Tetrahedron Vol. 48, No. 23, pp. 4919-4928, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Formation of Polycyclic Aromatic Compounds upon Electric Discharges in Liquid Toluene

Mihály T. Beck,* Zoltán Dinya and Sándor Kéki

Department of Physical Chemistry, Lajos Kossuth University and
Research Group of Antibiotics of the Hungarian Academy of Sciences
Debrecen 10, Hungary 4010

(*Received in UK* 4 *November* 1991)

Abstract: The formation of a great number of polycyclic aromatic compounds up to 604 mass number occurs when electric discharges are made in liquid toluene with one or both electrodes being graphite.

Recently Krätschmer et al.[1] prepared the C_{60} molecule, by making electric discharges between graphite electrodes in He atmosphere of about 100 Torr. From the soot formed, C_{60} was extracted with benzene. The compound was unambiguously characterized as C_{60} using mass spectrometric, NMR and IR spectroscopic and X-ray studies. Earlier observations[2] indicated that under certain condition a great number of cage molecules of the composition C_{30} - C_{100} can be formed, but C_{60} and C_{70} are of favourably high stability.

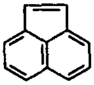
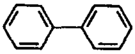
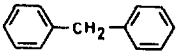
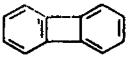
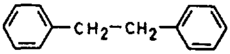
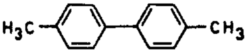
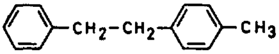
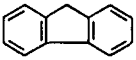
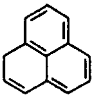
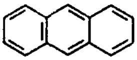
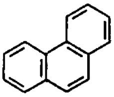
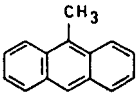
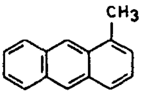
We expected that different all carbon cage molecules would be formed when electric discharges between graphite electrodes are made in certain organic solvents. We selected toluene for safety reasons as it can be cooled easily by adding solid carbon dioxide which provides inert atmosphere. Unfortunately, our experiments so far did not indicate the formation of the target molecules, but we observed that beside soot, coloured compounds soluble in toluene are formed.

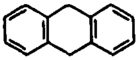
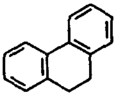
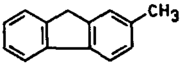
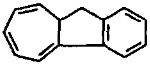
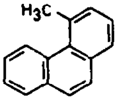
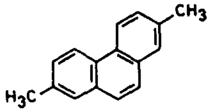
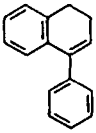
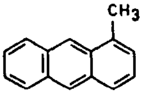
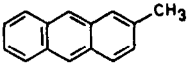
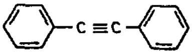
Table 1. summarizes the compounds unambiguously identified by GC-MS experiments.

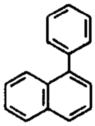
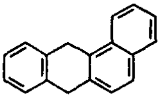
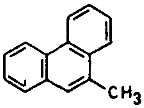
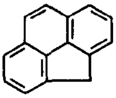
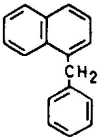
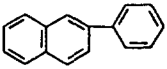
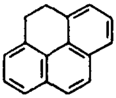
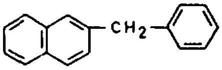
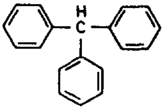
---

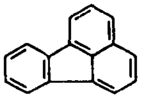
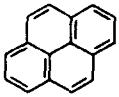
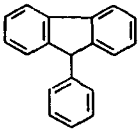
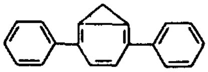
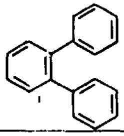
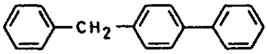
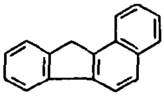
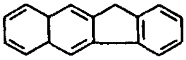
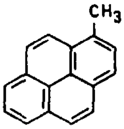
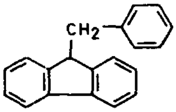
* Dedicated to Prof. G. Fodor on the occasion of his 75th birthday.

