# Thermal Decomposition of N-Methylpyrrole: Experimental and Modeling Study

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The thermal decomposition of N-methylpyrrole was studied behind reflected shocks in a pressurized driver single pulse shock tube over the temperature range 1050–1300 K at overall densities of  $\sim 3 \times 10^{-5}$  mol/cm<sup>3</sup>. A large number of decomposition products with and without bound nitrogen were obtained under shock heating. High concentrations of isomerization (2- and 3-methylpyrrole) and six-membered ring compounds (pyridine) were also found. The main decomposition channel is initiated by a rupture of the N–CH<sub>3</sub> bond with a rate constant of initiation  $k_{init} = 10^{16.26} \exp(-79.5 \times 10^3/RT) \text{ s}^{-1}$ , where R is expressed in units of cal/(K mol). Abstraction reactions and recombination of methyl radicals lead to the production of a line of hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>. Abstraction of a hydrogen atom from the N–CH<sub>3</sub> group leads to the production of C<sub>4</sub>H<sub>4</sub>N–CH<sub>2</sub><sup>•</sup> which upon ring enlargement produces pyridine. Toluene was used as a free radical scavenger to distinguish between radical chains and unimolecular processes. Reaction products such as CH<sub>3</sub>CN are obtained by a unimolecular decomposition of the N-methylpyrrole ring. The total decomposition of N-methylpyrrole in terms of a first-order rate constant is given by  $k_{total} = 10^{16.7} \exp(-79.2 \times 10^3/RT) \text{ s}^{-1}$ . First-order Arrhenius rate parameters for the formation of the various reaction products are given, a reaction scheme is suggested, and results of computer simulation and sensitivity analysis are shown. Differences and similarities in the reactions of pyrrole and N-methylpyrrole are discussed.

## Introduction

The investigation of the thermal reactions of N-methylpyrrole is part of a continued effort, undertaken in this laboratory, to elucidate the kinetics and mechanism of nitrogen-containing ring molecules which can be considered as prototypes of fuel nitrogen. In the frame of this effort we have recently reported studies on the decomposition pattern of pyrrolidine,<sup>1</sup> pyrrole,<sup>2</sup> isoxazole,<sup>3</sup> 3-methylisoxazole,<sup>4</sup> tetrahydropyridine,<sup>5</sup> and some other nitrogencontaining species.<sup>6,7</sup>

Replacement of the N-H bond by a N-CH<sub>3</sub> bond in the pyrrole ring introduces a relatively weak bond to the molecule as compared to pyrrole. Since the ejection of such a methyl group from the ring is usually characterized also by a high preexponential factor it is expected that, upon shock heating, this reaction will be a major initiation process. Products resulting from reactions of methyl radicals will thus be dominant.

The effort devoted by the scientific community to the study of the high-temperature reactions of nitrogen-containing heterocyclics is minimal. Reactions of pyridine<sup>8</sup> and pyrrole<sup>9</sup> and butenenitriles,<sup>10</sup> which are major isomerization products of pyrrole, have been recently reported. We are not aware of any recent study on the thermal reactions of *N*-methylpyrrole except for some preliminary, unpublished results.<sup>11</sup> There are some old studies on the thermal reactions of 1-methyl-,<sup>12</sup> 1-*n*-butyl-,<sup>13</sup> and 1-isopropylpyrrole.<sup>14</sup> Both flow and static methods were employed, but only the isomerizations of these reactants, resulting from the migration of the alkyl group from position 1 to positions 2 and 3 in the ring, were reported.

It is the purpose of this investigation to examine in detail the thermal reactions of N-methylpyrrole at combustion temperatures. In this frame, the product distribution over a wide temperature range is obtained, the Arrhenius parameters for the rate of their formation are determined, a reaction scheme describing the entire pyrolysis mechanism is suggested, and computer modeling, including sensitivity analysis, is shown. Differences and similarities in the thermal reactions of pyrrole and N-methylpyrrole are discussed.

# **Experimental Section**

I. Apparatus. The reactions of N-methylpyrrole were studied behind reflected shocks in a pressurized driver single pulse shock tube made of 2 in i.d. "double tough" Pyrex 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 a  $45^{\circ}$  angle toward the driver, near the diaphragm holder, to prevent reflection of transmitted waves and to reduce the final pressure in the tube to facilitate the extraction of gas samples. The driven section was separated from the driver by Mylar polyester films of various thickness depending upon the desired shock strength.

Prior to performing an experiment the tube was pumped down to approximately  $2 \times 10^{-5}$  Torr. After firing the shock, gas samples were collected through an outlet in the end block of the driven section and were analyzed by various methods as will be described later.

Reflected shock parameters were calculated from the measured incident shock velocities using the three conservation equations and the ideal gas equation of state. The incident shock velocities were measured with two miniature, high-frequency pressure transducers (Vibrometer Model 6QP500) placed 230 mm apart at the downstream end 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 (approximately 300  $\mu$ s) were obtained digitally with an accuracy of 2  $\mu$ s corresponding to 10–15 K 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<sup>5</sup> K/s.

A more detailed description of the tube and its mode of operation have been presented in previous publications.<sup>6</sup>

II. Materials and Analysis. Reaction mixtures containing 0.5%N-methylpyrrole in argon were prepared by injecting 0.22 mL of N-methylpyrrole into 12-L glass bulbs which were then filled with argon to 700 Torr. Both the bulbs and the vacuum line were pumped down to better than  $10^{-5}$  Torr before preparation of the mixtures.

