



## Comparative Study of Carbonization of Hydrocarbons. The 24/26 Rule.

Mihály T. Beck<sup>1\*</sup>, Sándor Kéki<sup>2</sup>, Pál T. Szabó<sup>3</sup> and Miklós Zsuga<sup>2</sup>

<sup>1</sup>*Department of Physical Chemistry, Kossuth Lajos University, Debrecen 10, Hungary, H-4010*

<sup>2</sup>*Department of Applied Chemistry, Kossuth Lajos University, Debrecen 10, Hungary, H-4010*

<sup>3</sup>*Department of Medical Chemistry, Albert Szent-Györgyi University, Szeged Dóm tér 8, Hungary H-6720*

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### Abstract

Comparative study of different types of carbonization of hydrocarbons, i.e., electric discharges, thermal pyrolysis and pyrolysis in flame is reported. On the basis of GC/MS experiments, it can be concluded that a large number of compounds, mainly polycyclic aromatic hydrocarbons (PAHs) were formed in each cases. Similar PAHs were formed independently of the starting material, i.e., hexane or naphthalene. The formation of PAHs was explained by the 24/26 rule, i.e., the molar mass of PAHs increases by C<sub>2</sub> or/and C<sub>2</sub>H<sub>2</sub> unit incorporation, regularly. The GC/MS investigation reveals that the C<sub>2</sub> or/and C<sub>2</sub>H<sub>2</sub> incorporation takes place in both odd and even series of carbon atom number of PAHs. Fullerene formation was, however, observed only in the case of high temperature process, i.e., electric discharges. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** carbonization, PAHs, fullerene

### Introduction

During the last ten years a new class of all-carbon compounds, called fullerenes, has become one of the hottest topics of scientific research [1-3]. Different types of production of fullerenes, like evaporation of carbon by resistive heating [4-6], arc discharge [7,8], high frequency furnace [9,10], low pressure flame [11-14] and pyrolysis [15] can be found in the literature. These methods provide soots containing fullerenes in a wide concentration range. Isolation and separation of the fullerenes can be achieved by extraction of the soot with different kinds of organic solvents (hexane, benzene, toluene, pyridine etc.) [8] followed by chromatography [16].

Since the discovery of fullerenes a great effort has been exercised in our laboratories to find out chemical methods, other than laser evaporation of graphite under inert atmosphere, for the synthesis of different carbon clusters. We tried to clarify the mechanism of formation of fullerenes and that of the carbonization processes.

Both aliphatic and aromatic compounds have been investigated under different temperature processes like electric discharges, pyrolysis and flame combustions in order to compare the carbonization processes at different temperatures.

### Results and Discussion

Different ionization techniques were applied in order to choose the most suitable one for obtaining the

best signal for fullerene type molecules. Electrospray ionization is basically used for polar, water soluble molecules, however, there are publications which report its application on fullerenes. Hiruoka et al. [19] recorded fullerene anions using NaK amalgam in benzene/dimethoxyethane. In our cases, however, where the samples are mixtures, this method was found unsuitable. Liu [20] describes a method to analyse fullerenes in ESI without performing any charge transfer chemical reactions. We tried to reproduce their experiments but were not satisfied with the result. FAB has been proved to be a powerful analytical tool for nonvolatile, thermally labile compounds, [21,22] and has been used for characterization of fullerenes [23-29]. Glycerol, which is used in most cases as a matrix in FAB MS, turned out to be unsuitable for fullerenes. There are some papers describing other matrices for FAB MS of fullerenes: Zhonping et al. [30] used different kinds of phthalates and p-toluenesulfonates and found the spectra of C<sub>60</sub> and C<sub>70</sub> much simpler. Dube et al. [31] reported the behaviour of polycyclic aromatic hydrocarbons (PAHs) under FAB using different hydrocarbon fractions as matrices. Groenewold et al. [32] used molten SbCl<sub>3</sub> solution as matrix for PAHs. Gas phase FAB spectra of fullerenes and PAHs have been presented by Takayama [33]. This method needs a special heated probe tip.

We tried different hydrocarbons, polyphenyl ethers (diffusion pump oil) and phthalates but these matrices were not suitable for complex mixtures. SbCl<sub>3</sub> seemed to be a good matrix not only for PAHs but fullerenes as well. Unfortunately it has a strong background peak exactly at m/z 720 so only C<sub>70</sub> could be detected. The best matrix for FAB analysis of our samples was 3-nitrobenzyl-alcohol (NBA).

