in winter, since preliminary results of a recent campaign²⁶ show that no BrO was detected during the night, whereas daytime mixing ratios ranging from 2 to 8 pptv were measured. Similarly to the Antarctic stratosphere, high abundance of OClO was also found. These observations seem to confirm that the reaction between BrO and ClO may play a significant role under the polar

(26) "Airborne Arctic Stratospheric Expedition", Preliminary Findings, February 1989.

stratospheric conditions either in the formation and variation of OClO or in the sequestration of BrO into BrCl. The latter effect is revealed by the new laboratory data presented in this paper and in that of Friedl and Sander.24

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Pyrolysis of Acetylene in Sonolytic Cavitation Bubbles in Aqueous Solution

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Water was irradiated with 1 MHz ultrasound (about 2 W/cm²) under mixtures of argon and acetylene of various compositions. A few experiments were performed using deuterated acetylene. Acetylene is rapidly consumed, the maximum rate occurring at a solution concentration of C_2H_2 of 2×10^{-3} M. The products are H_2 , CO, CH₄, a great number of hydrocarbons containing two to about eight C atoms, formic and acetic acids, formaldehyde and acetaldehyde, and insoluble soot. Some larger product molecules are benzene, isomers of benzene, phenylacetylene, styrene, and naphthalene. The products are similar to the ones observed in the pyrolysis and combustion of acetylene. The relative abundancies of the products change with acetylene concentration, which is in part attributed to the varying temperature of the adiabatically compressed cavitation bubbles. All products are initially formed proportional to the irradiation time, even at times in the 10-s range. Volatile products are, however, consumed in longer irradiations. It is concluded that all products are formed in single cavitation events and not by stepwise formation and subsequent sonolysis of intermediate compounds in different cavitation bubbles. A mechanism is proposed according to which water vapor decomposition is the main primary process at low C_2H_2 concentration, the OH radical and H and O atoms formed attacking acetylene molecules. At higher C_2H_2 concentrations, the direct pyrolysis of acetylene is the principal primary process, C_4H_2 and C_4H_4 being formed as the most important precursors of the higher C atom number products. Among the latter, even C atom numbers are more abundant than odd numbers. Small soot molecules form a colloid absorbing uniformly at all wavelengths in the UV/vis region, and larger molecules mainly scatter light. The results are discussed in terms of mechanisms developed in combustion chemistry.

Introduction

The chemical effects of ultrasound in aqueous solutions containing argon are due to the high temperatures in gas bubbles which are formed and compressed as a consequence of the periodic pressure changes in the liquid.¹ Two kinds of reactions may be distinguished: (1) reactions occurring directly in the hot gas bubbles, and (2) reactions in the solution as free radicals generated in the gas bubbles reach the liquid phase.² Solutes of high vapor pressure can readily move into the bubbles and undergo pyrolysis in the gas phase. Solutes of low vapor pressure are chemically changed by free-radical attack in solution, although even these compounds (such as ions^{2b} and polymers³) can also be pyrolyzed in the hot interface between bubble and solution. During the past few years many gas-phase reactions, such as H_2-D_2 isotope exchange,⁴ ${}^{15}N_2{}^{-14}N_2$ isotope exchange,⁵ ${}^{18}O_2{}^{-16}OH_2$ isotope exchange,6 and nitrous oxide7 and ozone8 decomposition have been studied. These reactions generally occur with more than 10 times greater yields than the liquid-phase reactions.

Studies on the sonolytic decomposition of pure hydrocarbons have been carried out by Suslick et al.⁹ Simple hydrocarbons, such as methane and ethane, in aqueous solution have been studied in our laboratory.¹⁰ In these experiments, water was irradiated under an argon atmosphere to which a certain amount of hydrocarbon gas had been added. The yields of the various products of sonolysis were determined as functions of the hydrocarbon concentration. With increasing amount of hydrocarbon in the argon bubbles the yields first increase as there is more and more reactant concentration. However, because of the lower ratio, γ , of the specific heats of the hydrocarbon (as compared to that of argon) the temperature reached in the adiabatic compression of the bubble becomes lower with increasing hydrocarbon content of the bubble. The two effects generally lead to a maximum in the yield vs hydrocarbon concentration curve. In addition, the spectrum of the products may change. For example, C₂H₂ and C_2H_4 are formed in the sonolysis of methane, and from the ratio of these products one may calculate the bubble temperature for