Pyrrole, listed as 99% pure, was obtained from Aldrich Chemical Company Inc. 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.

Gas analyses were performed in the following manner: shocked samples were injected into the gas chromatograph (HP Model 5890) and were then equally divided between two 2-m Porapak N columns. One column, connected to a nitrogen-phosphor detector (NPD), separated and quantitatively determined all the species with bound nitrogen. A second column, connected to a flame-ionization detector (FID), separated and quantitatively determined all the species in the post-shock mixture. In view of its low sensitivity for nitrogen-containing species as compared to the NPD, it was used only to determine the concentrations of the species without bound nitrogen.

In order to combine the GC peak areas in the two columns to one list, the area under the N-methylpyrrole peak in the FID column ( $A_{mp,FID}$ ) was set equal to that in the NPD column ( $A_{mp,NPD}$ ) and all the FID peaks were multiplied by the ratio ( $A_{mp,NPD}$ )/( $A_{mp,FID}$ ). In this way the sensitivities of all the products relative to N-methylpyrrole, which were determined separately from standard mixtures for each detector, could be used without further normalization.

The initial temperature of the columns was 35 °C. It was gradually elevated to 190 °C in an analysis which lasted about 45 min.

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 HP Model 5970 Mass Selective Detector. Each mass spectrum at the peak height was compared with a standard spectrum,<sup>15</sup> and the compounds could be identified.

GC peak areas were integrated with a Spectra Physics Model SP4200 dual channel computing integrator and were transferred to an IBM/PC for data reduction and graphical presentation.

## **Results and Discussion**

I. Arrhenius Rate Parameters. To determine the distribution of reaction products in N-methylpyrrole pyrolysis and the production rates of the various products, tests were run with mixtures containing 0.5% N-methylpyrrole in argon, covering the temperature range 1050–1300 K. Figures 1–5 show a line of first-order rate constants for product formation, defined as follows:

$$k_{1st}(\text{product}_i) = \{C_5(\text{product}_i)_t / [N-\text{methylpyrrole}]_0\}/t$$
 (I)

plotted on a logarithmic scale against reciprocal temperature and expressed in units of  $s^{-1}$ .

Values of E obtained from the slopes of the lines and their corresponding preexponential factors are summarized in Table I in units of kcal/mol and s<sup>-1</sup>, respectively.

Figure 6 shows the effective rate constant for the overall decomposition of N-methylpyrrole,  $k_{\text{total}}$ , expressed as a first-order rate constant as calculated from its disappearance rate:

$$k_{\text{total}} =$$

$$-(1/t) \ln\{[N-\text{methylpyrrole}]_t/[N-\text{methylpyrrole}]_0\}$$
 (II)

The Arrhenius parameters obtained for the overall disappearance of N-methylpyrrole (which is not a unimolecular reaction) are  $k_{\text{total}} = 10^{16.69} \exp(-79.2 \times 10^3/RT) \text{ s}^{-1}$ .

It should be stressed that although the values in Table I correspond to first-order rate parameters they do not necessarily

represent elementary unimolar reactions. We find it convenient, however, to initially summarize the results in this manner.

II. Nitrogen-Carbon Balance. The balance of nitrogen vs carbon in the decomposition and isomerization products is shown in Figure 7. The concentrations of all the nitrogen-containing products are plotted against one-fifth the sum of the concentrations of all the products each multiplied by the number of its carbon atoms. The diagonal in the figure represents a perfect mass balance. As can be seen, there is a slight deficiency of nitrogen. This can be the result of a slight error in the calibration. In general, nitrogen-carbon balance among the products is maintained.

**III. Reaction Mechanism.** Examination of the plethora of products in *N*-methylpyrrole pyrolysis suggests that they are obtained from three different modes of initiation. They can be grouped as follows:

1. Products resulting from the removal of the methyl group from the ring followed by reactions of (a) methyl radicals and, (b) nitrogen-containing intermediates which are formed in the same process.

2. Products resulting from a direct unimolecular cleavage of the pyrrole ring.

3. Products resulting from isomerization reactions of *N*-methylpyrrole.

The high concentrations of methane and ethane in the postshock samples clearly indicate that the ejection of the methyl group from the ring is an important initiation step.

$$\left\langle \sum_{\substack{N \\ CH_3}}^{N} \longrightarrow \left\langle \sum_{\substack{N \\ CH_3}}^{N} + CH_3^{\bullet} \right\rangle$$
(1)

The methyl radicals which are formed in this process yield methane by abstraction of a hydrogen atom, most likely from the methyl group on the *N*-methylpyrrole:

$$\left\langle \bigcup_{\substack{N\\ CH_3}}^{N} + CH_3^{\bullet} \longrightarrow \left\langle \bigcup_{\substack{N\\ CH_2}}^{N} + CH_4 \right\rangle$$
(2)

Ethane and ethylene are also obtained by the following sequence of reactions:

$$CH_3' + CH_3' \rightarrow C_2H_6 \tag{3}$$

$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_5^{\bullet} + H^{\bullet}$$
 (4)

$$C_2H_6 + H^\bullet \rightarrow C_2H_5^\bullet + H_2$$
 (5)

$$C_2H_5 \rightarrow C_2H_4 + H \tag{6}$$

It is possible to make a rough estimate of the initiation rate constant  $(k_1)$  by assuming that the concentration of methyl radicals formed in reaction 1 during the 2-ms reaction time is roughly equal to

$$[CH_3]_t = \{[CH_4] + 2([C_2H_4] + [C_2H_6])\}_t \quad (III)$$

An Arrhenius plot of  $\log k_1 vs 1/T$  where  $k_1$  is calculated from the relation

$$k_1 t \sim ([CH_3]_t / [mp]_0)$$
 (IV)

is shown in Figure 8 (mp = N-methylpyrrole). This yields  $k_1 = 10^{16.26} \exp(-79.5 \times 10^3/RT) \, \mathrm{s}^{-1}$ . This expression is in reasonable agreement with a rate constant for an allyl-like CH<sub>3</sub> bond rupture.

