Formation and Thermal Decomposition of Solid Carbon Particles during Pyrolysis of Carbon Suboxide behind Shock Waves

G. L. Agafonov¹, M. Nullmeier², P. A. Vlasov¹, J. Warnatz², and

I. S. Zaslonko¹

¹ Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygin str. 4, 117977 Moscow, Russia, iz@center.chph.ras.ru

² IWR, Universitat Heidelberg, Im Neuenheimer Feld 368, D-69120 Heidelberg, Germany, nullmeier@iwr.uni-heidelberg.de

The ability of carbon to form clusters in the gas phase at high temperatures has been known for a long time (Smalley, 1997). In contrast to the other refractory elements, the vapor of carbon in equilibrium with its solid phase at temperatures in the range of 3000–4000 K contains clusters with a substantial abundance of C_n particles, where 10<n<30. The first evidence of this fact extends back to early research on nuclear fission products by Hahn and Strassman (Hahn et al., 1942; Mattauch et al., 1943). The first quantum calculations of the structures responsible for such behavior of the vapor of carbon atoms up to carbon clusters C₂₀ (Pitzer and Clemente, 1959; Strictler and Pitzer, 1964) showed that they had the form of linear chains for C_2 up to C_{10} and the form of monocyclic rings for larger numbers of carbon atoms. Above the temperature of 1000 K, the vapor in equilibrium with the pure condensed phase of every element in the periodic table, except carbon, consists of dominantly either monoatomic or diatomic particles. Only carbon is able to form clusters that are so stable that they are the dominant species in the gas phase even at the temperature of 3000—4000 K. All the data available in the literature on the gas phase clusters of pure carbon up to 1985 could be well explained by the model of linear chains and monocyclic rings (Smalley, 1997). The cluster abundance dropped off so rapidly after the cluster size C_{23} — C_{25} has been achieved that for a long time there were no any speculations what would happen, as the clusters grew larger. In light of our knowledge about fullerenes, we can suppose that as the carbon cluster will grow larger, they have to form 2D and 3D structures. The first paper, which described the carbon in a soccer-ball structure, namely C_{60} , was the work of Osawa (Osawa, 1970) where it was suggested that such a structure should be stable. Bochvar and Gal'perin (Bochvar and Gal'perin, 1973) published a theoretical study in 1973 when they had completed the first of many Hückel calculations, which showed that C₆₀ structure would be a closed-shell molecule. Nevertheless, no one ever suggested that these structures could be formed spontaneously during condensation of carbon vapor.

The appearance of the laser-vaporization supersonic cluster beam technique (Dietz et al., 1981) made it possible to study the properties of carbon clusters in detail as they grew through the size range of 40 to 100 carbon atoms in cluster (Rohlfing, et al., 1984). One can observe three distinct regions that characterize the typical mass spectrum of carbon clusters produced by this method: first, the small clusters, containing less than 25 atoms, which consist of the chains and monocyclic rings (Yang, et al., 1988), that are well known from the earlier studies, second, a new region between the size of carbon clusters of approximately 25 and 35 atoms in which only few species of any sort were observed (a so-called "forbidden zone"), and, third, the distribution of even-numbered clusters extending from the size of 40 to well over

150 carbon atoms in cluster. This distribution of even-numbered carbon clusters is a unique feature of carbon and has never been observed for any other elements. The studies of reactivity of these even-numbered clusters (Zhang et al, 1986) with the use of the fast flow reactor made it possible to suggest that all these even-numbered carbon clusters exist in the form of hollow closed structures, that is fullerenes. Nevertheless, the question arises is it possible to observe carbon particles with n > n150-200. Recently, the first direct observations of large concentric shell fullerenes and fullerene-like nanoparticles were presented (Mordkovich, 2000). It was shown that carbon particles produced by iron carbonyl-catalyzed CO₂-laser pyrolysis of benzene are characterized by a two-level nanostructure, that is they consist of amorphous carbon nanoparticles 30-40 nm in diameter and fullerene molecules where the fullerenes are predominantly represented by C_{60} . Heat treatment of carbon particles at the temperature of 3000 K causes their rearrangement with the appearance of fullerene-like multishell nanoparticles of ~ 20 nm in diameter, higher fullerenes, and multishell fullerenes. In contrast to the classical fullerenes, which have a closed cage structure and are known to have been synthesized in a variety of sizes (C_{60} , C_{70} , C₈₄, C₁₀₂, etc.), multishell fullerenes have a cage-inside-cage structure. Direct transmission electron microscopy observation of the cage-inside-cage carbon clusters showed the occurrence of at least three varieties: two-shell 14-Å-sized $C_{60}@C_{240}$, two-shell 20-Å-sized C₂₄₀@C₅₆₀, and three-shell 20-Å-sized C₈₀@C₂₄₀@C₅₆₀.

The other promising approach to study the formation and thermal decomposition of carbon clusters and solid particles is the shock tube technique. The shock tube studies of soot formation process during pyrolysis of various hydrocarbons are well known. The presence of hydrogen makes the chemical kinetics of this process very complicated. Recently, carbon suboxide (C_3O_2 , or 1,2-propadiene-1,3-dione) molecule attracted the attention of researchers as a convenient source of pure carbon atoms for studying the reactions of small carbon clusters and the formation of the ensembles of solid carbon particles during pyrolysis behind shock waves (Dörge, et al., 1999; Friedrichs and Wagner, 1998). The condensation process occurs without participation of hydrogen in practically chemically inert atmosphere of CO and buffer gas.

