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FORMATION OF FULLERENES IN FLAMES

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Abstract

A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, and many other shapes. In this paper were considered works on formation and the synthesis of fullerenes in flames in the following sections, such as, the structure and properties of fullerenes; applications of fullerenes; methods for identification of fullerenes; methods for producing fullerenes; formation and synthesis of fullerenes in flame; synthesis of fullerenes in flames with applied electrical field; mechanism of fullerenes formation. Also was presented modified scheme for soot and fullerenes formation process in flames. It has been found that if the peripheral zone of the benzene flame is heated by some external source, such as a laser beam, which not just burns the soot but also creates the same conditions as in the middle of the flame, the concentration of fullerenes increases. The increase in the yield of fullerenes in the case where a ring electrode is positioned above the peripheral part of the reaction zone of a flame is due to the glow-discharge conditions providing an effective synthesis of fullerenes.

Keywords: fullerene, graphene, sphere, ellipsoid, tube

Introduction

The discovery of fullerenes representing a new form of existence of one of the most abundant elements on the Earth - carbon - has been recognized as one of the most significant achievements in 20th century science. Despite the fact that it has long been known that carbon atoms have a unique ability to bind into complex three-dimensional branched structures, which forms the basis of the whole subject of organic chemistry, the possibility of only one carbon forming stable skeleton.

The C60 and C70 fullerene ions were detected in premixed acethylene/oxygen/argon and benzene/oxygen/argon flames in 1987, identified by the mass-spectrometry method [1]. Howard et al. [2] have obtained large amounts of C60 and C70 in laminar premixed soot forming flames of benzene and oxygen at low pressures. Unlike the evaporation of graphite, in the fullerenes formed in flames the ratio C70/C60 changes from 0.26 to 8.8 (in the case of evaporation of graphite, this ratio changes from 0.02 to 0.18).

The synthesis of fullerenes in nature has been a subject of intense discussion for many years. It is unclear whether they form through assembly of small carbon bearing molecules (bottom-up) or fragmentations of large compounds (top-down).

The discovery of fullerenes in rocks (Buseck et al., 1992) suggests that fullerenes can be generated through a solid-state process.

Many interesting scenarios, such as cataclysmic impact, extensive wildfires, chondritic impactor, vaporization of carbon by lightning strike, and pyrolysis of organic matter, have been proposed to explain the formation of fullerenes in geological environments (Buseck, 2002, and references therein).

The hydrocarbon combustion process yields a C70/C60 ratio ranging from 0.26 to 0.57 (Howard et al., 1991), which tends to increase with increasing pressure.

This ratio is much larger than that obtained through graphite evaporation methods (0.02–0.18, e.g. Ajie et al., 1990). One cannot simply argue that the low C70/C60 ratio in PNs seems not to favor the top-down scenario, because the circumstellar envelopes have a significantly lower pressure than laboratories and the fullerene formation in combustion experiments is not completely understood.

The knowledge of fullerenes formation in flames has grown significantly during the short time since this process was first established. In this paper we present a review of the formation and the synthesis of fullerenes in flames in the following sections, such as, the structure and properties of fullerenes; applications of fullerenes; methods for identification of fullerenes; methods for producing fullerenes; formation and synthesis of fullerenes in flame; synthesis of fullerenes in flames with applied electrical field; mechanism of fullerenes formation.

The structure and properties of fullerenes

The structure of fullerene C60 proposed by R. Smalley resembles a football, so it is sometimes called footballene, and that of C70 resembles a rugby ball. Fullerenes C60 and C70 were identified in 1985 and prepared in macroscopic quantities in 1990, both by evaporation of graphite in an arc discharge [3]. In flames, fullerene ions were found in 1987, and in 1991, C60 and C70 were extracted in large quantities from laminar soot flames of premixed mixtures of benzene and oxygen at low pressures [4] and then was identified spectroscopically. Kr¨atschmer et al. (1990b) developed a method to efficiently produce C60 in the laboratory, making it possible to study in detail its electronic and vibrational properties. Because of its high stability and symmetry, C60 can be taken as a benchmark to study other fullerenes. C60 and its derivatives have long been suspected to be present in the universe. The search for this compound in nature started soon after its synthesis in the laboratory, and it has been detected in geological materials and meteorites and reported by several groups (e.g. Buseck et al., 1992; Becker and Bada, 1994; Becker et al., 1994; Heymann et al., 1996).

Fullerenes are closed hollow spherical shells or more complex 3D shapes, constructed from pentagonal and hexagonal carbon cells (C2n, $n \geq 15$), each of which has 60 or more carbon atoms. Molecular group known as fullerenes, contain other three-dimensional carbon molecules, including C70, C76, C78, C84, etc. Among these C60 is the most common fullerene consisting of 20 hexagons and 12 pentagons. C60 is a stable molecule crystal spheroid with a radius of 0.357 nm and the third allotropic form of carbon after diamond, graphite and carbon.

Fullerene C70 is formed in an amount of 5-6 times less than C60, in the electric method. In form it is close to an ellipsoid, whose axes size - 0,788 and 0,682 nm.

All the fullerenes relate into the class of carbons with a polyhedral-closed shell. They were detected as ionized particles in the fuel-rich plane of premixed acetylene and benzene-oxygen flames at low pressures with the use of molecular-beam sampling in combination with mass-spectrometry analysis [1].

