J. Phys. Chem. A **2004,** *108,* 3403−3405

Speciation of C_6H_6 Isomers by Gas Chromatography-Matrix Isolation Fourier Transform Infrared Spectroscopy−Mass Spectrometry

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Received: October 31, 2003; In Final Form: January 30, 2004

Isomeric C_6H_6 species produced by high-pressure shock tube pyrolysis of 1,5-hexadiyne have been investigated by gas chromatography-matrix isolation FTIR spectroscopy-mass spectrometry. In addition to benzene (stable end product) and 1,5-hexadiyne (starting material), six isomeric C_6H_6 species have been identified on the basis of spectroscopic characteristics. The results are consistent with theoretical predictions of stable species that will be formed in the pyrolysis of 1,5-hexadiyne and key species have been positively identified for the first time.

Soot formation in combustion systems is believed to begin by recombination of hydrocarbon radicals followed by isomerization of the recombinant species. These processes result in the formation of small aromatic species that subsequently undergo further addition of radical species resulting in molecular growth and eventually producing soot particles. Formation of the first aromatic ring, benzene, is of particular interest.

One of the dominant reaction pathways leading to benzene involves the recombination of two propargyl (C_3H_3) radicals. This process can produce any of three linear C_6H_6 species, one of which is 1,5-hexadiyne. Theoretical and experimental investigations[1−7] indicate that 1,5-hexadiyne can undergo a series of isomerizations passing through a number of stable species, ultimately resulting in formation of benzene. As part of an extensive study of this process,[8] we have investigated the nature of all of the stable isomeric C_6H_6 species produced by high pressure, single pulse shock tube (HPST) pyrolysis of 1,5-hexadiyne using integrated GC-matrix isolation FTIR-MS (GC-miFTIR-MS). Conventional GC-MS analyses have shown that these isomeric species are nearly impossible to positively identify on the basis of their mass spectra alone without authentic standards. GC−mi-FTIR−MS, however, allows simultaneous collection of both MS and FTIR data for nanogram quantities of individual chromatographic eluants. The results obtained from these analyses permit confident speciation of all products observed in the pyrolysis of 1,5-hexadiyne. These spectra, the associated structures, and the results of density functional theory calculations for the identified species are reported here; a detailed discussion of the shock tube work and the interpretation of the kinetic data is presented elsewhere.[8]

The high pressure shock tube has been fully described in other publications[9,10] and only a brief description of the technique will be given here. For the kinetic investigations initial 1,5-hexadiyne concentrations were 50−60 ppm. To obtain the spectra reported here, the initial 1,5-hexadiyne concentration was raised to 300 ppm. Careful checks were made to ensure that increasing the fuel concentration did not introduce additional species in the spectra and that the relative proportions of the respective peaks on the chromatogram were similar to those seen in the kinetic studies.

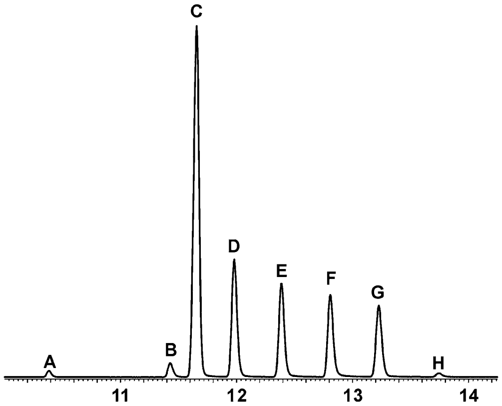

Figure 1. Total ion chromatogram illustrating the observed distribution of products obtained by shock-tube pyrolysis of 1,5-hexadiyne. $T = 1064$ K, $P = 550$ bar, reaction time = 1.2 ms.

Samples (around 1000 psi) are taken through the end wall of the shock tube into stainless steel vessels that are internally electropolished. These vessels were stored at 50 °C prior to transfer to Argonne from UIC, and it was confirmed that the samples could be stored for several days without degradation and that when the sample arrived at Argonne the chromatograms obtained at Argonne were consistent with those observed at UIC; i.e., sample integrity was preserved. The sample was prepared for injection into the GC−mi-FTIR−MS by condensing the contents of the gas sample vessel in a capped, vented (hypodermic needle) vial held in an acetone/dry ice bath. The vial was warmed to room temperature and placed in an autosampler on the GC-mi-FTIR-MS for normal headspace sampling.

