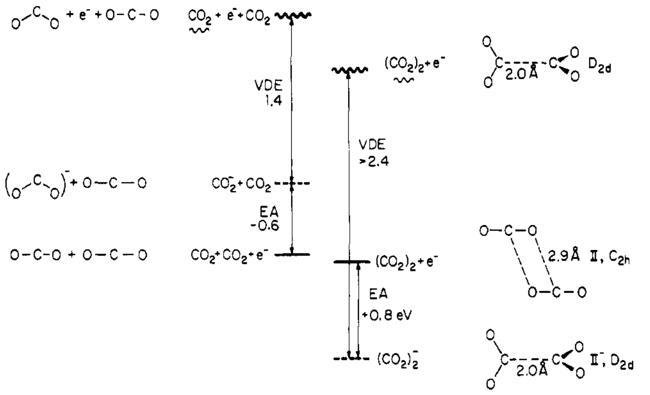

Figure 4. Estimates of energies and structures pertaining to carbon dioxide dimer neutral and anion. Double-headed arrows show vertical detachment energies in electron volts (from ref 10) and estimates of adiabatic electron affinities (from ref 5 for monomer, from present work for dimer). Corresponding geometrical structures are indicated, inferred from theory for monomer and dimer anions (ref 12) and from experiment for neutral dimer (ref 23-25).

While definitive results for electron attachment await improved experiments and calculations, we summarize in Figure 4 properties derived from several studies pertaining to $(CO_2)_2$ or its anion. For the neutral dimer, experiments and theory are in accord concerning both the structural parameters and dissociation energy.[22-25] There are two geometrical isomers of similar stability, both planar and involving nearly linear CO_2 monomer units: (I) a polar, T-shaped, C_{2v} isomer and (II) a nonpolar, "staggered side-by-side" C_{2h} isomer which is the prevalent form.[23-25] For the dimer anion, experiments and theory agree about some properties but not others. Evidence for two isomeric dimer anion species has been found by Margrave and co-workers[26] in infrared spectra of products from reaction of Li with CO_2 in argon matrices. One species is ascribed to an adduct $(Li^+CO_2^-)CO_2$ and the other to $Li^+C_2O_4^-$, corresponding to planar dimer anions of C_s and C_{2h} symmetry, respectively. Since on photolysis the latter species is converted to the former, the C_s isomer appears to be the more stable form in the matrix, but this might be affected by the proximity of the alkali-metal cation. The ab initio calculations[12] likewise indicate two isomers of similar stability, comprised of bent monomer units: (I^-) a polar, distorted-*T*, planar C_s isomer corresponding to a strongly bent CO_2^- ion solvated by a roughly linear CO_2 molecule and (II^-) a nonpolar, perpendicularly twisted nonplanar D_{2d} isomer. According to the calculations, the D_{2d} isomer is slightly more stable than the C_s isomer (by only ~0.2 eV) and its vertical detachment energy is more consistent with experiment,[10] but both isomers are predicted to be unstable with respect to the neutral dimer plus a free electron. Although in Figure 4 we portray the D_{2d} isomer as the ground state of the anion, this remains quite uncertain. Finally, we note that for the isoelectronic ions $(N_2O)_2^-$ and $(CS_2)_2^-$, Bowen and co-workers[27,28] find that the photodetachment spectra exhibit maxima at markedly lower electron binding energies than for the $(CO_2)_2^-$ anion. This offers further evidence for unusually strong bonding in the carbon dioxide dimer anion.

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Registry No. CO_2, 124-38-9; Rb, 7440-17-7.

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Thermal Reactions of Cyclic Ethers at High Temperatures. 5. Pyrolysis of 2,3-Dihydrofuran behind Reflected Shocks

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The thermal decomposition of 2,3-dihydrofuran was studied behind reflected shocks in a single-pulse shock tube over the temperature range 900–1300 K and overall densities of $\sim 2.5 \times 10^{-5}$ mol/cm^3. Under these conditions the following reaction products were found in the postshock analyses: c-C_3H_5CHO, $CH_3CH{=}CHCHO$, C_3H_6, CO, C_2H_4, C_2H_2, $CH_2{=}CO$, $CH_2{=}CHCH_2CH_3$, CH_4, C_2H_6, $CH_2{=}CHCHO$, butadiene, and small quantities of $CH_2{=}C{=}CH_2$, $CH_3{-}C{\equiv}CH$, and C_4H_4. The major reaction of 2,3-dihydrofuran is a unimolecular isomerization to cyclopropanecarboxaldehyde (c-C_3H_5CHO) with the following rate parameters: 2,3-dihydrofuran → c-C_3H_5CHO, $k_1 = 1.95 \times 10^{13} \exp(-49.38 \times 10^3/RT)$ s^{-1}, where *R* is expressed in units of cal/(K mol). The major fragmentation reaction of 2,3-dihydrofuran is the dissociation to ethylene and ketene with the following rate parameters: 2,3-dihydrofuran → C_2H_4 + $CH_2{=}CO$, $k_2 = 5.75 \times 10^{15} \exp(-69.28 \times 10^3/RT)$ s^{-1}. Propylene and carbon monoxide are the pyrolytic products of the highest concentration but are formed from the pyrolysis of cyclopropanecarboxaldehyde and not of 2,3-dihydrofuran. Rate parameters for the formation of the various reaction products are deduced, and the general reaction mechanism is discussed.

