THE IR LASER PHOTOCHEMISTRY OF METHYL-SUBSTITUTED TETRAHYDROFURANS

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Summary

The products from the decomposition of 2-methyltetrahydrofuran (2-MTHF), a mixture of *cis*- and *trans*-2,5-dimethyltetrahydrofuran (2,5-DMTHF) and 3-methyltetrahydrofuran (3-MTHF) induced by a pulsed CO_2 laser were determined by gas chromatography as a function of the reactant pressure, the focal length of the lens and the SiF_4 sensitization. The major hydrocarbon products at a pressure of 0.3 Torr were C_2H_4 (2-MTHF), C_3H_6 (2,5-DMTHF) and $1\text{-}C_4H_8$ (3-MTHF). With a tenfold increase in pressure C_2H_4 became a major hydrocarbon product for all three methyl-substituted tetrahydrofurans. At 10 Torr, CO was the major oxygenated species for 2-MTHF and 2,5-DMTHF, whereas for 3-MTHF it was H_2CO. For 2-MTHF the product distribution was interpreted as arising principally from breakage of the C—O bond and a ring C—C bond to form C_2H_4 and a 1,3 diradical. The product distribution from 2,5-DMTHF at low pressure was explained by cleavage of CH_3 followed by decomposition of the resulting tetrahydrofuranyl radical. Both the diradical and CH_3 cleavage mechanisms were used to account for the product distribution from 3-MTHF.

1. Introduction

The IR multiphoton decomposition of tetrahydrofuran (THF) has recently been studied in this laboratory [1]. The following mechanism was deduced from the distribution of stable products. At pressures of THF below about 2 Torr, breakage of the C—O bond occurred following absorption of a sufficiently large number of IR photons. The transient 1,5 diradical formed by the breakage of the C—O bond further decomposed via two different pathways by the breakage of different C—C bonds:
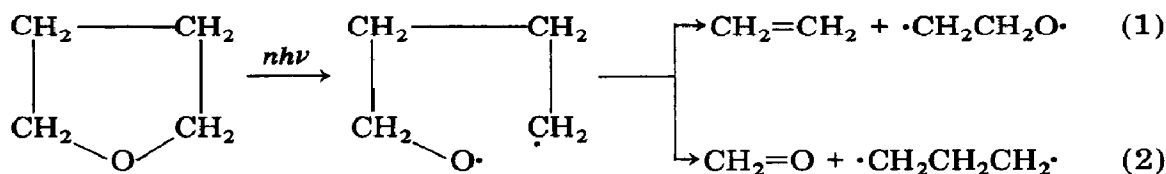
The $\cdot CH_2CH_2O\cdot$ diradical rearranged to form vibrationally excited CH_3CHO which decomposed to form CH_3 and CHO radicals. The energetics for the $\cdot CH_2CH_2CH_2\cdot$ diradical were different and it either closed to form cyclopropane or rearranged to propylene. At low THF pressures radical–radical reactions such as the dimerization of CH_3 to form C_2H_6 were very sensitive to the focal length of the lens used to irradiate the THF. At higher THF pressures CH_3 radical attack on THF became competitive and hydrogen abstraction by CH_3 led to one of two tetrahydrofuranyl radicals, which further dissociated and perturbed the product distribution.

We have investigated the IR-laser-induced decomposition of 2-methyltetrahydrofuran (2-MTHF), 3-methyltetrahydrofuran (3-MTHF) and a mixture of *cis-* and *trans-*2,5-dimethyltetrahydrofuran (2,5-DMTHF) in order to test some of the mechanistic ideas developed for THF. Introduction of methyl groups into the 2 and 3 positions on the THF ring lowers the THF symmetry and from the product distribution allows us to differentiate between different modes of fragmentation. Decomposition of methyl-substituted THFs is expected to produce both straight chain and branched methyl-substituted 1,3 diradicals. Rearrangement of these methyl-substituted 1,3 diradicals could lead to stable products which reflect the structure of the original diradical.

To the best of our knowledge, neither thermal decomposition studies of the methyl-substituted THFs nor the UV photolysis of gas phase methyl-substituted THFs have been reported in the literature. Thus the studies of laser-induced decomposition reported here represent the first data on the gas phase decomposition of these compounds. The liquid phase photolysis of THF, 2-MTHF, *cis-*2,5-DMTHF, *trans-*2,5-DMTHF and 2,2,5,5-tetramethyltetrahydrofuran at 185 nm has been studied [2, 3]. The major products from the liquid phase photolysis of all five THFs could formally be accounted for by the same bond-breaking scheme. However, rapid stabilization of the 1,5 diradical in the liquid phase suggests that many of the fragmentation products arise directly from molecular processes. Isomerization products involve the 1,5 diradical as an intermediate. The formal bond breaking in the liquid phase photolysis can be illustrated for 2-MTHF. Breakage of the C(5)—O bond (the least substituted carbon atom) and the C(2)—C(3) bond yields acetaldehyde and cyclopropane as major products. In contrast, the product distributions from the IR-laser-induced decomposition of the methyl-substituted THFs suggested different bond-breaking steps for each methyl-substituted THF. 2-MTHF can be explained by a diradical mechanism, but the bonds broken differ from those for 2-MTHF in the liquid phase. The products from the decomposition of 2,5-DMTHF are best explained by breakage of the CH_3 bond, and 3-MTHF is a hybrid of the diradical and CH_3 bond-breaking mechanisms. In general, final products which could be attributed to 1,3 diradicals are only minor products, but the products do reflect the structure of the methyl-substituted 1,3 diradical.

2. Experimental details

The experimental procedure has been described in ref. 1. Briefly, the radiation from a grating-tuned transversely excited atmospheric pressure pulsed CO_2 laser was passed through a 5 mm aperture and focused by an NaCl lens of focal length 10 or 30 cm into the center of a Pyrex cell of inside diameter 13.5 mm and length 76 mm with NaCl windows 45° to the optical axis. The relative laser energy was monitored by diverting about 1% of the radiation with a beam splitter after the aperture to a pyroelectric detector. The laser energy was calibrated using a disc calorimeter. 2-MTHF (Aldrich) and 3-MTHF (Aldrich) were irradiated at an energy of about 100 mJ and a wavelength of 1076 cm^{-1} (the R16 line of the 9 μm band), and the mixture of *cis*- and *trans*-2,5-DMTHF (Aldrich) was irradiated at a similar energy and a wavelength of 1087 cm^{-1} (the R34 line of the 9 μm band). The P42 line of the 9 μm band at 1025 cm^{-1} was used with SiF_4 as the sensitizer.