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Pyrolysis of Acetylene

various argon:methane ratios¹¹ making use of known kinetic data in combustion chemistry.¹²

In these studies on methane and ethane it was found that acetylene is an important product. Further, hydrocarbons of longer chain lengths were observed and it was reasoned that intermediate acetylene played a role in the buildup of these products. It was therefore decided to study the sonolysis of acetylene. As in the preceding work, aqueous solutions containing various mixtures of argon and acetylene were sonicated. It turned out that the decomposition rate of acetylene is very high. In some experiments, sonication times as short as a few seconds had to be applied to work under conditions where kinetic measurements are meaningful (i.e., at practically constant C_2H_2 concentration).

Experimental Section

The ultrasound was generated by a 1-MHz quartz generator. The generator and the irradiation vessels have been described previously.¹³ The vessels contained 37.5 mL of solution and 22.5 mL gas phase. They were closed during irradiation. The liquid was agitated by ultrasound as a small fountain was produced on the surface. This agitation was necessary to secure rapid equilibration of the solution with the gas atmosphere during irradiation. In some experiments a stream of an argon-acetylene mixture passed through the solution during irradiation to carry away the volatile products.

The identification of the volatile and nonvolatile compounds falls into five categories:

1. The simple volatile gases, consisting of H_2 , CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , CO, and CO_2 were analyzed on a Delsi gas chromatograph. Molecular sieve and Porapak columns were used. These gases were removed from the equilibrated vapor above the irradiated solution by transfer from the irradiation vessel into a Van Slyke manometric chamber and from there into an evacuated gas sample tube.

2. The group of gases consisting of hydrocarbons C₂'s through the C₄'s were analyzed on a Hewlett Packard 5890A gas chromatograph (50-m Al₂O₃/KCl fused-silica column; 0.32-mm internal diameter). The compounds consisted of propane, allene, propene, propyne, isobutane, *n*-butane, butadiene, and 1-butyne.

3. The hydrocarbons consisting of the C_5 's through the C_8 's were not found in the equilibrated gas phase. They were removed from the solution by a flowing mixture of C_2H_2 -Ar during irradiation. These products were condensed in a small trap cooled to -80 °C by a CO₂-acetone mixture. The products in this trap were extracted with ether or methanol and then analyzed in a UV spectrophotometer and in a mass spectrometer combined with a gas chromatograph.

4. The nonvolatile higher molecular weight hydrocarbons were extracted from the irradiated solution (saturated with NaCl) with diethyl ether. This extract was injected into a heated gas chromatograph column connected to a mass spectrometer. This extract contained hydrocarbons within the mass range of 100-200. In one case (Figure 10) 250 μ L of chloroform was used for extraction after 11 g of NaCl had been added to the irradiated solution.

5. The irradiated solutions contained compounds of rather large molecular weight which scattered light. Their relative concentration was followed by measuring the scattering absorbance at 300-800 nm in a spectrophotometer. About 50% of the particles scattering could be removed by a 0.45- μ m filter. On standing or during prolonged irradiations the colloidal particles precipitated as a yellowish or brownish solid.

Formaldehyde and acetaldehyde were determined gas by HPLC as dinitrophenylhydrazones. A 5-mL volume of a solution containing 2,4-dinitrophenylhydrazone (400 mg in 100 mL of 2 N HCl) was added to 30 mL of irradiated solution. Cyclohexane, 2 mL, was added after 10 min and the mixture was vigorously shaken for 3 min. A sample of the organic phase was then an-



Figure 1. Rate of consumption of acetylene and rates of formation of hydrogen and carbon monoxide as functions of acetylene concentration.



Figure 2. Irradiation of water under mixtures of argon and deuterated acetylene. Yield ratios H_2/HD and D_2/HD as functions of C_2D_2 concentration.

alyzed by HPLC (Waters RP 18 Cartridge with radial compression, 2 mL/min, 80% methanol-20% water). Formic acid and acetic acid were determined with an ion chromatograph.