In C70 there are five types of carbon atoms, i.e., there are five crystallochemical nonequivalent positions of carbon atoms (for example, there is the top where only six-membered rings converge). The length of the C-C take values 0,138-0,146 nm. The C70 molecule has a lower symmetry than C60. Fullerene C70 at room temperature forms a hexagonal close packing. Fullerene molecules perform a rotational motion around the equilibrium position with a frequency of 1012 Hz. With decreasing temperature, the fcc lattice becomes a simple cubic.

The solubility of fullerenes. Fullerenes are practically insoluble in polar solvents such as alcohols, acetone, tetrahydrofuran, etc. They are poorly soluble in alkanes (acyclic saturated hydrocarbons) of normal structure (pentane, hexane, decane, etc.), and the increasing number of carbon atoms increases the solubility in alkanes. Fullerenes with the highest solubility are characterized by aromatic hydrocarbons and their derivatives, among which naphthalene derivatives are the highest. The analysis shows that fullerenes are best dissolved in solvents, for which the value of the specific enthalpy of vaporization is divided by the volume of the solvent molecule close to the corresponding value for the fullerene molecule (around 100 kal/sm3).

Fullerenes have appreciable solubility in a broad class of organic solvents. This feature is explained by the unusual structure of fullerenes, with increased reactivity. Interest in investigating the behavior of fullerenes in solutions is due to the fact that fullerenes are the only soluble form of carbon that has both applied and fundamental importance. The uniqueness of the fullerene is also evident since they form clusters of several molecules in the solutions. Solvent interaction with fullerenes is due to van-der-Waals forces. Thus solutions of fullerenes begin to show unusual optical, thermodynamic, kinetic, and other properties.

Of the fullerene family, C60 and C70 are the major isomers obtained with 73 and 23% yield, respectively, a variety of molecules larger than C60 and C70 representing a total amount of 3 to 4% by weight. The colors of the fullerene family vary according to their molecular weight and symmetry: their colors in solution are magenta (C60), port-wine red (C70), brown (C76, C78) and yellow-green (C84).

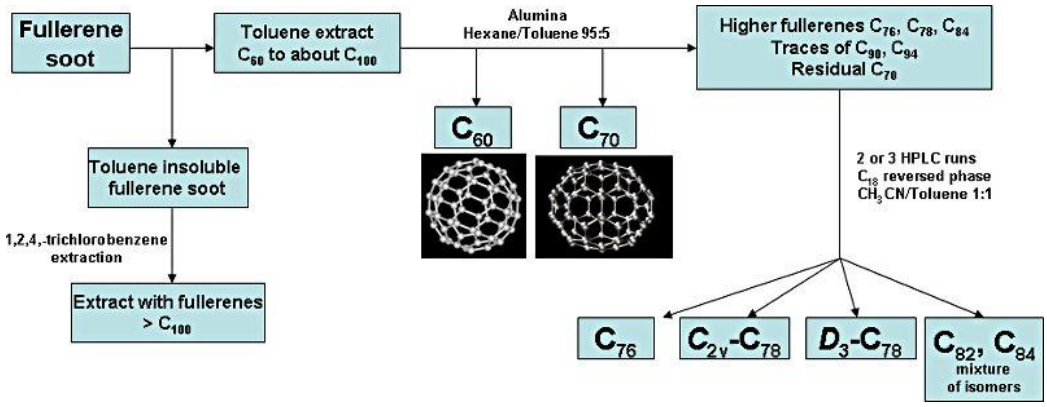

Figure 1 – Fullerenes purification and isolation protocol [36]

The physical properties. Due to the high reactivity of higher fullerenes and a small percentage of their output in the synthesis of fullerenes, their properties in literature are very poorly portrayed. The properties of fullerenes C60 and C70 are more widely studied and reported. Electron affinity in C60 is 2.65 eV, the ionization potential of - 7.61 eV binding energy per carbon atom - 7 eV, the polarizability is close to 80 Å3. The molecule can take up to 12 electrons and release one electron, i.e. the charge on the C60 can vary from 1 to 12. In the condensed state is a fullerene with molecular crystals - fullerites, in which the binding energy between molecules is 1.86 eV and is carried out by van der Waals forces. Fullerites have an orientational disorder of characterizing the ability of the thermal motion of molecules as to the relative change in the conditions of the spatial orientation of the crystal environment, which is typical for low energy barriers between the different positions of the molecules of the order of 0.2-0.3 eV.

Applications of fullerenes

The uniqueness of the fullerene structure determines their unusual physical and chemical properties that have great promise for practical use. Fullerenes are similar in their properties to graphite, and therefore inherit its high heat resistance and extraordinary electrical properties. Also, it is widely known for its graphite antifriction properties. The specific three-dimensional structure of fullerene molecules makes it possible to obtain a previously unknown class of heteroatomic compounds - doped fullerenes, and these compounds have begun a new turn in chemical (biochemical) science. Here are the most promising areas of application of fullerenes and their derivatives, some of which received a practical embodiment. The greatest number of patents from abroad dedicated the application of fullerenes in semiconductor technology and nanoelectronics as photodiodes, transistors and solar cells. C60, having high electro negativity, readily forms charge-transfer complexes, and acts as an electron acceptor. In diodes consisting of a fullerene as an acceptor covalently bound to a photoactive donor, and exposed to light, a photo induced electron transition occurs. High efficiency of light absorption and charge separation is a fundamental principle of solar panels. In the near future, this property of the fullerenes may be used in the creation of energy solar cells and other devices using photoconductivity. Application of fullerenes for growing diamond films also proves promising. In the process of destruction by microwave radiation of C60, a pair of carbon C-C is formed. Deposited on the surface of SiO2, they form diamond microcrystals forming the smooth diamond film. There are developments on the use of endohedral fullerenes and their derivatives, including inside the carcass half-integer spin atoms such as hydrogen or phosphorus, as the quantum computer parts [6].