Reactions 1 and 2 generate, in addition to  $CH_3$  and  $CH_4$ , two unstable intermediates containing nitrogen that play a very important role in generating the various nitrogen-containing



Figure 1. Plots of log{[prod]/[mp]<sub>0</sub>} as a function of reciprocal temperature of three reaction products. The Arrhenius parameters for the production rates of these products are evaluated from these plots.



Figure 2. Plots of  $\log\{[prod]/[mp]_0\}$  as a function of reciprocal temperature for four reaction products. The Arrhenius parameters for the production rates of these products are evaluated from these plots.



Figure 3. Plots of  $\log\{[prod]/[mp]_0\}$  as a function of reciprocal temperature for three reaction products. The Arrhenius parameters for the production rates of these products are evaluated from these plots. products. These intermediates are  $C_4H_4N^{\bullet}$  (reaction 1) and  $C_4H_4N$ -CH<sub>2</sub><sup>•</sup> (reaction 2). The questions that arise, therefore, are what nitrogen-containing species are formed by unimolecular reactions from the reactant and what species are formed from the above-mentioned nitrogen-containing intermediates. In order to answer these and other questions regarding the pyrolysis mechanism, we examined the effect of toluene on the production rate of some of the species and were also assisted by the results of modeling calculations as will be described later.

Figures 9-12 present a series of Arrhenius-type plots which show the effect of toluene on the rate of production of several nitrogen-containing species in mixtures containing 1% toluene and 0.1% N-methylpyrrole. GC peak areas of a given product are divided by those of N-methylpyrrole and plotted on a



Figure 4. Plots of log{[prod]/[mp]<sub>0</sub>} as a function of reciprocal temperature for two reaction products. The Arrhenius parameters for the production rates of these products are evaluated from these plots.



Figure 5. Plot of  $\log[C_3H_4]/[mp]_0]$  and  $\log[[CH_3CN]/[mp]_0]$  as a function of reciprocal temperature. The production of  $C_3H_4$  (allene and propyne) and  $CH_3CN$  is mainly due to reaction 7 (see Table II), and their concentrations are roughly the same.

 TABLE I: First-Order Arrhenius Parameters for Product

 Formation

molecule	$\log_{\mathbf{S}^{-1}} A$ ,	<i>E</i> , kcal/mol	k(1225 K)	<i>T</i> , K
total decomposition	16.69	79.2	3.66 × 10 <sup>2</sup>	1050-1240
initiation	16.26	79.5	$1.20 \times 10^{2}$	1050-1240
HCN	19.62	103	1.77 × 10 <sup>1</sup>	1075-1240
acetonitrile	15.60	79.4	$2.74 \times 10^{1}$	1075-1240
acrylonitrile	16.55	89.2	4.36	1130-1240
propionitrile	16.19	85.4	9.06	1090-1240
cis- and trans-crotononitrile	16.93	86.0	$3.89 \times 10^{1}$	1050-1240
vinylacetonitrile	14.81	79.7	3.93	1090-1240
pyridine	21.74	112	5.79 × 10 <sup>1</sup>	11601240
pyrrole	14.39	70.6	$6.27 \times 10^{1}$	1080-1240
3-methylpyrrole	11.24	45.8	$1.18 \times 10^{3}$	1130-1240
methane	15.70	78.3	$5.42 \times 10^{1}$	1050-1240
ethylene	16.60	88.6	6.26	1050-1240
ethane	16.89	86.9	$2.45 \times 10^{1}$	1050-1240
acetylene	22.24	117	$2.35 \times 10^{1}$	1050-1240
C <sub>3</sub> H <sub>4</sub>	15.41	79.4	$1.73 \times 10^{1}$	1100-1240

logarithmic scale against reciprocal temperature for runs with and without toluene. Figure 9 shows that there is no effect of toluene on the production rate of  $CH_3CN$ . We therefore suggest that the latter is formed from the reactant by the unimolecular reaction,

$$\begin{array}{c} \swarrow \\ N \\ \downarrow \\ CH_3 \end{array} \xrightarrow{} CH_3 CN + CH_3 - C \equiv CH \qquad (7)$$

Figure 10 shows the effect of toluene on the production rate of pyridine. The effect seen in this figure indicates that the production of pyridine is associated with free radical reactions.



1/TE4 (K<sup>-1</sup>)

Figure 6. Plot of log  $k_{total}$  as a function of reciprocal temperature. The plot gives the Arrhenius rate parameters for the overall decomposition of *N*-methylpyrrole.



[NITROGEN] (arbitrary units)

Figure 7. Carbon-nitrogen mass balance. Some slight deficiency in nitrogen can be seen. This might be due to slight errors in the calibration.

