Tetrahedron Vol 49, No 1, pp. 285-290, 1993
Printed in Great Britain

0040-4020/93 $5.00+.00

Formation of C_{60} and Polycyclic Aromatic Hydrocarbons upon Electric Discharges in Liquid Toluene

Mihály T. Beck,* Zoltán Dinya, Sándor Kéki and Lajos Papp

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

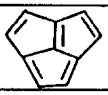
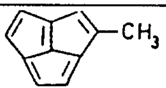
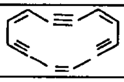
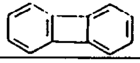
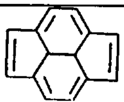
(*Received in UK* 13 *October* 1992)

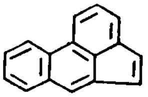
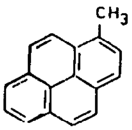
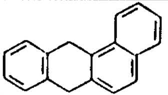
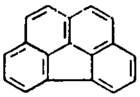
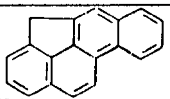
Abstract: A great number of polycyclic aromatic hydrocarbons and C_{60} are formed upon the effect of electric discharges in liquid toluene between graphite or pyrographite electrodes applying high voltage AC.

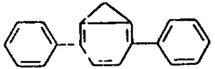
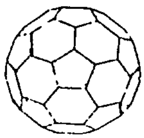
Recently the formation of a number of polycyclic aromatic hydrocarbons was found on the effect of electric discharges between graphite electrodes in liquid toluene.[1] However, no indication was found for the formation of C_{60}, the target molecule of these studies. In these experiments direct current of 24 - 48 V has been used. We observed that by using high voltage (about 20 kV) alternating current (50 Hz) C_{60} was formed besides a great number of polycyclic aromatic hydrocarbons, and that, surprisingly and also in contrast with the former experiments, the electrodes do not play any important role in the reaction. In the following, for sake of convenience, the term *scintillysis* is used for the reaction occurring on the effect of electrode discharges. Although decomposition and synthetic reactions on the effect of high temperature in the discharging zone are crucially important, it would be misleading to use the term pyrolysis. Plasmolysis would be more correct, however, the term scintillysis expresses the origin of the plasma where the reactions start. (The Referee suggested the term flash electrolysis. We prefer scintillysis since it is less committing than flash electrolysis. Obviously, no neutralization of organic ions occurs on the electrodes and it is far from being evident that on the effect of electric discharges ions are formed from the organic molecules.)

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

Table 1. The compounds formed upon low voltage DC and high voltage AC discharges and identified by GC-MS experiments.

No.	Name	Chemical Structure	I.	II.
1.	2-Methyl-phenylacetylene		-	++
2.	1H-indene		-	+
3.	Tricyclodecapentene		-	+
4.	Azulene		-	+
5.	1-Methylindene		-	+
6.	Naphthalene		-	++
7.	1-Methylene-1H-indene		-	++
8.	1 or 2-Methylazulene		-	+
9.	Methyltricyclodecapentene		-	+
10.	2-Methylnaphthalene		-	+
11.	1-Methylnaphthalene		-	+
12.	6,6’-Bifulvenil		-	+
13.	Cyclotetraheptatriene-triyne		-	+
14.	Acenaphthylene		++	++
15.	Biphenyl		++	++
16.	1,1’-Biphenylene		++	++
17.	3-Methylbiphenyl		-	+
18.	4-Methylbiphenyl		-	+
19.	9H-Fluorene		-	++
20.	Diphenylmethane		++	+
21.	1H-Phenalene		+	++
22.	Pyracylene		-	+
23.	1,2-Diphenylmethane		+	+
24.	4,4’-Dimethyl-1,1’-biphenyl		++	+
25.	Anthracene		++	+
26.	Phenanthrene		+	+
27.	9,10-Dihydroanthracene		++	+
28.	2-Methylfluorene		+	-
29.	9,10-Dihydrophenanthrene		+	-
30.	9a,10-Dihydrobenz[a]azulene		+	-
31.	Tolan		++	++
32.	2-Methylphenanthrene		-	+
33.	1-(p-Tolyl)-2-phenyl-ethane		+	-
34.	9-Methylanthracene		+	+
35.	1-Methylanthracene		+	+
36.	2-Methylanthracene		+	+
37.	4-Methylphenanthrene		+	-
38.	9-Methyphenanthrene		+	+
39.	4,5-Methylenephenanthrene		+	+
40.	2,7-Dimethylphenanthrene		+	+

No.	Name	Chemical Structure	I.	II.
41.	4-Phenyl-1,2-dihydronaphthalene		+	+
42.	Exo-5-Phenylbenzobicyclo-(2.1.1)hex-2-ene		+	-
43.	1-Phenylnaphthalene		+	+
44.	Acephenanthrylene		-	+
45.	2-Phenylnaphthalene		+	+
46.	3,6-Dimethyl-phenanthrene		-	+
47.	4,5-Dihydropyrene		+	+
48.	Fluoranthene		+	+
49.	Pyrene		+	+
50.	1-Benzylnaphthalene		+	-
51.	2-Benzylnaphthalene		+	-
52.	11H-Benzo[a]fluorene		+	+
53.	11H-Benzo[b]fluorene		+	+
54.	1-Methylpyrene		+	+
55.	Cyclopenta[c,d]pyrene		-	+
56.	Benzo[a]pyracylene		-	+
57.	Triphenylene		-	+
58.	o-Terphenyl		+	+
59.	p-Terphenyl		+	-
60.	m-Terphenyl		+	-
61.	9,10-Dihydrobenz[a]anthracene		+	-
62.	Benzo[g,h,i]fluoranthene		+	+
63.	Chrysene		++	++
64.	Naphthacene		+	+
65.	1-Methylchrysene		+	-
66.	4,5-Methanochrysene		+	+
67.	9-Phenylfluorene		+	-

