Decomposition of Crotonaldehyde at Elevated Temperatures. Studies with a Single-Pulse Shock Tube

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The thermal decomposition of crotonaldehyde (CH₃CH=CHCHO) in concentrations of ~0.5% in argon was studied behind reflected shocks in a pressurized driver single-pulse shock tube over the temperature range 960–1350 K and overall densities of ~3 × 10⁻⁵ mol/cm³. Under these experimental conditions the following decomposition products were found in the postshock mixtures: CO, CH₄, C₂H₂, C₃H₆, CH₂=CHCHO, CH₃C=CCH, CH₂=C=CH₂, C₂H₄, C₂H₆, C₄H₄, C₂H₆ and 1-C₄H₆. One dissociative H atom migration (resulting in the unimolecular formation of propylene and carbon monoxide) and two dissociation reactions initiate the decomposition of crotonaldehyde: (1) CH₃CH=CHCHO → CH₃CH=CH₂ + CO, (2) C₃H₅CHO → CH₃• + CH[•]=CHCHO, and (3) C₃H₅CHO → CH₃CH=CH[•] + CHO[•]. Following secondary reactions the two dissociative channels (reactions 2 and 3) yield hydrogen atoms, methyl radicals, acetylene, and carbon monoxide. The second channel yields also acrolein (CH₂=CHCHO), and the third contributes to the production of propylene at higher temperatures. The rate parameters obtained for the overall pyrolysis of crotonaldehyde over the temperature and pressure ranges of this experiment are k_{total} = 10^{16.04} exp(-73 × 10³/RT) s⁻¹ where *R* is expressed in units of cal/(K-mol). The reactions of the initiation products as well as of free radicals lead to the formation of plethora of reaction products. Arrhenius rate parameters for their formation are reported, and a general pyrolysis scheme is suggested.

Introduction

Whereas a lot of effort has been devoted to the study of the kinetics of formaldehyde and acetaldehyde decomposition, and a large volume of information on their reactions has been accumulated, relatively little has been done in trying to elucidate the pyrolysis patterns of higher molecular weight aldehydes. When C_3 and C_4 aldehydes are concerned we are aware of only one investigation of the homogeneous gas-phase decomposition of crotonaldehyde¹ and of several publications on propionaldehyde decomposition.²⁻⁴ As far as we are aware, the homogeneous gas-phase pyrolysis of acrolein has never been studied in the past.

Cleavage of the C–C bond in acetaldehyde as initiation followed by free-radical chain reactions was suggested as the general pyrolysis scheme of acetaldehyde.⁵ A similar mechanism was suggested also for propionaldehyde.² Grela and Colussi studied the pyrolysis of crotonaldehyde under very low pressure conditions.¹ They suggested on the other hand a three-center decarbolination mechanism for the formation of propylene and carbon monoxide as the only reaction channel in the pyrolysis. No other reaction products were discussed.

Crotonaldehyde is a major reaction product in the pyrolysis of 2,3-dihydrofuran which has been recently investigated in this laboratory.⁶ It is produced by the isomerization of cyclopropanecarboxaldehyde, which itself is a structural isomer and a primary product of the cyclic ether. In addition to the formation of the two isomerization products in the pyrolysis of 2,3-dihydrofuran, a large number of decomposition products were obtained. Similar to the findings in the pyrolysis of crotonaldehyde, propylene and carbon monoxide were the major decomposition products. It could be established that propylene was not a primary product, but it was unclear whether it was produced from crotonaldehyde or from its predecessor cyclopropanecarboxaldehyde. One of the objectives of this investigation is to clear up this question by comparing the production rates of propylene in both studies.

The present investigation is part of a continuous effort to elucidate the pyrolysis pattern, the kinetics, and mechanism of the C_4H_6O isomers.^{6,7} In this article the distribution of reaction

(2) Acs, G.; Toth, G.; Huhn, P. Magiar Kemiai Folyoirat 1973, 79, 386.

products in crotonaldehyde decomposition studied over the temperature range 960–1350 K is presented, Arrhenius rate parameters for the production of the various products are given, and the mechanism of the overall pyrolysis is discussed. Differences and similarities in the low- and the high-pressure results and in the pyrolysis of other C_4H_6O isomers are also discussed.

