2 torr of THF, the character of the laser induced decomposition of THF changes. In part this change arises from the increasing importance of  $CH_3$  attack on THF, but in addition evidence exists for collisional contributions to the dissociation yield. These collisional mechanisms involve both collisional energy pooling reactions and rotational hole filling.

When the decomposition of THF was followed as a function of the number of laser shots at 2.9 and 8.1 torr of THF, the data were fitted to an equation which describes a third-order kinetic equation. When the same experiment was repeated with 2-methyloxetane, similar results were obtained with a fourth-order equation best describing the data. Since the oxetanes are known to thermally decompose in a first-order reaction,<sup>10,19</sup> we conclude that the kinetic complexity of the THF reaction does not explain the failure to observe a linear relationship between ln ( $P_0/P$ ) and the number of laser shots. The most likely explanation for these results is that collision up-pumping is involved in accumulating sufficient energy for dissociation at pressures above ~2 torr of THF.

Supralinear pressure dependences which were observed for all of the reaction products, except  $C_3H_6$ , from 2 to 12 torr of THF are also consistent with collisional contributions to the dissociation yield.<sup>33,34</sup> The increased dissociation yield and increased absorption observed when 1 torr of N<sub>2</sub> was added to 3 torr of THF suggests that rotational hole filling as well as collisional energy pooling is involved. Evidence for rotational hole filling at pressures below 2 torr of THF is found in the supralinear pressure dependences of Table I and the increased dissociation yields with all added gases, except CH<sub>3</sub>CHO, which absorbs at 1076 cm<sup>-1</sup>.

The relationship between the dissociation yields and different focal length lenses is strikingly different at 0.3 and 3 torr of THF. The yield with a 50-cm lens is  $\sim 50\%$ of the yield with a 10-cm lens at 3 torr of THF, but only  $\sim 1\%$  at 0.3 torr of THF. Our interpretation of the severe drop in dissociation yield with a 50-cm lens at low THF pressure is that the laser energy density at the beam waist of the 50-cm lens is only slightly above the energy-density threshold for the reaction. By comparison the marginal decrease in yield with a 50-cm lens at 3 torr of THF suggests that collisional energy pooling reactions are only effective at the higher THF pressures. Part of the small decrease in yield at 3 torr of THF with a 50-cm lens compared to a 10-cm lens can also be related to the twofold increase in absorption with a 50-cm lens. This increase in absorption is related to the increasing absorption found with decreasing laser energy. At 3 torr of THF a threefold decrease in laser energy, focused with a 10-cm lens, increased the absorption from 5.8% to 8.8%.

At 3 torr of THF the relative product yields shown in Table II were insensitive to the focal length of the lens. The opposite effect was observed at 0.3 torr of THF. The disparity in these results can in part be rationalized by

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collisions randomizing internal energy at the higher THF pressure. Randomizing collisions are more graphically illustrated in the SiF<sub>4</sub>-sensitized reactions of THF, where energy is transferred solely by collisions. In these collision-dominated sensitization experiments the product distribution is much more thermal, as judged by the relative yields of  $C_2H_4$  and  $C_3H_6$ , independent of the THF pressure, and relatively insensitive to the focal length of the lens.

Collisions can also be effective in stabilizing vibrationally excited species.  $c-C_3H_6$  which is formed via the closure of •CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>• is initially formed with significant vibrational energy. The fractional yield of  $c-C_3H_6$  as a function of THF pressure has been used previously as a measure of collisional stabilization.<sup>4-6</sup> The shape of this curve, shown in Figure 4, is similar to that obtained in the UV or vacuum-UV photolysis of THF but levels off at lower fractional yields.<sup>4-6</sup> Although our results could be interpreted as collisional stabilization of excited cyclopropane, the changing character of the reaction with pressure, especially with regard to the decreased  $C_3H_6$  and  $c-C_3H_6$ products relative to  $C_2H_4$ , suggests caution in making such an interpretation. When  $N_2$  is added to 0.3 torr of THF, the fractional yield of  $c-C_3H_6$  decreases while the total yield increases. Clearly added N2 is doing more than stabilizing hot molecules.