The best results can, however, be obtained under EI. There are no background peaks but a lot of molecular and fragment ions can easily be detected. Using negative ion detection mode a large number of these peaks can be eliminated because carbon-cage type molecules produce much more intensive negative ions than the other compounds. Another advantage of EI is that samples can be evaporated slowly so only a fraction of the mixture goes into the ion source at one time.

Tandem mass spectrometry was also used in case of mixtures to separate and analyse separately the components of the mixtures.

#### *Carbonization during high voltage electric discharge*

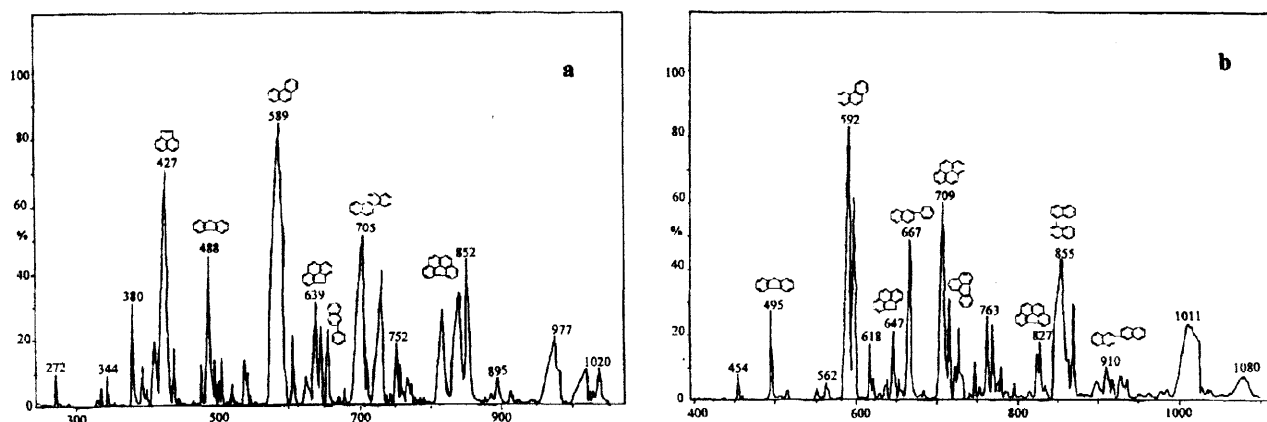
A large number of compounds and C<sub>60</sub> identified by GC/MS obtained by electric discharges have been published earlier [17,18]. Originally we hoped that by making electric discharges between carbon electrodes in benzene or toluene (instead of helium) the concentration of fullerenes might be increased. The fact that there was no significant difference if graphite or practically inert pyrographite electrodes were used clearly indicates that the electrode material does not play an important role in the chemical reactions. Independently of the starting materials, that were either aromatic or aliphatic compounds, PAHs were formed in each cases and the major components were almost the same.

#### *Carbonization at medium temperature*

Aliphatic (n-hexane) and aromatic (naphthalene, toluene) compounds were pyrolysed under inert atmosphere (argon and nitrogen) in order to study the carbonization process at about 1000-1500 °C. Each substance can be pyrolysed to soot. The yield of soot was found to be smaller when water was introduced. The amount of compounds extracted from the soot with toluene increased by decreasing the temperature. No

peak characteristic of fullerene or its derivatives can be found indicating that under these experimental conditions no fullerene formation takes place. The GC/MS chromatograms of pyrolysed hexane (a) and toluene (b) are presented in Figure 1. A comparison of these chromatograms shows that the major components of the extracts are rather similar.

The direct insertion mass spectrum (a) and GC/MS chromatogram (b) of pyrolysed naphthalene are shown in Figure 2. As it can be seen in Figure 2a there is a series with higher intensities, containing even number carbon atoms and another series between these peaks with smaller intensities, containing carbon atoms with odd number. On the basis of GC/MS analysis a possible explanation of this regularity is the propagation of  $C_2$  or/and  $C_2H_2$  chemical units, their incorporation and isomerization, leading to different types of PAHs (Fig. 1. and Fig. 2.). To elucidate the formation of PAHs from different compounds, the high temperature difference between the plasma or flame and the environment should be taken into account. The decomposition of the compounds such as toluene, hexane, naphthalene to different fragments including  $C_2H_2$  and  $C_2$  units takes place at high temperature, while the formation of PAHs by incorporating  $C_2H_2$  and  $C_2$  units occurs at low temperature. The amount of PAHs formed significantly depends on the temperature gradient between the plasma or flame and the environment.



