Air Force Research Laboratory

Ion-Molecule Reactions in a Nitrogen-Benzene Plasma: Implications for the Destruction of Aromatic Compounds

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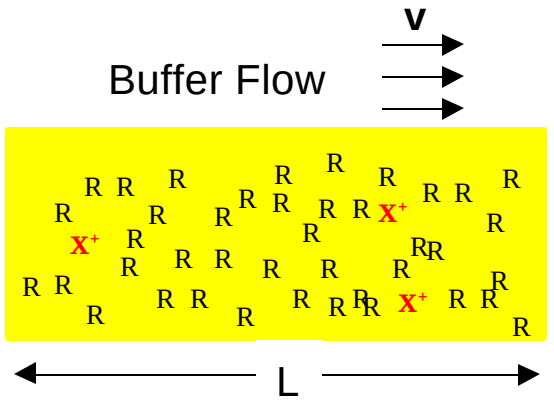
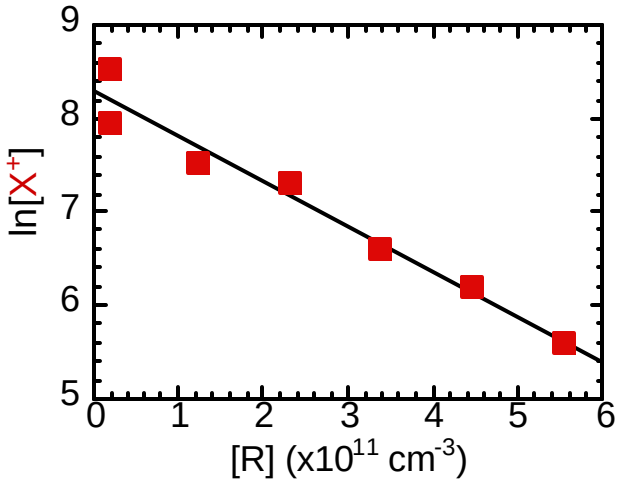
Introduction

Dielectric barrier discharges (DBDs) are attractive plasma sources for remediation of toxic gases, such as N_xO_y, SO_2, and VOCs, due to their ability to operate at higher pressures with moderate applied voltage. However, the destruction of aromatic compounds in these low temperature plasmas is problematic due to the small rate of ring-cleaving reactions by plasma generated oxidizing radicals at ambient gas temperatures. We report on a combination of laboratory flow tube kinetics measurements and computational modeling to investigate the question of whether a nitrogen plasma can be used for the destruction of waste aromatic compounds based on ion-molecule reactions.

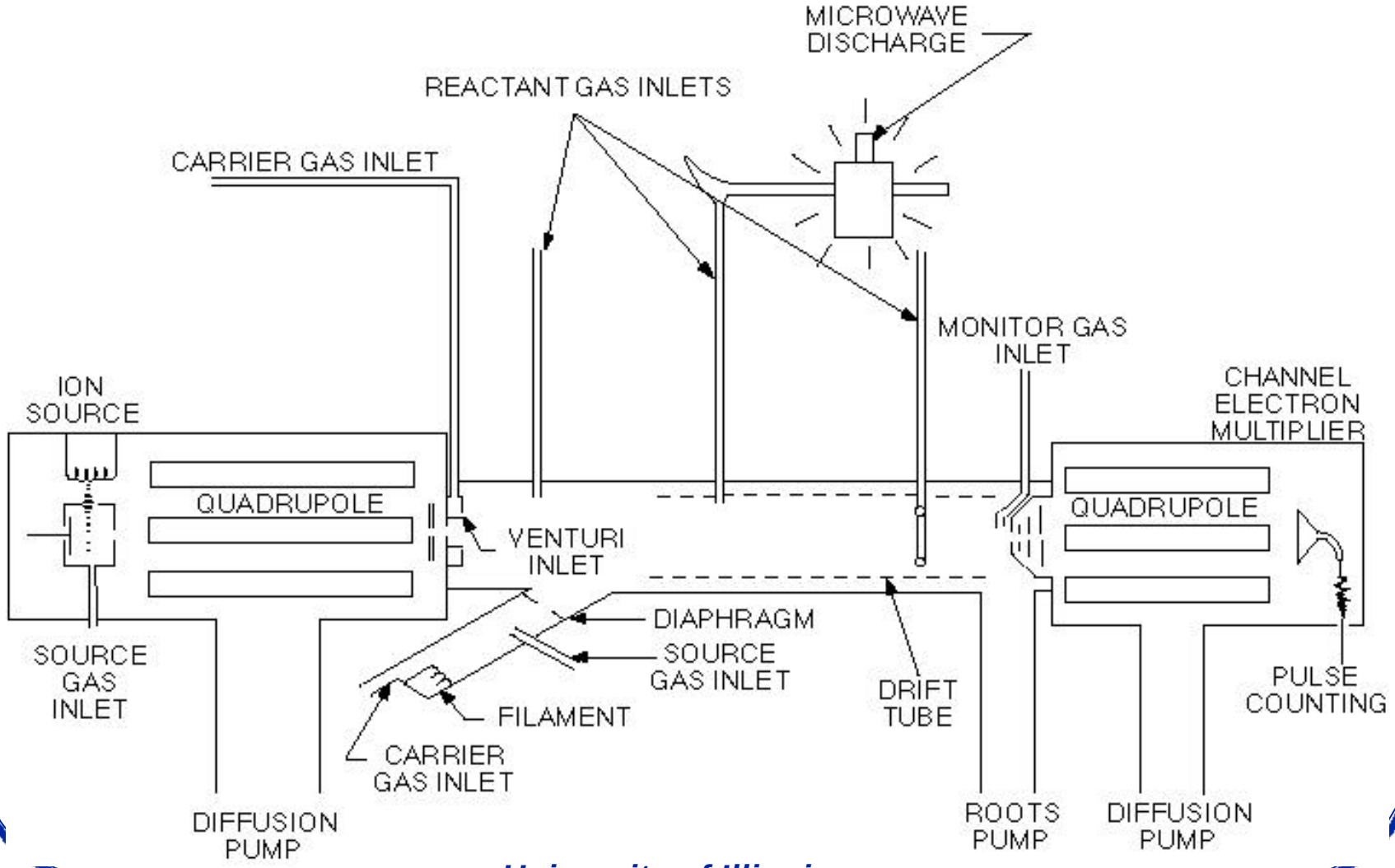
Flow Tube Kinetics

- Ion-molecule reaction $X^+ + R \rightarrow$ products
- Rate = $-d[X^+]/dt = k[X^+][R]$
  - R is present in a large excess
  - Pseudo first order kinetics
- $k = \frac{1}{[R]\,\tau} \ln\left(\frac{[X_o^+]}{[X^+]}\right)$
  - The reaction time is $\tau = L/\mathbf{v}_{ion}$
- Plot $\ln[X^+]$ vs [R] and the slope = $-k\tau$

