Os³⁸ClBr₅²⁻ but the respective contributions are not known.

Table IV shows the most important IMULA parameters for both investigated systems $K_2OsCl_6-K_2OsBr_6(n,\gamma)^{38}Cl$ and $K_2OsBr_6-K_2SnCl_6(n,\gamma)^{82}Br^1$ including the respective maximum and average recoil energies. As can be seen the simple reactions interstitial halide, $L_s(1)$ and $L_f(1)$ account for most of the reaction products indicating that in solids only little disorder is produced by (n,γ) recoil atoms. The differences, however, are very hard to understand. It is, indeed, expected that with increasing recoil energy $L_s(1)$ decreases which is found, but unexpectedly the $L_s(2)$ process disappears totally. Moreover the $L_{\rm f}(1)$ process increases and the $L_t(2)$ process decreases with increasing recoil energy which is quite opposite the expectation which predicts that processes responsible for more disorder increase when recoil atoms with higher energies react. Only ad hoc hypotheses might explain the large difference in D_c . Unfortunately it was not yet possible to apply IMULA to our previous $K_2 ReCl_6 - K_2 ReBr_6(n, \gamma)^{36} Cl$ experiments¹ (maximum ³⁶Cl recoil energy 1099 eV, average recoil energy 634 eV^{14}); it cannot be said if this failure is caused by deficient experimental data or because the model cannot be applied in its present state to such high recoil energies.

(14) Chang, J.; Ferro, L. J.; Spicer, L. D. J. Chem. Phys. 1983, 79, 6419.

Conclusions

It has been shown that the chemical effects of the nuclear process $K_2OsCl_6-K_2OsBr_6(n,\gamma)^{38}Cl$ can be quantitatively discussed by using the impact-induced multiple ligand abstraction (IMULA) model. For a more profound understanding of the relation between recoil energy and recoil atom mass, respectively, and the contributions of the different IMULA processes, further investigations seem necessary, using other (but similar) systems and other recoil energies.

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Thermal Reactions of Cyclic Ethers at High Temperatures. 2. Pyrolysis of Tetrahydrofuran behind Reflected Shocks

Assa Lifshitz,* Menashe Bidani,¹ and Shimon Bidani

Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel (Received: January 8, 1986)

The thermal decomposition of tetrahydrofuran was studied behind reflected shocks in a single-pulse shock tube over the temperature range 1070–1530 K and overall densities ranging from 2 to 8×10^{-5} mol/cm³. Over this temperature range the following products were obtained: H₂, CH₄, C₂H₂, C₃H₄ (allene), C₃H₄ (methylacetylene), 1-C₄H₈, C₄H₆, C₄H₄, C₄H₂, and small quantities of c-C₃H₆, C₆H₅, C₆H₆, and C₄H₄O. From a series of experiments using mixtures of tetrahydrofuran and tetrahydrofuran-d₈ and also partially deuterated (3,3,4,4-d₄) reactant, the following initiation steps were suggested: tetrahydrofuran \rightarrow C₂H₄ + (CH₂)₂-O, k_{uni} = 3.30 × 10¹⁶ exp(-83 × 10³/RT) s⁻¹; tetrahydrofuran \rightarrow C₃H₆ + CH₂O, k_{uni} = 8.25 × 10¹⁵ exp(-83 × 10³/RT) s⁻¹. The (CH₂)₂-O residue neither isomerizes to acetaldehyde nor dissociates from a potential surface of the latter. It dissociates to methyl and formyl radicals, producing carbon monoxide as the only oxygenated product of this channel. It was shown that ethylene is formed by elimination from the tetrahydrofuran ring at the 2-3 (4-5) and 3-4 positions at a ratio of ~2.2:1. A secondary isotope effect of ~1.65 in the production of both ethylene and propylene in favor of tetrahydrofuran over tetrahydrofuran-d₈ was noticed. It was also shown that allene and methylacetylene preserve the original skeleton of the tetrahydrofuran and are probably formed directly from propylene. 1-Butene on the other hand is produced by an attack of methyl radicals on propylene and does not preserve the skeleton of the tetrahydrofuran.

Introduction

Whereas a lot of effort has been devoted to the study of the pyrolysis of aliphatic and aromatic hydrocarbons, very little has been done in trying to elucidate the pyrolysis pattern of heterocyclic compounds.

Tetrahydrofuran is a very stable five-membered ring ether. The only attempt to study its thermal decomposition dates back some 35 years to Walters et al.,^{2,3} who studied the decomposition in a heated bulb over the temperature range 530-670 °C. As far as we are aware, nothing has been done since then to repeat the study or extend its temperature range in order to obtain more

accurate and elaborate information that could lead to the understanding of the pyrolysis mechanism.

In the early study,² the overall decomposition rate was determined from time-dependent pressure observations over the temperature range 529-569 °C at pressures ranging from 50 to 300 Torr. The authors concluded that the overall decomposition rate of tetrahydrofuran obeyed a 1.5-order rate law with a rate constant¹ $k = 1.15 \times 10^{12} \exp(-53.0 \times 10^3/RT) L^{1/2} mol^{-1/2} s^{-1}$. Among the reaction products obtained in the pyrolysis, ethylene and carbon monoxide were present at the highest concentrations, followed by methane together with smaller percentages of higher (unspecified) unsaturated compounds, and also hydrogen and ethane. Special care was taken in order to analyze for aldehydes during the pyrolysis, as acetaldehyde and formaldehyde might play the role of active intermediates in the reaction. A timedependent analysis did reveal the presence of aldehydes, which increased in the beginning, reached a peak, and then disappeared

⁽¹⁾ In partial fulfillment of the requirements for a Ph.D. Thesis submitted to the Senate of the Hebrew University by M.B.