Results

The effect of the C_2H_2 concentration on the consumption of acetylene and the formation of hydrogen and carbon monoxide are shown in Figure 1. The lower abscissa scale gives the concentration of acetylene in the aqueous solution before irradiation and the upper scale shows the volume percentage of C_2H_2 in the argon-acetylene gas above the liquid. As mentioned above, the yield vs C₂H₂ concentration curve has a maximum, the peak lying at $[C_2H_2] = 2 \times 10^{-3}$ M or 5 vol %. The curves for H₂ and CO also pass through a maximum (at 6×10^{-4} M), which, however, does not coincide with that of C_2H_2 consumption. Also note that almost no CO is formed at the maximum of the C_2H_2 consumption. Further, more H_2 is formed than C_2H_2 is consumed at C_2H_2 concentrations below 2×10^{-4} M. It has to be remembered at this point that acetylene is not the only compound that is sonolyzed in the argon bubbles as water vapor is also present. The decomposition of water vapor in argon bubbles leads to H₂, H_2O_2 , and a small amount of O_2 , free hydrogen and oxygen atoms and hydroxyl radicals being the intermediates.^{13,14} Experiments with deuterated acetylene, C_2D_2 , were also performed in which the D_2 and HD yields were determined. The D_2 yield also went through a maximum, the position of which is at a much higher acetylene concentration $(4 \times 10^{-3} \text{ M})$ than that of H₂. Very little D_2 appeared at acetylene concentrations where the yield of H_2 has its maximum, all these observations indicating that different mechanisms of hydrogen formation exist. In Figure 2, the yield ratios D_2/HD and H_2/HD are plotted as functions of C_2D_2 concentration. The opposing course of these curves also indicates that at about 1×10^{-3} M C₂D₂ there is a change in the mechanism of hydrogen formation, i.e., in the relative contributions of hydrogen from water and acetylene.

Figure 3 shows how the concentrations of H_2 and CO depend on the irradiation time. As can also be seen, very small amounts of carbon dioxide are also formed. The figure also shows the

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Figure 3. Concentration of various products as function of sonication time. The figure also shows the consumption of acetylene (or the concentration of remaining acetylene) and the scattering-absorbance of the irradiated solution. Initial acetylene concentration in the solution: 1.6×10^{-3} M.



Figure 4. Concentration of minor products of sonolysis as function of irradiation time. Initial acetylene concentration: 1.6×10^{-3} M.

decrease in C_2H_2 concentration as well as the concentration of remaining C_2H_2 . The initial concentration of C_2H_2 in solution is 1.6×10^{-3} M, the total concentration (adding the amount of C_2H_2 in the gas phase) being 2.6 × 10⁻³ M. For sonication periods exceeding about 8 min, over 90% of the acetylene is consumed. The solutions were turbid after sonication which indicates the formation of soot (organic compounds of rather high molecular weight). Figure 3 also shows how the amount of soot depends on irradiation time. The scattering absorbance is plotted as a function of time. The curve obtained roughly parallels that of C_2H_2 consumption; i.e., not much additional soot is formed after 5-10 min, when most of the acetylene has been consumed. The curves for H₂ and CO production, however, still increase at longer irradiation times. Under these conditions, one is dealing mainly with the sonolysis of water and the products from acetylene sonolvsis.

Methane and ethylene are also produced in the sonolysis of acetylene. Figure 4 shows how their concentrations vary with irradiation time. While the curve for CH_4 shows a behavior similar to that of C_2H_2 consumption in Figure 3 the curve for ethylene reaches a maximum at 10 min and then rapidly decreases. C_2H_4 obviously is a product that itself can readily be sonolyzed. Other products in Figure 4 are CO_2 , acetaldehyde, formaldehyde, and acetic and formic acids. The concentrations of ethylene and acetaldehyde decrease at longer times, while those of formaldehyde and formic acid continue to increase.