**Figure 1.** GC/MS chromatograms of pyrolysed hexane (a) and toluene (b)  
(The numbers below the structure formula of compounds refer to the scan numbers.)

Scheme 1. summarizes the formation of some PAHs identified by GC/MS. Molecular weights and the possible structures can be found on the top of the peaks in the chromatogram.

Experiments were done to find out the composition of the gases formed by electric discharges. The argon flow, which was used in the electric discharge experiments to provide inert atmosphere, was introduced to a reservoir kept in liquid nitrogen. Under this condition most of the gas phase products were trapped. These gases were then analysed by GC/MS and a huge amount of acetylene was found.

Naphthalene was burnt in a flame in order to obtain more details about the carbonization at medium temperature. The vapours were condensed on a cooled surface forming soot. The toluene extract of this soot was then analysed by MS in EI mode.

The same series of peaks can be found in the mass spectrum of the extract as shown in Fig. 1. Increasing the temperature of the probe tip the maximum of the most intensive peak in the spectrum was

shifted to the higher masses. Peaks can be detected over 700 amu, however, no fullerenes were formed under these conditions. A typical mass spectrum of the soot is shown in Figure 3.

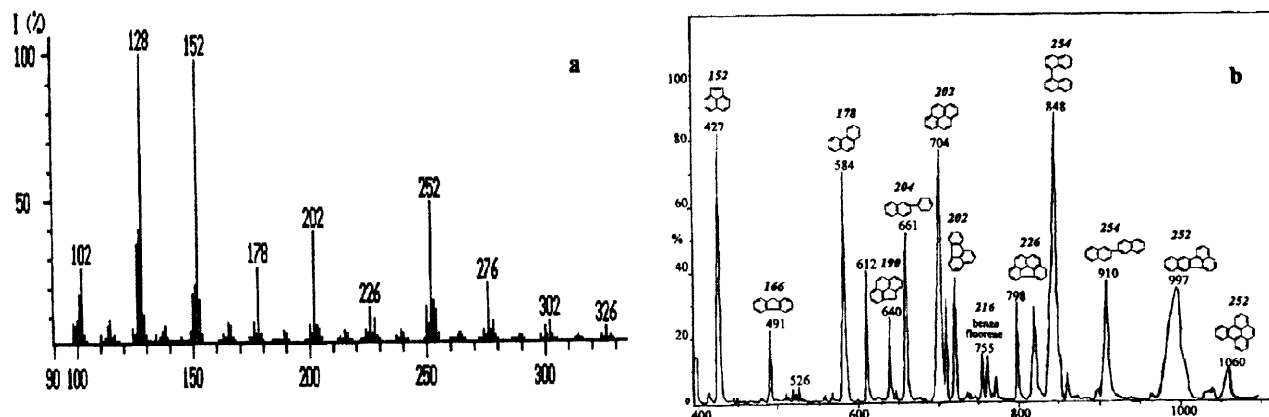
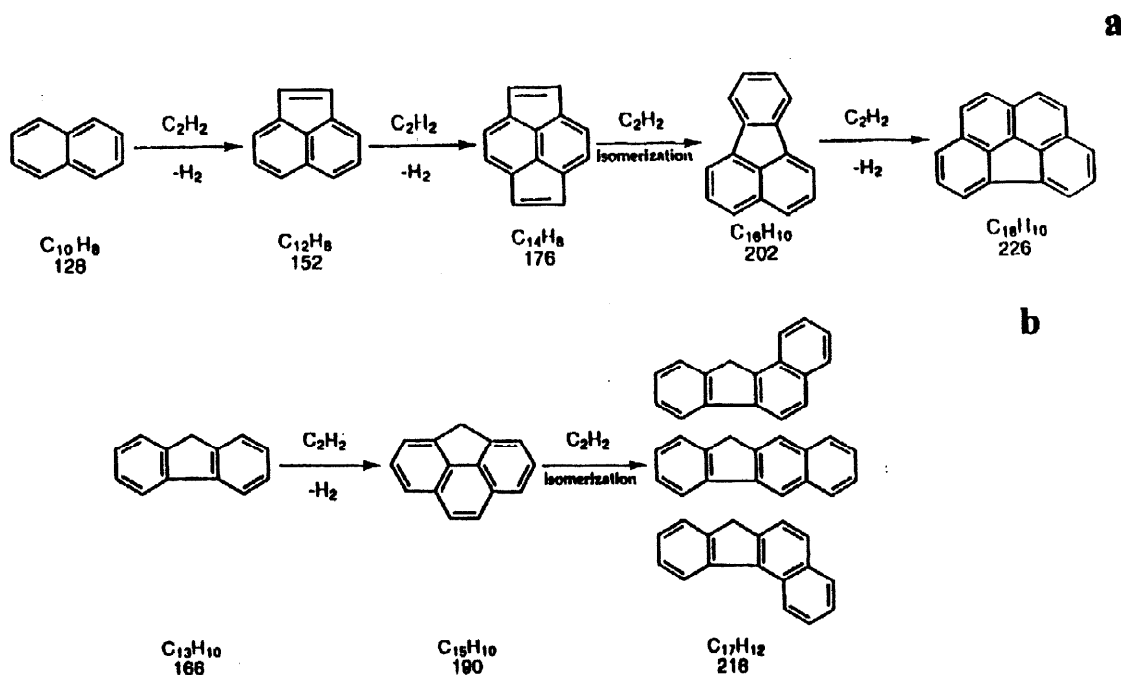


