Ideas on Soot Formation Spark Controversy

Notion that carbon shells play a role in the formation of soot draws fire from specialists researching this combustion phenomenon

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A great many ideas have been advanced over the years to account for the formation of soot in a flame, and something of a consensus now exists among soot researchers on how soot particles come by their distinctive morphology. However, many details about the mechanism of soot formation remain to be worked out and are the subject of controversy among scientists studying soot.

The chemistry of soot, at first glance, seems a fairly prosaic subject. Nevertheless, enough scientists and engineers are involved in probing that chemistry that they refer to themselves as the "soot community." That community has reacted with hostility to an alternative mechanism of soot formation proposed by Richard E. Smalley, Hackerman Professor of Chemistry at Rice University, Houston; and Harry W. Kroto, a professor in the School of Chemistry & Molecular Sciences at the University of Sussex in Brighton, England.

The attack on the ideas of Smalley and Kroto has been mounted principally by Michael Frenklach, a professor in the department of materials science and engineering at Pennsylvania State University, University Park; and Lawrence B. Ebert, Exxon Corporate Research in Annandale, N.J.

The hostility between the two camps has spilled beyond the scientific debate on soot and taken on personal tones. Frenklach and Ebert compare Smalley and Kroto's work on carbon clusters to research on cold fusion. Both are examples, they suggest, of "pathological science." Smalley and Kroto counter that soot research is a "backwater" of modern chemistry where researchers resent new ideas from outsiders.

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The structure of soot is the starting point for this dispute. As Frenklach points out in a 1989 article in the Penn State quarterly, "Earth and Mineral Sciences," soot is a "collection of carbonaceous particles around 1 μm in size, produced in combustion devices when the amount of oxygen is insufficient to burn the hydrocarbons into carbon dioxide and water." The particles are composed of chains of smaller spherical particles with diameters ranging from 20 to 50 nm.

These smaller particles can probably be considered the fundamental constituent of soot. Electron microscopy reveals that many of these particles possess a layered structure something like that of an onion. The conventional wisdom is that this structure results from packing together structural units that consist of stacks of polycyclic aromatic hydrocarbons (PAHs).

How the structural units pack to form soot particles isn't entirely clear, but the process is a rapid one. Frenklach writes, "The consensus of the research community has been that fuel molecules decompose in a high-temperature oxidative environment, forming radical and molecular species, with acetylene as the major reaction product. The subsequent reactions of these compounds lead to the formation and growth of polycyclic aromatic hydrocarbons that coalesce into the structural units, which, in turn, coagulate into the spherical particles."

In 1985, Smalley, Kroto, Rice chemistry professor Robert F. Curl, and coworkers published results of experiments involving laser vaporization of graphite (C&EN, Dec. 23, 1985, page 20). Their principal finding was that under certain conditions a remarkably stable species containing 60 carbon atoms was the dominant product of the vaporization reaction. The chemists proposed that the stability of the C_{60} cluster could be explained if it were a spherical aromatic molecule with a truncated icosahedral structure. They called the molecule "buckminsterfullerene" and came to refer to other closed carbon shells (which also are detected in the experiment) as "fullerenes."

Smalley and Kroto suggested in their paper that C_{60} might be found in flames. In 1987, Klaus H. Homann, a distinguished soot chemist at Institut für Physicalische Chemie in Darmstadt, West Germany, detected C_{60} in benzene and acetylene sooting flames.

A curved aromatic structure can result when five-membered rings are incorporated into a flat graphitic sheet made up of six-membered rings. Smalley and Kroto suggest that this occurs in a process that ties up reactive dangling bonds that would be expected at the edges of a graphitic sheet. Such a process could have two outcomes. As Smalley and Curl wrote in a 1988 review in *Science:* "In some cases a closed fullerene structure may result, tying up all remaining dangling bonds and precluding further growth.