Gases formed at lower yields are ethane, propene, propyne, allene, and butadiene. Figure 5 shows their yields together with those of methane and ethylene as functions of the C_2H_2 concentration in a double logarithmic plot. These gases show maximum yields again at about 4×10^{-3} M; they are formed with yields approximately 1/10th those of methane and ethylene. The rates given in Figure 5 are initial rates determined in experiments where the irradiation time was no longer than 3 min. In all cases, for sufficiently short irradiation times, the amount of product formed was proportional to the time. Trace concentrations of propane, butene, butyne, and the butanes were also observed.

Products having a larger number of C atoms are discussed next. The volatile products were removed continuously as mentioned



Figure 5. Initial rate of formation of minor products of sonolysis as function of acetylene concentration.



Figure 6. Ultraviolet absorption spectrum of purgeable compounds from a 1.6×10^{-3} M C₂H₂ solution. Irradiation time: 2 min. The acetylene concentration was kept constant during irradiation by flowing an Ar-C₂H₂ mixture through the solution.



Figure 7. (a) Absorption spectrum of an irradiated 1.6×10^{-3} M C₂H₂ solution at different times of irradiation. (b) Spectrum of the solutions in part a after purging with argon.

in the Experimental Section (procedure 3), i.e., by flowing an acetylene-argon mixture through the sonicated solution and freezing out the products at -80 °C. Figure 6 shows the absorption spectrum of these products. Several bands are seen in the UV region which are probably due to the presence of conjugated dienes, conjugated -ines as well as -enines. Among these compounds, diacetylene and vinylacetylene were identified by mass spectrometry.

Similar spectra were observed when the solution, which had been irradiated in the closed vessel, was investigated spectrophotometrically. Figure 7a shows the UV absorption spectrum at different times of irradiation. Note that the intensity of the bands is highest for the shortest irradiation, and progressively lower the longer the time of irradiation. This shows that the compounds that produce the sharp bands are consumed at longer irradiation times when most of the acetylene has been converted. Figure 7b



Figure 8. Relative abundances of compounds with mass numbers in the range from 64 to 104 for various acetylene concentrations.

shows the absorption spectra of the solutions of Figure 7a after purging with a stream of argon for 10 min. It can be seen that the volatile compounds that caused the sharp absorption bands were removed, the remaining absorption spectra being structureless and having increased intensity at longer irradiation times. The conclusion is drawn that the nonvolatile compounds in Figure 7b were formed by polymerization of the unsaturated compounds present in Figures 6 and 7a.

Figure 8 shows the relative intensities in the gas chromatographic/mass spectrometric investigation of the products that were removed by the flowing acetylene-argon stream. The three diagrams were determined for various steady-state acetylene concentrations. At the lower concentrations (0.46 and 0.94 mM) which lie on the left side of the maximum for acetylene consumption in Figure 1 a rather broad and uniform mass distribution is observed. At the higher acetylene concentration (3.72 mM), which is on the right side of the C_2H_2 maximum in Figure 1, the mass 78 peak of benzene is dominant. It should also be mentioned that the chromatogram contained various isomers of benzene at lower concentrations.

A chromatogram was taken from the ether extract of an 1.6 $\times 10^{-3}$ M C₂H₂ solution irradiated for 2 min in the closed vessel (experimental procedure 4, see above). It contained a very great number of products in the range of mass numbers up to 160. It was not attempted to identify all products. Only the most abundant ones, including phenylacetylene, styrene, indene, and naphthalene, were identified. The left part of Figure 9 shows that the most uniform distribution of products occurs at an acetylene concentration of 2.42 mM, i.e., close to the maximum for C₂H₂ conversion in Figure 1. At the higher acetylene concentration of 5.11 mM, the naphthalene peak is most pronounced. In the diagrams of the right side of Figure 9 the sums of all odd and even C number products in the C₇-C₁₀ range are shown. It can be seen that the intensity alternates, the even C numbered products being more abundant than the adjacent odd numbered ones.

It is important to note that all the products are formed at constant rate from the very beginning of sonication. Figure 10



Figure 9. (Left) Main products (mass numbers) in the irradiation of C_2H_2 solution of various concentrations. Products separated by extraction with ether and analyzed by combined gas chromatography-mass spectrometry. (Right) Relative abundancies of odd and even C number products.