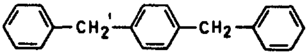
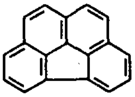
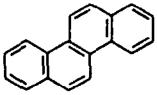
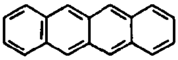
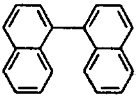
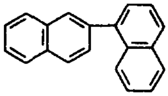
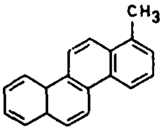
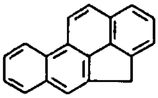
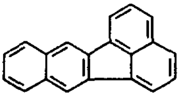
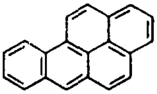
Table 1 Identified compounds by GC-MS

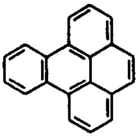
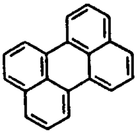
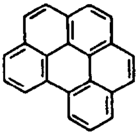
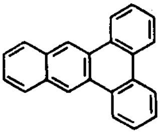
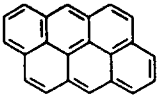
No.	Name	Chemical Structure
1.*	Acenaphthylene	
2.*	Biphenyl	
3.*	Diphenylmethane	
4.*	1,1'-Biphenylene	
5.*	1,2-Diphenylethane	
6.*	4.4'-Dimethyl-1,1'-biphenyl	
7.	1-(p-Tolyl)-2-phenyl-ethane	
8.	9H-Fluorene	
9.	1H-Phenalene	
10.*	Anthracene	
11.	Phenanthrene	
12.	9-Methylanthracene	
13.	1-Methylanthracene	

No.	Name	Chemical Structure
14.*	9,10-Dihydroanthracene	
15.	9,10-Dihydrophenanthrene	
16.	2-Methylfluorene	
17.	9a,10-Dihydrobenz[a]azulene	
18.	4-Methylphenanthrene	
19.	2,7-Dimethylphenanthrene	
20.	4-phenyl-1,2-dihydronaphthalene	
21.	1-Methylanthracene	
22.	2-Methylanthracene	
23.*	Tolan	
24.	Exo-5-Phenylbenzobicyclo-(2.1.1)hex-2-ene	

No.	Name	Chemical Structure
25.	1-Phenylnaphthalene	
26.	m-Terphenyl	
27.	7,12-Dihydrobenz[a]anthracene	
28.	9-Methylphenantrene	
29.	4,5-Methylenephenanthrene	
30.	1-Benzylnaphthalene	
31.	2-Phenylnaphtalene	
32.	4,5-Dihydropyrene	
33.	2-Benzylnaphthalene	
34.*	Triphenylmethane	

No.	Name	Chemical Structure
35.	Fluoranthene	
36.	Pyrene	
37.	9-Phenylfluorene	
38.	2,5-Diphenylcyclopropabenzene	
39.	o-Terphenyl	
40.	p-Terphenyl	
41.	4-Benzyl-1,1'-biphenyl	
42.	11H-Benzo[a]fluorene	
43.	11H-Benzo[b]fluorene	
44.	1-Methylpyrene	
45.	9-Benzyl-9H-fluorene	

No.	Name	Chemical Structure
46.	1,4-Dibenzylbenzene	
47.	Benzo[g,h,i]fluoranthene	
48.*	Chrysene	
49.	Naphthacene	
50.	1,1'-Binaphtalene	
51.	1,2'-Binaphtalene	
52.	1-Methylchrysene	
53.	4,5-Methanochrysene	
54.	Benzo(k)fluoranthene	
55.*	Benzo[a]pyrene	

No.	Name	Chemical Structure
56.	Benzo[e]perylene	
57.	Perylene	
58.	Benzo[g,h,i]prylene	
59.	1,2:3,4-Dibenzoanthracene	
60.	Anthanthrene	

---

*These are of relatively in large concentrations in the sample

There are a number of unidentified peaks assigned to some minor components. These compounds obviously are formed from the $C_6H_5^\cdot$ and $CH_3^\cdot$ radicals produced by the decomposition of toluene and from carbon atoms discharged from the graphite electrode(s). It would be easy to give plausible "mechanisms", however, to suggest chemically meaningful mechanisms requires the evaluation of experiments applying toluene appropriately labelled by ^{13}C, ^{2}D and ^{3}T atoms. It is, however, already obvious that both the liquid medium and the electrode(s) play a crucial role in these chemical reactions. If instead of toluene cyclohexane was used, no formation of compounds was observed and even the soot formation was rather small. If electric discharges were made in toluene between Pt electrodes, no significant extent of reaction was found, while the yield of the organic compounds (measured by the absorbancy of the filtered solution at 280 nm) was halved if only one of electrodes was graphite.