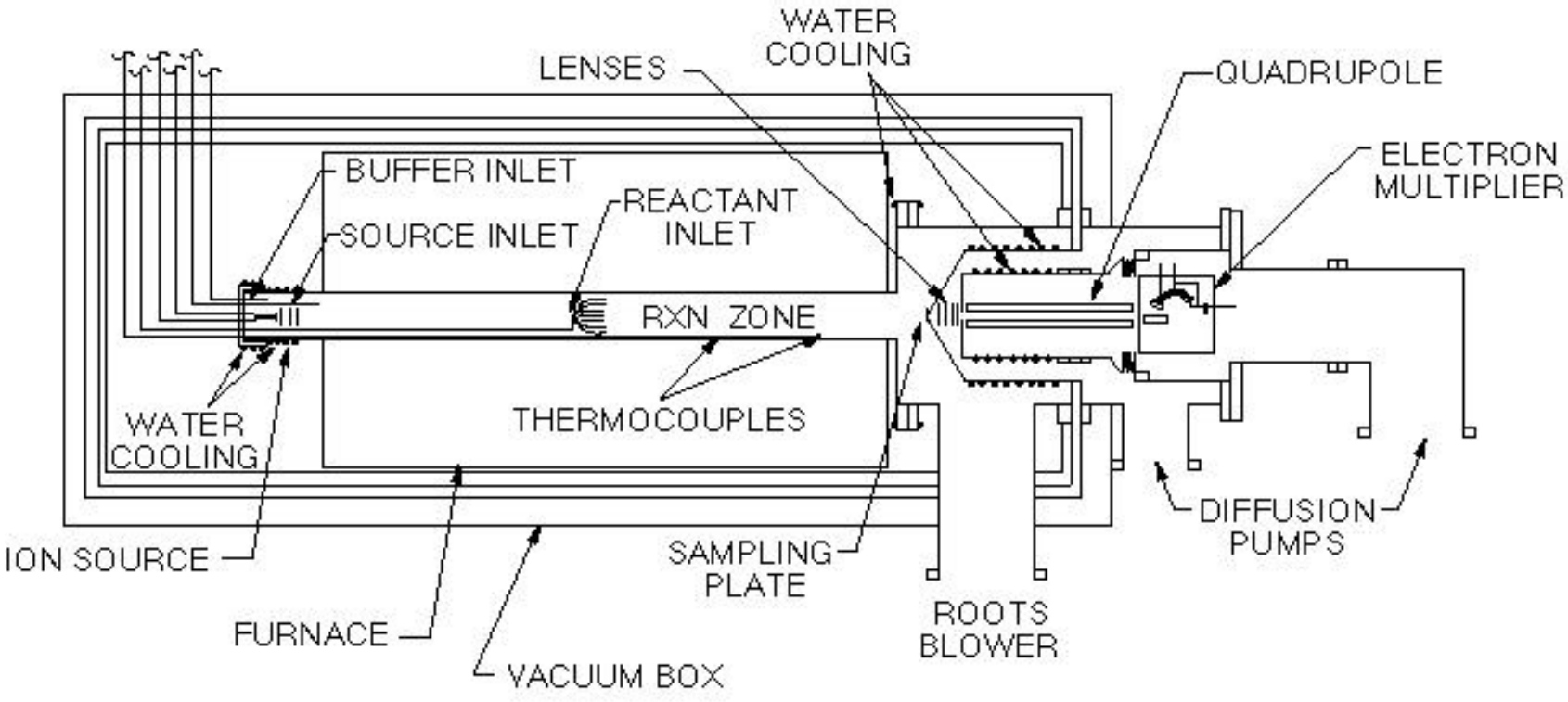




Selected Ion Flow Tube (SIFT)