We suggest that pyridine is formed by an isomerization (ring enlargement) of the radical which is formed in reaction 2, namely,

followed by an ejection of a hydrogen atom

An additional question is the mechanism by which crotonitrile (CH<sub>3</sub>CH=CHCN) and vinylacetonitrile (CH<sub>2</sub>=CHCH<sub>2</sub>CN) are formed. These compounds were found in substantial quantities in the post-shock mixtures. Figure 11 shows a strong effect of toluene on the formation rate of crotonitrile (and also on that of vinylacetonitrile, not shown here) indicating that these compounds are not formed from the reactant in a unimolecular process. It has been shown in the past that pyrrole<sup>2,9</sup> (found as a product in these experiments) isomerizes to these two compounds. However, when the isomerization reactions of pyrrole with their known rate constants were plugged into the reaction scheme and run in the computer, they produced only trace quantities of crotonitrile and vinylacetonitrile, in fact, several orders of magnitude below the quantities found in the post-shock mixtures. We therefore suggest that the intermediate that is formed in reaction 1, namely,  $C_4H_4N^{\bullet}$ , undergoes isomerization much faster than pyrrole and produces the radical  $CH_2$ =CHCH·CN  $\leftrightarrow$  CH<sub>2</sub>·CH=CHCN.



**Figure 8.** Plot of log  $k_{init}$  as a function of reciprocal temperature. The plot gives a rough estimate of the Arrhenius rate parameters for the ejection of a methyl from the pyrrole ring.

By abstraction of a hydrogen atom or recombination with one, crotonitrile and vinylacetonitrile are formed.

$$\langle N \rangle \longrightarrow CH_2 = CHCH^*CN$$
 (10)

$$\langle N \rangle \longrightarrow CH_2^*CH=CHCN$$
 (11)

 $CH_2 = CHCH^{\circ}CN + H \longrightarrow CH_2 = CHCH_2CN$  (12)

$$CH_2^{\bullet}CH = CHCN + H \longrightarrow CH_3CH = CHCN$$
 (13)

In Figure 12 the effect of toluene on the production rate of hydrogen cyanide is shown. The results are not as conclusive as those in the previous figures, but some effect can be seen. As will be discussed later, the production of HCN is the result of H atom attack on nitriles produced in the pyrolysis:  $RCN + H^* \rightarrow HCN + R^*$ .

The question of the mechanism of production of  $C_2H_5CN$  could not be clarified by the series of experiments with toluene. The results were inconclusive. The model calculations could not generate enough  $C_2H_5CN$  just by free radical processes. In fact the amount generated was orders of magnitude too low. We have introduced into the reaction scheme a direct production of  $C_2H_5CN$  from *N*-methylpyrrole

$$\left\langle \bigvee_{\substack{N \\ I \\ CH_3}} \longrightarrow C_2 H_5 CN + C_2 H_2 \right\rangle$$
(14)

with a rate constant obtained from Figure 2. As mentioned before, without this elementary step we could not produce enough  $C_2H_3$ -CN, although it is hard to visualize a transition state that would account for such a process. At low temperatures the concentrations of  $C_2H_5$ CN and  $C_2H_2$  are roughly the same as is indicated by reaction 14. At higher temperatures the production of acetylene is enhanced by additional free radical mechanisms and its log k vs 1/T plot shows a higher slope.

It is of interest to compare the pyrolysis pattern of N-methylpyrrole to that of pyrrole. Whereas the major reactions in pyrrole are isomerization reactions,<sup>5,9</sup> these are not found in N-methylpyrrole. Prior to the isomerizations in pyrrole a hydrogen atom migrates from the nitrogen to position 5 in the ring. Similar reactions for N-methylpyrrole would require a migration of a methyl group which is a much more energy demanding process.<sup>3,4</sup> The ejection of a methyl group from the nitrogen in the ring, which is much faster than the ejection of a



**Figure 9.** Plot of the GC peak area of  $CH_3CN$  divided by that of *N*-methylpyrrole as a function of reciprocal temperature with and without the free radical scavenger toluene. The scatter of the data points along one line indicates no involvement of free radicals in the formation of acetonitrile.



Figure 10. Plot of the GC peak area of pyridine divided to that of *N*-methylpyrrole as a function of reciprocal temperature with and without the free radical scavenger toluene. The distance between the lines indicates that the production of pyridine is associated with free radicals. It is obtained by a ring enlargement of  $C_4H_4N-CH_2^*$ .



Figure 11. Plot of the GC peak area of  $CH_3CH$ —CHCN as a function of reciprocal temperature with and without the free radical scavenger toluene. The distance between the lines indicates that the production of crotonitrile is associated with free radicals. It is obtained by isomerization of  $C_4H_4N^{\bullet}$ .

hydrogen atom in pyrrole, is thus the main initiation reaction and leads to the production of a plethora of products. We believe that the pyrrolyl radical ring  $C_4H_4N^{\bullet}$ , which remains after the dissociation, undergoes similar reactions to pyrrole considerably faster. This is strongly supported by the results of the computer modeling.