Figure 10. Concentration of phenylacetylene (\Box) and styrene (\bullet) as functions of sonication time for a 2.96 × 10⁻³ M C₂H₂ solution.

shows an example for a 2.96 mM C_2H_2 solution. The concentrations of phenylacetylene and styrene are plotted here as functions of irradiation time. In both cases the concentration of products is proportional to the irradiation time.

Figures 11–13 describe typical experiments on the soot which has already been mentioned in the discussion of Figure 3. Light scattering was found in all sonicated solutions even at the lowest C₂H₂ concentrations applied and after sonication times shorter than 1 min. Superimposed on the light scattering-absorption, which begins beyond 600 nm, is the UV absorption of the unsaturated compounds (Figures 6, 7, and 13). In the experiments of Figure 11, rather long irradiation times were used, at which times the unsaturated compounds were already converted into higher polymeric materials. The curves give the scattering-absorbance spectrum immediately after irradiation and after filtration of the irradiated solution through a 4×10^{-4} cm pore filter. The scattering after filtration was smaller as the largest soot particles had been removed. Note that the fraction of removed particles increased with increasing irradiation time. It should also be remembered that the acetylene in the closed vessel was consumed after a few minutes (Figure 3). These findings show that the soot particles became larger with time. In the experiments in which an acetylene-argon stream flowed through the solution, large amounts of soot were obtained. At longer sonication times the soot is no longer present as a colloid but as a brownish precipitate.

In the experiments of Figures 12 and 13 very short sonication times were applied to find out whether soot formation parallels that of the lower molecular weight products, i.e., does not have



Figure 11. Scattering-absorption of a 1.6×10^{-3} M C₂H₂ solution after different times of irradiation in the closed vessel: (full line) Immediately after irradiation; (dashed line) after filtration of the solution.



Figure 12. (Dashed line) Absorption spectra of an irradiated 3×10^{-3} M C₂H₂ solution before and after filtration. (Full line) Difference spectrum due to scattering. Irradiation time: 10 s.



Figure 13. Scattering-absorbance at 300 and 400 nm and 190-nm absorbance of benzene as functions of sonication time. C_2H_2 : 3×10^{-3} M. The scattering-absorbance was obtained as the difference of the spectra before and after filtration. The 190-nm absorbance was measured in the filtered solution.

an induction period. As can be seen from Figure 12, the absorption spectrum after sonication contained the sharp bands of unsaturated compounds on the scattering background. After filtration through a 2×10^{-6} cm pore filter which removed all larger particles the absorption spectrum was due to the lower molecular weight

compounds only. The scattering-absorption spectrum was obtained as the difference between the spectra before and after filtration. Experiments of this type were also made with longer irradiation times, i.e., 20 and 30 s. The scattering-absorbance at 300 and 400 nm is plotted in Figure 13 as function of irradiation time. The straight lines obtained indicate that soot is formed already in the very beginning of irradiation and its amount is proportional to the irradiation time. The figure also contains the absorbance of the sharp band at 190 nm after filtration which is typical for benzene. Its intensity also is proportional to the time.

The elementary composition of soot, produced in 3.4×10^{-3} and 5.9×10^{-3} M C₂H₂ solutions, was C_{4.8}H_{4.2}O, which shows that the decomposition of water contributed to soot formation. At very low C₂H₂ concentrations and short irradiation times the soot absorbed light instead of scattering it. The absorption spectrum extended rather uniformly over the whole UV/vis range.

Discussion

Combustion Character of C_2H_2 Sonolysis. The chemical effects of ultrasound are explained by the hot-spot theories of Noltingk and Neppiras,15 Griffing and co-workers,16 and more elaborate theories.^{1c,d,17} According to the Noltingk-Neppiras concept, a gas nucleus in the liquid grows slowly and isothermally in the ultrasonic field. The mechanism of growth is rectified diffusion¹⁷ as the bubble oscillates. The bubble's interior and the surrounding liquid are regions that undergo changes during bubble growth. Molecules diffuse into and out of the bubble, the concentration of gas molecules in the surrounding liquid varies, and hydrophobic molecules in the solution may be accumulated at the interface.^{2b,3} When a certain bubble size is reached, which is about 5×10^{-4} cm at a frequency of 1 MHz, it undergoes a rapid adiabatic compression or collapse. Temperatures of several thousand kelvin and pressures of up to 100 bar may be built up during this compression phase. As mentioned in the Introduction, the temperature will be lower with increasing C_2H_2 content of the bubble because of the greater heat capacity of this gas.

