論文の内容の要旨

A Kinetic Study on Polycyclic Aromatic Hydrocarbons
and Soot Generation Mechanisms
（多環芳香族炭化水素と煤生成機構に関する反応論的研究）

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Motivation and Objectives

Hazardous impacts of polycyclic aromatic hydrocarbons (PAHs), nano particles (NPs) and soot itself especially regarding the global warming and rarely curable diseases in animals particularly human beings, unfortunately will be the cause of big natural disasters in future as expected by the combustion and environmental scientists. On the other hand unsatisfactory improvement in research to control their emissions motivated us to think about this important and complex issue and accelerated us to contribute in terms of mechanistic investigation of their formations in the direction of resolving the complexities of this process.

It is well known that during combustion of a fuel, a part of fuel is oxidized to produce oxygenated inorganic and organic products while a significant portion of fuel is left unburnt. That unburnt fuel is pyrolyzed under same conditions to produce many smaller hydrocarbons, PAHs and soot. Due to this fact reason and considering the current research needs, the main objectives of Ph.D. study are determined to study the pyrolysis of mainly aromatic and some aliphatic hydrocarbons to achieve the following expected goals,

- Detection of large PAHs than coronene to fulfill the gap between coronene and the first fine soot particle and possible corresponding radicals.
- Understanding the effect of additives especially radicals like phenyl and methyl and C_2H_2 on the formation path ways of large PAHs.
- Construction of reaction mechanisms including large PAHs and their radicals in terms of elementary reactions to clarify the PAHs generation mechanism in detail.

Methods:

To achieve the goal, samples are pyrolyzed into a flow tube reactor and gas phase bimolecular reaction products have been detected by an in-situ direct sampling mass spectrometric technique by using a vacuum ultraviolet (VUV) single photon ionization (SPI) time of flight mass spectrometer (TOFMS) during the experimental procedure. CHEMKIN is under use for kinetic modeling and simulation purpose.

Achievements:

Until now I have collected experimental data for the pyrolysis of aromatic hydrocarbons, aliphatic hydrocarbons and their mixtures like toluene, benzene, toluene + acetylene, benzene + acetylene, toluene + benzene, toluene + acetone, toluene + benzene + acetylene, acetylene, ethylene and acetone. The gas phase reaction products from methyl radical (m/z = 15) to large PAHs, $C_{42}H_{18}$ (m/z =522) including smaller species, polyynes, radicals, PAHs, methyl-PAHs, phenyl-PAHs, ethynyl-PAHs and CP-PAHs resulted from methyl, phenyl and ethynyl-PAHs have been detected. Many sets of formation mechanisms of products of different samples have been developed. Four kinetic mechanisms for aliphatic and aromatic pyrolysis have also been prepared and used for simulation by CHEMKIN but due to some kinetic and thermodynamic problems, they can not be able to reproduce the observed experimental data. Modification of mechanism is under process.

The main cause of using toluene and benzene is to compare the products and their formation mechanisms as benzene is the simplest aromatic hydrocarbon and toluene is the simplest alkylated aromatic hydrocarbon. The main purpose of addition of some additives is to check the effect of some specific radicals on the formation pathways of products with and without addition to the main sample, like: addition of acetylene with both benzene and toluene is to check the effect of hydrogen abstraction and acetylene addition (HACA) mechanism. Addition of benzene with toluene is to understand the role of phenyl radical and addition of acetone is to understand the role of methyl radical in the PAHs formation mechanisms. Pyrolysis of typically selected aliphatic hydrocarbons is to compare the products with aromatics and to understand the differences in formation pathways of same products in both aliphatic and aromatic cases. The most prominent out puts of this work are the direct detection of large PAHs and new reaction pathways for the formation of PAHs with major role of cyclopenta fused, benzyl, phenyl and methyl radicals. At low temperatures (<1300 K), the products produced mainly from benzyl radicals were detected in the case of toluene while in the case of benzene phenyl products were found abundantly. At moderate temperature (~1300-1400 K), products mainly contributed by cyclopentafused, phenyl and methyl radicals together with some HACA were detected in the case of toluene while in the case of benzene dehydrocylization products of phenyl-PAHs and some HACA products were detected. But at high temperatures (>1400 K) in both cases mainly products contributed by the HACA and some polyynes could be detected due to self decomposition of almost all active species benzyl, phenyl, cyclopentadienyl radicals and benzene itself. Due to these reasons the formation routes of large PAHs were decelerated and resulted into the inhibition of large PAHs at high temperatures.

On addition of additives, the role of the HACA is only seemed important for the formation of stable condensed PAHs from unstable primary PAHs with zig-zag structure (having triple fusing sites, a bay structure of four carbons) in one step by ring growth with two carbon atoms.
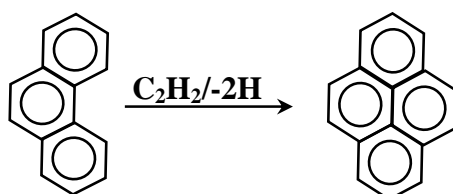
On the other hand PAC (phenyl addition / cyclization) mechanism is found highly efficient for the faster ring growth of PAHs having triple fusing sites due to its significances: (a) it increases the size by two aromatic rings in each step which is three times of the HACA. (b) It always produces only benzenoid PAHs. (c) All products PAHs contain one more active sites than that of reactant PAH. For example formation of benzo[e]pyrene from phenanthrene.
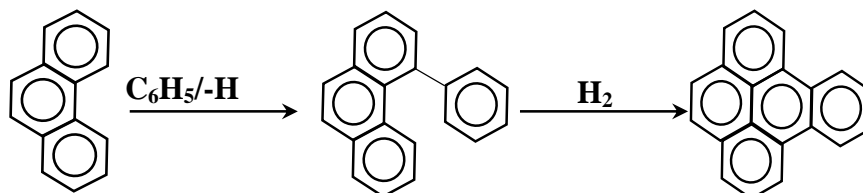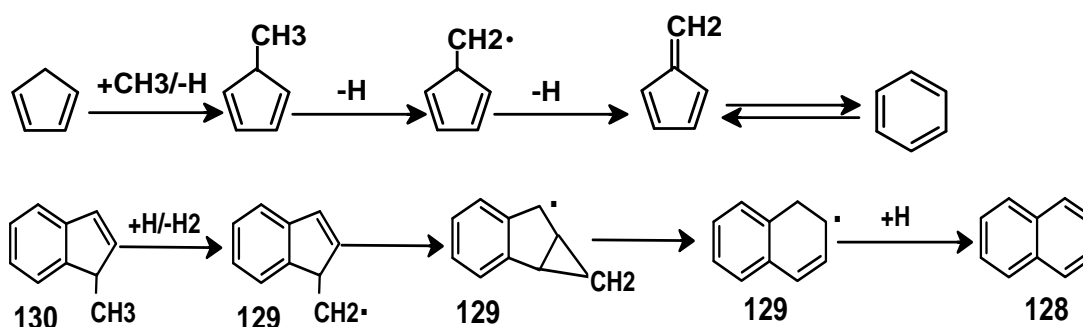

PAC mechanism is found also efficient for the growth of PAHs having double fusing site into cyclopentafused PAHs (CP-PAHs) having internally fused 5 membered ring like growth of naphthalene into fluoranthene for which HACA step is inefficient.
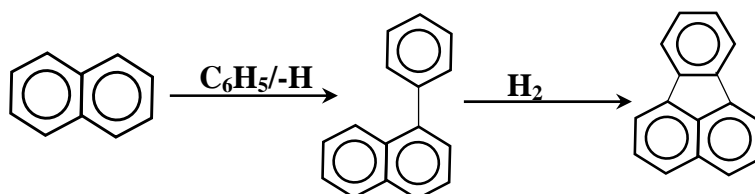
In this way PAC mechanism is found more efficient than the HACA for the formation of large PAHs.

Similarly, from the kinetic analysis of results on toluene with and without addition of acetone, it is found that MAC (methyl addition/cyclization) mechanism is only efficient for the growth of externally fused 5 membered ring CP-PAH into the closest primary PAHs through ring expansion. For example growth of cyclopentadiene, indene and 4H-cyclopenta[def]phenanthrene into benzene, naphthalene and pyrene.

But it is found that MAC mechanism is not efficient as HACA and PAC for the growth of large PAHs because of mass growth by only 14 u.