Application of fullerenes promise antifriction coatings, solid lubricants and lubricant additives. Experiments have shown that the introduction of fullerene additives to liquid oils and greases form fullerene coatings that can significantly improve the parameters of friction and wear parts and mechanisms, in some cases - repeatedly. This makes their application promising for a broad range of machinery and industrial equipment [7]. A small percentage of additives by weight are good enough in many cases. One result is shown using fullerene soot, which provides a real absorptive effect. Materials with improved

tribological properties are also prepared by introducing the polymeric binder in carbon Nanostructures polyhedral fulleroid multilayer type and high-temperature pressing of powder mixtures of iron and cobalt and fullerites [8]. In the second case, due to the formation of superhard carbon particles in a metal matrix, the wear resistance of the resulting composite is much higher than the high-tool-steels. Composites are versatile: they can be used in a variety of friction conditions.

Fullerenes are able to take over a large number of free electrons, so they are strong oxidizing agents and form many new chemical compounds. The possible applications of fullerenes in pharmacology are perhaps more numerous. At present fullerenes based on antiviral and neurotropic drugs, and hemosorption adsorbents is being developed, as well as methods of treatment using them.

Fullerene structures are promising catalysts of different transformations and provide high selectivity [9]. Dehydrogenate activity of fullerenic catalysts with respect to alkanes, including methane, are manifested in a high temperature range. Fullerenic catalysts can be considered as functional analogs of noble metals.

Fullerenes are able to connect a large number of free electrons, so they are strong oxidizing agents and form many new chemical compounds. Possible applications of fullerenes in pharmacology are perhaps the most numerous. Antiviral fullerenes and neurotropic drugs, adsorbents for hemosorption, as well as methods of treatment using them are currently being developed.

It was created a series of derivatives of fullerene C60 with pronounced membranotropic, antioxidant, antiviral and immunomodulatory properties, including inhibition of HIV and cytomegalovirus infections [10]. Organic derivatives of fullerenes have potentially wide applications in biology, in particular for photodisintegration DNA, inhibiting protease of a HIV, neuroprotection and apoptosis (natural cell death). Their use is planned for the treatment of Alzheimer's and Parkinson's, stroke, atherosclerosis. Their use also looks promising for particular compounds grafted to amino acid fullerenes. Fullerenes can be used for modification of proteins. Water-soluble derivatives of C60 have cytotoxic effects on cancer cells [11], and have antitumor activity [12].

Another potential use of fullerene derivatives is their use as materials for nonlinear optics to create optical fiber telecommunications, which do not require converting the optical signal into an electric signal and vice versa [13].

Recently, more and more attention has been paid to the use of such materials. Different organic molecules are formed by the donor and acceptor moieties are interconnected by a bridge of unsaturated bonds. The fullerene core is a powerful acceptor of electrons, so its derivatives may have a high hyperpolarizability, which are the main factors characterizing nonlinear optical properties of the molecule. Another method is the preparation of compounds with nonlinear fullerene-based optical properties, including derivatives of fullerenes, into a polymeric carrier.

Endo fullerenes (containing, for example, 3He or 129Xe) can be used as a label for the investigation of biological processes in the living body by NMR spectroscopy. Endohedral fullerenes containing Gd (for example, water-soluble polyhydroxylated Gd@C82 and Gd@C60, and Gd@C60 [C (COONa) 2] 10) is also promising for MRI studies of the human body. The uniqueness of the Gd3 + ion is that it has 7 unpaired electrons. It chelates with ion Gd3 + and acid dietiltetraminpenta, which has the commercial name "Magnevist", and are already used in medical practice. The compound enhances signals of water protons and produces higher contrast images of internal organs.

Methods for identification of fullerenes

One of the most common and reliable methods for the identification of fullerenes is spectral analysis. This method serves as a source of the most complete and reliable information on the structure and distinctive features of this class of compounds.

Studying the time-flight mass spectrometer with a laser ionization of the analyte is frequently used. Characteristic mass spectrum is generated in the flame of positively charged ions of fullerenes in acetylene - oxygen flame [2].

The mass-spectrometric investigations of benzene extracts of soot were carried out with the use of an ion-cyclotron-resonance Fourier spectrometer of the FT ICR MS Bruker "Apex Qe" type with an electric-spray ionization. They have shown that the fullerene oxides C60O, C60O2, C60O3, C70O, and C94O as well as the higher fullerenes C74, C78, C90, and C94 are present in the indicated extracts [14].

