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Pyrolysis and oxidation of benzene and cyclopentadiene by NO_x: a ReaxFF molecular dynamics study†

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Benzene (C₆H₆) and 1,3-cyclopentadiene (c-C₅H₆) are critical intermediate species in the combustion of fossil fuel and the formation of polycyclic aromatic hydrocarbons (PAHs). This study investigates the underlying mechanisms of pyrolysis and oxidation of C₆H₆ and c-C₅H₆ in the presence of O₂, NO and NO₂, respectively, under combustion conditions via ReaxFF molecular dynamics simulations. The size growth in the pyrolysis system is accompanied by an amorphous nature as well as an increase in the C/H ratio. In the oxidation systems, NO₂ is the most effective in the oxidation of both C₆H₆ and c-C₅H₆, followed by NO and O₂. In the presence of NO_x, O and N radicals generated in the high-temperature decomposition reactions of NO and NO₂ are actively involved in the addition and H-abstraction reactions of C₆H₆ and c-C₅H₆. Remarkably, the decomposition of NO₂ dramatically increases the number of O radicals in the system, which significantly accelerates the ring-opening of C₆H₆ and c-C₅H₆ by O-addition and forms linear-C₆H₆O and C₅H₆O species, respectively. Afterwards, the formation of -CH₂- by H-transfer plays an essential role in the decomposition of linear-C₆H₆O and -C₅H₆O. Reaction pathways of O and N radicals with C₆H₆ and c-C₅H₆ are reported in detail. The O and N-addition of C₆H₆ facilitate the decomposition to resonance-stabilized cyclopentadienyl radicals after the restructuring of the C-C bond.

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1. Introduction

Concerns about pollutant emissions together with the increasingly stringent emission specification worldwide have motivated research in clean combustion technologies. Soot is mainly exhausted from incomplete fuel combustion in diesel cylinders under high temperatures and pressures.¹ Benzene (C₆H₆), as the “first aromatic ring”, is an important intermediate species in the incomplete combustion of hydrocarbon fuels,² and it also contributed significantly to the formation of larger polycyclic aromatic hydrocarbons (PAHs) and soot.³ Recently, aromatics with a five-membered ring have drawn much attention in soot studies as PAHs with five-membered rings are observed in experiments *via* high-resolution atomic force microscopy.⁴ Meanwhile, the oxidation of six-membered aromatic rings leads to oxyradicals, which subsequently decompose into CO and a five-membered ring at the edge of PAHs such as free-edge, zigzag, and armchair. The in-depth study of C₆H₆ and 1,3-cyclopentadiene (c-C₅H₆) is instructive for extending large PAHs

since they are the basic units of PAHs.⁵ Moreover, because of the similarity of the structures, many investigations about PAH have been performed upon monocyclic rings to reduce the computational expense. The pyrolysis of C₆H₆ and c-C₅H₆ provides valuable insights into soot formation. Kashiwa *et al.*⁶ investigated C₆H₆ pyrolysis and the formation of particulate matter using a flow reactor. They found that a large amount of particulate matter with a less organic solvable fraction was formed from a C₆H₆-N₂ mixture above 1273 K. Shock tube experiments of C₆H₆ pyrolysis were conducted by Saggese *et al.*⁷ The results show that C₆H₆ pyrolysis begins with the cleavage of C-H bonds. Experimental studies by Wang *et al.*⁸ determined the reaction pathways of c-C₅H₆ pyrolysis. Kiefer *et al.*⁹ studied the c-C₅H₆ molecule and its radical using quantum simulations and estimated the thermodynamic properties. There is a general agreement that the initial step of c-C₅H₆ pyrolysis is C-H fission. Kern *et al.*¹⁰ first provided the first quantitative evidence for the H atom shift mechanism for the important secondary reaction c-C₅H₅ → C₃H₃ + C₂H₂. Pitsch *et al.*¹¹ investigated the H-abstraction and H-addition of c-C₅H₆ by quantum chemistry calculations. The results indicate that H-abstraction prefers to attack the -CH₂- group of c-C₅H₆. They also found that the reactions of c-C₅H₆ + H to form bimolecular products are prevalent at high temperatures and low pressures.¹²

Soot oxidation represents an essential and complex process in soot evolution, competing with surface growth, thus hampering

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particle emissions.¹³ High-temperature combustion takes place in the flame after PAH formation. NO_x is inherently produced when the temperature exceeds 2200 K.^{14,15} Experimental studies indicate that NO_x, especially NO₂, are more effective oxidizers than O₂ for soot oxidation.^{16,17} Oxidation and reburn types are two mechanisms responsible for the reduction of soot and NO_x.¹⁸ In the actual in-cylinder combustion, the oxidation of soot by NO_x inevitably occurs at the flame surface. By applying the flue gas recirculation technique, the presence of a given nitrogen oxide in the recirculated mixture can affect the emissions of soot, which could cause reburn type reactions of soot and NO_x. Therefore, the coexistence of soot and NO_x is worth studying. In the study of Setiabudi *et al.*¹⁹ by analyzing the soot combustion characteristic from room temperature to 900 K, NO₂ is first involved in the soot oxidation to produce surface complexes that are reactive to O₂. Shrivastava *et al.*²⁰ studied the kinetics of soot oxidation by NO₂ using the online aerosol technique, indicating that NO₂ decomposes to NO at temperatures higher than 773.15 K. They also found that the addition of NO₂ significantly reduces the activation energy of oxidation compared to the oxidation with air. Sander *et al.*²¹ investigated the reaction mechanism of the non-catalytic soot reduction by NO, which was validated using density functional theory. However, the subsequent pathway of the surface oxygen desorbing from the soot as CO was not elaborated. In the study of Abián *et al.*¹⁸ the effects of the presence and concentration of NO, NO₂ and N₂O on soot formation during ethylene pyrolysis in a quartz flow reactor have been determined. The experimental results indicate that the lowest soot tendency has been achieved in the presence of NO₂, followed by NO and N₂O. In addition, N radical is one of the products of the high-temperature reaction of NO.²² However, few studies have been performed on the chemistry of N radicals under conditions associated with combustion applications. In addition, the mixed combustion of ammonia and fossil fuels was proposed recently to meet the needs of 'carbon neutrality'. Therefore, the high-temperature reaction of N with PAHs has attracted more attention. Therefore, the oxidation mechanism with NO_x still needs to be theoretically studied for refinement.

In this paper, the ReaxFF MD method was utilized to investigate the reaction of C₆H₆ and c-C₅H₆ under high-temperature and pressure conditions including both the pyrolysis and the oxidation processes at the atomic level. In particular, the pyrolysis system focuses on the growth routes from reactants to large species. The oxidation by NO and NO₂ emphasizes the detailed pathways of O and N radicals in the reaction. A detailed understanding of the key reactive events related to pyrolysis and oxidation of monocyclic hydrocarbon will not only facilitate our understanding of combustion chemistry but also assist in developing comprehensive kinetic models.

2. Methodology

2.1 Simulation method

ReaxFF molecular dynamics (MD) is a novel simulation method that retains nearly the accuracy of quantum mechanics but

allows MD for computational costs nearly as low as for classical force fields. ReaxFF MD can simulate large-scale systems with complex chemical reactions, such as pyrolysis and combustion of hydrocarbons.²³

The ReaxFF MD is a general bond-order dependent potential method that can smoothly describe the bond breakage and formation among molecules in a system. The connectivity-dependent terms containing bond, angle and torsion are calculated from interatomic distances updated every MD step. Non-bonded interactions, including van der Waals and Coulomb, are calculated between every pair of atoms as they are independent of the bonded interactions. A geometry-dependent charge calculation scheme and Electronegative Equalization Method (EEM) are used to calculate atomic charges. ReaxFF force field includes the following energy components:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{vdW}} + E_{\text{Coulomb}} \quad (1)$$

where terms on the right-hand side of the equation represent bond energy, over-coordination energy penalty, under-coordination stability, lone pair energy, valence angle energy, torsion angle energy, van der Waals energy, and Coulomb energy, respectively. A more detailed description of the ReaxFF force field can be found in the work by van Duin *et al.*²⁴

2.2 Computational details

The ReaxFF MD simulation is carried out with the REAXC package in the Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS).²⁵ The CHON-2019 reactive force field developed by Kowalik *et al.*²⁶ is utilized for MD simulations in the current work. The bond/angle/dihedral parameters that involve any N atoms are trained against available experimental and quantum mechanics-based density functional theory data, which were validated in our previous work²⁷ and in the ESI.† The setups of the ReaxFF MD simulations of C₆H₆ and c-C₅H₆ are shown in Tables 1 and 2, respectively. There are 100 reactants in the pyrolysis systems. The system of C₆H₆ + O₂ contains 100 C₆H₆ and 375 O₂ molecules with an initial equivalence ratio of 2. Similarly, 100 c-C₅H₆ and 325 O₂ are set in the c-C₅H₆ + O₂ system. To investigate the effect of NO_x, O₂ is replaced by the same number of NO and NO₂. Ar is added as the bath gas to maintain the same initial mole fraction of C₆H₆ or c-C₅H₆ in pyrolysis and oxidation systems. The interaction between Ar and other species is *via* the van der Waals interaction. The periodic boundary conditions were applied in three directions. The bond order cutoff is set to be 0.2, which is related to species analysis and does not affect the actual simulation. Firstly, energy minimization is performed for every

