Carbon Clusters and Fullerene Formation in Turbulent Radial Jet from Graphite Contact Arc

G.I.Sukhinin, O.A.Nerushev

Inst. of Thermophysics, 630090 Novosibirsk, Russia

1. Introduction.

Since the discovery of fullerenes in the process of laser ablation of graphite 10 years ago [1], and introduction of a new method (5 years ago) of fullerenes synthesis from a graphite arc in macroscopic quantities [2] in the atmosphere of helium, they have become the object of intensive studies. There were registered non-monotonic distributions over the whole range of mass-spectra: odd-even alternation which is different for small and large clusters; the absence of clusters with 25 - 40 atoms per cluster. The family of fullerenes - large stable hollow clusters (with 60, 70, 76 etc. atoms) - was obtained. Different structural isomers (chains, mono- and polyrings, fullerenes) were identified by mobility measurements for a number of carbon clusters [3].

While some hypotheses of fullerene formation were offered [4], the kinetic description of this process was much less successful [5,6]. Gas dynamic processes in the flow under laser ablation or graphite arc evaporation were not considered at all. Besides, the cross sections of carbon clusters collisions were not selected with due regard to their real structures.

We present a simple kinetic model for the process of carbon cluster formation based upon real collisional cross sections of structural cluster isomers and gasdynamical structure of radial turbulent flow from a contact arc in the atmosphere of buffer gas (helium).

2. The model of flow and kinetics.

A typical scheme of a reactor for producing fullerenes in microscopic quantities is based on the use of a contact graphite arc [2,7,8]. Inside a vacuum chamber, there are two graphite electrodes. The cathode is movable to keep the gap between the electrodes constant. The chamber is filled with He to a pressure of 10-500 Torr. The parameters of the arc are: U_a=18-25 V, current $I_a \approx 100$ A.

As a result of electrode evaporation and mass and heat transfer process, a helium jet with some admixture of carbon (with mass flow rate of about 0.01 g/s) is formed. The flow between electrodes is determined by the influence of the self-magnetic field of an arc current according to approximate theory [9]. A maximum gas velocity is reached on the jet axis for a long enough arc:

$$v_a = \left[\frac{\mu_0 I_a^2}{4\pi S_a \rho} \right]^{0.5}, \qquad (1)$$

where I_a is arc current, S_a is the arc cross section, and ρ is the buffer gas density, μ_0 is the magnetic susceptibility of vacuum.

Gas-carbon mixture flows out of the inter-electrode gap, and a radial turbulent jet is formed. The fusion process of atomic particles begins in the inter-electrode gap, the result being the formation of C_2, C_3, and other carbon molecules (carbon clusters) in turbulent jet.

The Görtler theory for turbulent mixing is applied to the problem of a radial jet [10]. Suppose the gas flow is uncompressible and isobaric everywhere outside the gap. Such turbulent flow can be described by the mass and momentum conservation equations in the boundary layer approximation where molecular viscosity is ignored in comparison with turbulent viscosity:

A self-similar solution [11] can be obtained for radial velocity u and total density of carbon atoms.

$$u(r,z) = \frac{u_0 r_0}{r} \sqrt{\frac{3b_0\sigma}{2r_0}} \left[1-\mathrm{th}^2\varphi\right], \qquad (2)$$

$$n_c(r,z) = \frac{N_c r_0}{r} \sqrt{\frac{3b_0\sigma}{2r_0}} \left[1-\mathrm{th}^2\varphi\right], \qquad (3)$$

where $\varphi=\sigma z/r$ and u_0 is gas flow velocity on the gap exit, b_0, r_0 are half-width of the gap and the initial radius. N_c is carbon on the gap exit, $\sigma \approx 8.3$ is the only empirical constant of the theory. Thus, the profile of a small admixture behaves the same way the profile of the radial flow velocity does.

Due to the turbulent mixing across the flow, relative concentrations depend only on the radial coordinate. Taking into account the expressions for velocity, u , and carbon density, n_0, we can receive Smoluchowski equation for relative carbon cluster concentrations $c_k=n_k/n_c$:

$$\frac{dc_k}{dr/r_0} = \frac{N_c r_0}{u_0} \left[\sum_{j=1}^{k_m} K_{k-j,j} c_{k-j} c_j - \sum_{j=1}^{\infty} K_{kj} c_k c_j - K_{kk} c_k^2 \right], \qquad (4)$$

where boundary conditions are $c_k=c_k^o$ at $r=r_0$. In the equation (4) K_{ij} is the constant of (i+j)-mer formation in the collision of i-mer and j-mer:

$$K_{ij} = v_c\sqrt{(i+j)/ij}\ \sigma_{ij}P_{ij}, \qquad (5)$$

where $v_c=(8k_BT/\pi M_c)^{-1/2}$ is the carbon atoms thermal velocity at temperature T, M_c is the mass of carbon atom, and P_{ij} is the reactivity of forming a cluster of the (i+j) size in the collision of i-mer and j-mer.