Figure 2. Direct insertion mass spectrum (a) and GC/MS chromatogram (b) of pyrolysed naphthalene. (The numbers below the structure formula of compounds refer to the scan numbers.)



Scheme 1. Mechanism of formation of PAHs containing even (a) and odd (b) number of carbon atoms

The essence of 24/26 rule is summarized in Scheme 2, where the propagation of 24 units is shown in rows and that of 26 units in the columns.

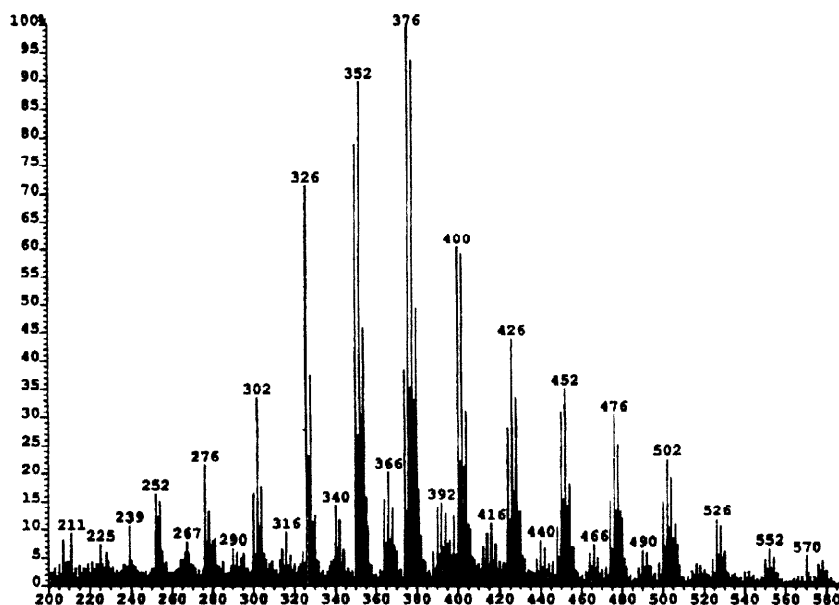


Figure 3. EI mass spectrum of the extract of the soot obtained from naphthalene in flame

a.

$C_{10}H_8$ 128	$C_{12}H_8$ 152	$C_{14}H_8$ 176																	
	$C_{14}H_{10}$ 178	$C_{16}H_{10}$ 202	$C_{18}H_{10}$ 226																
	$C_{16}H_{12}$ 204	$C_{18}H_{12}$ 228	$C_{20}H_{12}$ 252	$C_{22}H_{12}$ 276	$C_{24}H_{12}$ 300	$C_{26}H_{12}$ 324													
		$C_{20}H_{14}$ 254	$C_{22}H_{14}$ 278	$C_{24}H_{14}$ 302	$C_{26}H_{14}$ 326	$C_{28}H_{14}$ 350													
			$C_{24}H_{16}$ 304	$C_{26}H_{16}$ 328	$C_{28}H_{16}$ 352	$C_{30}H_{16}$ 376	$C_{32}H_{16}$ 400	$C_{34}H_{16}$ 424											
					$C_{30}H_{18}$ 378	$C_{32}H_{18}$ 402	$C_{34}H_{18}$ 426	$C_{36}H_{18}$ 450	$C_{38}H_{18}$ 474										
					$C_{32}H_{20}$ 404	$C_{34}H_{20}$ 428	$C_{36}H_{20}$ 452	$C_{38}H_{20}$ 476	$C_{40}H_{20}$ 500										

b.