⁽²⁾ Klute, C. H.; Walters, W. D. J. Am. Chem. Soc. 1946, 68, 506.

⁽³⁾ McDonald, G.; Lodege, N. M.; Walters, W. D. J. Am. Chem. Soc. 1951, 73, 1757.

together with the tetrahydrofuran.

On the basis of these results the authors suggested two main channels for the decomposition, both via the production of aldehydes.

$$\begin{array}{c} & \longrightarrow & CH_3CHO + C_2H_4 & \text{main channel} & (1) \\ & & \downarrow \\ & & CH_4 + CO \end{array}$$

$$CH_2 O + C_3 H_6 \quad \text{secondary channel} \quad (2)$$

In a later investigation,³ the effect of added gases and the effect of increased surface to volume ratio were studied. A series of gases, including free-radical scavengers, were added to the tetrahydrofuran, and the reaction rate was measured. In all of these studies, no effect or a very small effect on the overall decomposition was observed.

In this article the distribution of reaction products in tetrahydrofuran pyrolysis over the temperature range 1070-1530 K is presented and the mechanism of the reaction is discussed. Similarities and differences between the low- and the high-temperature results are emphasized. The article is the second part of a series on thermal reactions of cyclic ethers at high temperatures.⁴

Experimental Section

A. Apparatus. The thermal decomposition of tetrahydrofuran was studied behind reflected shocks in a pressurized driver, 52mm-i.d. single-pulse shock tube made of electropolished seamless stainless steel tubing.⁵ The driven section was 4-m long and the driver had a variable length up to 2.7 m. Its length could be tuned in 1-in. steps in order to obtain the best cooling conditions. Sections of the shock tube were connected with copper gaskets except for the last half of the driven section, which used gold gaskets to ensure a smooth flow in the region of the formed shock wave. A 36-L dump tank was connected to the driven section near the diaphragm holder in order to prevent reflection of transmitted shocks and in order to reduce the final pressure in the tube. The driven section was separated from the driver by Mylar polyester film of various thicknesses depending upon the desired shock strength. The tube was pumped down before each experiment to approximately 10⁻⁵ Torr and had a leak or degassing rate of about 5×10^{-4} Torr/min.

Reflected shock parameters were evaluated from the measured incident shock velocities by using the three conservation equations and the ideal gas equation of state. The molar enthalpies of tetrahydrofuran were taken from a report by Wilhoit et al.⁶

The incident shock velocities were measured with two miniature high-frequency pressure transducers (Vibrometer Model 6QP500) placed 300 mm apart near the end plate of the driven section. These transducers were connected in parallel. The signals generated by the shock waves passing over the transducers were fed through a home-built piezo amplifier into a Nicolet Model 3091 digital oscilloscope. Time intervals between the two signals shown on the oscilloscope were obtained digitally with an accuracy of $\pm 2 \,\mu$ s (out of about 400), corresponding to approximately ± 15 K. A third transducer placed in the center of the end plate provided measurement of the reaction dwell times (approximately 2 ms) with an accuracy of $\pm 5\%$. Cooling rates were approximately $(0.5-1) \times 10^6$ K/s.

B. Materials and Analysis. Two reaction mixtures containing 0.25 and 1% tetrahydrofuran in argon were prepared and stored at high pressure in stainless steel cylinders. Both the cylinders and the line were baked and pumped down to better than 10^{-5}



Figure 1. A typical chromatogram of postshock mixture of 0.25% tetrahydrofuran in argon heated to 1530 K. Ten reaction products can be seen. Not seen are hydrogen, carbon monoxide, and ethane.

Torr before the preparation of the mixtures.

The tetrahydrofuran was obtained from Fluka A.G. and was of puriss grade listed as 99.5% pure. None of the reaction products were found in the pure material. The argon used was Matheson ultrahigh-purity grade, listed as 99.9995% pure, and the helium was Matheson pure grade listed as 99.999% pure. All the materials were used without further purification.

Shocked samples were taken from the tube through an outlet in the driven section near the end plate, in $150-cm^3$ glass bulbs and analyzed on a Packard 800 series gas chromatograph using a flame ionization detector. Carbon monoxide was converted to methane prior to its analysis by using a Chrompak (Raney nickel) methanyzer operated at 400 °C with 50% H₂ + 50% Ar as a carrier.

The gas analysis was performed on 2-m Porapak N column. Its initial temperature of 35 °C was gradually elevated to 150 °C over about 80 min. A typical chromatogram obtained at the high-temperature end of this study is shown in Figure 1.

Several samples shocked to different temperatures were analyzed for ~ 3 h in the gas chromatograph to see whether high molecular weight products are formed behind the reflected shock waves. Nothing was eluted after 80 min. This of course does not exclude the possibility that some reaction products are absorbed on the walls of the shock tube or the glass bulbs and cannot be injected into the gas chromatograph. (This possibility is discussed later.)

Carbon monoxide was analyzed on a room temperature 3-m activated charcoal column from which the ratio CO/CH_4 could be obtained. This ratio in a standard mixture of methane and carbon monoxide was measured periodically in order to verify complete conversion of the latter to methane in the methanyzer.

Ethane could not be well separated from ethylene on the Porapak N column, especially when the ratio of ethylene to ethane was high. We therefore obtained the sum of the two on the Porapak N and the ratio on a 2-m silica gel column operated at room temperature.

We had difficulties in analyzing for hydrogen because of the low sensitivity of the thermal conductivity detector. Meaningful results for hydrogen were obtained only at high temperatures and did not assist in enlightening the pyrolysis mechanism. We therefore did not include hydrogen in our product distribution and based our mass balance calculations on carbon only.

