

Ring formation mechanism of C_4H_3 radical and acetylene in soot precursor formation

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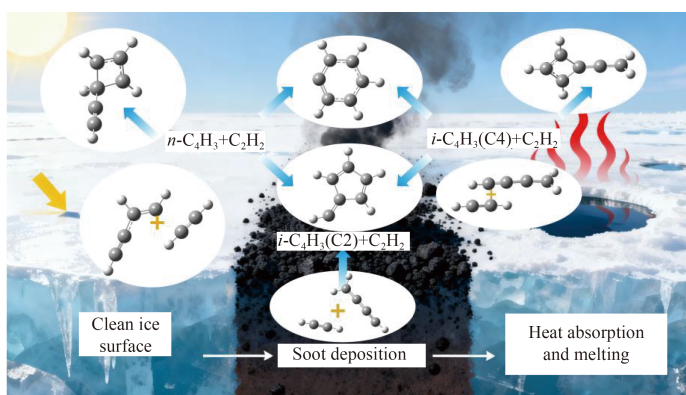
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Abstract: This study systematically investigates the cyclization reaction mechanisms between n - C_4H_3 (1-buten-3-yn-1-yl) and i - C_4H_3 (2-buten-3-yn-1-yl) radicals with acetylene (C_2H_2) using density functional theory (DFT) and transition state theory (TST). The results reveal that the reaction of n - C_4H_3 with acetylene proceeds via a radical chain mechanism through an addition-cyclization pathway, yielding phenyl (six-membered ring), fulvenyl (five-membered ring), and four-membered ring intermediates. The product formation rates follow the order:

fulvenyl (five-membered ring) > phenyl (six-membered ring) > four-membered ring. For i - C_4H_3 , the intermediate structures depend on the carbon position of i - C_4H_3 where acetylene addition occurs: addition at the C2 position predominantly generates fulvenyl (five-membered ring) as the primary product, whereas addition at the C4 position may lead to phenyl (six-membered ring), fulvenyl (five-membered ring), or four-membered ring intermediates, with the four-membered ring forming most rapidly and the six-membered ring the slowest. Theoretical analyses demonstrate that the selectivity of reaction pathways is primarily governed by structural differences between the isomers. This work provides atomic-scale insights into the cyclization processes between acetylene and C_4H_3 species, establishing a foundation for refining models of soot precursor formation.

Key words: density functional theory (DFT); transition state theory (TST); n - C_4H_3 ; i - C_4H_3 ; acetylene (C_2H_2); soot precursors



Soot refers to solid particles generated from incomplete combustion of fossil fuels in combustion systems such as gas turbines and internal combustion engines. It is primarily composed of carbon and often exists as polycyclic aromatic hydrocarbons (PAHs)^[1]. Macroscopically, soot typically appears as black smoke and is a type of pollutant emitted during combustion processes. Its particle size varies, with smaller particles remaining suspended in the atmosphere as aerosols. Soot not only reduces combustion efficiency^[2–3] but also poses health risks. Particularly significant is that black carbon deposition in the Arctic regions substantially reduces snow and ice albedo, accelerates glacier melting, and has profound impacts on global climate change^[4–5].

Furthermore, it is a major factor affecting atmospheric air quality^[6].

Benzene and polycyclic aromatic hydrocarbons (PAHs) are key precursors to soot formation. Under high-temperature conditions, hydrocarbon fuel decomposition generates numerous small molecular products with unsaturated structures, including neutral molecules and conjugated stable radicals such as C_2H_2 , C_3H_3 , C_4H_3 radical isomers, C_4H_4 and C_4H_5 radical isomers^[7]. These small molecules and radicals first form benzene through ring-formation reactions, followed by ring growth to generate stable polycyclic aromatic hydrocarbons (PAHs). The PAH molecules then undergo condensation and particle

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aggregation to form nascent soot^[8]. Georgievskii et al.^[9] suggested that C_3H_3 reacts with other radicals or stable small molecules to form precursors of polycyclic aromatic hydrocarbons, including fulvene and phenyl radicals. Senosiain et al.^[10] identified $C_2 + C_4$ reactions as significant benzene formation pathways, with $C_4H_3 + C_2H_2$ and $C_4H_5 + C_2H_2$ being primary pathways for forming C_6H_6 or C_6H_5 . Miller et al.^[11] found that the combination reaction of $C_3H_3 + C_3H_3$ yields fulvene ($C_5H_4CH_2$) containing a five-membered ring, thus revealing the $C_3 + C_3$ ring-formation pathway. Based on the first carbon ring formation mechanism, Zhang et al.^[12] used density functional theory (DFT) and transition state theory (TST) to calculate reaction pathways of propargyl (C_3H_3) and diacetylene (C_4H_2) forming the first carbon ring. The results showed that C_3H_3 and C_4H_2 could undergo addition reactions to form five-, six- and seven-membered rings. Trogolo et al.^[13] calculated the formation of five-, six- and seven-membered rings through the addition of 1,3-butadiene and C_3H_3 using the CBS-QB3 method, which enriched the thermodynamic and kinetic data for the first carbon ring formation.

Regarding the detection and identification of C_4H_3 radical isomers in flames, Yang et al.^[14] studied a benzene/oxygen/argon premixed flame using synchrotron radiation vacuum ultraviolet single-photon ionization method coupled with molecular beam mass spectrometry. They obtained photoionization efficiency (PIE) curves for radicals such as C_4H_3 and C_4H_5 in the range of 7.5 to 11.5 eV. By correlating experimental data with quantum chemical methods such as QCISD(T) and G3, they first confirmed the simultaneous presence of *i*- and *n*-isomers of the C_4H_3 radical in the flame. Mcenally et al.^[15] experimentally examined flames doped with diacetylene and vinylacetylene to verify whether the $C_4 + C_2$ reaction could be a significant pathway for aromatic hydrocarbon formation in fuel systems. Their observations indicated that in flames with abundant *n*- C_4H_3 , the addition reactions of *n*- C_4H_3 with acetylene and diacetylene could be important pathways for aromatic hydrocarbon formation. Acetylene (C_2H_2), as the simplest sp-hybridized hydrocarbon, was a key precursor for constructing carbon materials such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes. To refine the mechanism of the first carbon ring formation, this study adopted density functional theory (DFT) combined with transition state theory (TST) to calculate the potential energy profiles, reaction rate constants, and kinetic parameters for the reactions of *n*- C_4H_3 and *i*- C_4H_3 with acetylene.