Similarly in the case of aliphatic hydrocarbons, acetylene, ethylene and acetone are separately pyrolyzed and the gas phase reaction products were detected. Products range from C_2H_4 ($m/z = 28$) to $C_{24}H_{12}$ ($m/z = 300$) including polyacetylenes, PAHs and ethynyl-PAHs or CP-PAHs. From kinetic analysis it is found that the products formation mechanism is dominated by the aliphatic

radical-molecule reactions in addition to the HACA. In all cases benzene is found to be produced from the active role of C_4H_4/C_4H_3 with C_2H_2/C_2H_3 while the ring growth is found to be dominated by the role of C_4H_4. The HACA mechanism is found efficient for the formation of ethynyl or CP-PAHs in greater extent. Purpose and outputs of all the results are separately expressed as follows,

Benzene with and without addition of acetylene

Being the simplest aromatic hydrocarbon, benzene provides starting point for systematic study of thermal decomposition of aromatic hydrocarbons and an intermediate point of departure for theoretical and experimental studies of many aliphatics. Despite its limited presence in fuels, it is one of the primary intermediates that form during combustion and pyrolysis of almost all hydrocarbons. Its study of pyrolysis mechanism in detail will be the basis for other aromatic hydrocarbons. It will also focus on differences with pyrolysis mechanism of aliphatic hydrocarbons.
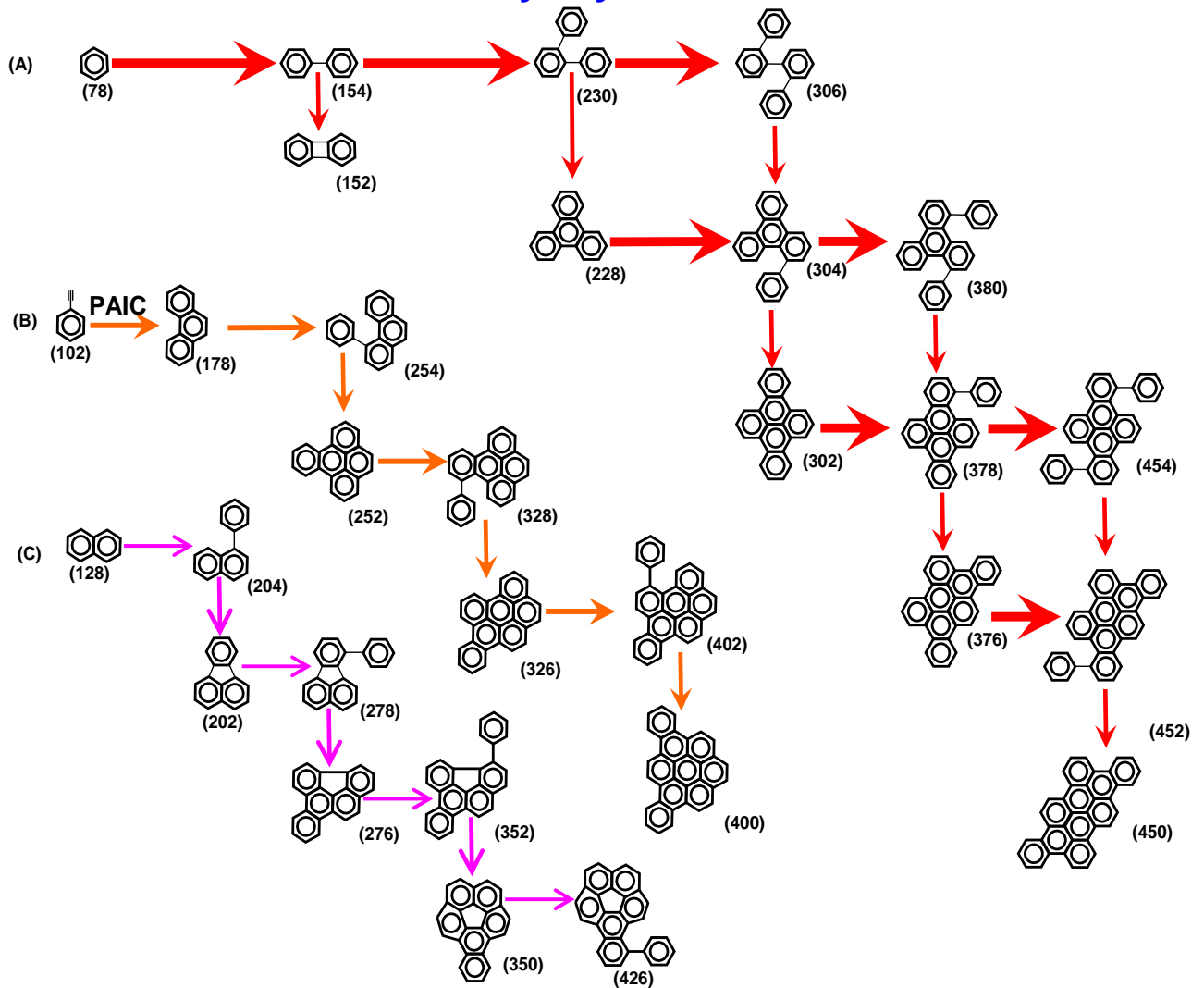
Purpose

The main purpose of this study is to detect the large PAHs directly in the gas phase and kinetic analysis of formation path ways of those products will help to decide the role of phenyl radical in the formation of large PAHs while addition of acetylene is to check the effect of HACA mechanism on formation pathways of those products.

Output

The gas phase reaction products of benzene pyrolysis with and without acetylene addition produced at pressures 10.18 Torr and temperatures 1140 K- 1473 K with constant residence time (0.61 s) have been detected. Those products are ranging from diacetylene to large polycyclic aromatic hydrocarbons (PAHs) of mass 454 amu ($C_{36}H_{22}$) including many polyphenyl-PAHs (especially biphenyl, terphenyl, phenyltriphenylene and quaterphenyl) and corresponding condensed benzenoid and non-benzenoid PAHs. The mass spectra showed a clear regular sequence with an interval of ~74 mass number, corresponding to the phenyl addition ($+C_6H_5$) followed by H-elimination (–H) and cyclization (–H_2). The chemical kinetic analysis showed that PAC (phenyl addition / cylization) mechanism is efficient for the growth of PAHs. Addition of acetylene significantly depleted the phenyl-PAHs by frequent conversion of only one active species phenyl radicals into phenylacetylene. Especially, acetylene is mixed with benzene to understand the effect of HACA (hydrogen abstraction / C_2H_2 addition) mechanism on the formation path ways of products in benzene pyrolysis. The HACA is only found efficient for the conversion of condensed PAHs resulted from phenyl-PAHs with zig-zag structure (having triple fusing sites) into spherical PAHs. The most prominent out puts of this work are the direct detection of large PAHs and a new chain mechanism, PAC for the formation of PAHs from the major role of phenyl radicals. The PAC process was found to be efficient in the subsequent growth of PAHs with five-membered rings for which HACA is inefficient. The role of PAC mechanism in combustion conditions is discussed in relation to the importance of disordered five-membered ring structure in fullerene or soot core.

Benzene Pyrolysis Mechanism

(A) (78) → (154) → (230) → (306)
(154) → (152)
(230) → (228) → (304) → (380)
(306) → (304)
(228) → (304) → (380)
(304) → (302)
(380) → (378) → (454)
(302) → (378) → (454)
(378) → (376) → (452)
(454) → (452)
(376) → (452) → (450)

(B) PAIC (102) → (178) → (254) → (252) → (328) → (326) → (402) → (400)

(C) (128) → (204) → (202) → (278) → (276) → (352) → (350) → (426)

Horizontal arrows = Phenyl addition
Vertical arrows = Dehydrocyclization
PAIC = Phenyl addition/ isomerization / cyclization

On Addition of Acetylene or at High Temperature

(78) (154) (228) (302) (376)

(102) PAIC (178) (252) (326)

(202) (226)

(152) (250)

