Identification of Chemi-Ions Formed by Reactions of Deuterated Fuels in the Reflected Shock Zone

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Dilute mixtures of various fuels with and without oxygen were analyzed dynamically from the reflected shock zone by time-of-flight mass spectrometry to test for the presence of chemi-ions. The identity of the major chemi-ion species and the amounts produced depended upon the fuel/O_2 ratio, temperature, observation time, and the cleanliness of the shock tube–mass spectrometer system. Chemi-ions were readily observed in oxidative mixtures of acetylene, ethylene, benzene, and acetaldehyde. Deuterated compounds of these fuels were employed to demonstrate the absence of chemi-ions in oxygen-free mixtures. It follows that the radical–molecule mechanism for soot formation is dominant in pyrolytic reaction systems.

Introduction

The question of the relative contributions of ionic and radical reactions to the soot formation process has been examined extensively. There is abundant evidence for the existence of chemi-ions in flames, and it has been argued that chemi-ions play a key role in the sequence of steps leading to polyaromatic species and eventually to soot.[1] A recent study of chemi-ionization in fuel-rich acetylene flames[2] supports previous work which reported that $C_3H_3^+$ is the dominant ion. However, $C_3H_3^+$ formation emanates from a sequence of ion–molecule reactions involving the primary chemi-ion HCO^+ which in turn is formed from reactions of CH in the ground state[3] and electronically excited states[4,5] with oxygen atom. Rate constants for ion–molecule reactions have been measured by the ion cyclotron resonance technique[6] and Fourier transform ion cyclotron resonance mass spectrometry.[7] Chemi-ions have been observed in the reflected shock zone of fuel–oxygen mixtures; their identities and reaction profiles have been recorded by time-of-flight (TOF) spectrometry.[8,9] In rich mixtures of C_2H_2–O_2[8] and C_2H_4–O_2,[9] $C_3H_3^+$ was reported to be the dominant ion. Ion–molecule studies on $C_3H_3^+$ have revealed that the linear isomer is more reactive than the cyclic form.[6] Δ_fH of the cyclopropenylium isomer is about 256 kcal/mol. Recent theoretical calculations place Δ_fH of the linear isomer 28 kcal/mol above the cyclic form.[10]

Shock tubes utilizing the laser extinction technique have been used to characterize the soot-forming tendencies of fuels in the absence of oxygen.[11-14] The shock tube has a decided advantage over flame studies since the fuel/O_2 ratio may be varied from totally rich to totally lean and a wide temperature and pressure range is accessible. The method of carbon atom balance revealed mass deficiencies between the initial amounts of various fuels decomposing in the absence of oxygen and the total gaseous product yield. These studies using the shock tube–TOF[15,16] and the single-pulse shock tube[17] techniques attributed the "missing" mass to soot formation. Reaction mechanisms have been proposed to describe the reaction sequence by which polyaromatic hydrocarbons are formed from the products and intermediates present in simple fuel decompositions[18] and from oxygen-free mixtures of fuels.[19] These modeling efforts involve exclusively radical–molecule reactions and do not include any ion–molecule reactions.

The major question addressed herein pertains to the existence of chemi-ions in oxygen-free reaction systems. A previous shock tube study reported the measurement of ion current in 100% C_2H_4 from 900 to 1800 K.[20] Since chemi-ions have relatively high values for their heats of formation, it is difficult to construct a sensible scheme for their production in the absence of exothermic reactions. In the experiments described herein, a shock tube is coupled to a TOF in order to conduct a systematic search for the identities of any chemi-ions formed in oxygen-free mixtures. The various mixture compositions selected are similar to those employed in previous studies.[11-17]

Experimental Section

The apparatus and the operating procedure have been described previously.[21] The gas heated in the reflected shock zone flows through a reentrant nozzle into the ion source. The sample may be ionized by pulsed electron bombardment, or in the case of dynamic analysis of chemi-ions, the filament current is turned off. Thus, by comparing beam-on with beam-off mass spectra, the chemi-ion mass peaks may be readily identified. A further check on the validity of the chemi-ion signals is provided by the option of placing a positive 4.7-V bias on a grid located between the nozzle and the ionization region.

