ARTICLE
Identification of Intermediates in Pyridine Pyrolysis with Molecular-beam Mass Spectrometry and Tunable Synchrotron VUV Photoionization†

Xin Hong, Tai-chang Zhang, Li-dong Zhang, Fei Qi∗
National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

(Dated: Received on March 6, 2009; Accepted on March 17, 2009)

The pyrolysis of pyridine (5.26% pyridine in argon) was performed with tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry technique at the temperature range of 1255-1765 K at 267 Pa. About 20 products and intermediates, containing major species H₂, HCN, C₂H₂, C₅H₃N, C₄H₇, and C₃H₃N, were identified by near-threshold measurements of photoionization mass spectra and their mole fractions vs. temperatures were estimated. The major reaction pathways are analyzed based on the experimental observations.

Key words: Pyridine pyrolysis, Intermediate, Tunable synchrotron VUV photoionization, Molecular-beam mass spectrometry

I. INTRODUCTION

Pyridine, the simplest six-membered heterocyclics, is the model and representative of nitrogen-containing compounds in the coal and coal-derived fuels [1-4], whose combustion leads to the NOₓ emission [5-7]. The pyrolysis of pyridine occurs in the pre-flame zone or during the initial heat-up period of the fuel prior to combustion [8,9], therefore the identification of the pyrolysis intermediates and quantitative determination are helpful for further understanding of the evolution of NOₓ [10].

The thermal decomposition of pyridine has been extensively studied. Hydrogen, acetylene and hydrogen cyanide were detected as the major pyrolysis products, along with minor components such as acrylonitrile (C₅H₄N), benzonitrile(C₆H₅N), and methane in flow systems at the temperature range of 950-1400 K [10,11]. Shock tube pyrolysis of pyridine shows major products (C₂H₂, HCN, C₆H₅N, and H₂) and minor ones vinylacetylene (C₂H₄), cyanovinylacetylene (C₅H₃N), and diacetylene (C₄H₂) at a rather high temperature range of 1200-1800 K [12,13]. As reported previously, HCN appears to be the key nitrogen-containing intermediate formed during the pyrolysis of this heterocyclic compound, however, some difference existed in the identification of some major and minor pyrolysis products, especially for acetonitrile (C₅H₃N) [10] and cyanoacetylene (C₅H₆N) [14]. It is noticeable that in previous investigations it has been difficult to identify radicals and isomeric species using electron-impact ionization mass spectrometry (EIMS) and/or gas chromatography (GC) due to the limited energy resolution of ionizing electrons and fragmental interference of EIMS, and the characteristics of the GC method.

In this work, molecular-beam mass spectrometric technique coupled with tunable synchrotron VUV photoionization method was applied to the pyrolysis investigation of pyridine to comprehensively determine the pyrolysis intermediates. This method has been adopted to identify the intermediates in combustion, especially radicals and isomers, by reducing fragmentation via near-threshold photoionization [15-17]. Moreover the mole fraction profiles and the schematics of the products formation are also provided in this work.

II. EXPERIMENTS

The experiment was carried out at the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. A detailed description of the instrument setup has been reported elsewhere [18], and only a brief description is presented here. An undulator radiation from the 800 MeV electron storage ring is dispersed by a 1 m Seya-Namioka monochromator with a 1.50 groove/m laminar grating covering the photon energy range from 7.80 eV to 24.00 eV. The energy resolving power is approximately 10⁴. The average photon flux can reach the magnitude of 10¹³ photon/s. A gas filter is used to eliminate higher-order harmonic radiation with Ne or Ar filled in the gas cell for this work. The apparatus is composed of a pyrolysis chamber equipped with a high temperature furnace, a differentially pumped chamber with a molecular-beam sampling system, and a photoioniza-

†Part of the special issue for “the 4th Sino-French Workshop on Molecular Spectroscopy, Dynamics and Quantum Control”.
∗Author to whom correspondence should be addressed. E-mail: fqi@ustc.edu.cn, FAX: +86-551-5141078, Tel.: +86-551-3602125