IV. Reaction Scheme and Computer Modeling. In order to account quantitatively for the production rate of some 15 products we have constructed a reaction scheme containing 46 elementary reactions and 23 species. The scheme is shown in Table II. The





[HCN] / [mep] arbt. units

Figure 12. Plot of the GC peak area of HCN as a function of reciprocal temperature with and without free the radical scavenger toluene. The results are not conclusive but indicate some effect of toluene. The main production channel of HCN is  $RCN + H^* \rightarrow HCN + R^*$ .

scheme does not account for the production of species that appeared at low concentrations such as  $C_3H_6$ ,  $C_4H_4$ ,  $C_4H_6$ , and  $CH \equiv C - CN$ . The first three columns in the table give the three parameters A, n, and E for the forward rate constants corresponding to the reactions as they are listed in the table. The rate constants are given by  $k = AT^n \exp(-E/RT)$  in units of cm<sup>3</sup> mol s. Column 4 gives the values of the forward rate constants as calculated from the rate parameters at a temperature of 1225 K, and column 5 shows the value for the reverse rate constants calculated from  $k_f$  and the equilibrium constants of the reactions, also at 1225 K. In column 6 the standard enthalpy change at 1000 K for each reaction is given. Column 7 shows the source of the rate parameters used.

The rate parameters assigned for the unimolecular reactions (reactions 1, 7, and 14) were based on the experimental findings in this investigation. The parameters for the isomerization reaction (45) were taken from studies at lower temperatures.<sup>11</sup>

The Arrhenius parameters for the other reactions were either estimated or taken from the NIST-Kinetic Data Base.<sup>16</sup> They were varied within the limits of their reported uncertainties. The Arrhenius rate parameters for each reaction that were taken from the NIST-Kinetic Data Base are the best fit to a large number of entries. In view of the very large number of citations involved they are not given as references in this article. Parameters for reactions which could not be found in available compilations were determined by comparison with similar reactions for which the rates parameters are known.

The thermodynamic properties of the species involved were taken from various literature sources.<sup>17–21</sup> The heats of formation of the various nitrogen-containing free radicals which are believed to play an important role in the decomposition of N-methylpyrrole were evaluated from estimated bond dissociation energies in the precursor molecules or in the products. The estimated bond energies of the relevant nitrogen-containing radicals can be seen in column 6 of Table II for reactions 1, 2, 8, 9, 12, and 13.

The computer program available to us can perform sensitivity analysis with respect to variations (or rather uncertainties) in the  $\Delta H_f^{\circ}$  of the species. In several tests that were performed we found that the results of the simulation were very insensitive to the estimated values and thus consider them adequate.

Figures 13–19 show experimental and calculated mole percents of the 15 products found in the decomposition and isomerization of N-methylpyrrole. The agreement for most of the products is satisfactory. Exceptions are pyridine, acetylene, and propylnitrile particularly in the reproduction of the log (mole percent) vs temperature slopes.

It should be mentioned again that the construction of the scheme was assisted largely by the toluene experiments. In several cases where known reactions could not account for the experimental production rates we have suggested new reactions like in the case of crotonitrile (CH<sub>3</sub>CH=CHCN) (reactions 11 and 13), viny-