Identification of the reaction products was based on their retention times in the gas chromatograph in comparison with the retention times of the pure substances. It was assisted also by GC-MS measurements. Complete mass spectra were taken at 3-s intervals during the 80-min run time of the chromatogram. Each mass spectrum at the peak height was compared to standard spectra⁷ and complete identification was achieved. The mass spectrometer used in these measurements, and also in determining the isotope distribution of various reaction products when labeled

⁽⁴⁾ Part 1. Lifshitz, A.; Ben-Hamou, H. J. Phys. Chem. 1983, 87, 1782.

⁽⁵⁾ Lifshitz, A.; Bidani, M.; Carroll, H. F. J. Chem. Phys. 1983, 79, 2742.
(6) Kudchadker, A. P.; Kudchadker, S. A.; Wilhoit, R. C. "Furan Dihydrofuran Tetrahydrofuran"; Key Chemical Data Books; Texas A&M University: College Station, TX, 1978.

⁽⁷⁾ Cornu, A.; Massot, R. Compilation of Mass Spectral Data; Heyden: London, 1966.

tetrahydrofuran was used, was V.G. ZAB-2F. Its sensitivity and resolution was not high enough to separate, for example, $C_2D_2^+$ from $C_2DH_2^+$ ($m/\Delta m = 1.8 \times 10^4$), creating some difficulties in the isotope analysis of the products, as will be discussed later.

The sensitivities of the various reaction products to the flame ionization detector were determined from standard mixtures. The areas under the various peaks in the gas chromatographic analysis were evaluated by a Spectra Physics Model SP4100 integrator. The information accumulated on the integrator was transferred after each analysis on line to a Digital Computer Controls D-116 computer in order to remove spurious peaks and noise, and then to a CDC-7600 for data reduction and graphic presentation.

Results

A. Evaluation of the Product Concentrations and Production Rates from the GC Peak Areas. Evaluation of the absolute concentrations of the various reaction products from the areas under their GC peaks was done in the following manner:

1. The concentration of tetrahydrofuran behind the reflected shock prior to decomposition, $C_5(\text{THF})_0$, is given by

$$C_5(\text{THF})_0 = \{p_1[\%(\text{THF})]\rho_5/\rho_1\}/100RT_1$$
(I)

where p_1 is the pressure in the tube prior to shock heating, %(THF) is the percentage of tetrahydrofuran in the original mixture, ρ_5/ρ_1 is the compression of the sample behind the reflected shock, and T_1 is the room temperature.

2. The concentration of tetrahydrofuran behind the reflected shock prior to decomposition in terms of its peak area, $A(THF)_0$ is given by

$$A(\text{THF})_0 = A(\text{THF})_t + 0.25 \sum N(\text{pr}_i) A(\text{pr}_i)_t / S(\text{pr}_i) \quad \text{(II)}$$

where $A(\text{THF})_i$ is the peak area of tetrahydrofuran in the shocked sample, $A(\text{pr}_i)t$ is the peak area of a product i in the shocked sample, $S(\text{pr}_i)$ is the sensitivity of a product i relative to tetrahydrofuran, and $N(\text{pr}_i)$ is the number of carbon atoms in a product i.

In tests where the shock temperature was low and the conversion small, $C_5(\text{THF})_0 \sim C_5(\text{THF})_i$, and the second term in the right-hand side of eq II which gives the amount of tetrahydrofuran decomposed is a second-order correction. When high conversions are concerned, the second term is important.

The concentration of a product i in the shocked sample is given by

$$C_5(\mathrm{pr})_{\mathrm{i}} = (A(\mathrm{pr}_{\mathrm{i}})_t / S(\mathrm{pr}_{\mathrm{i}}))(C_5(\mathrm{THF})_0 / A(\mathrm{THF})_0) \quad (\mathrm{III})$$

Since $A(THF)_0$ is not available in the postshock analysis, in order to calculate the concentration of each product in the mixture its value was calculated by using eq II. (Another alternative to obtain the value of $A(THF)_0$ per unit GC signal would be to use the peak area of the unshocked mixture of tetrahydrofuran, which was obtained in a separate run. We found that by doing so, the scatter in the data when many shocks are compared was larger than by using the value of $A(THF)_0$ calculated from eq II, probably because of the variation in the sensitivity of the flame ionization detector from day to day or during one long day.)

The rate of production of the various products after a reaction time t will be defined here as

$$rate(pr_i) = C_5(pr_i)_t / t$$
 (IV)

It represents an average rate of production over a time period t, which is approximately 2 ms. Since we shall discuss and deal with rates at the very early stages of production, they are close to linear and the average value over a period of 2 ms can very well represent $d[P_i]/dt$.

B. Presentation of the Experimental Results. In order to determine the distribution of reaction products in tetrahydrofuran pyrolysis, to determine the production rates of the various products and their dependence on the temperature, two groups of experiments (0.25 and 1% tetrahydrofuran in argon) were run, covering the temperature range 1070–1530 K. Details of the experimental conditions and the results of five representative tests from each group of experiments are given in Table I. The table shows the



Figure 2. Product distribution of postshock mixtures of 0.25% tetrahydrofuran in argon over the temperature range covered in this investigation.

temperature behind the reflected shock, T_5 , the overall density behind the reflected shock, C_5 , in units of mol/cm³, the reaction dwell time t in microseconds, and the fraction of the various reaction products as obtained in the postshock analysis, not including argon. The concentration of tetrahydrofuran behind the reflected shock prior to decomposition (C_5 (THF)₀) is given by the percent of tetrahydrofuran in the original mixture times C_5 .