No.	Name	Chemical Structure	I.	II.
68.	2,5-Diphenylcyclopropabenzene		+	-
69.	Triphenylmethane		+	-
70.	4-Benzyl-1,1'-biphenyl		+	-
71.	9-Benzyl-9H-fluorene		+	-
72.	1,1'-Binaphthalene		+	+
73.	1,2'-Binaphthalene		+	+
74.	Benzo(k)fluoranthene		+	+
75.	Benzo[a]pyrene		+	+
76.	Benzo[e]pyrene		+	-
77.	Perylene		+	+
78.	1,4-Dibenzylbenzene		+	-
79.	Benzo[g,h,i]perylene		+	+
80.	1,2:3,4-Dibenzoanthracene		+	-
81.	Anthanthrene		+	+
82.	Buckyball(C_{60})		-	+

For sake of comparison the results of three experiments are given in the Table. Column I. refers to the former experiments[1], column II. refers to high voltage discharges using either graphite or pyrographite electrodes. ++ indicates major, + minor products, while - shows that this compound could not be identified.

The fact that no difference occurs if graphite or the practically inert pyrographite electrodes were used in the high voltage AC experiments, clearly indicates that the electrode material does not play any important role in the chemical reactions. Using graphite electrode the corrosion of the electrodes could be seen, but the amount of carbon in the soot formed exceeded by orders of magnitude of the amount of the corroded graphite. Using pyrographite electrode no corrosion of the electrodes occurred and the amount of the carbon in the soot was practically the same as in the experiments using graphite electrodes. Applying low voltage DC scintillysis the graphite electrodes themselves take part in the chemical reactions.[1]

Another spectacular difference is that in the high voltage AC scintillysis experiments C_{60} could be found. The amount of C_{60} is small (about 2 mg, altogether about 1 % of the toluene soluble part of the soot). It seems likely that other fullerenes and perhaps their hydrogen containing derivatives were also formed, but our analytical facilities do not permit their detection.

Undoubtedly, the reaction taking place under the present condition is the gradual dehydrogenation, carbonization of toluene.

It seems likely that some of the polycyclic aromatic hydrocarbons are the precursors of C_{60}, while others mean dead ends from this point of view, just as in the case of formation of C_{60} in hydrocarbon flames.[2] It is possible, that the insoluble part of the soot contain higher fullerenes or nanotubes.[3] Electronmicroscopic experiments for their detection are in progress.[4]

Experiments are in progress in our laboratory to elucidate the effect of voltage end frequency on the distribution of the products as well as the possible role of electron impact reactions by changing the "inert" gases.

Experimental

Electric discharge experiments. Electric discharges were made between graphite (type RWO, produced by Ringsdorff), or pyrographite (home made, the surface covered by graphite balls of 10 - 100 µm diameter) electrodes of 6 mm diameter. The distance between the electrodes was 1 mm. The volume of toluene was 15 ml. The electrodes must be just covered by toluene, otherwise no discharges between the electrodes occurred. Before the start and during the experiment argon was bubbled through the liquid. The level of toluene was kept constant by adding fresh toluene. The discharges were applied for 10 minutes. The reactor itself (Fig.1) was a double wall glass cylinder, permitting the cooling of the liquid. The cooling water was precooled to 4 - 5 °C.

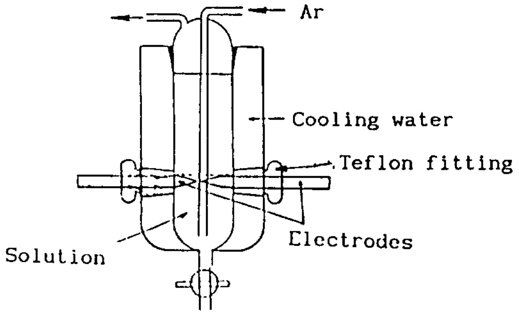


Figure 1

For the generation of discharges a Zeiss Type HF0002 Feussner apparatus was used. The 220 V, 50 Hz current is transformed to 10 - 20 kV. After charging condensers of variable capacity (1.5 - 24 nF) the revolving synchron switch discharges in each half-period. The time of the discharge can be varied by applying coils of 0 - 5 mH self-induction. In our experiments the inductivity and capacity values were constant (C = 12 nF, I_h = 0.02 mH). Under these conditions the duration of a discharge is 10^{-3} s, the frequency is 100 s^{-1}, E = 20 kV, I_{max} = 100 - 1000 A.

Gas chromatographic - Mass spectrometry experiments. To the product of the scintillysis experiments (liquid + soot) 100 ml toluene was added and boiled in reflux for one hour. The fitrate was distilled in vacuo and the brown paste like material was dissolved in dichloromethane. The samples were 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-20035 data system. The source conditions were: temperature 200 °C; electron energy 70 eV; accelerating voltage 4 kV; ionization curent 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; 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.

C_{60} was determined by comparative MS and FTIR study, using benzophenone as inner standard and authentic C_{60} product for calibration.

References

1. Beck,M.T. ; Dinya, Z.; Kéki, S. *Tetrahedron* 1992, *48*, 4919-4928
2. Baum, Th.; Löffler, Ph.; Weilmünster, P. and Homann, K.-H. *Ber. Bunsenges. Phys. Chem.* 1992, *96*, 841-857
3. Iijima, S. *Nature* 1992, *354*, 56-58
4. Barna, P.; Kéki, S.; Beck, M.T. to be published
5. McLafferty, F.W.; Stauffer, D.G. The Wiley/NBS Registry of Mass Spectral dada, Vol. 1-17, John Wiley and Sons, New York, *1988*