The following fuels were tested for chemi-ions: ethylene (Matheson); acetylene (Matheson); benzene (Baker, analyzed reagent grade); ethylene-d_4 (Cambridge Isotope Laboratories, 99%); acetaldehyde (Aldrich, 99%); acetaldehyde-d_4 (ICN Biomedicals, Inc., 99%); benzene-d_6 (Aldrich, 99%). Oxidative fuel mixtures were prepared with oxygen (Air Products and Chemicals, Inc.). All fuel gases were purified by bulb-to-bulb distillations, analyzed mass spectrometrically, and diluted with research grade neon (Matheson, 99.999%).

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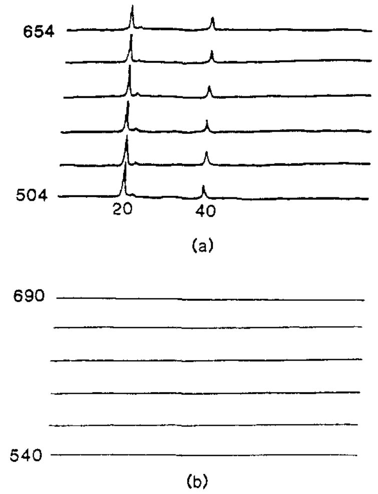

Figure 1. Appearance of mass spectra under "clean" conditions. Spacing between spectra is 30 μs, and observation time increases from lowest to highest line in Figures 1–3 and 5. (a) Mixture of 99% Ne–1% Ar at 1928 K, lowest spectral line at 504 μs, beam on. (b) Same mixture except at 2249 K, lowest spectral line at 540 μs, beam off.

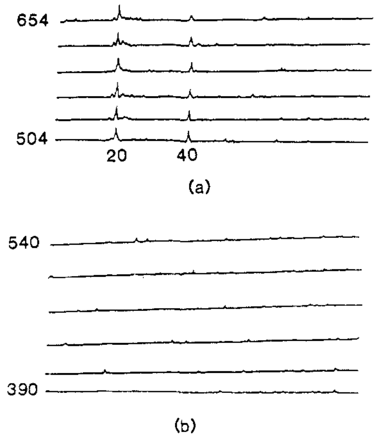

Figure 2. Appearance of mass spectra under "dirty" conditions. (a) Mixture of 99% Ne–1% Ar at 1992 K, lowest spectral line at 504 μs, beam on. (b) Same mixture except at 2234 K, lowest spectral line at 390 μs, beam off.

The entire vacuum system was monitored constantly for real and virtual leak rates to ensure that impurity levels were minimal. Typical test mixture pressures were initially 5.1 Torr. The diaphragm was ruptured routinely within 1 min of filling the shock tube.

In order to assess the cleanliness of the shock tube and TOF ion source, an inert gas mixture of Ne–1% Ar (Matheson, 99.999%) was shocked periodically. These tests were performed with the electron beam on, which allowed the location of *m/e* 20, 22, and 40, and with the beam off. The mass spectra were recorded at 30-μs intervals; four Polaroid pictures were taken for each run comprising a total of 25–30 mass spectra during typical observation times of 700–800 μs. Delay circuitry allowed extension of the observation recording time. Tracings of the mass spectra of "clean" runs are shown in Figure 1a,b. After many shocks with fuel-containing mixtures, a layer of soot accumulated on the nozzle, the shock tube wall, and the ion source. Spurious mass peaks appeared as is evident in Figure 2a,b. Occasionally, during extremely "dirty" conditions, a large peak of *m/e* 39 appeared at high temperatures and long observation times. Upon cleaning the apparatus, the Ne–Ar diagnostic returned to that shown in Figure 1a,b. The data on fuel mixtures reported herein were obtained during "clean" conditions.