Experimental Section

Apparatus. The decomposition of crotonaldehyde was studied behind reflected shocks in a single-pulse shock tube. The tube was made of 52-mm-i.d. electropolished stainless steel tubing. The driven section was 4 m long, and the driver had a variable length up to a maximum of 2.7 m and could be varied in small steps in order to tune for the best cooling conditions. A 36-L dump tank was connected to the driven section at 45° angle toward the driver, near the diaphragm holder, in order to prevent reflection of transmitted waves. The driven section was separated from the driver by Mylar polyester film of thickness ranging from 0.001 to 0.002 in., depending upon the desired shock strength. Prior to the experiment the tube was pumped down to approximately 2×10^{-5} Torr. After the shock was fired, gas samples were collected from the tube and were analyzed by gas chromatography using 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 crotonaldehyde were assumed to be the same as those of 2,3dihydrofuran and were taken from Wilhoit et al.^{8a} Since a mixture of only 0.5% crotonaldehyde in argon is used in these experiments, a small difference between the enthalpies of the latter and those of 2,3-dihydrofuran (if any) introduces a negligible error in the shock speed calculations. 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 piezo amplifier to a Nicolet Model 3091 digital oscilloscope. Time intervals between the two signals shown on the oscilloscope were obtained digitally with an accuracy of 2 μ s corresponding to 10–15 K

⁽¹⁾ Grela, M. A.; Colussi, A. J. J. Phys. Chem. 1986, 90, 434.

⁽³⁾ Acs, G.; Toth, G.; Huhn, P. Acta Chim. Hung. 1974, 82, 411.

⁽⁴⁾ Acs, G.; Toth, G.; Huhn, P. Acta Chim. Hung. 1974, 82, 425.

⁽⁵⁾ Colket, III, M. B.; Nageli, D. W.; Glassman, I. Int. J. Chem. Kinet. 1975, 7, 223.

⁽⁶⁾ Lifshitz, A.; Bidani, M. J. Phys. Chem. 1989, 93, 1139.

⁽⁷⁾ Lifshitz, A.; Bidani, M.; Bidani, S. J. Phys. Chem. 1986, 90, 6011.
(8) (a) Kudchadker, A. P.; Kudchadker, S. A.; Wilhoit, R. C. Furan Dihydrofuran Tetrahydrofuran; Key Chemical Data Books; Texas A&M University: College Station, TX, 1978. (b) Lifshitz, A.; Moran, A.; Bidani, S. Int. J. Chem. Kinet. 1987, 19, 61.

TABLE I: Experimental Conditions and Product Distribution (in Percent) in 10 Representative Experiments

| <i>T</i> , K | dwell time, µs | $\frac{C_5 \times 10^5}{\text{mol/cm}^3}$ | со | CH₄ | C₂H₄ | C ₂ H ₆ | C_2H_2 | C₃H ₆ | propyne | allene | 1-C₄H ₈ | C₄H ₆ | C₄H₄ | C₂H₃CHO | C₃H₅CHO |
|--------------|-------------------|---|-------|-------|--------|-------------------------------|----------|------------------|---------|--------|--------------------|------------------|-------|---------|---------|
| 987 | 1880 | 2.67 | 0.079 | 0.043 | 0.0026 | | 0.061 | 0.034 | | | | | | | 99.64 |
| 995 | 1800 | 2.65 | 0.133 | 0.041 | | | 0.056 | 0.027 | | | | | | 0.014 | 99.71 |
| 1020 | 1880 | 3.31 | 0.438 | 0.099 | 0.009 | | 0.13 | 0.054 | 0.0045 | | 0.012 | 0.014 | | 0.023 | 99.20 |
| 1065 | 1850 | 2.68 | 1.68 | 0.521 | 0.02 | 0.022 | 0.69 | 0.37 | 0.036 | | 0.026 | 0.127 | | 0.30 | 96.21 |
| 1078 | 1880 | 3.14 | 2.69 | 1.13 | 0.06 | 0.067 | 1.52 | 0.81 | 0.095 | | 0.060 | 0.293 | | 0.167 | 93.08 |
| 1102 | 1850 | 2.34 | 4.14 | 1.57 | 0.08 | 0.134 | 2.28 | 1.60 | 0.155 | | 0.14 | 0.380 | | 0.275 | 89.14 |
| 1122 | 1940 | 4.17 | 12.6 | 4.25 | 0.282 | 0.417 | 6.12 | 4.10 | 0.597 | 0.11 | 0.42 | 0.987 | 0.021 | 0.661 | 69.18 |
| 1185 | 1840 | 3.72 | 19.7 | 6.33 | 0.64 | 1.15 | 9.79 | 7.03 | 1.30 | 0.44 | 0.82 | 1.31 | 0.079 | 1.07 | 50.02 |
| 1232 | 1980 | 3.35 | 36.5 | 8.65 | 2.80 | 2.38 | 14.77 | 10.1 | 2.54 | 1.41 | 0.85 | 1.59 | | 1.26 | 16.46 |
| 1353 | 2000 | 3.57 | 41.8 | 11.1 | 8.01 | 1.10 | 19.23 | 6.28 | 3.25 | 1.72 | 0.23 | 1.08 | 0.54 | 0.50 | 4.43 |

