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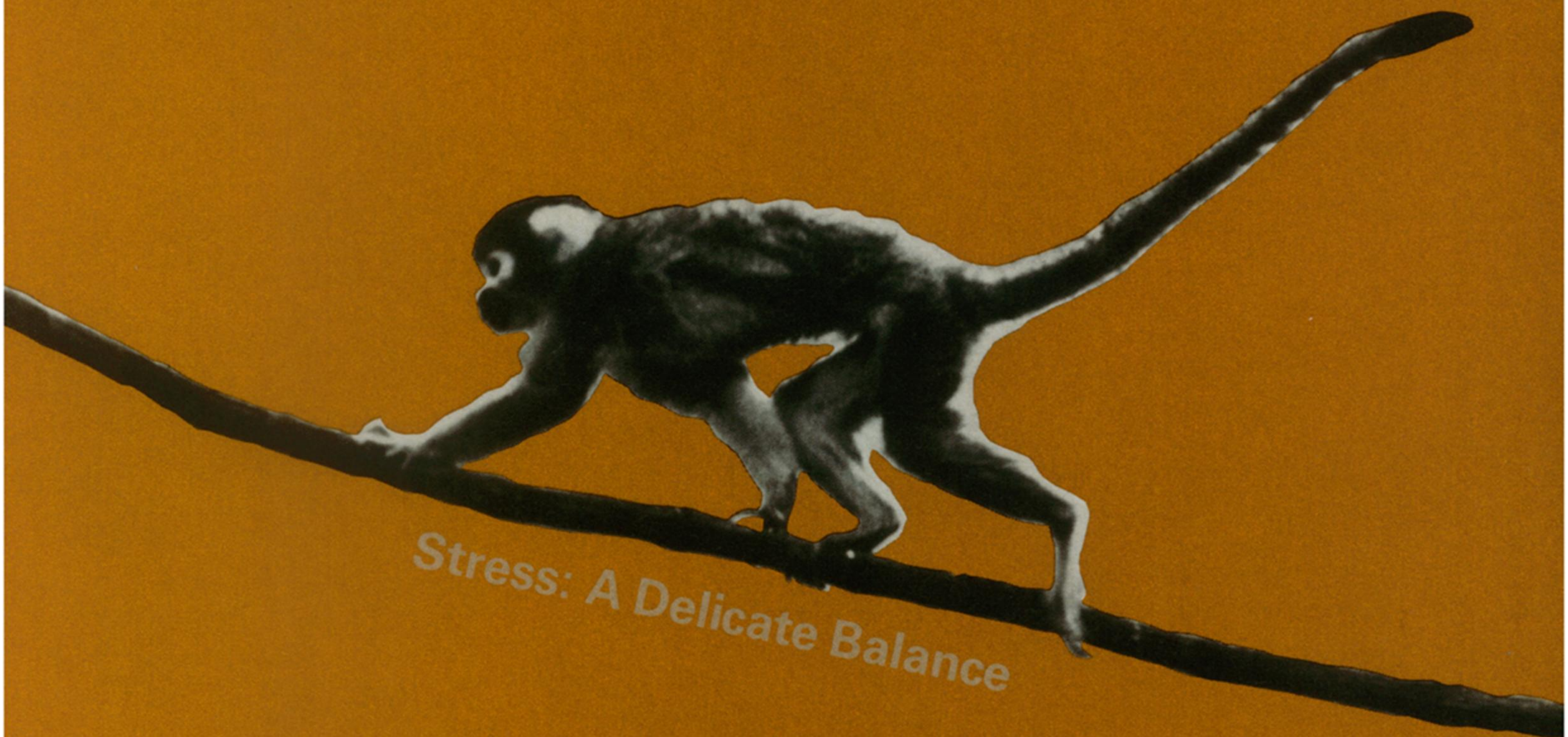


The Logical Suspect

Soot particle growth as it takes place in wood-burning fireplaces, diesel engines, and industrial furnaces, has been attributed to a complex set of interdependent chemical reactions. A researcher at the General Motors Research Laboratories has demonstrated that the decomposition of a single species is primarily responsible.

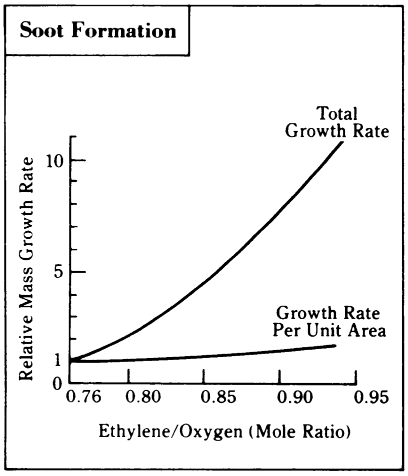
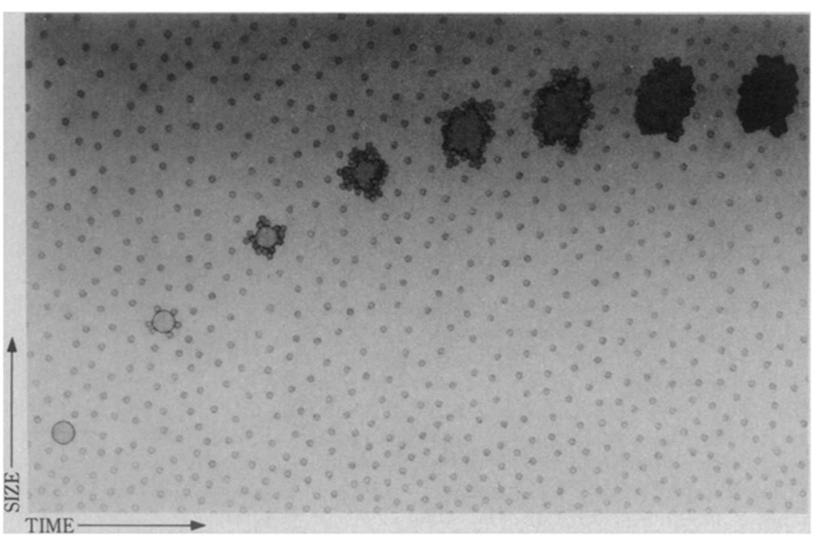


