

TAR CRACKING STUDIED WITH A PULSED MICROREACTOR

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ABSTRACT

We have developed a new technique for investigating reactions that are important during pyrolysis and combustion. Molecules of interest are pulsed through a small tubular furnace and the products analyzed using photoionization Time-of-Flight Mass Spectrometry (TOFMS) and matrix isolation Fourier-Transform Infrared (FTIR) spectroscopy. The short residence times (10–100 μ s) and high temperatures (up to 1800K) of these reactors make them ideal for measuring the initial products during thermal reactions since important reaction intermediates can be identified and quantified. We have used these reactors to study the pyrolysis of compounds of relevance to the pyrolysis and combustion of biomass. We have trapped and measured reactive intermediates as well as stable products. The combination of these two analytical techniques provides a powerful and unique method for understanding the thermal chemistry of biopolymers.

INTRODUCTION

Thermal treatment of biomass remains appealing as a source of energy, fuels and chemicals, but a thorough understanding of the chemical processes involved in pyrolysis and combustion remains elusive. The complicated chemical composition of lignocellulosic materials make development of complete elementary reaction mechanisms unrealistic for thermal processes, but an understanding of some of the most important reactions would be very valuable for understanding currently used biomass technologies and for developing new ones. Many of reactions associated with pyrolysis and combustion of biomass have been inferred from indirect experimental evidence. We have started an investigation to directly measure some of these reactions. Our initial studies focus on the formation and cracking of "tar" compounds and we will use new experimental and analytical techniques that will help unravel this chemistry. We will present experimental results which demonstrate these new capabilities.

EXPERIMENTAL

We use tubular reactors that are similar to the supersonic nozzles developed by Chen *et al.* [1] and used by others [2,3] for the preparation of radicals in molecular beams. Our version of the "Chen Nozzle" is shown in Figure 1 and it consists of a small tube (1mm i.d.) of silicon carbide that is resistively heated up to 1800 K. Gas mixtures are pulsed through the heated tube and expanded into a vacuum chamber for analysis. The supersonic cooling and low number densities in this expansion instantly quench and cool reactive intermediates, which are then analyzed using TOFMS or matrix isolation FTIR spectroscopy. The very high temperatures and short residence times (10–100 μ s) in the heated tubes allows one to trap and isolate primary intermediates from thermal reactions, while reducing secondary reactions.

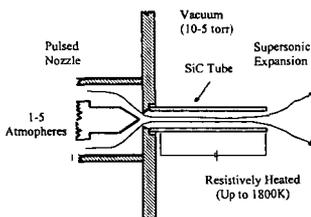


Figure 1. Schematic drawing of pulsed microreactor used in these experiments

TIME-OF-FLIGHT MASS SPECTROMETRY

We have used a newly built TOF mass spectrometer to investigate the pyrolytic reactions of a number of molecules. The expansion from the Chen Nozzle was skimmed and formed into a molecular beam, which was crossed by a vacuum ultraviolet (VUV) light beam. VUV (118 nm, 10.5 eV) photons were formed by tripling the third harmonic of a Nd/YAG laser in a xenon cell. The energy of these photons is sufficient to ionize most organic molecules and radicals while

reducing ion fragmentation relative to electron impact ionization. As an example, consider Figure 2. This figure shows the TOF mass spectrum of the products from the pyrolysis of furan in our Chen Nozzle (top) compared to the mass spectra obtained from a molecular beam mass spectrometer (MBMS). As can be seen, fragmentation is lower for the TOFMS even when the MBMS is run at an electron impact energy of 18 eV. TOFMS is also very sensitive (detection limits down to 10 ppb) and capable of high resolution. Figure 3 compares the mass resolution of peaks from the pyrolysis furan using TOF and quadrupole MBMS. TOF peak widths are about 0.06 AMU, while peak widths are about 0.7 AMU for quadrupole. The high resolution, low fragmentation and high sensitivity make TOFMS ideal for identifying pyrolysis products.

