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The feasible photoinduced growth of polycyclic aromatic hydrocarbons from cosmic benzene ice

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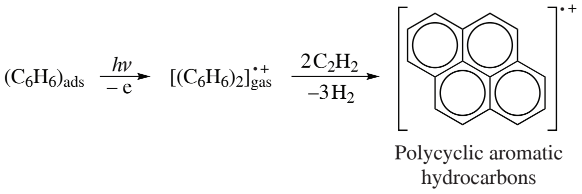
The reactive phenyl radical, electronically excited benzene monomer and dimer, their radical cations and low-atomic neutral hydrocarbons may be born *in situ via* the photodissociation/photoionization of a gaseous benzene monomer/dimer photo-desorbed from cosmic ice as well as *via* the subsequent dissociative recombination of the arisen benzene cations. The above-mentioned species can be the sources for the assembly into large polycyclic aromatic hydrocarbons, which can occur at very low temperatures and pressures in the interstellar medium.



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Dense interstellar molecular clouds are believed to be the main site for the formation of new stars and planetary systems. In addition to atomic and molecular hydrogen and dust grains of various compositions, the molecular clouds also contain the simplest inorganic and organic molecules, which, at low temperatures (<50 K), are mostly physically adsorbed on the cold surface of the dust grains, forming icy mantles.[1] The astronomical spectroscopy claims that large polycyclic aromatic hydrocarbon (PAH) molecules, including possible graphene nanostructures,[2] should be widespread in the interstellar medium (ISM), accounting for about 20% of carbon atoms in the Universe.[3] The brightest IR emission of gas-phase PAHs is observed in photodissociation regions (PDRs) localized at peripheral parts of dense molecular clouds illuminated by intense UV and VUV radiation of nearby massive stars. In the PDRs, the chemically active low-atomic hydrocarbons and free radicals are also observed.[4] Their list includes CCH, c-C_3H_2 and C_4H. The possible source of these species may be a photoinduced destruction of PAH molecules.[5] Small PAH molecules (including benzene C_6H_6) are assumed to be formed *via* the gas-phase free radical and ion-molecular reactions,[6,7] which are expected to occur in hot (>1000 K) circumstellar environments. However, the mechanism of the formation and growth of large PAH molecules is still questioned.

The photodissociation of benzene molecules and their derivatives (chlorobenzene and toluene) condensed on a cooled (~100 K) fused silica surface under pulsed KrF laser UV irradiation has been recently studied by mass spectrometry.[8–10] Besides the physically desorbed C_6H_6 molecules and their clusters $(C_6H_6)_n$ of various size, the release of hydrogen atoms and phenyl radicals, $C_6H_5^{\bullet}$, together with acetylene and ethylene molecules, from the substrate has demonstrated three dominant dissociative channels:

$$(C_6H_6)_{abs} + h\nu \longrightarrow C_6H_5^{\bullet} + H^{\bullet}, \tag{1}$$

$$(C_6H_6)_{abs} + h\nu \longrightarrow C_2H_2 + C_4H_4, \tag{2}$$

$$(C_6H_6)_{abs} + h\nu \longrightarrow C_2H_4 + C_4H_2, \tag{3}$$

when reactions (2) and (3) represent aromatic ring cleavage. The physical photodesorption plus the chemical photodissociation requires three photons of the KrF laser ($\lambda = 248$ nm) with the total energy 1.5 times higher than the ionization potential (IP) of the isolated C_6H_6 monomer (IP = 892 kJ mol^{-1}).

The benzene gas at low pressure was complementary studied in a molecular beam under irradiation by the same KrF laser line.[11] In addition to the reaction (1), two new pairs of fragments:

$$(C_6H_6)_{gas} + h\nu \longrightarrow (C_6H_4 + H_2) + (C_5H_3 + CH_3^{\bullet}) \tag{4}$$

were also observed due to the absorption of the single 248 nm photon, whereas two photons were required to release $C_3H_3^{\bullet}$:

$$(C_6H_6)_{gas} + 2h\nu \longrightarrow 2C_3H_3^{\bullet}. \tag{5}$$

The further photofragmentation of the C_6H_4 resulted in

$$C_6H_4 + h\nu \longrightarrow (C_6H_2 + H_2) + (C_4H_2 + C_2H_2). \tag{6}$$

Analysis of the laboratory experiments on laser-induced dissociation of benzene molecules both adsorbed and isolated in gas-phase elucidate a mechanism for the photoinduced formation and growth of PAH molecules in the interstellar medium from the electronically excited dimer $[(C_6H_6)_2]^*$ and its radical cation $[(C_6H_6)_2]^{\bullet+}$ as intermediate products.

