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In-situ Collection of Nanodrops of Polycyclic Aromatic Compounds from Ethane at 1184 K

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ABSTRACT

A distinct type of chemical intermediate has been observed, isolated, and partially characterized. Droplets were formed from ethane gas at 1184 K and 40 kPa and were collected on a quartz disk that had been preheated to the reactor temperature. The droplets were characterized by laser attenuation, electron microscopy, and fluorescence spectroscopy. The droplets are believed to be formed by condensation of polynuclear aromatic hydrocarbons and to be precursors to the formation of coke.

The formation of carbon from hydrocarbons at high temperatures has significant consequences. Carbon formation is necessary and desirable in the chemical vapor deposition (CVD) of carbon coatings[1] and in the commercial production of carbon black.[2] On the other hand, soot formed in the pyrolysis regions of flames is a serious pollutant.[3] In the industrial steam cracking of hydrocarbons to produce ethylene and propylene, carbon forms coke on the walls of the reactor tubes, ultimately choking off the flow.[4]

It is important to understand how carbon is formed at high temperatures. Some[5] suggest the source is acetylene or polyynes ($C_{2n}H_2$). Others[6] propose that fullerenes act as building blocks for larger carbon particles. Still others say carbon is formed from polycyclic aromatic hydrocarbons (PAHs).[7] The choice of mechanism is controversial.[8] In this letter we will describe a search for an elusive intermediate in the third of these mechanisms.

A highly developed theory[7] suggests that carbon is formed from PAHs. It is postulated that the feedstock breaks down to form free radicals, which react according to a chain mechanism. Hydrocarbon radicals with at least six consecutive carbon atoms can cyclize to form an aromatic ring, which can then add to an unsaturated hydrocarbon to form a larger aromatic compound, such as styrene or phenylacetylene. Further addition, abstraction, and dimerization steps can lead to larger, fused-ring aromatic compounds (PAHs), such as naphthalene, phenanthrene, pyrene, and so on. Ultimately, the partial pressures of even heavier PAHs could exceed their equilibrium vapor pressures, and these heavy PAHs could begin to condense as liquid droplets[9] or as solid particles. Further reactions of consolidation and dehydrogenation could occur in the liquid droplets to transform them into soot particles, or the droplets could collide with the reactor surface to form CVD carbon or coke.

Various aspects of this mechanism have been tested, but others remain unconfirmed. A key intermediate[9] would be a liquid droplet of PAH, formed by condensation of heavy, gaseous PAHs, but which has not yet progressed to carbon. Grisdale et al.[10] observed fogs during the CVD of carbon from methane. The fog was found in cooler parts of the reactor and could have been formed by the chilling of saturated gases coming from the hottest parts of the reactor. A number of workers have inserted cold probes into flames,[9,11,12] but others have commented that such probes could have cooled the gases, thus causing condensation.[13] These comments were supported by the observation that the sampled condensate contained compounds known to be volatile at flame temperatures.[14] Other workers have placed the orifices of molecular beam devices in flames,[15] but again this could have led to local cooling of the flame. Graham and others[12,16] have observed scattering of laser beams in hot pyrolysis and flame gases. The laser experiments left no doubt that aerosols were formed, but interpretation of the experiments was made difficult by the lack of knowledge of the optical properties of the condensate.

Because of the possible, important role of such aerosol particles, we decided to attempt to collect them using a hot probe, in contrast to the cold probes used previously. The system investigated was the pyrolysis of ethane (C_2H_6, Matheson, 99.95% pure) in a vertical, cylindrical, quartz reactor of 1-cm internal diameter (Figure 1). The reactor was heated to 1184 K by a 48-cm long, resistive furnace. (This temperature roughly corresponds to the conditions of industrial steam cracking.[4]) Flow (set by an MKS 1159B control-

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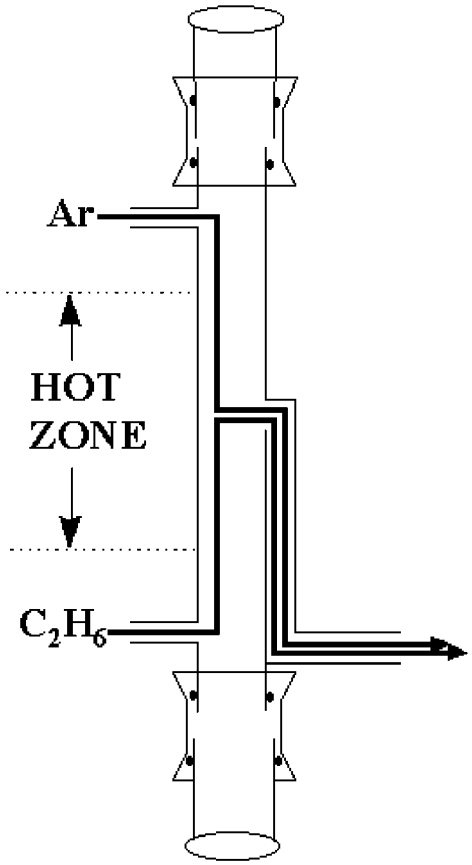

Figure 1. Schematic diagram of the vertical reactor and furnace.