In the case of C_3O_2 pyrolysis, in contrast to the pyrolysis of any arbitrary hydrocarbons, one can expect that because of a relatively simple composition of the products of C_3O_2 thermal decomposition the mechanism of formation of solid carbon particles will be more clear and simple as compared with the soot formation process due to the absence of hydrogen. On the other hand, hydrogen molecules and atoms play an important role in the kinetic mechanism of soot surface growth being actually the main species, which provide a sufficient level of active sites on the soot particle surface. In the case of C_3O_2 pyrolysis, the experiments show that the introduction of hydrogen into the reactive mixture results in a considerable decreasing of the total particle yield and hydrogen can be considered as an efficient inhibitor of solid carbon particle formation.

In the current work, we present a kinetic modeling of thermal decomposition of carbon suboxide and formation, transformation, and thermal decomposition of fullerene-like and soot-like solid carbon particles behind incident and reflected shock waves.

The experiments with C_3O_2 thermal decomposition behind shock waves demonstrate the formation of soot-like solid carbon particles for the temperatures below 1800 K and the concentration of C_3O_2 higher than 0.2% in argon (Kijewski et al., 1969) as well as within the temperature range of 1200-2400 K and for the pressure of about 5.4 MPa for the concentration of C_3O_2 between 0.03 and 1% in argon (Dörge et al., 1999). The two-step heating technique, which was applied in the work of (Deppe, 2000) to study the formation and thermal decomposition of solid carbon particles, made it possible to enlarge considerably the temperature range up to the temperatures of 4600 K. The typical curves of the experimentally measured and calculated time dependences of the solid carbon particle yield behind the reflected shock wave for the mixture of 1% C_3O_2 in Ar, for the total reaction time of 220 µs, the temperature and pressure behind reflected shock wave of T = 2650 K and p = 20 bar are shown in Fig. 1. After a short induction time, one can observe the growth of the total particle yield that means condensation of free C atoms into the solid carbon particles in these conditions. It was observed that the solid carbon particles are formed within not only the temperature range of 1300 to 2200 K, but, also, this process proceeds again above the temperature of 2300 K and attains the maximum at around 3000 K. After this, at the temperature above 3450 K, the process of thermal decomposition of solid carbon particles is observed, which depends on the prehistory of their formation behind the incident shock wave.



Fig. 1 Experimentally measured and calculated solid carbon particle yield as a function of the reaction time τ_r behind reflected shock wave for the mixture of 1% C₃O₂ in Ar for T = 2650 K and p = 20 bar.

Fig. 2. Kinetic curves of the calculated particle yield for the mixture of 1% C_3O_2 in Ar the conditions realized behind reflected shock wave ($\tau_r = 1000 \ \mu m$, $p = 20 \ bar$, 2400 K < T < 3700 K).

The kinetic curves of the calculated solid carbon particle yield for the mixture of 1% C_3O_2 in Ar for the conditions realized behind reflected shock wave ($\tau_r = 1000 \mu$ m, p = 20 bar, 2400 K < T < 3700 K) are presented in Fig. 2. One can see that the maximal value of the yield is attained at the temperature of 2800 K and, after the temperature of approximately 3550 K, thermal decomposition of carbon particles causes the decay of the yield.

Changing the distance between the observation section and the end plate of the shock tube, one can vary considerably the time of formation of solid carbon particles behind the incident shock wave. For instance, in the particular experiments presented in the work (Deppe et al., 2000), the variation of this distance from 4 to 128 mm resulted in the variation of time from 35 to 1200 μ s. In Fig. 3, one can see the calculated temperature dependence of the solid carbon particle yield for the mixture of 1% C₃O₂ in Ar for the pressure p = 20 bar, and for various values of the reaction time τ_r .



Fig. 3. Calculated temperature dependence of the solid carbon particle yield for the mixture of 1% C_3O_2 in Ar for the pressure p = 20 bar, and for various reaction times τ_r .

The comparison of the experimentally measured and calculated values of the solid carbon particle yield for the mixture of 1% C_3O_2 in Ar for three different values of the reaction time τ_r is shown in Fig. 4.



Fig. 4. Comparison of calculated (dotted lines and open symbols) and experimentally measured (solid symbols) values of the temperature dependences of solid carbon particle yield for the mixture of 1% C_3O_2 in Ar, p = 20 bar, for $\tau_r = 220$, 700, and 1100 µs.

The most surprising result of the experiments and calculations is the appearance of the second maximum of the total yield of solid carbon particles at the temperature of approximately 3000-3400 K, depending on the mixture composition and experimental conditions. As can be seen from Fig. 4, a considerable yield of solid carbon particles could be observed behind reflected shock waves within the temperature range of 2600-3500 K. Both, the experiments and our calculations demonstrate such behavior. The agreement between the experimentally measured and calculated values of the carbon particle yield is rather good. Our calculations showed that the second high temperature peak of the carbon particle yield has a specific fine structure, which is caused by the kinetics of condensation, growth, transformation,

and thermal decomposition of the ensembles of fullerene-like and soot-like solid carbon particles.

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