High Temp Flowing Afterglow



Ceramic tube-1800 K Quartz tube-1400 K

C_6H_6 Ion-Molecule Reactions

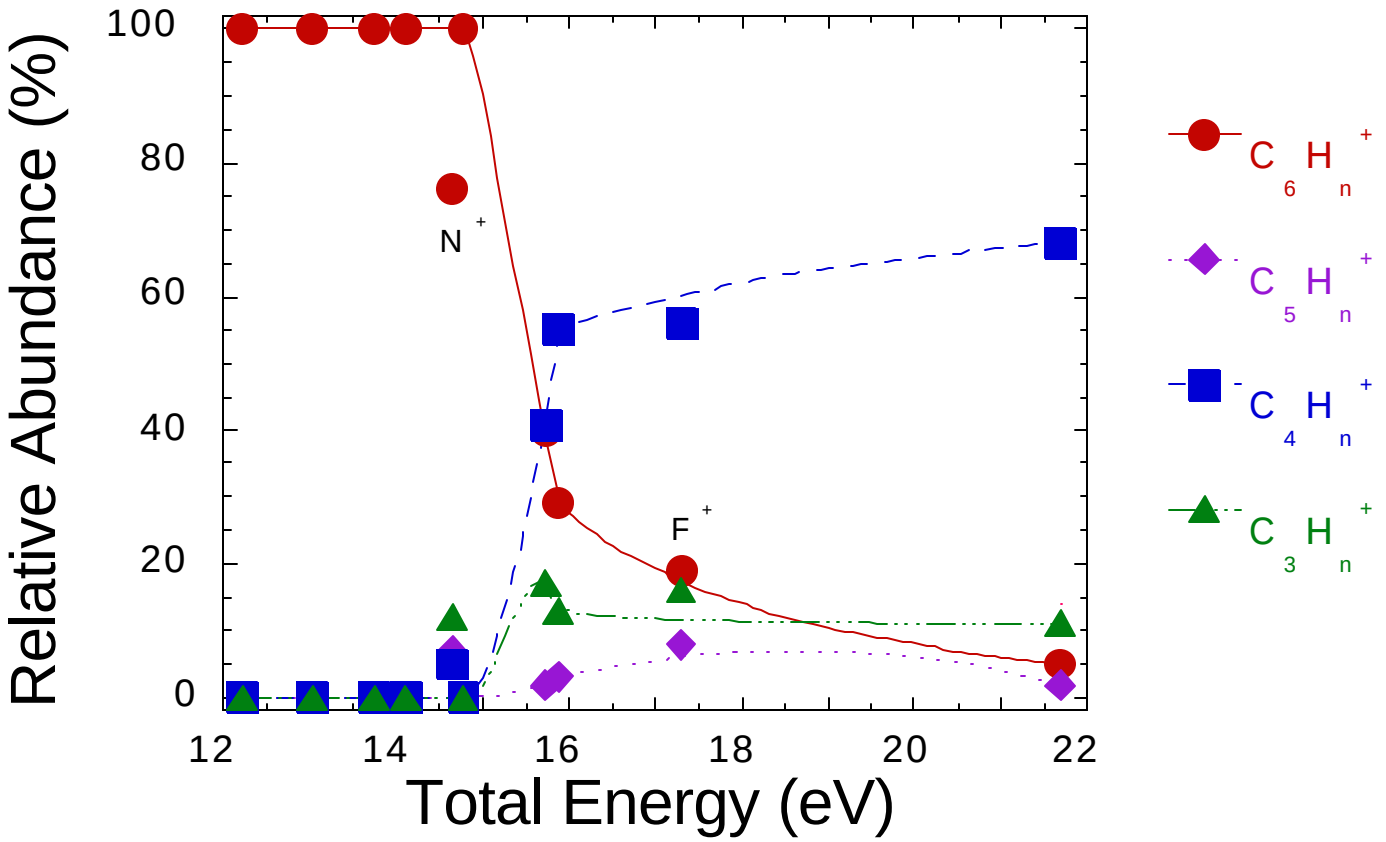
Reactant Ion	Recombination Energy (eV)	Temperature Range
NO^+	9.26	300 – 500
O_2^+	12.07	300 – 140 0
N_4^+	12.9	300 – 500
O^+	13.62	300 – 500
$Kr^+ (^2P_{3/2})$	14.00	300 – 500
N^+	14.53	300 – 500
$Kr^+ (^2P_{1/2})$	14.66	300 – 500
N_2^+	15.58	250 – 140 0
Ar^+	15.76	300 – 500
F^+	17.42	300
Ne^+	21.56	300 – 500

$X^+ + C_6H_6$ ® Products

X =	N_4	N	N_2	Ar	Ne
RE (eV) =	12.9	14.5	15.6	15.8	21.6
Ion Products (300K)					
$C_6H_6^+$	1.0	0.68	0.12	0.08	0.01
$C_6H_5^+$		0.07	0.24	0.18	0.02
$C_6H_4^+$		0.01	0.04	0.03	0.02
$C_5H_4^+$		0.07			
$C_5H_3^+$			0.02	0.03	0.02
$l\text{-}C_4H_4^+$		0.02	0.36	0.48	
$c\text{-}C_4H_4^+$		0.03	0.05	0.07	
$C_4H_3^+$					0.59
$C_4H_2^+$					0.09
$c\text{-}C_3H_3^+$		0.12	0.17	0.13	0.11
$C_2H_3^+$					0.07
$C_2H_2^+$					0.07
Rate (molecule-cm^3-s^{-1})	1.2×10^{-9}	2.0×10^{-9}	1.6×10^{-9}	1.3×10^{-9}	1.6×10^{-9}

Benzene Breakdown Diagram

Total Energy = $RE_{Ion} + E_{Int} + E_{Trans}$



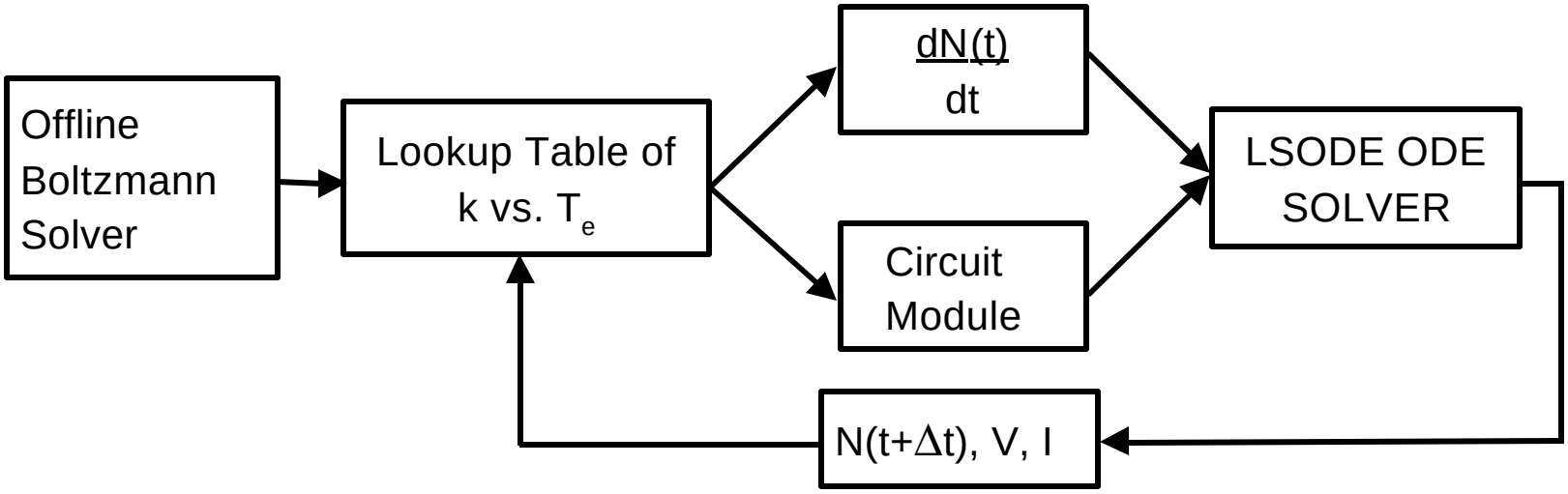
Kinetics Summary

- Series of benzene reactions all proceed at collisional rate.
- Mechanism changes from association to non-dissociative and then dissociative charge transfer with increasing reactant ion energy.
- Primary and secondary dissociation product ions are observed.
- Isomeric form of $C_3H_3^+$, $C_4H_4^+$, and $C_5H_3^+$ product ions was determined.
- Temp dependent branching fractions were converted to product ion breakdown curves. Pressure effect observed due to collisional stabiliztion of the charge transfer complex by He buffer.
- N^+ reaction with benzene involves many non-charge transfer processes.