(128) (202) (276)
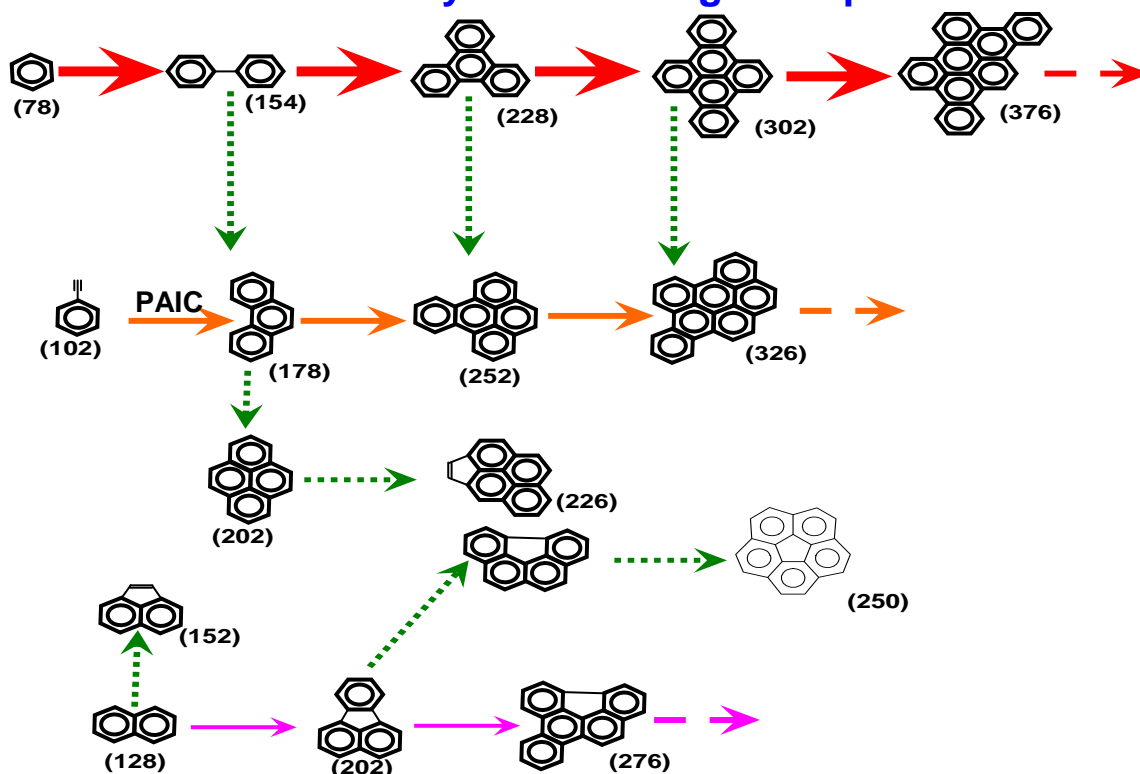
Horizontal arrows = PAC and Green arrows = HACA

Toluene with and without addition of acetylene

The main cause of selecting toluene as a main sample is its importance's. It is itself toxic and produces many toxic PAHs and carbonaceous nanoparticles during its pyrolysis and oxidation. It is the most abundant component of the majority of practical fuels. For example, jet fuels and gasoline contain 20-30% toluene due to its high energy density and anti-knocking capacity. It is also produced during the oxidation of other hydrocarbons and commercial fuels. It is the representative of aromatic compounds in model fuel.
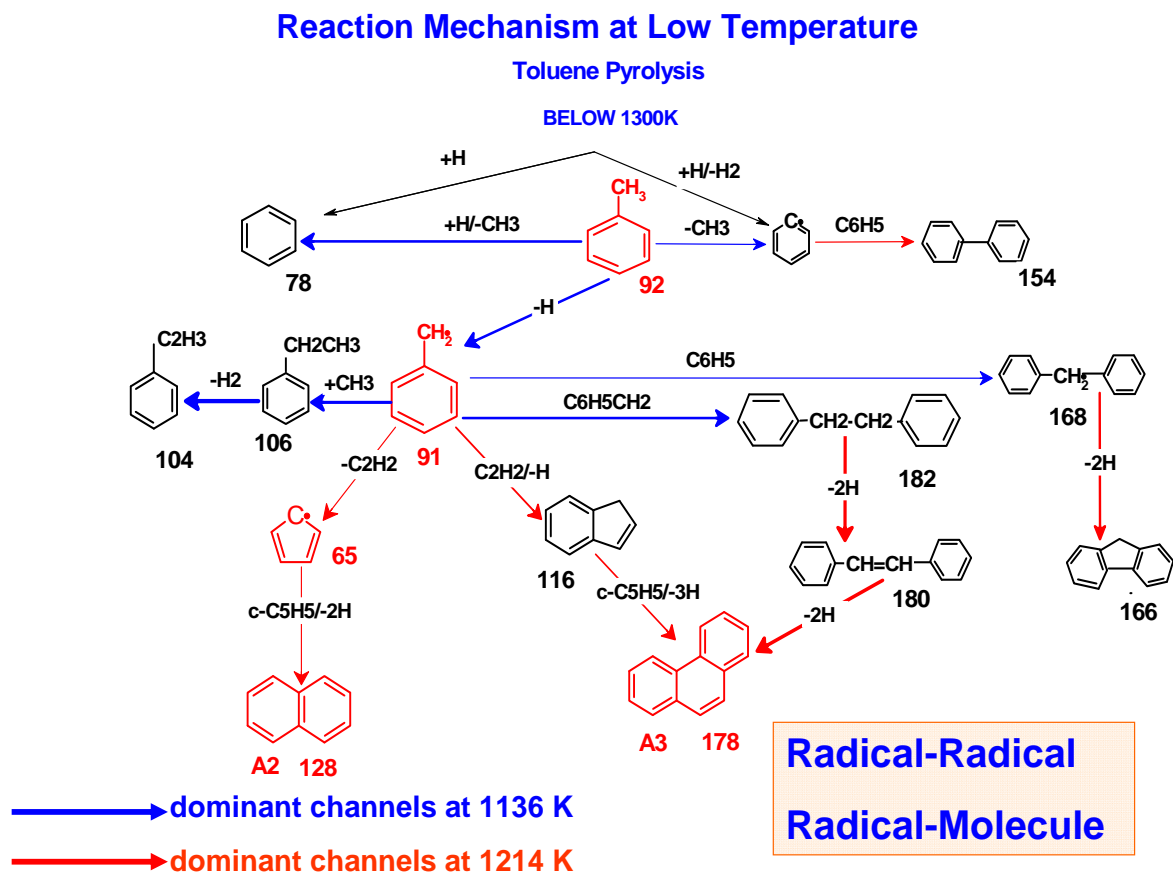
Purpose

Main objective of this study is to check the effect of the HACA mechanism in the formation pathways of large PAHs mainly produced by major role of benzyl, cyclopentadienyl, phenyl and cyclopentafused radicals during the pyrolysis of pure toluene.
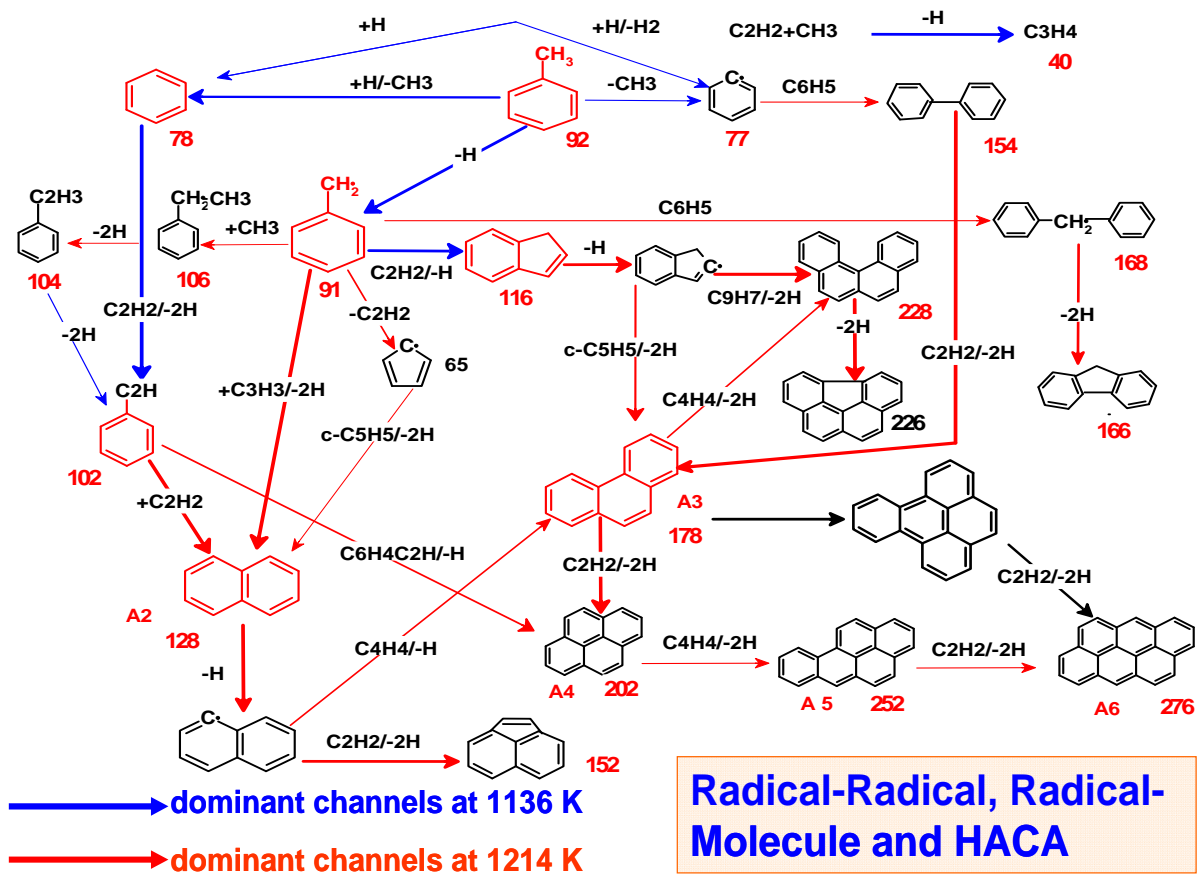
Outputs

