

Pulsed Pyrolysis Nozzle for Introducing Radicals into an ICR Cell

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Overview

- Devise an experiment to study ion/radical reactions in a modified FT-ICR
- Construct a pyrolysis nozzle to decompose specially designed organic precursors
- Construct a pulsed valve and driving circuit to introduce gas directly into the ICR vacuum chamber
- Employ computational fluid dynamics to predict gas flow properties both inside the pyrolysis tube and in the supersonic expansion

Introduction

We are interested in studying the reactions of gas phase ions with reactive intermediates such as radicals. It is straightforward with a variety of extant mass spectrometers to study reactions of ions with stable neutrals. Reactive species pose more of a problem since they are short-lived, difficult to make, and often dangerous to handle. Elegant experiments have been done generating such species by using chemistry, light, and heat. The generation of distonic ions in which the charge and radical sites are separated is an example.

Pyrolysis of suitable precursors possessing a weak bond can lead to intense beams of unstable species which can be seeded in a supersonic beam of inert carrier gas [1,2]. The precursors spend several microseconds in the hot-wall reactor where they are pyrolyzed the instant before they expand into

the vacuum. This technique is capable of making large densities of radicals, approximately 10^{14} cm^{-3} [3].

In this poster we describe the coupling of a pyrolysis nozzle, based on the work of Chen, with an FT-ICR. Although supersonic beams have been used previously with FT-ICRs [4], this is the first attempt to couple a pyrolysis jet for generating radicals to this instrument.

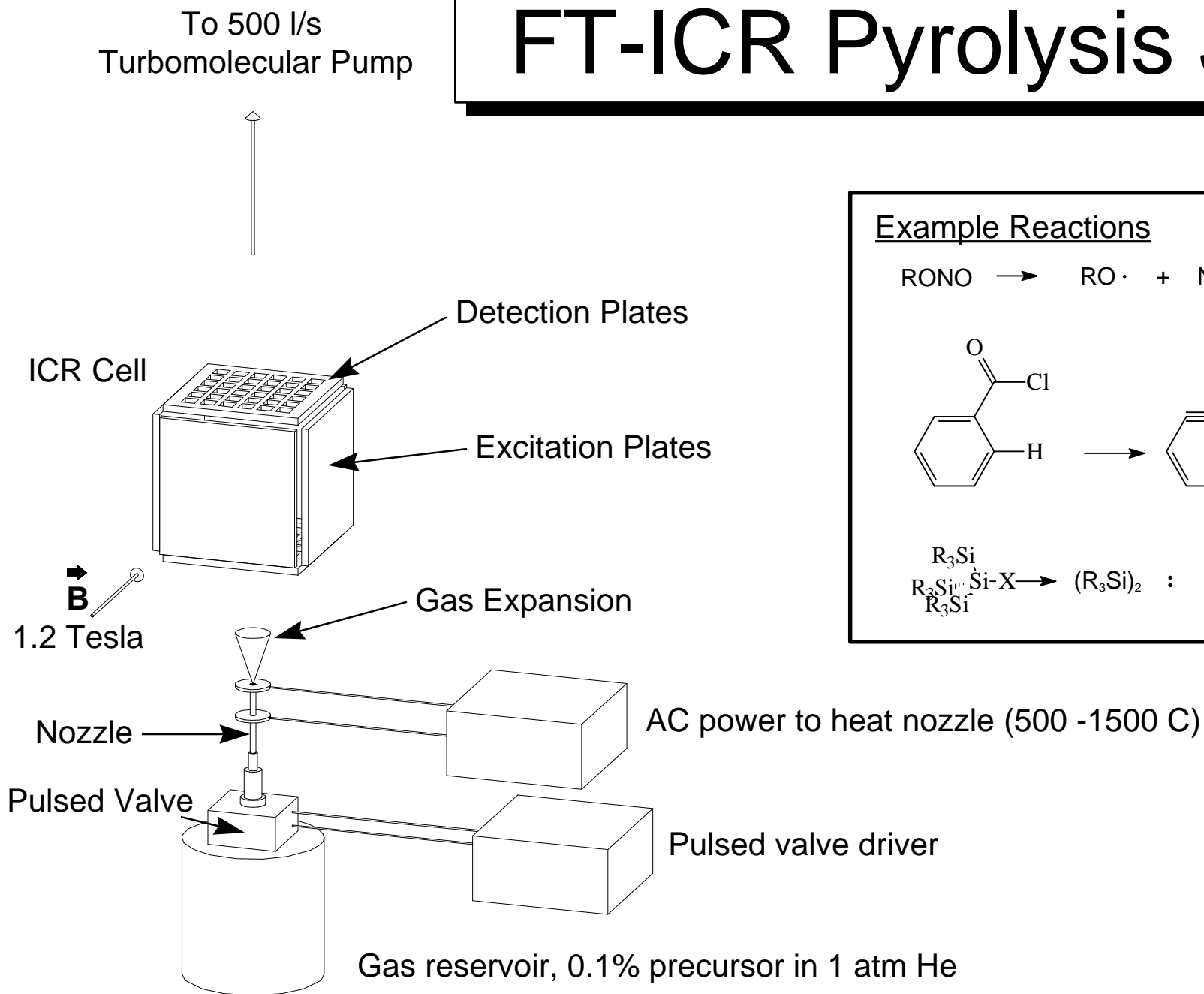
The pyrolysis nozzle operates at temperatures as high as 1850 K. The seeded beam it produces will intersect a small cloud of ions undergoing cyclotron motion inside of the ICR cell.