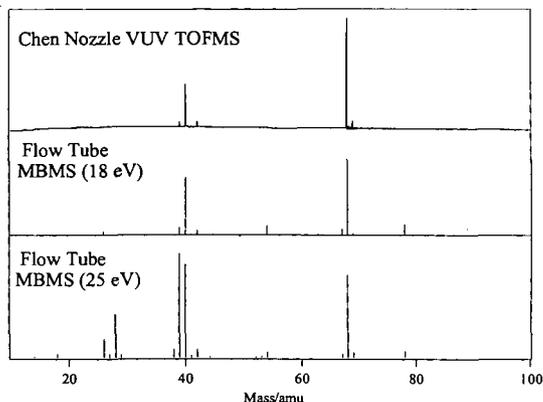


Figure 2 Mass spectra of the pyrolysis products of furan. The top spectrum shows the products from pyrolysis in a Chen Nozzle while the bottom two spectra show products from a heated flow tube reactor (1 cm i.d., ~1 sec. residence time, 750 °C).

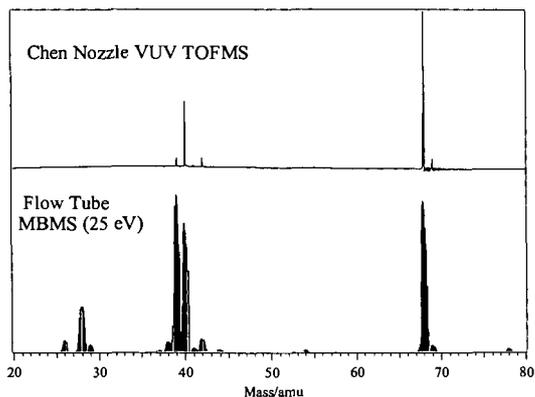


Figure 3 Mass spectra of the pyrolysis products of furan showing the superior mass resolution of the TOFMS (top) relative to the quadrupole MBMS (bottom).

We measured the pyrolysis TOF mass spectra of a number of different compounds using the Chen Nozzle. As an initial test of the Chen Nozzle, we pyrolyzed ethyl acetate and used the TOFMS to identify the well known products, ethylene and acetic acid[4]. We have also measured the products obtained from the pyrolysis of allyl bromide and allyl iodide. Our preliminary TOF mass spectra of allyl bromide and its pyrolysis products are shown in Figure 4. The middle spectrum in this figure shows that the pyrolysis of allyl bromide in the Chen Nozzle produces primarily allyl radical. This demonstrates that we can use this reactor to measure primary pyrolysis products such as radicals. When we conduct pyrolysis experiments using a

conventional flow tube reactor (1 cm diameter quartz tube heated to 500–800 °C, 100–1000 ms residence times) we only detect stable products that result from the reaction of ally radical. The spectrum at the top of Figure 4 shows the products produced when allyl bromide is heated above 1500 K (the exact temperatures could not be measured) in the Chen Nozzle. The products identified in this spectrum are similar to what is seen in conventional flow tubes. This demonstrates that the Chen Nozzle can also be used to study the thermal decomposition of reactive intermediates and bimolecular reactions.