The gas phase reaction products of toluene pyrolysis with and without acetylene addition produced at pressures 8.15-15.11 Torr and temperatures 1136K- 1507 K with constant residence time (0.56s) have been detected. Those products are ranging from methyl radical to large PAHs (polycyclic aromatic hydrocarbons) of mass 522 amu ($C_{42}H_{18}$) including smaller species, radicals, polyynes, PAHs and their ethynyl, methyl & phenyl derivatives. Based on observed Mass spectra, the chemical kinetic mechanisms of the formation of products are discussed. Especially, acetylene is mixed with toluene to understand the effect of HACA (hydrogen abstraction and acetylene addition) mechanism on the formation path ways of products in toluene pyrolysis. The most prominent out puts of this work

are the direct detection of large PAHs and new reaction pathways for the formation of PAHs with major role of cyclopenta fused radicals resulted from their corresponding methyl derivatives, with active participation of c-C_5H_5, C_6H_5, $C_6H_5CH_2$ and C_9H_7 in the formation of large PAHs. Role of the HACA is only seemed important for the formation of stable condensed PAHs from unstable primary PAHs with zig-zag structure (having triple fusing sites) in one step by ring growth with two carbon atoms.

Reaction Mechanism at Low Temperature

Toluene Pyrolysis

BELOW 1300K

+H   +H/-H2   C2H2+CH3 $\xrightarrow{-H}$ C3H4

+H/-CH3   -CH3   C6H5   **40**

78   **92**   **77**   **154**

C2H3   CH2CH3   -H

-2H   +CH3   C6H5

104   **106**   C2H2/-H   **116**   C9H7/-2H   **228**   **168**

C2H2/-2H   -C2H2   c-C5H5/-2H   -2H   **226**   C2H2/-2H   -2H

91   **65**   C4H4/-2H   **166**

+C3H3/-2H

C2H   c-C5H5/-2H

102   A3

+C3H3/-2H   **178**

+C2H2   C6H4C2H/-H   C2H2/-2H

A2   C4H4/-H   A4   **202**   C4H4/-2H   A5   **252**   C2H2/-2H   A6   **276**

128

-H

C2H2/-2H   **152**

→ **dominant channels at 1136 K**

→ **dominant channels at 1214 K**
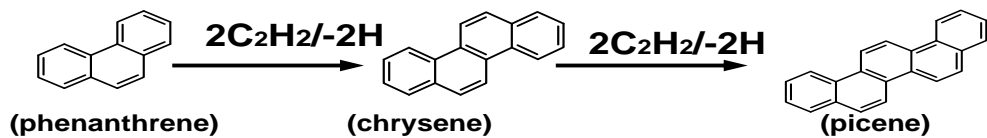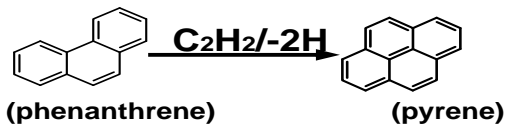
Radical-Radical, Radical-Molecule and HACA

Reaction Mechanism at 1315K

1. Role of HACA Mechanism

(a) Growth of linear PAH in two steps (Inefficient)

$2C_2H_2/-2H$ $2C_2H_2/-2H$

(phenanthrene)   (chrysene)   (picene)

(b) Growth of Condensed PAH in one step (Efficient)

$C_2H_2/-2H$

(phenanthrene)   (pyrene)

(c) Growth of Ethynyl species in one step (Efficient)

$C_2H_2/-2H$

(naphthalene)   (acenaphthalene)
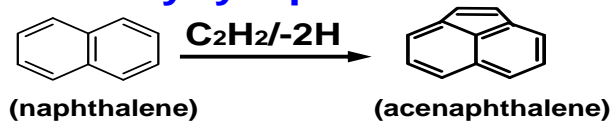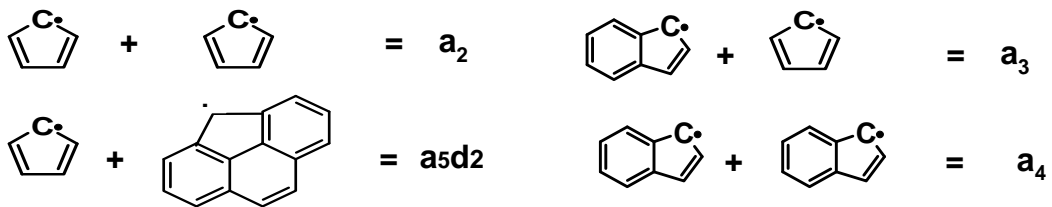
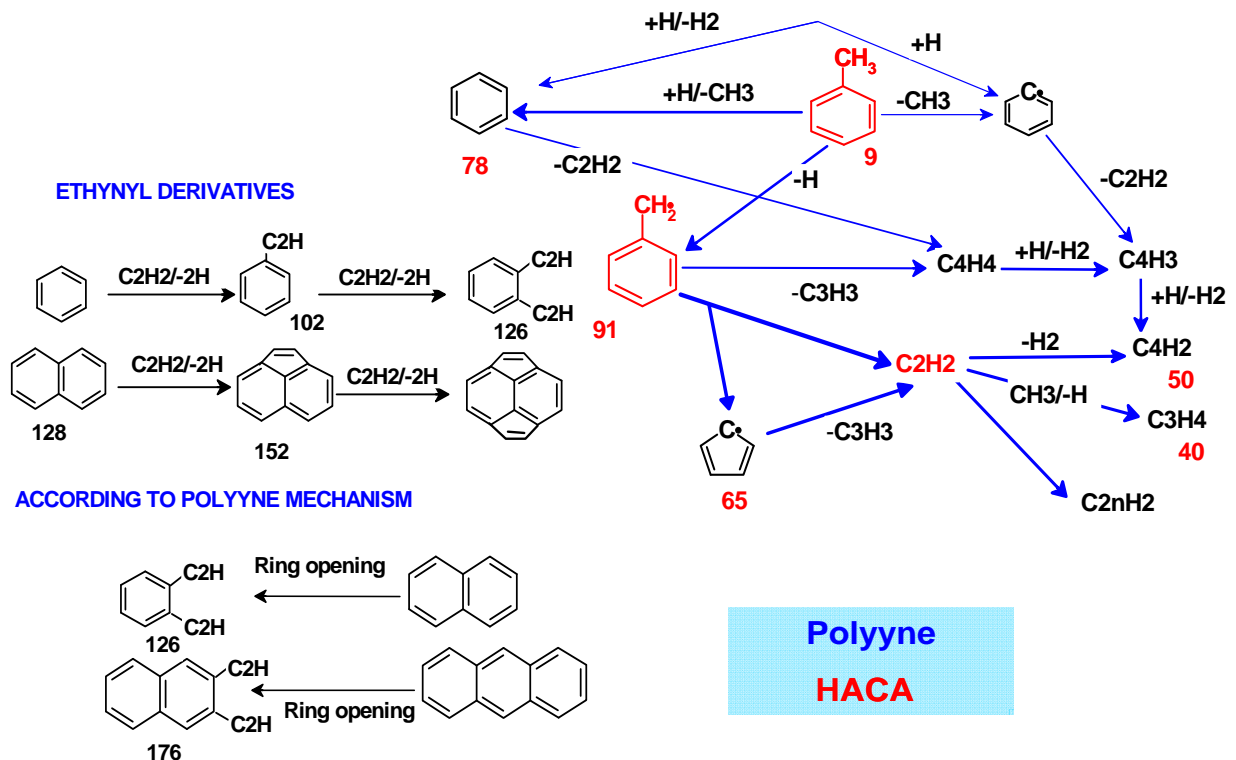## 2. PAHS resulted from Phenyl radical attack
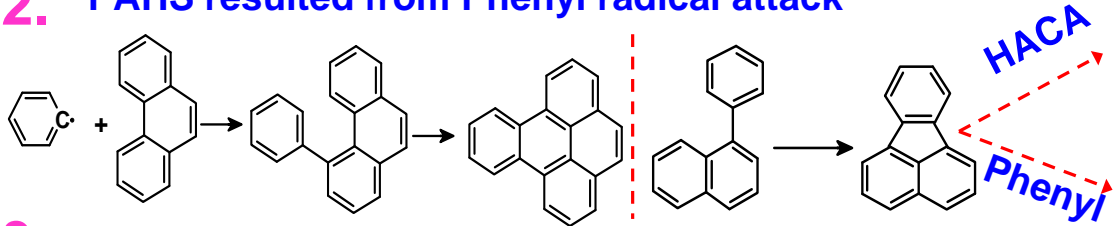
3. PAHS resulted from Methyl radical attack
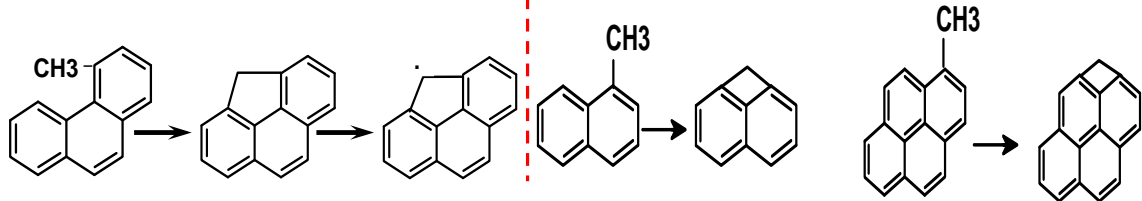
PAHS from Cyclopentafused radicals recombination