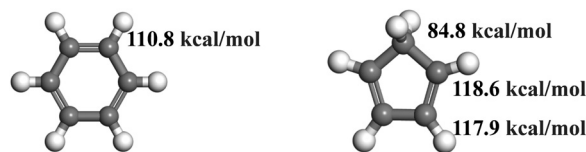
Table 1 Specific simulation conditions of C₆H₆ systems

System	Molecules	Temperature (K)	Pressure (atm)
C ₆ H ₆	100C ₆ H ₆ + 750Ar	2000, 2500	50
C ₆ H ₆ + O ₂	100C ₆ H ₆ + 375O ₂ + 375 Ar		
C ₆ H ₆ + NO	100C ₆ H ₆ + 375NO + 375Ar		
C ₆ H ₆ + NO ₂	100C ₆ H ₆ + 375NO ₂ + 375Ar		



Table 2 Specific simulation conditions of $c\text{-C}_5\text{H}_6$ systems

System	Molecules	Temperature (K)	Pressure (atm)
$c\text{-C}_5\text{H}_6$	$100c\text{-C}_5\text{H}_6 + 750\text{Ar}$	2000, 2500	50
$c\text{-C}_5\text{H}_6 + \text{O}_2$	$100c\text{-C}_5\text{H}_6 + 325\text{O}_2 + 425\text{Ar}$		
$c\text{-C}_5\text{H}_6 + \text{NO}$	$100c\text{-C}_5\text{H}_6 + 325\text{NO} + 425\text{Ar}$		
$c\text{-C}_5\text{H}_6 + \text{NO}_2$	$100c\text{-C}_5\text{H}_6 + 325\text{NO}_2 + 425\text{Ar}$		

Fig. 2 Molecular structures and C–H BDEs of C_6H_6 ¹² and $c\text{-C}_5\text{H}_6$.²⁹

system using a conjugate gradient algorithm to eliminate the artificial effects on the initial geometric configuration. The MD simulations are carried out through the isothermal–isobaric ensemble (NPT) with constant atom number, pressure, and temperature. NPT–MD simulations are performed at 50 atm, which on the one hand is high enough to ensure reactions occur at the ReaxFF MD simulation timescale,²⁸ and on the other hand, is of practical interest for high-pressure combustion engines. The system temperature is controlled by the Nosé–Hoover thermostat with a damping constant of 50 fs. A Nose–Hoover barostat is used to relax the pressure with a damping constant of 1000 timesteps. The starting configurations are equilibrated *via* low-temperature (300 K) ReaxFF simulations (time step of 0.1 fs for 200 ps) to prevent chemical reactions from occurring during equilibration. Then, the MD simulations are carried out for 5000 ps with a time step of 0.2 fs.²⁸ Note that each case is calculated three times with the same starting configurations.

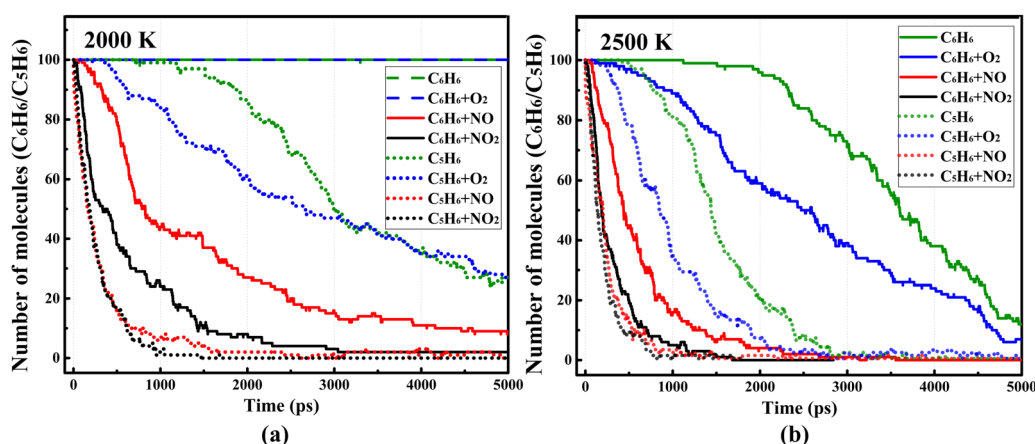
3. Results and discussion

Firstly, a global analysis of the pyrolysis and oxidation of (a) C_6H_6 and (b) $c\text{-C}_5\text{H}_6$ is conducted. Fig. 1 shows the time evolution of the molecular number of C_6H_6 and $c\text{-C}_5\text{H}_6$ under the pyrolysis and oxidation conditions with different oxidizers (O_2 , NO , NO_2) at 2000 K and 2500 K, respectively. Compared with the results at 2000 K, the number of the reactant decreases quicker at 2500 K. It is even significant for C_6H_6 as it is difficult to react at 2000 K under both the pyrolysis and the oxidation by O_2 conditions, whereas $c\text{-C}_5\text{H}_6$ is relatively easier to react at this temperature. In addition, at both 2000 K and 2500 K, systems containing C_6H_6

react more slowly than $c\text{-C}_5\text{H}_6$ with the same oxidizer. These phenomena can be explained by the lower C–H bond dissociation energy (BDEs) of $c\text{-C}_5\text{H}_6$ than that of C_6H_6 . The molecular structures and C–H BDEs of C_6H_6 and $c\text{-C}_5\text{H}_6$ are shown in Fig. 2. The $c\text{-C}_5\text{H}_6$ molecule has a symmetry number of two, and three different types of C–H bonds. The C–H bond dissociation energy of $-\text{CH}_2-$ in $c\text{-C}_5\text{H}_6$ is $84.8\text{ kcal mol}^{-1}$,¹² about $28.2\text{ kcal mol}^{-1}$ lower than the C–H bond dissociation energy of C_6H_6 .²⁹ The effects of different oxidizers on the five- and six-membered rings have similar trends. O_2 is the weakest in the oxidation of C_6H_6 and $c\text{-C}_5\text{H}_6$ compared to NO and NO_2 . NO_2 is the most significant for the oxidation of both $c\text{-C}_5\text{H}_6$ and C_6H_6 . However, the rate of elimination of $c\text{-C}_5\text{H}_6$ by NO essentially overlaps with that of NO_2 , which is caused by the superior H-abstraction by NO on $-\text{CH}_2-$. NO is abundant at the beginning in the system of $c\text{-C}_5\text{H}_6 + \text{NO}$. Moreover, NO prefers to react with $c\text{-C}_5\text{H}_6$ by H-abstractions instead of direct decomposition, which is significantly different from NO_2 as it is hard to be involved in the reaction directly. In the system of $c\text{-C}_5\text{H}_6 + \text{NO}_2$, NO_2 is first decomposed to NO and O . The detailed mechanisms of pyrolysis and oxidation by different oxidizers will be discussed later.

3.1 Pyrolysis of C_6H_6 and $c\text{-C}_5\text{H}_6$

The first-step reaction of monocyclic hydrocarbons is of great significance to understanding and controlling PAH growth. Fig. 3 shows the proportion of different reaction types that trigger the first-step reaction of C_6H_6 (blue columns) and $c\text{-C}_5\text{H}_6$ (red columns) in the pyrolysis systems. The upper and lower parts represent the ratio of forward and reverse reactions to the total net reaction. 35% of $c\text{-C}_5\text{H}_6$ molecules start by breaking the C–H bonds in $-\text{CH}_2-$, which is 30.4% higher than

Fig. 1 Time evolution of the number of C_6H_6 and C_5H_6 molecules under different conditions at (a) 2000 K and (b) 2500 K, respectively.