Introduction

We have recently published three studies describing the high-temperature pyrolysis of tetrahydrofuran,[1] furan,[2] and 2,5-dihydrofuran[3] behind reflected shocks in a single-pulse shock tube. Over the wide temperature range covered in these investigations extents of reaction below 0.01% up to close to 100% were mea-

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sured. A large number of products in each compound were found, and Arrhenius parameters for the rates of their formation were determined. The use of isotope labeling of the reactant and determining the isotope distribution in the products assisted in elucidating the general pyrolysis mechanism. This study presents a continued effort in trying to elucidate the pyrolysis mechanism of cyclic ethers and describes a study of the shock-initiated pyrolysis of 2,3-dihydrofuran.

As far as we are aware, the only report of a study on the pyrolysis of 2,3-dihydrofuran dates back to Wilson[4] in the late 1940s. In his study vapors of this compound were passed through a heated tube filled with pieces of broken glass, and an analysis of the reaction products was performed. Starting at 375 °C, the main product of the pyrolysis was cyclopropanecarboxaldehyde. As the temperature increased, the relative concentration of the latter decreased and crotonaldehyde, propylene, and carbon monoxide began to appear. At temperatures above 550 °C the only pyrolytic products were practically carbon monoxide and propylene.

The author explained his results by assuming two parallel decomposition channels in 2,3-dihydrofuran to yield cyclopropanecarboxaldehyde and crotonaldehyde which further decompose to carbon monoxide and propylene. No products other than those mentioned above were analyzed in the reacted mixture. Also, no rate parameters for the primary reactions were obtained.

In this article we present a detailed investigation of the high-temperature pyrolysis of 2,3-dihydrofuran over a wide temperature range. The distribution of reaction products is shown, the Arrhenius parameters for their formation rates are given, and the general pyrolysis mechanism is discussed.

Experimental Section

A. Apparatus. The pyrolysis of 2,3-dihydrofuran was studied behind reflected shocks in a pressurized driver 52-mm-i.d. single-pulse shock tube. The tube and the mode of its operation have already been discussed in a recent publication[5] and will be reported here only briefly.

The tube had a 4-m-long driven section divided in the middle by a 52-mm-i.d. ball valve and a variable driver section up to a maximum length of 2.7 m. The latter could be varied in small steps in order to obtain the best cooling conditions. A 36-L dump tank was connected to the driven section near the diaphragm position, in order to prevent reheating of the reaction mixture by the reflection of transmitted shocks. The high- and the low-pressure sections were separated by Mylar polyester film of various thickness depending upon the desired shock strength.

After the tube was pumped down to approximately 10^{-5} Torr, the reaction mixture was introduced into the section between the 52-mm-i.d. ball valve and the end plate and pure argon into the section between the diaphragm and the valve, including the dump tank. After the shock was fired, gas samples were collected from the tube through an outlet in the driven section (near the end plate) in 150-cm^3 glass bulbs and were analyzed on a Hewlett-Packard Model 5890A gas chromatograph using a flame ionization detector.

Reflected shock parameters were calculated from the measured incident shock velocities by using the three conservation equations and the ideal gas equation of state. The molar enthalpies of 2,3-dihydrofuran were taken from Wilhoit et al.[6]

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. The signals generated by the shock wave passing over the transducers were fed through a home-built piezo amplifier to a Nicolet Model 3091 digital oscilloscope. Time invervals between the two signals shown on the oscilloscope were obtained digitally with an accuracy of ~ 2 μs (out of about 450), corresponding to approximately 15 K. A third transducer (P.C.B. Model 113A26) placed in the center of the end plate provided measurements of the reaction times (approximately 1.8 ms) with an accuracy of $\sim 5\%$. Cooling rates were approximately 5×10^5 K/s.

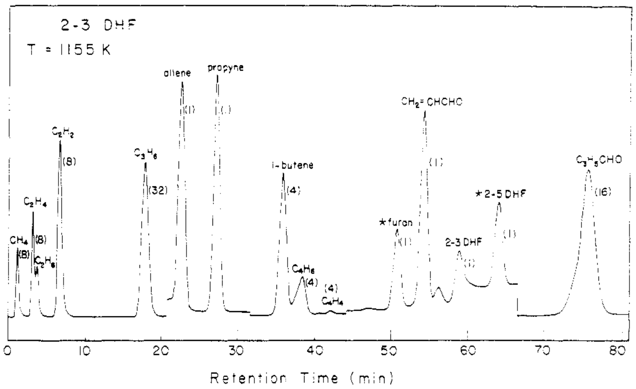

Figure 1. Gas chromatogram of a postshock mixture of 0.5% 2,3-dihydrofuran in argon at 1155 K where most of the reactant molecule has decomposed. The chromatogram is obtained on a Porapak N column. The numbers on the peaks indicate attenuations in powers of 2.

B. Materials and Analysis. A reaction mixture containing 0.5% 2,3-dihydrofuran in argon was prepared and stored at high pressure in a stainless steel cylinder. Both the gas handling system and the cylinder were pumped down to $\sim 10^{-5}$ Torr before the preparation of the mixtures.

2,3-Dihydrofuran was obtained from Fluka A.G. and was of purris grade listed as better than 99.5% pure. Argon and helium (driver gas) were obtained from the Matheson Gas Co. and were listed as 99.9995 and 99.999% pure, respectively. These materials were used without further purification.

