

Formation of Soot Particles

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Probable mechanisms are discussed of the formation processes of pyrolytic carbon films and soot particles, based on experimental investigations of their formation rates. Both are two-stage processes including nucleation and growth of nuclei. The formation of pyrolytic carbon from methane at temperatures below 1300 K is a molecular process. The activation energy of the formation of a plane nuclei is about 80, and of their growth about 50 kcal/mol. The formation of soot particles may take place in two ways differing in the nature of the nuclei as well as in the structure of the soot particles obtained.

The formation of soot particles during the burning and thermal decomposition of hydrocarbons is of a dual nature, the strictly physical laws of the creation of a new dispersed solid phase being complicated by a chemical process. The process as a whole is difficult to investigate and has not yet been adequately studied. Discussed below are recent experimental results on the kinetics of both formation and growth of soot particles as well as some ensuing conceptions about the mechanism of such processes.

STRUCTURE OF SOOT PARTICLES

The soot particles have a very compact structure. The density of their material ¹ equals 2.0 g/cm³ which is only 10 % less than that of three-dimensionally-ordered graphite (2.26 g/cm³). Following Biscoe and Warren ² and on the basis of the results of X-ray investigations, it has been assumed until recently that the soot particles comprised separate, irregularly located crystallites consisting of several approximately parallel graphite layers. Such a structure was termed "turbostratical".

The application of high-resolution electron microscopes ^{3, 4} provided proof, but graphite layers, and not crystallites serve as building blocks for soot particles. These layers are bent to conform to the shape of the particles and have the form of shells replicating the outer surface of the particle. Thermal soot particles consist of concentric spherical shells. In particles of other types of soot, only the external shells repeat the shape of the outer surface, the internal structure of such particles containing obviously several centres of growth. The distance between the layers has a spread conforming to the general distribution law.

The compact and largely regular structure of the soot particles should be taken into account when considering the growth mechanism. It is evident, for instance, that one cannot logically imagine the creation of such a structure by consecutive association of more or less large blocks. Most probably, such a structure is the result of a molecular growth process for which the term "chemical crystallization" would perhaps be the most exact one. Experimental results have actually proved this.

GROWTH OF SOOT PARTICLES

The growth process of a soot particle is similar to that of a pyrolytic carbon film on a wall. It can be experimentally investigated in the absence of soot particle formation within a wide range of temperatures. The growth stage of soot particles has therefore been better investigated than the formation stage. Nevertheless, reliable data about the kinetics of pyrolytic carbon growth during the thermal decomposition of methane are available up to 1300 K only.⁵ The growth rate of pyrolytic carbon is of the first order and is considerably inhibited by hydrogen. This inhibition effect can be well described by the Langmuir equation and can be attributed to a chemisorption of hydrogen. The growth rate of soot particles (in $\text{g cm}^{-2} \text{s}^{-1}$) can be expressed as follows:

$$W = 260 p_{\text{CH}_4} [1 - B p_{\text{H}_2} / (1 + B p_{\text{H}_2})] \exp(-66\,000/RT) \quad (1)$$

where p_{CH_4} and p_{H_2} are the partial pressures of methane and hydrogen, respectively, and R has units of $\text{cal mol}^{-1} \text{K}^{-1}$.

The inhibiting effect of hydrogen decreases when the temperature rises. The constant B in the Langmuir equation equals 40 at 1073 K and 25 at 1173 K. The activation energy of the process equals 66 ± 2 kcal/mol within a temperature range 1000-1300 K.

The growth rate of a pyrolytic carbon on a plane surface is governed by the same laws as that of the growth on the surface of soot particles and possesses the same activation energy but the rate constant is about 5 times higher. Possible causes of such a discrepancy are discussed below.

The growth rate of a pyrolytic carbon film is closely associated with the size of the crystallites being formed. Any individual hydrocarbon has at every temperature some constant average crystallite size for a stationary growth rate. It is reasonable to believe that the microcrystalline structure of the pyrolytic carbon film will reflect the molecular mechanism of its formation from molecules of the gaseous phase. Let us assume that each of the crystallites is being formed as a result of the growth of a nucleus in a basic plane, and that this growth continues until the crystallites, which expand towards each other, meet. Thus, the size of the crystallites depends on the rate of two processes, namely, the formation of nuclei and their growth. Consequently, if the growth rate and the average crystallite size are known from experiments, the formation rate of nuclei as well as the growth rate of crystallites can be determined by calculation.