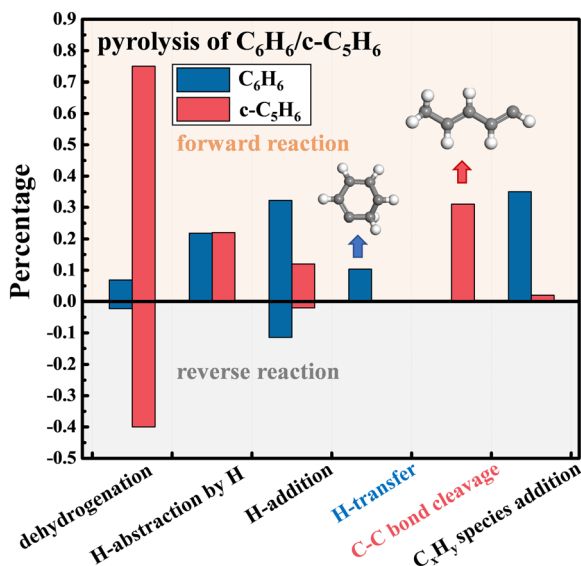


Fig. 3 Proportion of different first-step reactions of C_6H_6 (blue columns) and $c-C_5H_6$ (red columns) in the pyrolysis systems at 2500 K.

the percentage of dehydrogenation of C_6H_6 , attributed to the weaker C–H bond in $-CH_2-$ of $c-C_5H_6$. The C–C bond cleavage is observed during the pyrolysis of $c-C_5H_6$. However, the delocalized π bond of C_6H_6 is difficult to destroy directly, which is much stronger than the C–C bond in $c-C_5H_6$.^{7,30} One pathway for C_6H_6 pyrolysis begins with the C–H bond breaking. Among them, the probability of the H-addition reaction is slightly higher than that of H-abstraction. According to the potential energy surfaces, the energy barrier for the H-addition of C_6H_6 is $8.9 \text{ kcal mol}^{-1}$,³¹ while that of the H-abstraction by H is 16 kcal mol^{-1} .³² Another vital pathway of C_6H_6 pyrolysis is the addition of C_xH_y species generated by the decomposition of C_6H_6 .

As shown in Fig. 4 and 5, the time evolution of the number of species with different carbon numbers was monitored to

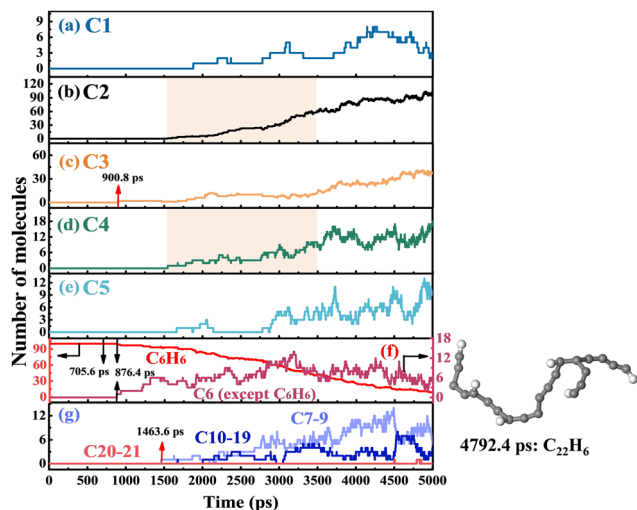


Fig. 4 Time evolution of the number of species with different carbon numbers in the system of C_6H_6 pyrolysis. In (a)–(g), C# represents the number of all species containing carbon atoms of #.

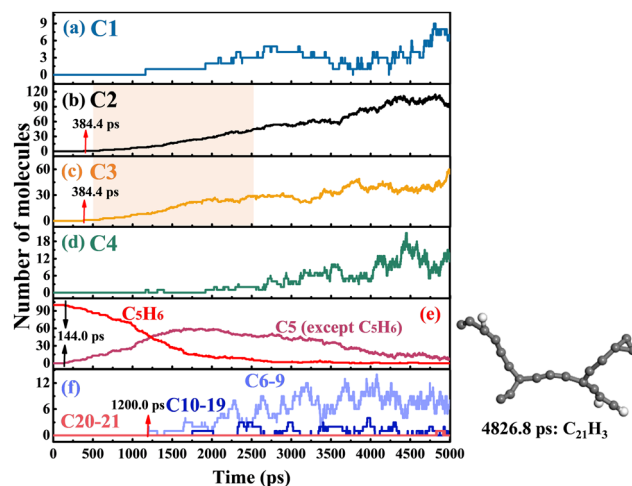


Fig. 5 Time evolution of the number of species with different carbon numbers in the system of $c-C_5H_6$ pyrolysis. In (a)–(f), C# represents the number of all species containing carbon atoms of #.

understand the soot formation. C# represents the number of all species containing carbon atoms of #. For C_6H_6 pyrolysis, the H-transfer of C_6H_6 is first observed at 705.6 ps, as shown in Fig. 4(f). Then, C_6H_6 is dehydrogenated at 876.4 ps. The hydrogen-related reactions including dehydrogenation, H-abstraction and H-addition have a lower percentage in the pyrolysis of C_6H_6 , as reflected by the consistently low amount of C6 (except C_6H_6). C6 species are mainly decomposed into C2 and C4, as shown in the shaded boxes in Fig. 4(b) and (d), with C2 and C4 growing simultaneously from 1500 ps to 3500 ps, which provide resources for species growth. C7 and heavier species are formed due to the successive C_xH_y addition after 1463.6 ps. The largest species, $C_{22}H_6$, is observed at 4792.4 ps. Fig. 5 shows that the pyrolysis of $c-C_5H_6$ starts with dehydrogenation at 144.0 ps. The C–C bond cleavage of $c-C_5H_6$ occurs almost simultaneously with dehydrogenation. Note that the pyrolysis of $c-C_5H_6$ begins much earlier than C_6H_6 because of the weaker C–H bond in $c-C_5H_6$. Since dehydrogenation accounts for a large proportion of the first-step reaction, the conversion between C_5H_6 and C5 (except C_5H_6) is frequent, as shown in Fig. 5(e). The production of C2 and C3 by the C–C bond fission of C5 is the most critical decomposition pathway, as illustrated by the rapid growth from 500 ps to 2500 ps by shaded boxes in Fig. 5(b) and (c). C6–C9 species are first observed at 1200.0 ps. $C_{21}H_3$, formed at 4826.8 ps, is the largest species in the pyrolysis system of $c-C_5H_6$. Notably, the pyrolysis of C_6H_6 produces significantly more C10–19 species than that in the pyrolysis system of $c-C_5H_6$, indicating that the addition reaction of graphitization in C_6H_6 pyrolysis is preferred. The study of Ossler *et al.*^{33,34} has demonstrated that high-temperature combustion generates more curved, more amorphous and less ordered structures. Notably, the carbon-to-hydrogen (C/H) ratio shows a considerable difference between the largest species ($C_{22}H_6/C_{21}H_3$) and reactants (C_6H_6/C_5H_6), indicating that the size growth is accompanied by an increase in mass as well as an increase in the C/H ratio.^{35,36}

The ring opening and decomposition of C_6H_6 and $c-C_5H_6$ at the atomic level are essential for understanding the growth



Pyrolysis at extremely high pressures and temperatures probably leads to the emergence of reactions rarely observed at medium and low temperatures, which should be considered. H-transfer of C_6H_6 to form S4 greatly facilitates the ring opening of C_6H_6 in the present work. Pathways (5) and (6) show the C-C β -scission of two types of C_6H_6 isomers (S3 and S4), respectively. C_6H_6 is converted to phenyl radicals (S5) *via* dehydrogenation and H-abstraction.⁷ Species that trigger H-abstraction include H radicals and C_xH_y , such as C_2H and C_2 . One of the first steps of c- C_6H_5 conversion is the C-C bond

Fig. 7 shows the main pathways of $\text{c-C}_5\text{H}_6$ pyrolysis. The carbon in $-\text{CH}_2-$ of $\text{c-C}_5\text{H}_6$ is defined as carbon (a). The *ortho*- and *para*-positions of carbon (a) are defined as carbon (b) and carbon (c), respectively. The elimination of hydrogen from carbon (a) to form cyclopentadienyl accounts for the largest proportion. Meanwhile, a great number of cyclopentadienyl radicals are produced by H-abstraction *via* H radicals. However, the abstraction of hydrogen from carbon (c) to produce S8 plays a minor role. The difference in probability between the two abstraction routes is attributed to the low barrier height of the H-abstraction at carbon (a), as calculated by the theoretical study by Mao *et al.*¹² Further H-abstraction of cyclopentadienyl radicals results in the formation of $\text{c-C}_5\text{H}_4$. The unsaturation degree rises with hydrogen removal, promoting the addition reactions. Carbon not connected to hydrogen in $\text{c-C}_5\text{H}_4$ is denoted as carbon (d). Except for the H-addition to carbon (d) to regenerate cyclopentadienyl radicals, few H-addition reactions take place at *ortho*- and *para*-positions to carbon (d), forming S7 and S8, respectively. As shown by pathway (11), S7 is converted into linear C_5H_5 radicals *via* C-C β -scission, which agrees well with the computational result obtained by Roy *et al.*⁴¹ S8 experiences ring-opening *via* C-C β -scission, as

