

THE VACUUM UV PHOTOLYSIS OF METHYL-SUBSTITUTED TETRAHYDROFURANS

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Summary

Product distributions from the gas and solid phase (77 K) 147 nm photolyses of tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran are reported. The mechanisms are similar to those proposed previously, and all involve the fragmentation of diradicals produced from initial carbon-oxygen bond cleavage. There is a pronounced preference for cleavage of the bond to the least substituted α -carbon. The products form from subsequent β cleavage of the initially formed diradicals. There is a pronounced preference for these β cleavages to produce a carbon-oxygen π bond and a trimethylene diradical, rather than a carbon-carbon π bond and the companion dimethylene oxide diradical. The hydrocarbon diradicals react further in a manner entirely consistent with predictions.

The simplicity of the results from the solid phase photolyses suggests either that secondary decomposition dominates product distributions from gas phase vacuum UV photolyses, or that the excited states involved have lifetimes sufficiently long to permit quenching and intersystem crossing.

1. Introduction

Because of the complexities of gas phase vacuum UV photolyses of even the simplest hydrocarbons, there has been little effort and few reports of work with more complex molecules [1 - 8]. Some complex molecules have been studied in the gas phase, but there has been little progress made at systematizing the information for any class of compound. There has been some recent effort to systematize the 184.9 nm liquid phase photolyses of complex molecules [9]. Nothing of this type has appeared that deals with photolyses at shorter wavelengths. Kizilkilic *et al.* [10] have reported a study which is similar to the present study. A direct comparison of that study with the present one is difficult because the previous study utilized 184.9 nm radiation and was primarily a liquid phase study. In this paper

we report on the 147 nm photochemistry of methyl-substituted tetrahydrofurans. The intent is not to go into the minutest details of the photolysis of each compound, but rather to identify the major primary processes for each molecule and to attempt to organize this information in such a fashion that it becomes possible to predict the photoreactions of structurally related molecules in these and related high energy systems. An attempt is also made to extend the ideas developed in the photolysis to the interpretation of both the γ radiolysis and the mass spectra of these compounds. This latter objective arises from the expectation that in high energy systems such as these, molecules should begin to behave statistically, *i.e.* the source of the energy should be less important than in lower energy systems.

2. Results

The product distributions observed when tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MTHF), 3-methyltetrahydrofuran (3-MTHF) and 2,5-dimethyltetrahydrofuran (2,5-DMTHF) are photolyzed at 147 nm in the gas phase, and in the solid phase at 77 K, both in the presence and absence of oxygen are presented in Tables 1 - 4.

TABLE 1

Comparison of the gas and solid phase (77 K) photolyses of tetrahydrofuran

<i>Product</i>	<i>Pressure</i>		
	<i>5 Torr</i>	<i>Solid</i>	<i>Solid in presence of oxygen</i>
CH ₄	17.1	104	—
C ₂ H ₂	9.9	0.0	0.0
C ₂ H ₄	90.1 (0.61) ^a	100	100
C ₂ H ₆	13.7	0.0	0.0
1-C ₃ H ₆	59.5	52.3	0.0
<i>c</i> -C ₃ H ₆	16.4	548	456
C ₃ H ₈	4.3	0.0	0.0
C ₃ H ₄	5.9	0.0	0.0
1-C ₄ H ₈	12.5	0.0	0.0

^aQuantum yield.

3. Discussion

In an attempt to systematize the vacuum UV photochemistry of ketones and organic heterocycles it has been proposed that these photoreactions are best interpreted and understood in terms of mechanisms which involve initial cleavage of the C—X bond, where X is the carbonyl group or

TABLE 2

Comparison of the gas and solid phase (77 K) photolyses of 2-methyltetrahydrofuran

Product	Pressure		
	5 Torr	Solid	Solid in presence of oxygen
CH ₄	20.1	3.6	2.3
C ₂ H ₂	10.3	0.2	0.0
C ₂ H ₄	130.0	13.1	8.3
C ₂ H ₆	34.0	3.2	0.0
1-C ₃ H ₆	85.2	12.0	0.0
c-C ₃ H ₆	14.8	88.0	100.0
CH ₃ CHO	33.0	—	103
C ₃ H ₈	7.9	0.0	0.0
C ₃ H ₄	6.7	0.0	0.0
1-C ₄ H ₈	31.2	2.0	0.0
i-C ₄ H ₈	3.0	0.0	0.0
2-C ₄ H ₈	13.3	2.1	0.0
c-C ₃ H ₅ CH ₃	8.0	25.4	16.8
CH ₃ COCH ₃	—	15.1	—