So, for instance, the growth rate of a film obtained from methane on a plane surface at 1273 K in absence of hydrogen equals 250 \AA/s , the average size of the crystallites L_g being 600 \AA . These values correspond to a nuclei formation rate of $C = 2.6 \times 10^9$ nuclei $\text{cm}^{-2} \text{s}^{-1}$ and to a crystallite growth rate of $W = 22 \text{ \AA/s}$.

The elementary collision theory permits one to determine from these data the activation energy of the nuclei formation as well as that of the crystallite growth. Assuming that a planar nucleus consists of a single atom of carbon, the activation energies of the nuclei formation E_n and crystallite growth E_g can be found from the equations:

$$E_n = 2.3 RT \log(N_f/C), \quad (2)$$

$$E_g = 2.3 RT \log(N_f/N_g), \quad (3)$$

where N_g = rate of film growth ($\text{atoms cm}^{-2} \text{s}^{-2}$) and N_f = number of collisions of methane molecules upon the surface ($\text{molecules cm}^{-2} \text{s}^{-1}$).

Substituting the values cited above for methane at 1073 K gives $E_n = 81$ and $E_g = 52$ kcal/mol. Consequently, the experimentally activation energy of the film growth

process ($E = 66$ kcal/mol) represents the gross activation energy of both elementary processes.

According to these concepts, the formation of pyrocarbon is a peculiar branched-chain molecular process taking place on surfaces. The carbon atoms are built-in into a planar graphite lattice as a result of the interaction of methane molecules with surface carbon atoms which have free-valence electrons. The hydrocarbon radicals of the gaseous phase do not participate in this process. On the contrary, some of the methane molecules decompose on the growing carbon surface and produce new radicals while others break down directly into carbon and hydrogen. Thus, the solid surface generates either CH_3 or CH_2 radicals.⁵

This mechanism considered explains the difference of the pyrocarbon formation rates on the surface of soot particles and on a plane surface as being due to different sizes of the crystallites. Owing to the small dimensions of the soot particles, the crystallites cannot reach their stable size corresponding to the given temperature, and this slows down the total growth rate. It is also possible that the growth rate of a curved graphite layer is less than that of a planar one. This molecular growth mechanism of pyrocarbon during the thermal decomposition of methane is common for other hydrocarbons. This can, however, be regarded as true only for temperatures below 1300 K.

There are not enough reliable data on the kinetics of the growth at higher temperatures,⁶ largely resulting from the undetermined composition of the gas interacting with the wall. Existing data on the formation kinetics and structure of the pyrocarbon, nevertheless, allows one to state that the chain process of its growth takes place at temperatures up to about 2500 K. Actually pyrocarbon films obtained at high temperatures show a pronounced texture and an anisotropic microcrystalline structure⁷ not differing substantially from those produced at lower temperatures. And kinetic data for the rate of pyrocarbon growth for methane and acetylene at 1800 to 2100 K allows one to conclude that, for films growing at such temperatures, one active collision of a molecule upon the surface takes place per 10^3 to 10^4 molecular collisions.

There is no reason definitely to claim that the growth of the film at higher temperatures is such a strictly molecular process as that below 1300 K. On the contrary, one may believe that radicals contained in the gaseous phase can play a more or less important role under such conditions.

FORMATION OF SOOT PARTICLES

The classical scheme of aerosol formation including nucleation and growth is fully applicable to soot formation processes. But, unlike condensation, nuclei of soot particles are products of a chemical reaction. And since the number of molecules required to form a nucleus cannot enter the reaction simultaneously, there is no doubt that the nucleation of a soot particle is of a complex nature and comprises a number of consecutive elementary acts. The understanding of the soot particle generation mechanism requires measurements of the process rate under various conditions. The obtaining of such data involves considerable difficulties due to the high rates of the process. Nevertheless, available results of such measurements, although far from complete, can be considered important.

They are briefly summarized: (i) the formation rate of soot particles has a sharp maximum corresponding to a small degree of total decomposition of the hydrocarbon.^{9, 10} (ii) The soot particle formation process is characterized by the presence of concentration thresholds and an induction period.⁶ (iii) The initial growth rate

of soot particles is considerably (in some instance, by two orders) higher than the stabilized growth rate of a pyrocarbon surface.¹¹

(iv) During the thermal decomposition of diluted acetylene, soot particles may form by two substantially different processes. The activation energy of one of them is 33 and of the other 175 kcal/mol.¹¹ (v) For self-combustion of acetylene, the dispersity of the soot formed will be the greater, the higher the temperature in the front of the flame. A maximum dispersity will be reached in detonation of acetylene, when—due to minimum losses of heat from the front by radiation—the temperature reaches its highest value. The specific surface of soot obtained from detonation of acetylene attains 180 m²/g (average particle size 170 Å). The specific surface of detonation soot does not depend on the initial pressure.¹² (vi) The absolute rate of soot particle formation in the diffusion-type burning of an acetylene+hydrogen mixture equals 10¹⁵ particles cm⁻³ s⁻¹. When acetylene detonates at an initial pressure of 10 kg/cm², this rate exceeds 10¹⁹ particles cm⁻³ s⁻¹.