Reaction Mechanism at High Temperature(>1400K)

ETHYNYL DERIVATIVES

ACCORDING TO POLYYNE MECHANISM

Polyyne

HACA

Toluene with and without addition of benzene

Purpose

Main aim of this study is to understand the role of phenyl radicals in the growth of polycyclic aromatic hydrocarbons initiated by benzyl radicals in toluene pyrolysis.
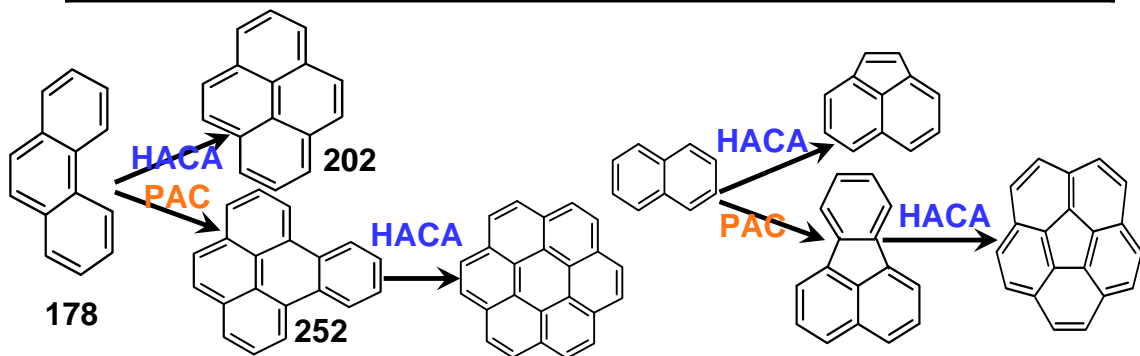
Outputs

Products produced at temperatures 1155–1467 K and pressure of 10.02 Torr with residence time 0.56 s have been detected. When benzene was added, products produced by benzyl radicals are significantly suppressed with significant increase in phenyl addition products (biphenyl, terphenyl, and triphenylene). Mass spectra showed a clear regular sequence with an interval of ~74 mass number, corresponding to the phenyl addition ($+C_6H_5$) followed by H-elimination ($-H$) and cyclization ($-H_2$). The analysis showed that PAC (phenyl addition / cylization) mechanism is also efficient for the growth of PAHs without triple fusing site, for which HACA (hydrogen abstraction / C_2H_2 addition) step is inefficient, and produces PAHs with five-membered rings.

Toluene + Benzene Pyrolysis Mechanism

Fullerene
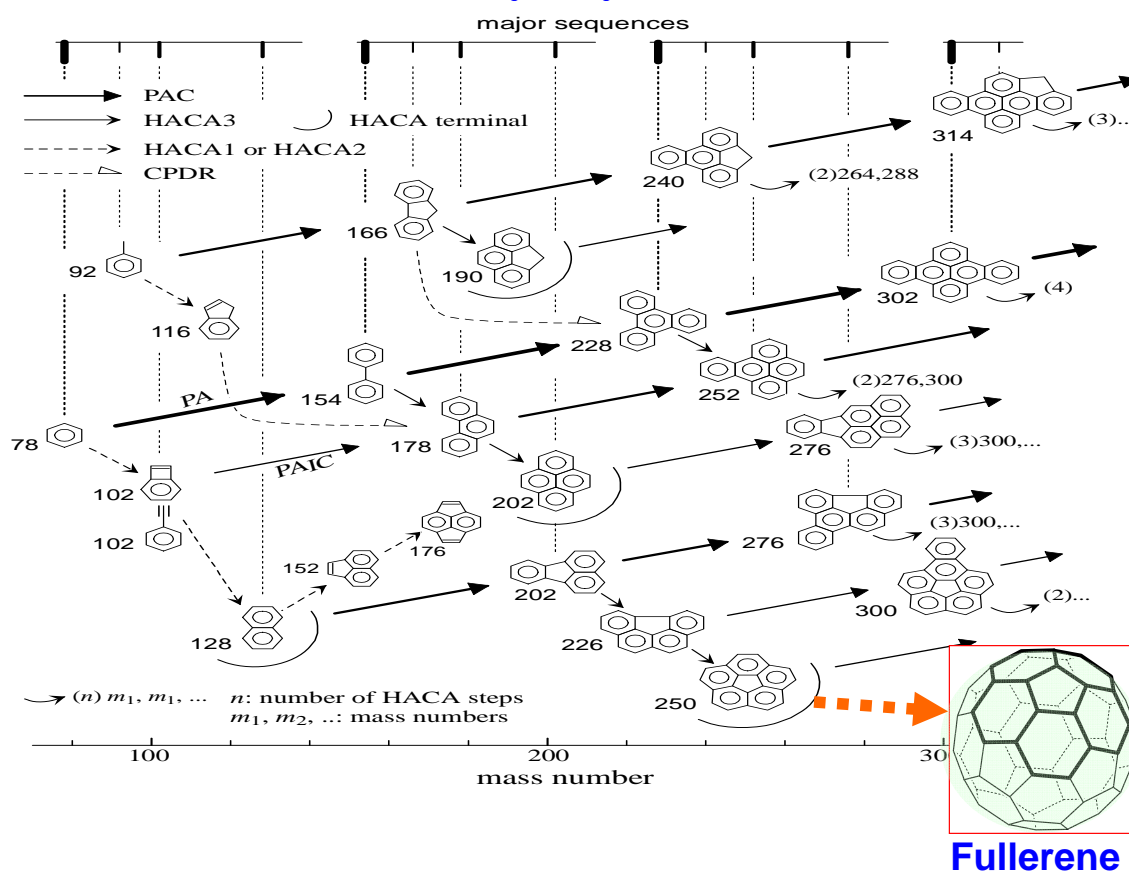
Comparison of HACA and PAC

Increases the product size by 24 u	Increases the size by 74u
Growth of one ring needs two steps	In each step two rings are increased
Inefficient for internal 5 membered PAHs	Efficient
It always stops the growth by closing the sites	It always opens new site for further growth
Important for spherical PAH	Cann't form spherical PAH

Toluene with and without addition of acetone

Purpose

Main aim of this study is to understand the role of methyl radicals in the growth of polycyclic aromatic hydrocarbons in toluene pyrolsysis.