depending upon the shock temperature. A third transducer (P.C.B. Model 113A26), placed at the center of the end plate, provided measurements of the reaction dwell times (approximately 2 ms) with an accuracy of ~5%. Cooling rates were approximately 5×10^5 K/s.

A more detailed description of the tube and its mode of operation have been described in previous publications.^{8b}

Materials and Analysis. Reaction mixtures containing 0.5% crotonaldehyde in argon were prepared manometrically and stored at 1 atm in 12-L glass bulbs. Both the bulbs and the vacuum line were pumped down to better than 10^{-5} Torr before the preparation of the mixtures.

Crotonaldehyde, listed as 99% pure, was obtained from Aldrich Chemical Co. None of the reaction products were found in the original material. Argon was Matheson ultra high-purity grade, listed as 99.9995%, and helium was Matheson pure grade, listed as 99.999%. All the materials were used without further purification.

The gas chromatographic analysis of the postshock mixtures was performed on two columns. The analysis of all the products except for CO was 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 an hour. Carbon monoxide was analyzed on a room-temperature 2-m molecular sieve 5A column. It was reduced at 400 °C to methane prior to its detection using a Chrompak methanyzer with a carrier composed of 50% hydrogen and 50% argon. This analysis gave the ratio $[CO]/[CH_4]$. From this ratio and the known methane concentration obtained in the Porapak N analysis, the concentration of CO could be calculated. The ratio [CO]/[CH₄] 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 typical chromatogram of a shocked mixture of 0.5% crotonaldehyde in argon heated to 1190 K is shown in Figure 1.

The identification of the reaction products was based on their retention times in the gas chromatograph. To assist in the gas chromatographic identification, chromatograms were run also on a VG ZAB-2F mass spectrometer which was used as a GC/MS. Each mass spectrum at the peak height was compared with standard spectra⁹ so that unknown peaks could be positively identified.

GC peak areas were integrated with a Spectra Physics Model SP4200 computing integrator and were transferred to a C.D.C. CYBER 180/855 main frame computer for data reduction and graphical presentations.

Experimental Results

Evaluation of Product Concentrations. Product concentrations were evaluated from their GC peak areas in the following manner:

1. The concentration of crotonaldehyde behind the reflected shock prior to decomposition, C_5 (crotonaldehyde)₀ is given by

 $C_5(crotonaldehyde)_0 =$

 $\{p_1 \times \% (crotonaldehyde)\rho_5/\rho_1\}/100RT_1$ (I)

where p_1 is the pressure in the tube prior to shock heating, %-(crotonaldehyde) is the percent of crotonaldehyde in the original



Figure 1. A gas chromatogram of a postshock mixture of 0.5% crotonaldehyde in argon heated to 1190 K. The chromatogram is obtained on a 2-m Porapak N column using flame ionization detector. The numbers on the peaks indicate relative attenuation factors.

mixture, ρ_5/ρ_1 is the compression behind the reflected shock, and T_1 is room temperature.

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

$$A(crotonaldehyde)_0 = A(crotonaldehyde)_t + \frac{1}{4} \sum N(pr_i) A(pr_i)_t / S(pr_i)$$
(II)

where $\mathcal{A}(crotonaldehyde)_i$ is the peak area of crotonaldehyde in the shocked sample, $\mathcal{A}(pr_i)_i$ is the peak area of a product *i* in the shocked sample, $S(pr_i)$ is its sensitivity relative to crotonaldehyde, and $N(pr_i)$ is the number of its carbon atoms.

