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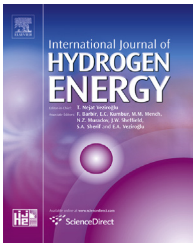

Formation of the first aromatic ring through the self-recombination of but-1-ene-3-yne with H-assistance in combustion

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ABSTRACT

The free H atom existing in flame plays vital role in combustion chemistry. As a continuation of our previous study, the possibility of forming the first aromatic ring via the self-recombination reaction of but-1-ene-3-yne (C_4H_4) with H-assistance was investigated in the present study. The potential energy surfaces were calculated with density functional theory and indicate that the $C_4H_4 + C_4H_4(+H)$ reaction can generate 6-membered ring, ring-opening and 5-membered ring structures. The zero point energies of the investigated molecules were obtained at CBS-QB3 level, and the reliability of energy calculation was checked with T1 diagnostic. The rate coefficients were calculated using conventional transition state theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory with solving master equation. By comparing the rate coefficients and branching ratio of product, we found that the CS10 + H, CS16, CS19 and CS38 are the dominant product of $C_4H_4 + C_4H_4(+H)$ reaction in the temperature range of 500–2500 K, and the formation of other products can be ignored. The self-dehydrogenation reaction is the essential step in the formation of the main product CS10 + H. Similar to H-transfer reactions, the self-dehydrogenation reactions are found to be sensitive to the molecular structure in terms of the energy barrier.

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Introduction

In the past three decades, great attention has been paid to the mechanism of polycyclic aromatic hydrocarbons (PAHs) evolution in flame [1–9]. It is widely accepted that the formation of the first aromatic ring (benzene and its derivatives) is a critical step of PAHs evolution and soot formation [10–13]. Specifically, the soot particle dynamics simulation is significantly depended on PAHs gas-phase kinetic, in which the growth of PAHs dominantly rests on the formation of the first aromatic ring [10,14–17].

Great efforts have been made to elucidate the mechanism of the formation of the first aromatic ring [18–23]. The addition reaction of C_4H_x and C_2H_2 molecules, the self-recombination reaction of two propargyl radicals (C_3H_3), and the cyclization reaction of C_6H_x molecule were regarded as the possible pathways to the formation of the first aromatic ring

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in flame [24–27]. In recent years, the role of C_4 species in the formation of the first ring was emphasized due to the high mole fraction in combustion, for example, the mole fraction of but-1-ene-3-yne (C_4H_4) can reach 2×10^{-3} in various premixed flame [28–30]. The possible pathways to the formation of the first ring in flame of aliphatic fuels were investigated by Cole et al. [31], who proposed that the dominant reaction pathway to benzene formation is 1,3-butadienyl(l-C_4H_5) + $C_2H_2 \rightarrow$ cyclohexadienyl $\rightarrow$ benzene + H in low pressure C_4H_6/O_2/Ar flame. By density functional theory (DFT) calculation, the recombination reaction of two C_4H_4 molecules was investigated in our previous study [32]. The results of potential energy surface (PES) shown that the styrene, phenylacetylene and 5-membered ring structure can be formed in $C_4H_4 + C_4H_4$ reaction, where the intramolecularly H-transfer reaction represents the rate-limiting step in some pathways due to the relative high energy barrier. On the other hand, it has reported that the redundant H atom can be abstracted with the help of the free H atom, and the energy barrier of this process is generally lower than 15 kcal/mol [33–35]. Furthermore, it has been experimentally confirmed that the free H atom existing in flame can directly participate in the formation of the first aromatic ring, and the isomerization of fulvene with H-assistance is the main pathway leading to benzene formation in a fuel-rich 1-hexene flame, while the reaction of $C_3H_3 + C_3H_3$ is only a minor contributor with 15% contribution [18]. In view of the works mentioned above, the pathways to the formation of the first ring through $C_4H_4 + C_4H_4$ reaction with H-assistance (namely $C_4H_4 + C_4H_4(+H)$ reaction) is valuable to be explored.