Outputs

The gas phase products of only toluene and toluene/acetone mixture produced at temperatures of 1140 K-1320 K, pressure of 10.38 Torr and residence time 0.585 s have been detected. Those species include a large number of methyl-PAHs, cyclopentafused PAHs (CP-PAHs), methyl CP-PAHs associated with their corresponding methylene radicals together with some other species. Peculiarity

of this result is the presence of mass peaks in a bundle of 2 to 5 peaks differ in mass number by one and two only in the case of mixture. This unique characteristic supports the significant role of methyl radical in the formation of polycyclic aromatic hydrocarbons (PAHs). Another feature of this result is the appearance of weak peaks at -1 mass associated to each significant peak in each

bundle are most probably of corresponding radicals which well explains the hydrogen elimination process as a step wise process. On the basis of methylderivatives of PAHs and CP-PAHs and their corresponding radicals, kinetic mechanism of formation of those detected species and their further consumption for the formation of primary PAHs are discussed in detail. This

kinetic analysis showed that MAC (methyl addition/cyclization) is efficient for the conversion of a CP-PAH into primary PAH for which both PAC and HACA

Formation mechanisms of one ring compounds
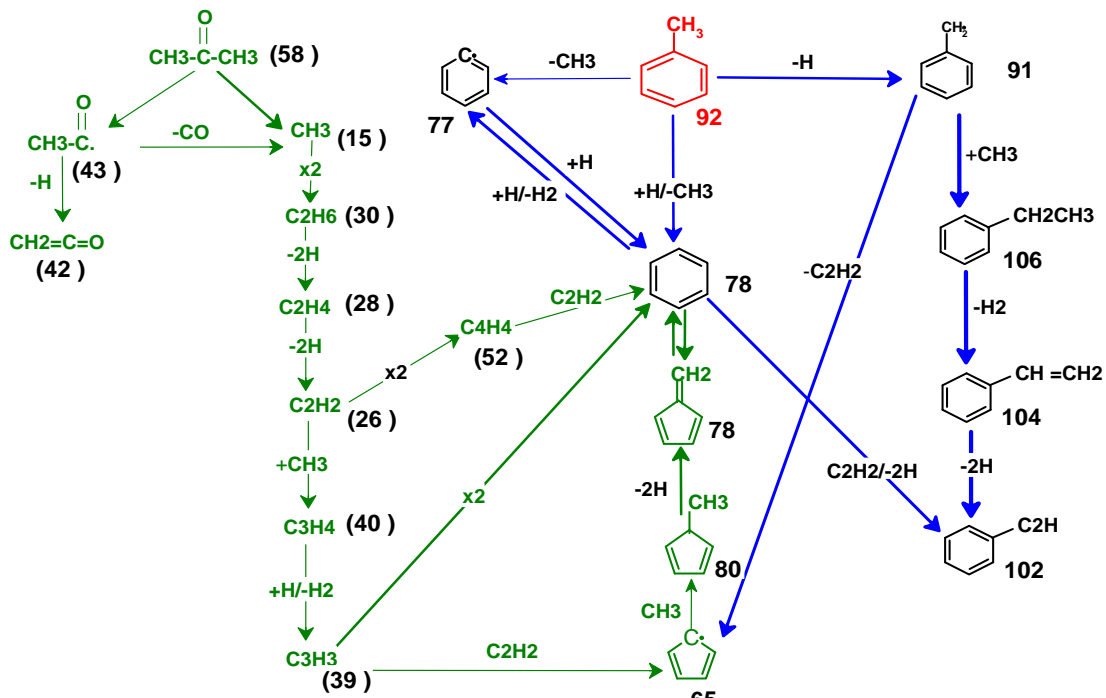
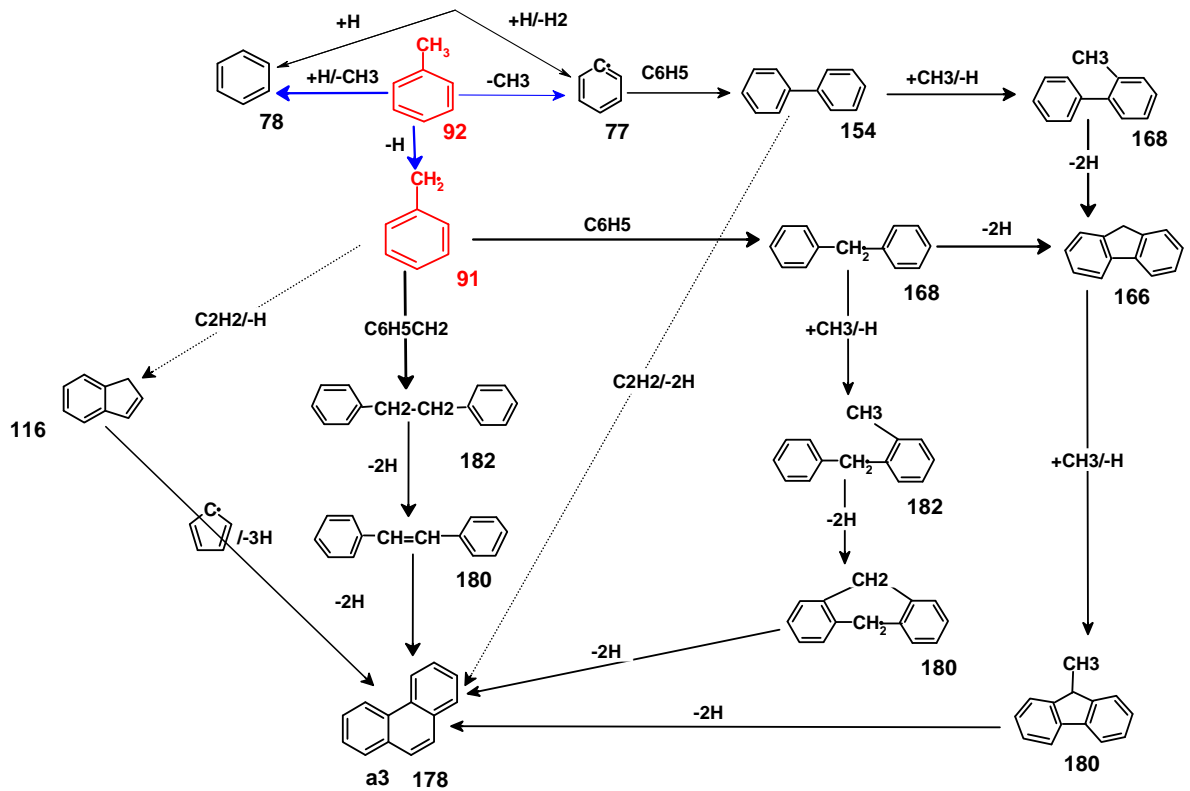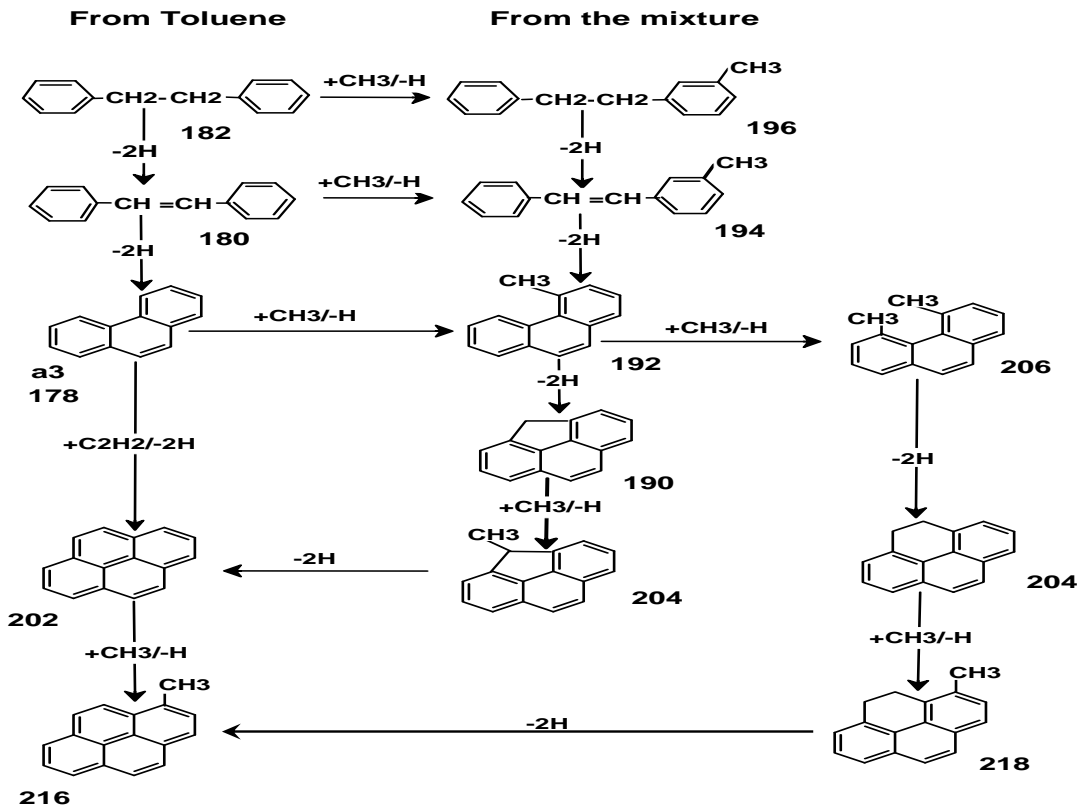