Figure 2 shows the product distribution obtained in postshock samples of 0.25% tetrahydrofuran in argon over the entire temperature range covered in this investigation. The percent of a given product out of the total shown in the figure corresponds to its mole fraction, $C_i / \sum C_i$, irrespective of the number of its carbon atoms. (Molecular hydrogen is not included.)

In Figures 3-5 the net rates of production of 13 reaction products, as defined by eq IV, are plotted against the reciprocal temperature. They are divided into C_1 - C_2 , C_3 , and C_4 products. As can be seen, the lines bend or even change their slopes as the temperature goes up. This behavior, resulting from the fact that the reactant is being depleted at high temperatures and there is further decomposition of some of the products, is typical for this type of study and has been found in the past.48 Because of this bend in the lines, any measured slope in the log (rate) vs. 1/Tplots provides only a lower limit for the Arrhenius temperature dependence. Table II summarizes the values of E_e as obtained from the slopes of the lines at the low-temperature end, before any significant bend has occurred. The table gives also the concentrations of all the products at 1300 K, following a reaction time of ~ 2 ms for 0.25% THF in argon. These quantities can serve at a later stage as a basis for computer modeling of the decomposition scheme, when the reaction mechanism is better understood and the necessary rate parameters become available.

Discussion

A. The Initiation Steps. In trying to understand the pyrolysis mechanism of a molecule like tetrahydrofuran, it is important to identify first the initiation steps. It has been suggested,² but not fully elucidated, that at low temperatures the molecule opens in two unimolecular channels to form ethylene and acetaldehyde in the major channel and propylene and formaldehyde in a second

⁽⁸⁾ Lifshitz, A.; Scheller, K.; Burcat, A. "Recent Development in Shock Tube Research"; *Proceedings of the 9th International Shock Tube Symposium (1973)*; Bershader, D., and Griffith, W., Eds.; Stanford University Press: Stanford, CA, 1973; p 690.



Figure 3. Plot of log (rate) vs. 1/T for C₁ and C₂ products.



Figure 4. Plot of log (rate) vs. 1/T for C₃ products.

and a slower channel. The aldehydes further decompose to yield additional reaction products.

In this section we will examine in more detail the suggested initiation.

a. Production of Ethylene. As can be seen in Figure 2, ethylene is indeed the major product of the pyrolysis and as such it is probably a primary product. We examined this thesis by shocking a mixture of 1% tetrahydrofuran and 1% tetrahydrofuran- d_8 , and looked at the isotope distribution in the ethylene. If the only



Figure 5. Plot of log (rate) vs. 1/T for C₄ products.



Figure 6. Isotopic distribution of ethylenes in postshock mixture of tetrahydrofuran and tetrahydrofuran- d_8 . The upper portion (a) shows the original GC-MS spectrum; in the lower portion only the parent ions are left. The intense peaks of C_2H_4 and C_2D_4 indicate that ethylene preserves the original tetrahydrofuran skeleton.

ethylenes that are formed are C_2H_4 and C_2D_4 and no scrambled product is found, then the ethylene retains the composition of the original skeleton and is being formed directly via the ring cleavage. At high temperatures like the ones in this study, some isotope exchange may occur, but at the low-temperture end of the range this should be minimal.

Figure 6 shows a mass spectrum of the ethylenes in the postshock mixture. In Figure 6a the spectrum is shown as obtained in the GC-MS experiment. It contains parent ions and daughter ions arising from the cracking pattern of the parents. These two groups of ions may overlap if the resolving power of the mass spectrometer is not high enough to separate them. In the present study, the mass spectrometer could not separate, for example, the ions $C_2D_2^+$ from $C_2H_4^+$ at m/z 28. The first ion is a daughter ion of $C_2D_4^+$ whereas $C_2H_4^+$ is a parent. It is relatively easy to remove the daughter ions from the spectrum when a small number of hydrogen atoms as in ethylene are present in the parent. It becomes, however, quite complicated when a mixture of large hydrogenated and deuterated molecules are involved. In Figure

TABLE I:	Details of	the Exper	imental	Results	of	Representative	Tests ^a		
						107 T-	and hard no ferra a	:	