TABLE 3

Comparison of the gas and solid phase (77 K) photolyses of 3-methyltetrahydrofuran

Product	Pressure		
	5 Torr	Solid	Solid in presence of oxygen
CH ₄	9.4	1.5	—
C ₂ H ₂	2.4	0.0	0.0
C ₂ H ₄	23.2	4.9	3.7
C ₂ H ₆	12.7	0.4	0.0
1-C ₃ H ₆	22.6	3.8	2.25
c-C ₃ H ₆	0.0	0.0	0.0
CH ₃ CHO	13.5	7.9	2.0
C ₃ H ₈	4.4	0.0	0.0
C ₃ H ₄	6.7	0.0	0.0
1-C ₄ H ₈	19.4	3.8	0.0
i-C ₄ H ₈	1.3	2.3	0.0
2-C ₄ H ₈	33.0	0.3	0.0
c-C ₃ H ₅ CH ₃	46.4	93.6	100
CH ₃ COCH ₃	12.6	—	—

the heteroatom, *i.e.* CO, O, S, SO, or SO₂ [5, 8, 10, 11]. Fragments of molecular formula (CH₂)_n and (CH₂)_{n-1}X, where X is a heteroatom, are usually putative intermediates which are insensitive to the trapping [10, 12 - 15]. When this is the case, and in the absence of other data, the

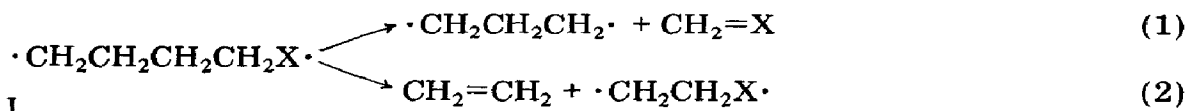
TABLE 4

Comparison of the gas and solid phase, 77 K photolyses of 2,5-dimethyltetrahydrofuran

Product	Pressure		
	5 Torr	Solid	Solid in presence of oxygen
CH ₄	—	24.1	—
C ₂ H ₂	15.3	0.0	0.0
C ₂ H ₄	170.0	10.6	8.4
C ₂ H ₆	22.0	3.5	0.0
1-C ₃ H ₆	162.0	12.0	11.6
CH ₃ CHO	—	32.0	23.0
C ₃ H ₈	6.3	0.0	0.0
C ₃ H ₄	1.2	0.0	0.0
1-C ₄ H ₈	13.6	6.8	0.0
<i>i</i> -C ₄ H ₈	7.1	0.5	0.0
2-C ₄ H ₈	35.5	12.4	0.0
<i>c</i> -C ₃ H ₅ CH ₃	43.9	80.3	100.0
CH ₃ COCH ₃	—	15.1	—

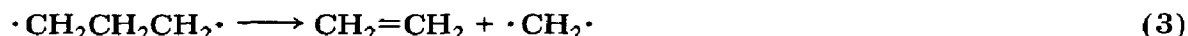
products of these intermediates can be ascribed to either molecular reactions or short-lived biradical intermediates. In the absence of definitive proof of either one or the other of these mechanisms the distinction between them is largely semantic. Because in certain cases evidence for a biradical is available, and because the existence of a biradical intermediate provides a unifying characteristic for the mechanisms of the photolyses of a large number of heterocyclic molecules, this mechanism is to be preferred and will be used in this paper. When energetically favorable the diradical produced undergoes loss of a small stable molecule, *e.g.* CO or SO₂, and a new diradical forms. The diradicals produced ultimately undergo subsequent β cleavage.