The gas chromatographic analyses of the postshock mixtures were performed on two different columns. The analyses of all the products except for CO were performed on a 2-m Porapak N column. Its initial temperature of 35 °C was gradually elevated to 150 °C in an analysis which lasted about 80 min. Carbon monoxide was reduced to methane prior to its analysis in a separate run and was then analyzed on a room-temperature, 2-m molecular sieve 5A column. This analysis gave the ratio $[CO]/[CH_4]$ which, together with the methane concentration obtained in the Porapak N analysis, enabled the calculation of the CO concentration. The reduction of CO to methane was done on a Chrompak (Raney nickel) methanyzer which operated at 400 °C with a carrier composed of 50% hydrogen and 50% argon. The ratio $[CO]/[CH_4]$ in a standard mixture of methane and carbon monoxide was determined periodically in order to verify a complete conversion of the latter to methane in the methanyzer.

A gas chromatogram of the products obtained at 1155 K is shown as an example in Figure 1.

Identification of the reaction products was based on their retention times but was assisted also by GC/MS analyses which were performed on a VG ZAB-2F mass spectrometer. The two isomerization products that could not be unambiguously identified by the GC/MS alone were collected from the gas chromatograph in repeated experiments and were identified by their NMR spectra. Qualitative identification of unstable ketene ($CH_2{=}CO$) as a reaction product was done in several runs by extracting a sample from the tube into a bulb containing methyl alcohol and analyzing for methyl acetate.

The sensitivities of the various reaction products to the flame ionization detector were determined from measurements in standard mixtures. The GC peak areas were evaluated by a Spectra-Physics Model SP-4200 computing integrator and were transferred after each analysis to an Apple IIe in order to remove spurious peaks and noise and then to a C.D.C. CYBER 855 for data reduction and graphical presentation.

Evaluation of the Product Concentrations

The evaluation of the absolute concentration of the various

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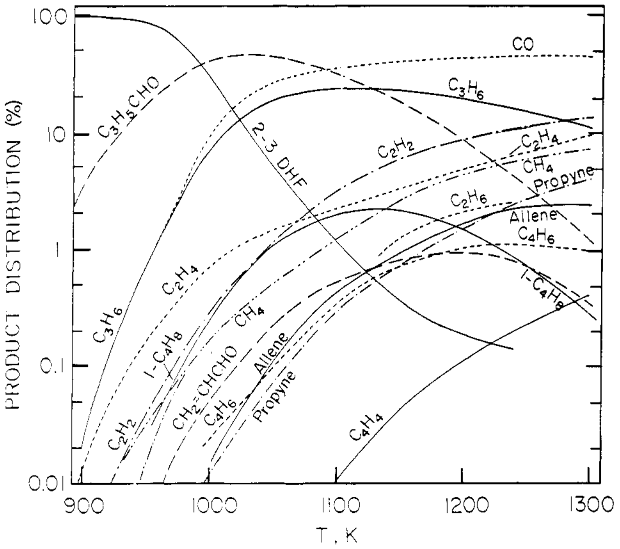


Figure 2. Product distribution in postshock mixtures of 0.5% 2,3-dihydrofuran in argon over the temperature range 900–1300 K. The species of the highest concentration are the isomerization products C_3H_5CHO.

reaction products from the area under their GC peaks was done in the following manner:

1. The concentration of 2,3-dihydrofuran behind the reflected shock prior to decomposition, $C_5(2,3\text{-DHF})_0$, is given by

$$C_5(2,3\text{-DHF})_0 = \{p_1[\%(2,3\text{-DHF})]\rho_5/\rho_1\}/100RT_1 \quad \text{(I)}$$

where p_1 is the pressure in the tube prior to shock heating, %(2,3-DHF) is the percent of 2,3-dihydrofuran in the original mixture, ρ_5/ρ_1 is the compression of the sample behind the reflected shock, T_1 is room temperature, and R is the gas constant.

2. The concentration of 2,3-dihydrofuran behind the reflected shock prior to decomposition in terms of its peak area, $A(2,3\text{-DHF})_0$, is given by

$$A(2,3\text{-DHF})_0 = A(2,3\text{-DHF})_t + 0.25\sum N(\text{pr}_i)\, A(\text{pr}_i)_t/S(\text{pr}_i) \quad \text{(II)}$$

where $A(2,3\text{-DHF})_t$ is the peak area of 2,3-dihydrofuran 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 its sensitivity relative to 2,3-dihydrofuran, and $N(\text{pr}_i)$ is the number of carbon atoms in a product i.

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

$$C_5(\text{pr})_i = A(\text{pr}_i)_t/S(\text{pr}_i)\{C_5(2,3\text{-DHF})_0/A(2,3\text{-DHF})_0\} \quad \text{(III)}$$

Since $A(2,3\text{-DHF})_0$ is not available in the postshock analysis, only $A(2,3\text{-DHF})_t$ is, its value must be calculated via eq II.

