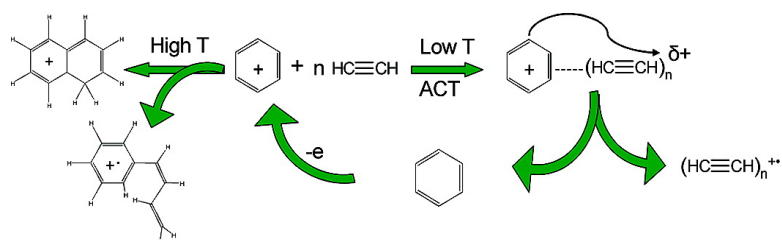


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J. Am. Chem. Soc., **2008**, 130 (39), 12848-12849 • DOI: 10.1021/ja803282c • Publication Date (Web): 09 September 2008

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Formation of Complex Organics from Acetylene Catalyzed by Ionized Benzene

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Received May 2, 2008; E-mail: mselshal@vcu.edu

Astronomical observations show > 100 organic molecules, including acetylene and benzene, are present in interstellar clouds, molecular clouds, solar nebulae, and envelopes expelled by evolved stars.^{1,2} Gas phase ion–molecule and intracluster reactions and catalysis on dust particles are among the most important synthetic pathways for formation of complex molecules in outer space. The wide range of temperature and pressure conditions in outer space environments allows diverse and unique chemistry to take place.^{1–4} These processes can lead to complex organics, clustering, and polymerization that produce nucleation centers for the formation of grains.^{1,2}

We reported evidence identifying the efficient formation of benzene ions within ionized acetylene clusters $(C_2H_2)^{+}_n$ with $n = 3–60$.⁵ Acetylene and benzene play a major role in the growth of complex organics made of hundreds of carbon atoms that could be responsible for the unidentified IR bands (UIBs).^{2,3} Here, we report new reactions of the benzene radical cation with acetylene from 120 to 680 K, showing acetylene undergoes sequential additions onto the benzene cation with two different mechanisms operating at low and high temperatures.

We studied the reactions of the benzene ion with acetylene using the mass-selected ion mobility (drift cell) technique (Figure S1).⁵ In the experiments, benzene cations ($C_6H_6^{+}$ or $C_6D_6^{+}$), generated by electron impact ionization (EI, 50–75 eV) of the clusters formed by supersonic beam expansion of a benzene (2%)/helium mixture, are mass-selected and injected into a drift cell containing pure acetylene vapor at well-defined pressures and temperatures. Residence times of the various ions are measured by monitoring the signals corresponding to each ion as a function of time after injection into the cell. Residence time can be varied by changing the voltage gradient in the cell. The reactant and product ions exiting the cell are analyzed and detected using a second quadrupole MS. Time-resolved studies allow identification of primary and secondary reaction products and measurement of rate coefficients.

Under ordinary conditions at 300 K, the benzene cation does not react with acetylene (Figure 1b) in agreement with previous work.⁶ At low temperatures (123 K, Figure 1a) clustering of several acetylene molecules onto the benzene cation is observed forming the products $C_6D_6^{+}(C_2H_2)_n$, with $n = 1–7$. A weak series corresponding to $(C_2H_2)_n^{+}$ with $n \geq 6$ to $n = 10$ is also observed. Because of the higher ionization energy (IE) of acetylene (11.4 eV) vs that of benzene (9.2 eV), no charge transfer (CT) within the $C_6D_6^{+}(C_2H_2)_n$ clusters is energetically possible.⁷ The generation of the $(C_2H_2)_n^{+}$ species with $n \geq 6$ can be explained by Associative Charge Transfer (ACT) reactions observed in the benzene⁺/propene system.⁸ Acetylene molecules bind noncovalently to $C_6D_6^{+}$, and partial charge transfer from the ion activates an acetylene molecule for addition polymerization with other associated acetylene molecules. Since the acetylene trimer ion, $(C_2H_2)_3^{+}$, has a structure similar to that of the benzene cation, the ACT process can generate the benzene cation from the associated acetylene molecules.