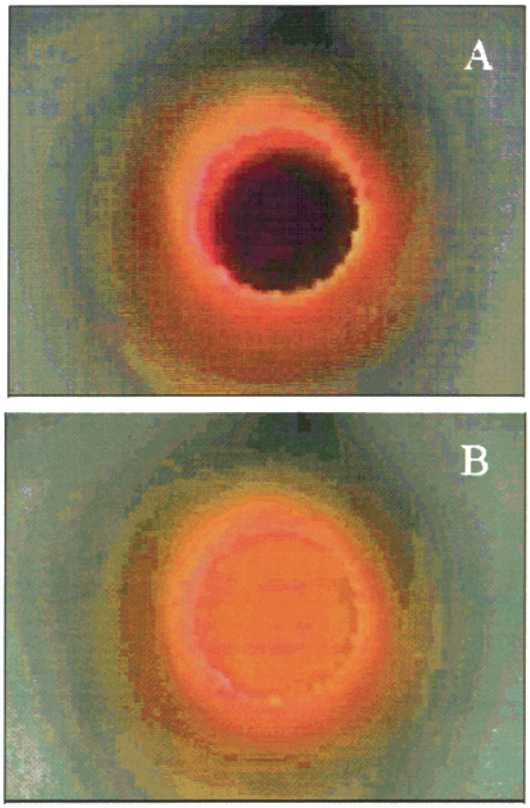

Figure 2. Two frames obtained from a digital video camera (Sony PC10) directed along the axis of the reactor. The total pressure was 40 kPa and the reactor temperature was 1184 K. (A) Ethane (39×10^{-6} mol s^{-1}) flowing in the top and Ar (39×10^{-6} mol s^{-1}) in the bottom. (B) Ethane and Ar flows both reduced to 4.5×10^{-6} mol s^{-1}.

ler) of ethane entered the reactor at the top and exited at a T-joint halfway down the heated section. A similar flow of argon entered the reactor at the bottom and also exited at the T-joint in the middle. The total pressure of gases in the reactor was controlled at 40 kPa, using a pressure transducer (MKS 122A), a controller (Omega CN-2000), a solenoid valve (MKS 159A), and a rotary vacuum pump (Welch 1397) attached to the reactor exit.

The reactor was examined by eye. The upper image in Figure 2 shows the hot zone of the reactor, viewed from above, with 3.9×10^{-5} mol s^{-1} each of ethane and of argon entering opposite ends of the reactor. This view shows the reactor walls glowing with a red to yellow light. The irregularities at the wall corresponded to the irregular carbon deposits on the wall. The gas in the center of the reactor was dark. The lower image was obtained after the flows of ethane and argon had been reduced to 4×10^{-6} mol s^{-1}. An orange glow appeared in the center of the reactor. This glow appeared to be caused by the scattering of light by gas-borne particles.

To learn more about this fog or smoke, the ethane and argon flows were interchanged. Circular gold wire grids (Electron Microscopy Sciences, 200-Au50) were suspended from a quartz thread in the upper, argon-blanketed region of the furnace. The quartz thread was, in turn, supported by a metal wire that entered the vacuum system through a septum. When the wire was retracted, the hot grids were allowed to fall down into the smoke or fog in the lower half of the reactor and then down through the incoming gas to the lower window. Here they were later collected for examination by microscopy.

Transmission electron microscopy (TEM, Philips, EM201) revealed the presence of tiny spheres and hemispheres on the surface of the grids, as seen in Figure 3. The hemispheres were much more common and ranged in diameter from 5 to 250 nm. Their shape was consistent with a population of fluid, aerosol nanospheres, which partially flattened on impact. The adhering nanodrop in Figure 3B has a fine structure consisting of circles of 5 to 15 nm in diameter. This droplet appears to have been formed by the coagulation of smaller droplets.

To attempt to collect enough of these fog nanodrops to begin chemical analysis, a spiral quartz substrate (with a larger surface area) was prepared. This was dropped through the fog, and the adhering droplets were washed off with dichloromethane (DCM). Examination of a washed substrate by scanning electron microscopy indicated that the droplets had been dissolved in the DCM. There was no sign of solid particles in the solution.