1 Computational methods

1.1 Calculations based on density functional theory

This investigation implemented the DFT/B3LYP methodological framework. A tiered strategy guided basis set selection: initial geometry optimizations and transition

state calculations were conducted by the cost-effective 6-31G(d) basis set, followed by 6-311G(d,p) for improving precision. The geometric optimizations and vibrational frequency analysis were ultimately performed using the 6-311++G(d,p) basis set. The incorporation of diffuse functions enabled superior treatment of electron correlation effects and weak intermolecular weak interactions. Method validation and computational reliability were verified through systematic comparison with existing literature data, geometry optimizations and frequency analyses were performed for *n*- C_4H_3 , *i*- C_4H_3 , C_2H_2 , transition states, and products within the Gaussian^[16] program package using the 6-311++G(d,p) basis set, complemented by CBS-QB3 method for single-point energy calculations. The optimized reactants and products showed no imaginary frequencies, while identified transition states had one and only one imaginary frequency, which was consistent with the single imaginary frequency criterion of TST. To verify the transition states, Intrinsic Reaction Coordinate (IRC) calculations were performed on the transition states using the same basis set and computational method. The results confirmed reactants and products reside at local minima, transition states occupy first-order saddle points, and each properly connects corresponding reactants with products.

1.2 Transition state theory

Transition State Theory provides the fundamental framework for describing chemical reaction rates in this study. Its central premise maintains that all chemical transformations proceed through a highest-energy transition state configuration during conversion from reactants to products. The primary mathematical description resides in the Eyring equation, which enables theoretical calculation of chemical reaction rate constants.

Based on the form involving the Gibbs free energy of activation ($\Delta G^\ddagger$):

$$k = \frac{k_b T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (1)$$

where k represents the reaction rate constant, k_b is the Boltzmann constant (1.380649×10^{-23} J/K), h is the Planck constant ($6.62607015 \times 10^{-34}$ J·s) and T is the absolute temperature (K). The terms $Q^\ddagger$, Q_A and Q_B correspond to molecular partition functions for the transition state, reactant A and reactant B, respectively. $\Delta G^\ddagger$ signifies the standard Gibbs free energy of activation (J/mol) and R is the ideal gas constant (8.314 J/(mol·K)).

1.3 Reaction rate constant calculation

This study determined reaction rate constants using KiSThelP^[17] and Gaussian software based on Transition State Theory. All calculated rate constants refer to the high-pressure limit values. The pre-exponential factor A , temperature exponent n , and activation energy E_a were

obtained by fitting the Arrhenius equation. Following frequency calculations at the B3LYP/6-311++G(d,p) level, energy values, vibrational frequencies, and molecular structure data were extracted from the Gaussian output files. Based on this information, KiSThelP was applied to obtain theoretical predictions of the benchmark gas-phase reaction rate constants. Generally, the empirical equation derived from the conventional TST method is adopted for this purpose:

$$k^{\text{TST}} = \sigma \frac{k_b T}{h} \frac{Q^{\text{TS}}(T)}{N_A Q^{\text{R}}(T)} e^{-\frac{V^\ddagger}{k_b T}} \quad (2)$$

In the equation above, σ represents the reaction path degeneracy, and N_A signifies Avogadro's constant (which cancels out for unimolecular reaction rate constants with units of s^{-1}). $V^\ddagger$ is the potential energy difference excluding zero-point vibrational energy. The terms (Q^{TS}) and (Q^{R}) denote the total partition functions for the transition state and the reactants, respectively. In rate constant calculations, the partition function incorporated the thermodynamic contributions from translational, rotational, and vibrational motions for all species (reactants and transition state). Consequently, the rate constants computed using the KiSThelP software inherently accounted for these effects, thus ensuring physical accuracy under high-temperature conditions. Comprehensive details concerning partition function treatment and rate constant derivation are available in reference^[18], and the complete computational methodology can be found in the KiSThelP software manual.

In KiSThelP, one-dimensional quantum mechanical effects were characterized using the transmission coefficient, expressed as $k^{\text{TST/T}}(T) = \chi(T) \times k^{\text{TST}}(T)$. This TST/T method introduced quantum tunneling corrections based on conventional TST. As an initial approximation, the Wigner correction method^[19] was applied, which relies solely on the imaginary frequency of the reaction mode to characterize the vibrational mode and quantifies its contribution as a multiplicative factor.

$$\chi(T) = 1 + \frac{1}{24} \left(\frac{h \text{Im} \nu^\ddagger}{k_b T} \right)^2 \quad (3)$$

where in $\text{Im} \nu^\ddagger$ denotes the magnitude (absolute value) of the imaginary frequency at the transition state.

To more accurately describe the relationship between the reaction rate constant k and temperature T and enhance predictive accuracy for reaction rates, the three-parameter Arrhenius equation^[20] was applied to calculate the rate constants over the temperature range of 300 to 4000 K. The equation is given as follows:

$$k = A T^n e^{-\frac{E_a}{RT}} \quad (4)$$

where A is the pre-exponential factor, n refers to the temperature exponent, and E_a denotes the activation energy.

For simplified kinetic expressions, the two-parameter Arrhenius formula was also used for rate constant fitting, which is expressed as follows:

$$k = A e^{-\frac{E_a}{RT}} \quad (5)$$

2 Reaction path analysis

2.1 Analysis of the reaction pathways between $n\text{-C}_4\text{H}_3$ and C_2H_2

The addition reaction mechanism of $n\text{-C}_4\text{H}_3$ with C_2H_2 was explored. Based on Gaussian calculations, the reactive site of the $n\text{-C}_4\text{H}_3$ radical was determined through analysis of its vibrational modes. The radical active center at the carbon 1 (C1) atom was selected for calculating the addition reaction pathways with the acetylene molecule. Molecular structures of $n\text{-C}_4\text{H}_3$ and $i\text{-C}_4\text{H}_3$ are presented in Figure 1, where TS denotes the transition state, and IM represents the intermediate. For potential energy surface calculations, the total energy was determined by combining single-point energy (SPE) and the zero-point energy (ZPE) correction, which is expressed as: $E(\text{total}) = E(\text{SPE}) + E(\text{ZPE})$.