For tetrahydrofuran there are two competing β -cleavage reactions, *i.e.* reactions (1) and (2). The results presented in Table 1 for the solid phase photolyses indicate that reaction (1), which forms the stronger carbon-oxygen π bond, is favored by a factor of 6. Similar experiments in this laboratory indicate that for tetrahydrothiophene ($X \equiv S$) reaction (2) is favored by a factor of 4. (Solid phase 77 K, 147 nm photolysis of tetrahydrothiophene produced a ratio of C₂H₄:C₃H₆ = 100:16.)



If the reaction mechanism proposed is operating in the molecules considered, then the products of each of these photolyses should be those shown in Table 5. The reaction path columns in Table 5 refer to the specific paths designated in Scheme 1. The products C₃H₆, *n*-C₄H₈ and *i*-C₄H₈ are all

methylenes accounts for the formation of lower molecular weight olefins which are not predicted by Scheme 1.



This reaction also accounts for the formation of methyl radicals since a sizable fraction of the CH_2 will abstract a hydrogen atom and form methyl radicals. The homolytic cleavage of $\text{CH}_3\text{—C}$ bonds does not appear to be an important primary process since methyl radicals are not very important products and most of these are formed from reaction (3) and the secondary decomposition of acetaldehyde or acetone.

Not only can the products be predicted from Table 5, but also the product distributions at 77 K in each case can be used to estimate the relative importance of each of the primary processes in Scheme 1. Because of the symmetry of THF and 2,5-DMTHF, their photochemistry can be described by reactions (1) and (2), *i.e.* paths A and B in Scheme 1 are degenerate for these molecules. For THF the products predicted are C_3H_6 (path a_1) and formaldehyde or C_2H_4 (path a_2) and acetaldehyde. Although the relative complexity of the gas phase data, because of reaction (3), indicates that reaction (2) is the major process, the solid phase photolyses make it clear that reaction (1) predominates by a factor of 6. A similar analysis of 2,5-DMTHF photolyses leads to the conclusion that reaction 1 is favored by a factor of about 8.3.

The lack of symmetry in both 2-MTHF and 3-MTHF requires that both reaction paths A and B be evaluated. For 2-MTHF it is only possible to place a limit on the relative importance of reaction paths A and B because paths a_1 and b_2 both produce C_3H_6 . However, the C_3H_6 produced from path b_2 is only propylene, while that produced from path a_1 is the trimethylene diradical which produces both cyclopropane and propylene. If all the propylene formed at 77 K is attributed to reaction path b_2 , then limits may be placed on the relative importance of each path in Scheme 1. The ratio of cyclopropane to ethylene gives a lower limit of 6.8 for the ratio of a_1 to a_2 , while the ratio of C_4H_8 to propylene gives a lower limit of 2.4 for the ratio of b_1 to b_2 . This last ratio may be considerably higher because any propylene produced in path a_1 , *i.e.* from the trimethylene diradical, obviously lowers the calculated ratio. On the basis of this analysis the lower limit, *i.e.* if all of the propylene originated from path a_1 , on the overall ratio of path A to path B is 2.5. The upper limit may be as high as 3.9.

The dominance of path A over path B is contrary to expectation on the basis of the relative stabilities of the diradicals produced by paths A and B. This preference for the formation of the least substituted radical has been observed previously in the liquid phase photolyses of cyclic ethers at 185 nm [6]. The propensity of the initially formed diradicals to β cleavage to produce a carbon-oxygen π bond as compared with a carbon-carbon π bond is estimated by the ratio $(a_1 + b_1)/(a_2 + b_2)$ which is equivalent to the ratio for the competition between reaction (1) and reaction (2) for the symmetric THF and 2,5-DMTHF molecules. Subject to the same uncertainty

regarding the source of the propylene, this ratio has a lower limit of 4.7 and an upper limit of 9.9 for 2-MTHF.

For 3-MTHF it is not possible to assign the individual paths unambiguously since, although in the solid phase methylcyclopropane would not undergo secondary decomposition and isobutene can only originate from path b_1 , methylcyclopropane can form by paths a_1 and b_1 . It is possible to evaluate the ratio $(a_1 + b_1)/(a_2 + b_2)$ which again is equivalent to the ratio for the competition between reaction (1) and reaction (2). In the present case there is no ambiguity and the ratio observed is 11.5. Again, the initial diradicals preferentially undergo the β cleavage which produces the strong carbon-oxygen π bond rather than the weaker carbon-carbon π bond. It is also significant that the mechanism predicts that no cyclopropane should be formed and none is.

