Electron density as the main parameter influencing the formation of fullerenes in a carbon plasma

© G.N. Churilov, P.V. Novikov*, V.A. Lopatin*, N.G. Vnukova*, N.V. Bulina, S.M. Bachilo**, D. Tsyboulski**, R.B. Weisman**

Kirensky Institute of Physics, Siberian Branch of Russian Academy of Sciences
660036 Krasnoyarsk, Russia
E-mail: churilov@iph.krasn.ru

*Krasnoyarsk State Technical University,
660074 Krasnoyarsk, Russia
**Rice University, TX 77005 Houston, USA

Thermodynamic estimates are presented for the formation of spheroidal and flat carbon clusters from reactant species of different charges. Charge is shown to strongly influence the geometry and stability of flat clusters. Changes in the charge of flat clusters can promote both their folding to spheroidal structures and their dissociation. It is cuncluded that the fluctuations of electron concentration in carbon plasmas can result in the accumulation of fullerene clusters and the dissociation of flat clusters. The research described in this publication was made possible in part by Award RE1-2231 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF). Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the CRDF. The work is also partially supported by the Russian State Program "Fullerenes and Atomic Clusters" (N 5-3-00) and RF Education Ministry program "Sceintific research of high school in priority directions of science and technique" (N 201.05.01.001).

The carbon-helium plasma at a pressure of 100 Torr is the optimal environment for synthesizing fullerenes, as was first demonstrated in Krätschmer's method [1]. Different modifications of this method now exist [2]. Usually, at these pressures and especially in a rare gas atmosphere, ionization waves can be observed [3].

The method used in our laboratory can be considered to be a modification of Krätschmer's method [2,4,5]. We designed and successfully used plasma-chemical reactor based on thermal graphite evaporation with formation of a carbon plasma jet, which is combined with helium flow at atmospheric pressure in a water-cooled chamber. A transformer matches the amplifier impedance with that of the plasmatron. The distinctive feature of our setup is that the synthesis is conducted at atmospheric pressure in the stream of carbon-helium plasma. The arc is fed by an alternating current at the frequency of 66 or 44 kHz.

Carbon evaporated from the central electrode acts as a plasma-forming gas. The temperature of this carbon plasma jet was measured both by the relative intensity technique and by a pyrometer. It was found to vary from 5000 K close to the outer electrode, to 2000 K in the tail part.

Our latest measurements have shown that the fullerene mixture synthesized in our setup contains approximately 60% of C_{60}, 25% C_{70} and 15% of higher fullerenes (Fig. 1). The total yield of fullerene from our setup is within the same range as obtained with other generally used methods. However, we are not aware of other reports of effective fullerene synthesis at atmospheric pressure, so in this rspect our experimental setup is unique.

We carried out investigations of a discharge in an argon stream between the water-cooled coil of copper tubing and a water-cooled copper electrode containing an axial hole for introducing the argon. The frequency of the current discharge was 44 kHz and the current was 10 to 15 A. It was found that the discharge at atmospheric pressure is stratified [6]. It has been known that such strata are the visual result of ionization waves (ionization instability). Until recently, however, strata were normally observed only at low pressure in regions restricted by glass tube walls.

Fig. 2 shows the discharge in the argon stream and a high-speed photograph of this discharge. Here, the presence of running ionization waves is easily visible. Thus, we observe that the discharges at atmospheric pressure can be stratified, too. Ionization waves arise when the discharge is driven by the alternating current.

In reference [7], the equilibrium states of rare gas plasmas were calculated by the method of level kinetics. According to these results, more than one value of the electron concentration can exist for definite values of gas density and

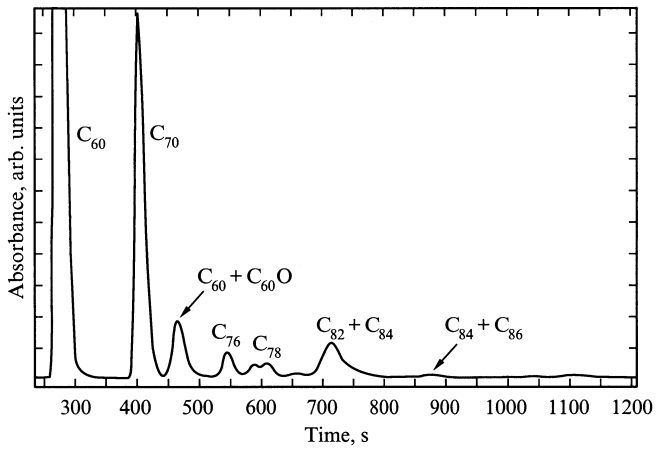

Figure 1. Typical HPLC chromatogram obtained from concentrated extract of fullerene mixture, using toluene eluent and Cosmosil Buckyprep column.