More generally, though, the growth process will be too fast to follow the minimum energy pathway. It seems likely that most growing nets will not close at all; instead, the growing edge will overrun and bury the opposite edge as it curls. Once this burying occurs, there is no ready way to terminate the growth process, and spiral structures ... seem likely to form. Such spirals could be a key factor in particle formation in the condensation of carbon vapor ... and may also be important to soot formation in flames."

In a companion review, Kroto presented a number of ideas concerning the fullerenes and spiral soot particles in combustion chemistry and astrophysics. Kroto asserted that Homann's findings support the idea that the fullerenes are involved in soot formation. Homann, however, has always maintained that his data indicate that C_{60} in flames is formed from highly excited soot particles, not the other way around.

C_{60} has never been isolated and probed spectroscopically, so its proposed structure has yet to be proven. (Smalley's group at Rice is working on that difficult problem.) Nevertheless, most chemists familiar with the research, including many in the soot community, accept the notion that C_{60} and the fullerenes are likely to be closed shell molecules. Ebert is an exception, as are a number of his colleagues at Exxon Research & Engineering.

Frenklach and Ebert believe the new theory amounts to "pathological" science and liken it to cold fusion

Soot researchers do not, however, accept the idea that incomplete closure of fullerenes plays a role in the formation of soot.

Frenklach says that calculations of the kinetics of soot formation and experimental evidence strongly indicate the closed carbon shells may exist, "but they have nothing to do with the formation of soot."

Frenklach has modeled the growth of PAHs in a flame environment. By making fairly straightforward changes in his computer code, the model can be applied to the growth of partially closed, curved carbon clusters of the sort Smalley and Kroto believe lead to soot particle formation. Simply put, Frenklach's results indicate that the reactions do not occur nearly rapidly enough to account for the observed kinetics of soot formation.

According to Ebert, several lines of experimental evidence argue against the spiraling particle model for soot formation. X-ray diffraction and carbon-13 nuclear magnetic resonance spectroscopy data suggest that the structural units making up soot particles are stacks of five or six planar benzenoid arrays. These arrays are about 2 nm × 2 nm in size, which corresponds to a molecule containing about 133 carbon atoms. A curved carbon network would result in significantly different x-ray diffraction patterns and ^{13}C NMR spectra, Ebert says, and these are simply not observed.

Ebert also takes issue with the notion that the carbon network curves by incorporation of five-membered rings in order to minimize dangling bonds. Actual soot contains plenty of atoms other than carbon to bond to carbon, he says, and these atoms are sufficient to eliminate any dangling bonds. Microanalysis of soot produced in his laboratory shows 92.06% carbon, 6.11% oxygen, 1.11% hydrogen, 0.46% sulfur, and 0.30% nitrogen. For a molecule with 133 carbon atoms, this corresponds to 26 additional atoms, which is enough to occupy all available edge positions on the molecule. Thus, for actual soot, there is no driving force for producing a curved network.

The chemistry of soot particles also argues against the Smalley and Kroto model, Ebert says. If soot were formed by the spiraling particle mechanism, its chemistry should resemble that of graphite, he adds. For example, very few reactive edges should exist in such a particle, making it resistant, as graphite is, to reductive methylation. But soot is susceptible to reductive methylation, and the extent of the reaction corresponds to reaction with polynuclear aromatics of about the size indicated by Ebert's diffraction data.

Kroto has made much of transmission electron microscope observations by Sumio Iijima, with NEC, Japan, of graphitic microparticles condensed from carbon vapor. These particles consist of a core of concentric graphitic shells surrounded by a layer of amorphous carbon. Kroto and Iijima now suggest that this structure is consistent with the spiraling carbon particle model.

Smalley and Kroto stand by their work contending that soot researchers resent new ideas posited by "outsiders"

Ebert, who is not fond of curved carbon networks of any kind, is unwilling to grant that the particles provide much support for such an interpretation. In any case, he insists that such particles, being composed almost entirely of carbon, have nothing to do with soot, which contains significant amounts of other atoms.

Ebert and Frenklach are not alone in their criticism. A number of combustion scientists tell C&EN the proposal is useless. Steven J. Harris, of General Motors Research Laboratories, for instance, says there is "unanimity in the soot community that C_{60} has nothing to do with soot."