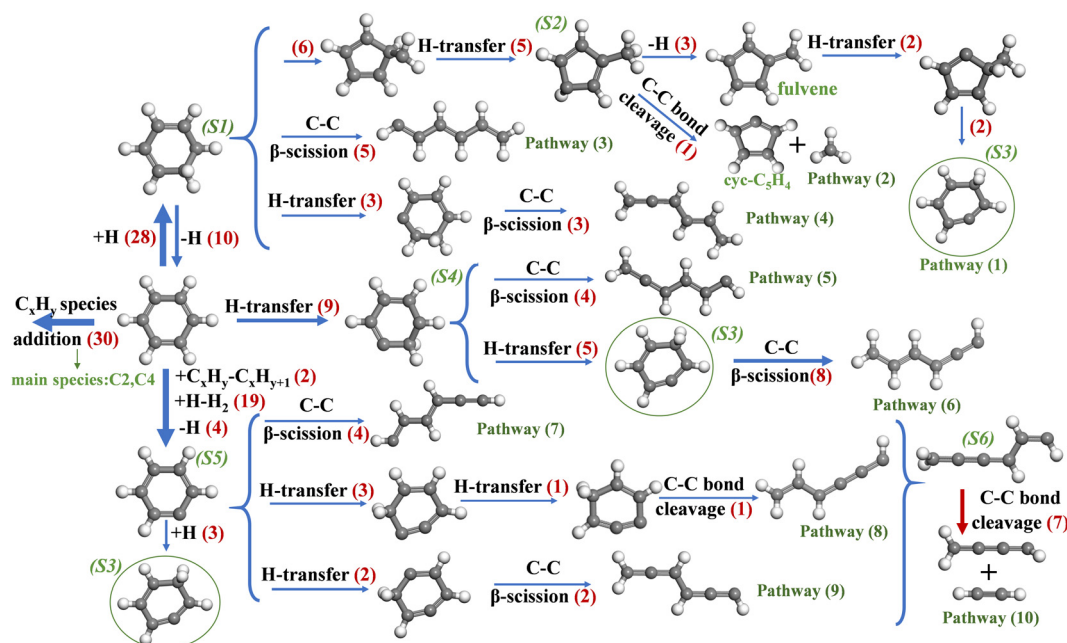


Fig. 6 Major reaction pathways of C_6H_6 pyrolysis at 2500 K. The number of reactions is indicated in red.

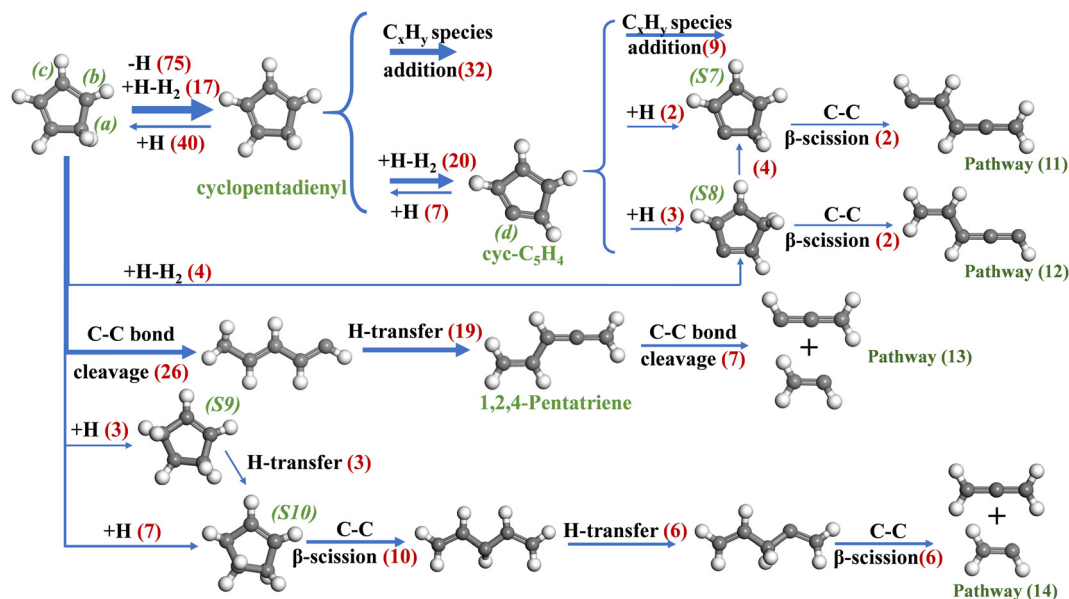


Fig. 7 Major reaction pathways of $c\text{-C}_5\text{H}_6$ pyrolysis at 2500 K.

presented by pathway (12), which has however been neglected in the previous studies.

The decomposition of $c\text{-C}_5\text{H}_6$ to C2 and C3 species follows pathways (13) and (14). Pathway (13) shows that $c\text{-C}_5\text{H}_6$ isomerizes by C–C bond cleavage and then experiences H-transfer to form a $-\text{CH}_2$ group in 1,2,4-pentatriene, which eventually decomposes to C_3H_3 and C_2H_3 . Pathway (13) is crucial for the accurate prediction of $c\text{-C}_5\text{H}_6$ consumption at 2500 K, which however has been ignored in the previous studies. Pathway (14) begins with the H-addition to carbon (b) to form S10, followed by isomerization *via* C–C β -scission and H-transfer, and eventually decomposition to C_2H_3 and C_3H_4 . Notably, a small number of H radicals is added to the carbon (c) of $c\text{-C}_5\text{H}_6$ to form S9. After that, all S9 species isomerize to S10 by H-transfer as the resonance-stabilized S10 is more stable.¹²

3.2 Oxidation of C_6H_6 and $c\text{-C}_5\text{H}_6$ by NO_x

Oxygen is one of the most significant oxidizers in combustion. Oxidation of soot by NO_x is more efficient than O_2 , obtained by

the global analysis from Fig. 1. In the presence of O_2 , O_2 is rarely involved in the oxidation of C_6H_6 or $c\text{-C}_5\text{H}_6$ directly. The oxidation rate is limited by the branching reaction: $\text{O}_2 + \text{H} = \text{O} + \text{OH}$. More details of C_6H_6 and $c\text{-C}_5\text{H}_6$ oxidation by O_2 are shown in the ESI.† In the presence of NO, the largest species in C_6H_6 and $c\text{-C}_5\text{H}_6$ systems are $\text{C}_{12}\text{H}_{10}\text{O}$ and $\text{C}_9\text{H}_5\text{N}_2$, respectively. Furthermore, $\text{C}_7\text{H}_6\text{O}_2\text{N}_2$ and $\text{C}_7\text{H}_7\text{O}$ are the largest species observed in the systems of $\text{C}_6\text{H}_6 + \text{NO}_2$ and $c\text{-C}_5\text{H}_6 + \text{NO}_2$, indicating that NO_x , especially NO_2 , effectively inhibits the growth of soot precursors. Fig. 8 shows the time evolution of the main species in the pure NO and pure NO_2 systems. The pure NO system has 375 NO molecules and 475 Ar atoms. Similarly, 375 NO_2 and 475 Ar are involved in the pure NO_2 system. Both systems are equilibrated at the 300 K for 200 ps, which subsequently performed high-temperature simulation at 2500 K for 5000 ps. Details of the settings are the same as for $\text{C}_6\text{H}_6 + \text{NO}/\text{C}_6\text{H}_6 + \text{NO}_2$ in section 2.2. Fig. 9 shows the main species in the reaction of $\text{C}_6\text{H}_6/c\text{-C}_5\text{H}_6$ with NO and NO_2 , respectively. The arrows on the right side present the number

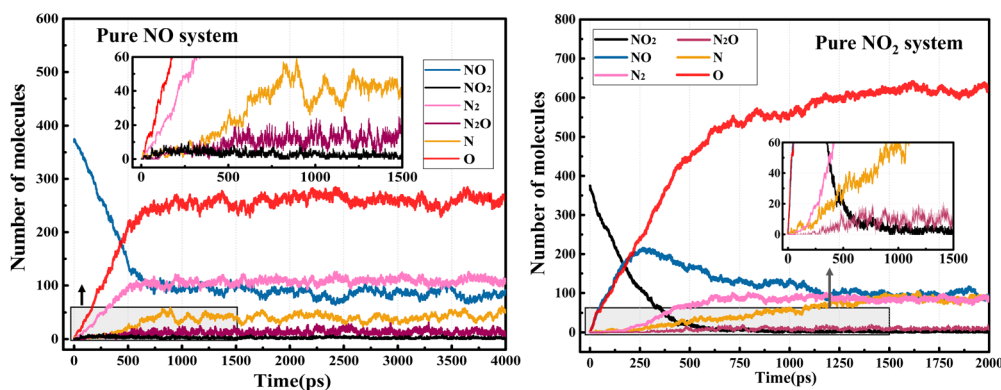
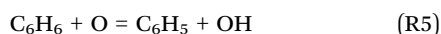


Fig. 8 Time evolution of the number of key species in the (a) pure NO system and (b) pure NO_2 system at 2500 K.

of O, N₂, NO and N in the pure NO/NO₂ system. The oxidation of C₆H₆ and c-C₅H₆ by NO_x is a chain reaction initiated at high temperatures. The mechanism of C₆H₆ oxidized by NO is as follows:



Once initiated, the chain propagation proceeds:



The production of N₂ in (R2) is consistent with that observed in the experiment.⁴² Notably, the consumption of NO in the presence of C₆H₆ and C₅H₆ is slower than that in the pure NO system. This is because a portion of N radicals produced by (R1) is involved in the reaction with C_xH_y species. Therefore, (R2) reacts slowly due to the reduction of N radicals.

