Thermal Reactions of Pyrrolidine at Elevated Temperatures. Studies with a Single-Pulse Shock Tube

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The thermal decomposition of pyrrolidine was studied behind reflected shocks in a single-pulse shock tube over the temperature range 900-1400 K and overall densities of $\sim 3 \times 10^{-5}$ mol/cm³. Under these conditions the following reaction products were found in the postshock mixtures: H_2 , CH_4 , C_2H_4 , C_2H_6 , C_2H_2 , C_3H_6 , CH_2 — CH_2 , CH_3C — CH_2 , CH_2 CH_2 , HCN, CH₃CN, CH₂=CHCN, C₂H₃CN, and small quantities of pyrrole and butadiene. Studies with a mixture of pyrrolidine and pyrrolidine- d_9 show that C_2H_4 and C_3H_6 are produced by direct ring cleavage with the following rate parameters: pyrrolidine $\rightarrow C_2H_4 + (CH_2)_2$ -NH, $k = 3.42 \times 10^{16} \exp(-75.2 \times 10^3/RT) \text{ s}^{-1}$ and pyrrolidine $\rightarrow C_3H_6 + CH_2$ =NH, $k = 1.35 \times 10^{16} \exp(-80.4 \times 10^3/RT) \text{ s}^{-1}$, where R is expressed in units of cal/(K mol). Hydrogen cyanide has the highest concentration among the nitrogen-containing products, followed by acetonitrile. No reaction products resulting from pyrrolidine isomerization were observed.

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. This is particularly true when heterocyclics containing nitrogen as the heteroatom are concerned. The pyrolyses of several 5-membered ring ethers have been recently studied.¹⁻⁴ However, except for the study of H₂ elimination from 2,5-dihydropyrrole⁶ we are not aware of any attempt to study the thermal reactions of other 5-membered rings containing nitrogen such as pyrrole (C_4H_5N) and pyrrolidine (C_4H_9N) .

In addition to the interest in the basic chemical kinetics of these compounds, their pyrolysis studies are of great importance to the understanding of the combustion of nitrogen-containing fuels. Since considerable fuel pyrolysis occurs parallel to the oxidation processes, it is essential to understand the pyrolysis mechanism before the complete combustion scheme can be constructed. The determination of the distribution of the nitrogen among the various pyrolytic products and its temperature dependence is an important task in this context.

In this article the distribution of reaction products in pyrrolidine pyrolysis over the temperature range 900-1400 K is presented, and the pyrolysis mechanism is discussed. Similarities and differences between pyrrolidine pyrolysis and the pyrolysis of its isoelectronic molecule tetrahydrofuran are emphasized.

Experimental Section

A. Apparatus. The thermal decomposition of pyrrolidine was studied behind reflected shocks in a pressurized driver, 52 mm i.d. single-pulse shock tube made of stainless steel tubing. The tube and the mode of its operation have been described in previous publications and will be reported here only very briefly $\hat{1}$.⁷ The driven section was 4 m long and was divided in the middle by a 52-mm ball valve. The driver had a variable length up to a maximum of 2.7 m and could be varied 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 smoothness 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.

Before the shock was fired and after the tube was pumped down to approximately 10⁻⁵ Torr, the reaction mixture was introduced into the section between the 52-mm ball valve and the end plate and pure argon was introduced into the section between the diaphragm and the valve, including the dump tank. After the shock was fired, gas samples were taken from the tube through an outlet in the driven section near the end plate in 150-cm³ glass bulbs and were analyzed on a Hewlett-Packard Model 5890A gas chromatograph with 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 pyrrolidine were taken from Stull et al.8

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. 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 intervals between the two signals shown on the oscilloscope were obtained digitally with an accuracy of $\sim 2 \mu s$ (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 dwell times (approximately 1.8 ms) with an accuracy of ~5%. Cooling rates were approximately 5×10^5 K/s.

B. Materials and Analysis. Reaction mixtures containing 1% pyrrolidine in argon were prepared and stored at 1 atm in 12-L glass bulbs. Both the bulbs and the line were pumped down to better than 10⁻⁵ Torr before the preparation of the mixtures.