Figure 1: Total growth rate contrasted with growth rate per unit area plotted as a function of ethylene/oxygen mole ratio measured at a given height above the burner face.

Figure 2: Artist's rendition of the surface growth of a single soot particle by the incorporation of acetylene molecules.

SOOT FORMATION may be divided into two stages. Microscopic soot particles are generated in the "inception" stage. They reach full size in the "growth" stage, which accounts for more than 95% of their final mass. Most scientific exploration has concentrated on particle inception which, despite all the effort, remains unexplained. Dr. Stephen J. Harris, a physical chemist at the General Motors Research Laboratories, has reversed traditional priorities. Combining experiment with logic, he has formulated the first quantitative explanation of the growth stage in soot formation.

Dr. Harris arrived at his mechanism through an elaborate process of elimination. To focus on the chemistry of soot growth, he began by eliminating from his investigation the complexities introduced by turbulence and mixing. He limited his research to premixed, ethylene/oxygen, laminar flames with one-dimensional flow.



Previous descriptions in the literature told him that two processes take place simultaneously during growth. Incipient particles collide and coalesce into larger particles, while growing at the same time by incorporating hydrocarbon molecules from the burned gases.

The first process reduces total surface area without changing total mass, while the second, called "surface growth," increases both total surface area and total mass. Hence, the increase in the total mass of soot can be entirely attributed to surface growth.

Dr. Harris set out to identify the hydrocarbon molecules—or "growth species"—responsible for surface growth. Increasing by increments the richness of the flame, he made the key discovery that although the total mass growth rate (gm/sec) increases strongly when the ratio of ethylene to oxygen is increased, the mass growth rate per unit surface area ($gm/cm^2/sec$) increases only slightly (see Figure 1). Thus, the controlling variable for how much soot is formed is not the concentration of growth species, but the surface area available for growth.

This finding led him to conclude that richer flames produce more total soot because they generate more particles in the inception stage. More incipient particles offer greater initial surface area for the incorporation of hydrocarbons.

Since the growth rate per unit area must depend on growth species concentration, this concentration must be similar from flame to flame. Dr. Harris went on to reason that there must either be enough growth species at the outset to account for the total soot growth in the richest flame, or the species must be rapidly formed within the flame from another hydrocarbon present in high enough concentration.

HE NARROWED his search to the four most abundant classes of hydrocarbons found in flames: acetylene, polyacetylenes, polycyclic aromatic hydrocarbons (PAH), and methane. Methane can be eliminated, because its concentration does not decrease as soot is produced. There is not enough PAH to account for soot formation in any flame. Neither of these two hydrocarbons can be readily formed from the other major species present. That left only acetylene and the polyacetylenes.

Acetylene contains enough hydrogen to account for the hydrogen content of soot measured in the early stages of growth. But among the polyacetylenes, only diacetylene could possibly supply enough hydrogen. That left acetylene and diacetylene.

There is more than enough acetylene to account for the mass of soot produced. There is not enough diacetylene, and while diacetylene can be formed from the abundant supply of acetylene, the reported rate of conversion is too slow for diacetylene to play a significant role. That left only acetylene.

Dr. Harris verified that acetylene is the growth species by determining that the slight increase in growth rate per unit area is proportional to the increase in acetylene concentration (see Figure 1). He also found that the rate constant he measured was in agreement with the reported rate constant for the decomposition of acetylene on carbon. These findings confirmed his hypothesis that soot particles grow in flames by the incorporation and subsequent decomposition of acetylene.

"Now that we know how soot grows," says Dr. Harris, "we can examine how it begins with greater understanding. Then, perhaps our knowledge will be complete enough to suggest better ways to reduce soot."

General Motors

MARK OF EXCELLENCE

THE MAN BEHIND THE WORK

Dr. Stephen J. Harris is a Staff Research Chemist at the General Motors Research Laboratories. He is a member of the Physical Chemistry Department.

Dr. Harris graduated from UCLA in 1971. He received his Master's and Ph.D. degrees in physical chemistry from Harvard University. His doctoral thesis concerned Van der Waals forces between molecules. Following his Ph.D. in 1975, a Miller Institute Fellowship brought him back to the University of California, this time at Berkeley, where he spent two years studying laser-induced chemistry. He joined General Motors in 1977.

Dr. Harris conducted his investigation into soot particle growth with the aid of Senior Science Assistant Anita Weiner. His research interests at GM also include the use of laser diagnostic techniques in combustion analysis, with special emphasis on intracavity spectroscopy.