In the presence of NO₂, the main reaction route of NO₂ acts as a rich source producing O radicals *via*:



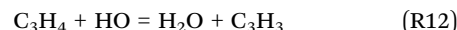
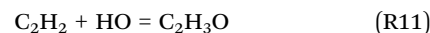
Subsequent NO reactions are the same as (R1) and (R2). NO can also be formed by the reaction of NO₂ and H radicals:



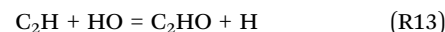
which provides OH radicals in the system. Some OH radicals react with H radicals and N radicals:



In addition, OH experiences OH addition and H-abstraction by OH with C_xH_y species, including:



The mechanism of reaction at high temperatures is dominated by OH addition with H-abstraction being a minor contributor.⁴³ The OH radicals can also provide O for C_xH_y species:



In the system of C₆H₆ + NO₂ (Fig. 9(b)), the number of O and N radicals is lower than those in the pure NO₂ system.

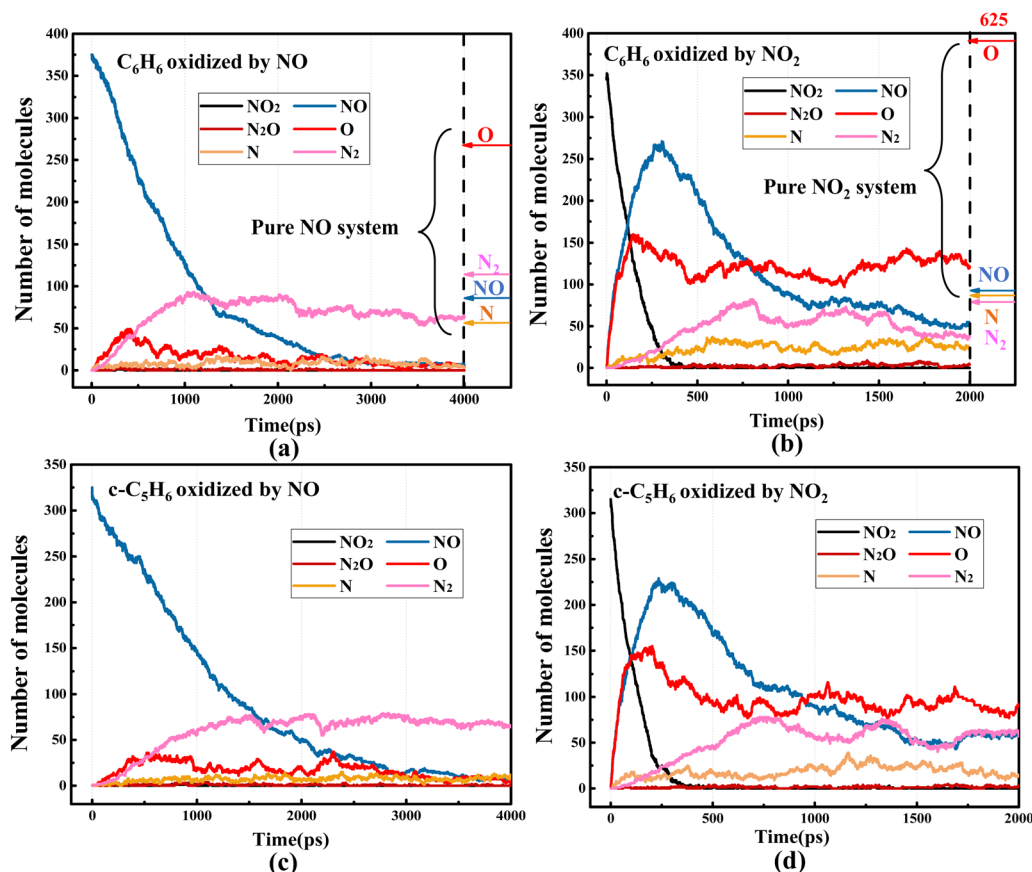


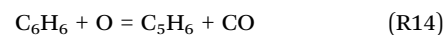
Fig. 9 Time evolution of the number of key species in the system of (a) C₆H₆ and NO, (b) C₆H₆ and NO₂, (c) c-C₅H₆ and NO, and (d) c-C₅H₆ and NO₂ at 2500 K. The arrows on the right side of (a) and (b) present the number of O, N₂, NO and N in the pure NO and pure NO₂ systems, respectively.



In particular, the reduction of O radicals is more noticeable than that in the pure NO₂ system, with a difference of approximately 500. Similarly, in the system where c-C₅H₆ reacts with NO or NO₂, a major role is played by O and N radicals in the c-C₅H₆ oxidation.

The increase in O radicals and N radicals significantly altered the types and distribution of the initial reaction. Fig. 10(a) shows the proportion of different reaction types that trigger the first-step reaction of C₆H₆ and c-C₅H₆ in the presence of NO. The percentage of reactions that take place in the pyrolysis system drops drastically. Notably, as seen from the red column, NO can abstract hydrogen from the -CH₂- of c-C₅H₆, with a percentage of about 65%. Xu *et al.*⁴⁴ found that NO is effective for H-abstraction of HCO. For the more stable C-H bond in -CH₂- of c-C₅H₆, NO still has an excellent ability to abstract hydrogen. However, for the C-H bond in C₆H₆, H-abstraction by NO is not dominant, which only accounts for about 4.4%. In the system of C₆H₆ + NO, more than half of the C₆H₆ molecules are activated by O and N radicals. Among them, reaction with O radicals accounts for more than 30%, which accounts for the highest percentage of all initial steps. O and N radicals participate in the reaction *via* H-abstraction and addition, represented by shaded and non-shaded parts, respectively. The probability of O-addition reactions is much higher than H-abstraction by O for both reactants of C₆H₆ and c-C₅H₆. However, nearly half of the reactions with N are achieved by H-abstraction in both systems. It is also worth noting that c-C₅H₆ is more likely to undergo H-abstraction by O or N radicals than C₆H₆. In the presence of NO₂ shown in Fig. 10(b), reactions in the pyrolysis system account for less than fifteen percent. Abundant O radicals greatly increase the probability of reaction with O radicals in both systems of C₆H₆ and c-C₅H₆, in proportions of 63.8% and 47.6%, respectively. NO₂ is rarely involved in the reaction with C₆H₆/c-C₅H₆ directly. NO, O and N produced during the decomposition of NO₂ are actively involved in the first-step reaction. NO has a strong capacity for H-abstraction. However, O and N radicals, especially O radicals, prefer to participate in reactions *via* addition.

The presence of NO_x greatly increases the number of O radicals in the system, which significantly accelerates PAH oxidation. Therefore, elucidating the reaction pathways of the elementary C₆H₆/C₅H₆ + O reaction at high temperature and pressure is of great importance to understanding the reaction mechanisms of hydrocarbon flames as well as the optimization of combustion processes. Fig. 11 shows the reaction pathway for C₆H₆ + O in the system where C₆H₆ is oxidized by NO₂ since this system has the largest proportion of reactions with O radicals. After connecting to the C atom on C₆H₆ to form C₆H₆O (S11), six subsequent reaction pathways are observed as depicted by blue arrows, where bold arrows indicate dominant reaction routes. The H-elimination after introducing O radical into C₆H₆ is one of the important pathways (C₆H₆ → S12).⁴⁵ The H radical then connects to O atoms of S12, forming a hydroxyl group (S12 → phenol), which is eventually abstracted by H radicals to produce H₂O and phenyl. The formation of phenol by H-transfer from S11 has also been found with a small probability. The isomerization of S11 *via* H-transfer between carbon atoms contributes to the ring-opening, as presented by pathway (15). The most important decomposition channel of S11 is to form linear-C₆H₆O (S15) *via* C-C β-scission. S15 experiences successive H-transfer, leading to the formation of the -CH₂- group in S17, which ultimately decomposes to C₅H₆ and CO, as shown by pathway (16).



The conversion of S11 to a stable species (S18) was found in abundance. The energy of forming S18 is 11.3 kcal mol⁻¹ lower than S11, as calculated in the study of Nguyen *et al.*⁴⁶ The bond cleavage of S18 is another key source of S15, followed by pathway (16). The isomerization of S11, S15 and S18 to S19 is found once each. After that, S19 experiences a decomposition reaction to the resonance-stabilized cyclopentadienyl radical and CHO, which agrees with the theoretical results of Hodgson *et al.*⁴⁵



NO₂ produce large amounts of O radicals at high temperature, which keeps the system at a high concentration of O radicals.