These conditions are even more drastic than in the combustion and pyrolysis studies on C_2H_2 that have often been reported.¹⁸ It is therefore not surprising that similar products are found in sonolysis and combustion. In our discussion, we will make use of the mechanisms developed in combustion chemistry. However, one should be aware that the sonolytic conditions are unique from various points of view. Firstly, the presence of oxygen is not necessary to initiate the reaction. Secondly, water vapor is present in the hot bubbles which can deliver O atoms to build up products containing oxygen. In the third place, the combustion in a cavitation event occurs in less than a microsecond and the products formed are immediately stabilized and cooled by the surrounding aqueous solvent.

The number of products from C_2H_2 sonolysis is large. Besides small gas molecules, such as CO and CH₄, various hydrocarbons with intermediate C atom numbers, such as benzene and various C_6H_6 isomers, high C number products, such as naphthalene, are formed. All these products have a common property when they are formed: Their concentration is proportional to the irradiation time, even at times as short as 10 s. An important conclusion can be drawn: All these products form in *single* cavitation events. If a product of higher C number was formed via accumulation of products of intermediate C numbers in the solution and subsequent pyrolysis in other cavitation events, the concentration would have increased in an S-shape manner.

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Pyrolysis of Acetylene

As already mentioned above, the temperature reached in a compressed argon bubble depends on its content of acetylene. At low acetylene concentration one expects a high temperature and the sonolysis of water vapor should play an important role. At high acetylene concentration, the temperature will be lower and mainly decomposition of acetylene take place.

The First Stages of Water and Acetylene Decomposition. Water is known to dissociate in cavitation bubbles to yield hydrogen atoms and hydroxyl radicals:

$$H_2O + M \to H + OH + M \tag{1}$$

It has previously been shown that oxygen atoms are also generated and that O atoms and OH radicals are interconvertible at the high temperatures existing in argon bubbles:6,13

$$2OH \rightarrow O + H_2O \tag{2}$$

$$O + H_2 O \to 2OH \tag{3}$$

In the pyrolysis of acetylene, the following processes play an important role:18

$$C_2H_2 + M \rightarrow C_2H + H + M \tag{4}$$

$$2C_2H_2 \rightarrow C_4H_3 + H \tag{5}$$

The specific rates of these reactions are known as functions of temperature.¹⁸ The temperature in argon cavitation bubbles is 3000 K or higher.¹¹ In this temperature range the specific rate of water decomposition is higher than that of acetylene.

At low acetylene concentrations, where one is dealing with high temperatures, the mechanism should consist mainly of an attack of acetylene by the free radicals and atoms from water. The following reactions are known from combustion studies:^{18a,b}

$$C_2H_2 + 0 \rightarrow CO + CH_2$$
 (6)

$$C_2H_2 + H + M \rightarrow C_2H_3 + M \tag{7}$$

$$C_2H + OH \rightarrow CH_2 + CO$$
 (8)

$$C_2H_2 + OH \rightarrow CH_2CO + H$$
 (9)

The CH₂ species formed in reactions 6 and 8 may undergo reactions with radicals leading to CH:^{18a}

$$CH_2 + OH \rightarrow CH + H_2O$$
 (10)

$$CH_2 + O \rightarrow CH + OH$$
 (11)

$$CH_2 + H \rightarrow CH + H_2 \tag{12}$$

The formation of CO via reaction 6 explains why the yield vs C_2H_2 concentration curve passes through a maximum at relatively low C_2H_2 concentration (Figure 1). At higher concentrations one moves into a range of lower temperatures where reaction 5 is the dominating primary decomposition process, the dissociation of water and acetylene becoming less important. Reaction 5 has the lowest activation energy among all the primary pyrolysis processes. For this reason and also for the bimolecular nature of this reaction, it should become faster than reaction 4 at higher acetylene concentrations and become the most important primary decomposition reaction.