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

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

$$C_5(\mathrm{pr})_i =$$

$$A(\text{pr}_i)_i / S(\text{pr}_i) \{C_5(\text{crotonaldehyde})_0 / A(\text{crotonaldehyde})_0 \}$$
(III)

Since $A(crotonaldehyde)_0$ is not available in the postshock analysis, only $A(crotonaldehyde)_t$ is, its value is calculated from eq II.

Product Distribution. In order to determine the distribution of reaction products in crotonaldehyde pyrolysis and to determine the production rates of the various products and their dependence on the temperature, tests were run with mixtures of 0.5% crotonaldehyde in argon, covering the temperature range 960–1350 K. Extents of pyrolysis as low as 0.1% could be determined. Details of the experimental conditions and the product distribution in 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 C_5 (in units of mol/cm³), and the percent of the various reaction products in the mixture as obtained in the postshock analysis (not including argon). The concentration of crotonaldehyde behind the reflected shock prior to decomposition { C_5 (crotonaldehyde)_0} is given by the percent

⁽⁹⁾ Cornu, A.; Massot, R. Compilation of Mass Spectral Data; Heyden: London, 1966.



Figure 2. A plot of {[CO] + [CH₂=CHCHO]} vs $^{1}/_{4}\sum(n_{C_{i}}[P_{C_{i}}])$ which demonstrates the oxygen-carbon mass balance among the decomposition products. $n_{C_{i}}$ is the number of carbon atoms in a product *i*, and $[P_{C_{i}}]$ is its concentration.



Figure 3. Production of carbon monoxide, acrolein, and ethylene. The points on the straight lines correspond to first-order rate constants from which Arrhenius parameters can be evaluated.



Figure 4. Production of acetylene, butadiene, and 1-butene. The points on the straight lines correspond to first-order rate constants from which Arrhenius temperature dependences and preexponential factors can be evaluated.



Figure 5. Production of propylene, propyne, and allene. The points on the straight lines correspond to first-order rate constants from which Arrhenius parameters can be evaluated.



Figure 6. Production of methane, ethane, and cumulene. The points on the straight lines correspond to first-order rate constants from which Arrhenius temperature dependences and preexponential factors can be evaluated.

of crotonaldehyde in the original mixture times C_5 . As can readily be seen, carbon monoxide, acetylene, propylene, and methane are the species of the highest concentration. As will be discussed later, all of these species are the result of unimolecular decomposition or abstraction by the unstable products of initiation.

Oxygen-Carbon Balance. The balance of oxygen vs carbon in the decomposition products is shown in Figure 2. The concentrations of carbon monoxide and acrolein (the only oxygencontaining products found in the postshock analysis) are plotted against the sum of the concentrations of all the species $1/4\sum$ $(n_{C_i}[P_{C_i}])$, where n_{C_i} is the number of carbon atoms in a species *i* and $[P_{C_i}]$ is the concentration of a species *i*. The 45° line in the figure represents a perfect mass balance. As can be seen, oxygen-carbon balance is maintained over the entire range of the experiments with some very slight tendency toward a loss of oxygen relative to four carbon atoms. The species that carries almost all the oxygen in the system is carbon monoxide.

Arrhenius Parameters. In Figure 3-6, rates of production of all the reaction products, defined as

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

and divided by the initial crotonaldehyde concentration are plotted against reciprocal temperature. They are expressed in units of

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

| | | F | | | | | | | | |
|--|-----------------|----------|-------------|--|--|--|--|--|--|--|
| compound | $\log A/s^{-1}$ | kcal/mol | Т, К | | | | | | | |
| C ₃ H ₅ CHO ^a | 16.04 | 73 | 950-1200 | | | | | | | |
| Major Reaction Products | | | | | | | | | | |
| CO | 16.60 | 77 | 1000-1150 | | | | | | | |
| C ₂ H ₂ | 15.94 | 74 | 950-1150 | | | | | | | |
| C ₂ H ₂ | 16.11 | 76 | 950-1150 | | | | | | | |
| CH₄ | 15.40 | 72 | 950-1150 | | | | | | | |
| Products of Medium Concentration | | | | | | | | | | |
| C.H.CHO | 14 08 | 69 | . 1000-1150 | | | | | | | |
| $C_{2}H_{4}$ (propyene) | 18 47 | 92 | 1000-1150 | | | | | | | |
| C.H. (butadiene) | 15 20 | 74 | 1075-1335 | | | | | | | |
| C_2H_6 | 18.50 | 93 | 1025-1200 | | | | | | | |
| Products of Minute Concentration | | | | | | | | | | |
| C.H 11000 | | 79 | 1075-1225 | | | | | | | |
| C_{2114} | 13.10 | 70 | 1000 1250 | | | | | | | |
| | 12.60 | 70 | 1000-1350 | | | | | | | |
| 1-C4H8 | 18.89 | 95 | 1020-1150 | | | | | | | |
| C ₃ H ₄ (allene) | 21.39 | 111 | 1060-1200 | | | | | | | |