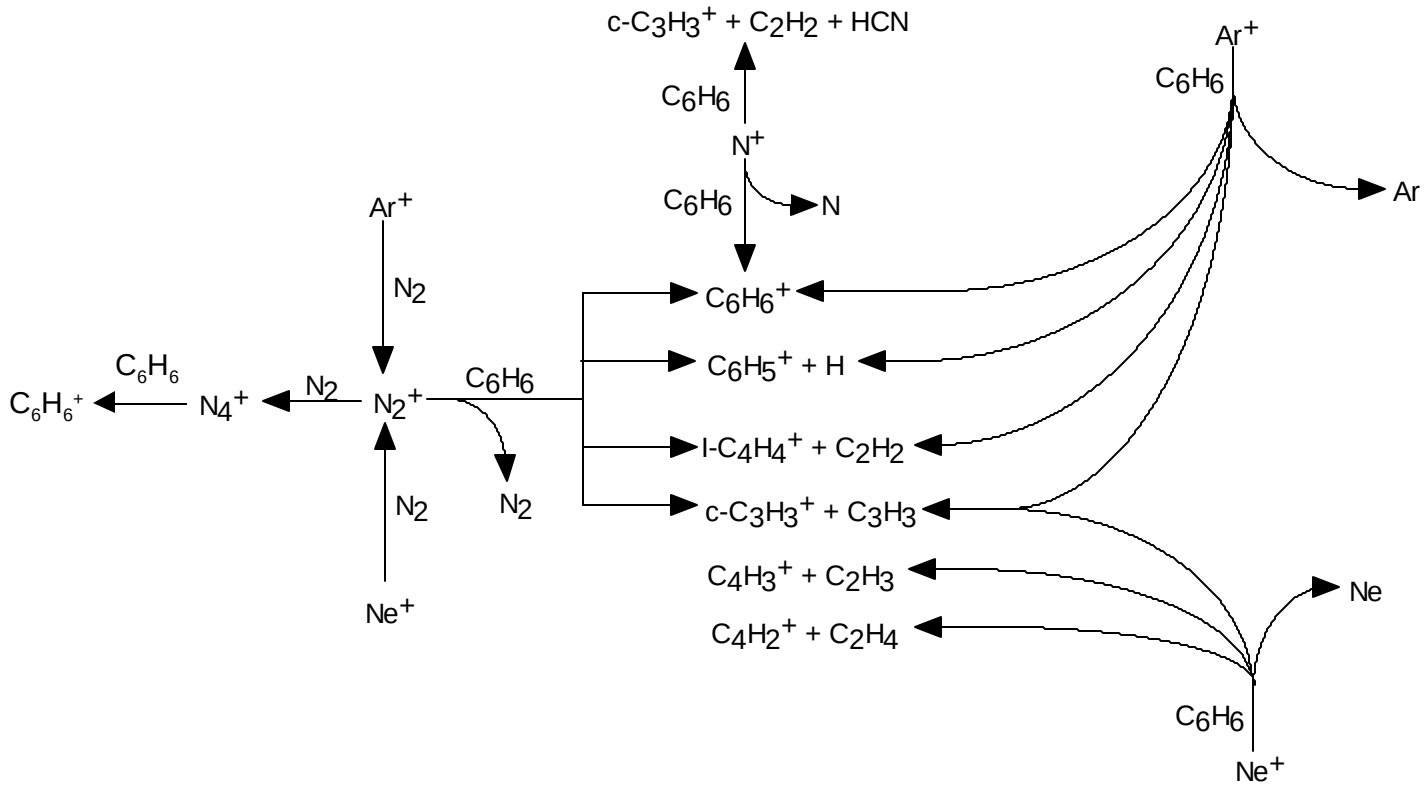
Thanks to AFOSR

DBD Model Description

- The basis of the model is to integrate the nonlinear ordinary differential equations describing the reaction chemistry over the residence time with the simultaneous solution of the equations for the circuit parameters.
- The rate coefficients for the electron impact reactions are obtained from a lookup table produced by an offline Boltzmann solver.



Dominating Reactions



Dissociative Recombination

Reaction	Rate (molecule-cm^3-s^{-1})
E + C_6H_6+ = C_6H_5 + H	5.00 x 10^{-7}
E + C_6H_6+ = products	5.00 x 10^{-7}
E + C_6H_5+ = C_6H_4 + H	2.76 x 10^{-7}
E + C_6H_5+ = products	8.27 x 10^{-7}
E+C_6H_4+ = products	11.0 x 10^{-7}
E+C_5H_4+ = products	**9.00 x 10^{-7}**
E+C_5H_3+ = products	9.00 x 10^{-7}
E + l-C_4H_4+ = products	**5.77 x 10^{-7}**
E + c-C_4H_4+ = products	**5.77 x 10^{-7}**
E + C_4H_3+ = products	6.20 x 10^{-7}
E + C_4H_2+ = products	**5.77 x 10^{-7}**
E + c-C_3H_3+ = products	7.00 x 10^{-7}
E + C_2H_3+ = products	4.50 x 10^{-7}
E + C_2H_2+ = products	2.70 x 10^{-7}

- Thermal rate coefficients are listed. The model assumes a $T^{-0.5}$ temperature dependence.
- The category "products" signifies species lacking a six membered aromatic ring
- Rates in red are estimated.
- Rates in black are measured (see references).