Thus, it has been established that the yield of fullerenes increases under the action of a glow

discharge in the case where an electrode (a needle or a ring) is positioned directly above a flame, and the maximum yield of fullerenes is attained with the use of a ring electrode positioned above the central region of the flame front. The maximum yield of the fullerene C60 was β=15% of the soot formed.

Methods for producing fullerenes

Methods of producing fullerenes are quite varied, and in particular, include an arc discharge in an inert gas atmosphere using a graphite electrode, laser vaporization of a graphite surface, the laser pyrolysis of hydrocarbons, the combustion of aliphatic and aromatic hydrocarbons at higher equivalence ratio, the pyrolysis of hydrocarbons in a reactor, and an arc plasma jet at atmospheric pressure. Analysis methods for obtaining fullerenes on an industrial scale have shown that not all of them are suitable for industrial production because of high energy costs and low productivity. Recently, however, they have all been developed to some extent. At the present time the predominant method of industrial production of fullerenes is arc evaporation of graphite proposed in 1990 by B. Krechmer. Optimization of the production process of the arc is a certain relation between the carbon concentrations, temperature and gas flow rate flowing out of the electrode gap. However, to obtain such optimum ratio in the arc is almost impossible, since the arc current changes the three parameters simultaneously. The most comprehensive study was carried out in [6], where the rate of erosion of the graphite anode, the growth rate of carbon formation on the cathode and the content of fullerenes in the soot on the arc current, type and pressure of the gas, and the inter electrode gap were obtained. For a graphite anode with a diameter of 6 mm, maximum values of the fullerene yield of 10-15% are obtained at a current of 80 A, a helium pressure of 100 Torr, and the gap between the electrodes is 3-5 mm. With the decrease and increase of current and pressure at the optimal electrode spacing a drop in the yield of fullerenes was observed.

Formation and synthesis of fullerenes in the flame

Evidence that fullerenes can be formed in flames was at first elusive but progress was eventually made. In 1991 significant quantities of C60 and C70 were found in samples collected from low pressure premixed benzene/oxygen flames. Further investigations showed that fullerenes could be produced in sustainable quantities by sub-atmospheric pressure, laminar, and premixed flames of benzene in an oxygen-deficient atmosphere with or without the presence of an inert gas.

The experimental results of Ugarte (1992) presented evidence of the spontaneous tendency of electron irradiated graphite to include pentagons in its hexagonal network, and hence form curved structures. This has been further confirmed by Chuvilin et al. (2010), who have shown that fullerenes can form directly from grapheme in a similar fashion. In the experiment of Chuvilin and co-workers, a sheet of graphene was exposed to a beam of energetic 80 keV electrons. The energy transferred to the graphene results in the loss of carbon atoms from the edges of the sheet. If the size of the graphene arc is not too big (less than a few hundreds of carbon atoms), the loss of carbon atoms at the edge will lead to the formation of pentagons, which triggers the curving of graphene into a bowl-shaped structure. Further carbon removal from the edges using the electron beam will reduce the size of the curved structure until it is sufficiently small to zip up its open edges and isomerize into a closed fullerene structure.

All the fullerenes fall into the class of carbons with a polyhedral-closed shell. They were detected as ionized particles in the fuel-rich plane of premixed acetylene and benzene-oxygen flames at low pressures with the use of molecular-beam sampling in combination with mass-spectrometry analysis [15].

Dunk et al. (2012) claim to have identified the fundamental processes leading to the formation of fullerenes in a recent experimental work, based on laser vaporization of pure C60 in the presence of carbon vapor. According to this study, fullerenes would self-assemble bottom up through a closed network growth (CNG) mechanism based on the ingestion of atomic carbon and C2 clusters.

More recently, macroscopic amounts of not only C60 and C70 fullerenes [16], but also of larger ones, such as C116 [17], were extracted from the low-pressure laminar premixed benzene flames with the use of soot solvents. The reactions of formation of fullerenes and soot in an arc discharge can have much in common with the reactions occurring in the fuel-rich flames. The Bulb-like fullerene nanostructures, formed along with fullerenes and soot, were detected in soot with the

use of high-resolution transmission electron microscopy (HRTEM).

It has been shown [3] that the maximum fullerene formation is shifted to the right relative to the maximum soot formation. In a detailed study of fullerene formation from benzene flames, the second maximum at 70 mm from the burner matrix was detected.

The influence of gas discharge, the type of electrode, and the inter electrode spacing on the yield of fullerenes in combustion was studied. The experimental setup is shown in Figure 2.

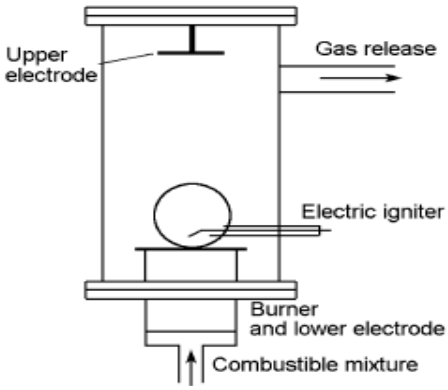

Figure 2 – The scheme of the setup

It was established that polycyclic aromatic hydrocarbons were positively and negatively charged; therefore the process could be controlled with an electric field.