After irradiation by typically 200 pulses, the remaining reactant (about 95%) and products were frozen into a sample loop using liquid nitrogen. (Small volatile products such as H_2, CO and CH_4 were not effectively trapped.) The products were introduced via a sampling valve into a gas chromatograph containing a Carbopack C–0.19% picric acid column of outside diameter 1/8 in and length 6 ft and a flame ionization detector. The products were initially identified by gas chromatography–mass spectroscopy. The peak height was used as a measure of product yield. Although the product yields were not corrected for gas chromatographic sensitivity, the relative sensitivities of the three major hydrocarbon products (ethylene, propylene and 1-butene) differed by less than 15%.

H_2, CO, CH_4 and C_2H_4 were determined in separate runs using a Carbosieve B column of outside diameter 1/8 in and length 6 ft and the thermal conductivity detector of the gas chromatograph. Sensitivity factors for these four gases were determined using pure samples. The products and reactants were expanded directly into the sample loop. Typically, pressures of methyl-substituted THF of 5 or 10 Torr and 2000 pulses were required to generate sufficient product for analysis. Under these conditions, the conversion was as high as 58%.

3. Results

3.1. Major products

At low conversions, the major hydrocarbon products in the laser-induced decomposition of the three methyl-substituted THFs were ethylene, propylene and 1-butene. For each methyl-substituted THF, 1,3-butadiene became a major hydrocarbon product at higher reactant pressures. Ethane was also a major product for 2,5-DMTHF and 3-MTHF, but not 2-MTHF, and isobutene was only a major product for 3-MTHF. The distributions of these hydrocarbons are shown in Table 1 for each of the methyl-substituted

TABLE 1

The distribution of major hydrocarbon products produced in the laser-induced decomposition of methyl-substituted tetrahydrofurans

Pressure (Torr)	Focal length of lens (cm)	SiF_4 (Torr)	C_2H_4[a] (%)	C_3H_6[a] (%)	$1\text{-}C_4H_8$[a] (%)	C_2H_6[a] (%)	$1,3\text{-}C_4H_6$[a] (%)	$i\text{-}C_4H_8$[a] (%)	Percentage of total[b] (%)
2-MTHF, $\nu = 1076\ cm^{-1}$									
0.3	30	—	70	13	15	t[c]	1.8	t	81
3.0	30	—	70	12	11	t	5.8	t	90
0.3	10	—	70	13	15	t	2.2	t	80
3.0	10	—	71	13	11	t	5.6	t	90
0.3	10	5.0[d]	69	14	9.8	t	7.2	t	90
3.0	10	5.0[d]	74	12	7.8	t	6.3	t	88
2,5-DMTHF, $\nu = 1087\ cm^{-1}$									
0.3	30	—	7.1	56	13	21	3.2	t	71
3.0	30	—	30	45	11	7.2	7.1	t	87
0.3	10	—	5.8	53	13	25	3.8	t	79
3.0	10	—	33	41	9.0	10	6.6	t	88
0.3	10	5.0[d]	44	35	8.2	6.5	6.5	t	86
3.0	10	5.0[d]	46	35	7.8	4.0	7.4	t	85
3-MTHF, $\nu = 1076\ cm^{-1}$									
0.3	30	—	21	23	32	13	3.6	7.8	66
3.0	30	—	34	24	21	2.6	12	5.7	81
0.3	10	—	23	23	27	15	5.7	6.3	73
3.0	10	—	41	22	17	5.3	9.7	4.9	83
0.3	10	5.0[d]	60	21	7.6	t	8.5	2.2	88
3.0	10	5.0[d]	54	22	10	t	11	3.5	84

[a] The yields of the six hydrocarbons total 100%.
[b] The yield of the six hydrocarbons as a percentage of the total analyzed peak height on the Carbopack C–0.19% picric acid column.
[c] t, trace.
[d] $\nu = 1025\ cm^{-1}$.

TABLE 2

The distribution of products produced in the laser-induced decomposition of 2-MTHF and 2,5-DMTHF and determined using the Carbosieve B column and the thermal conductivity detector

Pressure (Torr)	Focal length of lens (cm)	Shots	H_2 (Torr)	CO (Torr)	CH_4 (Torr)	C_2H_4 (Torr)	ΔP^a (Torr)
2-MTHF, $\nu = 1076\ cm^{-1}$							
10	10	2000	4.7	4.3	1.8	4.4	5.8
2,5-DMTHF, $\nu = 1087\ cm^{-1}$							
10	10	2000	≈ 1.1	2.0	1.2	0.75	2.5

[a]Decrease in reactant pressure determined by IR spectroscopy.

THFs as a function of pressure and focal length of the lens, and with SiF_4 as the sensitizer. (SiF_4 was irradiated using the P42 line of the 9 μm band at 1025 cm^{-1}.)

The H_2, CO, CH_4 and C_2H_4 yields from the laser-induced decomposition of 2-MTHF and 2,5-DMTHF determined using the Carbosieve B column and the thermal conductivity detector are shown in Table 2. The decrease in the methyl-substituted THF pressure measured by IR spectroscopy corresponded to a conversion of 58% for 2-MTHF and 25% for 2,5-DMTHF. The major oxygenated species for 2-MTHF and 2,5-DMTHF is CO. The ratio of CO to the decrease in the methyl-substituted THF pressure was 0.74 for 2-MTHF and 0.80 for 2,5-DMTHF. For 2-MTHF the CO yield was equal to the C_2H_4 yield and large amounts of H_2 were formed. From IR data only very small amounts of H_2CO were observed, and by gas chromatography larger aldehydes and ketones were only present as minor products. This result is consistent with CO being the major oxygenated product from 2-MTHF and 2,5-DMTHF. Similar studies on 3-MTHF could not be carried out because of catastrophic failure of the gas chromatograph temperature programmer. However, IR data revealed that H_2CO was a major product of the laser-induced decomposition of 3-MTHF. (Previous measurements [1] on oxetane have shown that H_2CO is stable with respect to decomposition to H_2 and CO under the present experimental conditions.)

3.2. Minor products

The minor products of the laser-induced decomposition of the methyl-substituted THFs were those which represented less than 5% of the total products detected using the Carbopack C–0.19% picric acid column. In addition to 1-butene, four different C_4H_8 isomers were produced: cis- and trans-2-butene, isobutene and methylcyclopropane. Four C_5H_{10} isomers were detected by gas chromatography–mass spectroscopy. Because it was impossible to distinguish between the various isomers from the mass spectral cracking patterns, retention times of known samples were used to identify 1-pentene, cis- and trans-2-pentene and 3-methyl-1-butene. One C_6H_{10}

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product was identified and corresponded to 1,5-hexadiene (diallyl). Other minor hydrocarbon species included propane, cyclopropane, methylacetylene, isobutane and n-butane. The minor oxygenated species were acetone, methyl ethyl ketone, acetaldehyde, propionaldehyde and furan.