Formation Mechanism of two ring compounds
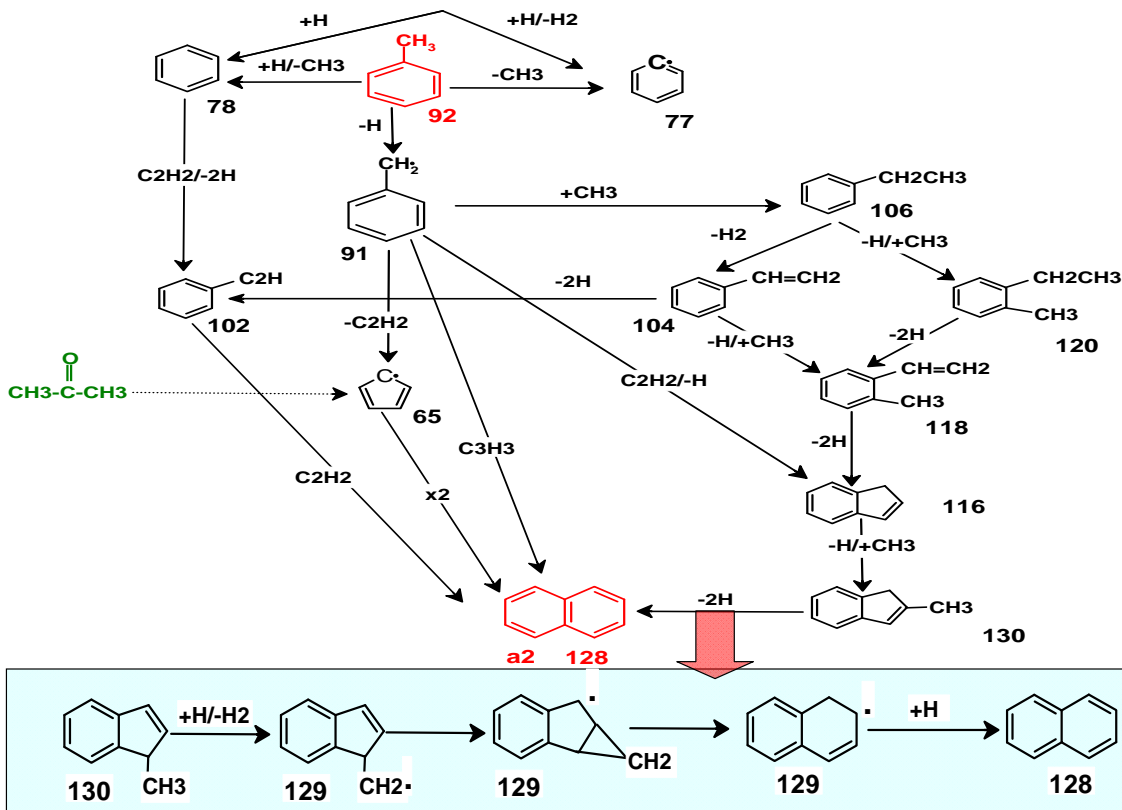
mechanisms are not so efficient. Finally it is found MAC mechanism is not efficient as HACA and PAC, as it increase the mass of species by 14 u.

Formation mechanisms of three ring compounds

Formation mechanism of four ring compounds

From Toluene

From the mixture

Toluene with and without addition of benzene and acetylene

Purpose

Main aim of this work is to check the combined effect of HACA, PAC and MAC mechanism on the formation path ways of PAHs and to evaluate which one seems to be the dominant process for the growth of large PAHs.

Outputs

The gas phase reaction produts of toluene with and without addition of benzene + acetylene at temperatures, 1147- 1473 K, total Pressure; 15.51 Torr and constant residence time; 0.62 s have been detected. Those products were ranging from C_2H_4 (*m/z* = 28) to $C_{36}H_{18}$ (*m/z* = 450). Mass spectra clearly show that the addition of acetylene consumed significantly the benzyl radicals and strongly depleted it products and accelerated the formation of methyl-PAHs without showing any significant change in phenyl products. Chemical kinetic analysis of formation pathways of detected products showed that addition of acetylene in the mixture causes the deceleration of benzyl and phenyl initiated products by trapping active species benzyl and phenyl radicals. Reactions of radicals methyl, phenyl and benzyl with acetylene are found dominant over radical self recombination and other radical-radical reactions. Enhancement in methyl-PAHs concentration even after the significant consumption of methyl radical by acetylene to produce propyne favors the acceleration of toluene decomposition into phenyl and methyl radicals on addition of benzene and acetylene which might be caused by acceleration of chain reactions by one or more products. Addition of benzene did not show any significant effect on products formation.

Pyrolysis of aliphatic hydrocarbons acetylene, ethylene and acetone

Acetylene is the simplest alkyne and it is produced during the pyrolysis and oxidation of almost all hydrocarbons. Study on formation mechanism of first aromatic ring has concluded that it is the most important starting species for the formation of first aromatic compound benzene or phenyl radical from aliphatic hydrocarbons. It is the main chain carrier of HACA mechanism. Although C_2H_2 is a very simple molecule, it's pyrolysis mechanism is too complicated due to different views about the initial dissociation mechanisms as well as the formation routes of first aromatic ring i.e benzene or phenyl radical. Its pyrolysis mechanism is highly important to understand the PAHs formation path ways in detail in its own as well as in other hydrocarbons.

Similar to C_2H_2, ethylene is an important species produced during oxidation and pyrolysis of many aliphatic and aromatic hydrocarbons. On hydrogen abstraction it produces vinyl radical which is highly active chain carrier for the formation of large species and PAH as well. Although it is so important its pyrolysis mechanism for the formation of PAHs is not well known.

Although, acetone is the best compound to produce sufficient methyl radical, an important radical for the acceleration of production of PAHs especially in the case of aliphatic hydrocarbons and alkylated aromatic hydrocarbons as well, until now acetone pyrolysis is only limited to the estimation of rates of initial uni-molecular decomposition channels and ketene formation. To our knowledge, the identification of bimolecular gas phase products of its pyrolysis has not been reported in any studies.

Purpose

The main objective of this study is to detect products larger than benzene and kinetic analysis of their formation pathways. Another aim is to check the effect of HACA as well as the role of methyl radical in the formation of PAHs from aliphatic hydrocarbons.
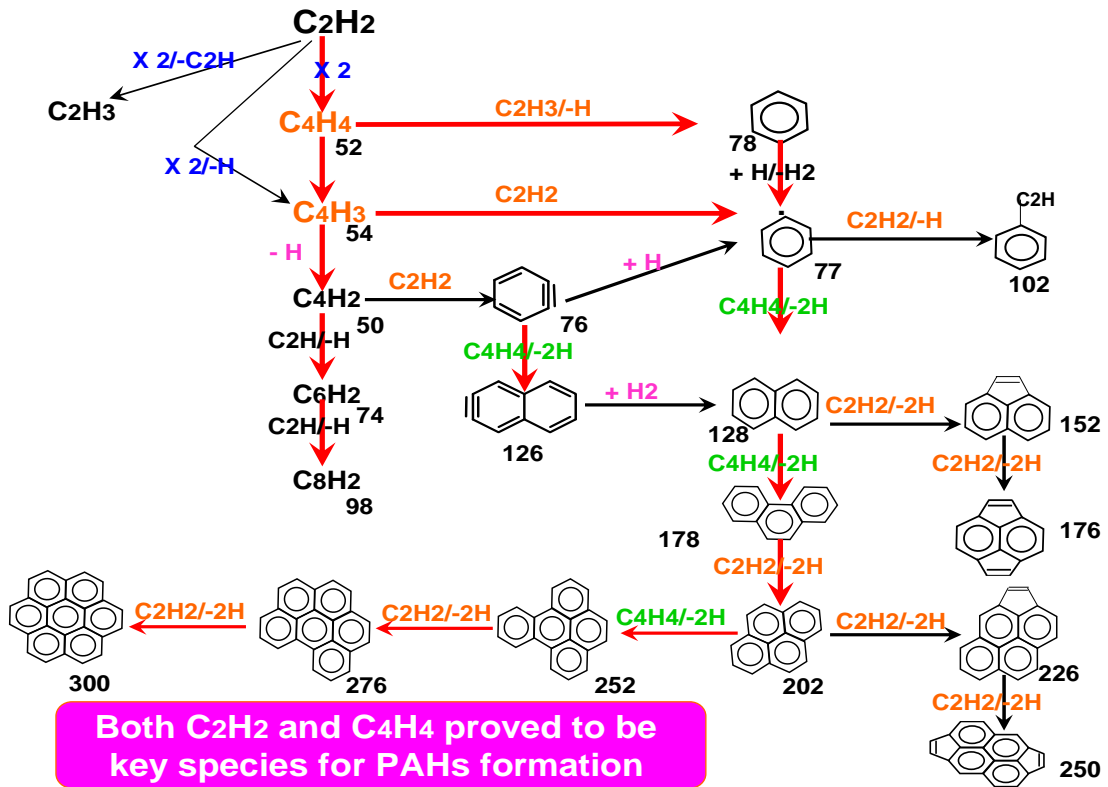
Outputs