^a First-order rate constant for the overall decomposition of crotonaldehyde.

s⁻¹ and at low extents of reaction resemble first-order rate constants. As can be seen, the lines bend as they approach the high-temperature end of the range. There are several reasons for these bends. Since the overall decomposition of crotonaldehyde is very complex, neither the disappearance of the reactant nor the production of any of the reaction products obeys a simple firstorder relation. The only way to evaluate a first-order rate constant is by calculating a pseudo-zero-order constant and dividing it by the initial crotonaldehyde concentration. This will be a good approximation as long as [crotonaldehyde]_t \simeq [crotonaldehyde]₀. At high conversions and therefore at high temperatures this condition is not fulfilled and the evaluation of the rate constant is incorrect. The rate constants are underestimated at high temperatures, causing bends in the log k vs 1/T plots. An additional reason for these bends is the temperature drop during the course of the reaction owing to the endothermicity of the overall decomposition which amounts in the present study to some 100 K for complete decomposition. Since the decrease in the rate constants owing to the drop in temperature will be more pronounced at high conversions (high temperatures), this again causes a bend in the log k vs 1/T plots. Values of E in units of kcal/mol as obtained from the slopes of the lines and their corresponding preexponential factors are summarized in Table II. They are obtained from the low-temperature, low-conversion range in the figures before the bends begin. It should be mentioned that although the points on each figure are calculated as first-order rate constants, they do not necessarily represent elementary unimolecular reactions. This is however a useful way to present the experimental data from which Arrhenius temperature dependencies and preexponential factors can be evaluated. These quantities can serve as a basis for computer modeling of the decomposition scheme.

In Figure 7 the first-order rate constant for the overall rate of decomposition of crotonaldehyde, $k_{\text{total}} = -\ln \{[\text{croton-aldehyde}]_t/[\text{crotonaldehyde}]_0]/t$, is shown. The value obtained is $k_{\text{total}} = 10^{16.04} \exp(-73 \times 10^3/RT) \text{ s}^{-1}$.

Discussion

It has been shown by Grela and Colussi¹ that the formation of propylene and carbon monoxide in the very low pressure pyrolysis (vlpp) of crotonaldehyde takes place via a three-center decarbolination mechanism

with a high-pressure rate constant (calculated from the low-



Figure 7. An Arrhenius plot for the overall decomposition of crotonaldehyde. $k_{\text{total}} = 10^{16.04} \exp(-73 \times 10^3/RT) \text{ s}^{-1}$.

pressure data) of $k_{\infty} = 10^{13.5} \exp(-59.7 \times 10^3/RT) \text{ s}^{-1}$. There was no mention of formation of other species in the pyrolysis.

Since a plethora of products at concentrations similar to that of propylene appear under the conditions of the present experiment, additional reactions do take place. The mechanism of their formation is straightforward. It is based on two parallel carbon-carbon bond cleavages adjacent to the C=C double bond.

$$CH_3CH = CH - CHO \rightarrow CH_3CH = CH^{\bullet} + CHO^{\bullet}$$
(2)

$$CH_3 - CH = CHCHO \rightarrow CH_3 + CH = CHCHO \quad (3)$$

Thus, in addition to the three-center production of propylene and carbon monoxide (reaction 1), the formation of the major products in the pyrolysis (Figures 3-6) results from the reactions of the unstable intermediates which are formed in reactions 2 and 3. They fall into the three categories of unimolecular dissociations, abstractions, and recombinations.