#### TABLE II: Reaction Scheme for the Decomposition of N-Methylpyrrole

reaction	A	n	E	k <sub>f</sub> (1225 K) <sup>a</sup>	k <sub>r</sub> (1225 K) <sup>a</sup>	$\Delta H_{r}^{\circ b}$	source
1. N-methylpyrrole $\rightarrow C_4H_4N^{\bullet} + CH_3$	$2.32 \times 10^{16}$	0	80.0	$1.24 \times 10^{2}$	$3.65 \times 10^{12}$	76.0	this work
2. N-methylpyrrole + CH <sub>3</sub> $\rightarrow$ C <sub>4</sub> H <sub>4</sub> N-CH <sub>2</sub> • + CH <sub>4</sub>	$5.00 \times 10^{12}$	0	10.0	$8.22 \times 10^{10}$	$2.61 \times 10^{9}$	-9.43	est
3. $CH_3 + CH_3 \rightarrow C_2H_6$	$1.80 \times 10^{13}$	0	0	$1.80 \times 10^{13}$	$9.87 \times 10^{\circ}$	-90.8	16
4. $CH_3 + CH_3 \rightarrow C_2H_5 + H$	$2.80 \times 10^{13}$	0	13.5	$1.07 \times 10^{11}$	$1.76 \times 10^{14}$	11.6	22
5. $C_2H_6 + H \rightarrow C_2H_5 + H_2$	$1.43 \times 10^{14}$	0	9.58	$2.80 \times 10^{12}$	7.79 × 10 <sup>9</sup>	-3.75	16
6. $C_2H_5 \rightarrow C_2H_4 + H$	$6.21 \times 10^{12}$	0	38.0	$1.05 \times 10^{6}$	$4.36 \times 10^{12}$	38.0	16
7. N-methylpyrrole $\rightarrow$ CH <sub>3</sub> —C=CH + CH <sub>3</sub> CN	$4.00 \times 10^{15}$	0	79.4	$2.68 \times 10^{1}$	$1.25 \times 10^{5}$	39.6	this work
8. $C_4H_4N - CH_2 \rightarrow C_5H_6N$	$1.00 \times 10^{14}$	0	55.0	$1.54 \times 10^{4}$	$2.17 \times 10^{4}$	-9.9	est
9. $C_5H_6N^{\bullet} \rightarrow \text{pyridine} + H$	$2.00 \times 10^{13}$	0	28.0	$2.02 \times 10^{8}$	$8.39 \times 10^{12}$	27.4	est
10. $C_4H_4N^\bullet \rightarrow CH_2 = CH - CH^\bullet CN$	$5.00 \times 10^{14}$	0	62.5	$3.54 \times 10^{3}$	$1.67 \times 10^{3}$	11.4	est
11. $C_4H_4N^{\bullet} \rightarrow CH_2^{\bullet}CH = CHCN$	$5.00 \times 10^{14}$	0	54.0	$1.16 \times 10^{5}$	4.25 × 10 <sup>4</sup>	7.39	est
12. $CH_2 = CH - CH \cdot CN + H \rightarrow CH_2 = CHCH_2CN$	$2.00 \times 10^{14}$	0	0	$2.00 \times 10^{14}$	$5.39 \times 10^{-1}$	-94.5	est
13. $CH_2$ ·CH=CHCN + H $\rightarrow$ CH <sub>3</sub> CH=CHCN	$2.00 \times 10^{14}$	0	0	$2.00 \times 10^{14}$	$6.38 \times 10^{-1}$	-94.1	est
14. N-methylpyrrole $\rightarrow C_2H_2 + C_2H_5CN$	$1.55 \times 10^{16}$	0	85.4	$9.02 \times 10^{\circ}$	$7.24 \times 10^{4}$	41.3	this work
15. N-methylpyrrole + H $\rightarrow$ C <sub>4</sub> H <sub>4</sub> N-CH <sub>2</sub> • + H <sub>2</sub>	$5.00 \times 10^{13}$	0	9.00	$1.24 \times 10^{12}$	$1.70 \times 10^{9}$	-8.21	est
16. N-methylpyrrole + $C_4H_4N^{\bullet} \rightarrow pyrrole + C_4H_4N - CH_2^{\bullet}$	$3.00 \times 10^{12}$	0	9.00	$7.44 \times 10^{10}$	$2.41 \times 10^{11}$	3.00	est
17. $C_4H_4N^{\bullet} + CH_3 \rightarrow 2$ - and 3-methylpyrrole	$2.00 \times 10^{12}$	0	0	$2.00 \times 10^{12}$	$6.81 \times 10^{1}$	-76.0	est
18. $C_4H_4N^{\bullet} + H \rightarrow pyrrole$	$2.00 \times 10^{14}$	0	0	$2.00 \times 10^{14}$	$4.41 \times 10^{-1}$	-95.0	est
19. $CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3$	$6.62 \times 10^{\circ}$	3.7	9.50	$3.57 \times 10^{10}$	$2.07 \times 10^{11}$	2.38	16
20. $CH_3 + CH_2CN \rightarrow C_2H_5CN$	$2.45 \times 10^{14}$	-0.5	0	$7.00 \times 10^{12}$	$1.42 \times 10^{1}$	-84.0	est
21. $CH_3CN \rightarrow CH_2CN + H$	$1.02 \times 10^{15}$	0	94.0	$1.74 \times 10^{-2}$	$1.13 \times 10^{13}$	94.0	6
22. $CH_3CN + H \rightarrow CH_3 + HCN$	$5.01 \times 10^{13}$	0	2.00	$2.20 \times 10^{13}$	$1.63 \times 10^{10}$	-7.93	est
23. $CH_3CN + CH_3 \rightarrow CH_4 + CH_2CN$	$5.00 \times 10^{11}$	0	9.00	$1.24 \times 10^{10}$	$1.73 \times 10^{8}$	-13.4	est
24. $CH_3CN + H \rightarrow H_2 + CH_2CN$	$1.38 \times 10^{14}$	0	9.54	$2.75 \times 10^{12}$	$1.65 \times 10^{9}$	-12.2	est
25. $C_2H_3 + Ar \rightarrow C_2H_2 + H + Ar$	$3.00 \times 10^{15}$	0	32.0	$5.80 \times 10^{9}$	$1.70 \times 10^{16}$	40.7	16
26. $C_2H_3 + CH_2CN \rightarrow CH_2CH = CH_2CH_2CN$	$1.23 \times 10^{14}$	-0.5	0	$3.50 \times 10^{12}$	9.65 × 10 <sup>-2</sup>	-91.7	est
27. $C_2H_3CN \rightarrow C_2H_2 + HCN$	$1.78 \times 10^{12}$	0	68.0	$1.32 \times 10^{\circ}$	$2.83 \times 10^{\circ}$	42.1	7
$28. C_2H_3CN + H \rightarrow HCN + C_2H_3$	$1.50 \times 10^{14}$	0	2.00	$6.60 \times 10^{13}$	$4.85 \times 10^{12}$	1.41	est
29. $C_2H_5CN + H \rightarrow C_2H_5 + HCN$	$1.50 \times 10^{14}$	0	2.00	$6.60 \times 10^{13}$	$6.10 \times 10^{10}$	-6.35	est
$30. C_2H_5CN \rightarrow C_2H_4 + HCN$	$6.00 \times 10^{12}$	0	72.0	8.58 × 10 <sup>-1</sup>	$3.31 \times 10^{3}$	31.6	est
31. $C_2H_5CN \rightarrow H_2 + C_2H_3CN$	$2.51 \times 10^{13}$	0	77.0	$4.60 \times 10^{-1}$	$6.06 \times 10^{3}$	33.8	est
32. $C_2H_5CN + H \rightarrow C_2H_4CN + H_2$	$1.38 \times 10^{14}$	0	9.54	$2.75 \times 10^{12}$	$6.01 \times 10^{10}$	-4.21	est
33. $C_2H_5CN + CH_3 \rightarrow C_2H_4CN + CH_4$	9.00 × 10 <sup>12</sup>	0	8.00	3.37 × 10 <sup>11</sup>	1.70 × 10 <sup>11</sup>	-5.43	est
34. $C_4H_4N_2 \rightarrow C_2H_3CN + HCN$	1.14 × 10 <sup>13</sup>	0	08.0	$8.42 \times 10^{6}$	1.80 × 10°	39.1	est
35. $CH_4 \rightarrow CH_3 + H$	$7.80 \times 10^{19}$	20	103.8	2.34 × 10 <sup>-7</sup>	1.09 × 10 <sup>10</sup>	100	10
36. $CH_4 + H \rightarrow CH_3 + H_2$	2.25 × 10 <sup>4</sup>	3.0	8.70	$1.13 \times 10^{12}$	4.90 × 10 <sup>10</sup>	1.22	10
$37. C_2H_4 + H \rightarrow C_2H_3 + H_2$	$2.03 \times 10^{13}$	0	20.7	$3.37 \times 10^{11}$	1.35 × 10 <sup>11</sup>	3.60	10
38. $CH_2 = C = CH_2 \rightarrow CH_3 = C = CH$	$1.48 \times 10^{13}$	0	00.4 70.5	$2.48 \times 10^{2}$	$7.77 \times 10^{10}$	-1.70	23
39. $CH_3 - C = CH + AI \rightarrow C_3H_3 + H + AI$	$2.53 \times 10^{17}$	0	72.5	$2.97 \times 10^{4}$	$0.8 / \times 10^{18}$	91.5	10
$40. CH_2 = C = CH_2 + Ar \rightarrow C_3H_3 + H + Ar$	$4.05 \times 10^{17}$	0	/3.1	$1.03 \times 10^{\circ}$	$1.18 \times 10^{10}$	09.0	10
41. $C_2H_4CN \rightarrow C_2H_3CN + H$	$3.00 \times 10^{15}$	0	40.0	$2.19 \times 10^{\circ}$	$1.32 \times 10^{12}$	38.0	est
42. $CH_2CN + CH_2CN \rightarrow C_4H_4N_2$	$1.23 \times 10^{14}$	-0.5	0	$5.50 \times 10^{12}$	$5.34 \times 10^{-1}$	-85.0	est
45. $\Pi + \mathbb{C}_{2}\Pi_{4}\mathbb{C} \mathbb{N} \rightarrow \mathbb{C}_{2}\Pi_{5}\mathbb{C} \mathbb{N}$	$3.00 \times 10^{12}$	0	67.0	$3.00 \times 10^{12}$	$2.13 \times 10^{-1}$	-102	est
44. $U_4\Pi_4IN \rightarrow U_{12}^{-} \rightarrow U_2\Pi_4UIN + U_2\Pi_2$	$1.39 \times 10^{13}$	0	0/.U 58.0	$1.77 \times 10^{3}$	$2.27 \times 10^{\circ}$	43.3	est
45. $IV$ -methylpytrole $\rightarrow 2$ - and 3-methylpytrole	2.39 × 1012	0	20.00	$1.00 \times 10^{2}$	$1.00 \times 10^{2}$	0 21	14
$40.  \Box_3 = \Box = \Box_1 + H \rightarrow \Box_1 + \Box_2 = \Box_2$	2.01 × 10.2	U	2.00	2.20 × 10 <sup>13</sup>	7'AI V 1010	-0.31	10