3.3. Pressure dependence

The pressure dependence of the IR-laser-induced decomposition of the three methyl-substituted THFs was studied from 0.2 to 10 Torr. The methyl-substituted THFs were irradiated with 200 laser shots focused with a 10 cm lens. Logarithmic plots of the relative product yields *versus* pressure are shown in Figs. 1 and 2 for C_2H_4 and C_3H_6 respectively. The pressure dependences shown in Table 3 were determined from these types of plots. The ratio of products as a function of pressure could be determined from the same data. The ratios of propylene to 1,3-butadiene and ethylene to 1,3-butadiene as a function of pressure are shown for the three methyl-substituted THFs in Figs. 3 and 4.
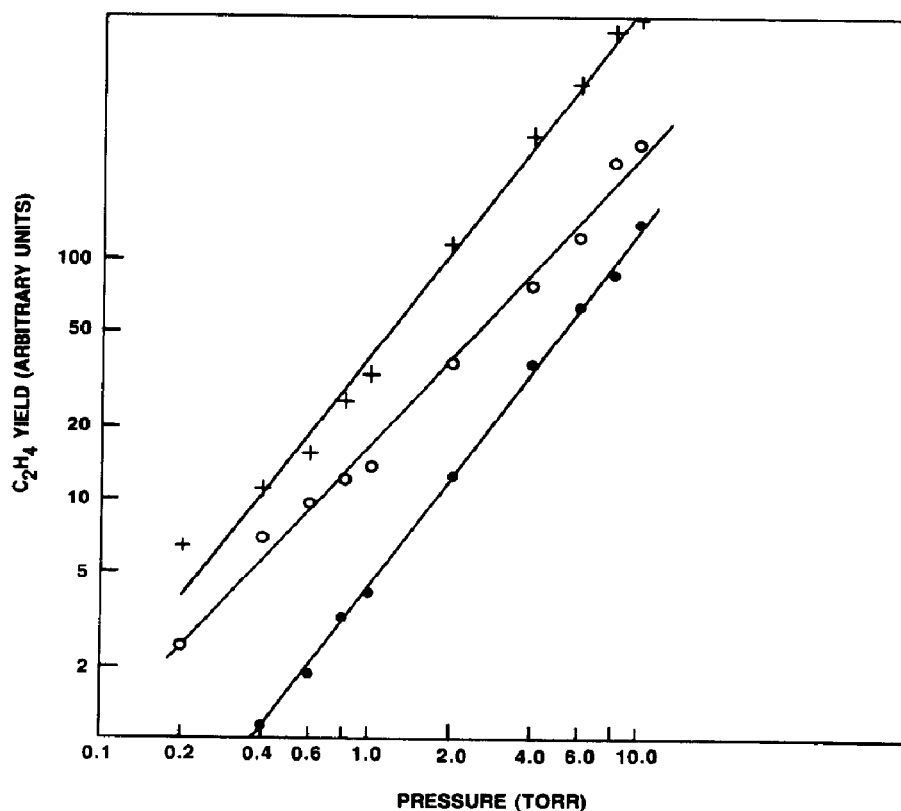

Fig. 1. Logarithmic plots of the relative product yield of C_2H_4 *vs.* the 2-MTHF (O), 3-MTHF (+) and 2,5-DMTHF (●) pressures. Each point corresponds to 200 laser shots focused using a lens of focal length 10 cm. 2-MTHF and 3-MTHF were irradiated with the R16 line of the 9 μm band and 2,5-DMTHF was irradiated with the R34 line of the 9 μm band.
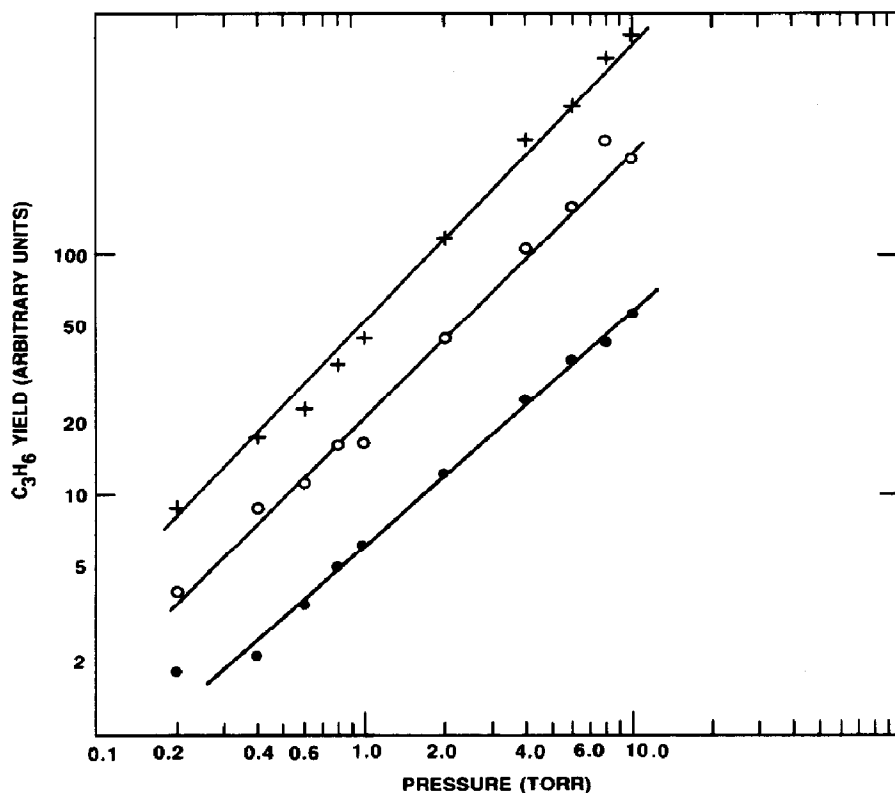
Fig. 2. Logarithmic plots of the relative product yield of C_3H_6 vs. the 2-MTHF (○), 3-MTHF (+) and 2,5-DMTHF (●) pressures. The experimental conditions were the same as in Fig. 1.

TABLE 3

Power dependence of the product yield on methyl-substituted THF pressure from 0.2 to 10 Torr for product yield proportional to (pressure)^n

Product	n^a for the following compounds		
	2-MTHF	2,5-DMTHF	3-MTHF
CH_4	—^{b}	1.5 (0.99)	1.5 (0.99)
C_2H_4	1.2 (0.99)	1.5 (0.99)	1.4 (0.99)
C_3H_6	1.1 (0.99)	1.0 (0.99)	1.2 (0.99)
1-C_4H_8	1.0 (0.99)	1.1 (0.99)	1.0 (0.99)
1,3-butadiene	1.5 (0.99)	1.5 (0.99)	1.5 (0.99)

^{a}Correlation coefficients are given in parentheses.
^{b}Not determined.

