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Reaction between propargyl radical and 1,3-butadiene to form five to seven membered rings. Theoretical study

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ABSTRACT

Propargyl radical addition to 1,3-butadiene seems to be a promising channel to form 5-, 6-, and 7-membered rings. These are important steps in the growth of polycyclic aromatic hydrocarbons and soot platelets. The reaction mechanism, involving 97 intermediates and 115 transition structures, was studied by CBS-QB3 method (reported here) and density functional theory. All these structures were included in the subsequent RRKM study at different combustion pressures ($P = 30\text{--}0.01$ atm) and temperatures ($T = 1200\text{--}2100$ K). At $P = 30$ atm, open-chain products dominate in the whole range of temperatures. The importance of 5- and 6-membered rings rises with T , reaching a maximum in the T range 1500–1800 K. A more modest yield in 7-rings is present at $T = 1500$ K. At $P = 1$ atm, in the range 1200–1500 K, the yield in 5- and 6-rings dominate. 5- and 6-rings yields are about 41% at 1200 K (CBS-QB3 data). At $P = 0.1$ atm, 6-rings become the main products a 1000 K (35%), and then they decrease to 12% (2100 K) and 5-rings rise up to 44% (1200 K), and then decrease to 14% (2100 K). Open-chains are the main products at $T < 1000$ K and $T > 1500$ K. Then, at $P = 0.01$ atm, open-chain products are important below 900 K and above 1500 K, 6-rings are main contributors between 900 K and 1500 K. 6-Rings reach a maximum yield of 47% (1200 K) and 5-rings 44% (1200 K) and 7-rings 17% (900 K). The main products form through to H losses.

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1. Introduction

Particulate is a major contribution to the overall mass of atmospheric aerosol, and PAHs exhibit an ubiquitous presence. The impact of carbonaceous particulate [1,2] and polycyclic aromatic hydrocarbons (PAHs) on the environment is significant [3,4]. PAHs and amorphous carbon have been also identified in planetary atmospheres [5,6], in the envelopes of carbon-rich stars [6–9], and in the interstellar medium [10]. Graphene sheets and graphene nanoribbons are also interesting from a technological point of view [11–15]. PAHs are considered as soot precursors [16,17], by sharing the same origin [18–22]. We have studied theoretically the growth of an aromatic system adsorbed on a model soot platelet [23] and the feasibility of van der Waals associations and σ bond formation between PAH-like molecules as a function of temperature [24,25]. Formation of aromatics, in particular the first ring, and soot particles, have been reviewed and discussed by Richter and Howard in 2000 [26], and by Frenklach in 2002 [27]. The first ring formation has been studied both experimentally and computationally. Investigations have involved cyclopentene flame [28], 1,3-

butadiene + C_2 [29] and C_2H [30] reactions. Bittner and Howard have suggested benzene formation via the butadienyl plus ethyne reaction [31]. Similar mechanisms (vinyl addition to ethyne, or to but-1-ene-3-yne) has also been proposed by the same groups [32–35]. Jones et al. proposed barrierless reactions of ethynyl radicals with substituted 1,3-butadiene molecule to form benzene in the interstellar medium [36]. We have previously studied [37] the first growth steps of aromatic systems through radical-breeding mechanism proposed by Krestinin [38–40], and by radical addition of propargyl to But-1-ene-3-yne [41].

The propargyl has been considered a species capable of generating aromatics through self-addition: recombination of two propargyl radicals can be the dominant pathway to benzene and phenyl formation [35,42–47]. It plays also an important role in the hydrocarbon growth process: for instance, the kinetics of the reaction between the propargyl radical and ethyne [48,49] and butadiene [50,51] has been investigated both experimentally and theoretically. Similar reaction, the thermal decomposition of benzyl radical has been also computationally investigated [52].

Butadiene has also been considered important in combustion and astrochemistry and $C_2H + 1,3$ -butadiene reaction has also been recently investigated both theoretically and experimentally [30].

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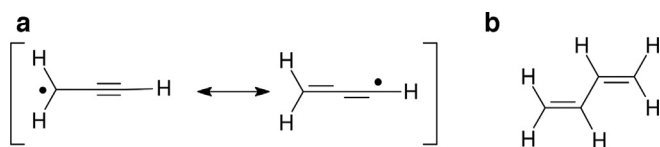


Chart 1. Propargyl radical (a) and 1,3-butadiene (b).

Both the propargyl radical and 1,3-butadiene have been measured in molar fractions x , in the ranges $x = 2\text{--}3 \times 10^{-3}$ and $8 \times 10^{-5}\text{--}6 \times 10^{-3}$, respectively [53–56]. They have been detected in premixed ethyne [53], benzene [54], toluene [55], or gasoline [56] flames. Propargyl radical has also been detected in molar fraction up to $x = 1 \times 10^{-3}$ or 2.4×10^{-4} in low-pressure flames [57,58].

In this paper we explore the possible formation of 4-, 5-, 6-, or 7-membered ring intermediates, which could be involved in subsequent PAH growth processes under combustion conditions. We simulate also the effect of four pressure values (30, 1, 0.1, and 0.01 atm): the highest pressure value could be related to internal combustion engine [59,60], while the low pressure data could be pertinent to low-pressure flames [58,61–67]. The reacting system examined is defined by the radical addition of propargyl to 1,3-butadiene (Chart 1).