				170 Tetrany	uroruran in Ar	gon			
				[product]/ ∑[products]					
shock	τ <i>T</i> ₅ , Κ	<i>C</i> ₅	t	CH4	СО	C2	H ₆	C ₂ H ₄	C ₂ H ₂
42	1075	2.64×10^{-5}	⁵ 2190	8.94 × 10 ⁻⁴	9.22 × 1	0-4	1.1	2×10^{-3}	
62	1107	2.77×10^{-3}	5 2000	1.96×10^{-3}	2.34×10^{-10}	0 ⁻³	3.5	5×10^{-3}	1.74 × 10 ⁻⁵
31	1205	2.97×10^{-5}	5 2140	3.46×10^{-2}	5.35×10^{-10}	0 ⁻² 1.62 >	< 10 ⁻³ 7.1	9 × 10 ⁻²	4.42×10^{-4}
25	1385	3.45×10^{-5}	5 2040	1.50×10^{-1}	3.00×10^{-10}	0 ⁻¹ 1.78 >	< 10 ⁻² 2.6	1×10^{-1}	3.71×10^{-2}
29	1415	4.20×10^{-5}	2010	1.65×10^{-1}	3.32×10^{-10}	0 ⁻¹ 1.40 >	< 10 ⁻² 2.7	7×10^{-1}	4.77×10^{-2}
1% Tetrahydrofuran in Argon									
[product]/ [products]									
shock	C ₃ H ₆	<i>c</i> -C₃H ₆	allene	propyne	C_4H_8	C₄H ₆	C ₄ H ₄	C₄H₂	THF
42	2.44×10^{-4}	9.87 × 10 ⁻⁵	2.84×10^{-5}		2.17×10^{-4}	1.92×10^{-4}			9.94 × 10 ⁻¹
62	8.16×10^{-4}	2.23×10^{-4}	2.28×10^{-4}		2.81×10^{-4}	2.53×10^{-4}			9.90 × 10 ⁻¹
31	1.88×10^{-2}	7.97×10^{-4}	4.95×10^{-3}	1.12×10^{-3}	8.90×10^{-3}	2.22×10^{-3}			7.95×10^{-1}
25	4.73×10^{-2}		1.33×10^{-2}	1.99×10^{-2}	2.88×10^{-3}	7.68×10^{-3}	2.85×10^{-3}	3.73×10^{-4}	1.34×10^{-1}
29	4.30×10^{-2}		1.34×10^{-4}	2.25×10^{-2}	1.76×10^{-3}	7.72×10^{-3}	3.51×10^{-3}	1.08×10^{-3}	5.52×10^{-2}
0.25% Tetrahydrofuran in Argon									
	$[product]/\sum[products]$								
shock	: T ₅ , K	<i>C</i> ₅	t	CH4	CO	C ₂	H ₆	C ₂ H ₄	C ₂ H ₂
33	1160	2.53×10^{-5}	⁵ 2175	8.36 × 10 ⁻³	1.20 × 1	0-2 5.14 >	< 10 ⁻⁴ 1.6	1×10^{-2}	
50	1205	2.69×10^{-5}	5 2110	3.39×10^{-2}	6.10×10	0 ⁻² 5.37 >	< 10 ⁻³ 8.4	3×10^{-2}	1.03×10^{-3}
59	1260	2.78×10^{-5}	2200	7.81×10^{-2}	1.60×10^{-1}	0 ⁻¹ 1.90 >	< 10 ⁻² 2.0	2×10^{-1}	6.24×10^{-3}
17	1340	2.90×10^{-5}	2000	1.12×10^{-1}	2.81×10^{-10}	0 ⁻¹ 3.13 >	< 10 ⁻² 2.7	0×10^{-1}	1.91×10^{-2}
34	1520	3.05×10^{-5}	2015	1.59×10^{-1}	3.82×10^{-10}	D ⁻¹ 5.07 >	< 10 ⁻³ 1.9	5×10^{-1}	1.94×10^{-1}
0.25% Tetrahydrofuran in Argon									
				[pro	duct]/∑[produ	icts]			
shock	C ₃ H ₆	c-C ₃ H ₆	allene	propyne	C₄H ₈	C ₄ H ₆	C ₄ H ₄	C ₄ H ₂	THF
33	6.16×10^{-3}	5.20×10^{-4}	9.11×10^{-4}		2.48×10^{-3}	6.18×10^{-4}			9.37×10^{-1}
50	2.41×10^{-2}	1.16×10^{-3}	8.51×10^{-3}	2.07×10^{-3}	9.75×10^{-3}	1.97×10^{-3}			7.51×10^{-1}
59	5.46×10^{-2}	6.97 × 10 ⁻⁴	2.03×10^{-2}	1.13×10^{-2}	1.13×10^{-2}	5.01×10^{-3}	7.08×10^{-4}		4.29×10^{-1}
17	5.87×10^{-2}		2.03×10^{-2}	1.87×10^{-2}	8.81×10^{-3}	7.03×10^{-3}	2.19×10^{-3}		1.50×10^{-1}
34	6.96×10^{-3}		7.23×10^{-3}	1.44×10^{-2}	1.86×10^{-4}	2.25×10^{-3}	3.68×10^{-3}	3.28×10^{-3}	1.89×10^{-2}

^aDwell times are expressed in μ s and concentrations are in mol/cm³.



Figure 7. Isotopic distribution of ethylenes in postshock mixture of 1% 3,3,4,4-tetrahydrofuran- d_4 in argon. In part a the original GC-MS spectrum is shown and in part b only the parent ions. The intense peaks of C₂D₄ and C₂D₂H₂ indicate that ethylene is formed by elimination from the 2-3 (4-5) as well as the 3-4 positions.

6b the spectrum contains only parent ions after removal of all the peaks which belong to the daughter ions and also m/z 32 and 28 coming from the air background. As can be seen the peak at m/z 30 which is present in Figure 6a disappears completely in Figure

TABLE II: E_a , the Arrhenius Temperature Dependence of the Production Rate, in kcal/mol, and the Product Concentrations after 2 ms at 1300 K, in mol/cm³, for 0.25% THF in Ar

molecule E_{a}		concn	molecule	Ea	concn		
CO	80	2.8×10^{-8}	C ₃ H ₆	83	8.0 × 10 ⁻⁹		
CH₄	72	1.1 × 10 ⁻⁸	C_3H_4 (allene)	105	2.5×10^{-9}		
C_2H_4	83	3.2×10^{-8}	$C_3H_4(propyne)$	95	2.0×10^{-9}		
C_2H_6	98	3.5 × 10 ⁻⁹	C ₄ H ₆	65	7.0×10^{-10}		
C_2H_2	95	1.5 × 10 ⁻⁹	C ₄ H ₈	76	1.0×10^{-9}		

6b, since it is nothing but $C_2D_3^+$ (62% of the parent $C_2D_4^+$). Some small residues of m/z 29 and 31 are still present owing to either small isotope exchange or some deviation from the published cracking pattern which is somewhat instrument-dependent. These results clearly show that both ethylenes preserve the original skeleton of the tetrahydrofuran molecule and are thus formed by unimolecular ring cleavage.