The fluorescence spectrum of the solution was recorded using a Shimadzu spectrofluorophotometer (RF-5301 PC). A fluorescence spectrum obtained with an excitation wavelength of 270 nm is shown in Figure 4. The fluorescence maxima occurred at 380, 415, and 440 nm. This is the spectral region where emission is expected from three- and

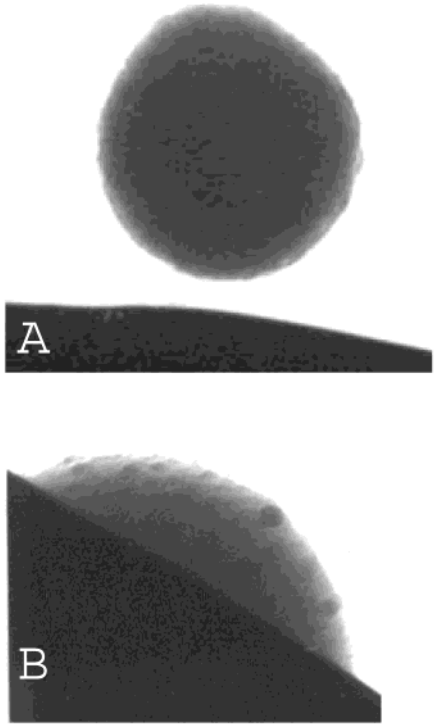

Figure 3. Transmission electron microscope images of droplets (× 220,000) adhering to a hot gold grid that was dropped through the lower part of the reactor when 4.4×10^{-6} mol s^{-1} of ethane flowed in the bottom and an equal amount of Ar flowed in the top.

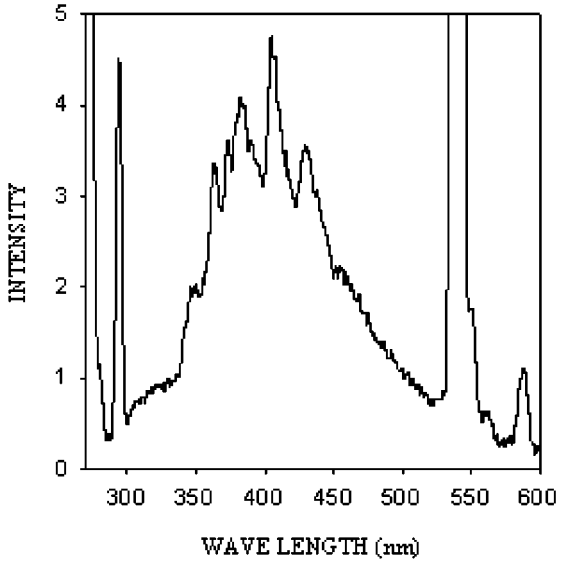

Figure 4. Fluorescence spectrum of material collected on a hot, spiral, quartz substrate that had dropped through a fog (formed at the same conditions as in Figure 3) and that was then washed in 2 cm^3 of DCM. The sharp peaks at 270 and 540 nm were caused by scattered, incident, 270-nm light.

four-ring PAH units, such as phenanthrene, anthracene, fluoranthene, and pyrene units.[17] Unsubstituted three- and four-ring PAHs are too volatile to condense at 1184 K, but these PAH units could have been linked to other units in nonvolatile compounds. On the other hand, fullerenes fluoresce[18] between 600 and 800 nm and linear polyenes ($C_{2n}H_{2n+2}$) fluoresce[19] weakly between 500 and 700 nm.

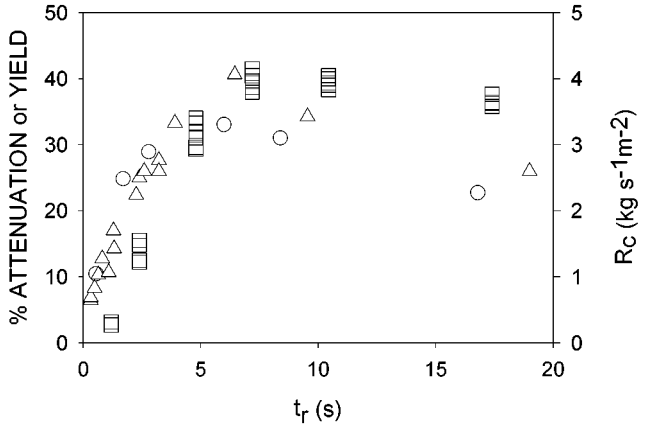

Figure 5. Attenuation of the laser beam (squares), total yield of liquid products (triangles), and rate of carbon deposition (circles) as a function of the residence time.