It is possible to show [11] that effective cross sections of atoms C collisions with C_k clusters change linearly with the k number and depend on the structure of clusters; the dependence of cross sections of linear and plane C_k clusters on k is quadratic; the dependence of C_k fullerenes cross sections on k is linear again. Therefore, carbon clusters are dramatically different from compact clusters, whose collision cross sections are proportional to $k^{2/3}$.

The reactivities P_{ij} should be either estimated with the help of quantum chemistry methods or determined experimentally. The collision of two clusters, C_i and C_j, does not automatically lead to the formation of a new C_{i+j} cluster. With a certain probability $P_{ij}(T)$, an intermediate complex is formed, the energy of which is redistributed between various internal degrees of cluster freedom. As a result of collisions with hot He atoms, their annealing into the most stable (i+j)-isomer [4] and thermolization to the surrounding gas conditions take place.

In this paper, we deal with the simplest assumptions only. We will assume that $P_{ij}=\langle P\rangle$ for each i and j not equal to 60,70, and some other stable fullerenes. For these selected i and j, probabilities were assumed to be constant and equal to $P_{ij} = \beta\langle P\rangle$ ($\beta < 1$). Parameter β could be chosen from comparison of calculated fullerenes yield with experimental data [7,8].

Results and discussion.

The kinetic equation (4) is fully equivalent to the non-stationary kinetic equation with a dimensionless coordinate $x = (n_0v_c\sigma_{11}r)/u_0$. We were looking for a solution of kinetic equation (4) for mass k numbers from 1 to 120 at x=X corresponding to the chamber radius $r=R_c$. The population c_{120} represents the total cluster population of all sizes equal to and larger than 120. Figure 1 shows cluster size distribution at X=25 for standard initial conditions (SIC): $c_1^o=1$, $c_k^o=0$ for $k>1$ (curve 1). It is remarkable that significant variations of initial conditions (spectrum 2: $c_1^o=0.1$, $c_2^o=0.45$, $c_k^o=0$ for $k>2$) are not reflected in resulting mass-spectra for $k\geq 10$. Mass-spectra substantially depend on the initial distribution only at small distances

(X≤10). This indicates that the initial distribution of clusters is relatively unimportant for large cluster size distributions. However, small regular variations of reactivities may cause changes ("even - odd alternation") in mass-spectra. Curve 3 shows size distribution (initial conditions are the same as for curve 1) for the case when even clusters reactivities are decreased by the factor of 0.7. Nevertheless, overall spectra shape does not changes significantly.

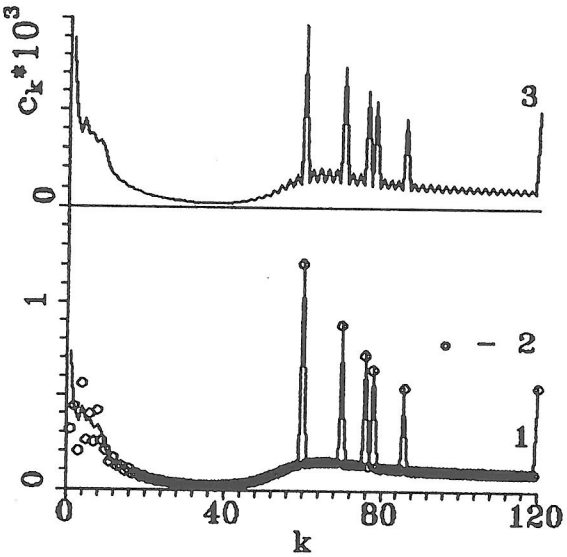

Fig.1. Clusters size distribution. Effects of initial conditions (1,2) and reactivity (3).

To illustrate the dynamics of the change of cluster distribution function, figure 2 shows the results for X=25, 50, 100 (with the conditions of fig.1). It is clear that there is a distinctive "gap" for k numbers in the range from 20 to 40 in the distribution of clusters which is connected with large cross sections of plane cyclic clusters. Getting into this size range, smaller clusters pass it quickly to get into fullerene range. The distribution function becomes non-monotonic. On the background of this distribution, there appear clearly marked peaks for relatively stable C_{60}, C_{70}, C_{76}, C_{78} and some other fullerenes which grow with the distance from the source.