In this study, the possibility of forming the first aromatic ring through the $C_4H_4 + C_4H_4(+H)$ was investigated. For this purpose, the PES of $C_4H_4 + C_4H_4(+H)$ reaction were explored by using DFT method, followed by calculating the reaction rate coefficients using conventional transition state theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory with solving master equation.

Computational details

Quantum chemistry calculations

In this study, all local minimum and transition state structures were optimized using DFT/B3LYP method with 6-311 + G(d,p) basis set [36–39]. The vibrational frequencies of optimized structures were calculated with the same method, and were scaled by a factor of 0.967 [40] in subsequent kinetic calculation. The zero-point energies (ZPE) were obtained at CBS-QB3 level as suggested by Montgomety et al. [41] and Cavallotti et al. [42]. The reaction energy calculated with CBS-QB3 is close to the experimental data, and the mean deviation is as small as 1.0 kcal/mol [43]. Each transition state was firstly checked by inspecting the normal modes of the corresponding imaginary frequencies, and was reconfirmed through the intrinsic reaction coordinate (IRC) [44] calculation to ensure that the transition state was correctly connected with the reactant and product. Both close-shell and open-shell systems were appeared in $C_4H_4 + C_4H_4(+H)$ reaction, and were calculated with the restricted wave function and unrestricted wave function respectively. The CBS-QB3 method is a single-reference-based electron correlation procedure, therefore it is necessary to evaluate whether such a formalism is suitable, especially for open-shell systems [45]. To this end, T1 diagnostic was performed at CCSD(T)/6-311 + G(d,p) level [46] with DFT/B3LYP/6-311 + G(d,p) geometries. In this study, all quantum-chemical calculations were performed using the Gaussian 09 suite of programs [47].

Reaction rate coefficient calculations

In $C_4H_4 + C_4H_4(+H)$ system, both one-step bimolecular reaction and unimolecular thermal decomposition reaction will be involved in. For one-step bimolecular reaction, the RRKM theory combined with equilibrium constants will be used if the product is unimolecule. Specifically, the rate coefficients of the backward reaction were calculated at 1 atm by RRKM method, and rate coefficients of the forward reaction were the multiplier of corresponding equilibrium constants and the rate coefficients of the backward reaction. Otherwise, the rate coefficients of one-step bimolecular reaction were calculated with TST method. The rate coefficients of unimolecular thermal decomposition reaction were computed at 1 atm using a combined RRKM/Master Equation method via MultiWell suite of codes (MultiWell-2013.1) [48,49].

In MultiWell calculation, the density and sum of states were calculated by exact count with an energy grain size of 10 cm^{-1} for the first segment of the double array, and the maximum energy was set as 500,000 cm^{-1}. The exponential-down model with $<\Delta E_{down}> = 260\ cm^{-1}$ was employed to describe the collisional energy transfer [50]. The bath gas collider in this study is argon, which Lennard–Jones parameters of σ and ε/k_B equal to 3.47 Å and 114 K respectively [50]. The Lennard–Jones parameters of all investigated structures were assumed be the same as that of phenylacetylene with $\sigma = 5.72$ Å and $\varepsilon/k_B = 535.6$ K [51]. The internal rotations were treated as 1-D unsymmetrical hindered rotations [52,53], and the torsional potential energy and rotational constant as functions of the dihedral angle were obtained by scanning the relaxed PES at DFT B3LYP 6-31G level. Quantum tunneling corrections were performed with considering one-dimensional unsymmetrical Eckart barriers [54]. The translational and vibrational temperatures in MultiWell calculation were regarded to be equal. The number of stochastic trials was varied from 1×10^4 to 6×10^6 to keep the statistical fluctuations within 3%.

Results and discussion

Multireference diagnostics

The starting point should be the multireference diagnostics used to assess whether the single-determinant reference state CBS-QB3 method used in this study is suitable, since the PES of some H abstraction reactions present obvious multireference effects [55,56]. The T1 diagnostic proposed by Lee and Taylor [45] provides an approximate measure of mutltireference character in the wave function. A large T1 value indicates that a multireference electron correlation procedure is needed,

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