3.4. Extent of the reaction

The disappearance corresponding to 10 Torr of each methyl-substituted THF was followed as a function of the number of laser shots by IR spectroscopy. The number of laser shots required to halve the reactant pressure was
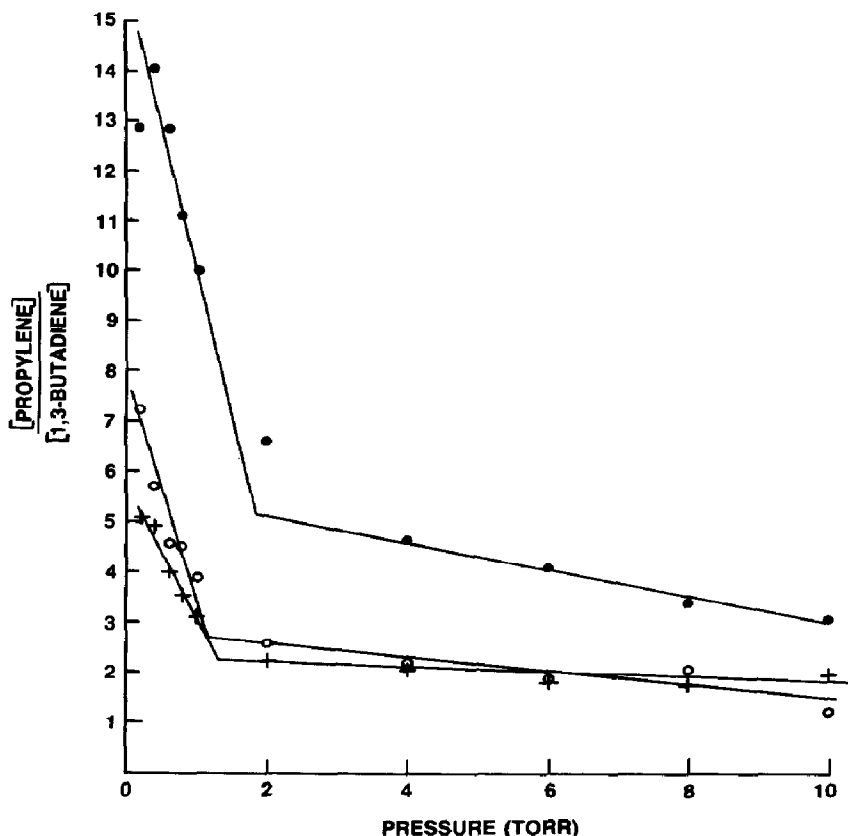
Fig. 3. A plot of the ratio of propylene to 1,3-butadiene peak heights *vs.* the 2-MTHF (○), 3-MTHF (+) and 2,5-DMTHF (●) pressures. The experimental conditions were the same as in Fig. 1.

1300 for 2-MTHF, 2500 for 2,5-DMTHF and 3000 for 3-MTHF. In each case the plot of $\ln(P_0/P)$ *versus* the number of laser shots, where P is the methyl-substituted THF pressure after s shots, was not a straight line. In the laser-induced decomposition of THF, a plot of $(1/P_{THF})^{n-1}$ *versus* s was found to be linear for $n = 3$. These types of plots were attempted for the methyl-substituted THFs, and straight line plots were obtained for $n = 3$ for 2-MTHF and 2,5-DMTHF while 3-MTHF was best fitted to a plot where $n = 2$. These results are shown in Fig. 5.

4. Discussion

The products from the IR-laser-induced decomposition of THF were previously interpreted as arising from the breakage of a C—O bond and one of two C—C bonds [1]. Calculations based on a thermodynamic cycle yield a bond strength of 74.6 kcal mol^{-1} for the C—O bond in THF. Comparable values are obtained for the ring C—C bonds. The C—H bond strength is
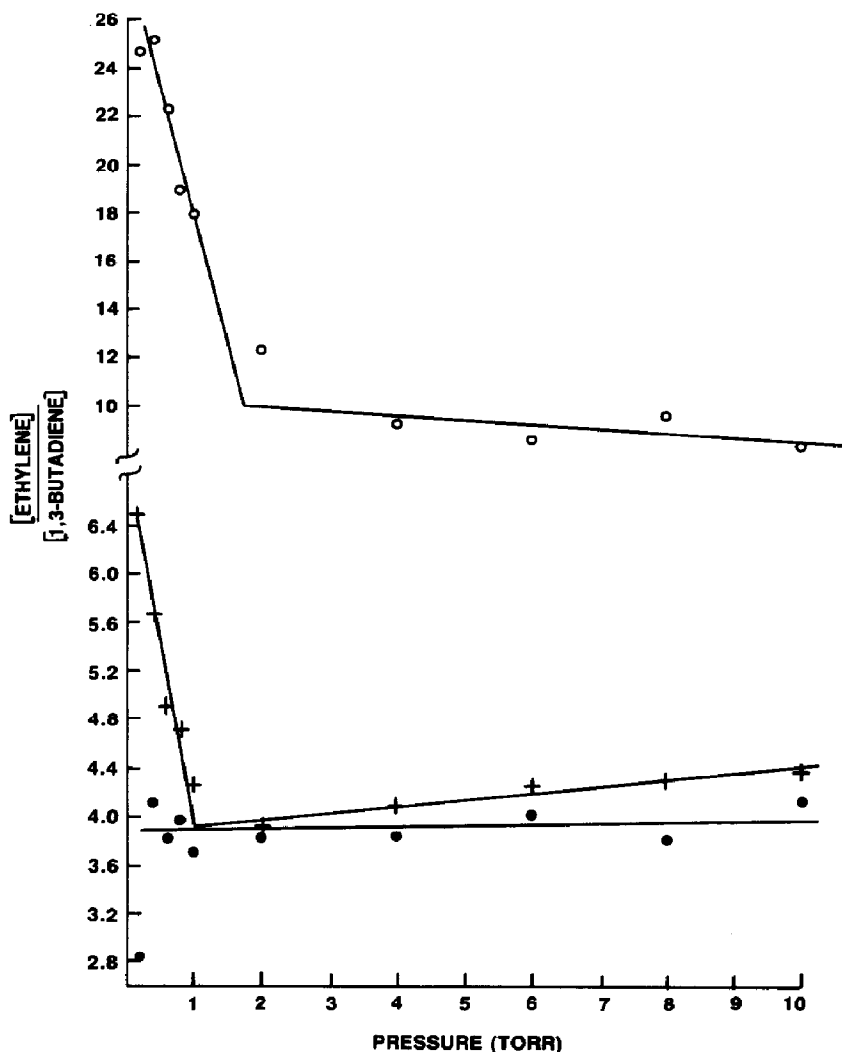
Fig. 4. A plot of the ratio of ethylene to 1,3-butadiene peak heights *vs.* the 2-MTHF (O), 3-MTHF (+) and 2,5-DMTHF (●) pressures. The experimental conditions were the same as in Fig. 1.