The pyrrolidine, listed as 99% pure, was obtained from Fluka A.G. The argon used was Matheson ultrahigh purity grade, listed as 99.9995%, and the helium was Matheson pure grade listed as 99.999%. Isotopically labeled pyrrolidine (C₄D₉N) was obtained from Stohler/Kor Stable Isotopes and was 98% isotopically pure. All the materials were used without further purification.

Gas analyses of the shocked samples were performed on two different columns in the following manner:

1. A 2-m Porapak N column was used to separate and quantitatively determine all the reaction products excluding pyrrole and pyrrolidine. The column's initial temperature of 35 °C was gradually elevated to 150 °C in an analysis which lasted about 80 min. A typical chromatogram of a mixture of 1% pyrrolidine in argon heated to 1245 K is shown in Figure 1.

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⁽⁸⁾ Stull, D. R.; Westrum, Jr., E. F.; Sinke, G. C. The Chemical Thermodynamics of Organic Compounds; Wiley: New York, 1969.

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



Figure 1. A typical gas chromatogram of a postshock mixture of 1% pyrrolidine in argon obtained on a Porapak N column. Pyrrolidine is not eluted from this column.

Retention Time (min)

40

50

60

70

(16) (16

30

20

10

2. A 2-m Tenax column was used to determine pyrrole and pyrrolidine. The latter were eluted from the Porapak N column only after several hours at 170 °C and could not be conveniently analyzed on that column. They were quantitatively determined relative to the light hydrocarbons C1-C3 and HCN which appeared as a single peak on the Tenax. Since the latter are known also from the Porapak N analyses, the two chromatograms could be combined and the concentration of each product relative to pyrrolidine could be determined. A typical Tenax chromatogram of a mixture shocked to 1000 K is shown in Figure 2.

We were unable to analyze the hydrogen in the GC because of the presence of relatively large quantities of helium which are trapped in the postshock mixtures and are eluted from the column very close to the hydrogen. Since the hydrogen peaks appear immediately after those of helium, they ride on their tail preventing a meaningful analysis to be performed. We therefore did not include molecular hydrogen in our product distribution and based our mass balance calculations on the carbon atoms only.

The identification of the reaction products was based on their retention time in the gas chromatograph in comparison with the retention time of the pure substance. The identification was assisted also by GC/MS measurements. Mass spectra were taken in 3-s intervals during the 80-min run time of the chromatogram. Each mass spectrum at the peak height was then compared with standard spectra9 in order to identify the product. The mass spectrometer used in these measurements and in the measurements of the isotopic distribution in the products was V.G. ZAB-2F.

The sensitivities of the reaction products to the flame ionization detector were determined relative to pyrrolidine from standard mixtures. The areas under the GC peaks were integrated by a Spectra Physics Model SP4200 computing integrator. The information accumulated on the integrator was transferred after each analysis to an Apple IIe in order to remove spurious peaks and noise, and then to a C.D.C. CYBER 180/855 for data reduction and graphical presentation.

Results

A. Evaluation of the Product Concentrations from the GC Peak Areas. The evaluation of the absolute concentrations of the various reaction products from the area under their GC peaks was done in the following manner:¹

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

 $C_5(\text{pyrrolidine})_0 = \{p_1 \times (\% \text{ pyrrolidine}) \rho_5 / \rho_1\} / 100RT_1 \quad (I)$ where p_1 is the pressure in the tube prior to shock heating, (%



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



Figure 2. A gas chromatogram of a postshock mixture of 1% pyrrolidine in argon obtained on a Tenax column. The concentration of pyrrolidine (and pyrrole) relative to C_1 - C_3 hydrocarbons and HCN are obtained from this column.

pyrrolidine) is the percent of pyrrolidine in the original mixture, ρ_5/ρ_1 is the compression behind the reflected shock, and T_1 is room temperature.