DOI:10.1088/1674-0068/22/02/204-209
tion chamber with a reflection time-of-flight mass spectrometer (RTOF-MS). Pyridine was controlled by a syringe pump (ISCO 1000D) with the liquid flow rate of 0.10 mL/min (equivalent to $27.75 \times 10^{-3}$ SLM in gas phase) at room temperature. Subsequently, pyridine was vaporized and mixed with Ar which was controlled by a MKS mass flow controller with the flow rate of 0.50 SLM. The vaporizer was kept at a temperature of 450 K. Then the mixture of pyridine and Ar was fed into a 3.0-mm-ID (inside diameter) and 300-mm length alumina flow tube with 60 mm stationed inside the furnace. The pyrolysis species, including the reactant, intermediates, and products, were sampled by a quartz nozzle with a $\sim 500 \mu$m orifice at the tip. The formed molecular beam in the differentially pumped chamber then passed into the photoionization chamber through a nickel skimmer and was crossed by the tunable synchrotron VUV light. A digital delay generator (DG 535, SRS) was used to trigger a pulsed power supply and the multiscaler (P7888, FAST Comtec) as well. The ions were drawn out of the photoionization region by the pulse extraction field and subsequently collected by a microchannel plate (MCP) detector. Finally, the ions were detected by a silicon photodiode (SXUV-100, International Radiation Detectors, Inc.) used to monitor the photon flux for normalizing ion signals. Pyridine was purchased from Sinopharm Chemical Reagent Limited Co., Shanghai, China with a purity of $\geq 99.5\%$. No further purification was performed for this study.

To reduce collisions of the pyrolysis species and detect the primary and secondary products including radicals, the pyrolysis chamber was kept at low pressure (267 Pa) controlled by a MKS throttle valve in this work. The temperature was measured by a Pt-30%Rh/Pt-6%Rh thermocouple inserted in the heating region inside the flow tube. The temperature uncertainty is within 50 K.

A series of mass spectra were measured with the variation of photon energy at specified temperature for measurements of photoionization efficiency (PIE) spectra. The integrated ion intensities for a specified mass were normalized by the photon flux and then plotted as a function of the photon energy, which yielded PIE spectra containing information of ionization energies (IEs) of specific species. Mass spectra can also be recorded at fixed photon energy for various pyrolysis temperatures. In order to avoid fragmentation, mass spectra were recorded near-ionization thresholds for temperature scanning. In this work, the measurements were carried out at the selected photon energies of 16.00, 11.70, 11.00, 10.78, 10.00, and 9.50 eV. The temperature ranged from 1255 K to 1765 K.

III. RESULTS AND DISCUSSION

A. Species Identification

The identification of pyrolysis species is based on the measurement of photoionization mass spectra and the photoionization efficiency spectra (PIE). A stack plot of photoionization mass spectra within the temperature range of 1255-1765 K is presented in Fig.1. The selected energy is 11.70 eV, at which most of the pyrolysis intermediates and products can be ionized and detected. Partial signals are amplified by a factor of 4 in order to clearly reveal the weak peaks. The intensities of pyrolysis intermediates and products varies as the temperature increases. The amount of pyridine decreases to about 25% at 1765 K.

A stack plot of photoionization mass spectra of pyridine with four different photon energies ranging from 9.50 eV to 16.00 eV at 1745 K is presented in Fig.2. Part of the mass spectra (from $m/z=88$ to 110) are amplified by a factor of 2 for the better illustration of the mass peaks of $m/z=103$ and 104. Mass peaks of $m/z=52, 74$ can be recognized together with trace amount of $m/z=53, 54, 78, 103$ at the energies lower than 11.00 eV. As the energy increases, the peaks become abundant which correspond to most of the pyrolysis intermediates and products, such as $m/z=28, 40, 50, 65, 77, 79$. Specially, $m/z=26, 53$ and trace amount of $m/z=51$ began to emerge at energy higher than 11.70 eV. The mass peaks of $m/z=16$ and 27 can be observed at the high energy of 16.00 eV. Furthermore, the identification of pyrolysis species can be obtained by the further measurement of PIE spectra which are selectively depicted in Fig.3. Clear onsets on PIE spectra of $m/z=26$ and 51 are located at 11.40 and 11.61 eV, as shown in Fig.3, which correspond to the IEs of acetylene (11.40 eV [19]) and cyanoacetylene (11.61 eV [19]), respectively. In this work, about 20

![FIG. 1 The stack plot of photoionization mass spectra for the pyrolysis of pyridine with temperatures at the photon energy of 11.70 eV.](image-url)
intermediates and products are identified and listed in Table I.