In the case of CH<sub>3</sub>CHO no evidence exists for the collisional stabilization of "hot" CH<sub>3</sub>CHO formed from  $\cdot$  CH<sub>2</sub>CH<sub>2</sub>O $\cdot$ . The relative yield of CH<sub>3</sub>CHO decreases with increasing THF presence, suggesting the indirect formation of CH<sub>3</sub>CHO. In experiments at 3 torr of THF, 25 torr of added N<sub>2</sub> led to a ninefold increase in CH<sub>4</sub> and almost a twofold decrease in CH<sub>3</sub>CHO, implying that removal of CH<sub>3</sub> as CH<sub>4</sub> competes with formation of CH<sub>3</sub>CHO.

Added Gases. The inert gases, N<sub>2</sub> and CH<sub>4</sub>, were observed to quench the formation of some of the highly unsaturated hydrocarbons and the aldehydes. The opposite effect was observed when  $C_2H_4$  and  $C_3H_6$  were added to THF. One explanation for these results may involve pyrolysis reactions which occur during the thermal pulse produced by  $V \rightarrow T/R$  relaxation. Highly unsaturated hydrocarbons might be expected as pyrolysis products either via loss of hydrogen from more saturated hydrocarbons or by radical reactions. The addition of inert gases

will increase the heat capacity of the gas mixture, decrease the maximum temperature following  $V \rightarrow T/R$  relaxation, and decrease the extent of any pyrolysis reactions. Although  $C_2H_4$  and  $C_3H_6$  when added to THF will also increase the heat capacity, exothermic reactions between radicals formed in the laser induced dissociation of THF and  $C_2H_4$  or  $C_3H_6$  could actually raise the peak temperature following the laser pulse. The large increase in the *i*- $C_4H_{10}$  yield when  $C_3H_6$  was added to THF provides evidence for radical reactions between  $C_3H_6$  and  $CH_3$ .

CH<sub>3</sub>CHO is dissociated by itself at 1076 cm<sup>-1</sup> predominantly to CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The decrease in total yield when CH<sub>3</sub>CHO is added to THF reflects the competition between dissociation of THF and CH<sub>3</sub>CHO. The increase in C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> relates to the dimerization of CH<sub>3</sub> radicals and abstraction of H to form CH<sub>4</sub>. The C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> ratio remained constant even with 1 torr of CH<sub>3</sub>CHO and 3 torr of THF. This result is consistent with CH<sub>3</sub> attack on CH<sub>3</sub>CHO being much faster than attack on THF and may explain why added CH<sub>3</sub>CHO had little effect on the thermal decomposition of THF.<sup>2</sup>

NO had a dramatic effect on the photodissociation of THF. All of the products which we have associated with CH<sub>3</sub> radicals decreased, suggesting that NO reacted with CH<sub>3</sub> to form an adduct. At the low pressures of our experiments, we would not expect the adduct to be stabilized and, hence, the CH<sub>3</sub> and NO would be regenerated. Although there is no net reaction of CH<sub>3</sub> and NO at low pressure, NO can increase the effective lifetime of the CH<sub>3</sub> radical and presumably allow less-favorable reactions of CH<sub>3</sub> to compete with the very fast dimerization reaction to form C<sub>2</sub>H<sub>6</sub>. A physical analogy for the role of NO would be radiation trapping in a low-pressure discharge which increases the effective lifetime of the radiating state.

HI had the effect of increasing the CH<sub>4</sub> yield at the expense of  $1-C_4H_8$ . This result suggests that HI acted as a radical trap for CH<sub>3</sub> radicals. However, the removal of CH<sub>3</sub> radicals by HI should also have decreased the  $C_2H_6$  yield more than was observed. H<sub>2</sub> was ineffective as a radical trap.

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