References:

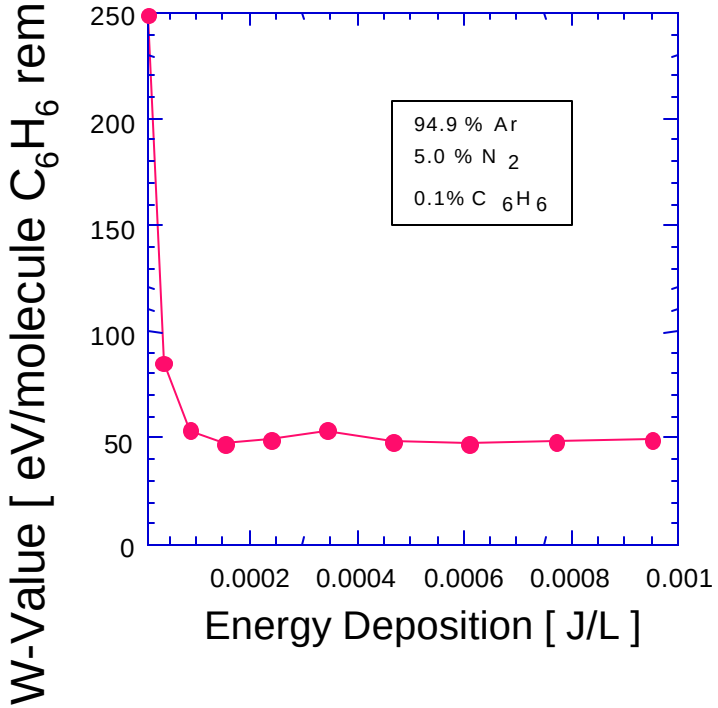
1) Lehfaoui et al., J. Chem. Phys. **106**:5406-5412 (1997).
2) Rebrion-Rowe et al., J. Chem. Phys. **108**:7185-7189 (1998).
3) Mitchell and Rebrion-Rowe, Int. Rev. Phys. Chem. **16**:201-213 (1997).

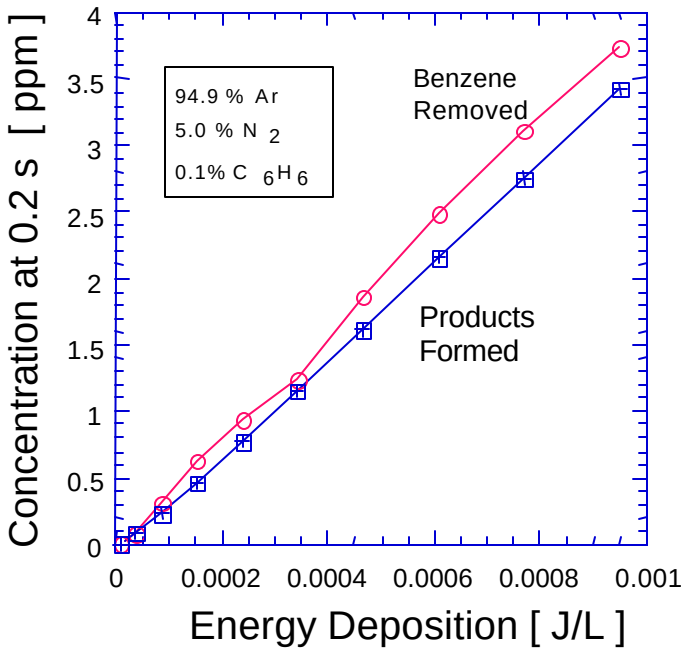
Experimental Setup Modeled

- A pulsed low pressure discharge has been modeled as follows:
  - •Dielectric discharge height = 2.5 mm.
  - •Reactor pressure = 1 Torr
  - •Operating temperature = 300 K
  - •Single pulse input (ca. 100 ns duration)
  - •Input benzene = 0.1%
- Key assumptions are as follows:
  - •The dissociative recombination rates of many organic molecular ions have been measured, but the product distributions have not. It is assumed here that for $C_6H_6^+ + e^-$ and $C_6H_5^+ + e^-$ only only 50% and 25%, respectively, of the reactions produce products with the six membered ring intact. The remainder of the species are classified as “products”.

Effect of Energy on Benzene Removal ($Ar/N_2/C_6H_6$)

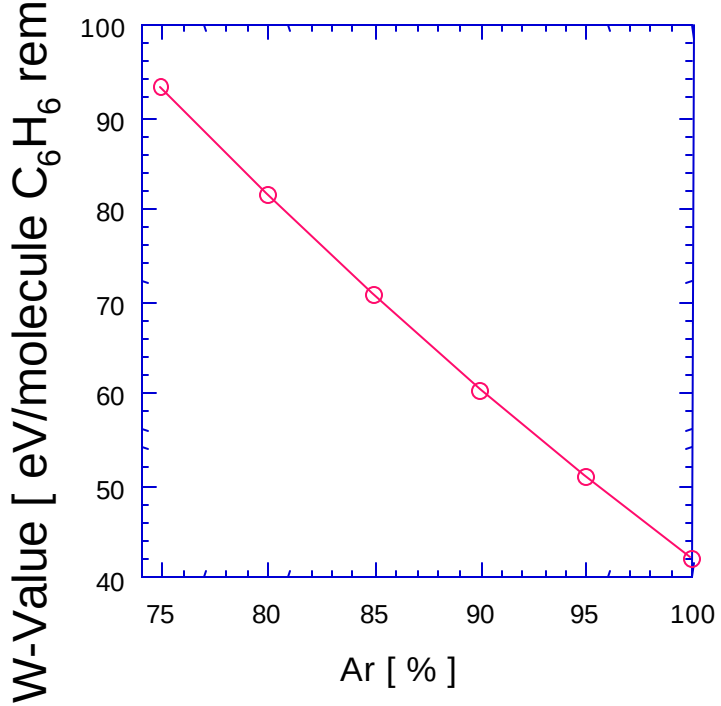
- Most of the benzene removal involves breaking of the aromatic ring since the reaction of Ar^+ with C_6H_6 predominantly produced $l\text{-}C_4H_4^+$ and other lower order hydrocarbons

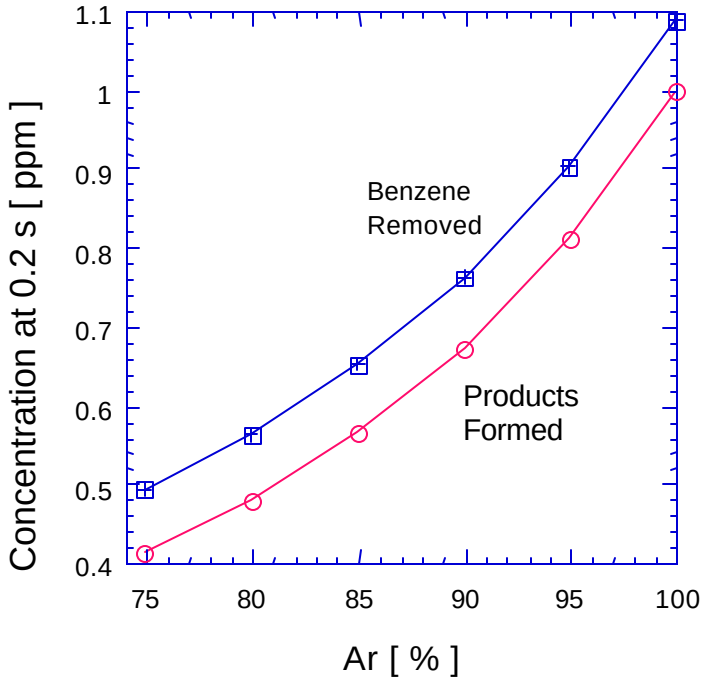




Effect of N_2 on Benzene Removal ($Ar/N_2/C_6H_6$)