To initiate any feasible chemical network at low temperatures and pressures occurring in the ISM, the physically adsorbed C_6H_6 molecules should apparently be transformed into both kinetically active and electronically excited states, preferably, in a radical and/or a radical cation form in a gas phase. Indeed, the phenyl radical $C_6H_5^{\bullet}$ can react with vinylacetylene to create a neutral naphthalene molecule and a hydrogen atom (the so-called HAVA mechanism[6]):

$$C_6H_5^{\bullet} + C_4H_4 \longrightarrow C_{10}H_8 + H^{\bullet}. \tag{7}$$

Benzene radical cations can form naphthalene radical cations and molecular hydrogen by subsequently adding two acetylene molecules in the course of the ion-neutral reaction:[7]

$$[C_6H_6]^{\bullet+} + C_2H_2 \longrightarrow [C_6H_6–C_2H_2]^{\bullet+}, \tag{8a}$$

$$[C_6H_6–C_2H_2]^{\bullet+} + C_2H_2 \longrightarrow [C_{10}H_8]^{\bullet+} + H_2. \tag{8b}$$

Both radical (7) and ion-neutral (8) reactions are exothermic ones, and their intermediate stages are accompanied by negative activation barriers.

In the present work, we start from the guess that high local density of benzene monomers, dimers and clusters can arise in the gas phase of ISM due to a physical photodesorption of benzene from dust icy mantles:

$$n(C_6H_6)_{\text{abs}} + h\nu \longrightarrow [(C_6H_6)_n]_{\text{gas}},\ n \geqslant 1. \tag{9}$$

Then, the gas-phase derived benzene particles may transfer to their excited electronic states and/or even ionized states adsorbing the second photon of the appropriate energy (above a dissociation threshold and/or IP value, respectively):

$$[(C_6H_6)_n]_{\text{gas}} + h\nu_1 \longrightarrow [(C_6H_6)_n]^{*}, \tag{10}$$

$$[(C_6H_6)_n]_{\text{gas}} + h\nu_2 \longrightarrow [(C_6H_6)_n]^{\bullet+} + e. \tag{11}$$

The chemically active low-atomic hydrocarbons, also needed for the large PAH photosynthesis, may be produced by destruction of hydrogenated amorphous carbon grains[12] and during the photodissociation of the electronically excited $(C_6H_6)_n^{*}$ neutral molecules, as well as because of the dissociative recombination of their radical cations $(C_6H_6)_n^{\bullet+}$:

$$(C_6H_6)_n^{\bullet+} + e \longrightarrow (C_6H_6)_n^{*} \longrightarrow (C_6H_6)_{n-1} + C_mH_l + C_{6-m}H_{6-l}. \tag{12}$$

Among clusters of various sizes n, the simplest benzene dimer $(C_6H_6)_2$ is of particular interest because it corresponds to the excimer molecules[13] that are loosely bound only in their ground state due to very weak van der Waals interactions, whereas the most excited electronic states of $(C_6H_6)_2$ are well bound. The radiative lifetime of the excited states of $(C_6H_6)_2$ is long enough[14] to interact efficiently with other highly reactive particles. It has been established that $(C_6H_6)_2$ can exist in the form of parallel stacked (PS), parallel displaced (PD), and T-shaped and tipped T-shaped configurations, the transition between which is accompanied by overcoming small energy barriers (Figure 1).

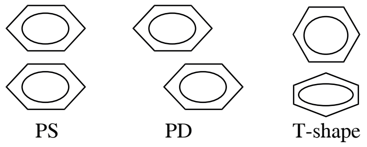

Figure 1 Stable geometric configurations of the benzene excimer molecule.

The next presumable stage of the photoinduced synthesis of PAHs molecules in the ISM gas phase is the formation of the $C_6H_5^{\bullet}$ radical from the electronically excited C_6H_6 monomer or dimer:

$$[C_6H_6]^{*} \longrightarrow C_6H_5^{\bullet} + H^{\bullet}, \tag{13}$$

$$[(C_6H_6)_2]^{*} \longrightarrow C_6H_6 + C_6H_5^{\bullet} + H^{\bullet}. \tag{14}$$