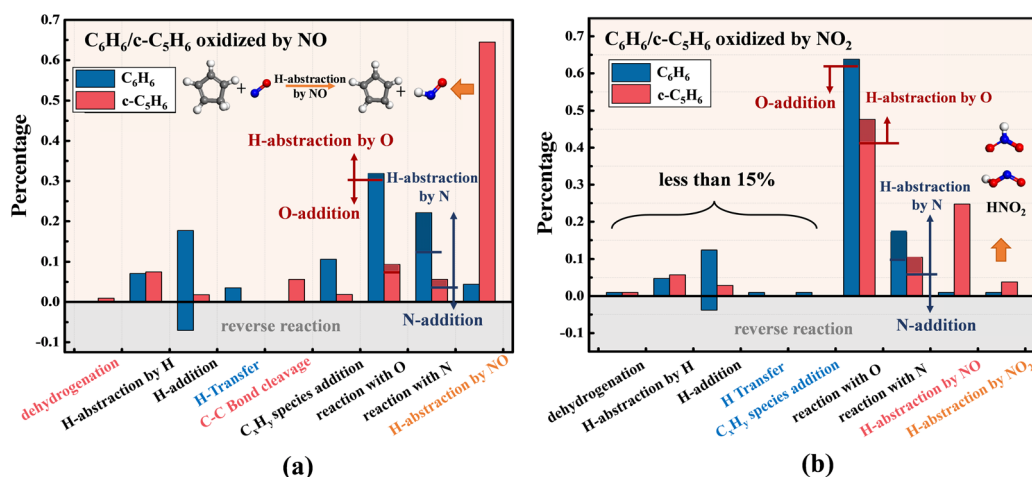


Fig. 10 Proportion of different first-step reactions of C₆H₆ (blue columns) and c-C₅H₆ (red columns) in the presence of (a) NO and (b) NO₂ at 2500 K.

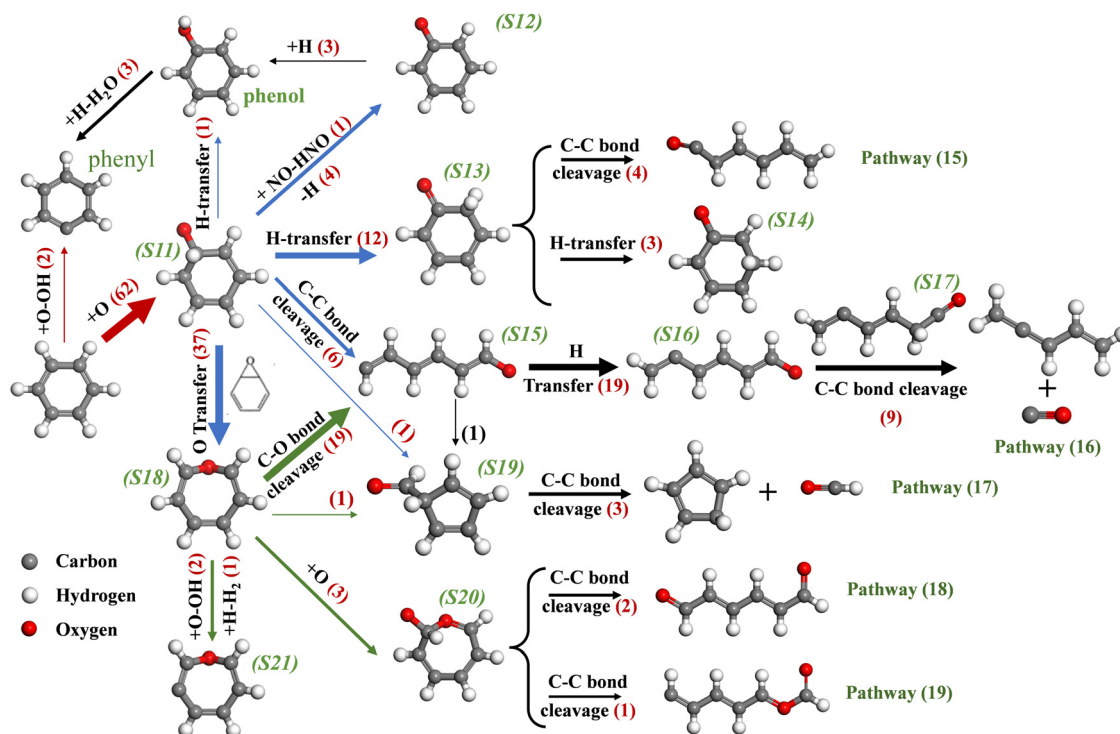
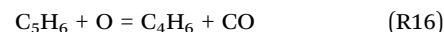


Fig. 11 Major reaction pathways of C_6H_6 and O radicals in the system of C_6H_6 and NO_2 .

Therefore, the continued attack on C_6H_6O by O radicals is inevitable, which however has rarely been focused on in the literature. For S18, the addition of O radicals on the carbon that connected to the initial oxygen atom is observed. After that, S20 isomerizes to form linear- $C_6H_6O_2$ via two routes, as shown by pathways (18) and (19). At last, the H-abstraction of S18 by O and H radicals to form S21 is found.

In the system of $c-C_5H_6 + NO_2$, about 47% of the $c-C_5H_6$ molecules experience O-addition reactions as the initial step. Fig. 12 shows the reaction pathways of $c-C_5H_6$ and O radicals. As indicated by the red arrows, O radicals attack carbon (b) or carbon (c) of $c-C_5H_6$ to generate C_5H_6O . O-addition on carbon (b) is more important. Both S22 and S23 are found to form S24.

Pathway (20) shows the ring-opening of $c-C_5H_6O$ (S22) via C–C β -scission. As shown by the blue arrows, both S23 and S24 can proceed with bond cleavage, forming a linear species including S26 and S31. S26 is the main product of ring-opening, which experience H-transfer to S27 with a $-CH_2-$ group. In addition, after the H-transfer of S23, S25 undergoes bond cleavage to form S27, which is also an important pathway for generating S27. After that, S27 decomposes into C_4H_6 and CO.



The decomposition route via $S23 \rightarrow S26 \rightarrow S27 \rightarrow C_4H_6 + CO$ is important for C_5H_6O consumption, which is in great

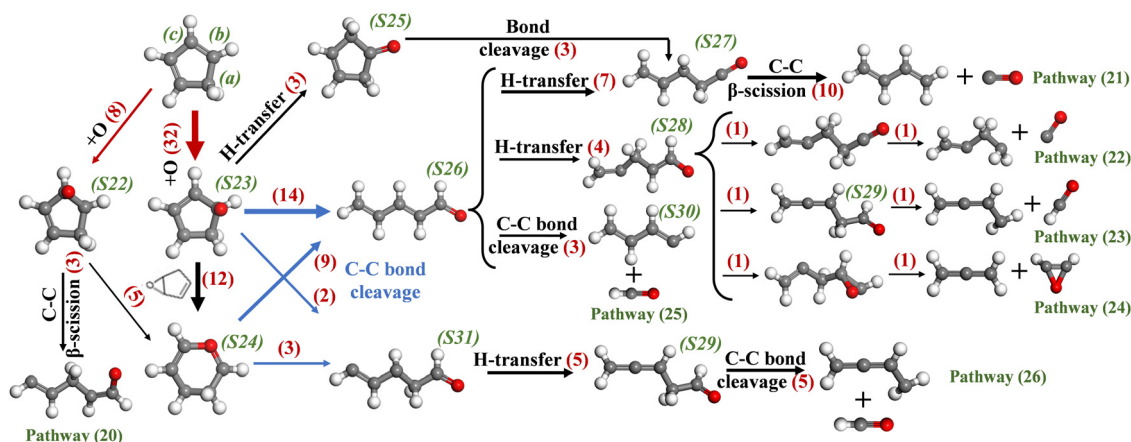


Fig. 12 Major reaction pathways of $c-C_5H_6$ and O radicals in the system of $c-C_5H_6$ and NO_2 .

agreement with the theoretical results by Robinson.⁴⁷ For the oxidation of C₆H₆ and C₅H₆ by O radicals, the key reactions that produce CO are the transfer of the hydrogen from the carbon connected with oxygen to the adjacent carbon, forming –CH₂–C=O. After that, CO is removed from the linear C₆H₆O or C₅H₆O. In addition, –CH₂– formed by successive H-transfer drives the decomposition reaction, as shown by pathways (22), (23) and (24), which produce CO, CHO and C₂H₂O, respectively. S31 is another isomer of linear-C₅H₆O after ring-opening, which experiences H-transfer and decomposes to C₄H₅ and CHO.