estimated to be significantly higher at 90.7 kcal mol^{-1} [1]. In the methyl-substituted THFs, C—CH$_3$ bond breakage can also occur between the carbon in the THF ring and the methyl carbon. We estimate that breakage of the C—CH$_3$ bond is only 5.4 - 7.8 kcal mol^{-1} greater than breakage of the C—O bond or ring C—C bonds depending on the particular methyl-substituted THF. (The thermochemical data were taken from ref. 4 or were estimated from group additivity values in the appendix to ref. 4.)

The product distributions of each methyl-substituted THF will be discussed within the context of a bond-breaking scheme. Sufficient differences exist in the laser-induced chemistry of these three methyl-substituted THFs to warrant separate discussions.
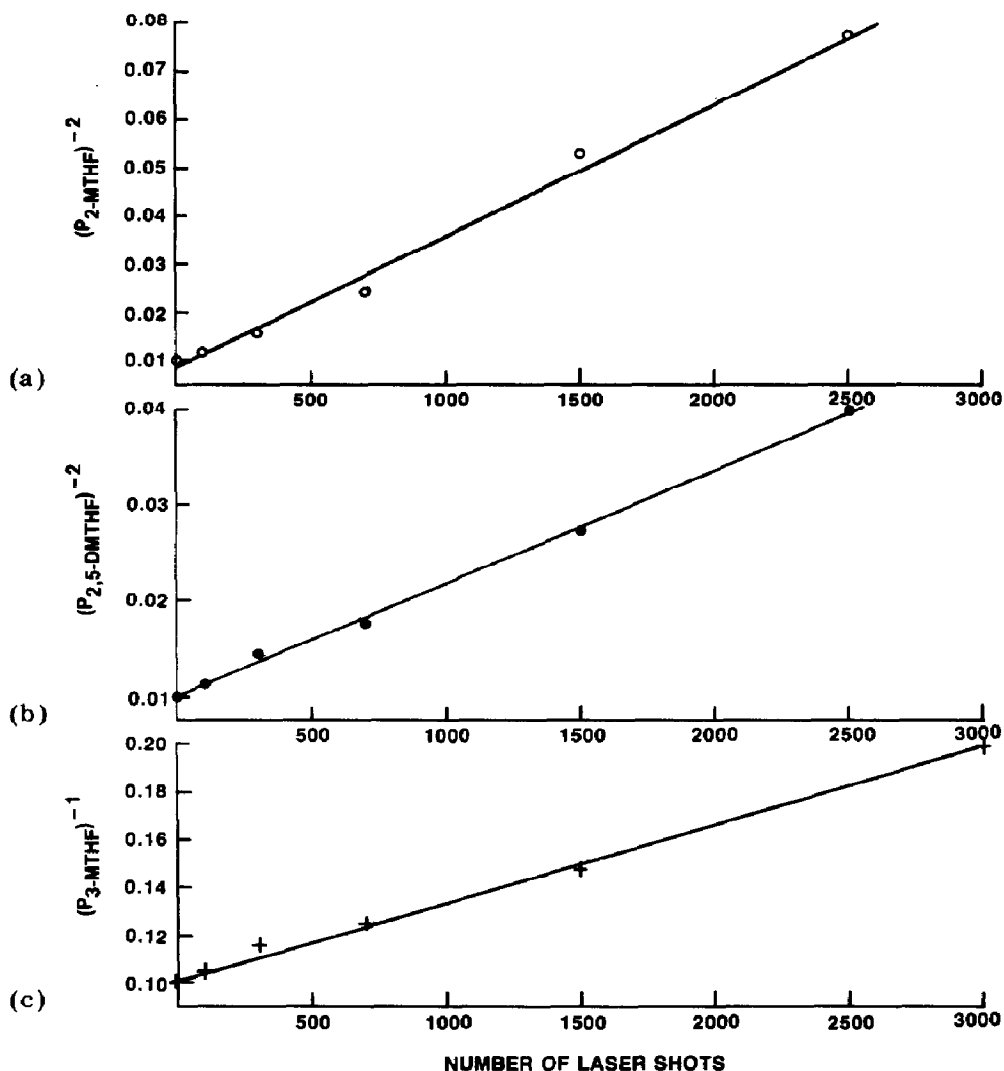
Fig. 5. Plots of (a) the 2-MTHF and (b) 2,5-DMTHF pressures remaining after s laser shots raised to the power -2 and (c) the 3-MTHF pressure remaining after s laser shots raised to the power -1 vs. the number of laser shots. The initial pressure in each case was 10 Torr. The irradiating wavelengths and lens were the same as in Fig. 1.

4.1. 2-methyltetrahydrofuran

The major hydrocarbon product in the laser-induced decomposition of 2-MTHF was ethylene. As shown in Table 1, the C_2H_4 yield was very insensitive to the 2-MTHF pressure, the focal length of the lens and even sensitization by SiF_4. These results are in direct contrast with THF where the products of radical–radical and radical–molecule reactions were strongly perturbed by the focal length of the lens and the THF pressure.

The production of C_2H_4 as the major hydrocarbon product is compatible with the breakage of the C(3)—C(4) and C(5)—O bonds in 2-MTHF.