The experimental conditions were as follows: C/O=1, p=40 torr, flow rate of benzene 250 cm3/min, oxygen 758 cm3/min, argon 101 cm3/min, v=18.4 cm/s, T=1200 K, and δ=0.5–0.8 cm; electrode systems are the needle–plane, plane–plane, and ring–plane with an inter-electrode spacing of 4–21 cm; voltage U = 0.5–20 kV. A premixed C6H6/O2/Ar flame under conditions corresponding to the maximum yield of fullerenes was studied [18]. Processing of the experimental data revealed the advantage of the ring electrode over the electrode in the form of a needle and showed that the yield of fullerene C60 (≈15%) was the highest when the electrode was placed in the middle of the flame (L = 4 cm).

The effect of acetylene–oxygen flames on the different zones along the height of the benzene–oxygen flames have been studied using a ring burner. It has been found that fullerene formation is activated at the boundary of contact of the acetylene–oxygen and benzene–oxygen flames. The positive effect of the acetylene flame consists of increasing the temperature in the upper part of the reaction zone of the main benzene–oxygen flame by 50 0C, increasing the degree of ionization, and intense conversion of PAHs present in the benzene–oxygen flame to fullerenes.

It has been established that in the soot at the front of a flame the number of structures with a closed shell as well as the concentration of the fullerene molecules in the gas phase increases with their time of stay in this region. In the region located at a height of 70 mm above a burner the concentrations of the fullerenes and structures with a closed shell are lower than those in regions located at heights of 60–120 mm. The highly ordered nanostructures, such as nanotubes and fullerene bulbs, were detected in solid samples taken from the walls and the upper part of the combustion chamber, which points to the fact that they are formed in the internal-redistribution processes occurring in the solid carbon during a time not longer than 100 ms [4].

The photographs of soot samples obtained with the use of a high-resolution JEM-3010 electron microscope of the JEOL firm with a magnifying power of up to 1,500,000 times at an accelerating voltage of 300 keV, show that these samples are highly structured, which is characteristic of fullerene formations. It is known that the fullerenes formed in a flame are adsorbed, along with the polycyclic hydrocarbons, on the soot particles. The indicated photographs are presented in Figure 2 [19, 20].

The soot samples shown on them comprise agglomerates consisting of spherical and nonspherical particles and an amorphous soot (Figure 3a). In these samples, spherical nanostructures with a diameter of up to 2 nm are also present (Figure 3b). In (Figure 3c), straight and bent carbon structures are seen. In photographs obtained with high magnifying power (Figure 3d), one can see a layered carbonaceous material.

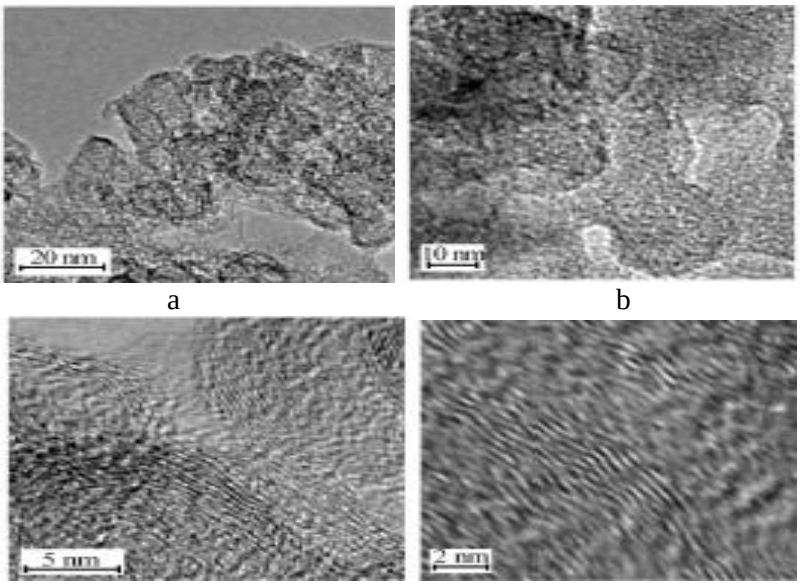

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Figure 3 – Microscopic photographs of fullerene containing soot samples obtained with different magnifying powers

Contrary to the supposition that the fullerene structures are the precursors of soot [17], the results of Grieco point to the fact that a gas-phase growth of fullerene molecules along their vertical path in a flame takes place simultaneously with the nucleation of soot particles and fullerenes are deposited on the growing soot particles.

Two ways of formation of fullerenes in flames were discussed. Frenklach and Ebert suggest that the number of the bent structures, i.e., PAHs containing five- and six-membered rings, increase successively, which leads to the formation of fullerenes. They believe that the "bent" PAHs are formed more rarely than the plane PAHs in flames, which is in agreement with measurements of the concentrations of the PAHs (including corannulene - a bent molecule) in the fullerene-forming flames [21].

The kinetic reliability of the successive formation of fullerenes in a homogeneous gas-phase reaction was theoretically proved in [22], where calculations for a piston reactor were carried out on the basis of the experimentally measured concentrations of different-type particles. The authors of the indicated work described the formation of the C60 and C70 fullerenes, beginning with fluoranthene, and their growth provided by the successive emission of hydrogen, the addition of C2H2, or the use of corannulene as an intermediate compound.