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

$$A(\text{pyrrolidine})_0 =$$

$$A(\text{pyrrolidine})_t + 0.25 \sum N(\text{pr}_i) A(\text{pr}_i)_t / S(\text{pr}_i)$$
 (II)

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

In tests where the shock temperature is low and the conversion is small, $C_5(\text{pyrrolidine})_0 \simeq C_5(\text{pyrrolidine})_t$ and the second term in the right-hand side of eq II which gives the amount of pyrrolidine 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

$$C_{5}(pr)_{i} = A(pr_{i})_{t} / S(pr_{i}) \{C_{5}(pyrrolidine)_{0} / A(pyrrolidine)_{0} \}$$
(III)

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

B. Presentation of the Experimental Results. In order to determine the distribution of reaction products in pyrrolidine pyrolysis and to determine the production rates of the various products and their dependence on the temperature, some 60 tests were run, covering the temperature range 900-1400 K. Extents of pyrolysis as low as a few hundredths of one percent could be determined. Details of the experimental conditions and the product distribution in five representative tests are 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 the argon). The concentration of pyrrolidine behind the reflected shock prior to decomposition $\{C_5(\text{pyrrolidine})_0\}$ is given by the percent of pyrrolidine in the original mixture times C_5 .

Figure 3 shows the product distribution obtained in shocked samples of 1% pyrrolidine in argon over the temperature range



Figure 3. Product distribution in postshock mixtures of 1% pyrrolidine in argon over the temperature range covered in this investigation. The major products are ethylene and hydrogen cyanide.



Figure 4. A plot of $\log \{[C_2H_4]_t/[pyrrolidine]_0\}/t$ against the reciprocal temperature. The slope of the line taken at the low-temperature range gives the Arrhenius activation energy for the major initiation reaction. $E_a = 75.2 \text{ kcal/mol.}$



Figure 5. A plot of $\log \{[C_3H_6]_i/[pyrrolidine]_0\}/t$ against the reciprocal temperature. Over the low-temperature range the line corresponds to the first-order rate constant of the minor initiation reaction pyrrolidine $\rightarrow C_3H_6 + CH_2 = NH$.



Figure 6. A plot of $\log \{[HCN]_t/[pyrrolidine]_0\}/t$ against the reciprocal temperature. The slope of the line in the figure corresponds to an activation energy of 75.4 kcal/mol.



Figure 7. A plot of $\{[CH_4]_{i}[pyrrolidine]_{0}/t \text{ vs } 1/T$. Methane is obtained by a reaction between pyrrolidine and CH₃. The latter is obtained by the decomposition of the biradical $(CH_2)_2$ -NH.



Figure 8. A plot of $\log \{[CH_3CN], [pyrrolidine]_0]/t vs 1/T$. Acetonitrile is the major nitrogen-containing product after HCN. The Arrhenius temperature dependence for the rate of its formation is 78.0 kcal/mol.

covered in this investigation. The percent of a given product out of the total shown in the figure corresponds to its mole fraction, $100C_i/\sum C_i$, irrespective of the number of its carbon atoms. (Molecular hydrogen is not included.)



Figure 9. A plot of log $\{[C_2H_2]_t/[pyrrolidine]_0\}/t$ against the reciprocal temperature. Both the preexponential factor and the Arrhenius temperature dependence are very high indicating that acetylene is not formed in a single-step unimolecular reaction.

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

molecule	A, s ⁻¹	$E_{\rm a}$, kcal/mol	<i>T</i> , K
CH₄	1.29×10^{16}	77.7	1000-1250
C ₂ H ₄	3.42×10^{16}	75.2	900-1200
C,H,	2.27×10^{19}	99.5	1100-1280
C ₁ H ₆	1.35×10^{16}	80.4	1000-1200
CH ₂ =C=CH ₂	2.97×10^{19}	98.0	1000-1200
CH ₃ C=CH	1.65×10^{18}	97.4	1100-1250
HCN	1.59×10^{16}	75.4	950-1180
CH ₂ =CHCH ₂ CH ₃	1.35×10^{15}	81.1	1000-1280
CHICN	1.08×10^{16}	78.0	1000-1200
pyrrolidine ^a	4.68×10^{16}	77.0	900-1250

^a Arrhenius parameters for the overall decomposition of pyrrolidine.

In Figures 4-9, the rates of production of the major reaction products, defined as

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

divided by the initial pyrrolidine concentration are plotted against the reciprocal temperature. They are expressed in units of 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 where the reactant is highly depleted (a typical behavior for this kind of a linear presentation).^{1,2,7} Values of E_a 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 range in the figures before the bends begin. Although the points on the figures resemble first-order rate constants ($k_{\text{first order}}$), not all of them necessarily represent elementary unimolecular reactions. This is, however, a useful manner to present the experimental data from which Arrhenius temperature dependencies and preexponential factors can be evaluated. 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.