The diradical $\cdot CH_2CH(CH_3)O\cdot$, which is produced with C_2H_4, can either close to form propylene oxide or isomerize by hydrogen transfer to acetone:

$$CH_2{-}{-}CH{-}CH_3{}^* \xrightarrow{M} CH_2{-}{-}CH{-}CH_3 \qquad (3)$$

$$\begin{array}{c} CH_3 \\ | \\ \cdot CH_2{-}CH{-}O\cdot \end{array}$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_3{}^* \xrightarrow{\quad M \quad} CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (4)$$

$$\longrightarrow CH_3CO + CH_3 \qquad (5)$$

$$\longrightarrow CH_3 + CO \qquad (6)$$
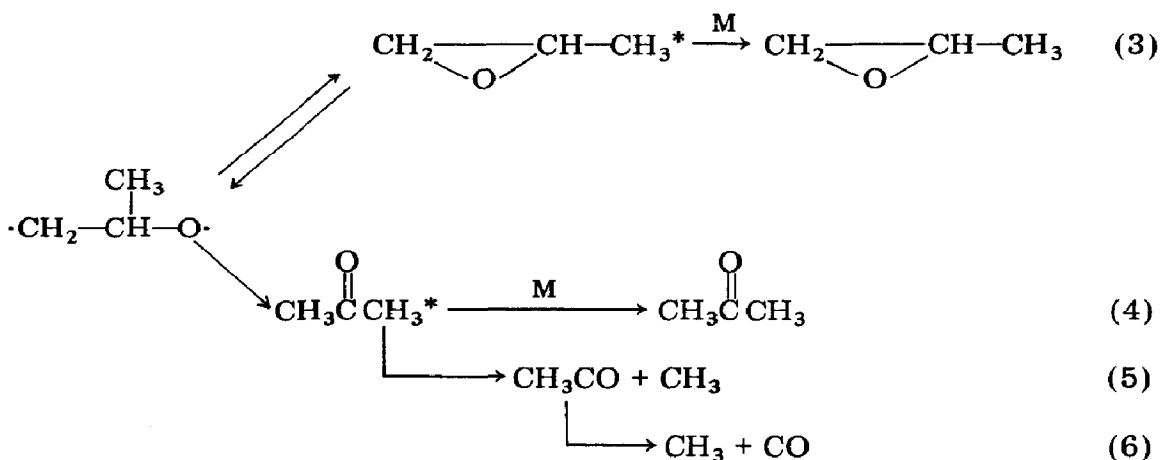
From the exothermicity of the reaction, acetone will be formed with at least 85 kcal mol^{-1} of excess energy and will dissociate to CO and CH_3 radicals. Collisions are not very effective in stabilizing the excited a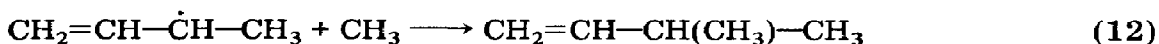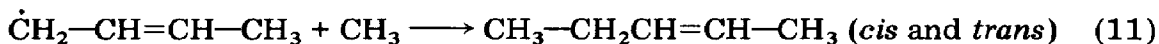cetone. Acetone is detected in low yield, and the yield does not increase with 2-MTHF pressure. Propylene oxide is not observed as a product of the reaction. At high conversion, CO is the major oxygenated species with a yield equal to that of C_2H_4 as shown in Table 2. This result is consistent with the above reaction scheme. The fate of the CH_3 radicals from excited acetone is unclear. Judging from the relatively low C_2H_6 yield and the absence of significant change in product distribution with focal length, CH_3 radicals must be at a low concentration within the focal zone. Acetone, with ten atoms and 24 vibrational modes, may have a dissociative lifetime which is long with respect to both the CO_2 laser pulse duration and diffusion out of the focal zone. Slow reactions between CH_3 and other products or the reactant outside the focal zone could dissipate the CH_3 radicals. Hydrogen abstraction reactions by CH_3 could account for the large CH_4 yield obtained at high conversion and shown in Table 2. However, it is difficult to draw conclusions from high conversion studies because of secondary reactions. For this reason, we cannot comment on the formation of H_2, which is a major product at high conversion.

The formation of propylene and 1-butene as minor hydrocarbon products implies that 2-MTHF can decompose by alternate pathways. C_3H_6 can be formed by breakage of the C(3)—C(4) and C(2)—O bonds or the C(2)—C(3) and C(5)—O bonds. The former route produces propylene directly, whereas the latter yields $\cdot CH_2CH_2CH_2\cdot$. Evidence for the production of the trimethylene diradical is provided by the formation of small amounts of cyclopropane. The $\cdot CH_2CH_2CH_2\cdot$ diradical cannot be produced in either 3-MTHF or 2,5-DMTHF and cyclopropane is not observed in these two methyl-substituted THFs.

Breakage of the C(4)—C(5) and C(2)—O bonds will yield $CH_3\dot{C}HCH_2CH_2\cdot$. This diradical can either close to form methylcyclopropane or isomerize to the four isomeric butenes:

$$CH_3\dot{C}HCH_2CH_2\cdot$$

$$CH_3\text{—CH}\underset{CH_2}{\text{————}}CH_2^* \xrightarrow{\text{M}} CH_3\text{—CH}\underset{CH_2}{\text{————}}CH_2 \qquad (7)$$

$$\rightarrow CH_3CH_2CH=CH_2 \qquad (8)$$

$$\rightarrow CH_3CH=CH\ CH_3\ (cis\ \text{and}\ trans) \qquad (9)$$

$$\rightarrow (CH_3)_2C=CH_2 \qquad (10)$$

1-butene and *cis-* and *trans-*2-butene can be formed directly from the $CH_3\dot{C}HCH_2CH_2\cdot$ diradical by a hydrogen shift. Isobutene must arise from a hydrogen shift followed by a CH_3 shift, or more likely via closure of the original diradical followed by ring opening of the methylcyclopropane to yield the $\cdot CH_3CH(CH_3)CH_2\cdot$ diradical.

Studies of the thermal or chemical activation of methylcyclopropane provide an estimate of the distribution of butene isomers expected from isomerization of the $CH_3\dot{C}HCH_2CH_2\cdot$ diradical. Methylcyclopropane presumably rearranges via a 1,3 diradical intermediate. Breakage of either of two C—C bonds yields $CH_3\dot{C}HCH_2CH_2\cdot$ (leading to 1- and 2-butenes), while breakage of the third bond produces $\cdot CH_2CH(CH_3)CH_2\cdot$ (which should lead to isobutylene). In the thermal decomposition of methylcyclopropane, the relative distribution of butene isomers was [1-butene]:[*cis*-2-butene]:[*trans*-2-butene]:[isobutene] = 1.0:0.63:0.28:0.16 at a temperature of 468 °C [5]. (Setser and Rabinovitch [6] report very similar butene distributions in the decomposition of 1,2-dideutero-3-methylcyclopropane.) This distribution reflects both the Arrhenius A factor and the activation energy which for isobutene is 2.3 kcal mol^{-1} greater than for 1-butene. Chemically activated methylcyclopropane has sufficient internal energy so that the butene distribution should not be affected by small differences in the activation energy. Chemically activated methylcyclopropane has been prepared by the reaction of methylene with propylene and cyclopropane [7] or via the reaction of methyl and cyclopropyl radicals [8]. The relative distributions of butene isomers in the order above were 1.0:0.51:0.51:0.31 [7] and 1.0:0.31:0.38:0.30 [8].