There are several advantages to coupling pyrolysis and ICR. First, the ICR is highly sensitive, unlike other spectroscopic techniques [3]. Thus, large quantities of dangerous precursors will not be needed. Second, m/z 1000 ions in the cell with a radius of 1 cm are traveling at

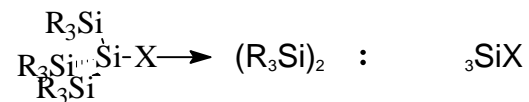
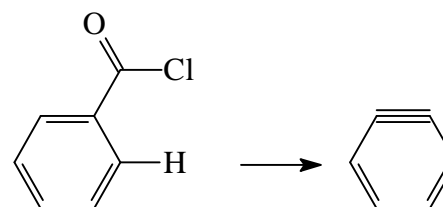
roughly the same velocities as neutrals in the seeded beam ($\sim 10^3$ m/s). This may allow gentle reactions (e.g., charge exchange) if the experiment is set up such that the ions and the neutral beam are moving in the same direction. Third, the trapped products of ion-radical reactions can be studied since the detection of the ions in an FT-ICR is nondestructive. For example, ionized radicals could be stored for subsequent studies of their reactivity.

The high speed gas flow is needed for short residence times inside the hot nozzle and for creating a directional beam in the vacuum chamber. However, the ICR is a low pressure instrument, $< 1 \times 10^{-6}$ Torr. We elect to bring these two techniques together using a piezoelectric pulsed valve capable of remaining open for 10 μ s or longer. The inclusion of the valve complicates the gas dynamics so we have resorted to numerical calculations to model the flow behavior.