Experimental Results

In order to determine the distribution of reaction products and to determine their production rates and their temperature dependence, a series of experiments with mixtures containing 0.5% 2,3-dihydrofuran in argon were run, covering the temperature range 900–1300 K. The total gas densities behind the reflected shocks were approximately 2.5×10^{-5} mol/cm^3. Details of several representative tests are given in Table I. The table shows the temperature behind the reflected shock (T_5), the overall density behind the reflected shock in units of mol/cm^3 (C_5), and the percent of the various reaction products as obtained in the postshock analysis (not including argon). The concentration of 2,3-dihydrofuran behind the reflected shock prior to decomposition $\{C_5(2,3\text{-DHF})_0\}$ is given by the mole fraction of 2,3-dihydrofuran in the original mixture times C_5.

Figure 2 shows the product distribution obtained in postshock mixtures of 0.5% 2,3-dihydrofuran in argon over the 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

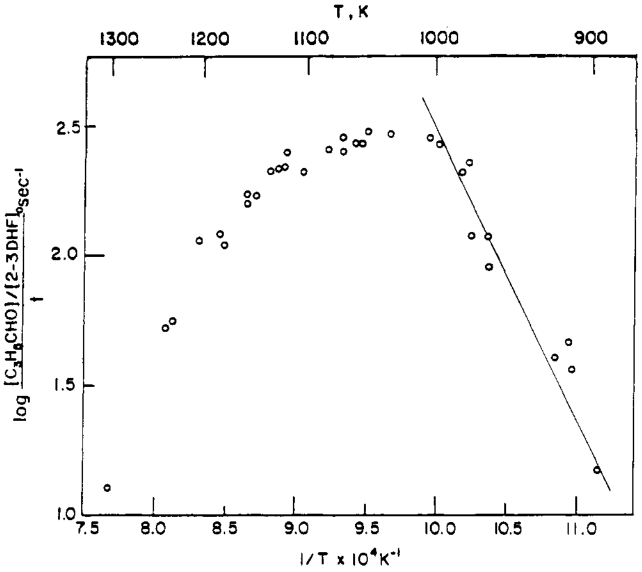


Figure 3. Plot of log $\{[C_3H_5CHO]_t/[2,3\text{-dihydrofuran}]_0\}/t$ against the reciprocal temperature. The slope of the line taken at the low-temperature range gives the Arrhenius activation energy for the unimolecular isomerization of 2,3-dihydrofuran, the major reaction in the system. E = 49.4 kcal/mol and $A = 1.95 \times 10^{13}$ s^{-1}.

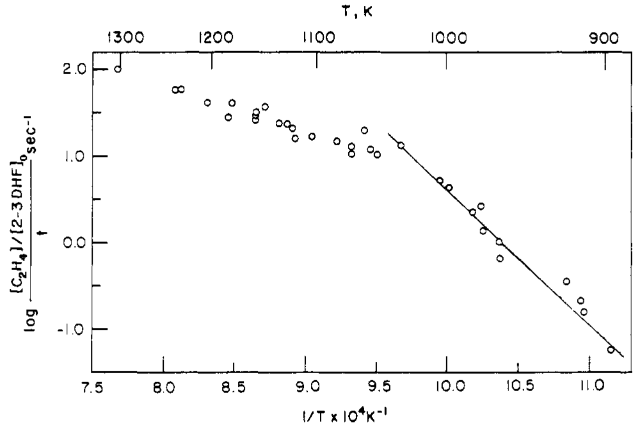


Figure 4. Plot of log $\{[C_2H_4]_t/[2,3\text{-dihydrofuran}]_0\}/t$ against the reciprocal temperature. Ethylene is obtained by a unimolecular decomposition of 2,3-dihydrofuran. The slope of the line taken at the low-temperature end gives the Arrhenius activation energy for this reaction. E = 69.3 kcal/mol and $A = 5.75 \times 10^{15}$ s^{-1}.

($100C_i/\sum C_i$), irrespective of the number of its carbon atoms. As can be seen, the major reaction products at the low-temperature end are the isomerization products, followed by equal concentrations of propylene and carbon monoxide. The latter become the main products at high temperatures. In addition to these, a large number of other products appear and disappear as the temperature is increased.

First-order rate constants for the production of the reaction products are calculated from the relation

$$k_{\text{first order}} = ([\text{Pr}_i]/t)/[2,3\text{-DHF}]_0 \quad \text{(IV)}$$

where $[\text{Pr}_i]$ is the concentration of a product i following a reaction time t and $[2,3\text{-DHF}]_0$ is the concentration of 2,3-dihydrofuran immediately behind the reflected shock prior to decomposition. It should be mentioned that eq IV is a good approximation for a first-order rate constant under the condition of low total conversion, namely, $[2,3\text{-DHF}]_t \simeq [2,3\text{-DHF}]_0$. At high conversions and therefore at high temperatures eq IV is no longer correct, in particular for reaction products that are formed and disappear at the same time.

As has been done in the previous studies,[2,5] rate constants and their temperature dependence $E(\text{Pr}_i)$ are calculated from the Arrhenius plots only from the lower section of the temperature range before bending of the Arrhenius curves begins to occur.