The formation of the C60 and C70 fullerenes through the splitting out of hydrogen or the addition of C2H2 was also tested in the process of simulation of a fullerene-forming flat premixed benzene–oxygen–argon flame at low pressure with an equivalent ratio of 2.4 [22].

The concentration profiles of fullerenes are characterized by two local maxima. Based on the fact that the concentrations of fullerenes, PAHs, and soot change with increase in the distance above a burner, Grieco et al. arrived at the conclusion that the first maximum can be due to the active coagulation of the PAHs, accompanied by their intramolecular condensation, including the dehydrogenation, rearrangement, and formation of rings.

Most of the PAHs are evidently expended for the soot formation and a much smaller part of them is expended for the formation of fullerenes. Grieco et al. concluded that the second, largest concentration maximum, corresponding to the region of the most intensive fullerene formation, cannot be explained by only the reaction of the PAHs, the concentrations of which in this region are at the detection limit of the analytical equipment or are lower than it; this maximum can be explained by the successive addition of acetylene to the PAHs.

Detailed investigations of the ways of formation of fullerenes in flames were carried out by Homman's group who studied the structure of a flame mainly by the direct introduction of ions and neutral particles into a mass spectrometer [19]. They investigated the premixed flames of acetylene, benzene, butadiene, and naphthalene with oxygen at a low pressure with the use of molecular-beam sampling in combination with the mass-spectrometric analysis. It has been estab-

lished that the bimolecular reaction between two PAHs with a coordinated detachment of hydrogen — the so-called zipper mechanism - plays an important role in the growth of fullerenes.

Synthesis of fullerenes in flames with applied electrical field

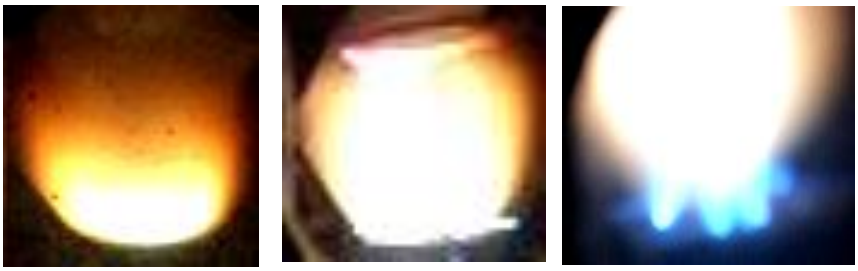
It is practically impossible to increase the yield of fullerenes in combustion using a traditional method. The authors of [18] have shown that the synthesis of fullerenes formed in the plasma of an electric arc increases with the increase in the electron density and in the ionization instability, causing a change in the electron concentration from 1010 to 1011 cm–3. Despite the fact that the conditions of formation of fullerenes in a flame differ from those in an electric arc, they share a common trait: the initial products are ionized. An electric field applied to a flame changes the electron concentration and the flame temperature, with the result that conditions necessary for the formation of fullerenes are established.

A series of experiments on the study of the yield of fullerenes in a premixed benzene-argon-oxygen flame exposed to a longitudinal electric field in the region of a dark corona discharge and a glow discharge at C/O = 1.0, P = 40 torr, benzene-flow rate $Q1$ = 250 cm3/min, oxygen-flow rate $Q2$ = 758 cm3/min, argon-flow rate $Q3$ = 101 cm3/min (10% of the combustion-mixture volume), and velocity of the cold mixture inflow from a perforated stabilizer v = 18.4 cm/s have been carried out [18]. Under these conditions, created with a margin of steady burning flame front from the burner δ = 0,5 ÷ 0,8 cm, studies were conducted in a voltage range of 0.5 - 20 kV with needle electrode systems. The ring plane-plane at different inter-electrode distances varying ranging from 1 to 18 cm length of one experiment was τ = 20 min. After completion of the experiment soot was collected from the combustion chamber and filter. After that samples of the soot were weighed and were extracted with benzene and examined using physico-chemical methods. Identification of C60 and C70 was carried out by absorption spectra obtained in the infrared wavelength range in the study sample of soot extracts using a FTIR spectrometer from Perkin Elmer.

It has been established in [24] that a negative-polarity upper electrode exerts a large influence on the fullerene formation as compared to a positive-polarity one. However, in experiments conducted with a negative-polarity, the upper electrode in the region of dark, corona, and glow discharges at an inter-electrode distance H = 18 cm with the use of a needle–plane electrode system, a significant increase in the yield of fullerenes was not detected. At an inter-electrode distance of H = 18 cm, the upper electrode was positioned at a height of 10–11 cm above the upper edge of a flame. Under the indicated conditions, a discharge acted on the upper part of the flame, where a smaller number of ions are found [25] and the formation of the output combustion products is practically absent. In this case, the calculated electron density did not exceed ~105–107 cm̃3. It has been established in earlier investigations that the optimum density of the free electrons, providing a maximum yield of fullerenes, is ~109 cm̃3. It is known [26] that, if the density of the charged particles in a gas is very small, they interact mainly with neutral particles. This interaction is short-lived and the pair collisions are of main importance in such an ionized gas. When the density of the charged particles increases, the role of their interactions with each other increases gradually too. It is apparent that, under the above-described experimental conditions, the density of the charged particles is insufficient to effectively influence the fullerene formation at an interelectrode distance of 18 cm.