To summarize, in the initial cleavage of oxygen heterocycles such as the molecules at present under consideration, there is a pronounced preference for cleavage of the carbon-oxygen bond at the position of the least substituted carbon atom. The initially formed diradicals either I, A or B each having five atoms separating the radical centers, one of which is on carbon and the other on oxygen, undergo β cleavage preferentially to produce the carbon-oxygen π bond (reaction (1)), rather than the carbon-carbon π bond (reaction (2)). This preference is substantial and the estimated ratios of reaction (1) to reaction (2) for THF, 2-MTHF, 3-MTHF and 2,5-DMTHF are 6, 4.7 - 9.9, 11.5 and 8.3 respectively.

The results in this laboratory on a large number of heterocycles suggest that following photon absorption a quasi-equilibrium is established which permits a sampling of the energy surfaces available for reaction. Despite the large amount of energy deposited in the molecule, thermodynamic factors such as bond energies and product stabilities affect the partitioning of the excited molecule among the available reaction channels. This involvement of thermodynamic factors is nothing more than a restatement of Hammond's postulate and the Bell-Evans-Polanyi principle [16]. Couched in theoretical terms, it may be stated that the slopes of the potential surfaces leading to the more stable products are steeper, or that the density-of-states leading to the more stable products is higher. Furthermore, the conclusions also seem to apply to the γ radiolyses and the mass spectra of these compounds. The products from the γ radiolysis of THF in the gas phase are quite similar to those presented in Table 1, with the exception that secondary decomposition products, acetylene, allene and saturated hydrocarbons are more prevalent in the radiolysis than in the photolysis. Table 6 presents the mass spectra of THF, 2-MTHF, 3-MTHF and 2,5-DMTHF. These spectra represent the eight most intense peaks for each compound [17]. Each of the peaks has been assigned to one of the following categories: photolysis mechanism, molecular ion, $M-CH_3$ and other. In each case, ions with appropriate m/e or one less than that m/e have been assigned to a particular category of reaction. In Table 7 the fraction of the ion current attributable to each process is indicated. Ions corresponding to processes similar to those discussed

TABLE 6

Mass spectra of methyltetrahydrofurans

<i>THF</i>		<i>2-MTHF</i>		<i>3-MTHF</i>		<i>2,5-DMTHF</i>	
<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>
42	100 ^a	71	100 ^c	56	100 ^a	56	100 ^a
72	39 ^b	43	91 ^a	41	58 ^a	41	81 ^a
71	33 ^b	41	68 ^a	86	30 ^b	85	58 ^c
41	31 ^a	42	55 ^a	29	13 ^a	43	46 ^a
43	16 ^a	27	46 ^a	55	13 ^a	45	22 ^d
27	10 ^a	29	33 ^a	28	12 ^a	29	31 ^d
40	7 ^d	39	31 ^d	39	9 ^d	27	19 ^d
39	7 ^d	45	25 ^d	57	9 ^a	57	14 ^a

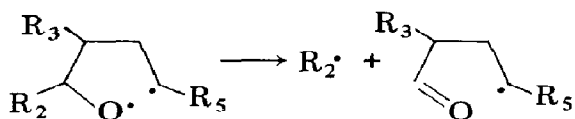
^aPhotolysis mechanism.^bM or M - 1.^cM-CH₃.^dOther.

TABLE 7

Fraction of the ion current attributable to the various categories of reaction

<i>Category</i>	<i>Fraction of ion current</i>			
	<i>THF</i>	<i>2-MTHF</i>	<i>3-MTHF</i>	<i>2,5-DMTHF</i>
Photolysis mechanism	0.65	0.65	0.83	0.65
M or M - 1	0.30	0.00	0.12	0.00
M-CH ₃	0.00	0.22	0.00	0.16
Other	0.06	0.13	0.04	0.19

above, *i.e.* β -cleavage processes, account for 65% of the ion current from THF, 2-MTHF and 2,5-DMTHF, and 85% for 3-MTHF. It is also worth noting that the M-H and M-CH₃ processes seem to compete. When there is a methyl group in the 2-position, M-CH₃ is important and no M-H is observed. However, when there is no methyl group in either the 2- or the 5-position then M-H is observed. Both of these ions, M-CH₃ and M-H, are in fact β -cleavage reactions of an ion of structure similar to A in Scheme 1. This suggests that in the photolyses of 2-MTHF and 2,5-DMTHF the diradical A may undergo the β -cleavage reaction shown in reaction (4).