Among them, (H)CO has an inhibitory effect on soot formation, as it ties up carbon atoms, limiting their involvement in the soot formation processes.

As seen from the decomposition of C₆H₆O and C₅H₆O, the formation of –CH₂– plays an important role in the fragmentation of linear species. The C–C bond between –CH₂– and the carbon attached to the oxygen is easily broken. Notably, linear-C₅H₆O decomposes more readily than linear-C₆H₆O, which is probably because the high H/C ratio is more likely to form the –CH₂–.

The N radical is one of the key products of the high-temperature reaction of NO_x. Fig. 13 shows the reaction pathway of C₆H₆ with N radicals in the system of C₆H₆ + NO since C₆H₆ has the highest proportion of initial reactions with N radicals compared to other systems. S32 is formed after the N-addition of C₆H₆. The study of Balucani *et al.*⁴⁸ shows that the N-addition of C₆H₆ proceeds through the formation of a van der Waals complex (T1), which is barrierless. Then, T1 isomerizes to form S32 through the nitrogen bridging of two carbon atoms of the ring, with a low barrier of 0.7 kcal mol^{–1}.⁴⁹ The rapid reaction leads to difficulty in the observation of T1. S32 can evolve in two different ways. Firstly, it can undergo C–C bond breaking to form the seven-membered c-S33, where a nitrogen atom is inserted into the C–C bond of C₆H₆. Secondly, the hydrogen of S32 transfers from carbon to the nitrogen atom, then anilino radical (S34) is produced by the cleavage of the HC–NH bond. Notably, the hydrogen on the carbon attached to the nitrogen tends to

transfer to the nitrogen to form –CNH, which is also observed after the N-addition reaction of c-C₅H₆, which will be discussed later. The route of C₆H₆ → S32 → S34 is the most important pathway for N-addition reactions of C₆H₆, and S34 is the most stable isomer of C₆H₆N.⁴⁸ S34 species isomerize to S35, which subsequently lose an NH₂ group, and the following reaction is proposed:



Pathway (28) shows the main decomposition reaction of C₆H₆N (S34):



S34 isomerizes to S36 *via* C–C ring-closure and then S37 is produced from the bicyclic intermediate (S36) through C–C cleavage. After that, S37 experiences H-transfer to form S38 and then decomposes to c-C₅H₅ and HCN, which have been proven to be reasonable with a low energy barrier height.⁴⁹ Overall, O and N radicals can react with C₆H₆ and form the resonance-stabilized cyclopentadienyl radical. Notably, the ring-opening reaction of C₆H₆ assisted by N radicals has not been found at low temperatures. In the present work, pathway (29) shows the route of C₆H₆N isomerization to linear-C₆H₆N in high-temperature systems for the first time. In addition, H-elimination of S34 forming cyc-C₆H₅N is observed in the system.

The reaction of N radicals with c-C₅H₆ has received less attention in previous studies, which however has important implications for assisting in developing comprehensive kinetic models. The pathways in the system of c-C₅H₆ + NO and c-C₅H₆ + NO₂ are investigated as indicated by blue and black, respectively, as shown in Fig. 14. The red arrows indicate that the reaction is found in both systems. Attacking carbon (b) and carbon (c) of c-C₅H₆ are two main routes for N-addition of c-C₅H₆, which generate S39 and S42, respectively. After that, S39 produces S40 and S43 sequentially *via* successive H-transfer and finally experiences the cleavage of the C–C bond as shown by pathway (31). In addition, S41 forms *via* C–N ring-closure of S40 in the

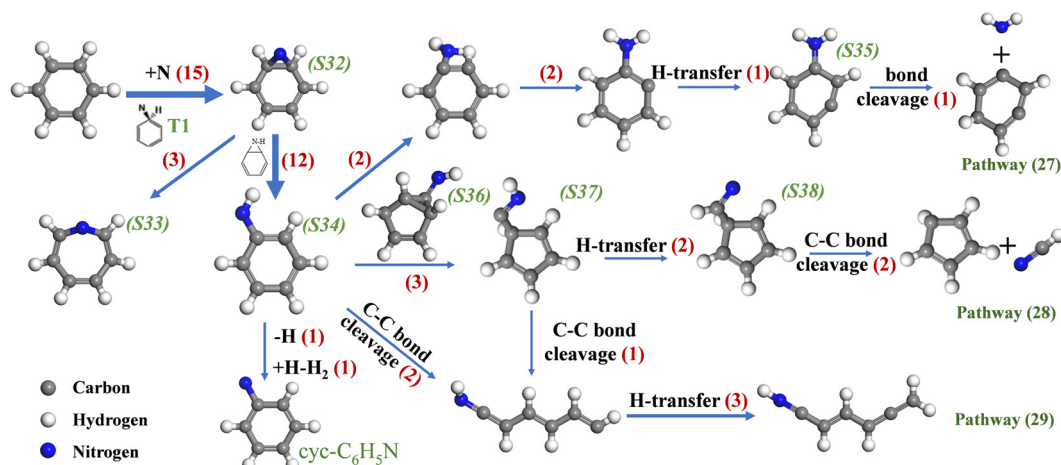


Fig. 13 Major reaction pathways of C₆H₆ and N radicals in the system of C₆H₆ and NO.



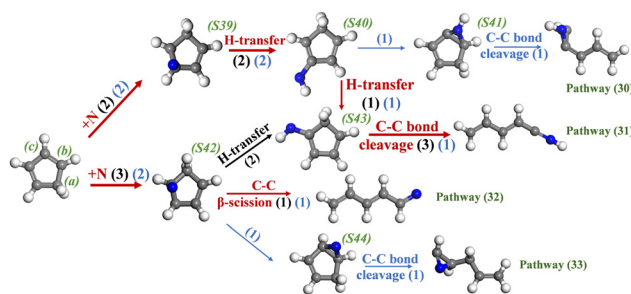


Fig. 14 Major reaction pathways of $c\text{-C}_5\text{H}_6$ and N radicals in the system of $c\text{-C}_5\text{H}_6$ and NO (blue arrows) and system of $c\text{-C}_5\text{H}_6$ and NO_2 (black arrows). The red arrows indicate that the reaction occurs in both systems.

system of $c\text{-C}_5\text{H}_6$ and NO, which finally breaks the C–C bond to a linear- $\text{C}_5\text{H}_6\text{N}$. Three reaction routes are observed for S42. Among them, C–C β -scission of S42, shown by pathway (32), is observed in both the $\text{C}_5\text{H}_6 + \text{NO}$ and $\text{C}_5\text{H}_6 + \text{NO}_2$ systems. In the system of $c\text{-C}_5\text{H}_6$ and NO_2 , the hydrogen atom of S42 shifts from carbon to the nitrogen atom to form the –NH group of S43, which subsequently experiences ring-opening as mentioned above. The third reaction route of S42 is found in the system of $c\text{-C}_5\text{H}_6$ and NO. As shown by pathway (33), the isomer (S44) is formed via C–N bond fusion of S42, which then isomerizes to linear- $\text{C}_5\text{H}_6\text{N}$ via C–C bond cleavage. In summary, both C_6H_6 and $c\text{-C}_5\text{H}_6$ take the ring-opening and fragmentation with the assistance of N radicals.

4. Conclusion

In this study, ReaxFF MD simulations are performed to investigate both the pyrolysis and oxidation of C_6H_6 and $c\text{-C}_5\text{H}_6$ at high temperatures and pressures. The pyrolysis of $c\text{-C}_5\text{H}_6$ mainly starts with the dehydrogenation in the methylene ($-\text{CH}_2-$) group. However, C_6H_6 prefers to undergo addition reactions with H radicals and C_xH_y species. C_{22}H_6 and C_{21}H_3 are the largest species in the pyrolysis system of C_6H_6 and $c\text{-C}_5\text{H}_6$. The size growth is accompanied by an increase in mass as well as an increase in the C/H ratio. Among the three oxidizers of O_2 , NO and NO_2 , NO_2 is the most effective in aromatic elimination, followed by NO and O_2 . The chain-branching reaction of $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ leads to the formation of O radicals in systems with O_2 as the oxidizer. The presence of NO_x effectively inhibits the growth of the species due to the formation of abundant O and N radicals in the high-temperature decomposition of NO_x by reactions: $\text{NO}_2 = \text{NO} + \text{O}$, $\text{NO} = \text{N} + \text{O}$, and $\text{N} + \text{NO} = \text{N}_2 + \text{O}$. Note that NO shows a remarkable ability to abstract hydrogen atoms from the $-\text{CH}_2-$ group of $c\text{-C}_5\text{H}_6$. However, H-abstraction by NO on C_6H_6 is not dominant. The reaction pathways of O and N radicals with C_6H_6 and $c\text{-C}_5\text{H}_6$ have been studied. The addition of O radicals to $c\text{-C}_5\text{H}_6$ is more likely to occur on the carbon adjacent to $-\text{CH}_2-$. Addition reactions of O and N radicals lead to the ring-opening of C_6H_6 and $c\text{-C}_5\text{H}_6$, and the formation of $-\text{CH}_2-$ by H-transfer promotes the decomposition of linear- $\text{C}_6\text{H}_6\text{O}$ and $\text{C}_5\text{H}_6\text{O}$. Anilino radical is the main product of N-addition to C_6H_6 . N radicals are added at both the *ortho*- and *para*-carbon sites of

$-\text{CH}_2-$ of $c\text{-C}_5\text{H}_6$. Species containing nitrogen readily form $-\text{CNH}$, and the addition of N radicals assists the ring-opening. Notably, the addition of O and N radicals to C_6H_6 also assists in their decomposition to the resonance-stabilized cyclopentadienyl radical and HCO/HCN. Overall, novel insights into the key reactive events related to the pyrolysis and oxidation of C_6H_6 and $c\text{-C}_5\text{H}_6$ are obtained, which could improve comprehensive kinetic mechanisms and soot reduction strategies.