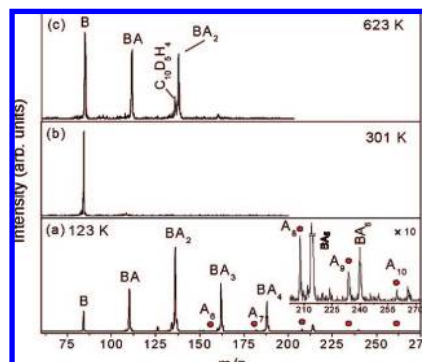
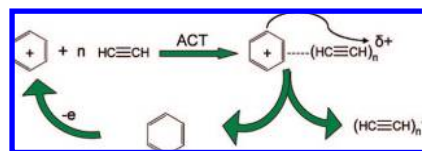


Figure 1. Mass spectra obtained following the injection of $C_6D_6^{+}$ (B) into drift cell containing purified acetylene (A) at cell pressures of (a) 0.35, (b) 0.42, and (c) 0.73 Torr.

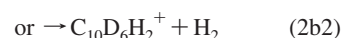
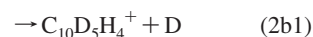
Scheme 1



For clusters containing few acetylene molecules such as $C_6D_6^{+}(C_2H_2)_3$, less charge will reside on acetylene which may not be sufficient to induce cyclization of the acetylene trimer, and we do not observe a $C_6H_6^{+}$ product ion. For larger clusters partial CT may be assisted by the stabilizing effect resulting from the formation of covalent bonds in the adduct ions making the overall process thermodynamically favorable. Similar to benzene⁺/propene,⁸ the polymerized adducts can have lower IEs than benzene (e.g., the cyclic acetylene polymer $(C_2H_2)_6 = C_{12}H_{12} = 1,5,9$ -cyclododecatriyne, IE = 9.2 eV or alkynaphthalene isomers, IE < 8.5 eV) that can take up the charge and leave benzene neutral. The remaining benzene molecule can be reionized with ionizing radiation in space, and the overall process will amount to catalytic cyclization and/or polymerization of acetylene (Scheme 1).

By this mechanism at low temperatures the benzene cation can act as a catalyst to convert acetylene molecules into ionized acetylene polymer cations through the ACT activation process.

At higher temperatures we observed reactions (1) and (2) apparently leading to covalent adducts (Figure 1c).



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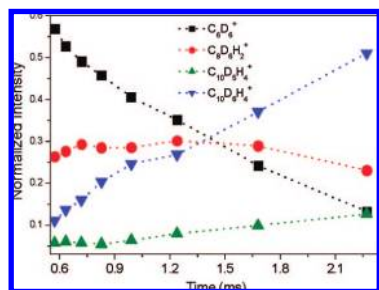


Figure 2. Integrated arrival time distributions of the reactant and product ions as a function of reaction time following the injection of $C_6D_6^+$ into drift cell containing 2.4 Torr acetylene at 623 K.

The evolution of the products with temperature is shown in Figure S2, and the time dependence product distributions at 673 K are demonstrated by changing the voltage gradient in the drift cell (Figure S3). The fact that these reactions are observed only at high temperatures suggests they have energy barriers. This is confirmed by measuring the overall rate for the disappearance of $C_6D_6^+$ (m/z 84), and the generation of the first adduct $C_8D_6H_2^+$ (m/z 110), the second adduct $C_{10}D_6H_4^+$ (m/z 136), and the elimination product $C_{10}D_5H_4^+$ (m/z 134) or $C_{10}D_6H_2^+$ (possibly D_6 -naphthalene $^{++}$) (Figure 2). The rate coefficient measured at 623 K is $3.7 (\pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ indicating a reaction efficiency of $\sim 10^{-5}$. This is consistent with SIFT results reported by Bohme et al. where the rate coefficient at ~ 300 K was estimated as $\leq 4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.⁶ The rate coefficient shows weak temperature dependence and no pressure dependence indicating the reaction is second-order. An Arrhenius plot obtained over a narrow temperature range (623–683 K) yields an activation energy of $3.5 \pm 1.5 \text{ kcal/mol}$ (Figure S4). In light of the slow reaction rate and the narrow temperature range imposed by experimental limitations, the measured activation energy should be considered an approximate value.