The gas phase reaction products ranging from C_2H_4 ($m/z = 28$) to $C_{24}H_{12}$ ($m/z = 300$) have been detected. Mass spectra showed the dominant species at interval of mass ~24 u which corresponds to HACA mechanism. On the other hand very significant concentration of vinylacetylene and its corresponding radical C_4H_4/C_4H_3, indicate that these species are actively participating in the ring growth. As HACA mechanism needs two steps while vinylacetylene needs only one step for ring growth, latter is expected to be the most probable route. In addition to those products, methyl-PAHs products have also been detected in the case of acetone pyrolysis and observation of methylcyclopentadienyl proves its contribution in benzene formation.

Results on aliphatic pyrolyis can be summarized as follows,

❖ Gas phase species from ethylene (m/z = 28) to coronene (m/z = 300) were detected and their formation path ways were explored through the kinetic analysis.

❖ In the case of acetylene pyrolysis, the main key species were found to be C_4H_4/C_4H_3 and C_2H_2.

❖ In the pyrolysis of ethylene, the key species were found to be C_2H_3 as main chain carrier until first ring and C_4H_4/C_4H_3 for ring growth.

❖ The main key species in the case of acetone pyrolysis were found to be methyl radical for aliphatic products and C_4H_4/C_4H_3 for the aromatic products.

Acetylene Pyrolysis Mechanism

Both C2H2 and C4H4 proved to be key species for PAHs formation

Ethylene Pyrolysis Mechanism

C2H3 is found as chain carrier for the formation of aliphatic products and C4H4 for PAHs formation
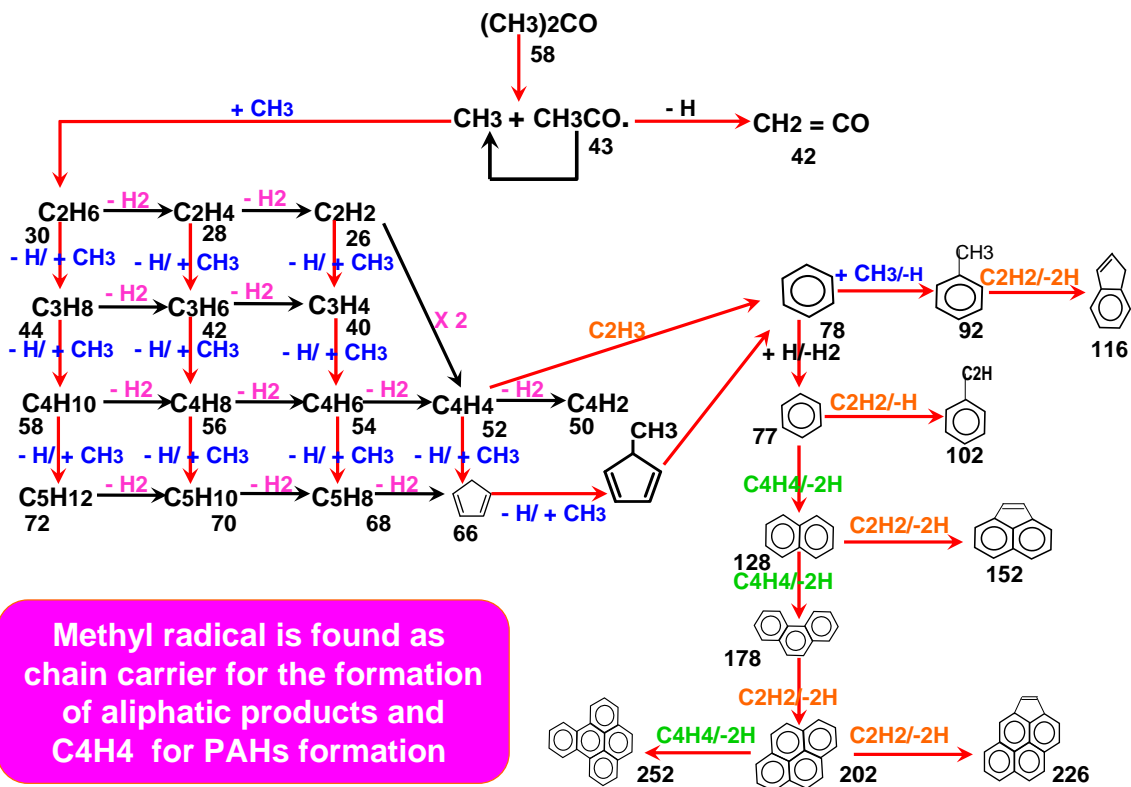
Acetone Pyrolysis Mechanism

(CH3)2CO
58

+ CH3 → CH3 + CH3CO. — -H → CH2 = CO
43   42

C2H6 — -H2 → C2H4 — -H2 → C2H2
30   28   26
- H/ + CH3   - H/ + CH3   - H/ + CH3

C3H8 — -H2 → C3H6 — -H2 → C3H4
44   42   40
- H/ + CH3   - H/ + CH3   - H/ + CH3

C4H10 — -H2 → C4H8 — -H2 → C4H6 — -H2 → C4H4 — -H2 → C4H2
58   56   54   52   50
- H/ + CH3   - H/ + CH3   - H/ + CH3   - H/ + CH3

X 2

C2H3

C5H12 — -H2 → C5H10 — -H2 → C5H8 — -H2 →
72   70   68   66
- H/ + CH3

CH3

- H/ + CH3

+ CH3/-H → (CH3) 92 — C2H2/-2H → 116
78

+ H/-H2

77 — C2H2/-H → (C2H) 102

C4H4/-2H

128 — C2H2/-2H → 152
C4H4/-2H

178

C2H2/-2H

252 ← C4H4/-2H — 202 — C2H2/-2H → 226

Methyl radical is found as chain carrier for the formation of aliphatic products and C4H4 for PAHs formation

Major Conclusions

- ❖ Gas phase products from methyl radical ($m/z = 15$,) to large PAHs ($m/z = 522$, ($C_{42}H_{18}$) including smaller species, radicals, polyynes, PAHs and their ethynyl, methyl & phenyl derivatives have been detected.
- ❖ The best temperature range at which large PAHs could be detected was 1300-1400 k and the growth of PAHs was found decelerated either by decreasing or increasing the temperature.
- ❖ New formation mechanisms PAC (phenyl addition/ cyclization) and MAC (methyl addition/ cyclization) have been investigated.
- ❖ Role of HACA mechanism was found only efficient to convert PAHs having triple fusing site into spherical PAHs so called soot precursor.
- ❖ This investigation believes that PAH greater than coronene should be the soot precursor.
- ❖ Radical-Molecule reaction was found dominant over radical-radical and the HACA for the fast formation of PAHs.
- ❖ In the case of aromatic pyrolysis with and without additives, key species were found to be benzyl, phenyl, methyl and cyclopenta fused radicals (like: cyclopentadienyl, indenyl and 4H-cyclopenta[def] phenanthrenyl).
- ❖ In the case of aliphatic pyrolysis, the main key species were found to be C_4H_4/C_4H_3 and C_2H_3/C_2H_2.
- ❖ Finally it can be concluded that HACA mechanism is only efficient to convert primary PAHs into CP-PAHs but it is not efficient for the formation of large PAHs as chain carrier even in the case of aliphatic hydrocarbons.

Significances:

1. It will be helpful to understand the soot nucleation process in detail.
2. It has opened the door for the preparation of kinetic model including elementary reactions for practical combustion process.
3. It will help to understand the real combustion process and to control the emission of environmental pollutants.
4. It will help to decide suitable additives for fuels.
5. It will help in preparation of model fuel for future.
6. It will be helpful to understand chemically the carbon nanotube and tyre manufacturing processes.

Future Works

1. **Publication of results.**
2. **Construction of Kinetic mechanism suitable to reproduce the experimental data.**
3. **Quantum mechanical calculation of some important reactions.**