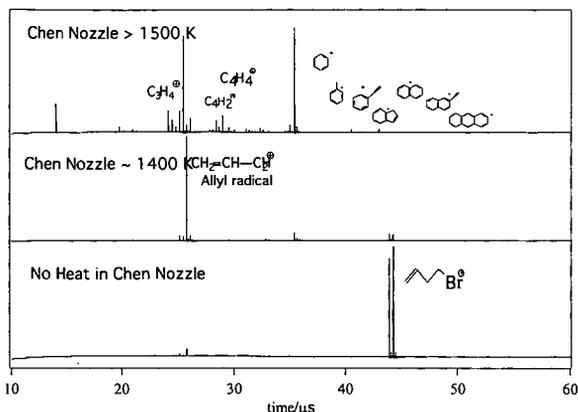


Figure 4 The products from the pyrolysis of allyl bromide in a Chen Nozzle

MATRIX ISOLATION ANALYSIS

While mass spectrometry is a powerful technique for identifying products from thermal reactions, it suffers from its inability to distinguish isomers and from its difficulty with quantitative analysis. Thus, we have developed experimental hardware that allows us to trap the pyrolysis products from a Chen Nozzle in an argon matrix. The compound of interest is diluted in argon and passed through our Chen Nozzle and the products are deposited on a cold (12K) CsI window. Identification of the pyrolysis products is then carried out using FTIR spectroscopy.

Figures 5 show some results for the pyrolysis of allyl iodide. The products from allyl iodide should be the same as those from allyl bromide, but the iodide requires a lower pyrolysis temperature. The matrix isolation spectrum shown in Figure 5 is obtained by subtracting our any residual allyl iodide and clearly shows the formation of allyl radical, allene, ethylene and acetylene. These peak assignments are made based upon the literature assignments of matrix isolation spectra [5-8]. The matrix results are consistent with the TOFMS results and demonstrate that matrix isolation spectroscopy is ideal for unambiguous product identification

THE PYROLYSIS OF FURAN

Furan was initially chosen as a model compound because it is known to be an important intermediate in the pyrolysis and combustion of biopolymers [9]. Figure 6 shows the TOF mass spectra resulting from the pyrolysis of furan in our Chen Nozzle. Our TOFMS measurements agree qualitatively with those reported in the literature [10,11]. As with allyl bromide, higher temperature allows the measurement of products from secondary, bimolecular reactions.

Matrix isolation FTIR spectroscopy was used to identify the molecular structure of the compounds products identified by TOFMS. The preliminary results from this experiment are shown in Figure 7. The bottom spectrum shows portions of the furan spectrum when the Chen Nozzle is unheated, while the top shows the spectrum when the nozzle is heated to approximately 1400 K. As can be seen, the matrix isolation technique can differentiate between methyl acetylene, allene and cyclopropene, all of which have the same mass and so are indistinguishable with TOFMS. Thus, both the allyl bromide and the furan example demonstrate the complementary and consistent nature and matrix isolation FTIR and TOFMS.

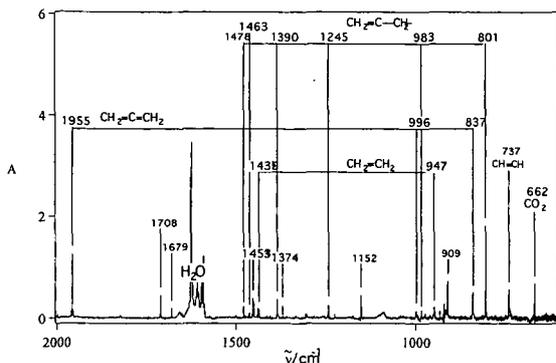


Figure 5 Matrix isolation FTIR spectrum of the products obtained from the pyrolysis of allyl iodide in a Chen Nozzle. Allyl radical ($\text{CH}_2=\text{CH}-\text{CH}_2^\bullet$), allene ($\text{CH}_2=\text{C}=\text{CH}_2$), ethylene ($\text{CH}_2=\text{CH}_2$), and acetylene ($\text{CH}\equiv\text{CH}$) are identified in the spectrum

Pyrolysis of Furan: Time-of-Flight Mass Spectra

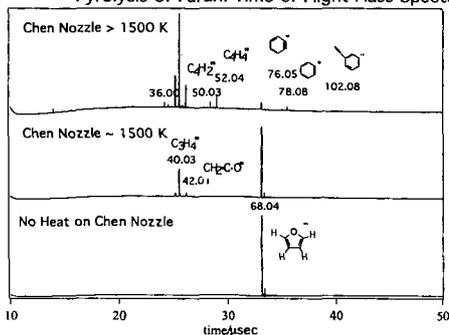
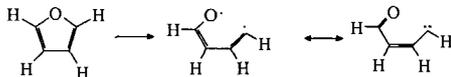


Figure 6 TOF mass spectra of the products of pyrolysis of furan in a Chen Nozzle (top and middle) compared to the TOF mass spectrum of furan (bottom).