In Figure 10 the first-order rate constant for the overall rate of decomposition of pyrrolidine, $k = \ln \{[pyrrolidine]_0/[pyrrol$ $idine_{t}/t$ is shown. It is roughly equal to the sum of the rate constants for the production of ethylene and propylene.

Discussion

A. The Pyrolysis Mechanism. a. The Initiation Reactions. In our recent study on the thermal reactions of the isoelectronic molecule tetrahydrofuran,¹ we suggested that the decomposition



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1400

1300

1200

Figure 10. A plot of log k vs 1/T for the overall rate of pyrrolidine decomposition.



Figure 11. Isotopic distribution of ethylene in a postshock mixture of pyrrolidine and pyrrolidine- d_9 . The upper part of the figure (a) shows the obtained mass spectrum at the ethylene peak height. The lower part (b) shows only the parent ions after removing the daughter ions and the background. The intense peaks of C_2H_4 and C_2D_4 indicate that ethylene preserve the original pyrrolidine skeleton.

was initiated by parallel reactions that involved the ring cleavage and elimination of ethylene and propylene according to the reaction

$$\Box_{0} \longrightarrow C_{2}H_{4} + (CH_{2}-)_{2}-0$$
(1)

$$\Box_{0} \longrightarrow C_{3}H_{6} + CH_{2}O \qquad (2)$$

This suggestion was based on the measurements of the isotopic distribution in the products obtained from experiments with mixtures containing tetrahydrofuran and tetrahydrofuran- d_8 . Since ethylene and propylene showed no isotopically scrambled products but only C_2H_4 as well as C_2D_4 and C_3H_6 as well as C_3D_6 , it was concluded that these products preserve the original skeleton of tetrahydrofuran and are thus formed by unimolecular elimination from the ring

We have repeated the same type of experiment in pyrrolidine by shock heating mixtures of pyrrolidine and pyrrolidine- d_9 and examining again the isotopic distribution in the ethylene and propylene formed in the pyrolysis. The results of this experimental are shown in Figures 11 and 12. Figure 11a shows the original mass spectrum of the ethylene and Figure 11b shows the spectrum



Figure 12. Isotopic distribution of propylene in a postshock mixture of pyrrolidine and pyrrolidine- d_9 . The upper part of the figure (a) shows the original GC/MS spectrum and the lower part (b) shows only the parent ions. The negligible contribution at m/z 44, 45, and 46 indicates that the propylene preserves the original skeleton of pyrrolidine and is therefore produced mainly via unimolecular elimination from the ring.

after removal of the background peaks of the ion source and the daughter ions, leaving only the parents. As can be seen, only C_2H_4 (m/z 28) and C_2D_4 (m/z 32) with some slight contribution from C_2H_3D (m/z 29) and C_2D_3H (m/z 31) (probably due to isotope exchange) are present. No $C_2H_2D_2$ (m/z 30) is observed. Similar results are shown in Figure 12a (original spectrum) and Figure 12b where only the parent ions are left. Here too the main contribution to propylene comes from C_3H_6 (m/z 42) and C_3D_6 (m/z 48). There is a contribution from C_3H_5D (m/z 43) and C_3D_5H (m/z 47), again, probably due to isotope exchange. The species $C_3H_4D_2$ (m/z 44), $C_3H_3D_3$ (m/z 45), and $C_3D_4H_2$ (m/z 46) which might be formed via a biomolecular free-radical mechanism (reactions 3–6) are either not present in the mixture or have a very small contribution.

$$CH_3 + CD_2 = CD_2 \rightarrow CH_3 - CD_2 - CD_2 \rightarrow D + CH_3 - CD = CD_2 (m/z \ 45) \ (3)$$

$$\rightarrow H + CD_3 - CD = CH_2 (m/z \ 46) \tag{4}$$

$$CD_3 + CH_2 = CH_2 \rightarrow CD_3 - CH_2 - CH_2 \rightarrow H + CD_3 - CH = CH_2 (m/z \ 45) \ (5)$$

$$\rightarrow D + CH_3 - CH = CD_2 (m/z \ 44) \tag{6}$$

We may therefore conclude that the initiation reactions in pyrrolidine pyrolysis are the same as those in tetrahydrofuran:

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$$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

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The rate constants obtained for these reactions are

$$k_7 = 3.42 \times 10^{16} \exp(-75.2 \times 10^3 / RT) \text{ s}^{-1}$$

 $k_8 = 1.35 \times 10^{16} \exp(-80.4 \times 10^3 / RT) \text{ s}^{-1}$

In view of the high preexponential factors (as has been obtained also in tetrahydrofuran decomposition) it can be concluded that the reaction proceeds via a biradical transition state rather than a concerted one.