As shown in Figure 2, DFT calculations reveal the reaction mechanism for acetylene addition to the radical site of $n\text{-C}_4\text{H}_3$. The acetylene molecule initially overcame an energy barrier of 2.99 kcal/mol to attack the C1 radical site of $n\text{-C}_4\text{H}_3$, forming intermediate IM1 with an exothermicity of 36.73 kcal/mol. This calculated barrier compares favorably with the value of 4.85 kcal/mol reported by Lorries et al.^[21] using B3LYP/6-31G(d)//G3B3 methodology, with the 1.86 kcal/mol difference. This is attributed to our implementation of basis sets incorporating diffuse and polarization functions that more accurately described electron distribution, particularly in high electron-density regions like multiple bonds, and thus the precision of both geometric optimization and energy calculations was improved. Subsequently, the newly formed C–C single bond in IM1 underwent a conformational transformation through a rotational transition state, absorbing 2.29 kcal/mol of energy to form intermediate IM2. IM2 is then converted to IM3 via C–H bond torsional motion with a rotation angle of 81.8°. Finally, IM3 proceeded through three competing cyclization pathways: forming a cyclobutadiene derivative via the four-membered ring transition state TS6 (energy barrier 33.4 kcal/mol), generating a fulvene structure through the five-membered ring transition state TS5 (energy barrier 4.2 kcal/mol), and constructing a benzene ring skeleton via the six-membered ring transition state TS4 (energy barrier 4.38 kcal/mol). The IRC analysis confirmed that the six-membered ring formation proceeded through multiple intermediates (IM1→IM2→IM3→TS4→IM4) without evidence of a concerted transition state for direct six-membered ring formation.

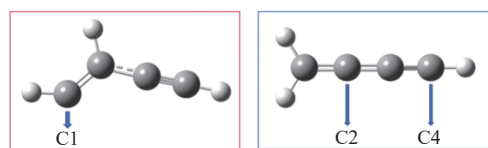


Fig. 1 Structures of $n\text{-C}_4\text{H}_3$ (left) and $i\text{-C}_4\text{H}_3$ (right)

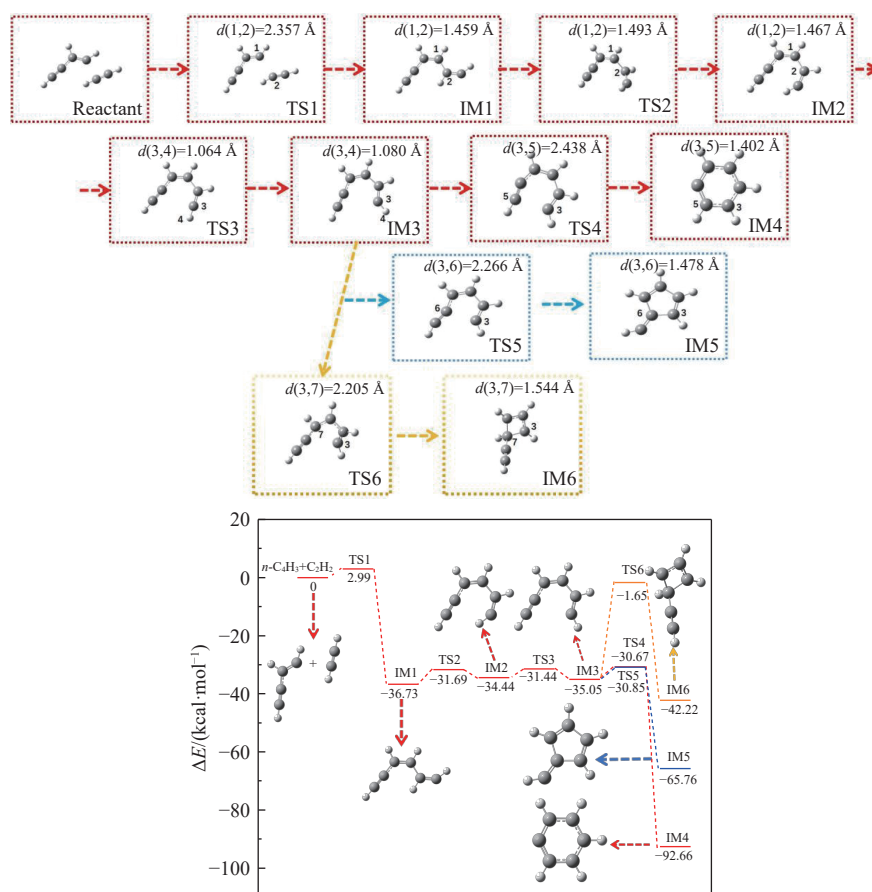


Fig. 2 Addition reaction pathways and potential energy surfaces for the n - C_4H_3 radical and C_2H_2 molecule based on DFT calculations

Although a theoretical possibility exists for concerted [4+2] cycloaddition of acetylene to the n - C_4H_3 conjugated system directly generating a phenyl radical, the initial reaction of the n - C_4H_3 radical preferentially followed the stepwise radical addition mechanism, which represents the commonly accepted pathway in the literature. The energy barriers for IM3 to IM4, IM5 and IM6 calculated in this work show differences of 1.15, 1.48 and 0.06 kcal/mol, respectively, compared to the corresponding values of 5.53, 2.72 and 33.34 kcal/mol reported in the reference [21].

2.2 Analysis of the reaction pathways between i - C_4H_3 and C_2H_2

Geometrical optimization and frequency analysis of the i - C_4H_3 radical were performed using DFT with the B3LYP/6-311++G(d,p) functional and basis set. It is revealed that the C_2H_2 molecule preferentially underwent addition reactions with the carbon atoms at the C2 and C4 positions of the i - C_4H_3 radical.