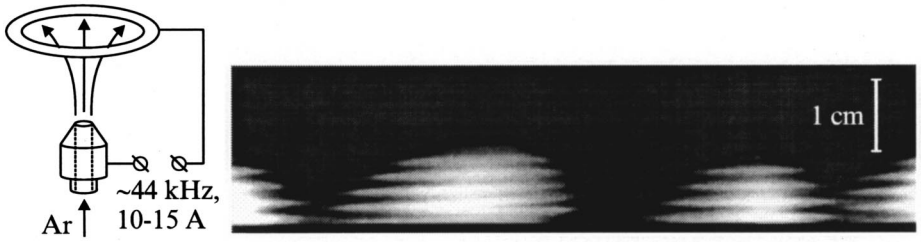

Figure 2. The principal scheme of the discharge in an argon flow at atmospheric pressure and a photo-registration of the irradiation intensity of the plasma discharge revealing forced running ionization waves. The current of the discharge arc is 7 A, the frequency is 44 kHz, and the linear rate of argon flow is 42 m/s. The hole of the central electrode is about 2.0 mm in diameter.

electron temperature. This effect of ionization instability is usually observed in experiments on the generation and study of ionization waves in rare gases, at pressures ranging from fractions of 1 up to 200 Torr. In the well known and popular experimental setup of Krätschmer, fullerene synthesis is usually carried out at pressures between 100 and 200 Torr. At these pressures the local electron concentration in a carbon-helium plasma can vary over a wide range because of the presence of spontaneous ionization waves.

The above considerations suggest that electron concentration pulsations are also present in our atmospheric pressure carbon-helium plasma arc. The commom feature for effective fullerene synthesis in the experimental setups at low and atmosperic pressures is the plasma instability related to electron concentration fluctuations. So, it is possible to deduce that electron concentration (and especially the variations in electron concentration) may be a major parameter that influences the production of carbon clusters in the form of fullerene molecules.

Many publications have now appeared concerning the local redistribution of electrons in plasmas caused by the injection of dust particles. As the electrons are condensed on the particles of dust [8], so they will also be condensed on carbon clusters during their formation. Thus, in reviewing the formation of fullerene molecules from carbon clusters, it is necessary to take into account the charge of these clusters.

1. Calculations

We carried out computer simulations of fullerene C_{60} formation from carbon clusters having different charges. The simulations were carried out using the program HyperChem 5 to calculate the optimal geometry of molecules and their molecular dynamics at different temperatures. All of the calculations were performed with the PM3 semi-empirical quantum chemical method.

Estimations of the formation energies of different carbon clusters were made at a temperature of 1000 K because fullerene formation occurs at about 1000 to 2000 K. The influence of the charge of clusters on the process of their formation was investigated. We considered the formation of flat clusters consisting only of hexagons, as well as non-planar ones, containing at least one pentagon. After calculating the total energy of different clusters, the energy of formation was estimated using the following relation:

$$C_n + C_m \rightarrow C_{n+m},$$

$$\Delta E = E_t(C_{n+m}) - E_t(C_n) - E_t(C_m),$$

where ΔE is the energy of reaction and $E_t(C_i)$ is the calculated total energy of cluster C_i.

Our estimations showed that spheroidal cluster formation at 1000 K is more favorable than the formation of flat clusters having the same number of atoms (Fig. 3, *a,b* and Table 1). This result can be explained by the increased number of carbon atoms with non-saturated bonds in the flat clusters.

The energy of the reaction $C_n + C_m \rightarrow C_{n+m}$ for the formation of a cluster C_{n+m} depends on the charges of the reacting clusters. Table 2 shows the calculated energies of formation of fullerene C_{60} from the clusters C_{20} and C_{40} with different charges, as well as the energies of formation of the flat cluster C_{60} from the flat clusters C_{20} and C_{40}.

The most favorable are the "neutral–ion" and the "anion–cation" reactions. The least favorable are reactions between ions with the same charge. Reactions between neutral clusters are intermediate in energy. Formation reactions for small-sized clusters follow the same pattern as described above for fullerene C_{60}.