FT-ICR Pyrolysis Jet



Example Reactions



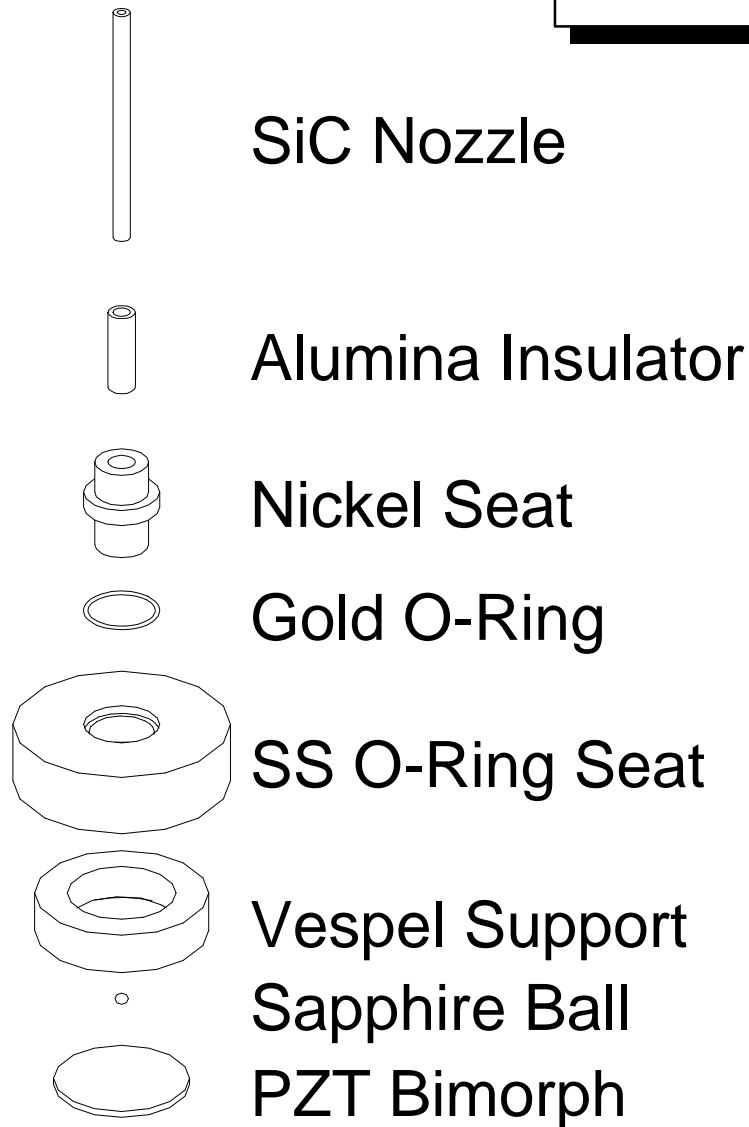
Description of the FT-ICR

The FT-ICR consists of a 1.2 Tesla magnet (Varian) and a 2" ICR cell. The data system is a Nicolet FTMS 1280. The vacuum system consists of a custom chamber pumped by a 500 L/s turbomolecular pump (Balzers TPU500) backed by a two stage roughing pump (Welch 1397). The chamber is equipped with the new pulsed valve as well as ports for a desorption probe, a laser beam, and a gas inlet system.

The original cell had solid excitation and detection plates. It was modified for these nozzle experiments since the supersonic beam has to move through the cell. New detection plates were made with 67% transmitting stainless steel mesh.

At the moment the pulsing of the valve is controlled manually but it will be interfaced to the experimental sequence generated by the FTMS 1280 software.

Pulsed Valve



The pulsed valve consists of a sapphire ball driven into a nickel seat by a lead zirconate titanate (PZT) piezoelectric bimorph. A spring, not shown, provides the restoring force that keeps the valve closed. It is capable of sealing from atmosphere to 10^{-8} Torr. The pulse duration is $10\ \mu\text{s}$ (FWHM) or longer and the repetition rate varies from 0 - 20 kHz.

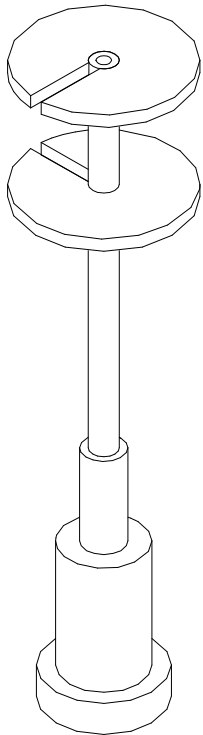
U.S. Patent 3,895,231 and Cross, J. B. and Valentini, J. J. *Rev. Sci. Instrum.* **53** 38-42 (1982).

Description of Pulsed Valve

Copper leads were soldered to the PZT bimorph. The sapphire ball was glued to the bimorph with epoxy. Alumina adhesive (903 HP Cotronics, Brooklyn, NY) bonds the nickel seat, alumina insulator, and silicon carbide tube together. The gold seal was made according to A. Roth, Vacuum Sealing Techniques pp. 380-381 (1994).