As illustrated in Figure 3, different from the study by Lorries et al.^[21], this work computed the addition-cyclization reaction pathway involving the C4 site of i - C_4H_3 and acetylene. The C_2H_2 molecule and the i - C_4H_3 radical first overcame an energy barrier of 11.02 kcal/mol to form intermediate IM7 *via* addition. However, computational results from Wang et al.^[22] at the B2PLYP-D3/6-

311++G(d,p), B2PLYP-D3/cc-pVTZ, B3LYP/6-311++G(d,p), B3LYP/cc-pVTZ, and B3LYP/cc-pV5Z levels reported a barrier of 14.59 kcal/mol for this step, which exceeded our value by 3.57 kcal/mol. Subsequently, the newly formed C–C single bond in IM7 underwent conformational rotation, generating intermediate IM8 *via* an endothermic process ($\Delta H = +2.41$ kcal/mol). IM8 then underwent intramolecular C–H bond rotation to adjust its spatial configuration, forming intermediate IM9 with a suitable orientation for subsequent cyclization. IM9 proceeded through competitive pathways to form four-membered, five-membered, and six-membered ring products, with corresponding transition state barriers of 20.65 (four-membered ring, TS12), 16.70 (five-membered ring, TS10) and 33.14 kcal/mol (six-membered ring, TS13), respectively. A 1,3-hydrogen migration occurred within the five-membered ring intermediate IM10 ($\Delta G^\ddagger = 54.14$ kcal/mol, TS11), which transferred a hydrogen atom to the meta-unsaturated carbon atom and yielded the fulvenyl intermediate IM11 with an extended conjugated system. Although this pathway produced a thermodynamically more stable product, its significantly elevated activation energy severely restricted the reaction. In contrast, the six-membered ring intermediate IM13 underwent a 1,2-hydrogen migration ($\Delta G^\ddagger = 23.32$ kcal/mol, TS14) to form the aromatic phenyl-structured IM14 *via* ortho-hydrogen transfer.

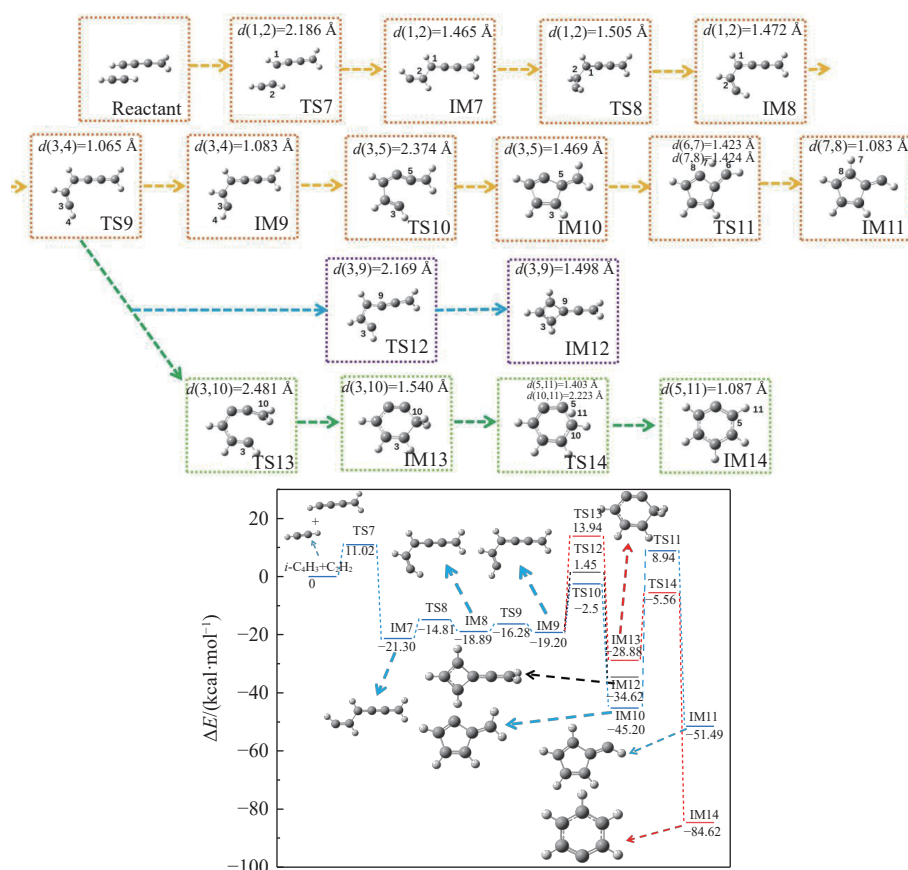


Fig. 3 Reaction pathway and potential energy surface for the addition of the i - C_4H_3 radical at the C4 position to the C_2H_2 molecule based on DFT calculations

As shown in Figure 4, an alternative reaction pathway involved the addition of the C_2H_2 molecule to the radical site at the C2 position of i - C_4H_3 . This step needs to surmount a 12.55 kcal/mol barrier to form intermediate IM15. The calculated barrier reported in reference [21] is 8.49 kcal/mol, which results in a difference of 4.06 kcal/mol between the computational results. In the subsequent step, IM15 underwent conformational isomerization to form IM16 by surmounting a barrier of 2.14 kcal/mol, which was consistent with typical rotational barriers for C–C single bonds. IM16 then experienced an intramolecular conformational adjustment induced by C–H bond rotation, and yielded IM17 through a low-barrier structural rearrangement driven by non-bonding interactions. The final step involved a concerted ring-closure reaction of IM17, which overcame an activation energy of 14.92 kcal/mol to form IM18, with the cyclization barrier differing from reference [21] by 1.29 kcal/mol. Subsequently, the transformation from IM18 to IM19 followed an identical pathway to that from IM10 to IM11.

3 Reaction rate analysis

3.1 Analysis of addition reaction rates for n - C_4H_3 (C1) and i - C_4H_3 (C2, C4) with C_2H_2

This study combined DFT with TST and the Wigner

tunneling correction (TST/W) method to calculate reaction rate constants. All calculations were performed at the B3LYP/6-311++G(d,p) level of theory, and applied a frequency scaling factor of 0.998 (based on Kanchanakunghui et al., 2021, Version 5)^[23]. Using KiSTheP software, geometric structures and vibrational frequency data of reactants and transition states were extracted from Gaussian output files to determine rate constants for addition reactions, ring-closure steps, and rate-determining elementary reactions. Compared to the temperature range of 300–3000 K reported in reference [20], this work extended the computational range for reaction rate constants to 300–4000 K. This expansion covered kinetic processes under extreme combustion conditions like those in high-temperature gas turbine combustion chambers, and provided the first reported kinetic predictions for the ultra-high temperature regime (>3000 K), as illustrated in Figures 5–7.