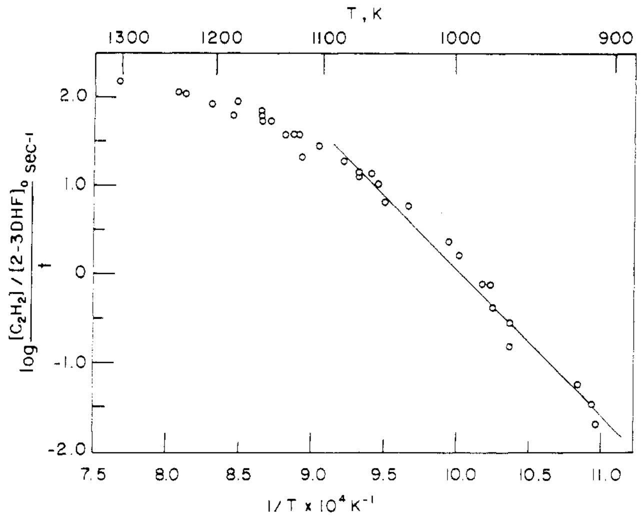


Figure 5. Plot of log $\{[C_2H_2]_t/[2,3\text{-dihydrofuran}]_0\}/t$ against the reciprocal temperature. Over the low-temperature range the line corresponds to a first-order rate constant of acetylene formation.

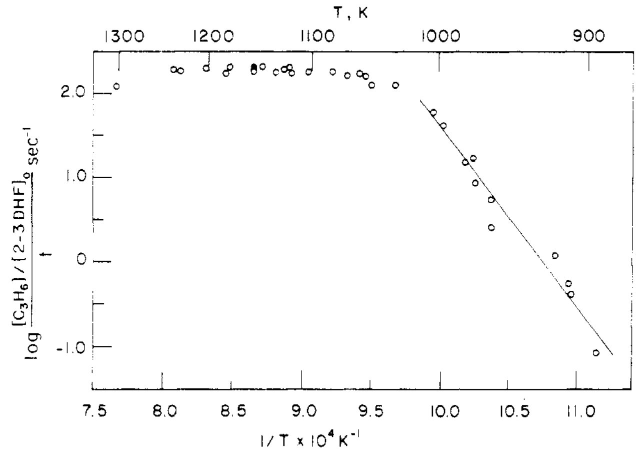


Figure 6. Plot of log $\{[C_3H_6]_t/[2,3\text{-dihydrofuran}]_0\}/t$ against the reciprocal temperature. Propylene is the major pyrolysis product. However, it is not formed directly from the decomposition of 2,3-dihydrofuran but through the decomposition of its isomerization product cyclopropanecarboxaldehyde.

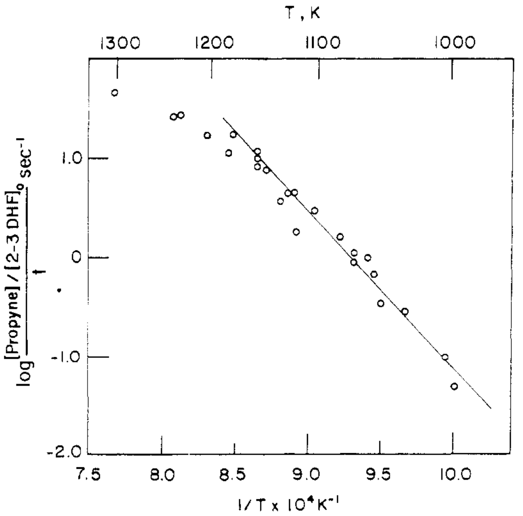


Figure 7. Plot of log $\{[CH_3C{\equiv}CH]_t/[2,3\text{-dihydrofuran}]_0\}/t$ vs $1/T$. Propyne is a minor reaction product and is formed by the decomposition of propylene. The Arrhenius temperature dependence for the rate of its formation is 74.0 kcal/mol.

In Figures 3–9 such curves for seven reaction products are shown, where the logarithm of $[\text{product}_i]_t/[2,3\text{-DHF}]_0$ divided by the reaction time t is plotted against the reciprocal temperature. The points on the curves are first-order rate constants ($k_{\text{first order}}$), although not all the products are formed in a unimolecular process. It provides, however, a convenient way to present the experimental data from which Arrhenius temperature dependencies and preexponential factors can be calculated and can serve as a basis for computer modeling of the general pyrolysis scheme.

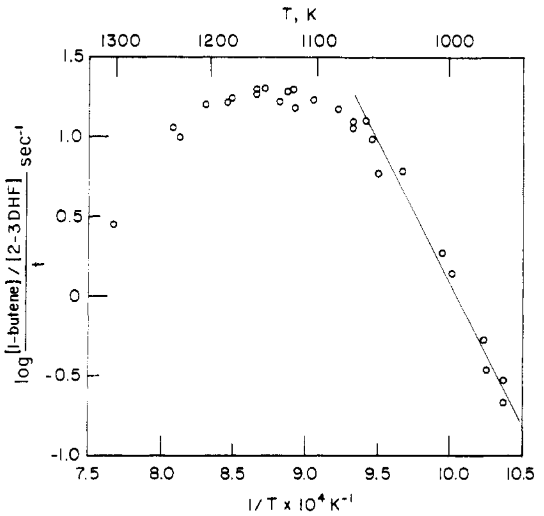


Figure 8. Plot of log $\{[1\text{-butene}]_t/[2,3\text{-dihydrofuran}]_0\}/t$ vs $1/T$.