Homann's position is somewhat less adamant. He says one "cannot rule out the spiraling particle mechanism entirely, but it does not account for the majority of soot particles." Nevertheless, his research is beginning to suggest that soot may form through the coalescence of "atypical" PAHs, ones that are somewhat curved because of five-membered rings incorporated into them.

Smalley and Kroto respond somewhat differently to these criticisms. "I continue to think it is an interesting hypothesis that hasn't been disproven," Smalley says. On the other hand, he says, he is not committed to the notion that this is how soot forms. "The answer to the question is to be found in experiments and detailed calculations and not in the rhetoric of this game."

Kroto, by contrast, is adamant that the theory is correct and that Frenklach and Ebert are "more motivated by emotion than clear scientific thought." He dismisses the kinetic argument because Frenklach limits growth to a single leading edge of the spiraling particle. "Our hypothesis implies that once growth reaches the stage of overlapping the first shell, it is fast and epitaxial, more akin to growth at a step on a graphite surface," he says. "This invalidates their whole argument."

Unfortunately, it does not, and Kroto never responds to the chemical arguments advanced by Ebert.

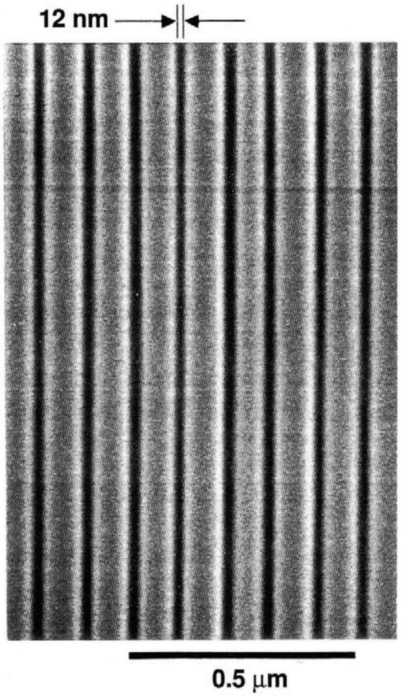
There are a number of unfortunate aspects to this tale. It isn't clear that anybody knows precisely how soot forms. Thus, mounting diatribes against new ideas because, supposedly, they are not needed, is counterproductive. Homann, though, is willing to consider whether the ideas of Smalley and Kroto can be incorporated into a fuller picture of soot formation within the constraints imposed by experimental observations.

On the other hand, some fundamental chemical properties of soot as determined by Ebert appear to pose significant problems for the model developed by Smalley and Kroto. Kroto, in particular, refuses to discuss coherently how such properties can be reconciled with his model. Those properties are not annoying details to be brushed aside, as Kroto insists on treating them.

In fact, neither side appears to comprehend fully what the other side is saying. Ebert, for example, insists that Smalley has claimed that up to three potassium ions can fit inside the closed C_{60} molecule, when in fact he has never made such a claim. Smalley concedes that his reading of the soot literature has been "casual."

If there is a moral to the story, it is probably that scientists should be wary of becoming overly enamored with their hypotheses. That's certainly not a novel observation, but it is worth repeating, because in the case of soot, ignoring it has led to the breakdown of rational discussion. □

Rapid etching of 12-nm lines for semiconductors achieved



In a development that could ease the ability to construct integrated circuit devices that utilize quantum effects, Randall L. Kubena and colleagues in the optical physics department of Hughes Research Laboratories, Malibu, Calif., have etched lines as small as 12 nm across on semiconductor substrates at speeds fast enough to be used in production. Currently, most commercial integrated circuits contain features at least 100 times larger. To produce the lines, a high-intensity focused gallium ion beam was scanned electronically over a gallium arsenide wafer coated with poly(methyl methacrylate) resist material. According to the Hughes scientists, ultrasmall structures such as these will play a critical role in an emerging integrated circuit technology based on quantum effects, in which subatomic particles behave like waves by passing through formerly impenetrable barriers.