2. Theoretical method

The high-level composite method CBS-QB3 [68,69] was used to study the energy hypersurface. All stationary points were determined by gradient procedures [70–74]. The nature of the minima and first order saddle points was confirmed by vibrational frequency analysis. The CBS-QB3 energies including zero point vibrational energies (ΔE_{ZPE}) are reported throughout in the text.

For comparison purpose, all the critical points were also optimized at the DFT [75] level, by using the M06-2X functional [76–79]. The cc-pVTZ basis set [80] was used in these optimizations. The optimizations were followed by cc-pVQZ [81] single-point energy calculations, to finally obtain M06-2X/CBS (complete basis set) energy estimates through the extrapolation formula put forward by Halkier et al. [82]. A validation of the computational level adopted in this study was done in a previous study [41]. The DFT energies are reported in the Supplementary Material.

Geometry optimizations and thermochemistry calculations were carried out by using the Gaussian 09 system of programs [83].

The Rice Ramsperger Kassel Marcus (RRKM) theory [84,85], was then used to obtain the distribution of the reaction products. In order to obtain these distributions as functions of time, RRKM and Master Equation calculations (RRKM-ME) were carried out by using the MultiWell program suite [86,87]. It allows us to calculate sum and densities of states, then assesses micro-canonical rate constants according to RRKM theory, and finally solves the master equation. Corrections for quantum tunneling were included for all hydrogen transfer reactions (not H dissociations) by incorporating the contributions for one-dimensional unsymmetrical Eckart barriers [88]. MultiWell stores densities and sums of states in double arrays: the lower part of the array consisted of 600 array elements, which range in energy from 0 to 2995 cm^{-1} . The higher energy part of the double array consisted of 600 elements ranging in energy from 0 to 150,000 cm^{-1} with an energy spacing of 250.4 cm^{-1} . The Lennard–Jones parameters necessary for the collision frequency calculations were assumed to be the same for all the structures, and were: $\sigma = 5.9 \text{ \AA}$, and $\epsilon/k_B = 410 \text{ K}$. Energy transfer was treated by assuming the exponential-down model for collision step-size distributions: $E_{\text{down}} = 2000 \text{ cm}^{-1}$, independent from the temperature [52,89]. This value was found to accurately reproduce the experimental falloff behavior for decomposition of benzyl

Table 1

Entrance channels: ΔE_{ZPE} (kcal mol $^{-1}$) barriers and adduct for the initial radical additions.

Channel	Barrier	Adduct
1	5.7	–22.1
2	11.1	–6.1
3	7.8	–23.1
4	13.6	–7.2

radical with a good agreement between calculations and experimental data across the temperature range 300–3000 K [52].

Low-frequency modes were treated as harmonic oscillators. Rate constants were calculated in the range 1200–2100 K. In this work, the number of stochastic trials was set to 10^7 , for 300 collisions. Simulations were carried out for combustion temperatures, at different pressures (of N_2 buffer gas), namely at $P = 0.01, 0.1, 1, \text{ and } 30 \text{ atm}$, to simulate combustions under low, normal, and high [59,60] pressure conditions. Low-pressure flames are often times preferred because of their nearly one dimensional structure and extended reaction zone [58,61–66].

3. Results and discussion

3.1. Potential energy surface

Four entrance channels are conceivable: they are due to the addition of each of the external carbons (1 and 3) of the delocalized propargyl radical (a) to the positions 1 and 2 of 1,3-butadiene (b) (Chart 1). The propargyl additions to the external carbons of 1,3-butadiene have lower energy barriers compared to the additions to the internal carbons (Table 1), and the their adducts are more stable because the possibility of delocalization of the unpaired electron. Making reference to the reagents, the adducts are located at –22.1 (1), –6.1 (2), –23.1 (3), –7.2 (4) kcal mol $^{-1}$, respectively.

The reaction pathways that start from 1–4 are shown in Schemes 1–3. Because of the complexity of the system, the reaction mechanism (entailing 97 intermediates and 115 transition structures) has been necessarily split in three schemes, and red numbers in each scheme indicate connections to another scheme. Due to the complexity of the reaction mechanism, the numeric labels will be often mentioned not sequentially. The bold lines in Scheme 1–3 show the favorable routes leading to the most abundant products: the complete list of all the products and their yields is reported in Section 2 of the Supplementary Material. Other connections between the intermediates could be conceivable, but we arbitrarily chose to neglect transition structures with energies above 20 kcal mol $^{-1}$ with respect to reactants.

The four initial adducts 1–4 are interconnected: 1 (Scheme 1) and 4 (Scheme 3) are connected through the intermediate 37. Initial adducts 2 and 3 through structure 39 (Scheme 2). All the above-mentioned steps involve fairly moderate energies (up to 12 kcal mol $^{-1}$ above the reactants). On the other hand, connection between 1–3 and 2–4 is much more indirect (1–12–38–50–3 and 2–39–3–40–4, respectively).

In Scheme 1 the most stable intermediate is the 7-ring 8 at –60.6 kcal mol $^{-1}$ with respect to the reactants. It is formed starting from 1, by cyclization (5), and then ring opening (6) followed by another cyclization (7). However, the H migration 7–8 involves a high barrier (21.0 kcal mol $^{-1}$) and in case the system was thermalized, this barrier could be demanding enough to make the formation of the 8 (and 9) difficult (see Section 3.2).

Other important structures are the 5-rings due to H losses 18, 30 and 31. These H losses have high barriers but they are irreversible and they possibly “pump away” from the C_7H_9 system.

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