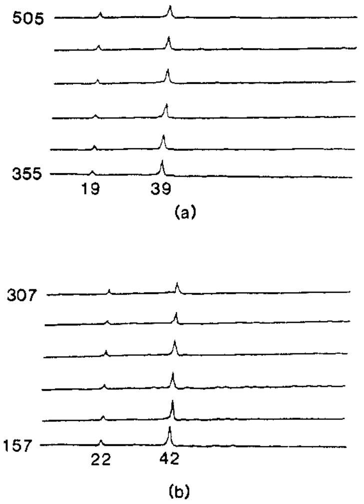

Figure 3. Chemi-ion formation in oxidative mixtures of ethylene, beam off. (a) 2% C_2H_4–3% O_2–95% Ne mixture at 1892 K, peak on left side is *m/e* 19 (H_3O^+) followed by *m/e* 39 ($C_3H_3^+$), lowest spectral line at 355 μs. (b) 2% C_2D_4–3% O_2–95% Ne mixture at 2004 K, peak on left side is *m/e* 22 (D_3O^+) followed by *m/e* 42 ($C_3D_3^+$), lowest spectral line at 157 μs.

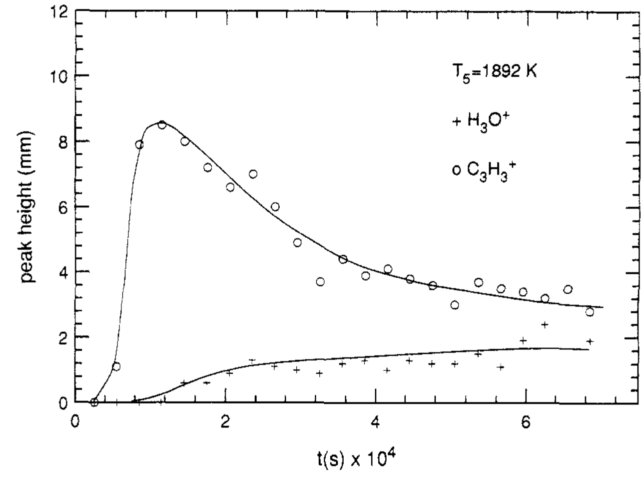

Figure 4. Reaction profile recorded for 2% C_2H_4–3% O_2 mixture at 1892 K: +, H_3O^+; o, $C_3H_3^+$.

Results and Discussion

Fuel–Oxygen Mixtures. In order to demonstrate that our apparatus yields valid chemi-ion data, a mixture of 2% C_2H_4–3% O_2 was investigated. Chemi-ions at *m/e* 19 (H_3O^+) and 39 ($C_3H_3^+$) were readily observed as displayed in Figure 3a in accordance with previous work.[9] A smaller peak height ascribed to $C_5H_3^+$ was also recorded. The chemi-ion profiles were dependent upon reaction time and temperature. A typical plot is displayed in Figure 4.

H_3O^+, $C_3H_3^+$, and traces of $C_5H_3^+$ were recorded from a 2% C_2H_2–3% O_2 mixture over a temperature range 1300–1700 K during observation times of 100–700 μs in agreement with previous work.[8]

A mixture of 1% C_6H_6–4.2% O_2 (which has the same C/H/O ratio employed in Bittner and Howard's flame study of C_6H_6[22]) reveal the chemi-ions $C_3H_3^+$, H_3O^+, and $C_6H_6^+$ from the beginning of the observation period and over the temperature range 1600–2000 K. The peak due to $C_6H_6^+$ disappeared within 100 μs. Chemi-ions were not detected at temperatures lower than 1500 K.

A mixture of 0.86% C_7H_8–4.2% O_2 at 1805 K produces $C_7H_7^+$ at early times followed by $C_3H_3^+$ and then H_3O^+ at 80 and 170 μs, respectively.