$C_9H_{10}$ 118	$C_{11}H_{10}$ 142	$C_{13}H_{10}$ 166																	
	$C_{13}H_{12}$ 168	$C_{15}H_{12}$ 192	$C_{17}H_{12}$ 216																
	$C_{15}H_{14}$ 194	$C_{17}H_{14}$ 218	$C_{19}H_{14}$ 242	$C_{19}H_{14}$ 266	$C_{19}H_{14}$ 290	$C_{19}H_{14}$ 314													
		$C_{19}H_{16}$ 244	$C_{21}H_{16}$ 268	$C_{23}H_{16}$ 292	$C_{25}H_{16}$ 316	$C_{27}H_{16}$ 340													
			$C_{23}H_{18}$ 294	$C_{25}H_{18}$ 318	$C_{27}H_{18}$ 342	$C_{29}H_{18}$ 366	$C_{31}H_{18}$ 390	$C_{33}H_{18}$ 414											
					$C_{29}H_{20}$ 368	$C_{31}H_{20}$ 392	$C_{33}H_{20}$ 416	$C_{35}H_{20}$ 440	$C_{37}H_{20}$ 464										
					$C_{31}H_{22}$ 394	$C_{33}H_{22}$ 418	$C_{35}H_{22}$ 442	$C_{37}H_{22}$ 466	$C_{39}H_{22}$ 490										

Scheme 2. The essence of 24/26 rule for even (a) and odd (b) number of carbon atoms

## Conclusion

Similar results can be obtained in each case of different carbonization processes but the concentration of the components were found to be different.

A large number of polycyclic aromatic hydrocarbons were formed in each cases. With the help of the 24/26 rule the formation of these PAHs can be explained. Fullerene formation was observed only in the case of the high temperature process.

## Experimental

Electric discharges were made between graphite or pyrographite electrodes. Detailed experimental data on the apparatus and the sample processing procedure have already been published [17].

A resistively heated ceramic tube of 270 mm length and 20 mm diameter was used as a reactor in the pyrolysis experiments, where the temperature was kept at 1000 °C or 1500 °C. The pyrolysis was carried out under a N<sub>2</sub> or Ar atmosphere. The organic components were evaporated and carried by the N<sub>2</sub> or Ar stream into the reactor. The products were trapped in a cooled reservoir and the condensed soot was extracted with toluene. The mixture of PAHs was prepared by evaporation of toluene.

In the flame combustion experiments a simple burner was used and the samples were introduced into the flame by a spoon. The vapours were trapped on a cooled surface and the soot was collected, then extracted with toluene. The preparation of PAHs was carried out similarly to the thermal pyrolysis.

Electrospray measurements were run on a Finnigan TSQ 7000 instrument equipped with an ESI/APCI ion source. The spray voltage was 4.5 kV. Benzene was used as a mobile phase with a flow rate of 0.2 mL/min. FAB spectra were performed on a VG 7070HS double focusing instrument equipped with a FAB ion source. Xe was used in these experiments as a reagent gas. The voltage of the FAB gun was 8 kV, the ion current was 1.5 mA.

EI and GC/MS measurements were done on a VG 7035 double focusing GC/MS instrument. Source conditions were: temperature: 300 °C, accelerating voltage: 4 kV, electron energy: 70 eV. Probe temperature could be varied between 50–350 °C.

Separations of PAHs were carried out on a Hewlett-Packard HP5710A gas chromatograph coupled to the mass spectrometer described above. A fused silica capillary column (30m x 0.32mm id, DB1, J&W) was used. Carrier gas was He at 1.6 mL/min flow rate. The temperature program was: 80 °C for 2 min, then increased by 6 °C /min to 280 °C. Compounds in the chromatograms have been identified on the basis of their relative retention time and with the help of NBS registry of MS data.

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