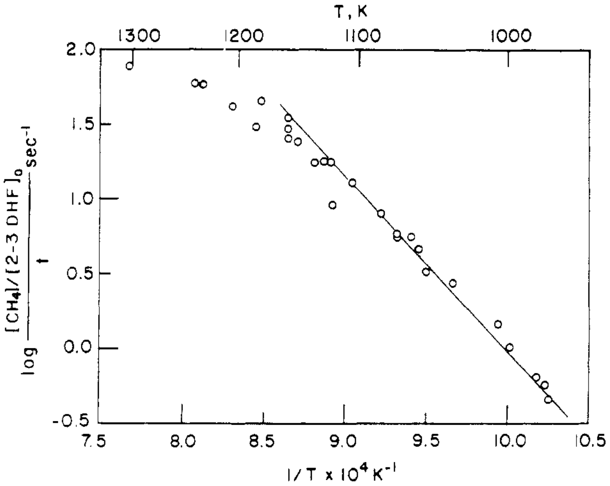


Figure 9. Plot of log $\{[CH_4]_t/[2,3\text{-dihydrofuran}]_0\}/t$ vs $1/T$. Methane is obtained by a reaction between methyl radicals and 2,3-dihydrofuran. These radicals are formed by the decomposition of the biradical $(CH_2)_2$–O.

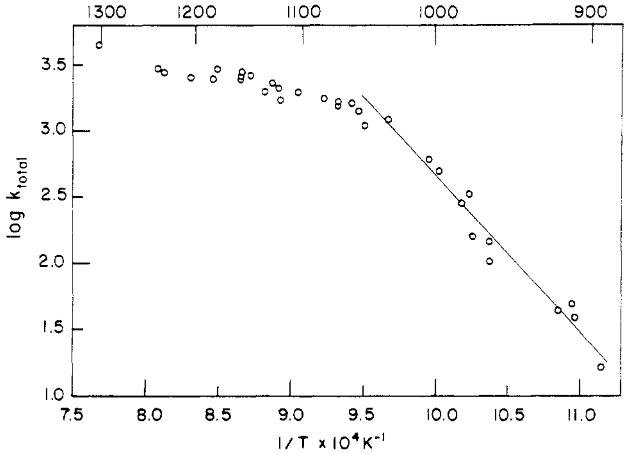


Figure 10. Plot of log k_{total} vs $1/T$ for the overall rate of 2,3-dihydrofuran decomposition.

Values of preexponential factors and Arrhenius temperature dependencies for the formation of the products obtained in this

TABLE I: Experimental Conditions and Product Distribution (in %) of Representative Tests

T, K	$10^5 C_5$, mol/cm^3	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	allene	propyne	1-butene	C_4H_6	C_4H_4	CH_2-CHCHO	CO	C_3H_5-CHO	2,3-DHF
922	1.89		0.063	0.010		0.20								6.81	92.6
964	1.87	0.039	0.20	0.054		1.02			0.056				0.95	21.9	74.8
1005	2.87	0.25	0.90	0.40		10.1	0.019	0.017	0.32	0.034		0.051	12.56	48.6	25.9
1072	2.32	0.73	1.41	1.68	0.28	21.2	0.22	0.12	1.48	0.16		0.32	30.4	37.1	2.89
1105	2.27	1.67	2.19	3.57	0.44	23.1	0.50	0.38	2.17	0.44	0.013	0.58	36.3	26.6	1.06
1155	2.23	3.85	3.57	7.77	1.55	23.5	1.19	1.28	2.19	0.98	0.077	0.97	34.9	17.2	0.26
1237	2.66	5.44	5.41	10.2	2.53	17.7	2.06	2.39	1.04	1.17	0.19	0.87	45.5	4.82	0.14
1303	2.79	7.12	9.49	13.9	4.29	11.4	2.40	4.21	0.26	1.06	0.41	0.33	43.9	1.18	0.0032

TABLE II: Preexponential Factors (A) and Arrhenius Temperature Dependencies (E) for the First-Order Rate Constants of Formation of the Various Products

molecule	log A/s^{-1}	E, kcal/mol	T, K
CH_4	11.88	54.4	900–1100
C_2H_4	15.76	69.3	900–1030
C_2H_2	16.60	75.8	900–1080
C_2H_6	14.90	72.6	1060–1175
C_3H_6	22.17	94.4	900–1030
$CH_2{=}C{=}CH_2$	18.73	90.9	960–1150
$CH_3C{=}CH$	15.00	74.0	1000–1150
$CH_2{=}CH{-}CH_2{-}CH_3$	17.94	81.7	970–1070
C_4H_6	14.96	72.5	980–1100
C_4H_4	18.37	98.7	1075–1175
$CH_2{=}CHCHO$	16.00	75.8	960–1080
C_3H_5CHO	13.29	49.4	900–1000
2,3-DHF[a]	14.47	54.2	900–1030

[a] First-order rate constant for the overall decomposition of 2,3-dihydrofuran.

investigation are summarized in Table II. The parameters are calculated from the above-mentioned figures by using the low-temperature section of the plots before bends begin to occur.

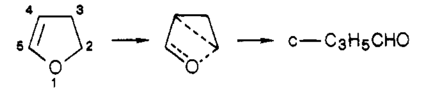
Figure 10 shows a plot of log k_{total} vs $1/T$ where k_{total}, which corresponds to overall rate of 2,3-dihydrofuran decomposition, is calculated from the relation

$$k_{total}t = -\ln\{(1 - x_t)/(1 - x_0)\} \tag{V}$$

where x_t is $\sum[Pr_i]_t/[2,3\text{-DHF}]_0$, x_0 is $\sum[Pr_i]_0/[2,3\text{-DHF}]_0$, and t is the reaction time.