The most important characteristic of a fullerene factory is the yield of fullerenes, $Y_k = kc_k$. Figure 3 shows the Y_{60} dependence on dimensionless distance. Solid line presents the calculated yield of C_{60} for β=0.2 parameter value. In this case, there is a maximum of $Y^*_{60} = 0.12$ at $X^*_{60} = 125$ and then there is a slow decrease due to the collisional transitions of some unstable C_{60} clusters into larger size clusters.

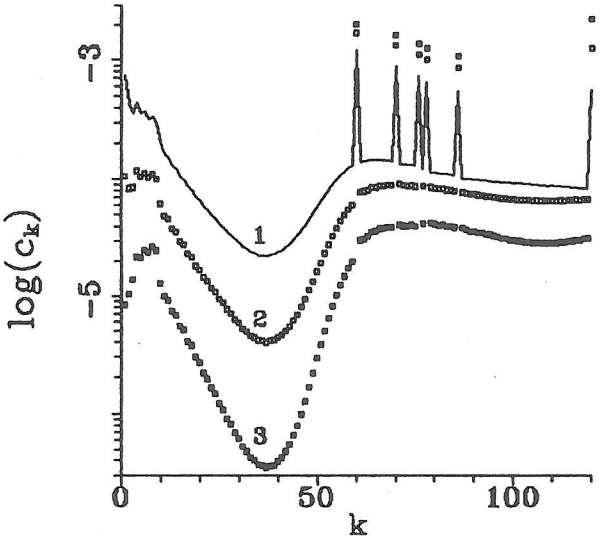

Fig.2. Clusters size distribution. Evolution with radial distance.

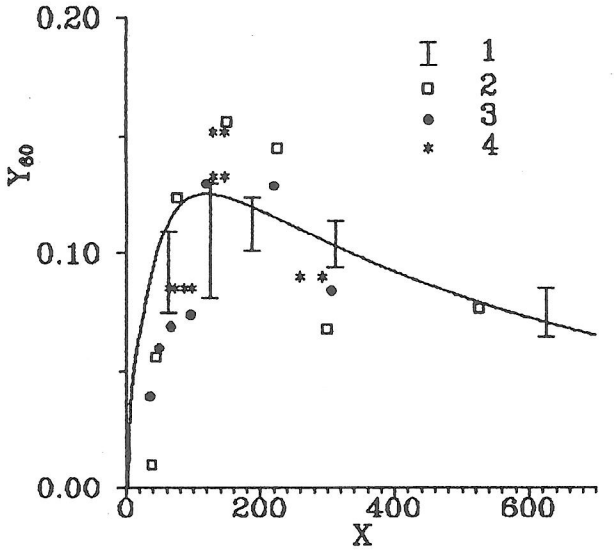

Fig.3. Fullerene yield.
Solid line - calculation for β=0.2.
Experimental data: 1 - [7], 2-4 - [8], dependences on He pressure (2), arc current(3), inter-electrode gap (4).

In view of the fact that for actual installations the radial coordinate is determined by the location of chamber wall of soot-collecting cooled screen, the change of X coordinate is connected with the change of other parameters (gas pressure, arc current, interelectrode gap, etc). Making use of equation (1) for estimating the initial flow velocity, we get the following:

$$X = \langle P \rangle \frac{n_0 v_c \sigma_{11} R_c}{u_0} = \frac{Q}{m_c} \frac{\langle P \rangle}{\chi^2} \frac{v_c \sigma_{11}}{\mu_0} \frac{p \mu_g}{RT I^2} \frac{\pi R_c r_0}{b_0} \qquad (10)$$

where Q is the carbon mass flow rate, p is the gas pressure, μ_g is the molar mass of buffer gas, R is the gas constant. We assume also that initial radial jet velocity u_0 is proportional to velocity inside the gap: $u_0 = \chi v_a$. Thus the value of X is the parameter of the problem. From the following comparison with experimental data it is seen, that $\langle P \rangle / \chi^2$ turns out to be close to one.

The obtained results can be compared with the measured dependencies of fullerene yield. Experimental data from [7] are also presented in Fig.3 by bars. Due to the lack of full experimental information in the Ref.[7], the data are connected by X^*_{60} parameter - corresponding to maximum yield of C_{60} ($Y^*_{60} = Y_{60}(X^*)$ is the maximum value which coincides in the experiments and calculations for β=0.2). Other points in Fig.3 present experimental dependence of Y_{60} on gas pressure, arc current and interelectrode gap [8]. The agreement of experimental and calculated results is fairy good, though the chamber diameters in [7] and [8] are differ by the factor 6.

Thus, the present results reveal the crucial role of collisional cross sections and mobilities of clusters and the importance of gas dynamic processes in the evolution of carbon clusters.

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