

PRODUCTION AND CHARACTERIZATION OF FULLERENES IN FLAMES

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ABSTRACT

Closed-cage all-carbon molecules referred to as fullerenes were discovered in carbon vapor from laser heating of graphite and subsequently produced in macroscopic quantities by resistive heating of carbon rods. Suggestions that fullerenes may be involved in soot formation, and the detection, in flames, of all-carbon ions having the same masses as fullerenes, have generated much interest in the possible formation of fullerenes in flames. Combustion experiments and chemical analyses will be reported which have been conducted over ranges of flame conditions to determine if fullerenes can be produced in flames and to assess the relationship between fullerenes and soot.

INTRODUCTION

Fullerenes were discovered¹ in carbon vapor produced by laser irradiation of graphite, and have recently been produced in macroscopic quantities^{2,3,4} by graphite vaporization with resistive heating. Fullerene C_{60} is a closed cage carbon structure containing 20 six-membered rings and 12 five-membered rings with the appearance of a soccer ball. There has been a surge of scientific interest in these compounds because they represent a new class of carbon in addition to the two known forms, graphite and diamond. There has also been much practical interest in fullerenes. Many potential applications have been suggested, including catalysts and superconductors produced by incorporation of metal atoms with the fullerenes, and super lubricants produced by fluorination of fullerenes.

That fullerenes may be formed in sooting flames has frequently been suggested^{5,6,7,8} since the early days of fullerene research. Zang et al.⁵ considered the possible role of carbon shell structures in the formation and morphology of soot. They envisioned the growth of successive shells, separated by roughly the 0.33 nm intersheet distance in graphite, producing a soot nucleus consisting of concentric but slightly imperfect spheres, with the edge of the outermost shell giving a very rapid growth front. Kroto and McKay⁶ described a carbon nucleation scheme involving quasi-icosahedral spiral shell carbon particles, and suggested it may apply to soot. Curl and Smalley⁷ suggested carbon nets in the form of spiral structures may be important to soot formation in flames.

In spite of early predictions that fullerenes may be associated with soot formation and morphology, confirming evidence has not been produced although all-carbon ions having the same molecular weights as fullerenes have been detected in flames^{9,10,11}. Also, Pope¹² (see Pope and Howard, Fuel Chemistry Div. Preprints, this Meeting) has determined that compounds in the mass range 700-750 amu in a flame behave in a manner consistent with the relatively stable fullerene C_{60} being a substantial fraction of the material in this mass range. This conclusion

resulted from a study of molecular beam mass spectrometer data obtained by Bittner¹³ in a near-sooting benzene-oxygen flame. Similar flames but in the sooting regime were studied by McKinnon¹⁴, whose data on high molecular weight soot precursors gave interesting but inconclusive evidence pertinent to the possible presence of fullerenes. The subsequent application of soot extraction techniques similar to those employed in the graphite vaporization studies revealed the presence of fullerenes in soot deposited on surfaces of the combustion chamber in McKinnon's studies (McKinnon and co-workers, submitted for publication).

EXPERIMENTAL

In order to determine if fullerenes are formed in flames, soot samples were collected from flames under ranges of conditions and analyzed using conventional techniques. Premixed laminar flames of benzene and oxygen with argon diluent were stabilized on a water-cooled burner in a low-pressure chamber equipped with windows and feed-throughs for visual observation, optical diagnostics and probes, and exhausted into a vacuum pump. The burner consists of a horizontal drilled copper plate (100 mm diameter, 12 mm thick, 1 mm diameter holes centered 2.5 mm apart in a triangular grid) in the end of a tube, upward through which the feed mixture is delivered. The flame is stabilized with a flat front uniformly displaced from a drilled copper burner plate by a short distance which depends on the velocity of the gas leaving the burner and the flame speed of the mixture. The flame is surrounded by an annular nonsooting flame which provides a thermal shield, giving an approximately one-dimensional core within which temperature and species concentrations vary only with distance, or residence time, from the burner surface. The burner was previously used in mechanistic studies of soot nucleation and growth¹³, and the flames studied are of a type for which considerable data on temperature and chemical composition are available⁹⁻¹⁸.

Flames were produced under different sets of conditions over the ranges: burner chamber pressure, 1.60-13.35 kPa; atomic C/O ratio, 0.96-1.07; mol % Ar, 0-39; gas velocity at the burner (298 K), 14-75 cm/s. Each flame was maintained for 1.6 to 2.8 hr, during which a soot sample was withdrawn from the flame at a given distance from the burner using a quartz probe connected to a room-temperature filter, vacuum pump, and gas meter. Soot was also collected from the inside surface of the burner chamber after each run. Using flame temperature and gas composition information, the soot masses and gas volumes collected with the probe in the different flames are found to correspond to soot yields in the range 0.8 to 12% of the carbon fed.

The soot samples were extracted with toluene, using an ultrasonic bath at room temperature, and filtered. The solution from one of the samples was evaporated to dryness and analyzed with a Varian-MAT model 731 mass spectrometer interfaced to a Teknivent data system using a direct injection probe heated from 373 K to 673 K and electron impact ionization. The mass spectrum has been submitted for publication.

The toluene extracts were fractionated with a high performance liquid chromatograph (HPLC) coupled to a spectrophotometric diode-array detector (DAD). A separation scheme proven effective for large polycyclic aromatic hydrocarbons (PAH)²⁰⁻²² was used. The column (4.6 mm i.d., 250 mm length) was packed with 5 μ m Nucleosil octadecylsilyl-bonded silica having 300 Å pore size. A reverse-phase solvent system of methanol/dichloromethane was used. The mobile phase program consisted of a linear increase in dichloromethane concentration from 10-100% in 40 min with a 10 min hold time at 100%. The flow rate was 1.0 mL/min. In HPLC chromatograms for the toluene extracts, the broadband DAD response

is roughly proportional to mass for PAH²³.

In order to obtain broadband ultraviolet-visible (UV-Vis) spectra, solutions from HPLC fractionation of the soot extracts were concentrated by evaporation under nitrogen and the HPLC mobile phase was replaced with spectro-grade decalin. The UV-Vis spectra of the different peaks of interest were acquired over the 200-800 nm wavelength interval using a Hewlett-Packard 8450 A spectrophotometer. Mass spectra of these HPLC fractions were acquired using the equipment and technique mentioned above. The identities of the HPLC peaks suggested by UV-Vis spectra were confirmed by mass spectra. The HPLC method was then used to analyze the toluene extracts of all the soot samples.

The experimental results, which have been submitted for publication, not only show whether fullerenes are formed in flames but also reveal behavior of interest in comparison with that of the graphite vaporization technique for fullerenes production.

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