It can also be seen in Figure 6b that the C_2H_4 peak is higher than the C_2D_4 peak by a factor of ~1.65 indicating a secondary isotope effect. This is a typical behavior for secondary isotope effects near or at the high-pressure limit of unimolecular reactions.⁹ At the high overall densities behind the reflected shock ((2-8) × 10⁻⁵ mol/cm³) the ring cleavage is probably near the highpressure limit. Since ethylene is the major product of the pyrolysis, the mass spectrum of the remaining tetrahydrofuran shows a higher concentration of the deuterated compound.

Ethylene can be formed via elimination from tetrahydrofuran at the 2-3 (or 5-4) positions (reaction 3), or alternatively from the 3-4 positions (reaction 4). In order to clarify which channel is operative, we shocked 3,3,4,4-tetrahydrofuran- d_4 . Elimination of ethylene from the 3-4 positions leads to the production of

⁽⁹⁾ Robinson, P. J.; Holbrook, K. A. Unimolecular Reactions; Wiley-Interscience: New York, 1972; p 302.

$$\sum_{s=0}^{D_2} \sum_{z=0}^{J_2} - CD_2 = CD_2 + CH_2 - O - CH_2$$
 (3)

$$D_2 \longrightarrow D_2 \longrightarrow CD_2 = CH_2 + CD_2 - CH_2 - 0 \qquad (4)$$

 CD_2 =CD₂ (reaction 3) whereas elimination from the 2-3 (or 5-4) positions leads to the production of a scrambled ethylene CD_2 = CH₂ (reaction 4). The results of this experiment are shown in Figure 7. In Figure 7a the original GC-MS spectrum is shown and in Figure 7b the spectrum after removing peaks resulting from the cracking pattern of C_2D_4 and $C_2D_2H_2$ as well as the air peaks. As can be seen, both molecules are present, which means that both reactions 3 and 4 take place. The ratio of CD_2 =CH₂ to CD₂=CD₂ is roughly 2:1, indicating that their rates are practically identical except for a statistical factor of 2 which results from the fact that there are two ways to obtain CH₂=CD₂ (2-3 and 4-5) and only one to get CD₂=CD₂.

The production of ethylene in a unimolecular dissociation of tetrahydrofuran leaves the two fragments CH_2 -O- CH_2 and CH_2 - CH_2 -O as residues. Since the CO concentration is practically equal to that of the ethylene, and since the formation of ethane in the pyrolysis indicates that methyl radicals are involved, it is reasonable to assume that the two $(CH_2)_2$ -O residues decompose to HCO and CH_3 :

$$(CH_2)_2 - O \rightarrow HCO + CH_3^{\bullet}$$
(5)

$$HCO \rightarrow H^{\bullet} + CO$$
 (6)

It was suggested in the low-temperature study that the residue is acetaldehyde,² which is known to decompose to HCO and CH_3 .¹⁰ We looked very carefully for acetaldehyde in the vapor-phase chromatography (VPC) and in the GC-MS chromatograms, but could not find even traces of the latter. We also looked at the remote possibility that the acetaldehyde was absorbed on the shock tube walls, on the walls of the glass bulbs, or on the injection system and was therefore not injected to the column together with the rest of the sample.

We shocked a mixture of 0.1% ethylene oxide in argon to ~ 1000 K where considerable isomerization of ethylene oxide to acetaldehyde takes place.⁴ Both ethylene oxide and acetaldehyde were clearly detected in the postshock analysis both on the gas chromatograph and on the GC-MS, meaning that if acetaldehyde is being formed, it can be detected and identified.

At 1200 K, for example, the half-life of acetaldehyde decomposition is \sim 75 ms.¹⁰ This will leave almost all the acetaldehyde in the mixture at 2 ms for detection were acetaldehyde an intermediate in the pyrolysis.

One can therefore reach the conclusion that neither of the $(CH_2)_2$ -O residues passes through the potential energy surface of acetaldehyde toward its decomposition to methyl and formyl radicals. This is a marked difference from the results at low temperatures where aldehydes were found.

From the known rate of formation of ethylene and its Arrhenius temperature dependence at the lower end of the temperature range, one can calculate the unimolecular rate parameters for the elimination to produce ethylene using the relation:

$$rate(C_2H_4) = k(C_2H_4)[THF]_0$$
(V)

The result obtained is $k(C_2H_4) = 3.30 \times 10^{16} \exp(-83 \times 10^3/RT) \text{ s}^{-1}$. Such a high preexponential factor is very typical of ring cleavage of this type. The isoelectronic molecule cyclopentane¹¹ decomposes to ethylene and cyclopropane with a preexponential factor of $2 \times 10^{16} \text{ s}^{-1}$, very similar to the one obtained for tetrahydrofuran.

b. Production of Propylene. After establishing that the production of ethylene is an initiation step, let us examine now the



Figure 8. Isotopic distribution of propylenes in postshock mixture of tetrahydrofuran and tetrahydrofuran- d_8 . In the upper portion (a) the original GC-MS spectrum is shown, and in the lower section (b) the peaks left after removing the cracking pattern of the parents are shown. The intense peaks of C_3H_6 and C_3D_6 indicate that propylene is formed directly via the ring opening.

reaction channel for production of propylene. Propylene can in principle be formed by elimination from the ring

$$(7) \longrightarrow CH_2O + C_3H_6$$

or by methyl radical attack on ethylene.

$$C_2H_4 + CH_3 \rightarrow C_3H_7 \rightarrow C_3H_6 + H$$
(8)

Since the concentration of ethylene is much higher than that of propylene, the ethylene can be the precursor of the latter.