Investigations carried out under conditions where the upper electrode was positioned directly above a flame have shown that, in this case, the yield of fullerenes increases. The influence of the type of electrode and the height of its position above a flame on the formation of fullerenes was investigated to determine the conditions providing their maximum yield. Electrodes in the form of a needle and a ring were used. The investigations were carried out at a negative polarity of the upper electrode under conditions where U = 7 kV and H = 1–9 cm (with a step of 1 cm). A glow discharge appeared independently of the type of electrode at different heights of its disposition above a flame; this discharge caused an intense glow of the whole flame (Figure 4). In this case, the average temperature of the flame increased to 1200oC (without a field, this temperature was equal to 950oC).

Thus, in the case where the upper electrode is placed directly above a flame, the near-cathode region of the glow discharge exerts a stronger influence on the processes occurring in the flame. In this case, in the IR spectra of soot extracts, all the spectral lines corresponding to the fullerenes C60 (λ= 528, 577, 1183, and 1429 cm-1) appeared.



a b c

a) a flame without a discharge; b) the flame exposed to a discharge (U = 7 kV); c) strimer

Figure 4 – Action of a glow discharge on the yield of fullerenes in the case where a ring cathode is positioned above the central part of a flame

It has been established that a ring electrode offers an advantage over a needle one, and a maximum yield of the C60 fullerene (β=15% of the soot formed) was obtained in the case where this electrode was positioned above the peripheral part of the central reaction zone of the flame [27].

The increase in the yield of fullerenes, in the case where a ring electrode is positioned above the peripheral part of the reaction zone of a flame, is due to the glow-discharge conditions providing an effective synthesis of fullerenes.

This supposition is based on the results of earlier investigations [23], showing that, if the peripheral zone of a benzene flame is heated by any external heat source, e.g., a laser beam, which does not simply burn the soot but forms conditions identical to those at the center of the flame, the concentration of fullerenes increase.

The mechanism of fullerenes formation

The combustion method is by far more important than the carbon vapor condensation method [28], giving C60/C70 yields of 20% and higher based on the weight of extractable and solid products. The mechanism of C60/C70 formation in combustion has long been considered to be different from that of the carbon vapor method because the combustion method involves hydrogen atoms in addition to carbon and leads to polyaromatic hydrocarbon (PAHs) (or nanographenes) as the major products, with C60/C70 as very minor by-products. This view was held by Homann who constructed his own formation mechanism for C60 based on the intermediacy of PAHs [29].

However, the situation changed when Howard used benzene premixed with oxygen flame. Although he never clearly described the flame temperature, he once mentioned about 1,800 K [16], which is close to 2,000 K used in the size-up stage by Irle/Morokuma.

Howard initially achieved only 0.003–9.0% yields [16], but they increased to 20% and, shortly before his untimely death in 2007, to quantitative yield [28].

Fullerenes formation in flames can be viewed as a molecule weight growth process, analogous to the formation of polycyclic aromatic hydrocarbons and soot. An oxygen deficiency leads to the formation of soot, and PAHs are nuclei of soot particles. From Figure 5, it is evident that PCAHs can be converted to soot or fullerenes, depending on combustion conditions, among which the determining parameter is pressure.

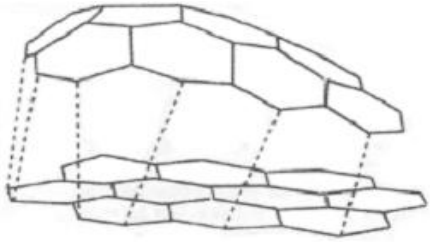


Figure 5 – Model of formation of five- and six-member rings as a result of the binding of two PAHs by the zipper mechanism

Fullerenes are formed in the process of step-by-step monomolecular reactions, such as the cyclization of C30 cells, the rupture of the C–H bonds, and the intramolecular rearrangement; therefore, a high-temperature process is preferred. Fullerenes can also be formed by a combined mechanism. Since the majority of aromers are geometrically incompatible for the formation of fullerenes as the finite products of the reaction between different PAHs, it is suggested that reactions with acetylene can lead to further growth of the molecules as long as they become geometrically compatible for the cell closure.

It is known that the formation and synthesis of fullerenes in the traditional method of arc

evaporation of graphite is performed at pressures p < 40 torr.

A necessary condition for this mechanism is low pressure. As the pressure increases, i.e., with transition to atmospheric pressure or above, where triple collisions dominate, PCAHs coagulate to form soot clusters.

As noted in [29], nano- and subnano size particles are formed by gas-phase condensation in asymptotic giant branched stars. The experiments were carried out at pressures of 0.1-2.6 and 7 mbar, close to the values of p in the astrophysical atmosphere at temperatures T<1700 K, at which the formation of fullerenes was observed. As fullerenes are formed at low pressures, the corresponding spatial orientation is important, which requires that the steric factor should be considered. For a molecule of C60 to form, a spatial orientation of two molecules of C30 is required. There are various models of formation of fullerenes C60, one of which is the zip mechanism [1, 30].