The secondary reactions in which species which are formed in the first dissociation channel (reaction 2) participate are

$$CH_3CH = CH^* \rightarrow CH_3C \equiv CH + H^*$$
(4)

$$CH_{3}CH = CH^{\bullet} \rightarrow CH_{3}^{\bullet} + CH = CH$$
(5)

$$CH_{3}CH = CH^{\bullet} + H^{\bullet} \rightarrow CH_{3}CH = CH_{2}$$
(6)

$$CH_3CH = CH - CHO + H^{\bullet} \rightarrow CH_3CH = CH_2 + CHO^{\bullet} \quad (6')$$

 $CH_{3}CH = CH^{\bullet} + C_{4}H_{6}O \rightarrow CH_{3}CH = CH_{2} + (C_{4}H_{5}O)^{\bullet} (7)$

$$CHO^{\bullet} \to H^{\bullet} + CO \tag{8}$$

The secondary reactions resulting from the second dissociation channel (reaction 3) are

$$CH^{\bullet} = CHCHO \rightarrow CH = CH + CHO^{\bullet}$$
(9)

$$CH^{\bullet} = CHCHO \rightarrow CH_2 = C = CO + H^{\bullet}$$
(10)

$$CH' = CHCHO + H' \rightarrow CH_2 = CHCHO$$
(11)

$$CH_{3}-CH=CHCHO + H^{\bullet} \rightarrow CH_{3}^{\bullet} + CH_{2}=CHCHO$$
(11)

$$CH^{\bullet} = CHCHO + C_4H_6O \rightarrow CH_2 = CHCHO + (C_4H_5O)^{\bullet}$$
(12)

$$CH_3 \cdot + C_4H_6O \rightarrow CH_4 + (C_4H_5O) \cdot$$
(13)

$$CH_3 \cdot + CH_3 \cdot \rightarrow C_2H_6$$
 (14)

Subsequent reactions which involve isomerizations and bimolecular reactions between free radicals and secondary products are the following:

$$CH_3^{\bullet} + CH_3CH = CH_2 \rightarrow CH_2 = CHCH_2CH_3 + H^{\bullet}$$
 (15)

2

$$CH_2 = CHCHO \rightarrow CH_2 = CH^{\bullet} + CHO^{\bullet}$$
 (16)

$$CH = CH + H^{\bullet} \rightarrow CH_2 = CH^{\bullet}$$
(17)

$$CH_2 = CH^{\bullet} + CH_2 = CH^{\bullet} \rightarrow C_4H_6$$
(18)

$$CH_2 = CH^{\bullet} + CH_3^{\bullet} \rightarrow CH_3CH = CH_2$$
(19)

$$CH_3C = CH \rightarrow CH_2 = C = CH_2$$
(20)

$$2CH_2 = C = CH_2 \rightarrow C_4H_4 + C_2H_4$$
(21)

$$H^{\bullet} + C_4 H_6 O \rightarrow H_2 + (C_4 H_5 O)^{\bullet}$$
 (22)

$$C_2H_6 + H^{\bullet} \rightarrow C_2H_5^{\bullet} + H_2$$
 (23)

$$C_2H_5^{\bullet} \to C_2H_4 + H^{\bullet}$$
(24)

$$H^{\bullet} + H^{\bullet} + M \rightarrow H_2 + M$$
 (25)

$$(C_4H_5O)^{\bullet} \to CH_3C = CH + CHO^{\bullet}$$
(26)

$$(C_4H_5O)^{\bullet} \rightarrow CH_3^{\bullet} + CH_2 = C = CO$$
 (27)

$$(C_4H_5O)^{\bullet} \rightarrow CH_3CH = CH^{\bullet} + CO$$
 (28)

It is of interest to compare the results obtained by Grela and Colussi in the vlpp of crotonaldehyde¹ to the results obtained in the present study in terms of the products obtained as well as the rate parameters. Before such a comparison is made, it should be stressed that the temperature range over which most of the data points were collected is roughly the same in both studies, but the pressure regimes are different. This study involves relatively high total pressures ($p \sim 2.5$ atm) and higher crotonaldehyde partial pressures.

It is not clear whether reaction products other than propylene were not formed under the conditions of the vlpp study or whether they were not identified. If the first case is true, then it is not clear why acetylene was not produced in the pyrolysis.