B. Mole fraction profiles of pyrolysis species

The mole fractions of the observed pyrolysis species versus the temperature can be evaluated from the measurements of near-threshold photoionization mass spectra. The evaluation method of mole fraction has been reported in detail elsewhere [18]. It should be pointed out that the photoionization cross-section data of some nitrogenous compounds are not available, but fortunately, at the selected near-threshold photon energies they can be deduced from previous PIE measurements [15,20-25]. The mole fraction profiles of pyrolysis intermediates versus temperatures are shown in Fig.4 and Fig.5.

The mole fraction profiles of pyridine and major products are displayed in Fig.4. The mole fractions of C$_2$H$_2$, H$_2$, and the nitrogenous products HCN are of the magnitude order of $10^{-2}$. The concentration of HCN increases continuously as the temperature increases with the highest yield. The initial formation temperatures ($T_F$) of C$_2$H$_2$ and HCN are around 1405 K which indicate they are not the primary product [10]. Lower concentration of C$_5$H$_3$N (cyanovinylacetylene) is detected with the $T_F$ of 1255 K, which indicates C$_5$H$_3$N formed at the early stage of pyrolysis. The smallest molecule H$_2$ has the relative low $T_F$ of 1330 K with abundant amount and its mole fraction increases monotonically. It is worth noting that no C$_5$H$_4$N was detected, which is in consistent with the previous results [10].

The mole fractions of most hydrocarbons, nitrogenous pyrolysis intermediates, and products are of the magnitude orders of $10^{-3}$ and $10^{-4}$, as shown in Fig.5. The mole fraction profiles of intermediates including C$_2$H$_4$, C$_4$H$_4$, C$_6$H$_5$, C$_6$H$_2$, CH$_4$, and nitrogenous compounds vinylcyanide (C$_5$H$_3$N) and cyanoacetylene (C$_4$HN) are displayed in Fig.5(a). $T_F$ values for C$_4$H$_4$ and C$_5$H$_3$N are 1405 K indicating they are the earliest formed species in Fig.5(a). Those products with $T_F$ values of 1560 and 1630 K are produced in the secondary process. Figure 5(b) presents the mole fraction profiles of propyne (C$_3$H$_4$), C$_4$H$_3$, C$_4$H$_5$, cyanoalene (C$_5$H$_3$N) with the $T_F$ in the range from 1440 K to 1520 K. Ben-
TABLE I Intermediates and products identified in the pyrolysis of pyridine.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Formula</th>
<th>Species</th>
<th>IE/eV</th>
<th>$X_M$</th>
<th>$T_F$/K</th>
<th>$T_M$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>H$_2$</td>
<td>Hydrogen</td>
<td>15.43</td>
<td>15.43</td>
<td>3.02 $\times 10^{-2}$</td>
<td>1330</td>
</tr>
<tr>
<td>16</td>
<td>CH$_4$</td>
<td>Methane</td>
<td>12.61</td>
<td>12.60</td>
<td>7.17 $\times 10^{-4}$</td>
<td>1595</td>
</tr>
<tr>
<td>26</td>
<td>C$_2$H$_2$</td>
<td>Acetylene</td>
<td>11.40</td>
<td>11.40</td>
<td>3.49 $\times 10^{-2}$</td>
<td>1405</td>
</tr>
<tr>
<td>27</td>
<td>HCN</td>
<td>Hydrogen cyanide</td>
<td>13.60</td>
<td>13.60</td>
<td>5.07 $\times 10^{-2}$</td>
<td>1405</td>
</tr>
<tr>
<td>28</td>
<td>C$_2$H$_4$</td>
<td>Ethylene</td>
<td>10.51</td>
<td>10.51</td>
<td>1.13 $\times 10^{-3}$</td>
<td>1480</td>
</tr>
<tr>
<td>40</td>
<td>C$_3$H$_6$</td>
<td>Propyne</td>
<td>10.36</td>
<td>10.35</td>
<td>2.07 $\times 10^{-4}$</td>
<td>1440</td>
</tr>
<tr>
<td>50</td>
<td>C$_4$H$_2$</td>
<td>1,3-butadiyne</td>
<td>10.17</td>
<td>10.17</td>
<td>4.94 $\times 10^{-3}$</td>
<td>1520</td>
</tr>
<tr>
<td>51</td>
<td>C$_5$HN</td>
<td>Cyanoacetylene</td>
<td>11.62</td>
<td>11.60</td>
<td>6.58 $\times 10^{-4}$</td>
<td>1480</td>
</tr>
<tr>
<td>52</td>
<td>C$_5$H$_4$</td>
<td>Vinylcyclopropane</td>
<td>9.58</td>
<td>9.58</td>
<td>1.85 $\times 10^{-3}$</td>
<td>1405</td>
</tr>
<tr>
<td>53</td>
<td>C$_5$H$_5$</td>
<td>Vinylycine</td>
<td>10.91</td>
<td>10.91</td>
<td>3.12 $\times 10^{-3}$</td>
<td>1405</td>
</tr>
<tr>
<td>54</td>
<td>C$_6$H$_6$</td>
<td>1,3-butadiene</td>
<td>9.07</td>
<td>9.07</td>
<td>1.08 $\times 10^{-4}$</td>
<td>1520</td>
</tr>
<tr>
<td>65</td>
<td>C$_7$H$_8$N</td>
<td>Cyanoallene</td>
<td>10.35</td>
<td>10.37</td>
<td>8.38 $\times 10^{-5}$</td>
<td>1560</td>
</tr>
<tr>
<td>74</td>
<td>C$_8$H$_2$</td>
<td>1,3,5-hexatriyne</td>
<td>9.50</td>
<td>9.48</td>
<td>8.08 $\times 10^{-4}$</td>
<td>1630</td>
</tr>
<tr>
<td>77</td>
<td>C$_8$H$_4$N</td>
<td>Cyanoallene</td>
<td>9.33</td>
<td>9.33</td>
<td>2.59 $\times 10^{-3}$</td>
<td>1255</td>
</tr>
<tr>
<td>78</td>
<td>C$_8$H$_6$</td>
<td>Benzene</td>
<td>9.24</td>
<td>&lt;10$^{-5}$</td>
<td>1670</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>C$_8$H$_4$N</td>
<td>Pyridine</td>
<td>9.26</td>
<td>9.26</td>
<td>2.73 $\times 10^{-4}$</td>
<td>1560</td>
</tr>
<tr>
<td>93</td>
<td>C$_8$H$_4$N</td>
<td>Pyridine</td>
<td>9.73</td>
<td>9.71</td>
<td>3.25 $\times 10^{-4}$</td>
<td>1560</td>
</tr>
<tr>
<td>103</td>
<td>C$_9$H$_4$N</td>
<td>Pyridine</td>
<td>10.10</td>
<td>9.96</td>
<td>2.73 $\times 10^{-4}$</td>
<td>1560</td>
</tr>
</tbody>
</table>