Since partially deuteriated pyrrolidine was not available to us, the type of experiment that would clarify the question from what positions in pyrrolidine ethylene is eliminated could not be performed. However, as has been observed in tetrahydrofuran, we SCHEME I

$$C_{2}H_{4} + (CH_{2})_{2}-NH$$

$$C_{3}H_{6} + CH_{2} = NH$$

$$(CH_{2})_{2}-NH \longrightarrow HCN + CH_{3} + H$$

$$CH_{2} = NH \longrightarrow HCN + H_{2}$$

$$(CH_{2})_{2}-NH \longrightarrow CH_{3}CN + H_{2} (?)$$

$$CH_{3} + HCN \longrightarrow CH_{3}CN + H$$

$$CH_{3} + CH_{3} \longrightarrow C_{2}H_{6}$$

$$CH_{3} + C_{3}H_{6} \longrightarrow C_{4}H_{8} + H$$

$$C_{2}H_{4} \longrightarrow C_{2}H_{2} (schematic presentation)$$

$$C_{3}H_{6} \longrightarrow allene (schematic presentation)$$

$$C_{3}H_{6} \longrightarrow c_{4}H_{6} (schematic presentation)$$

$$C_{3}H_{8} \longrightarrow C_{4}H_{6} (schematic presentation)$$

$$C_{4}H_{8} \longrightarrow C_{4}H_{6} (schematic presentation)$$

$$R(CH_{3}, H) + N \longrightarrow C_{2}H_{4} + HCN + CH_{3}$$

$$\left(\bigcap_{N} \stackrel{\circ}{\longrightarrow} \stackrel{$$

believe that in pyrrolidine pyrolysis as well, ethylene is eliminated from both the 3,4 and the 2,3 (4,5) positions.

A marked difference between the initiation reactions in the two decomposition studies is the relative reaction rates of reactions 1 and 2 in tetrahydrofuran as compared to reactions 7 and 8 in pyrrolidine. Whereas the ratio [ethylene]/[propylene] in tetrahydrofuran is about 4, in pyrrolidine it is much higher, about 20.

b. The Subsequent Reactions. The reactions that follow the initiation steps are determined by the reactions of the species CH_2 —NH and $(CH_2)_2$ -NH which are formed in reactions 7 and 8. These reactions determine also the distribution of the nitrogen among the various reaction products. We are not aware of previous investigations dealing with the thermal reactions of these species. They should therefore be examined in analogy with the reactions of the isoelectronic species containing oxygen that are formed in the initiation steps of tetrahydrofuran pyrolysis (reactions 1 and 2). These are formaldehyde and $(CH_2)_2$ -O.

Formaldehyde is known to decompose to carbon monoxide¹⁰ by reactions 9 and (probably) 10.

It is therefore reasonable to assume that the species CH_2 —NH will decompose in a similar manner to yield HCN and H_2 by either one- or two-step mechanism.

$$CH_2 = NH \rightarrow HCN + H_2$$
 (11)

⁽¹⁰⁾ Warnatz, J. In Combustion Chemistry; Gardiner, Jr., W. C., Ed., Springer-Verlag: New York, 1984; p 338.

The biradical which is formed in tetrahydrofuran decomposition (reaction 1), $(CH_2)_2$ -O, decomposes according to the reaction¹

$$(CH_2)_2 - O \rightarrow H + CH_3 + CO$$
(12)

where the methyl radicals are the source for the large quantities of methane found in tetrahydrofuran decomposition. A similar reaction in pyrrolidine would be

$$(CH_2)_2 - NH \rightarrow H + CH_3 + HCN$$
 (13)

Since reaction 7 has the highest rate in the pyrolysis, the large quantities of HCN found in the shocked samples support the conclusion that reaction 13 is the main supplier of hydrogen cyanide.