The reaction of OH with C_2H_2 according to eq 9 leads to ketene. However, the formation of CO has also been postulated¹⁹ via the reaction

$$OH + C_2H_2 \rightarrow CH_3 + CO \tag{13}$$

a methyl radical being formed, too. This reaction explains why methane is such an important product (Figure 4), as the CH₃ radical may pick up a hydrogen atom. C_2H_4 may be formed in the reaction of methyl radicals:

$$2CH_3 \rightarrow C_2H_4 + H_2 \tag{14}$$

At low acetylene concentrations, the H_2 yield is greater by a factor of about 2 than the yield of C_2H_2 consumption (Figure 1). H_2 can be formed in dilute solutions by the combination of H atoms from the decomposition of water or via the reaction

$$H + H_2 O \rightarrow H_2 + OH \tag{15}$$

In the presence of rather little acetylene, the H_2 yield is increased substantially (Figure 1). This is not due to hydrogen coming from acetylene molecules as the experiments with C2D2 showed that almost no D₂ was formed at these low concentrations. Small amounts of hydrogen peroxide could still be detected at low acetylene concentrations, which indicates that oxidizing species, such as OH radicals and oxygen atoms, were not completely scavenged by C_2H_2 . The increase in H_2 yield is attributed to the scavenging of O and OH which in the absence of C_2H_2 decrease the hydrogen yield by reactions with H or H_2 .

Isotopic studies with C_2D_2 have revealed the concentration ranges where the water-initiated reactions play a role, and where the bimolecular pyrolysis reaction 5 begins (Figure 2). D_2 is the dominant product at acetylene concentrations above 2×10^{-3} M, where the yield of H_2 drops to zero. The D_2 formation is attributed to direct pyrolysis of C_2D_2 .

Formaldehyde and acetaldehyde may be formed from CH₃ and C_2H_5 radicals:

$$CH_3 + O \rightarrow CH_2O + H \tag{16}$$

$$C_2H_5 + O \rightarrow CH_2O + H \tag{17}$$

Formaldehyde may also be formed by insertion of CH radicals into water molecules:20

$$CH + H_2O \rightarrow CH_2OH \rightarrow HCHO + H$$
 (18)

Ketene from reaction 9 may be hydrolyzed to acetic acid

$$CH_2 = C = 0 + H_2 O \rightarrow CH_3 COOH$$
(19)

and HCHO oxidized to formic acid:

$$HCHO + O \rightarrow HCOOH$$
(20)

 C_3 and C_4 Hydrocarbons. Propyne and allene form in yields about a factor of 10 less than methane and ethylene, whereas propene and propane form in yields lower still (Figure 5). Propyne and allene are probably in equilibrium and formed by the reactions:21

$$CH_2 + C_2H_2 \rightarrow C_3H_3 + H \tag{21}$$

$$C_3H_3 + RH \rightarrow C_3H_4 + R \tag{22}$$

$$CH_3 \rightarrow CH_2 \rightarrow CH_2 = C = CH_2$$
 (23)

Butadiene, diacetylene, and vinylacetylene have been identified. There exists a group of intensely absorbing compounds that have absorption bands at 200, 214, 224, 245, 260, 273, and 295 nm (Figure 6 and 7). These volatile compounds, when left in the solution, react to form nonpurgeable derivatives that absorb the scatter light (Figures 7b and 13). These compounds have not been identified, but their banded structures suggest mixed polyenesynes. For example, the 245-nm band of Figure 6 is the same as the 244-nm band of R--(CH=CH)--(C= \overline{C})₂--(CH=CH)--R with $\epsilon = 23\,000 \text{ M}^{-1} \text{ cm}^{-1}$. The 295-nm band is close to the 294-nm band of R-(CH=CH)₂-(C=C)₂-R with ϵ = 31 000 M⁻¹ cm⁻¹.²²

Products of Greater C Atom Number. The similarity of the products with those reported in combustion studies provides excellent evidence that the sonolysis of acetylene generates compounds that are similar if not identical with those found in flames and shock tubes.23