The formation of methane requires a collision between methyl and crotonaldehyde and would probably be too slow to be observed under the very low pressure conditions, but acetylene is formed by consecutive unimolecular dissociations (reactions 2 and 5) that should not be affected by pressure more than the three-center reaction that leads to the production of propylene. If acetylene was simply not identified (which we believe is the case), then the results are understood except that the high-pressure rate constant for propylene production does not correspond to the overall decomposition of crotonaldehyde.

Another possibility that should be examined is whether products such as acetylene and methane could not be produced by the decomposition of propylene. This however can be unequivocally ruled out on the basis of its known decomposition rate. As can be seen in Figures 4–6, acetylene and methane have production rates (and hence concentrations) similar to that of propylene. Over the temperature range 1000–1100 K where most of the data points in this study were collected, the thermal decomposition of propylene is extremely slow¹⁰ and cannot account for the observed high concentrations of methane and acetylene. It is clear that they are produced directly by the decomposition of crotonaldehyde.

The rate parameters for the production of propylene which were obtained in this study, i.e., $\log A/s^{-1} = 16.11$ and E = 76 kcal/mol, are very different from those calculated by Grela and Colussi and cannot correspond to a three-center mechanism. It should be stressed that these parameters do not correspond to an elementary unimolecular reaction since there are additional reactions that

produce propylene, such as reactions 6, 7, and 19. The contribution of these additional reactions to the production of propylene increases with temperature since it involves recombinations of free radicals whose concentrations increase with temperature by more than 60 kcal/mol. Such a behavior increases the slope of the Arrhenius curve which represents the production rate of the species in question. This very well explains the high preexponential factor and the high Arrhenius temperature dependence for the production rate of propylene obtained in this study.

The high-pressure rate constant calculated from the lowpressure data by Grela and Colussi is somewhat higher than the one obtained in this study for the overall decomposition of crotonaldehyde. This is particularly true in the low-temperature range of the present study. It is however by a factor of ~ 10 higher than the rate constant of propylene production at the low-temperature range and by about a factor of 3 higher at the high-temperature range of this investigation. There might be a slight slide into the falloff region in the present study, but this cannot explain such a big difference in production rates unless the calculated highpressure rate constant represent more than just the production of propylene. In any case the rate constant obtained by Grela and Colussi cannot be used for computer simulation of the results obtained in this study.

In the pyrolysis of 2,3-dihydrofuran, a structural isomer of crotonaldehyde, the latter is one of the major reaction products. It is preceded by cyclopropanecarboxaldehyde which isomerizes to crotonaldehyde. Propylene is the major *decomposition* product, and a question was raised whether the latter is a direct product of 2.3-dihydrofuran or whether it comes from the decomposition of one of the aldehydes. It has been established, on the basis of the extremely high preexponential factor in its Arrhenius plot, that propylene could not be a direct product of 2,3-dihydrofuran and must have been a secondary product, namely, a product of either cyclopropanecarboxaldehyde or crotonaldehyde. A comparison of the production rates of propylene in 2,3-dihydrofuran to those in the present study shows that propylene in 2,3-dihydrofuran cannot be produced from the decomposition of crotonaldehyde. At 1000 K the production rate of propylene in 2,3-dihydrofuran is higher by 2 orders of magnitude from its production rate in crotonaldehyde. It must therefore be produced from cyclopropanecarboxaldehyde. The latter isomerizes to crotonaldehyde and decomposes to propylene (and carbon monoxide) at the same time.

It has been shown that ethylene and acetylene are produced directly by unimolecular reactions of 2,3-dihydrofuran. In crotonaldehyde they are formed by dissociation of unstable intermediates produced by bond cleavage reactions. This is a marked difference which is due to the cyclic structure of 2,3-dihydrofuran.

Conclusion

The thermal decomposition of crotonaldehyde is initiated by three unimolecular reactions of which two are bond fission reaction and one involves a three-center decarbolination process. The overall rate of decomposition of crotonaldehyde is given by k_{total} = $10^{16.04} \exp(-73 \times 10^3/RT) \text{ s}^{-1}$. Acetylene and methylacetylene are obtained by successive unimolecular dissociations. Their ratio at very low conversions (~18) is a good measure for the ratio k_5/k_4 . These two products were not found in the vlpp of crotonaldehyde which is in disagreement with the results of the present experiment.

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⁽¹⁰⁾ Burcat, A. Fuel 1975, 54, 87.