In order to clarify this point we again examined the isotopic distribution of propylene in the postshock mixture of tetrahydrofuran and tetrahydrofuran- d_8 . If reaction 7 is operative then the propylenes should be unscrambled (except for some slight isotope exchange). If reaction 8 is operative, in addition to unscrambled propylenes there should be a considerable concentration of $C_3D_4H_2$ and $C_3D_2H_4$ from the attack of CH_3 on C_2D_4 and CD_3 on C_2H_4

$$CH_2 = CH_2 + CD_3 \rightarrow CH_2 - CH_2 - CD_3 \rightarrow C_3H_4D_2 + D \qquad (9)$$

$$CD_2 = CD_2 + CH_3 \rightarrow CD_2 - CD_2 - CH_3 \rightarrow C_3D_4H_2 + H \quad (10)$$

The results are shown in Figure 8. Again, in Figure 8a the original GC-MS spectrum is shown and in Figure 8b only the parent molecules are left. It can be seen that $C_3H_2D_4$ (m/z 46) is absent and $C_3H_4D_2$ (m/z 44) is negligible, indicating that the propylene is not formed by a chain mechanism but by unimolecular ring elimination. The only scrambling seen is of C_3D_5H and C_3H_5D which are present probably due to isotopic exchange.

In view of the conclusion regarding the origin of the propylene, we looked very carefully for the presence of formaldehyde (reaction 7) in the GC-MS since it was not found in the routine GC analyses. We did find in the background of the GC-MS chromatograms, starting at ~ 35 min and ending at ~ 43 min, lowintensity peaks at m/z 29 and 30 at a ratio of 1:0.9, typical of formaldehyde. This smeared peak of formaldehyde could not be detected in the vapor-phase chromatograph. We cannot determine quantitatively the formaldehyde concentration from these experiments but it is clear that formaldehyde is present and is probably formed by reaction 7. It should be mentioned here that since the concentration of formaldehyde is relatively small, its

⁽¹⁰⁾ Colket, III, M. B.; Neageli, Neageli, D. W.; Glassman, I. Int. J. Chem. Kinet. 1975, 7, 223.

⁽¹¹⁾ Tsang, W. Int. J. Chem. Kinet. 1978, 10, 599.



Figure 9. Effect of 1% toluene on the pyrolysis of 0.1% tetrahydrofuran in argon: (•) no toluene; (0) 1% toluene. There is no effect on the rate of production of propylene (b), a weak effect on that of ethylene (a), and a strong effect on the production rate of 1-butene (c). These effects reflect the extent of free-radical involvement in the process.

nondetection introduces a negligible error in the mass balance calculation.

The production rate of propylene is about 4 times slower than that of ethylene (Figure 2) but has the same Arrhenius temperature dependence. A calculation similar to the one done for ethylene (eq V) yields for propylene production (reaction 7) a rate constant $k = 8.25 \times 10^{15} \exp(-83 \times 10^3/RT) \text{ s}^{-1}$.

B. Effect of Toluene on the Production Rate of Ethylene, Propylene, and 1-Butene. There is a marked difference between reaction 7 and reaction 3 by which ethylene is formed. In reaction 7 the two species are stable molecules and free radicals are not involved. In reaction 5 the residue $(CH_2)_2$ -O further decomposes to produce the free radicals H and CH₃.

Following an attack on the tetrahydrofuran ring by these radicals the species $C_4H_7O^{\bullet}$ is formed. Similar to tetrahydrofuran, $C_4H_7O^{\bullet}$ will decompose to yield

$$\bigcup_{0} - C_2 H_4 + CO + CH_3$$
 (11)

and a chain reaction can then propagate.

The importance of the chain depends on how fast the decomposition of tetrahydrofuran radical (reaction 11) is in comparison to the decomposition rate of tetrahydrofuran (reaction 3). If, for example, the rates are identical, then the production of ethylene will be independent of the presence of free radicals.

To what extent the free radicals play a role in the initiation reactions can be clarified by the introduction of free-radical scavengers.

We ran several shocks in a mixture containing 0.1% tetrahydrofuran and 1% toluene in argon and compared the findings to runs in 0.1% tetrahydrofuran without toluene. The results are shown in Figure 9. Although the scatter is somewhat higher than usual, the picture is very clear. In propylene (Figure 9b) there is no effect of toluene. The open and closed circles scatter along one line. This is in agreement with the already established fact that propylene is formed in a unimolecular reaction. Also, the contribution of reaction 8 to its production is negligible.

The production of ethylene (Figure 9a) is inhibited by about a factor of 2 in the presence of 1% toluene as can be seen in the figure. This relatively weak inhibition implies only that the tetrahydrofuryl radical $C_4H_7O^{\bullet}$ decomposes to yield ethylene (reaction 11) somewhat faster than tetrahydrofuran.



Figure 10. Isotopic distribution of allene in postshock mixture of tetrahydrofuran and tetrahydrofuran- d_8 . The upper portion shows the original GC-MS spectrum; the lower portion shows only the parent ions. The intense peaks of C_3H_4 and C_3D_4 indicate that the allene is formed directly from the propylene.

The effect of toluene on the production of 1-butene is on the other hand very strong. It inhibits the rate by approximately a factor of 8. The production mechanism of butene clearly depends on free radicals. This is also strongly supported by the isotopic analysis of the butenes.

Following the elucidation of the initiation steps in the tetrahydrofuran pyrolysis, and determining the primary products, the remaining reaction products can be accounted for by consecutive uni- and bimolecular reactions. The methyl radicals and the hydrogen atoms produced by the decomposition of the intermediate $(CH_2)_2$ -O attack tetrahydrofuran and recombine (CH_3) to yield methane, ethane, and hydrogen.