As shown in Figure 5, kinetic calculations revealed strong temperature dependence for the n - C_4H_3 (C1) addition reaction with acetylene, and thus exhibited exponential rate enhancement with increasing temperature. The low energy barrier of this reaction, consistent with prior theoretical analysis, indicated facile reaction proceeding. The results showed a reaction rate constant of $3.08 \times 10^9 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ at 300 K.

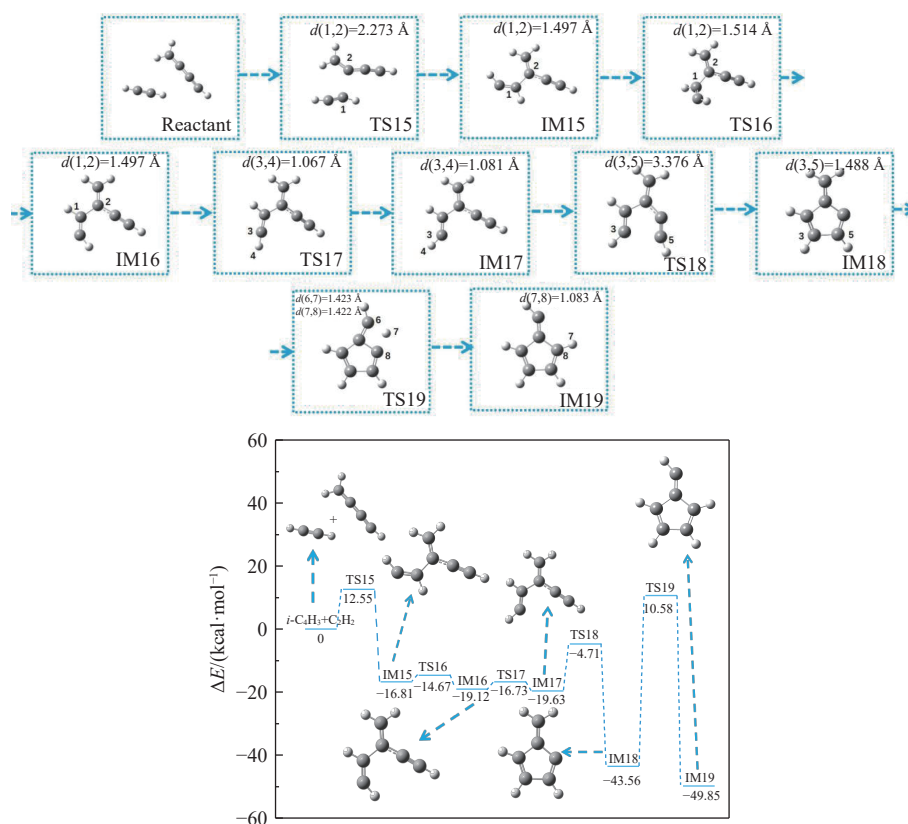


Fig. 4 Reaction pathway and potential energy surface for the addition of the $i\text{-C}_4\text{H}_3$ radical at the C2 position to the C_2H_2 molecule based on DFT calculations

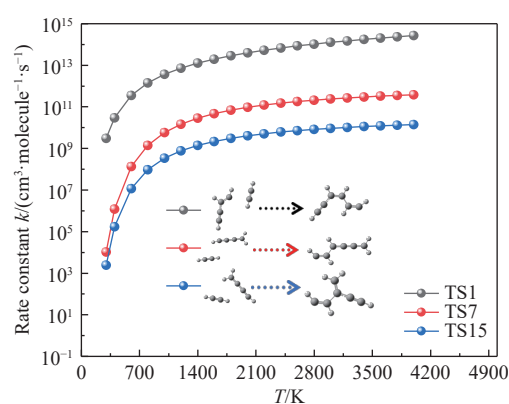


Fig. 5 Comparison of addition reaction rates of $n\text{-C}_4\text{H}_3$ (C1) and $i\text{-C}_4\text{H}_3$ (C2, C4) with C_2H_2

When the temperature increased to 1000, 2000 and 3000 K, the reaction rate constants reached 3.65×10^{12} , 3.98×10^{13} and $1.26 \times 10^{14} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively, which demonstrated a significant temperature effect of spanning five orders of magnitude. This confirmed the substantial promoting effect of high-temperature combustion environments on the formation of soot precursors. This temperature sensitivity also aligned with the Arrhenius-type dependence predicted by transition state theory.

A notable site sensitivity was observed for the addition reaction of acetylene to $i\text{-C}_4\text{H}_3$, with the carbon 4 site having 1–2 orders of magnitude faster than that at the carbon 2 site. The results show rates of $5.69 \times$

$10^9 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (C4) and $3.23 \times 10^8 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (C2) at 1000 K, which increased to 1.64×10^{11} and $6.62 \times 10^9 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively, at 2500 K. The molecular structure of $i\text{-C}_4\text{H}_3$ illustrated its conformation: the carbon 4 site experienced less steric hindrance than the carbon 2 site, resulting in a more favorable stereochemical orientation for the addition transition state and a correspondingly lower activation energy barrier (approximately 1.53 kcal/mol), which preferentially directed reaction flux towards the more accessible C4 position. This finding was consistent with the Hammond Postulate prediction regarding the influence of spatial effects on reaction path selectivity. Molecular dynamics simulations further indicated that differences in configurational entropy could also influence the competition between reaction channels.