The uncertainty for IE is 0.05 eV.

b The maximum mole fractions.

c $T_F$ refers to the initial temperature for formation of species.

d $T_M$ refers to the temperature relating to the maximum mole fraction.

e The value is total maximum mole fraction of CH$_3$CCCH$_2$ and CH$_3$CHCCH.

f The value is for both CH$_3$CCCH$_2$ and CH$_3$CHCCH.

The mole fraction profiles of most species in Fig.5 ascend to their highest values as temperature increases, except for those of CH$_4$ and C$_4$H$_3$.

C. Schematic reaction pathways

The reaction mechanism developed to interpret the above results involves a chain reaction initiated by C–H bond scission, as suggested in Refs.[13,14,26-29]. An es-

FIG. 5 Mole fraction profiles for the other pyrolysis intermediates and products formed from pyridine pyrolysis.

zonitrile (C$_2$H$_5$N) and 3-pyridinecarbonitrile (C$_6$H$_4$N$_2$) are the recombination products with high $T_F$ values of 1560 K. The mole fraction profiles of most species in Fig.5 ascend to their highest values as temperature increases, except for those of CH$_4$ and C$_4$H$_3$. DOI:10.1088/1674-0068/22/02/204-209
FIG. 6 A schematic decomposition pathways of pyridine pyrolysis at temperatures from 1255 K to 1765 K.

The estimation of the bond energies in the pyridine molecule would lead to the conclusion that the ring opening is less likely than C−H breakage [30]. The C−H and C−C bond energies in pyridine are the same as those in benzene, 428.0 and 489.9 kJ/mol, respectively, and the C−N bond energy is calculated to be 445.2 kJ/mol, supporting the conclusion that the C−H bond is more likely to be broken [10,12]. Thus the subsequent reactions are dependent on the thermochemistry of the cyclic pyridyl radicals produced by the scission of C−H bond. o-pyridyl, p-pyridyl, and m-pyridyl are the three possible C−H cleavage products which may all undergo ring opening. Among them o-pyridyl is unique in its ability to produce directly an open-chain cyano radical (CHCHCHCN, R1) [13,26].