C. Production of Allene and Methylacetylene. Together with these bimolecular reactions, we can account at this stage for the formation mechanism of H₂, CH₄, CO, C₂H₄, C₂H₆, C₃H₆, and CH₂O. The remaining products are obtained by further reactions of these molecules, both unimolecular reactions and reactions with the free radicals in the system. These reactions were discussed in the past in various publications. Methane,¹² ethane,¹³ and and ethylene,¹⁴ are known to produce acetylene at high temperatures as do all the C₃ compounds^{15,16} found in this pyrolysis. Burcat has shown that in propylene pyrolysis, allene is produced first, followed by the production of methylacetylene, probably via isomerization.¹⁷ The same behavior is found in this study as can be seen in the product distributions (Figure 2).

In Figure 10, the results of the GC-MS analysis in a postshock mixture of 1% tetrahydrofuran and 1% tetrahydrofuran- d_8 in argon for allene is presented. In Figure 10a the original spectrum is shown and in Figure 10b only the peaks of the parents are left. Allene, like propylene, preserves the original skeleton of the tetrahydrofuran. It consists mostly of C₃H₄ and C₃D₄, with small contributions from C₃D₃H and C₃H₃D, probably owing to isotope exchange. This picture clearly supports the conclusion that allene is formed from propylene.

The isotope effect for allene is somewhat smaller than for propylene, 1.36 compared to 1.63. This result is unclear.

Methylacetylene is formed from allene by unimolecular isomerization¹⁷ and must also be unscrambled. However, its mass spectrum is more complex and shows a high C_3D_3H peak. This is the result of the almost complete exchange of the acidic deu-

(17) Lifshitz, A.; Frenklach, M.; Burcat, A. J. Phys. Chem. 1975, 79, 1148.

⁽¹²⁾ Hertzberg, A.; Glick, H. A. In Fundamental Data Obtained from Shock Tube Experiments; Ferri, A., Ed.; Pergamon: New York, 1961; p 161. (13) Burcat, A.; Skinner, G. B.; Crossley, R. W.; Scheller, K. Int. J. Chem. Kinet. 1973, 5, 345.

 ⁽¹⁴⁾ Tanzawa, T.; Gardiner, Jr., W. C. Combust. Flame 1980, 39, 241.
 (15) Burcat, A. Fuel 1975, 54, 87.

⁽¹⁶⁾ Lifshitz, A.; Frenklach, M.; Burcat, A. J. Phys. Chem. 1976, 80, 2437.



Figure 11. Mass spectrum of 1-butene obtained by GC-MS analysis of postshock mixture of tetrahydrofuran and tetrahydrofuran- d_8 . The intense peaks of C₄H₅D₃ and C₄H₃D₅ support the conclusion that 1-butene is formed by attack of methyl radicals on propylene.

terium \underline{D} —C=C—CD₃, with the water absorbed on the walls of the ion source of the mass spectrometer.¹⁷ Its spectrum does not represent its original isotope distribution and is not useful for discussion.

D. Production of C_4 Compounds. The mechanism for 1-butene can be also elucidated from the isotope distribution of the butenes in a postshock mixture of tetrahydrofuran and tetrahydrofuran- d_8 . The original spectrum is shown in Figure 11. Fortunately, although the molecule has eight hydrogen atoms, its cracking pattern is rather simple. There is a loss of H, CH₃, and CH₅ (or D, CD₃, and CD₅ in the deuterated molecule), but not of two and three hydrogens which might complicate the interpretation. m/z 59 and 61, seen as intense peaks in the spectrum (in addition to m/z64 and 56), are ions corresponding to C₄H₅D₃ and C₄D₅H₃.

These two scrambled molecules are formed in the following two reactions:

$$CH_2 = CH - CH_3 + CD_3 \rightarrow CD_3 - CH_2 - CH - CH_3 \rightarrow CD_3 - CH_2 - CH = CH_2 + H (12)$$
$$CD_2 = CD - CD_3 + CH_3 \rightarrow CH_3 - CD_2 - CD - CD_3 \rightarrow CH_3 - CD_2 - CD = CD_2 + D (13)$$

We cannot comment as to whether there is a contribution to 1-butene from attachment of a hydrogen atom to the oxygen in the tetrahydrofuran followed by decomposition of the radical to 1-butene and OH. Such a possibility was raised in the discussion of ethylene oxide pyrolysis,⁴ when the formation of ethylene was considered. We believe that the main channel for 1-butene formation is methyl radical attack on propylene.

We could not obtain meaningful mass spectra for the rest of the C_4 molecules since they begin to appear in sufficient concentrations only at high temperatures, where extensive isotope exchange occurs. These C_4H_n molecules can be produced by degradation of C_4H_{n+2} precursors, but additional reaction channels probably do play a role in their production. At high temperatures the system approaches a semiequilibrium and the product distribution is controlled more by thermochemistry than by kinetics. The stable products at the high temperatures are H_2 , C_2H_2 , C_4H_2 , and other C_nH_m , where n > m, and the pyrolysis system approaches this composition.

It should be added that at high temperatures small concentrations of C_4H_4O , C_6H_6 , and C_6H_5 were also observed, but in very small concentrations. Also, no opening of the ring to produce isomers of tetrahydrofuran such as butyraldehyde was noticed.

E. The General Reaction Scheme. The overall pyrolysis of tetrahydrofuran can be summarized by the following reaction scheme, representing the major reactions that participate in the pyrolysis. (Some of the channels are represented in a schematic manner).

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