Both (13) and (14) monomolecular decay reactions are characterized by a decrease in the total internal energy of the systems and relatively small activation barriers. Moreover, a lack of aromatic character in the excited excimer provides a minimal energy barrier that is essentially lower than that for the monomer. Although both reactions lead to the formation of the $C_6H_5^{\bullet}$ radical, the further chemical role of the second benzene ring in reaction (14) is still unclear for the moment. So, it would be interesting to consider alternative reactions in which both benzene rings of the C_6H_6 excimer participate simultaneously in the subsequent formation of PAHs. For instance, the $[(C_6H_6)_2]^{\bullet+}$ radical cation [arisen *via* reaction (11)] can take place as an active particle as well. Despite the large IP of the $(C_6H_6)_2$ dimer, its radical cation is more energetically stable than the ionized monomer. The higher chemical stability of the radical cation is confirmed by the dissociation energy of the radical cation *versus* a neutral dimer[15] (64 *versus* 10 kJ mol^{-1}). Species $[(C_6H_6)_2]^{\bullet+}$ may enter into the bimolecular ion-neutral reactions with the acetylene molecules:

$$[(C_6H_6)_2]^{\bullet+} + C_2H_2 \longrightarrow [C_{14}H_{10}]^{\bullet+} + 2\,H_2, \tag{15}$$

$$[C_{14}H_{10}]^{\bullet+} + C_2H_2 \longrightarrow [C_{16}H_{10}]^{\bullet+} + H_2, \tag{16}$$

which greatly facilitate the PAH formation compared to those proposed in works[6,7] by reducing the number of successive chemical stages with the low activation barriers. Then, the produced PAH cations can transform into the corresponding neutral molecules due to the electron recombination $[\text{PAH}]^{+} + e \rightarrow \text{PAH}$, or take part in the further benzene network leading to the growth of the PAH cation size.

A quantum-chemistry treatment of reaction (15) results in a complex geometry transformation, including the stage of addition of an acetylene molecule to one of the benzene rings, accompanied by a change in the configuration from PS to PD-like structures and a subsequent transition to a T-shaped structure (see Figure 1). At the stage of formation of the bond between the second benzene ring and the C_2H_2 molecule, a transition from a T-shaped structure to a phenanthrene-like molecule and further isomerization into stable phenanthrene radical cation occurs (Figure 2).

As a summary, we proposed the multi-stage growth of the PAH molecules under low temperature ISM conditions *via* the electronically excited $(C_6H_6)_2$ excimer and its radical cation as an intermediate product of the photoinduced desorption of a cosmic benzene ice mantle. On an example of how a gas-phase

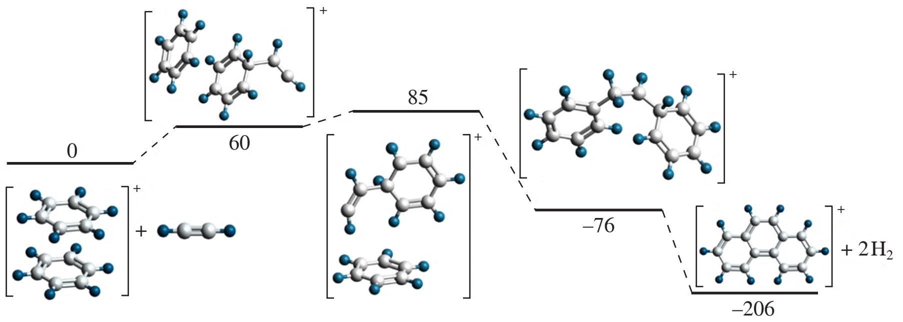

Figure 2 Energies (in kJ mol^{-1}) of the multistage formation of a phenanthrene radical cation from a benzene dimer radical cation and an acetylene molecule.

interaction of the $[(C_6H_6)]_2^{\bullet+}$ radical cation with the two acetylene molecules subsequently may lead to the ISM formation of the phenanthrene and pyrene cations avoiding the naphthalene one is shown. From an astrochemistry viewpoint, we do encourage to search for phenanthrene and pyrene in space since the last attempts of the naphthalene detection have not been successful.

In the present work, the electronic structure calculations were carried out using the ORCA software package.[16] Geometry optimization and single-point energy calculations were performed at the density functional theory level with the B3LYP/G hybrid functional and cc-pVTZ basis set (TD-DFT/B3LYP/G and cc-pVTZ level of theory in case of the benzene excimer excited electronic state). The PS geometry of the neutral $[(C_6H_6)_2]^*$ dimer in the first excited singlet state was chosen as the starting point for transformation (14). It was also tacitly assumed that the precursor $[C_6H_6]_2^{\bullet+}$ corresponds to the ground doublet state.

We intend to accomplish soon *ab initio* calculation of relevant rate constants for the low temperature domain to provide the astrochemists with the required facilities for modelling the photoinduced PAHs growing under the ISM conditions.

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