Oxygen-Free Nondeuterated Mixtures. A 3% C_2H_2 mixture was shocked over the temperature range of 1700–2500 K. Chemi-ions were not detected during observation periods up to

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900 μs. Similar negative results were obtained for a 5% C_2H_2 mixture.

For 3.0% C_2H_4–Ne mixtures, over the temperature range of 1700–2350 K and observation periods of 700 μs, chemi-ion signals were not recorded. But at higher temperatures, 2320–2730 K, signals at *m*/*e* 39 corresponding $C_3H_3^+$ appeared at late observation times. The appearance time depended inversely upon the reaction temperature; at 2332 K, $C_3H_3^+$ starts appearing at 900 μs while at 2520 K, $C_3H_3^+$ appeared at 732 μs.

Mixtures of 2.0% C_6H_6 and 3.0% CH_3CHO displayed like results. Chemi-ion signals were observed only at higher temperatures and late observation times. For instance, at 2100 K $C_3H_3^+$ appeared after 460 μs for 2.0% C_6H_6–Ne; in 3.0% CH_3CHO–Ne mixtures, $C_3H_3^+$ signals were recorded after 690 μs at 2370 K.

The chemi-ion results for the oxidative mixtures were expected and confirmed that the present apparatus was recording valid chemi-ion signals as evidenced by the following observations: the signals disappeared upon application of a positive bias; the species detected were fuel dependent; the appearance times were temperature dependent, and the profiles recorded during an experiment were reaction time dependent as shown in Figure 4.

The results from the oxygen-free mixtures were not understandable. Pyrolyses are endothermic reaction systems; the temperature of the reflected shock zone decreases during the decomposition. Since the reaction zone is energy deficient, it is difficult to propose a sensible set of reactions that will produce chemi-ions. The second problem is the finding that $C_3H_3^+$ is a secondary ion and is produced from reactions[1,2] involving the primary chemi-ion HCO^+.

$$HCO^+ + CH_2 \rightarrow CH_3^+ + CO \qquad (1)$$

$$CH_3^+ + C_2H_2 \rightarrow C_3H_3^+ + H_2 \qquad (2)$$

The direct chemi-ionization reaction involving electronically excited CH^*

$$CH^* + C_2H_2 \rightarrow C_3H_3^+ + e^- \qquad (3)$$

was shown not to be important in modeling rich acetylene flames.[2] Although CH^* is highly reactive[4,5] in forming HCO^+, the same effect is apparently diminished in $C_3H_3^+$ formation since the contribution of reaction 3 to the total ion density is minor.[23] Furthermore, the formation of CH^* is likely to involve oxygen and/or oxygen-containing radicals.[2] Therefore, removing O_2 from the system presents a severe obstacle to the production of CH^* and $C_3H_3^+$. This reasoning is the basis for the guide that three elements are required for chemi-ion formation: C, O, and H. If any one of the three is missing, chemi-ions will not be formed. However, Hanson et al.[24] measured CH radical concentrations in a shock tube by laser absorption and by emission at 431 nm ($A^2\Delta$–$X^2\pi$) in O_2-free mixtures of ethane and diketene, both highly diluted in argon. This suggests that there might be other routes to excited CH. Unfortunately, they were not equipped to measure ion currents.

Deuterated Fuel Mixtures. Since the *m*/*e* 39 signal appeared at late observation times and at high temperatures in oxygen-free systems albeit under "clean" conditions, a series of experiments using deuterated compounds were initiated to test further the validity of the TOF chemi-ion signals. Mixtures of C_2D_4 with and without O_2 were investigated. The results from a 2.0% C_2D_4–3.0% O_2–Ne mixture displayed the expected isotope shifts, H_3O^+ (*m*/*e* 19) → D_3O^+ (*m*/*e* 22) and $C_3H_3^+$ (*m*/*e* 39) → $C_3D_3^+$ (*m*/*e* 42) as shown in Figure 3b. Increasing the C_2D_4/O_2 ratio also produced expected results; the peak heights due to D_3O^+ and $C_3D_3^+$ decreased as shown in Figure 5a. An unexpected result is the appearance of *m*/*e* 39 at late observation times in Figure 5a.