<sup>a</sup> Rate constants are expressed as  $k = AT^n \exp(-E/RT)$  in units of cm<sup>3</sup> s mol cal. <sup>b</sup>  $\Delta H_f^{\circ}$  are given at 1000 K and are expressed in units of kcal/mol.





Figure 13. Comparison between experimental  $(\blacksquare, \square)$  and calculated (lines) mole percents of  $CH_4$  and  $C_2H_4$ .

lacetonitrile (CH<sub>2</sub>=CHCH<sub>2</sub>CN) (reactions 10 and 12) and propylnitrile ( $C_2H_3CN$ ) (reaction 14).

Tables III and IV show the sensitivity spectra of the reaction scheme at 1050 and 1250 K, respectively. The sensitivity  $S_{ij}$  is given by  $(\Delta \log C_i / \Delta \log k_j)$  at t = 2 ms. The sensitivity factor  $S_{ij}$  was evaluated by changing  $k_j$  by a factor of 2. Reactions that show no effect on the production rate on all the products both at high and at low temperatures were not included in the tables.  $(S_{ij} = 1 \text{ means a factor of 2 change in } C_i$  for a factor of 2 change in  $k_j$ .) The tables show that the main initiation reaction (reaction

Figure 14. Comparison between experimental  $(\blacksquare, \square)$  and calculated (lines) mole percents of  $C_2H_2$  and  $C_2H_3CN$ .

1) has an effect on all the products whose productions involve free radical reactions. Most of the entries in the table are self evident. On the other hand, the production rate of pyridine, for example, is independent of the rates of both reactions 8 and 9. It is determined by the production rate of  $C_4H_4N-CH_2$  which is expressed by reactions 2, 15, and 16.