Based on the assumption of the stability of R1, the dominant mechanism in the pyrolysis of pyridine at low temperature range is proposed to be the following [13]:

\[ C_2H_5N \rightarrow o-, p-, m-C_5H_4N + H \]  
(1)

\[ o-C_2H_4N \rightarrow R1 \]  
(2)

\[ R1 \rightarrow C_2H_2 + HC=CHCN \]  
(3)

\[ H + C_5H_5N \rightarrow o-, p-, m-C_5H_4N + H_2 \]  
(4)

The above short-chain mechanism is in accord with the experimental observations that C5H4N, C2H2, and C5H4 are the principal products at low temperature. C2H2 is the precursor for the formation of C4H2 and C6H2 by polymerization process [31]. Other than the major low-temperature chain mechanism, there is also a minor chain process which may arise via fission of a secondary H from R1, producing cyanovinylacetylene (CVA) [13].

\[ R1 \rightarrow HC=CH=CHCN + H \]  
(5)

It is proposed that both pyridyl and open-chain radicals could undergo molecular elimination of HCN to produce the C4H3 radical as follows.

\[ o-, p-, m-C_5H_4N \rightarrow HCN + C_4H_3 \]  
(6)

\[ R1 \rightarrow HCN + C_4H_3 \]  
(7)

HCN is mainly deduced from the m-pyridyl and its subsequent open-ring radical [13,28]. Although the authors are unaware of any previous studies of HCN elimination from cyclic radicals, HCN elimination is an analogous process to the decomposition of benzyl radicals by invoking a rearrangement to a bicyclic C7H7 radical which can molecularly eliminate C2H2 [13]. The counterpart C4H3 radical is unstable and could readily form either C4H4 by H addition or C4H2 by H abstraction. Free radical and decomposition of unstable intermediates may attribute to the formation of minor reaction products. When C5H4N is formed, they may be consumed through different channels and produce C3H3N by H addition or C3HN by H abstraction as described in Fig.6.

The m-pyridyl radical can also undergo a C2H2 radical elimination process together with the formation of C3HN. It is possible that the recombinant of the C2H2 radical may be slow due to the low concentration of the product 1,3-butadiene (C4H6). The direct ring opening of pyridine for the formation of HCN and C4H2, C3H2 and C4H2, C3H2N and C4H2 may also make potential contributions to the pyrolysis product. In the previous studies, the sooting tendency of pyridine decomposition has been reported to be substantially less than that of other aromatics (e.g. benzene) and even less than that of pyrrole [32,33]. The result of this investigation is consistent with the previous ones, since very few species with molecular weights higher than that of pyridine were observed [13]. Only mass 103 and 104 were found in this pyrolysis process. Mass 103 and mass 104 corre-
spond to benzonitrile and 3-pyridinecarbonitrile which have also been identified in investigation of the low-pressure premixed pyridine rich flame [34]. Based on the present experimental results, it appears that it is also difficult to grow a second ring. The reason for this may be the short lifetime of the pyridyl radical. Another explanation relates to the relative reactivity of the carbon atoms on pyridine. Analogous to the growth mechanism for polyaromatic hydrocarbons, acetylene will add to the pyridyl radical. But the carbon atom located at meta position has the lowest reactivity and will inhibit the addition of the additional second C_{2}H_{2} needed for the ring formation [13,14]. The schematic decomposition pathways of pyridine pyrolysis at temperatures from 1400 K to 1845 K are summarized in Fig.6.

IV. CONCLUSION

The pyrolysis of pyridine was studied with tunable synchrotron VUV photoionization and molecular beam mass spectrometry. The evolution of the major and minor products in the pyrolytic process was imaged by both the temperature scanning profile and the energy scanning profile. The dominant pathways of the preferable open chain of o-pyridyl and m-pyridyl are presented schematically together with some free radical reactions accompanied by decomposition of unstable intermediates for the formation of minor products. Further analysis and theoretical calculation will be carried out to enrich the reaction network of the precursors for NOx evolution.

V. ACKNOWLEDGMENTS

This work was supported by the Chinese Academy of Sciences, the Natural Science Foundation of China (No.20533040), the National Basic Research Program of China (973) (No.2007CB815204Hm), and the Ministry of Science and Technology of China (No.2007DFA61310).