The pulsed valve driver circuit is modified from a design made for Washington University in 1982. Briefly, a 555 timer is used to generate a variable width pulse of about 5 V which is input to a comparator (LF347). This comparator controls a transistor (SN3440) which switches the larger voltage (up to 120 V) for valve operation.

Pyrolysis Nozzle



Graphite Contacts

Silicon Carbide Nozzle

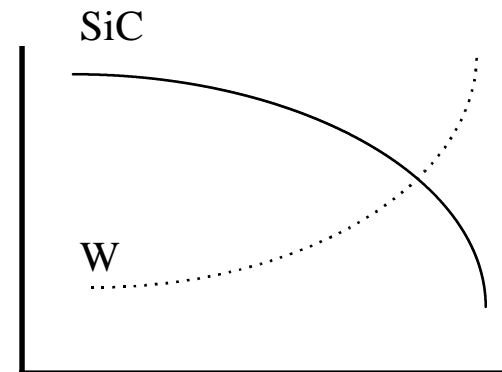
Alumina Insulator

Nickel Base

<u>Voltage (V)</u>	<u>Current (A)</u>	<u>Ballast (W)</u>	<u>Temp. (C)</u>
21.2	0.50	100	700
19.0	1.05	150	953
20.3	1.39	200	1108
24.3	2.00	100+200	1375
23.8	2.89	150+200	1536

Ballast resistance (light bulbs) were parallel when two were used.

Ω



T

Description of Pyrolysis Nozzle

The pyrolysis nozzle is based on a design of Chen.[1,2] It employs a 0.040" I.D., 0.020" wall silicon carbide tube (Hexoloy SA, Carborundum, Niagara Falls, NY). The tube is heated resistively until it reaches the desired temperature. The SiC nozzle is ground to an ID that nested in a standard aluminum oxide tube and cemented into this tube with ceramic adhesive (903HP, Cotronics, Brooklyn, NY). The Al_2O_3 tube, which provides both thermal and electrical insulation, is cemented into the nickel seat in the same manner. Electrical contact to the nozzle is provided by disks machined from high quality graphite (AXF-5Q, Poco Graphite, Decatur, TX). Clips fashioned from 0.020" molybdenum sheet carry the AC power to the graphite disks. The heated portion of the tube is 1 cm long.

Since the resistance of SiC is a negative function of temperature, ballast resistance is needed to prevent thermal runaway. This is provided by standard light bulbs with various powers. The tungsten filament inside of these bulbs has a resistance that is a strong positive function of temperature and thus limits the current. (See Ω vs. T plot)

A single-color infrared pyrometer (Ircon Ultimax UX-20) was used to measure the temperature of the nozzle in a test chamber. The wall temperature of the nozzle could be adjusted to any temperature between 900 K and 1850 K depending upon the ballast resistance.

Gas molecules spend several microseconds inside the hot portion of the nozzle. This should be sufficient time for decomposition, but not long enough for destruction of the radicals from bimolecular collisions.

Future Plans

Our goal is to create an experiment to probe ion interactions with a wide variety of reactive intermediates. In the future, we will incorporate an RF-only-mode event [7] to relax ions back to the center of the trap so we can carry out further reactions with neutrals and improve our sensitivity. We are also working on improving our calculations that model the gas pulse and we are creating a Direct Simulation Monte Carlo model of the supersonic expansion.

We plan to pursue studies of several kinds of chemistry using the pulsed pyrolysis nozzle. These include reactions of radicals with distonic ions, decompositions of a variety of compounds to generate singlet and triplet silylenes, and the interactions of charged biomolecules with radicals.

Conclusions

A pulsed pyrolysis nozzle that can achieve 10- μ s pulse widths and temperatures up to 1850 K has been interfaced to an FT-ICR with a modified trap. Although all of the parts are work separately, it is too early to gauge the effectiveness of the combined instrument. Gas dynamics calculations suggest that the residence times and temperatures inside the nozzle should lead to effective pyrolysis while the supersonic expansion will cool the seeded intermediates to approximately 10 K. Among the details to be addressed are interfacing the pulsed valve to the software that controls the rest of the experimental sequence.

References

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Acknowledgments

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