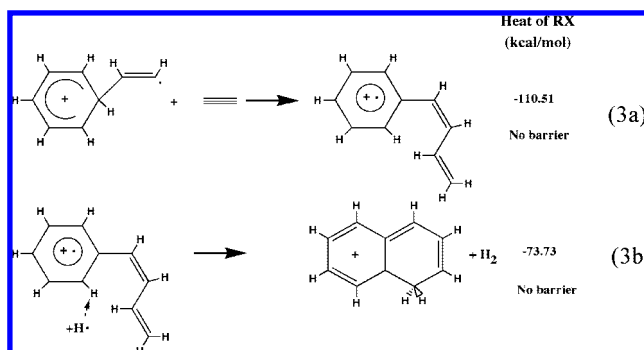
The first product (1) is likely a styrene-type cation while the second product (2a) could be an open-chain isomer, and the elimination product $C_{10}D_5H_4^+$ is likely to be a naphthalene-type (2b1) or the $C_{10}D_6H_2^+$, D_6 -naphthalene $^{++}$ cation itself (2b2).

For structural information on the first adduct, we measured the reduced mobility of the $C_6D_6^+C_2H_2$ ion in He. Mobility can provide structural characterization of the ion based on its collision integral (Ω) which depends on the geometric shape of the ion.^{5,9} The $C_6D_6^+C_2H_2$ ion was formed by EI ionization of the $C_6D_6-C_2H_2$ neutral clusters generated by supersonic beam expansion. The reduced mobility of the $C_6D_6^+C_2H_2$ ion was measured as $9.8 \pm 0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ corresponding to $\Omega = 53.1 \pm 3 \text{ \AA}^2$ (in He at 300 K). The calculated Ω values for several low energy $C_8D_8^+$ covalent isomers are 52–56 \AA^2 (Table S5). This suggests that the $C_6D_6^+C_2H_2$ ion has a covalent structure probably similar to the styrene-type cation.

For more information on the reaction mechanism, we calculated the energetics of the addition of a second acetylene to the $C_8H_8^+$ ion (3a). The geometries were optimized and the harmonic frequencies were computed using the B3LYP hybrid functional in conjunction with the 6-31G* basis sets,¹⁰ and the calculations were performed using Gaussian 03.¹¹

According to the calculations, the formation of the $C_{10}H_{10}^+$ ion by the addition of acetylene to the $C_8H_8^+$ ion (3a) is highly exothermic and does not involve a barrier. Also, the abstraction of H from the $C_{10}H_{10}^+$ ion by another H to form the naphthalene-type structure ($C_{10}H_9^+$) occurs in an exothermic and barrierless process.¹⁰ Although the D loss (2b) was observed in the absence of other radicals, the conditions in interstellar space and combustion

processes typically involve reactive radical species that can lead to exothermic and barrierless H abstraction reactions (3b).



Since the formation of $C_{10}D_6H_4^+$ (2a) is barrierless, the observed barrier (3.5 kcal/mol) can be attributed to the formation of $C_8D_6H_2^+$ (1) which is the most likely rate-limiting step.

We present here direct evidence for low temperature ACT reactions of acetylene onto the benzene cation that catalyzes the conversion of acetylene molecules into cyclic/polymerized ions and for high temperature addition/elimination reactions that lead to possible generation of naphthalene-type ions. Under low pressure, radiative association may be possible at interstellar temperatures of 10 K where the lifetime of the adducts is longer. Alternatively, these reactions can take place on benzene adsorbed on grain surfaces. The observed reactions can explain the formation of complex organics under a wide range of temperature and pressure in astrochemical environments.

Acknowledgment. We thank the NSF (CHE-0414613) and NASA (NNX07AU16G) for support and Dr. Sam Abrash (UR) for calculations.

Supporting Information Available: The temperature and time evolutions of the reaction products, Arrhenius plot, Table of relative energies, Ω s for $C_8D_8^+$ covalent isomers, and complete ref 11. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA803282C