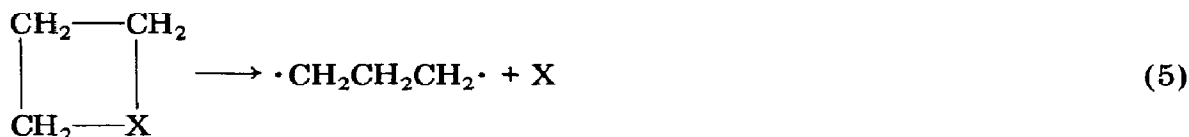


(4)

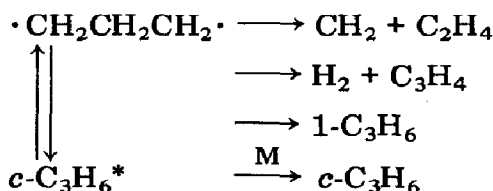
A

This is a distinct possibility since methyl radicals (R_2) are produced from other sources and the analysis would not detect the companion aldehyde radical or products from it.

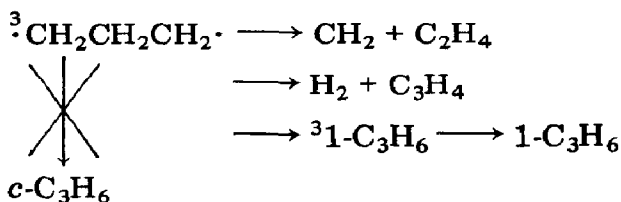
In previous studies from this laboratory it has been suggested that both singlet and triplet trimethylene diradicals were intermediates in the vacuum UV photolyses of both cyclobutanone and trimethylene sulfone [8, 11].



The evidence for this reaction is mainly the formation of cyclopropane and the pressure dependence of the cyclopropane to propylene ratio. The triplet state was implicated because oxygen is able to interfere with the formation of propylene and ethylene but had no effect on the formation of cyclopropane [8, 11]. The singlet and triplet diradicals react in the gas phase according to Schemes 2 and 3 respectively. The major difference between Schemes 2 and 3 is that the triplet trimethylene cannot form cyclopropane owing to spin restrictions.



Scheme 2.



Scheme 3.

Just as the comparison of the gas with the solid phase (77 K) data allows a better estimate of the primary processes by minimizing secondary decomposition, assuming that triplet diradicals cannot cyclize and that oxygen will react with triplet states (essentially all the alkenes derived from the diradicals are in fact quenched by oxygen), a comparison at 77 K of the product distributions in the presence and absence of oxygen allows the estimation of the relative importance of singlet and triplet trimethylene diradicals and methyl-substituted trimethylene diradicals. This estimate

does not necessarily relate to the total number of singlets and triplets since there is no evaluation of the number of singlets and triplets in the carbonyl products. However, as an approximation of the ratio of singlets to triplets, the data for the trimethylene diradical from THF and 2-MTFH are 10 and 7 respectively. A similar analysis for the methyl-substituted trimethylene diradicals produced from the photolyses of 2-MTHF, 3-MTHF and 2,5-DMTHF gives singlet to triplet ratios of 6, 15 and 4 respectively.

The yields of the C_4H_8 isomers produced from each of the methyl-substituted tetrahydrofurans are presented in Table 8. If it is assumed that no diradical intermediates are involved in these reactions, and that the acyclic C_4H_8 isomers originate from the secondary decomposition of methylcyclopropane, then no evidence for the source of the methylcyclopropane in the C_4H_8 isomer distribution would be expected. However, if diradical intermediates are involved, then 3-MTHF should produce higher yields of *i*- C_4H_8 because the diradical in that instance would be the 2-methyltrimethylene, *i.e.* it would have the *i*-butene carbon skeleton. Although the differences are small, they are significant. 3-MTHF produces higher yields of *i*- C_4H_8 than either 2-MTHF or 2,5-DMTHF, thus supporting the intermediacy of diradicals in these systems. In the solid phase the olefin yields are quite small but definitely support the diradical hypothesis.