The Reaction Mechanism

A. Unimolecular Reactions of 2,3-Dihydrofuran. a. Isomerization Reactions. Contrary to the thermal behavior of tetrahydrofuran,[1] furan,[2] and 2,5-dihydrofuran,[3] the main reaction channel in 2,3-dihydrofuran involves an isomerization process. The bridging between the 2- and 4-positions in 2,3-dihydrofuran and the cleavage of the 1–2 CO bond produce cyclopropanecarboxaldehyde as the major reaction product.



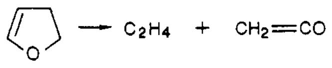
(1)

As can be seen in Figure 11, the latter isomerizes to crotonaldehyde as the temperature increases, in a similar process to the cyclopropane → propylene isomerization.

$$c\text{-}C_3H_5CHO \rightarrow CH_3CH{=}CHCHO \tag{3}$$

Owing to an incomplete separation of the GC signals of these two aldehydes (despite a serious effort to achieve one), we could not derive the rate constant for reaction 3 but only obtain the isomerization rate constant for reaction 1. This is shown in Figure 3 where the logarithm of [R-CHO]/[2,3-DHF]$_0$ (where [R-CHO] is the total aldehyde concentration) divided by the reaction time t is plotted against $1/T$. The rate constant obtained for this reaction is $k_1 = 1.95 \times 10^{13} \exp(-49.38 \times 10^3/RT)$ s^{-1}.

b. Production of Ethylene. The second unimolecular reaction that 2,3-dihydrofuran undergoes is the dissociation to ethylene and ketene



(2)

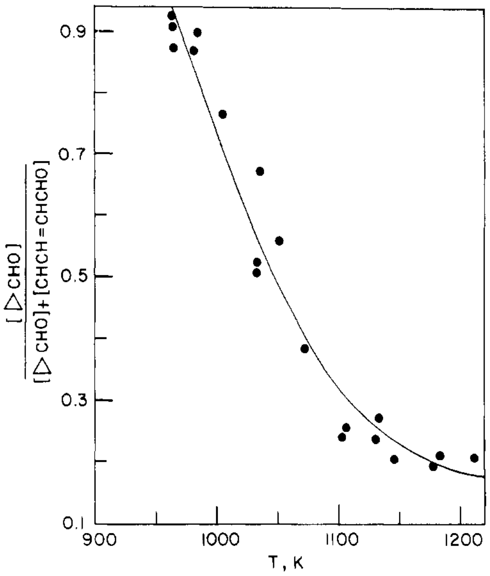
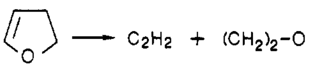


Figure 11. Fraction of cyclopropanecarboxaldehyde (c-C_3H_5CHO) in the total aldehyde concentration as a function of temperature, showing isomerization of the latter to crotonaldehyde.

with a rate constant of $k_2 = 5.75 \times 10^{15} \exp(-69.28 \times 10^3/RT)$ s^{-1} (Figure 4). This rate constant is very similar to the ones obtained for the same type of reaction in other five-membered ring ethers.[1,2] It corresponds to a loose transition state and suggests a biradical rather than a concerted dissociation. Since isotopically labeled reactant was not available to us, we could not perform experiments that will unambiguously show whether ethylene preserves the original skeleton of the dihydrofuran.[1] The presence of ketene ($CH_2{=}CO$) in the postshock samples is, however, a strong support for the assumption of a unimolecular dissociation of the 2,3-dihydrofuran to ethylene and ketene.

c. Production of Acetylene. A unimolecular dissociation of 2,3-dihydrofuran to yield acetylene takes place according to the reaction



(4)

It has already been shown[1] that the biradical $(CH_2)_2$-O which is obtained in this reaction decomposes to methyl radicals, H, and CO according to the reaction

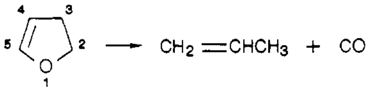
$$(CH_2)_2\text{-}O \rightarrow CH_3 + H + CO \tag{5}$$

If this reaction is indeed an elementary unimolecular reaction, then the concentration of acetylene should be roughly equal to $[CH_4] + 2[C_2H_6]$ since the methyl radicals will either abstract a hydrogen atom from 2,3-dihydrofuran to form methane or recombine to produce ethane. This fact is reflected in the product distribution as shown in Figure 2. The rate constant obtained for reaction 4 (Figure 5) is $k_4 = 3.98 \times 10^{16} \exp(-75.80 \times 10^3/RT)$ s^{-1}.

An interesting feature in the distribution of reaction products in 2,3- and 2,5-dihydrofuran is the ratio $[C_2H_4]/[C_2H_2]$. This ratio is higher than unity in 2,3-dihydrofuran (at least before C_2H_4 begins to decompose) and is considerably less than unity in the 2,5 isomer.[3] This can be very well understood by examining the structure of the two isomers, namely, the position of the C=C double bond in the molecules. Owing to the existence of a C=C bond in the 3,4-positions in 2,5-dihydrofuran, the elimination of acetylene from this molecule involves only a cleavage of a single C–C bond and is thus likely to occur. Ethylene cannot be formed from this molecule by a simple elimination, without the migration of hydrogen atoms and a change in the molecular structure. Whereas the production of acetylene in 2,5-dihydrofuran corresponds to a primary reaction, ethylene is formed in a secondary reaction and its concentration is thus very small.