The flame front structure of soot formation flames can be considered in close connection with the mechanism of fuel conversion. A scheme that was suggested by Bockhorn [31] in 1994 is known, where polycyclic aromatic hydrocarbons (PAH) are precursors of soot particles. Since then, in rich fuel flames the nano-sized particles such as fullerenes and graphenes are found. The fullerenes formation is generally observed at pressures below 60 Torr, because for fullerenes formation an adherence of steric spatial factor is necessary, but in flames at atmospheric pressure this factor is prevented by triple collisions. Therefore, the pressure coordinate can be introduced to the general scheme for soot formation. At low pressure the formation of fullerenes from polycyclic aromatic hydrocarbon (PAH) occurs, but with pressure increase the polycyclic aromatic hydrocarbons (PAH) are coagulates to soot particles. On the basis of data on the synthesis of fullerenes in the flame it is possible to modify the general scheme proposed by H. Bockhorn for rich fuel flames, namely to make a pressure-coordinate, which allows for the formation of fullerenes at low pressures, and soot at high pressures.

The fuel flames lacks of oxygen leads to soot formation, at that PAH are the nucleus of soot particles. From Figure 6 we can see that PAH can be converted to soot or fullerenes, depending on combustion conditions, [34, 35].

Conclusion

In review, works on formation and the synthesis of fullerenes in flames were considered in the sections, such as, the structure and properties of fullerenes; applications of fullerenes; methods for identification of fullerenes; methods for producing fullerenes; formation and synthesis of fullerenes in flame; synthesis of fullerenes in flames with applied electrical field; mechanism of fullerenes formation. A modified scheme for soot and fullerenes formation process in flames was also presented.

It was found that if the peripheral zone of the benzene flame is heated by some external source, such as a laser beam that does not just burn soot but also creates the same conditions as in the middle of the flame, the concentration of fullerenes increases.

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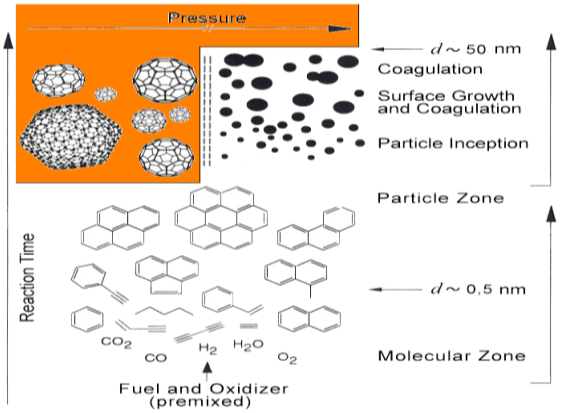

Figure 6 – Modified scheme for soot and fullerenes formation process in flames [32, 33, 34]

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[35] http://www-ipcms.u-strasbg.fr/spip.php?article2166&lang=en. *(Endo) fullerenes: from production to isolation*

ОБРАЗОВАНИЕ ФУЛЛЕРЕНОВ В ПЛАМЕНИ

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Аннотация

Фуллерен - молекула, состоящая целиком из углерода, в виде либо полой сферы, эллипсоида, трубки, и многих других форм. В данной работе были рассмотрены работы по формированию и синтеза фуллеренов в пламени в направлениях, таких как, структура и свойства фуллеренов; применение фуллеренов; методы идентификации фуллеренов; способы получения фуллеренов; формирование и синтез фуллеренов в пламени; синтез фуллеренов в пламени с наложением электрического поля; механизм образования фуллеренов. Представлена модифицированная схема для процессов сажеобразования и фуллеренов в пламени. Было обнаружено, что если периферийную зону пламени бензола нагревать с помощью некоторого внешнего источника, такого как лазерный луч, который не только сжигает сажу, но также создает такие же условия, как и в середине пламени, концентрация фуллеренов увеличивается. Увеличение выхода фуллеренов в случае, когда кольцевой электрод расположен над периферийной частью реакционной зоны пламени, обусловлено условиями тлеющего разряда, обеспечивающего эффективный синтеза фуллеренов.

ЖАЛЫНДА ФУЛЛЕРЕНДЕРДІ ҚАЛЫПТАСТЫРУ

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Аннотация

Фуллерен эллипсоида қуыс саладағы түтік- көміртегі кез келген молекуласы болып және басқа да көптеген нысандары түрінде, толығымен тұрады. Бұл мақалада осындай фуллерен құрылымы мен қасиеттеріне, сондай қалыптастыру бойынша жұмыстар мен төмендегі бөлімдерде жалында фуллеренді синтездеу қаралды; фуллеренді қолдану; фуллеренді анықтау әдістері; фуллерен өндіру үшін әдістері; жалын фуллерендер қалыптастыру және синтездеу; қолданбалы электр өрісі бар жалында фуллерендер синтезі; фуллереннің қалыптастыру механизмі. Сондай-ақ, жалын күйе және фуллеренді қалыптастыру процесі үшін өзгертілген схемасын таныстырылды. Бұл, мысалы, жай ғана күйе жағылып, сонымен қатар жалын ортасында бірдей жағдай лазерлік сәуленің, фуллерендер концентрациясы ретінде, бензол жалын перифериялық аймағы кейбір сыртқы көзі қызып артады. Сақина электрод жалын реакция аймағында перифериялық бөлігі жоғарыда орналасқан жағдайда фуллерендер кірістілігінің өсуі фуллерендер тиімді синтезін қамтамасыз бықсып-разряд жағдайларына байланысты.