The second largest nitrogen-containing product is acetonitrile. The question is whether the latter can be formed via the rearrangement of the biradical

$$(CH_2)_2 - NH \longrightarrow CH_3 - CH = NH$$
 (14)
 \downarrow
 $CH_3CN + H_2$

or whether it is formed by a reaction between methyl radicals and hydrogen cyanide, both reaction products:

$$CH_3 + HCN \rightarrow CH_3CN + H$$
 (15)

The equivalent of reaction 14 with $(CH_2)_2$ -O would be its rearrangement to acetaldehyde:

$$(CH_2)_2 \rightarrow CH_3CHO$$
 (16)

As has been discussed in our tetrahydrofuran pyrolysis article,¹ no traces of acetaldehyde were found among the reaction products, thus ruling out completely the existence of reaction 16.

Whether reaction 14 takes place or not, can be determined by using a specifically labeled pyrrolidine:



Acetonitrile with two isotopically identical carbon atoms would then rule out reaction 14. Unfortunately, we were unable to obtain such a labeled pyrrolidine and the question of reaction 14 remains an open question until such a molecule can be made available.

The production mechanism of the additional two nitriles which are found among the reaction products, acrylonitrile and ethane nitrile, has been described in a previous article⁵ dealing with the thermal reactions of acetonitrile. Since a similar environment prevails under the experimental conditions of the present study, their production mechanism may be assumed to be the same.

Similar to the observations in tetrahydrofuran decomposition we did not observe any products resulting from isomerization reactions of pyrrolidine. It should be mentioned that preliminary results on the reactions of pyrrole (C_4H_4NH) show a number of isomerization products resulting from the ring opening of the latter.⁵ Similar reactions in furan could not be established.²

B. The Pyrolysis Scheme. The overall pyrolysis of pyrrolidine can be summarized in Scheme I. It contains the major reactions that participate in the pyrolysis. Some of the later reactions in the pyrolysis are given as overall (schematic) processes for simplicity.

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Scattering Anisotropy of Partially Oriented Samples. Turbidity Flow Linear Dichroism (Conservative Dichroism) of Rod-Shaped Macromolecules

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Light-scattering anisotropy of partially oriented macromolecules or particles is important in several contexts; however, owing to the generally rather complex forms of both the scattering expressions and the orientational distributions that these have to be integrated over, very few calculations have been made. We calculate here the scattering flow linear dichroism ("conservative dichroism") of rodlike, nonabsorbing and noninteracting particles of varying size and shape that are partially oriented in a Couette flow cell and observed along a radial optical direction. The scattering is calculated according to the Rayleigh-Gans-Debye approach and the flow orientation described by the Peterlin-Stuart theory for rigid particles. It is found convenient to define a "reduced turbidity linear dichroism", $LD_r^r = (\tau_{\parallel} - \tau_{\perp})/\tau_{iso}$, analogous to the ordinary, absorptive reduced dichroism, LD_A^r . Unlike LD_A^r , however, LD_r^r is generally not factorizable into separate "optical" and "structural" terms but is expected to depend on higher moments of the orientational distribution. The scattering anisotropy at complete orientation varies with particle geometry and increases monotonically with the length of particles whose diameter is small compared to the wavelength of light. Measured linear dichroism of very long, rod-shaped aggregates of the protein tubulin, oriented in Couette flow, shows fair agreement with the calculated dependence of LD^r, with gradient and, furthermore, allows comparison between turbidity dichroism and absorptive dichroism to be made.

Introduction

Among current methods for studying macroscopically oriented samples, linear dichroism is finding increasing use. An advantage to dispersive phenomena, such as polarized scattering and birefringence, is that linear dichroism can often be directly related to structure, through the directional properties of the light-absorbing electronic or vibrational transitions.¹⁻³ In addition, linear dichroism is today very sensitively measured by modulation techniques,^{4,5} as has been exploited extensively, for example, for

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⁽¹⁾ Thulstrup, E. W. Aspects of the LD and MCD of Planar Organic Molecules; Springer: Berlin, 1980.

⁽²⁾ Nordén, B. Appl. Spectrosc. Rev. 1978, 14, 157-248.

⁽³⁾ Michl, J., Thulstrup, E. Spectroscopy with Polarized Light; VCH Verlagsgesellschaft: Weinheim, FRG, 1986.