Earlier studies of the pyrolysis of furan are consistent with our results in that allene, methyl acetylene, acetylene and ketene are reported as primary pyrolysis products. Our possible observation of cyclopropene is unique but consistent with proposed mechanisms. In the mechanisms proposed in the literature [11], the first step in the destruction of furan is the breaking of the C-O bond in the ring:



It is unclear how much energy would be required to break this bond. Typically, ether C-O bonds are weak (82 kcal/mol) [12], but aromatic stabilization energy will be sacrificed, though some stabilization energy will be regained in the resulting diradical. An alternative mechanism involving the attack of furan by hydrogen atoms is shown in Scheme I. Hydrogen atom is reformed in each branch of the mechanism, making the reaction catalytic. This could account for the low observed Arrhenius activation energy (78 kcal/mol) [6,7]. Hydrogen atom could be formed by the rupture of the C-H bond. The bond dissociation energy for this bond has not been measured though our *ab initio* calculations give a value of 118 kcal/mol.

Matrix Isolation FTIR

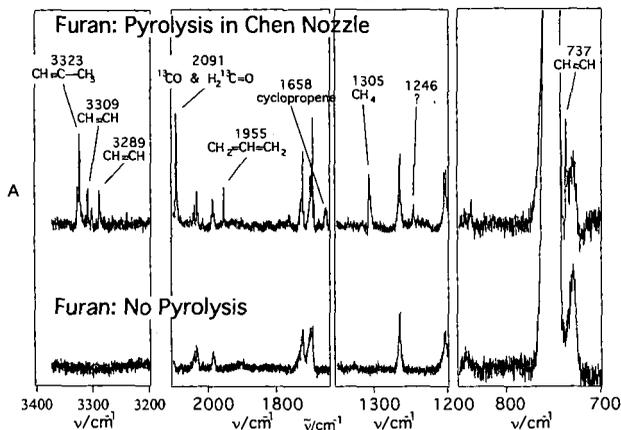
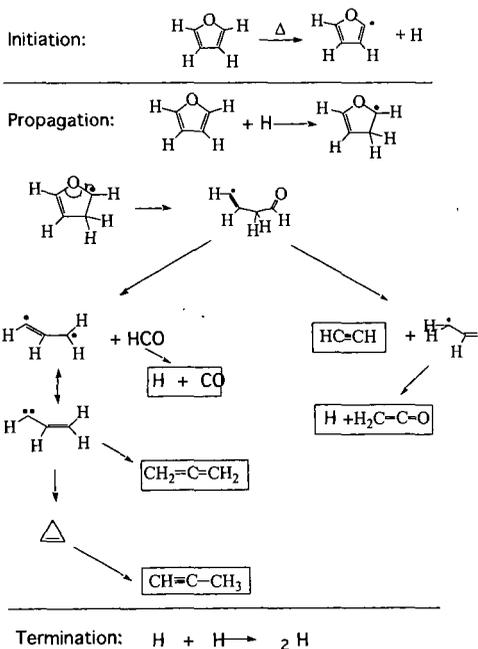


Figure 7 Matrix isolation FTIR spectrum of the pyrolysis products of furan (top) compared to the spectrum of furan alone.

Scheme I: Mechanism for Furan Decomposition



CONCLUSIONS

The combination of high temperature Chen Nozzles with TOFMS and matrix isolation FTIR spectroscopy is a powerful tool for understanding the thermal chemistry occurring during the combustion and pyrolysis of biopolymers. It allows the unambiguous identification of reaction intermediates as well as stable products.

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