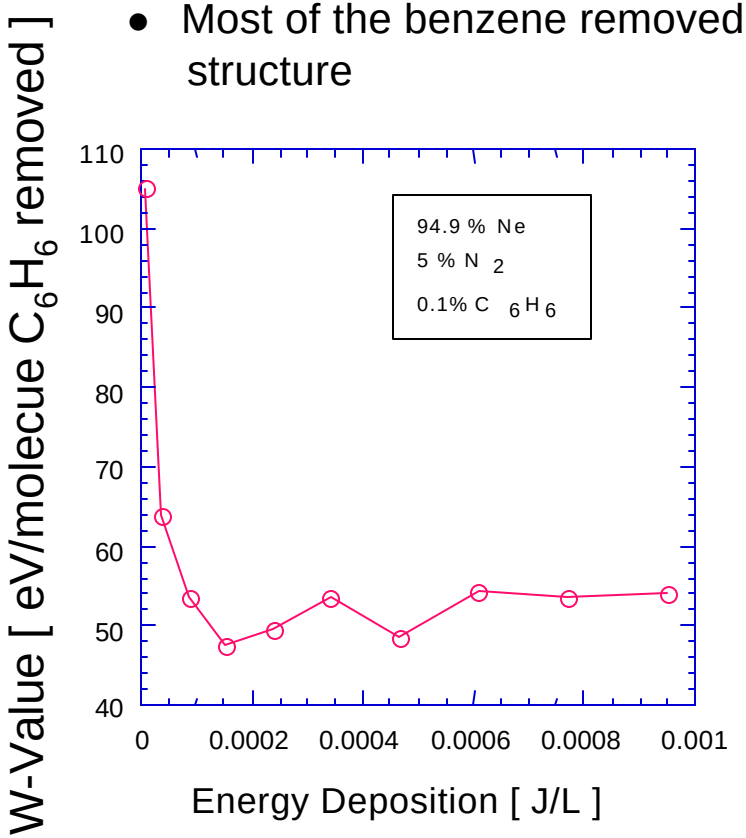
- End products mainly included the recombination products of l-$C_4H_4^+$, $C_6H_5^+$ c-$C_3H_3^+$.

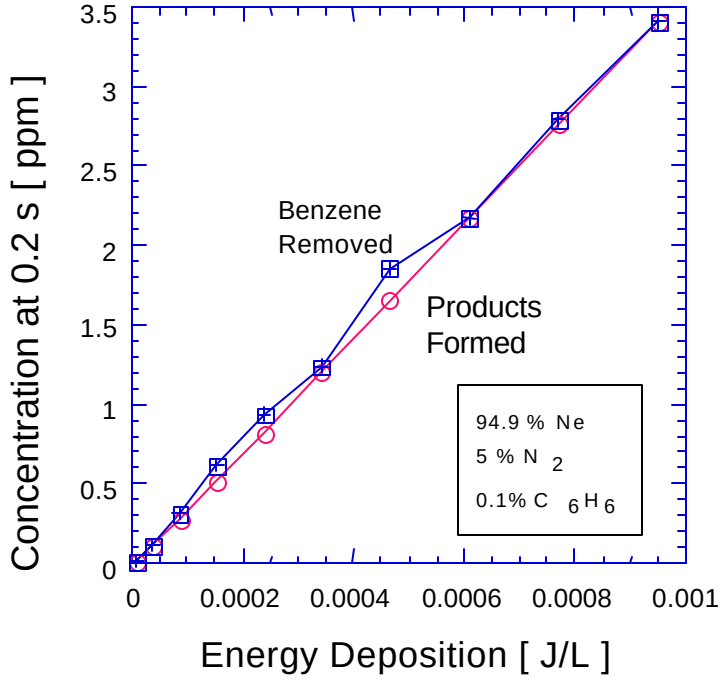




Effect of Energy on Benzene Removal ($Ne/N_2/C_6H_6$)

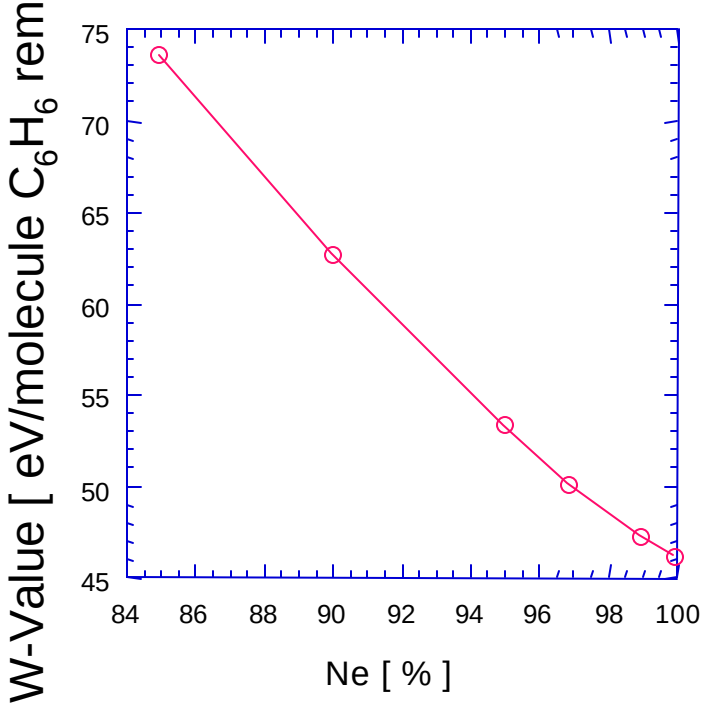
- Most of the benzene removed resulted in breaking of the aromatic ring structure