The most intersting results were obtained when analyzing the influence of charge on the geometry and stability of the clusters. In Table 2, missing data indicate that the final cluster does not exist. The charge of a cluster influences its geometry and stability significantly (Fig. 2, *c*). Although the spherically symmetric molecule fullerene C_{60} keeps its structure regardless of its charge, the flat cluster C_{60} behaves differently depending on charge. The neutral cluster C_{60}

Table 1. Reaction energy for forming flat and spheroidal carbon clusters

Number in Fig. 3	Reaction	Spheroidal clusters, ΔE, kJ/mol	Flat clusters, ΔE, kJ/mol
I	$C_{14} + C_4 \rightarrow C_{18}$	−1484	−886
II	$C_{18} + C_2 \rightarrow C_{20}$	−1237	−853
III	$C_{20} + C_{20} \rightarrow C_{40}$	−2337	−1379
IV	$C_{20} + C_{40} \rightarrow C_{60}$	−3290	−1873

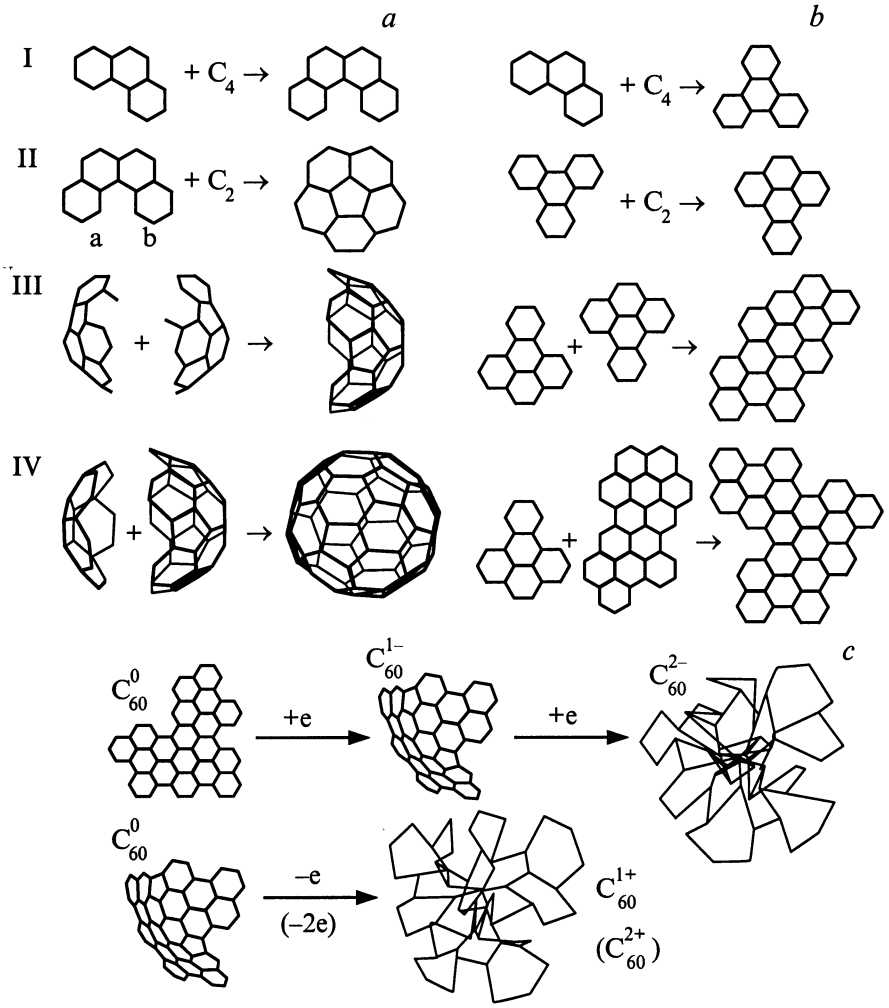

Figure 3. Formation reactions of spheroidal (a) and flat (b) carbon clusters (the calculated reaction energies are presented in Table 1) and energy minimization of a large flat cluster C_{60} with different charges (c).

and singly-charged anion C_{60}^- are folded into a portion of a spherical surface and remain stable at 1000 K. The folding happens in the places where two hexagons are divided by an unfinished hexagon having four bonds. In this place the fifth bond appears and the cluster becomes curved due to the appearance of pentagon. In our calculations, the flat singly-charged cation C_{60}^+ and the doubly-charged ions C_{60}^{2-} and C_{60}^{2+} dissociate in the process of geometry optimization.