Based on the mass spectra, the formation of 1:12, 2:3, 4:5, 6:7, 8:9, 10:11 and 1:2, 3:4, 5:6, 7:8, 9:10, 11:12 hexabenzocoronene isomers is also likely,[4] but not proven unambiguously yet.

Several oxygen containing compounds also formed in small amounts, e.g., dibenzo[b,d]furan. The source of oxygen was the water content of dry ice added to the liquid toluene.

The reactions in the electric discharges are related to the thermal reactions when the reactant is subjected to a very big temperature gradient. Very recently Kawakami et al.[3] published that in the thermal decomposition of p-xylene (gas phase, the temperature of the spiral heater 1050-1150°C) a number of compounds was formed, the main products being toluene, 4,4'-dimethylbibenzyl and [2,2]-paracyclophane. The differences between this type of reaction and those taking place in electric discharges in liquids using graphite electrodes are as follows:i) In addition to thermal activation the activation by electron impact should be taken into consideration; ii) The graphite electrodes themselves are sources of carbon atoms; iii) The thermal gradient is considerably different in the two reactions, consequently the diffusion of the reactive radicals from the high temperature zone is also different.

Experiments are in progress in our laboratory with benzene, the three xylene isomers and with isotopically labelled compounds. We intend to apply different conditions to the electric discharges both in liquids and gases, including high voltage, high frequency (Tesla) currents.

Experimental

Electric discharge experiments. Electric discharges were made between two graphite electrodes, using direct current of 24-28 V, 10-15 A. The electrodes were mounted into a three-necked flask of 250 ml, the distance between the electrodes was at most 2mm, but the best result was obtained when the two electrodes were scratched by each other. From time to time solid carbon dioxide was added to the freshly distilled toluene, the volume of which was 100 ml. After treatment the toluene was removed in a rotary evaporator. The brown paste-like residue was dissolved in dichloromethane and then heated to dryness. This material was used in the GC-MS experiment. The amount of material obtained after a two-hour discharge treatment was 150 mg.

When one of the electrodes was graphite and the other platinum, the yield of material, based on the absorbance of the solution at 280 nm, was about the half, independently whether the carbon anode or the cathode was replaced by Pt.

Gas chromatographic - Mass spectrometry experiments: The samples were dissolved in dichloromethane and analyzed by using a VG-7035 (VG Analytical Ltd.,U.K.) mass spectrometer equipped with a combined electron impact chemical ionization source and coupled with a Hewlett-Packard 5010A gas chromatograph. The system was controlled by a VG-2035 data system. The source conditions were: temperature 200°C; electron energy 70 eV; accelerating voltage 4 kV; ionization current 200 μA. Chromatographic conditions were: fused silica capillary column, 50 m x 0.25 mm id DB-5 (J & W), directly interfaced to the ion source; injection port temperature 250 °C ; interface temperature 250 °C; column initial temperature 100 °C, hold 2 min , increase 4 °C/min to 260 °C; splitless valve on for 0.5 min, carrier gas helium at 2 ml/min.

Structural identification of individual organic compounds was based on comparison of their retention times and electron impact mass spectra with those of authentic compounds of the Wiley/NBS Registry of Mass Spectral Data Base[5] and spectral interpretation.

Acknowledgement: We are much obliged to Mr. András Berki and Mr. László Maglóczki for the constuction of the discharge apparatus.

References

1. Krätschmer, W.; Lamb, L.D.; Fostiropoulos, K.; Huffamn, D.R. *Nature* 1990, *347*, 354-358

2. Rohlfing, E.A.; Cox, D.M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322-3330

3. Kawakami, S.; Iwaki, S.; Nakada, M.; Yamaguchi T. *Bull. Chem. Soc. Japan* 1991, *64*, 1000-1004

4. Reed, R.I.; Tennent, A. *Org. Mass Spectrometry* 1971, *5*, 619-621

5. McLafferty, F.W.; Stauffer, D.G. The Wiley/NBS Registry of Mass Spectral Data, Vol 1-17, John Wiley and Sons, New York, *1988*