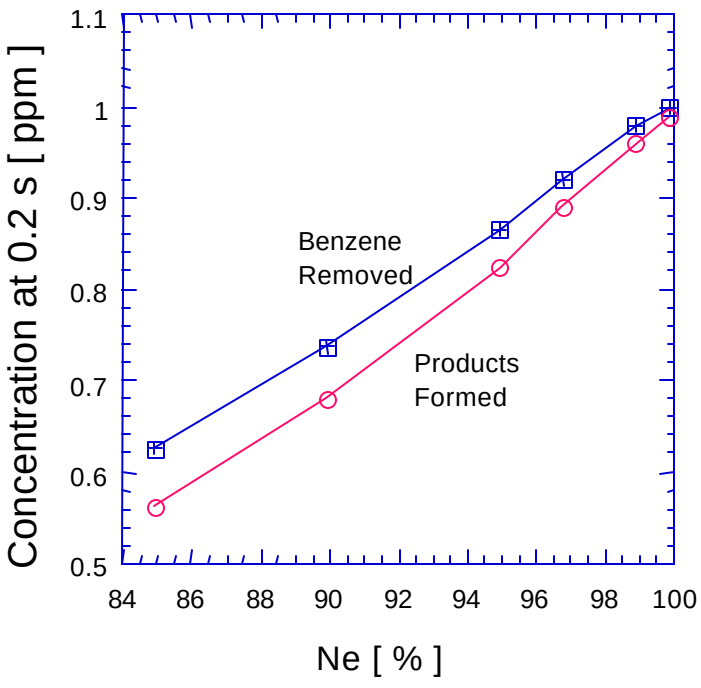




Effect of N_2 on Benzene Removal ($Ne/N_2/C_6H_6$)

- Both benzene removal and energy efficiency improve with increasing Ne concentration.