The problem of pentagon formation in flat clusters is very important. Using the example of cluster C_{18} (Fig. 3, a) with one incomplete pentagon, it is possible to observe that the changes in its geometry depend on its charge. A pentagon forms during the geometry optimization of the singly-charged ions C_{18}^- and C_{18}^+ and the doubly-charged cation C_{18}^{2+}. The ab length (Fig. 3, a) decreases to a typical C–C bond length of about 1.4 Å. And with geometry

Table 2. Dependence of the reaction energy on the charges of reacting clusters

Type of reaction	Reaction $n = 40$, $m = 20$	Fullerene C_{60}, ΔE, kJ/mol	Flat cluster C_{60}, ΔE, kJ/mol
Neutral–ion	$C_n + C_m^+ \rightarrow C_{n+m}^+$	−3440	*
	$C_n + C_m^- \rightarrow C_{n+m}^-$	−3423	−2709
Anion–cation	$C_n^- + C_m^+ \rightarrow C_{n+m}$	−3302	−949
Neutral–neutral	$C_n + C_m \rightarrow C_{n+m}$	−3290	−1873
Anion–anion	$C_n^- + C_m^- \rightarrow C_{n+m^{2-}}$	−2851	*
Cation–cation	$C_n^+ + C_m^+ \rightarrow C_{n+m}^{2+}$	−2784	*

* — cluster is unstable.

optimization of the neutral cluster and doubly-charged anion C_{18}^{2-}, the ab length between outer hexagons increases. This example cleary suggests that a lower electron concentration in the plasma is necessary for the formation of spheroidal clusters containing pentagons.

2. Conclusions

In the phase of an ionization wave with a low electron concentration, the formation of clusters containing pentagons is favored. Further decrease of the electron concentration to a minimum reduces the effeciency of cluster formation because of higher energy of "cation–cation" reactions.

As the electron concentration increases in the opposite phase of the ionization wave, the large flat clusters acquire negative charge and dissociate into smaller clusters or separate atoms. Because the time of elementary reactions is about 10^{-12} s, while the period of the electron concentration wave in the plasma is 10^{-3}–10^{-5} s, the cluster distributions can stay near equilibrium as the electron concentration varies. Therefore small-sized clusters, including the spheroidal ones, have time to be generated from separate atoms. With the increase of the electron concentration, the efficiency of their formation decreases due to the higher energy of "anion–anion" reactions. Because the electron concentration does not have such a strong effect on the stability of small spheroidal clusters and fullerene shells, the clusters and fullerene molecules already generated are not destroyed.

The large flat clusters tend to dissociate into smaller sized clusters during oscillations of the electron concentration. As the energies of formation of small-sized clusters with and without pentagons are similar, there are always a number of clusters in the plasma suitable for forming fullerenes. These clusters remain stable once they have been formed.

Thus, the ionization wave executes two functions during the synthesis of fullerenes. At low electron concentrations, it favors the formation of clucters, especially spheroidal ones, whereas at high electron concentrations it tends to preferentially destroy the flat clusters.

We note that the proposed mechanism does not consider statistical processes, but only the driving role of electron concentration variations. Recognition of the importance of electron concentration variations may provide an essential step on the way to the controlled synthesis of fullerenes and, possibly, fullerene derivatives.

References

[1] W. Krätschmer, K. Fostiropoulos, D.R. Huffman. Chem. Phys. Lett. **170**, 167 (1990).
[2] G.N. Churilov. Instruments and Experimental Techniques **43**, *1*, 1 (2000).
[3] P.S. Landa, N.A. Miskinova, Yu.V. Ponomarev. Soviet Physics-Uspekhi **132**, *4*, 601 (1980).
[4] G.N. Churilov. Int. Winterschool on Electronic Properties of Novel Materials "Progress in Fullerene Research" (Kirchberg, Tyrol, Austria) World Scientific (1994). P. 135.
[5] G.N. Churilov, L.A. Solovyov, Y.N. Churilova, O.V. Chupina, S.S. Malcieva. Carbon **37**, *3*, 427 (1999).
[6] G.N. Churilov, V.A. Lopatin, P.V. Novikov, N.G. Vnukova. The proceedings of the 1st International Congress on Radiation Physics and Chemistry of Condensed Matter, High Current Electronics, and Modification of Materials with Particle Beams and Plasma Flows. Tomsk, **2**, 223 (2000).
[7] A.Yu. Gavrilova, A.G. Kiselyov, E.P. Skorokhod, M.E. Stanishevskaya. Matematicheskoe Modelirovanie (Math. Modelling) **8**, *6*, 103 (1996).
[8] V.I. Molotkov, M.Yu. Nefedov, M.Yu. Pustyl'nik, V.M. Torchinsky, V.E. Fortov, A.G. Khrapak, K. Yoshino. JETP Letters **71**, *3*, 102 (2000).