MS and matrix isolation FTIR data were collected using a ClearIR integrated GC−mi-FTIR−MS. The instrument consists of a conventional GC-MS (Agilent 6890/5973) coupled with a

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10.1021/jp037311r CCC: $27.50

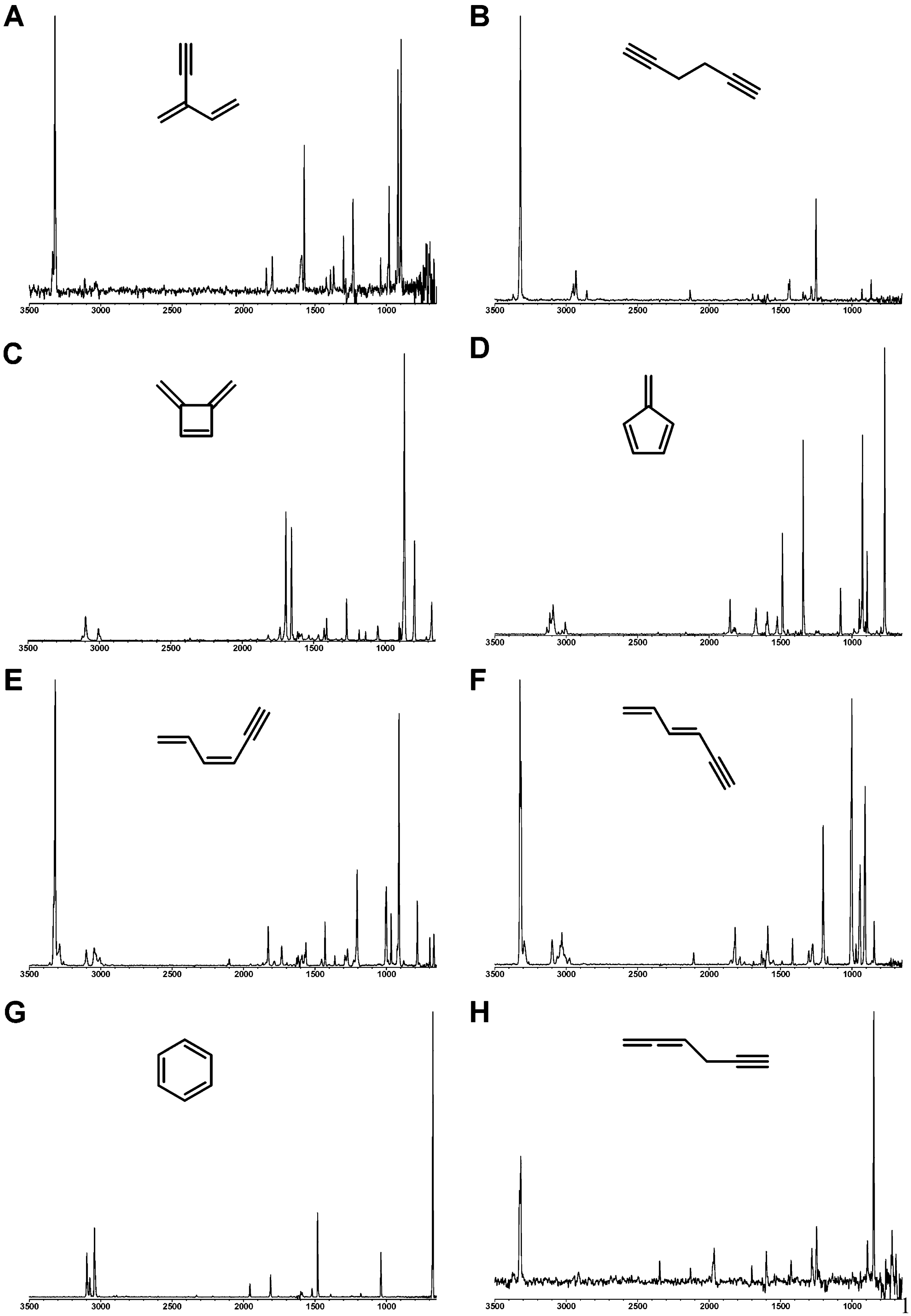

Figure 2. Matrix isolation FTIR spectra and assigned structures for isomeric C_6H_6 species observed from shock-tube pyrolysis of 1,5-hexadiyne (compound B).