3.2 Kinetic analysis of competitive multi-pathways in the ring-closure reaction system

As shown in Figure 6, investigation of $n\text{-C}_4\text{H}_3$ (C1) addition to acetylene revealed distinct ring-size selectivity in subsequent cyclization: the formation rate of the five-membered ring (fulvenyl) was the fastest, the four-membered ring formation was the slowest, and the six-membered ring (phenyl) formation rate was intermediate, indicating a clear preference for five-membered ring formation. These results were consistent with the experimental findings from reference [15], where doping

flames with diacetylene (C_4H_2 , a precursor to $n-C_4H_3$) led to a significant increase in aromatic hydrocarbon yields. However, the primary products were not benzene-based compounds but five-membered ring fulvene derivatives, whose mass spectrometric signal intensity showed a linear positive correlation with the doping concentration. Kinetic analysis of the temperature dependence suggested that at 300 K, the reaction rates for the five- and six-membered ring pathways exceeded that of the four-membered ring pathway by 21 orders of magnitude. When the temperature increased to 2500 K, the rate ratio between the five- and six-membered ring pathways and the four-membered ring pathway decreased to 2 orders of magnitude. The calculated transition state energy barriers indicated higher reactivity for the five- and six-membered ring pathways than for the four-membered ring pathway, with an advantage of over 29 kcal/mol compared to the four-membered ring path, consistent with observed kinetic trends in ring-size dependent temperature effects. Furthermore, this kinetic preference for five- and six-membered rings was in agreement with the ring strain effects described by Baldwin's Rules for ring closure^[24], where reduced ring strain corresponded to enhanced cyclization probability and lower-energy reaction pathways.

The selectivity for cyclic products in the reaction pathway involving the addition of acetylene to the C4 site of $i-C_4H_3$ exhibits substantial temperature dependence. Within the temperature range of 300–1800 K, the formation rate of the five-membered ring is higher than that of the four-membered ring, with the rate difference between them being approximately one order of magnitude.

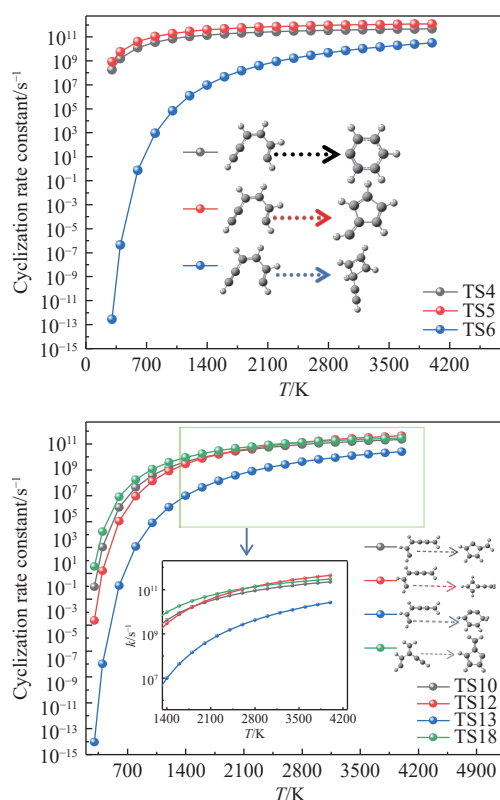


Fig. 6 Cyclization reaction rates for various pathways

However, at temperatures above 1800 K, the four-membered ring pathway becomes faster, owing to its higher temperature sensitivity (as reflected by a larger temperature exponent in the Arrhenius pre-exponential factor). Compared to the four- and five-membered rings, the six-membered ring transition state experiences significant steric hindrance, resulting in a formation rate nearly 12 orders of magnitude slower at 300 K. As the temperature increases (1000–3000 K), the difference in rate constants gradually narrows to 1–2 orders of magnitude. This indicates that while the influence of energy barrier differences diminishes at high temperatures, it still dominates the pathway selectivity in the low-to-medium temperature combustion range. The rate differences among the various cyclization pathways could span several orders of magnitude, and temperature could even lead to a crossover in pathway dominance (for example, the intersection observed around 1800 K for the $i-C_4H_3$ pathways), all of which highlight the critical importance of kinetic analysis for predicting the actual product distribution in combustion systems. The influence of ring strain (kinetic control) and entropy effects on ring-size selectivity changed with temperature: lower temperatures suppressed the higher-barrier six-membered ring pathway, while higher temperatures reduced activation energy disparities and moderated selectivity. These findings were consistent with the trend predicted by Baldwin's rules for ring closure regarding the effect of ring strain on transition state stability. For the reaction pathway involving acetylene addition to the C2 site, the rate constants at 300, 1000 and 3000 K were 3.40×10^1 , 1.12×10^9 and $1.58 \times 10^{11} \text{ s}^{-1}$, respectively. This represented a span of 10 orders of magnitude (10^1 – 10^{11} s^{-1}), with the reaction rate increasing exponentially with temperature.

3.3 Mechanistic analysis of the rate-determining steps in the reaction kinetics of various pathways

Based on DFT calculations, the cyclization reaction pathways of $n-C_4H_3$ and $i-C_4H_3$ with C_2H_2 were studied. Each pathway comprised multiple elementary reaction steps. According to the definition of the rate-determining step (RDS), the overall rate of a multi-step reaction is governed by the elementary step with the highest activation energy (i.e., the slowest step)^[25]. Theoretical calculations identified the respective RDS for each pathway as follows: Path A: IM1 $\rightarrow$ IM4, IM1 $\rightarrow$ IM5, IM1 $\rightarrow$ IM6; Path B: IM7 $\rightarrow$ IM11, IM7 $\rightarrow$ IM12, IM7 $\rightarrow$ IM13; Path C: IM18 $\rightarrow$ IM19. The calculation results are shown in Figure 7. In this study, due to the broad reaction temperature range (300 – 4000 K) and significant differences in energy barriers among the different reactions, the variation of reaction rates with temperature exhibited a complex trend. Furthermore, the rate constants showed a gradual plateauing with increasing temperature in the high-temperature regime. This phenomenon occurred because the influence of activation energy on the rate diminishes at elevated temperatures,

while the influences of factors such as entropy change and tunneling effects become progressively more significant.