Conflicts of interest

There are no conflicts to declare.

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References

- B. Frank, R. Schlögl and D. S. Su, *Environ. Sci. Technol.*, 2013, **47**, 3026–3027.
- J. D. Kubicki, *Environ. Sci. Technol.*, 2006, **40**, 2298–2303.
- A. Drakon, A. Eremin, M. Korshunova and E. Mikheyeva, *Combust. Flame*, 2021, **232**, 111548.
- M. Commodo, K. Kaiser, G. De Falco, P. Minutolo, F. Schulz, A. D'Anna and L. Gross, *Combust. Flame*, 2019, **205**, 154–164.
- M. Frenklach and A. M. Mebel, *Phys. Chem. Chem. Phys.*, 2020, **22**, 5314–5331.
- K. Kashiwa, T. Kitahara, M. Arai and Y. Kobayashi, *Fuel*, 2018, **230**, 185–193.
- C. Saggese, A. Frassoldati, A. Cuoci, T. Faravelli and E. Ranzi, *Combust. Flame*, 2013, **160**, 1168–1190.
- H. Wang, Z. Liu, S. Gong, Y. Liu, L. Wang, X. Zhang and G. Liu, *Combust. Flame*, 2020, **212**, 189–204.
- J. H. Kiefer, R. S. Tranter, H. Wang and A. F. Wagner, *Int. J. Chem. Kinet.*, 2001, **33**, 834–845.
- R. D. Kern, Q. Zhang, J. Yao, B. S. Jursic, R. S. Tranter, M. A. Greybill and J. H. Kiefer, *Symp. (Int.) Combust., [Proc.]*, 1998, **27**, 143–150.
- M. Baroncelli, Q. Mao, S. Galle, N. Hansen and H. Pitsch, *Phys. Chem. Chem. Phys.*, 2020, **22**, 4699–4714.
- Q. Mao, L. Cai and H. Pitsch, *Combust. Flame*, 2020, **222**, 423–433.
- C. Qiu, A. F. Khalizov and R. Zhang, *Environ. Sci. Technol.*, 2012, **46**, 9464–9472.
- F. Arens, L. Gutzwiller, U. Baltensperger, H. W. Gäggeler and M. Ammann, *Environ. Sci. Technol.*, 2001, **35**, 2191–2199.
- A. K. Agarwal, A. P. Singh and R. K. Maurya, *Prog. Energy Combust. Sci.*, 2017, **61**, 1–56.



- 16 I. P. Kandylas, O. A. Haralampous and G. C. Koltsakis, *Ind. Eng. Chem. Res.*, 2002, **41**, 5372–5384.
- 17 M. Jeguirim, V. Tschamber, J. F. Brilhac and P. Ehrburger, *J. Anal. Appl. Pyrolysis*, 2004, **72**, 171–181.
- 18 M. Abián, E. Peribáñez, Á. Millera, R. Bilbao and M. U. Alzueta, *Combust. Flame*, 2014, **161**, 280–287.
- 19 A. Setiabudi, M. Makkee and J. A. Moulijn, *Appl. Catal., B*, 2004, **50**, 185–194.
- 20 M. Shrivastava, A. Nguyen, Z. Zheng, H.-W. Wu and H. S. Jung, *Environ. Sci. Technol.*, 2010, **44**, 4796–4801.
- 21 M. Sander, A. Raj, O. Inderwildi, M. Kraft, S. Kureti and H. Bockhorn, *Carbon*, 2009, **47**, 866–875.
- 22 K. L. Wray and J. D. Teare, *J. Chem. Phys.*, 1962, **36**, 2582–2596.
- 23 Q. Zhong, Q. Mao, J. Xiao, A. C. T. van Duin and J. P. Mathews, *Combust. Flame*, 2018, **198**, 146–157.
- 24 A. C. Van Duin, S. Dasgupta, F. Lorant and W. A. Goddard, *J. Phys. Chem. A*, 2001, **105**, 9396–9409.
- 25 H. M. Aktulga, J. C. Fogarty, S. A. Pandit and A. Y. Grama, *Parallel Comput.*, 2012, **38**, 245–259.
- 26 M. Kowalik, C. Ashraf, B. Damirchi, D. Akbarian, S. Rajabpour and A. C. Van Duin, *J. Phys. Chem. B*, 2019, **123**, 5357–5367.
- 27 Y. Wang, Q. Mao, Z. Wang, K. H. Luo, L. Zhou and H. Wei, *Combust. Flame*, 2023, **248**, 112571.
- 28 M. Feng, X. Z. Jiang and K. H. Luo, *Proc. Combust. Inst.*, 2019, **37**, 5473–5480.
- 29 C. Barckholtz, T. A. Barckholtz and C. M. Hadad, *J. Am. Chem. Soc.*, 1999, **121**, 491–500.
- 30 R. D. Kern and K. Xie, *Prog. Energy Combust. Sci.*, 1991, **17**, 191–210.
- 31 A. Mebel, M.-C. Lin, T. Yu and K. Morokuma, *J. Phys. Chem. A*, 1997, **101**, 3189–3196.
- 32 D. Hou and X. You, *Phys. Chem. Chem. Phys.*, 2017, **19**, 30772–30780.
- 33 F. Ossler, S. E. Canton and J. Larsson, *Carbon*, 2009, **47**, 3498–3507.
- 34 F. Ossler, S. E. Canton, L. R. Wallenberg, A. Engdahl, S. Seifert, J. P. Hessler and R. S. Tranter, *Carbon*, 2016, **96**, 782–798.
- 35 Q. Mao, A. C. Van Duin and K. Luo, *Carbon*, 2017, **121**, 380–388.
- 36 H. Michelsen, *Proc. Combust. Inst.*, 2017, **36**, 717–735.
- 37 L. Madden, L. Moskaleva, S. Kristyan and M.-C. Lin, *J. Phys. Chem. A*, 1997, **101**, 6790–6797.
- 38 Y. Guo and J. J. Grabowski, *J. Am. Chem. Soc.*, 1991, **113**, 5923–5931.
- 39 V. S. Rao and G. B. Skinner, *J. Phys. Chem.*, 1988, **92**, 2442–2448.
- 40 W. Sun, A. Hamadi, S. Abid, N. Chaumeix and A. Comandini, *Proc. Combust. Inst.*, 2021, **38**, 891–900.
- 41 K. Roy, C. Horn, P. Frank, V. G. Slutsky and T. Just, *Symp. (Int.) Combust.*, 1998, **27**, 329–336.
- 42 J. Rodriguez-Mirasol, A. C. Ooms, J. R. Pels, F. Kapteijn and J. A. Moulijn, *Combust. Flame*, 1994, **99**, 499–507.
- 43 R. Ananthula, T. Yamada and P. H. Taylor, *J. Phys. Chem. A*, 2006, **110**, 3559–3566.
- 44 Z. F. Xu, C.-H. Hsu and M. C. Lin, *J. Chem. Phys.*, 2005, **122**, 234308.
- 45 D. Hodgson, H.-Y. Zhang, M. R. Nimlos and J. T. McKinnon, *J. Phys. Chem. A*, 2001, **105**, 4316–4327.
- 46 T. L. Nguyen, J. Peeters and L. Vereecken, *J. Phys. Chem. A*, 2007, **111**, 3836–3849.
- 47 R. K. Robinson and R. P. Lindstedt, *Combust. Flame*, 2011, **158**, 666–686.
- 48 N. Balucani, L. Pacifici, D. Skouteris, A. Caracciolo, P. Casavecchia and M. Rosi, *Computational Science and Its Applications – ICCSA*, 2018, pp. 763–772.
- 49 C.-H. Chin, T. Zhu and J. Z. H. Zhang, *Phys. Chem. Chem. Phys.*, 2021, **23**, 12408–12420.