The relative distribution of butene isomers produced in the laser-induced decomposition of 2-MTHF at 0.3 Torr with a 10 cm focal length lens was [1-butene]:[*cis*-2-butene]:[*trans*-2-butene]:[isobutene] = 1.0:0.03:0.05:trace. This large excess of 1-butene compared with the thermal and chemical activation distribution was observed at all 2-MTHF pressures and with a lens of longer focal length. We conclude that the major mechanism for formation of 1-C_4H_8 does not involve a diradical. 1-C_4H_8 could also be formed by the reaction of allyl radicals and methyl radicals as in THF.

Allyl radicals were certainly present in the laser-induced decomposition of 2,5-DMTHF and 3-MTHF as deduced by the formation of 1,5-hexadiene (diallyl). However, 2-MTHF and diallyl had the same retention time, thus shedding no light on the formation of 1-butene by radical–radical reaction. The absence of significant CH_3 radical concentration as judged by the C_2H_6 yield does not offer strong support for the radical–radical reaction.

1-pentene, *cis*- and *trans*-2-pentene and 3-methyl-1-butene were the four different C_5H_{10} isomers identified as products from all three methyl-substituted THFs. It is possible to rationalize the formation of the last three C_5H_{10} compounds by the addition of a CH_3 radical to two equivalent methyl-allyl radicals:

$$\dot{C}H_2\text{—}CH{=}CH\text{—}CH_3 + CH_3 \longrightarrow CH_3\text{—}CH_2CH{=}CH\text{—}CH_3 \ (cis \text{ and } trans) \quad (11)$$

$$CH_2{=}CH\text{—}\dot{C}H\text{—}CH_3 + CH_3 \longrightarrow CH_2{=}CH\text{—}CH(CH_3)\text{—}CH_3 \quad (12)$$

The methylallyl radicals presumably arise from loss of hydrogen from 1-butene. Methyl addition to a methylallyl radical with the methyl substituted on the central carbon, *i.e.* $\cdot CH_2\text{—}C(CH_3){=}CH_2$ (arising from loss of hydrogen from isobutene), would lead to 2-methyl-1-butene as a product. No evidence for the formation of 2-methyl-1-butene was obtained. *Cis*- and *trans*-2-pentene, 3-methyl-1-butene and 2-methyl-1-butene have been observed as minor products from methylcyclopropane chemically activated by methyl and cyclopropyl radicals [8]. The absence of 2-methyl-1-butene in our experiments reflects our much lower isobutene yield relative to 1-butene. The formation of 1-pentene must involve a different mechanism. 1-pentene was a product in the laser-induced decomposition of THF, whereas the three other C_5H_{10} products were not.

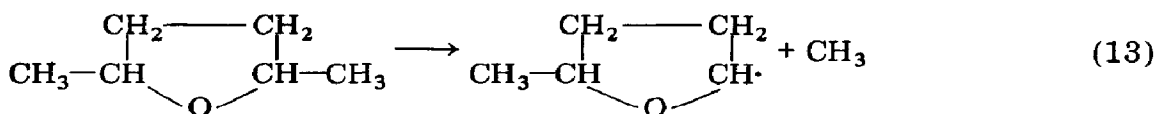A non-diradical decomposition mode for 2-MTHF would be breakage of the C(2)—CH_3 bond as a primary step to form CH_3 and C_4H_7O radicals. The C_4H_7O radical would be expected to split out a molecule of C_2H_4 along with a CH_2CHO radical. Formation of C_2H_4 as the major hydrocarbon from 2-MTHF is compatible with C(2)—CH_3 bond breakage. However, direct formation of CH_3 would be expected to produce a large C_2H_6 yield which is sensitive to the pressure and the focal length of the lens. The fact that this is not observed argues against C(2)—CH_3 bond breakage as the primary bond-breaking step.

The distribution of hydrocarbon yields from 2-MTHF was very insensitive to the 2-MTHF pressure and to the sensitized decomposition. Although these results appear to indicate that collisional effects are not important, the increase in the 1,3-butadiene yield at higher pressures did suggest additional reactions, perhaps involving C_2H_3 radicals. The increasing importance of 1,3-butadiene at higher pressures can also be seen in Figs. 3 and 4, where a change in slope of the [C_3H_6]/[1,3-butadiene] and [C_2H_4]/[1,3-butadiene] curves *versus* the 2-MTHF pressure is observed in the region 1 - 2 Torr. The effect of the 2-MTHF pressure could also be masked by the large yield of C_2H_4 at low pressure. As discussed later, C_2H_4 becomes

an increasingly important product with 2,5-DMTHF and 3-MTHF at higher pressure. The influence of collisions on the dissociation yield can be seen in the pressure dependences in Table 3. Whereas 1-butene and propylene scale with the 2-MTHF pressure, the ethylene yield has a small collisional contribution and 1,3-butadiene has a greater collisional contribution. Collisions could influence the decomposition by rotational hole filling, collisional up-pumping or reaction between a radical and 2-MTHF. Evidence for collisional up-pumping is found in the experiments which followed the extent of the reaction *versus* the number of laser shots. As with THF, a plot of $\ln(P/P_0)$ *versus* s for 2-MTHF initially at 10 Torr was not linear. As shown in Fig. 5, a linear plot was found for the function $(1/P)^{n-1}$ *versus* s where $n = 3$ for 2-MTHF. This functional dependence was observed for THF and 2-methyloxetane and was attributed to collisional up-pumping.

4.2. 2,5-dimethyltetrahydrofuran

Table 1 shows that the major hydrocarbon product in the laser-induced decomposition of a mixture of *cis*- and *trans*-2,5-DMTHF at low pressure was propylene. In contrast with 2-MTHF, the hydrocarbon distribution was a strong function of pressure or sensitization and C_2H_6 was a major product. Breakage of the C(3)—C(4) and C(2)—O bonds or the C(3)—C(4) and C(5)—O bonds are predicted to yield C_3H_6 and a $\cdot CH_2CH(CH_3)O\cdot$ diradical. This is the same diradical implicated in 2-MTHF. Based on the experimental results with 2-MTHF, we would expect $\cdot CH_2CH(CH_3)O\cdot$ to decompose predominantly to CO and CH_3, with the CH_3 radicals being in low concentration in the focal zone so that C_2H_6 would be obtained in low yield. Table 2 shows that at 25% conversion CO is in fact the major oxygenated product. However, at 0.3 Torr of 2,5-DMTHF and low conversion, C_2H_6 is the second largest product of the reaction and the C_2H_6 yield is very sensitive to the focal length of the lens. With a shorter focal length lens, a larger yield of C_2H_6 was produced. One explanation for these results with 2,5-DMTHF which could reconcile the disparate results concerning the expected $\cdot CH_2CH(CH_3)O\cdot$ diradical would be C(2)—CH_3 or C(5)—CH_3 bond breakage as the primary step in the laser-induced decomposition of 2,5-DMTHF:

$$
\begin{array}{ccc}
\text{CH}_2\text{——CH}_2 & & \text{CH}_2\text{——CH}_2 \\
\text{CH}_3\text{—CH} \quad \text{CH—CH}_3 & \longrightarrow & \text{CH}_3\text{—CH} \quad \text{CH·} + \text{CH}_3 \\
\diagdown \text{O} \diagup & & \diagdown \text{O} \diagup \\
\end{array} \qquad (13)
$$

$$
C_3H_6 + CH_2CHO \qquad (14)
$$

$$
\longrightarrow CH_3 + CO \qquad (15)
$$

Loss of CH_3 from 2,5-DMTHF would yield a C_5H_9O radical which could further decompose to C_3H_6 and a CH_2CHO radical. The CH_2CHO radical could isomerize to CH_3CO and decompose to CH_3 and CO. Thus the major products C_3H_6 and CO would be accounted for, and C_2H_6 would be formed by the dimerization of CH_3 radicals, initially at high concentrations.

The distribution of decomposition products from 2,5-DMTHF is very sensitive to pressure. Increasing the 2,5-DMTHF pressure or using a sensitizer increases the C_2H_4 yield dramatically. Breakage of a C—O bond in the 2,5-DMTHF ring cannot lead directly to C_2H_4. C_2H_4 could be produced by either breakage of two C—C bonds in the 2,5-DMTHF ring, which has no precedent and as an alternative reaction pathway would be more probable at lower 2,5-DMTHF pressures, or further decomposition of a primary reaction product. The increased formation of 1,3-butadiene at higher 2,5-DMTHF pressures suggests formation of C_2H_3 radicals which could also produce C_2H_4 by hydrogen abstraction. The one-to-one correspondence between C_2H_4 and 1,3-butadiene can be seen both in the ratio of products and the pressure dependence of the two products. In Fig. 3 the plot of the $[C_3H_6]/$ [1,3-butadiene] ratio *versus* the 2,5-DMTHF pressure changes slope in the region 1 - 2 Torr as do those for the other two methyl-substituted THFs, whereas in Fig. 4 the slope remains essentially constant over the entire 2,5-DMTHF pressure range. From the pressure dependences shown in Table 3 both C_2H_4 and 1,3-butadiene scale with the 2,5-DMTHF pressure to the power 1.5, illustrating the same collisional contribution to these yields. CH_4 also scales with the power 1.5 of the 2,5-DMTHF pressure, whereas C_3H_6 and 1-C_4H_8 both depend linearly on the pressure. In THF the CH_4 yield had a power dependence twice that of C_2H_4, implying that CH_4 was formed by CH_3 attack on THF. From the CH_4 power dependence in 2,5-DMTHF, CH_3 attack on 2,5-DMTHF appears to be a much less important source of CH_4 than in THF. As with 2-MTHF, evidence for collisional up-pumping was found in the experiments which measured the extent of the reaction *versus* the number of laser shots for 2,5-DMTHF at 10 Torr. These results are shown in Fig. 5.

4.3. 3-methyltetrahydrofuran

Although the major hydrocarbon product in the laser-induced decomposition of 3-MTHF at low pressure was 1-butene, large yields of ethylene and propylene were also found. As with 2,5-DMTHF, the product distribution shifts increasingly towards C_2H_4 as the pressure is raised or when the reaction is sensitized, and C_2H_6 is a major product of the reaction (at least at low pressure) whose yield increases with a shorter focal length lens. H_2CO was observed in substantial yield by IR spectroscopy, in contrast with the two other methyl-substituted THFs which both have CH_3 groups substituted on an α carbon atom.

As was the case with the other two methyl-substituted THFs, the 1-C_4H_8 yield, when compared with the other C_4H_8 isomers, was significantly higher than could be accounted for by the isomerization of diradicals. We believe that 1-C_4H_8 is formed primarily by the addition of allyl and methyl radicals. The detection of 1,5-hexadiene confirms the presence of allyl radicals while substantial C_2H_6 yields must arise from the CH_3 radicals. One source of CH_3 radicals would be direct C—CH_3 bond breakage. Loss of CH_3 from 3-MTHF would produce a C_4H_7O radical which would be expected to

split out an allyl radical and a molecule of H_2CO. Thus a $C—CH_3$ bond-breaking mechanism could explain the high $1\text{-}C_4H_8$ yield (allyl plus methyl), the CH_3-related products H_2CO and perhaps even the C_3H_6 yield if C_3H_5 radicals were to abstract hydrogen atoms from 3-MTHF. (The C_3H_6 yield does show a pressure dependence of 1.2.)

The relative distribution of butene isomers produced from 3-MTHF at 0.3 Torr with a lens of focal length 10 cm was [1-butene]:[cis-2-butene]:[trans-2-butene]:[isobutene] = 1.0:0.06:0.12:0.23. The isobutene yield from 3-MTHF relative to cis- and trans-2-butene was a factor of 23 larger than that from 2,5-DMTHF. We attribute this large isobutene yield to the formation and isomerization of the $\cdot CH_2CH(CH_3)CH_2\cdot$ diradical formed by breakage of the C(4)—C(5) and C(2)—O bonds of 3-MTHF.

C_2H_4 at low 3-MTHF pressure could be formed by breakage of the C(3)—C(4) and C(5)—O bonds. At higher 3-MTHF pressures, and especially under sensitized conditions, C_2H_4 becomes the predominant product. Although it could be argued that breakage of bonds C(3)—C(4) and C(5)—O is favored at higher pressure, the substantial yield of H_2CO from 3-MTHF at 10 Torr suggests that the primary bond breakages continue to be important. Additional C_2H_4 probably originates from decomposition of a primary product, just as in 2,5-DMTHF. The increased yield of 1,3-butadiene at higher pressures, the matching dependence of the $[C_2H_4]/[1,3\text{-butadiene}]$ and $[C_3H_6]/[1,3\text{-butadiene}]$ ratios on both 2-MTHF and 3-MTHF pressure, and the similar pressure dependence for both C_2H_4 and 1,3-butadiene (1.4 and 1.5 respectively) all suggest the involvement of a C_2H_3 radical. Of the five products whose pressure dependences were determined, only 1-butene was linearly dependent on the 3-MTHF pressure. CH_4 had a pressure dependence of 1.5, pointing out the diminished importance of CH_3 attack on 3-MTHF as a source of CH_4 compared with THF. As with the other two methyl-substituted THFs, evidence for collisional up-pumping was found in the experiments which measured the extent of reaction.

Acknowledgments

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