In Path A, the calculated kinetic parameters for the initial $n\text{-C}_4\text{H}_3 + \text{C}_2\text{H}_2$ addition revealed a substantial temperature exponent ($n = 2.03$). It was indicated that the energy of $n\text{-C}_4\text{H}_3$ was approximately 13.66 kcal/mol higher than that of $i\text{-C}_4\text{H}_3$, suggesting that $n\text{-C}_4\text{H}_3$ is a structurally more rigid and thermodynamically less stable radical isomer. Its initial addition reaction with acetylene (via TS1) was a bimolecular process requiring highly oriented collisions, resulting in a highly ordered transition state and consequently a significant entropy penalty (i.e., a large negative activation entropy). In the Arrhenius equation, the large positive n value compensates for this entropic effect. The total rate for forming five- and six-membered rings (fulvenyl and phenyl) from the reaction of $n\text{-C}_4\text{H}_3$ (C1) with acetylene exceeded that for four-membered ring formation by approximately 14–15 orders of magnitude or more. This difference exhibits a distinct temperature dependence: at low temperature (300 K), the rate difference is 14–15 orders of magnitude, narrowing to 1–2 orders of magnitude in the high-temperature range (3000–4000 K).

On reaction Path B, the reaction between $i\text{-C}_4\text{H}_3$ (C4) and acetylene exhibited distinct ring-size selective kinetic behavior. DFT calculations revealed that the formation of the six-membered ring product requires overcoming a high activation energy due to significant steric hindrance in the transition state, arising from twisting of the conjugated carbon chain.

Consequently, at a low temperature of 300 K, the six-membered ring channel proceeded at a negligible rate ($k = 3.12 \times 10^{-45} \text{ s}^{-1}$), which lags behind the four-membered ring ($k = 1.02 \times 10^{-4} \text{ s}^{-1}$) and the five-membered ring ($k = 2.26 \times 10^{-10} \text{ s}^{-1}$) by 41 and 35 orders of magnitude, respectively. However, at a high temperature of 1500 K, the rate difference between the six-membered ring and the four-/five-membered rings narrowed to 6–8 orders of magnitude, which indicates a gradual reduction in disparity as temperature increases. In the reaction of $i\text{-C}_4\text{H}_3$ (C2) with acetylene, the hydrogen migration step leading to five-membered ring (fulvenyl) formation was highly sensitive to the energy barrier. Transition state analysis identified a substantial barrier of 54.14 kcal/mol for this process, resulting in a minimal rate constant ($k = 1.03 \times 10^{-28} \text{ s}^{-1}$). The rate increased exponentially through the medium-temperature range (1000–2000 K), reaching $1.41 \times 10^1 \text{ s}^{-1}$ at 1000 K and $3.32 \times 10^7 \text{ s}^{-1}$ at 2000 K. In the high-temperature dominant regime (3000–4000 K), the rate constant surpassed the $10^9\text{--}10^{10} \text{ s}^{-1}$ magnitude.

Regarding the experimental evidence supporting the computational results, this study primarily focused on elucidating the reaction mechanisms at the atomic and molecular level through quantum chemistry calculations and transition state theory. The fitted kinetic parameters are listed in Table 1 (three-parameter Arrhenius equation) and Table 2 (two-parameter Arrhenius equation).

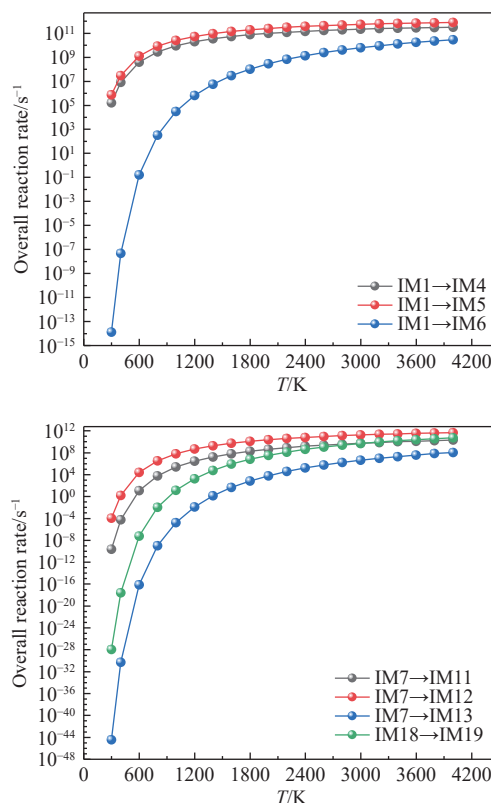


Fig. 7 Reaction rates for various pathways

Table 1 Kinetic parameter fitting for cyclization reactions of $n\text{-C}_4\text{H}_3/i\text{-C}_4\text{H}_3$ radicals with acetylene based on the three-parameter Arrhenius equation (temperature range: 300–4000 K)

	A	n	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$E/(\text{kcal}\cdot\text{mol}^{-1})$
TS1	2.059×10^7	2.03	16.16	3.87
TS2	3.791×10^{12}	0.05	27.78	6.65
TS3	1.091×10^{13}	0.19	12.43	2.97
TS4	6.925×10^{11}	0.03	20.71	4.95
TS5	8.427×10^{11}	0.11	18.42	4.41
TS6	3.997×10^{11}	0.20	140.86	33.70
TS7	1.513×10^{12}	0.01	46.26	11.07
TS8	4.848×10^{12}	0.06	27.62	6.61
TS9	8.736×10^{12}	0.18	13.30	3.18
TS10	7.418×10^{11}	0.08	69.30	16.58
TS11	2.602×10^{11}	0.66	230.90	55.24
TS12	1.30×10^{12}	0.18	86.62	20.72
TS13	4.003×10^{11}	0.17	137.79	32.96
TS14	9.850×10^{11}	0.26	97.16	23.24
TS15	6.159×10^{10}	−0.03	41.65	9.96
TS16	1.482×10^{12}	0.01	8.86	2.12
TS17	5.199×10^{12}	0.18	13.58	3.25
TS18	1.226×10^{12}	0.05	60.85	14.56
TS19	2.602×10^{11}	0.66	230.90	55.24

Table 2 Kinetic parameter fitting for cyclization reactions of n - C_4H_3 / i - C_4H_3 radicals with acetylene based on the two-parameter Arrhenius equation (temperature range: 300–4000 K)