Polyynes ($C_{2n}H_2$) have ultraviolet absorption wavelengths that depend on the square root of n.[20] When n is 13, the maximum absorption occurs at 350 nm.[21] When n is 25, the maximum would be expected at 485 nm, and any fluorescence would be at longer wavelengths, beyond the spectrum observed here. The boiling point of a polyyne with n equal to 25 has been estimated to be 800 K,[22] too low to condense at the temperatures used in this work. Evidently fullerenes, polyenes, and polyynes are not responsible for the fluorescence observed in this work.

The material collected on the spiral "fog-catcher" was also placed on the thermal desorption probe in the electron impact source of a quadrupole mass spectrometer (VG Quattro). No mass spectrum was observed, suggesting that the material was nonvolatile.

Light from a diode laser (Alpec, 670 nm) was directed through the upper quartz window, down the axis of the reactor, out the other quartz window, through an aperture, and onto a photodiode (Texas Instruments TSL 220). The signal from the detector was attenuated, depending on the flow rate of ethane into the reactor (or on the residence time of the gases in the reactor), as shown by the squares in Figure 5. Overlapping squares at the same residence times show the results of experiments performed on different days to check reproducibility. At the shortest residence time of about 1 s, (corresponding to flow rates of each gas of 19×10^{-6} mol s^{-1}), the attenuation was only about 3%. The attenuation reached a maximum of about 40% when the residence time was 7 s and then declined slightly for longer residence times or slower flow rates.

The total yield of liquid products leaving the reactor had been determined in previous experiments.[23] This yield is also plotted as a function of residence time in Figure 5. It can be seen that the amount of light attenuation by the aerosol was parallel to the concentration of liquid products. It had been found previously that the liquid products consisted of aromatic hydrocarbons,[23] with the masses detected extending up to 700 amu. These observations are consistent with condensation of the heavier PAHs to form the nanodrops.

The deposition rates of carbon from hot ethane had previously been measured in experiments[24] in which a quartz

substrate was suspended from one arm of an electronic microbalance (Cahn RG2000). The dependence of the laser attenuation on the residence time, shown by the squares in Figure 5, also paralleled the dependence of the deposition rate (shown by the circles) on the residence time. This close parallel was consistent with the hypothesis that the aerosol responsible for attenuating the light beam also formed carbon in a direct, first-order process.

Each time the reactor was removed from the furnace, it was observed that carbon had deposited on the parts of the reactor that had been in contact with hot ethane. The parts of the reactor that had always been blanketed by argon remained clear.

Reviewing and interpreting these experiments, we believe that we have observed an unusual type of chemical intermediate, lying between two phase transitions, from gas to liquid and then from liquid to solid. Ethane, a light hydrocarbon gas, can be transformed in part, at high temperatures and long residence times, to form heavy PAHs, which can condense as liquid nanodrops. These droplets can deflect and attenuate a laser beam just as the droplets in fog or a cloud can block the sunlight. When viewed with the naked eye, the fog appears to glow with an orange light because of the scattering of light originating at the furnace and at the reactor walls. The droplets were collected on hot dropped substrates and were examined by transmission electron microscopy and by fluorescence spectroscopy. The fluorescence spectrum was consistent with the presence of high molecular weight PAHs. The rate of chemical vapor deposition on a solid surface within the reactor was proportional to the concentration of the droplets, as measured approximately by the attenuation of the laser beam.

These results are consistent with the suggestion[7,9] that large PAHs form, condense, and then dehydrogenate and carbonize to form coke. Most of the droplets observed were unlike the solid soot particles observed elsewhere,[15] which were usually chains of attached spherules, like strings of pearls.

The present technique is well suited to the collection of these nanodrops. Pyrolysis at a moderate temperature but a high conversion allows the droplets to grow to a convenient size before they start to carbonize. In combustion, temperatures would be higher, oxygen-containing radicals would be present, and time scales would be much shorter; these factors would make experiments more difficult. The use of a hot substrate in this work enabled the collection of droplets that were formed prior to the passage of the substrate, whereas a cold probe could chill the gases, thus triggering the formation of droplets.

Direct, experimental research on this new intermediate is just beginning. We would like to study the dependence of the size and concentration of the droplets on such experimental parameters as the pressure and temperature. It would also be interesting to study the bulk and surface reactions of these droplets, and their possible transformation to soot, carbon black, or pyrolytic carbon. It would be challenging, but potentially rewarding, to adapt the present techniques to combustion systems.

With better understanding of these droplets of aromatic hydrocarbons, we can hope to find ways of reducing the formation of soot and coke or of controlling the chemical vapor deposition of carbon.

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