All the experimental facts and theoretical considerations suggest the following model. The formation of soot particles is, like any process of the initiation of a new dispersed phase, limited by the nucleation. Nuclei may be of two types, namely, either complex unsaturated polymer molecules, or simple radicals. The properties of the primary nucleus define the process of its further growth and the properties of the soot particles produced. A rough analogy may here be drawn between a nucleus and a DNA molecule in which a genetical code is incorporated.

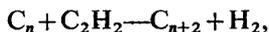
The “molecular nucleus” obtained as a result of reactions including condensation, aromatisation and dehydrogenation, continues to grow by virtue of the same reactions. The product will be a soot particle having an indefinite structure, being X-ray amorphous, and containing a considerable amount of volatiles. Such a process was investigated by Homann *et al.*^{13, 14} in rich premixed flames of acetylene, and was observed by Johnson and Andersen¹⁵ as well as by Tesner and Altshuler¹¹ during the thermal decomposition of acetylene. It seems that the growth rate of these soot particles considerably exceeds that of the pyrocarbon.

A “radical nucleus” initiates a quite different chain of transformations which finally produce soot particles with a compact, regular, and well-investigated structure. The first step of these transformations should be the conversion of the radical nucleus into a nucleus having a physical surface, i.e., into one which is similar to the nucleus of an aerosol particle produced by condensation. Such a nucleus is a soot particle of a minimum size and its further growth process is similar to the pyrocarbon growth described above.

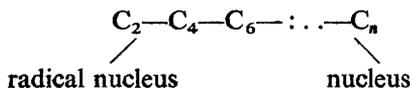
The formation process of a nucleus from a radical-nucleus has not yet been investigated and is most difficult to investigate. Taking into account all that is known about radical processes, this stage may be conceived as follows. The initial interactions between the radical nucleus and the original hydrocarbon molecules are radical reactions resulting in the formation of new radicals. It is quite clear that the activity of the radicals falls in the course of this process by formation of carbon-carbon bonds. Hence, the rate of their interaction with the original molecules will decrease too. At a certain moment the radical nucleus will lose its radical properties, attain the properties of a physical surface, and become a soot particle of minimum size thereby representing a nucleus.

Consequently, in contrast to the usual radical chain, in the chain under consideration more and more heavy and less active radicals will be formed and its propagation rate will gradually slow down. So, for instance, for acetylene the elementary reaction act and the chain leading to the formation of a nucleus are as follows :

elementary act :



chain :



The formation of a great number of soot particles from radical nuclei may be described by equations similar to those of a branched chain process with mutual termination of chains.⁹ The termination represents in this process the destruction of radical nuclei on the surface of the particles formed. Concerning the branching, which was postulated in order to explain the experimentally observed increase of the particle formation rate, its mechanism is not understood.

A comparison of calculations and experimental data permits the determination of the activation energy of the formation of radical nuclei. For the formation of soot from acetylene its value is around 170 kcal/mol. Obviously, the C_2 radical is the only one requiring such an activation energy for its formation from acetylene.

The chain-type scheme of the nucleation and growth described above cannot be regarded as strictly proved but it explains satisfactorily the experimentally observed regularities. This scheme does not take into account the coagulation of the growing particles which actually takes place and results at late stages of particle growth in the formation of a chain-like structure.

The regions of existence of both soot formation processes described above are still indefinite. Probably the first process initiated by a molecular nucleus takes place at lower temperatures and at small concentrations of hydrocarbons. It seems that industrial soot production technology is probably based on an application of the second process, since the structure of all industrial soots is practically identical and they do not contain any considerable amounts of volatiles.

Finally, a great resemblance must be noted between the formation mechanisms of pyrocarbon and soot. Both are two-stage processes limited by nucleation. And both are branched chain processes. The growth process of a carbon surface is similar to a planar model of the three-dimensional soot formation process. The difference consists in that the growth of crystallites on a surface is limited by their coming into contact. The formation rate of planar nuclei and their growth rate at a constant hydrocarbon concentration in the gaseous phase is constant. But the growth of nuclei in volume is not limited, although the generated surface of the particles results in the destruction of radical nuclei and in the slowing down of the particle formation rate.

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