2,3-Dihydrofuran on the other hand can in principle produce both ethylene and acetylene (reactions 2 and 4). However, owing to the existence of a C=C double bond in the 4,5-positions, the 1–5 C–O bond is stronger than the 1–2 bond and the production of ethylene by elimination from the 2,3-positions is more likely to occur than the production of acetylene by elimination from the 4,5-positions. This explains the high $[C_2H_4]/[C_2H_2]$ ratio in the product distribution of 2,3-dihydrofuran.

B. Production of Propylene. As can be seen in Figure 2, excluding the isomerization, propylene and carbon monoxide are the major pyrolysis products. It is interesting to see whether these products are formed directly from 2,3-dihydrofuran (reaction 6) or whether they are formed through the decomposition of one or both isomerization products.

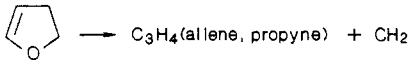


(6)

In order that a direct formation of propylene can take place, a migration of one hydrogen atom from the 2- to the 3-position with a simultaneous cleavage of the ring at the 1,5- and 2,3-positions must take place. Apparently such a process does not occur.

By examining the Arrhenius preexponential factor for propylene production (Figure 6 and Table II), it becomes obvious that propylene is not formed directly from 2,3-dihydrofuran. A preexponential factor of 10^{22} s^{-1} is not compatible with a preexponential factor of a single-step unimolecular reaction and is probably composed of a combination of preexponential factors. The thermal decomposition of the aldehydes must be the source of propylene and carbon monoxide and not the decomposition of 2,3-dihydrofuran.

C. Subsequent Reactions and the Production of Minor Reaction Products. Additional reaction products such as methane, ethane, allene, propyne, 1-butene, butadiene, etc., are also found in the postshock mixtures but at much lower concentrations. In the high-temperature environment that prevails behind the reflected shocks methyl radicals and hydrogen atoms are always present. Under these conditions products such as ethylene, propylene, etc., are known to be formed, and the mechanism of their formation will not be discussed here. An interesting question, however, is the mechanism of the formation of methylacetylene. This substance can be formed directly from the ring according to the reaction

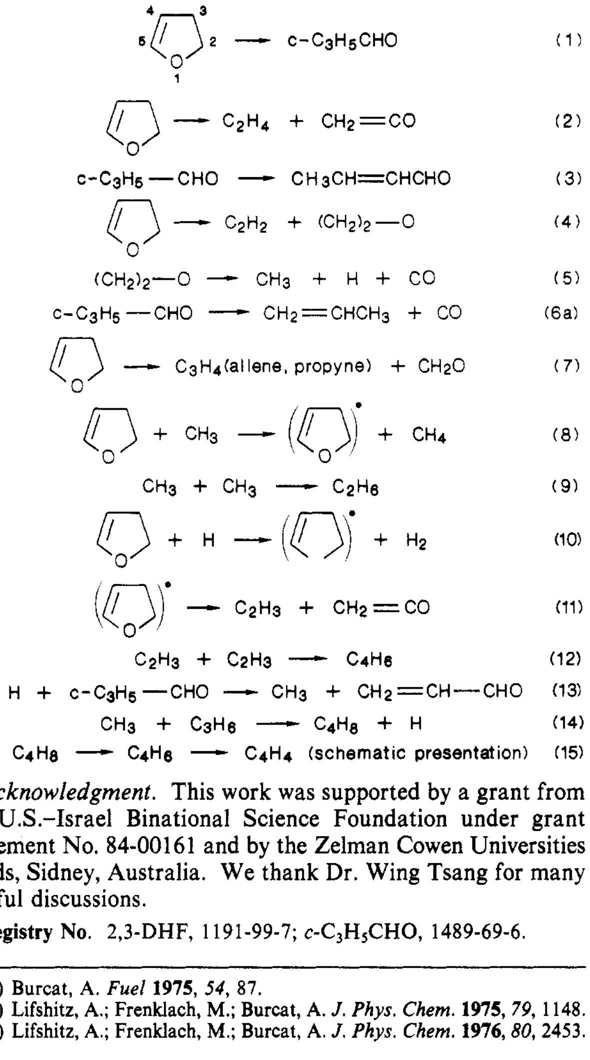


(7)

or alternatively from propylene as has been shown in the past.[7] We could not detect even traces of formaldehyde in the postshock samples to support the existence of reaction 7 although it is very hard to detect such small quantities of formaldehyde. In view of its very small concentration, we believe that methylacetylene is produced from propylene[7] with (or without) a small contribution from 2,3-dihydrofuran ring opening (reaction 7). Allene is known to be produced by the isomerization of methylacetylene.[8,9]

General Reaction Scheme of 2,3-Dihydrofuran Pyrolysis

The overall pyrolysis of 2,3-dihydrofuran can be summarized in the following reaction scheme. It contains the major reactions that participate in the pyrolysis.



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Registry No. 2,3-DHF, 1191-99-7; *c*-C_3H_5CHO, 1489-69-6.

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