TABLE 1

		ref
A	2-ethynyl-1,3-butadiene	11
B	1,5-hexadiyne	*a*
C	3,4-dimethylenecyclobutene	12
D	fulvene	13, 14
E	1,3-hexadien-5-yne (*Z*)	15
F	1,3-hexadien-5-yne (*E*)	15
G	benzene	*a*
H	propargylallene	16

[a] Authentic standard available.

Nicolet FTIR via a matrix isolation cell. GC carrier gas is doped with ∼2% Ar and the column effluent is split ∼70% to the matrix isolation cell, ∼30% to MS. The Ar matrix, with entrained analytes is collected at 9−10 K on a highly polished rotating gold cylinder, giving a time-resolved record of the eluants from which FTIR spectra can be obtained after the GC run is completed, thereby permitting multiple spectra to be recorded and averaged, a feature that is particularly valuable for trace species analysis. FTIR spectra are collected by positioning the matrix into the focal point of an FTIR microscope attached to the spectrometer with the simultaneously recorded total ion chromatogram, TIC, being used to identify the portion of the matrix to probe. Separation of individual eluants was achieved using a 60 m ZB-5 capillary GC column programmed from 30 to 60 °C at 1 °C/min.

The TIC obtained from analysis of the post shock gas from the shock-tube pyrolysis of 1,5-hexadiyne ($T = 1064$ K, $P = 550$ bar, reaction time = 1.2 ms) is illustrated in Figure 1. Eight species (A−H) are observed in these data. The mass spectra for each of the peaks in the TIC are available in the Supporting Information, and though differences exist between these spectra, they are not particularly useful for structural assignment but are used by the GC-mi-FTIR software for determining which segments of the argon matrix are to be examined by FTIR. Matrix isolation FTIR spectra and assignments for all eluants are illustrated in Figure 2. Compounds B and G are readily unambiguously identified by comparison with authentic standards as 1,5-hexadiyne and benzene, respectively, and spectroscopic data confirm these assignments. For the remaining eluants authentic standards are not readily available and these have been assigned from matrix isolation FTIR data by (i) interpretation, (ii) comparison with literature data (see Table 1), and (iii) comparison of experimental spectra with theoretical data calculated using DFT (B3LYP/6-31G*) (see Supporting Information).

The observed distribution of products is consistent with the results of theoretical studies of propargyl recombination reactions and subsequent isomerization pathways leading to the formation of benzene.[1] Of particular interest are species E and F, which are consistent with a route to benzene from propargyl radicals that does not involve the formation of fulvene. The relative concentrations of E and F are in accord with a recent theoretical paper by Miller and Klippenstein[1] that reexamined the potential energy surface for propargyl radical recombination. The observation of E and F is also consistent with work by Hopf and Muso[16] on 1,3,-hexadiyne-5-yne isomerization at 275 °C. 1,3-Hexadien-5-yne, not resolved into cis and trans forms, was observed in work by Alkemade and Homann[5] and is probably one of two unidentified species in a recent study by Shafir et al.[7] This is the first time the cis and trans isomers have been resolved and positively identified in a kinetic study.

Acknowledgment. K.B.A. and L.B.H. gratefully acknowledge the support of the US Department of Energy under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under contract number W-31-109-ENG-38. K.B. and co-workers at UIC gratefully acknowledge the support of the National Science Foundation under contract CTS 0109053.

Supporting Information Available: MS data and vibrational spectra data. This material is available free of charge via the Internet at http://pubs.acs.org.

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