#### Conclusions

Production rates and distribution of products obtained in the thermal decomposition of N-methylpyrrole are successfully

······································	reaction																			
compound	1	2	3	5	7	8	10	12	13	14	15	16	18	22	28	29	38	44	45	46
CH <sub>4</sub>	0.91	0.10	~0.06																	
$C_2H_4$	0.93	0.01	-0.01	-	0.01	0.89				0.96	-0.86					0.93		0.06		
$C_2H_6$	1.83	-1.79	0.86													0.75		0.00		
$C_2H_2$	0.43	0.03			0.04	0.04				0.69	-0.01							0.42		
$CH_2 = C = CH_2$	-0.01				0.99												0.99	0.12		
CH <sub>3</sub> C=CH	0.01				0.99	-0.01											0.77			
HCN	1.0				0.61	0.92				0.39	-0.92			0.62		0.38		0.23		
CH <sub>3</sub> CN	-0.01				0.99	-0.01								-0.01				0.20		
C <sub>2</sub> H <sub>3</sub> CN	0.90					-0.04					0.01						0.99			
C <sub>2</sub> H <sub>5</sub> CN	-0.04					-0.04				0.99	0.01				-0.04					
CH <sub>3</sub> CH==CHCN	1.80					0.87			0.895		-0.89	-0.69								
CH <sub>2</sub> =CHCH <sub>2</sub> CN	1.77					0.84	0.94	0.90	-0.03		-0.86	0.67								
pyridine	0.93					0.97						0.10								
pyrrole	0.96											0.14								
2- and 3-methylpyrrole																		0.99		

TABLE III: Sensitivity Analysis at 1050 K: ( $\Delta \log C / \Delta \log k$ ) at t = 2 ms, k is Changed by a Factor of 2

TABLE IV: Sensitivity Analysis at 1225 K: ( $\Delta \log C / \Delta \log k$ ) at t = 2 ms, k is Changed by a Factor of 2

	reaction																			
compound	1	2	3	5	7	8	10	12	13	14	15	16	18	22	28	29	38	44	45	46
CH <sub>4</sub>	0.21	0.65	-0.36		-	0.01						0.01								0.01
C <sub>2</sub> H <sub>4</sub>	-0.06	0.16	-0.09	0.27	-0.18	0.07			-0.32	0.73		0.31				0.32				-0.03
C <sub>2</sub> H <sub>6</sub>	0.69	-0.54	0.23	0.04	0.03	0.03				-0.03		0.03						-0.01		0.03
$C_2H_2$		0.29	-0.11		0.1	-0.32			-0.17	0.35		0.21						0.49		0.15
$CH_2 = C = CH_2$	-0.04	-0.25	-0.07		0.99				0.15	-0.03		-0.22					0.73	-0.03		-0.23
CH <sub>3</sub> -C=CH	-0.04	-0.25	0.07		1.03	-0.03			0.16	-0.01		-0.22					-0.04	0.01		-0.27
HCN	-0.18	0.40			0.20	0.12			-0.36	0.33		0.36		0.26	0.14	0.11		0.32		
CH <sub>3</sub> CN	-0.07	-0.25			1.03	0.01			0.15	-0.03		-0.22		-0.32			0.03			
C <sub>2</sub> H <sub>3</sub> CN	0.40	-0.09			0.16	-0.81			0.19	0.11		-0.20		0.07	-0.6	-0.04		0.77		
C <sub>2</sub> H <sub>5</sub> CN	-0.04	-0.36			0.21	-0.04			0.26	0.88		0.32		0.01		-0.64		-0.04		
CH <sub>3</sub> CH=CHCN	0.55	0.26					-0.11	0.04	0.36		0.03	0.01	-0.29						-0.06	
CH2=CHCH2CN	0.63	-0.03					0.57	0.35	-0.32			-0.25	-0.14						-0.01	
pyridine	0.26	0.35					-0.01		-0.11		0.20	0.19	-0.06						-0.09	
pyrrole	0.55	0.15					0.04		-0.17		-0.04	0.14	0.21						-0.04	
2- and 3-methylpyrrole	-0.06	-0.06									-0.03	-0.04							0.71	



Figure 15. Comparison between experimental  $(\blacksquare, \square)$  and calculated (lines) mole percents of pyridine and  $C_2H_6$ .



т, к

Figure 16. Comparison between experimental  $(\blacksquare, \square)$  and calculated (lines) mole percents of 2- and 3-methylpyrrole and C<sub>2</sub>H<sub>5</sub>CN. The agreement with C<sub>2</sub>H<sub>5</sub>CN is not very evident.



Т, К

Figure 17. Comparison between experimental  $(\blacksquare, \square)$  and calculated (lines) mole percents of HCN and pyrrole.



Figure 18. Comparison between experimental ( $\blacksquare$ ,  $\square$ ) and calculated (lines) mole percents of CH<sub>3</sub>CH=CHCN and CH<sub>2</sub>=CHCH<sub>2</sub>CN.

simulated with a kinetic scheme containing 46 elementary reactions and 23 species. The major initiation process in the decomposition of N-methylpyrrole is fission of the methyl group from the pyrrole ring.  $CH_3^{\bullet}$  and  $C_4H_4N^{\bullet}$ , which are formed in this process, initiate a free radical mechanism and are responsible for a plethora of products. N-methylpyrrole also undergoes several



Figure 19. Comparison between experimental  $(\blacksquare, \square)$  and calculated (lines) mole percents of CH<sub>3</sub>CN and C<sub>3</sub>H<sub>4</sub>.

unimolecular reactions including ring cleavage and migration of the methyl group to positions 2 and 3 in the ring.

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