TABLE 8

Comparison of the C_4H_8 isomer distribution from the gas phase photolyses of 2-methyltetrahydrofuran, 3-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran

	<i>1-C₄H₈</i>		<i>i-C₄H₈</i>		<i>2-C₄H₈</i>		<i>c-C₃H₅CH₃</i>		<i>i-C₄H₈/n-C₄H₈^a</i>	
	<i>Gas</i>	77 (K)	<i>Gas</i>	77 (K)	<i>Gas</i>	77 (K)	<i>Gas</i>	77 (K)	<i>Gas</i>	77 (K)
2-MTHF	46.9	2.0	5.3	0.0	25.6	2.1	22.2	25.4	0.053	0.000
2,5-DMTHF	13.6	6.8	7.1	0.5	35.5	12.4	43.9	80.3	0.071	0.005
3-MTHF	28.1	3.8	13.5	2.3	33.1	0.3	25.3	93.6	0.135	0.023

^a1-Butene + 2-butene.

The simplicity of the product distributions in the solid phase is worthy of some comment. Firstly, it appears that the gas phase product distributions are largely the result of secondary decompositions. This suggests that primary processes may be very simple despite the large amounts of energy in vacuum UV photons. A case in point is THF which, in the gas phase at 147 nm, apparently decomposes by seven different primary processes. The entire mechanism requires 48 different reactions [7]. In the solid phase the mechanism requires only one primary process together with the description of diradical behavior presented. If it is considered that excited states rather than secondary decomposition are being quenched in the experiments at 77 K, then an equally interesting conclusion is required. That conclusion

is that these highly excited states produced by 147 nm (813 kJ) photons are not predissociative but have lifetimes sufficiently long to be quenched. Fluorescence lifetimes of 2 ns have been measured for liquid *p*-dioxane excited by 185 nm photons [18, 19]. Although a collision frequency is ill-defined in the solid phase the implication of a triplet state confirms that long lifetimes may be involved. Few intersystem crossing rate constants exceed 10^7 s^{-1} .

4. Experimental details

4.1. Materials

THF, 2-MTHF, 3-MTHF and 2,5-DMTHF (cis and trans) were all purchased from Aldrich Chemical Company and were the best grade available. Each compound was distilled twice in a nitrogen atmosphere on a 30 theoretical plate spinning band column. From each distillation only the middle third was used. Oxygen (research grade) obtained from Matheson Gas Products was used as received.

4.2. Irradiation and analyses

The design and preparation of the microwave-powered discharge lamps used in this study have been described previously [11]. The photolyses were conducted in a 1 l bulb to which the lamp was attached with a ground-glass joint. The bulb was filled with the reactant on a grease-free vacuum line. The pressure was measured with a Wallace and Tiernan FA-160 pressure gauge. The lamp, with the bulb attached, was placed in the antenna of a Raytheon PGM 101 microwave generator (2450 MHz). The discharge was initiated by sparking with a Tesla coil and was maintained by the microwave generator. Solid phase photolyses were conducted in a 0.050 l cell with the surface opposite the lamp window immersed in liquid nitrogen. Periodically the photolysis was interrupted and a new surface of the reactant was deposited opposite the window. The photolysis was then resumed. This was done about five times during each experiment and minimized the photolysis of products. In gas phase experiments, product photolysis was negligible because conversions were always less than 0.1% and changes in the conversion had no effect on the product distributions.

After the photolysis, a 0.025 l sample was introduced into an F and M 810 gas chromatograph equipped with a flame ionization detector and a column (10 M 30% squalane on Chromosorb P) operated at ambient temperature and a helium flow of 0.060 l min^{-1} . The presence of both formaldehyde and acetaldehyde among the products was confirmed by chromatographic analyses on squalane and di-isodecyl phthalate; however, the reproducibility of these yields was very poor.

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