	A	$E/(kJ \cdot mol^{-1})$	$E/(kcal \cdot mol^{-1})$
TS1	2.805×10^9	15.54	3.72
TS2	5.626×10^{12}	28.18	6.74
TS3	3.772×10^{13}	12.79	3.06
TS4	8.588×10^{11}	20.81	4.98
TS5	1.779×10^{12}	18.71	4.48
TS6	1.654×10^{12}	141.50	33.85
TS7	1.532×10^{12}	46.27	11.07
TS8	7.224×10^{12}	27.77	6.64
TS9	3.885×10^{13}	14.80	3.54
TS10	1.789×10^{12}	70.25	16.81
TS11	8.036×10^{13}	228.49	54.66
TS12	5.929×10^{12}	88.13	21.08
TS13	1.630×10^{12}	139.20	33.30
TS14	8.613×10^{12}	99.33	23.76
TS15	5.738×10^{10}	41.79	9.99
TS16	1.040×10^{12}	8.86	2.12
TS17	2.242×10^{13}	15.04	3.60
TS18	1.596×10^{12}	60.30	14.43
TS19	8.036×10^{13}	228.49	54.66

Although the present work is a theoretical investigation without direct experimental data, the main conclusions are consistent with experimental observations reported in the literature. Specifically, the finding that the n - C_4H_3 pathway predominantly led to five-membered ring (fulvene) formation aligns with experimental results from flame-doping studies by McEnally et al.^[15]. Additionally, the premise that both i - C_4H_3 and n - C_4H_3 isomers coexisted is directly supported by the experimental discovery of Yang et al.^[14] using synchrotron radiation vacuum ultraviolet photoionization technology.

4 Conclusions

This work systematically elucidated the ring-formation mechanisms of n - C_4H_3 and i - C_4H_3 radical isomers with acetylene (C_2H_2) and their regulatory effects on product selectivity, through integrated DFT and kinetic calculations. The main conclusions are as follows:

(1) The reaction of n - C_4H_3 at the C1 site with acetylene could form four-, five- and six-membered ring products. Kinetic studies indicated higher rate constants for the five-membered ring (fulvenyl) pathway, primarily due to its minimal ring-closure energy barrier (≈ 4.2 kcal/mol).

Although the benzene ring (six-membered) was thermodynamically more stable, its formation barrier (≈ 4.38 kcal/mol) was slightly higher than that of the five-membered ring pathway. The four-membered ring pathway exhibited the slowest rate due to its substantially higher energy barrier (≈ 33.4 kcal/mol). Consequently, under kinetically controlled combustion conditions, the five-membered ring product dominated.

(2) For i - C_4H_3 , site selectivity was related to steric effects for a fixed carbon atom count:

C4 site: This site exhibited the fastest addition rate. The cyclization product selectivity showed significant temperature dependence: the five-membered ring pathway dominated at low temperatures (<1800 K), while the four-membered ring pathway became faster at high temperatures (>1800 K) due to its higher temperature sensitivity. The six-membered ring pathway remained the slowest due to its extremely high ring-closure barrier (≈ 33.14 kcal/mol), although its relative disadvantage decreased at elevated temperatures.

C2 site: This site exhibited a slower addition rate. Its reaction mechanism differed from that at the C4 site, which favored direct formation of a five-membered ring intermediate *via* a concerted ring-closure step with a relatively lower barrier (≈ 14.92 kcal/mol).

(3) The five-membered ring structure (fulvenyl) presented significant kinetic advantages in both the n - C_4H_3 pathway and the C2 site pathway of i - C_4H_3 . This finding is consistent with experimental observations of fulvene species in combustion environments, and thus provides crucial quantum chemistry evidence and kinetic support for a potential “five-membered ring priority” growth route in initial soot particle formation.

(4) The reaction mechanisms, energy barriers, and temperature-dependent rate constants elucidated in this study, specifically, the universal kinetic preference for five-membered ring formation, the distinct site selectivity and fundamentally different mechanisms for i - C_4H_3 , and the temperature-induced reversal in ring-size selectivity for the C4 site pathway, provide a theoretical foundation for constructing and refining more accurate chemical kinetic models of soot precursor formation.

(5) The reaction path selectivity and kinetic parameters clarified at the atomic level in this work offer potential insights for understanding and controlling soot formation. Theoretical calculations suggest that manipulating the reaction microenvironment (e.g., temperature) for C_4H_3 isomers with acetylene could influence cyclization pathway selection, and thus modulate soot precursor evolution. Specifically, high-temperature conditions might promote the formation of less stable intermediates (e.g., four-membered rings) with limited growth potential.

Declaration of Competing Interest

The authors declare no conflict of interest.

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碳烟前驱体形成中 C_4H_3 自由基和乙炔成环机理

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摘 要: 本工作运用密度泛函理论(DFT)以及过渡态理论(TST), 对 *n*- C_4H_3 (1-丁烯基-3-炔)和 *i*- C_4H_3 (2-丁烯基-3-炔)与 C_2H_2 (乙炔)成环反应机理进行了系统的理论研究。对比了 *n*- C_4H_3 与 *i*- C_4H_3 异构体的成环路径差异, 结果表明, *n*- C_4H_3 与乙炔采用自由基链式反应方式结合, 以加成环化反应形成产物, 产物为苯基(六元环)、富烯基(五元环)和四元环中间体, 产物生成速率大小依次为: 富烯基(五元环)>苯基(六元环)>四元环; *i*- C_4H_3 与乙炔发生成环反应生成的中间体结构取决于

乙炔加到 $i-C_4H_3$ 的哪个碳原子上, 如果乙炔加到 $i-C_4H_3$ 的 2 号碳原子, 则得到主要产物富烯基 (五元环); 而加到 $i-C_4H_3$ 的 4 号碳原子, 则可能得到产物为苯基 (六元环)、富烯基 (五元环) 或四元环, 四元环最快生成, 六元环最慢。理论上阐明了反应路径选择性的原因主要是由于异构体结构的不同, 本研究从原子级层次解析了乙炔与 C_4H_3 物种成环的过程, 从而为进一步完善碳烟前驱体生成的模型打下了基础。

关键词: 密度泛函理论; 过渡态理论; $n-C_4H_3$; $i-C_4H_3$; 乙炔; 碳烟前驱体

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