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The main precursor of the products that contain a greater number of C atoms is possibly C_4H_3 formed in reaction 5. It can react according to

$$C_4H_3 + M \rightarrow C_4H_2 + H + M \tag{24}$$

the activation energy being 59.7 kcal/mol.^{18a} Diacetylene, C₄H₂, is formed in this reaction. It is a very reactive species through which many higher hydrocarbon products including soot are possibly produced. C_4H_2 is also formed in a reaction of C_2H (see eq 4):^{18d}

$$C_2H_2 + C_2H \rightarrow C_4H_2 + H \tag{25}$$

Diacetylene can also react with the OH radical:^{18d}

$$C_4H_2 + OH \rightarrow C_3H_2 + HCO$$
(26)

The sequence of reactions 25 and 26 plays an important role in C_2H_2 combustion. HCO may be a precursor of formaldehyde. C_3H_2 is an unsaturated carbene which could also be the precursor of many products of higher C atom number.

The relative proportion of products in the C_5-C_7 range is strongly dependent on the C_2H_2 concentration. In the 0.46 mM solution of Figure 8 the nonaromatic C_5 and C_6 hydrocarbons form a greater portion relative to the aromatic compounds than in the 0.94 and 3.72 mM C₂H₂ solutions. These nonaromatic compounds have the compositions C₅H₄, C₅H₆, C₆H₂, C₆H₄, C₆H₆, and C₇H₈ and consist of di- and triacetylenes as well as mixed olefin-acetylenes. These compounds may be identical with those responsible for the absorption bands in Figures 6 and 7, extending from 200 to 300 nm. Compounds of higher mass have been obtained from ether extracts of the irradiated solutions. Only the most abundant ones have been positively identified. Again the relative proportion of these products is a function of C_2H_2 concentration (Figure 9).

The fact that higher products with an even C atom number are found more frequently than those with an odd C atom number (Figure 11) indicates that polymerization and condensation reactions of an even number precursor, such as diacetylene, play a dominant role. The formation of diacetylene as the first intermediate to form solid carbon and hydrogen has already been discussed in the early shock tube work on soot formation.²⁴

The aromatic compounds benzene, styrene, phenylacetylene, indene, and naphthalene are prominent products of C₂H₂ sonolysis,

(24) Greene, E. F.; Taylor, R. L.; Patterson, W. L. J. Phys. Chem. 1958, 62, 238.

especially in the concentration range above 1 mM. In the sonolysis of aqueous benzene solutions (unpublished work) C_2H_2 is a very important product, so there is an interconversion of C_2H_2 and C_6H_6 , just as is reported in combustion.²⁵

Soot Formation. The absorption spectrum of very small soot particles resembles that of a black substance. It could be the spectrum of graphite particles. One therefore may conclude that the pyrolysis at the highest temperatures, i.e., lowest C₂H₂ concentrations, leads partly to complete stripping off of all hydrogen atoms in acetylene. Carbon formation has been attributed to the reaction²⁶

$$CH + H \rightarrow C + H_{2}$$
 (27)

The pathways to soot formation have been treated in the combustion literature.^{18c,23c,27} Polycyclic hydrocarbons are considered to be a major component of soot. And soot is defined as the fraction of carbon accumulated in species larger than coronene.^{23a} Although the mechanism of acetylene pyrolysis remains unchanged in an oxidative environment, combustion soot is considered primarily to consist of hydrogen and carbon, although oxygen is reported in some soot. The sonolytically produced soot contains about 1 oxygen atom per 5 carbon atoms.

Up until now we have mentioned only free-radical reactions to explain the formation of various products. It should, however, be remembered that ion-molecule reactions can occur under comparable conditions, i.e., in flames and shock tube experiments.²⁸ Ionic reactions, which often are faster by orders of magnitude than radical reactions, become possible when chemiionization processes occur between radicals and atoms, such as

$$CH + O \rightarrow CHO^+ + e^-$$
(28)

the CHO⁺ ion initiating various reactions with neutral molecules including the polymerization of C_2H_2 .

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