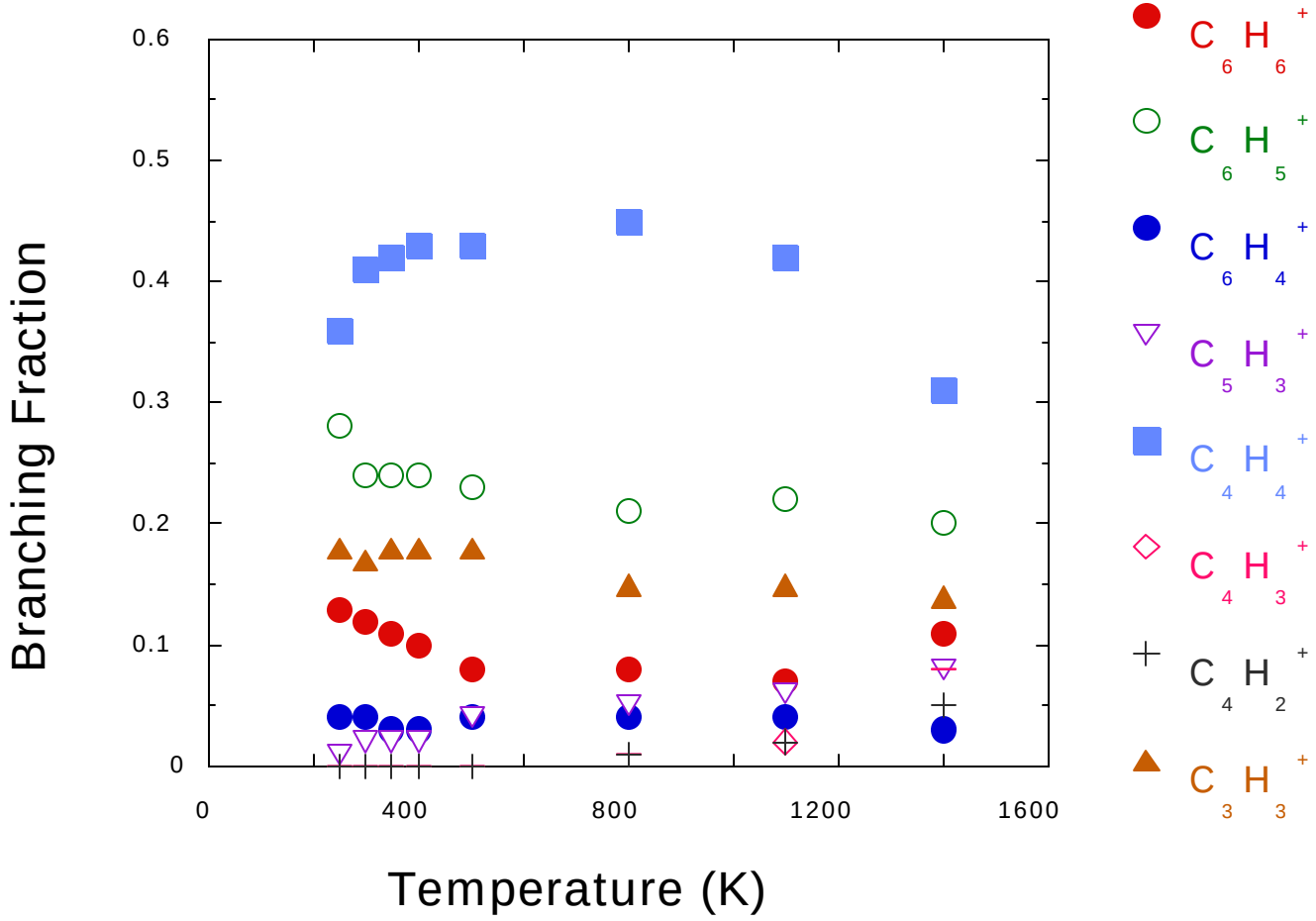


Modeling Summary

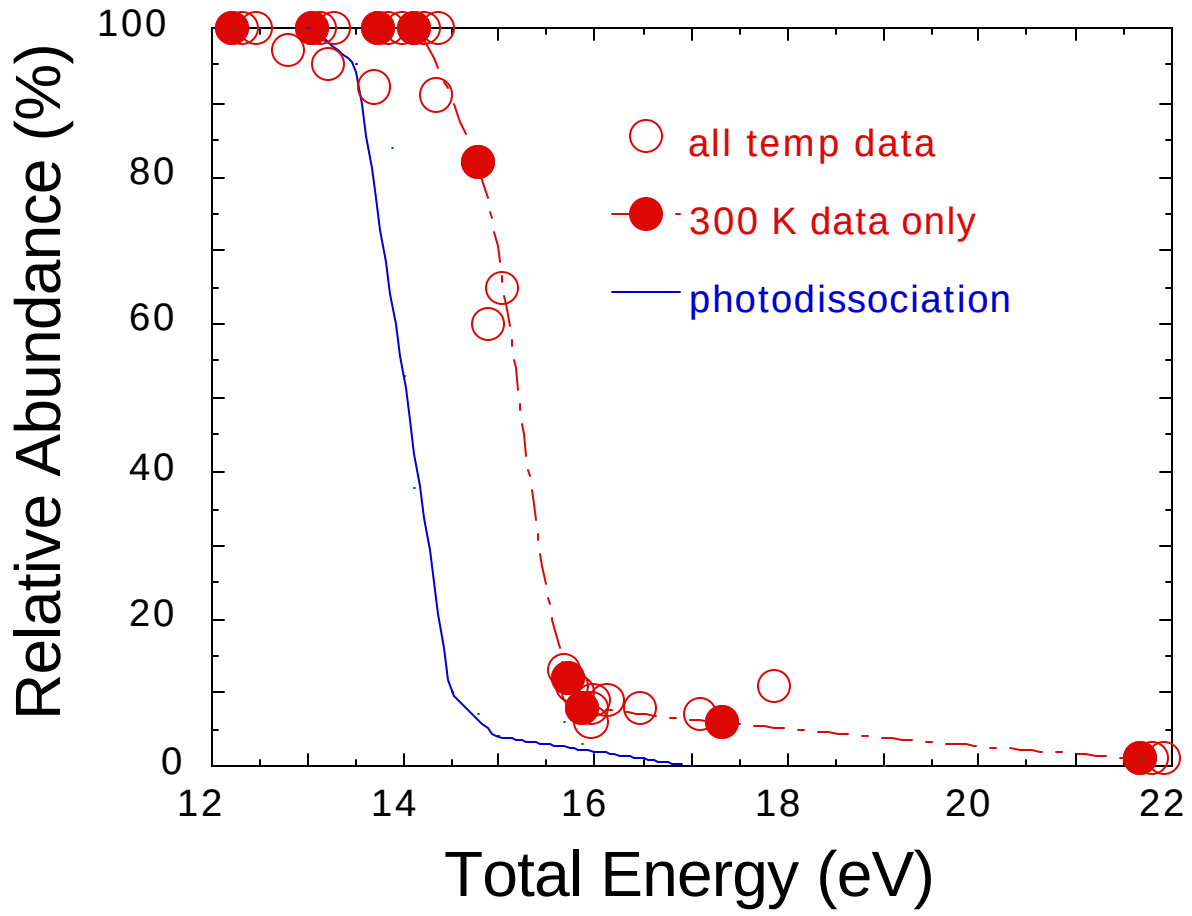
- The energy efficiency increases initially with increasing energy deposition and remains constant a higher input energies.
- Benzene removal increases with increasing input energy.
- The best results are obtained for pure Ar and Ne discharges which is due to the large rate of ring-cleaving reactions by plasma generated Ar^+ and Ne^+ ions. At lower input energies, Ne discharges are better degraders of benzene.
- The presence of N_2 inhibits the benzene degradation efficiency mainly because the energy efficiency in the absence of N_2 is much higher than in the presence of N_2.
- Dielectric barrier discharges operating with Ar or Ne show potential as sources for remediation of aromatic compounds.

Thanks to NSF

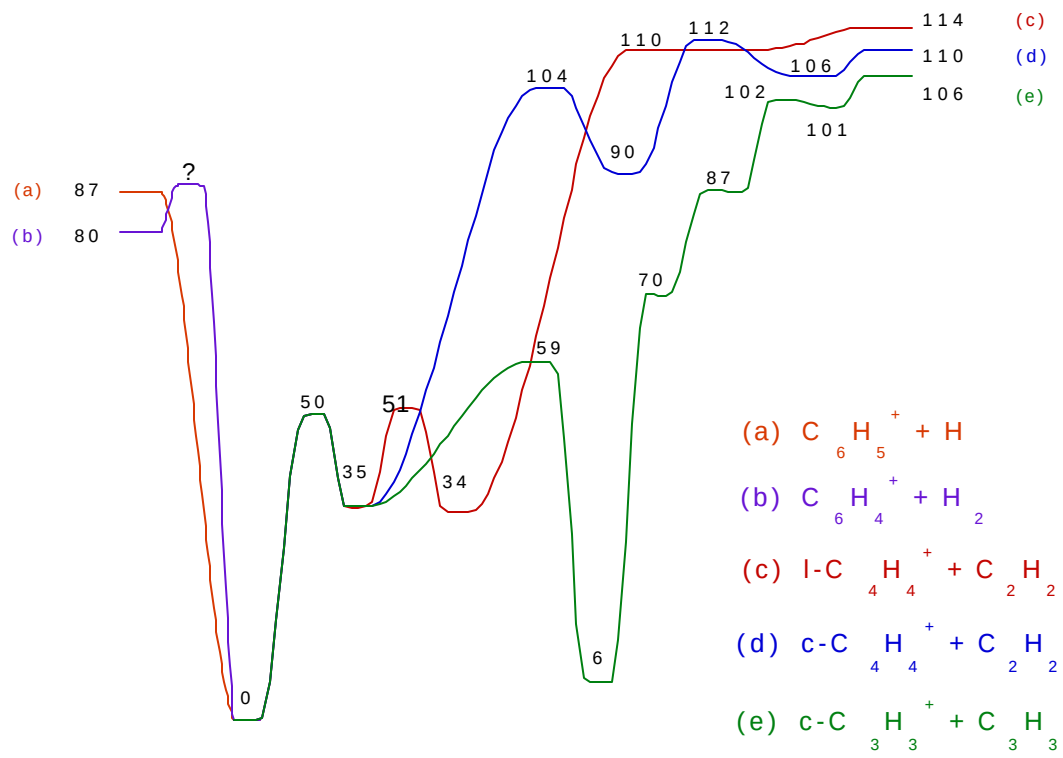
$N_2^+ + C_6H_6$


Branching Fraction
0.6
0.5
0.4
0.3
0.2
0.1
0
0
400
800
1200
1600
Temperature (K)
C6H6+
C6H5+
C6H4+
C5H3+
C4H4+
C4H3+
C4H2+
C3H3+

Parent Ion: $C_6H_6^+$



Reaction Coordinate Diagram



H fissure(s) | H migration | Ring rearrangment and opening