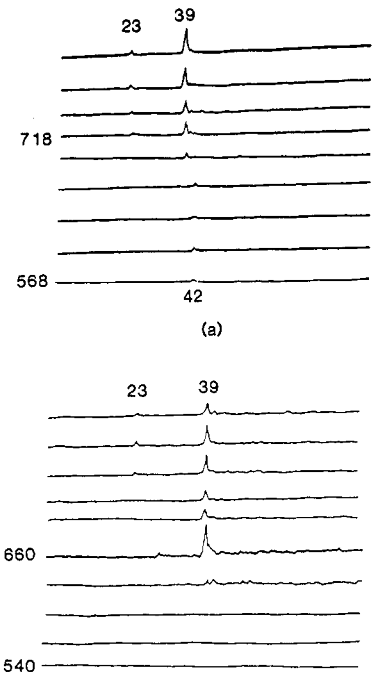

Figure 5. (a) Mixture of 3% C_2D_4–1% O_2–96% Ne at 2261 K, lowest spectral line at 568 μs, small peak at *m*/*e* 42 ($C_3D_3^+$) appears at early time followed by large peak at *m*/*e* 39 at 718 μs, beam off. (b) 3% C_2D_4–97% Ne mixture at 2283 K, lowest spectral line at 540 μs, large peak at *m*/*e* 39 appears at 660 μs, along with smaller peaks at *m*/*e* 23 and 41.

Furthermore, O_2-free mixtures of C_2D_4, CD_3CDO, and C_6D_6 each diluted in inert gas all revealed the absence of *m*/*e* 42 and the presence of *m*/*e* 39 at late observation times which was similar to that observed in the nondeuterated mixtures. The chemi-ion spectra from a 3.0% C_2D_4 mixture at 2283 K are displayed in Figure 5b. The peak at *m*/*e* 42 ($C_3D_3^+$) is missing, but large signals at *m*/*e* 39 are detected after 660 μs along with a very small peak at *m*/*e* 23. The mass spectral traces recorded after shock arrival and continuing to the onset of *m*/*e* 39 are "clean", resembling those in Figure 1b. Also appearing are small peaks at *m*/*e* 23 and 41. The ratio of *m*/*e* 39:41 is about 10.

Despite exhaustive efforts to discover and remove the late occurring *m*/*e* 39 peak by thorough cleaning of the shock tube, ultrasonic cleaning of the nozzle and ion source parts, and exclusion of any detergent containing potassium, the *m*/*e* 39 peak as shown in Figure 5a,b persists. We regard it as an artifact and use its appearance to mark the end of the observation period.

Conclusions

The chemi-ion mass spectra recorded by the shock tube–TOF apparatus in oxidative mixtures are understandable. Increasing the fuel/O_2 ratio from 2:3 to 3:1 in the ethylene mixture decreased markedly the chemi-ion signals. An oxygen-free mixture displayed an absence of chemi-ions during well-defined observation periods. Deuterated fuel mixtures demonstrated the validity of the chemi-ion signals during the observation period and identified the *m*/*e* 39 peak at late times as an artifact. The absence of chemi-ions in oxygen-free systems supports the dominance of the radical–molecule reaction mechanism with regard to soot formation in pyrolytic systems. The question concerning the relative contributions of radical–molecule and ion–molecule reactions in combustion mixtures is not answered here except to say that they are both operative.

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Registry No. C_2H_4, 74-85-1; C_6H_6, 71-43-2; C_2D_4, 683-73-8; C_6D_6, 1076-43-3; acetylene, 74-86-2; toluene, 108-88-3; acetaldehyde, 75-07-0; acetaldehyde-*d*$_4$, 1632-89-9.

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