



Initiation mechanism of 1,3-butadiene combustion and its effect on soot precursors



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ABSTRACT

1,3-Butadiene ($13C_4H_6$, $CH_2=CH-CH=CH_2$) is of great importance as a ubiquitous intermediate in hydrocarbon combustion. Besides its toxic nature, it is involved in the formation of major soot precursors such as C_3H_3 and $n-i-C_4H_5$. In the present study, the initiation mechanism of 1,3-butadiene combustion has been systematically investigated. It includes the thermal decomposition and mutual isomerization on the C_4H_6 potential energy surface (PES), the H-assisted isomerization reaction on the C_4H_7 PES and the H addition-elimination and H abstraction reactions. The temperature- and pressure-dependent rate coefficients for the first two categories of reactions were computed extensively while the H-addition and H-abstraction reactions were adopted from literature. The updated initiation mechanism was then incorporated into Aramco Mech 2.0 to reveal the initiation pathways in 1,3-butadiene pyrolysis and pre-mixed flame. The previously missing “well-skipping” path $13C_4H_6=CH_3 + C_3H_3$ is found to be important in 1,3-butadiene pyrolysis. The H-assisted isomerization has a minor contribution to conversion between 1,3- and 1,2-butadiene, while the similar reactions were suggested to play important roles in fulvene/benzene and allene/propyne interconversion. Using the updated model that includes the above pressure-dependent reactions, the effect of the well-skipping paths on the formation of several well-recognized soot precursors (such as C_3H_3 , C_4H_5) are discussed.

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1. Introduction

With two conjugated double C=C bonds, 1,3-butadiene ($13C_4H_6$, $CH_2=CH-CH=CH_2$) is a stable intermediate species which is produced in large quantities during the combustion of olefins [1–4]. It is not only an air pollutant due to its toxic nature [5] but also a potential PAH precursor [6–9]. Furthermore, the products of its decomposition are the most important benzene precursors (C_3H_3 , $i-/n-C_4H_5$) [10–14]. As a part of the foundational fuel model, the combustion mechanism of 1,3-butadiene has been continuously studied in respect of its pyrolysis and oxidation mechanism [15–22], with some recent studies focusing on the PAH formation kinetics [23–28] and the interaction chemistry when blended with other important fuels [29–31].

The initial decomposition step of 1,3-butadiene pyrolysis is usually thought to take place through C–C bond fission to produce two vinyl radicals [16,32,33] or via a tight transition state to form ethylene and acetylene [16,34]. However a series of pyrolysis ex-

periment of C_4H_6 isomers by Hidaka et al. [18] suggested fast isomerization among 1,3-butadiene, 1,2-butadiene and 2-butyne before 1,3-butadiene decomposition; Chambreau et al. [19] conducted flash pyrolysis experiments with time-of-flight (TOF) mass spectrometry and their observation implied that fast isomerization of the C_4H_6 species happens prior to C–C bond cleavage to form methyl and propargyl radicals. In flame conditions, bimolecular reactions are usually more important than unimolecular decompositions. As the smallest diene, 1,3-butadiene possesses six vinylic bonds C–H bonds which are stronger than the allylic and allylic bonds. Rate constants of the H abstraction reactions of 1,3-butadiene are consequently lower than that in alkanes or alkenes [35]. With limited rates of H abstraction reactions, the H-addition reaction to yield C_2H_3 and C_2H_4 was found to play an important role in 1,3-butadiene oxidation [16] where two double bonds can be attacked by hydrogen atoms. Another plausible initiation mechanism of 1,3-butadiene is the H-assisted isomerization: $H + 12C_4H_6 = H + 13C_4H_6$. This reaction was included in recent modeling studies of hydrocarbons such as 2-methyl-2-butene and n-heptane [4,36,37]. Ruwe et al. [4] proposed this reaction to suggest a fast conversion from 1,2-butadiene to 1,3-butadiene in a 2-methyl-2-butene flame where 1,2-butadiene is supposed to be

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produced but not detected. However the H-assisted isomerization reaction of 1,2-butadiene to 1,3-butadiene is not yet well understood and its potential contribution remains unclear [4]. To resolve the conflicts in experimental observations, theoretical efforts that unravel the fundamental reaction mechanisms of 1,3-butadiene are needed.

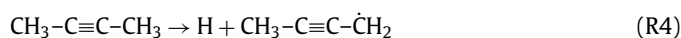
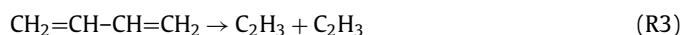
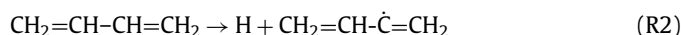
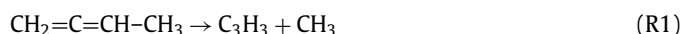
Lee et al. [38] explored the C_4H_6 PES with G2M(MP2)//B3LYP/6-311G** and calculated the energy-resolved rate constants of all the reactions under photodissociation conditions. Chin et al. [39] recharacterized the C_4H_6 PES at CCSD(T)/6-311+G(3df,2p) level and captured the energy-resolved rate constants with RRKM method. Du et al. [40] calculated the T-P- dependent kinetics of C_4H_6 with only direct dissociation pathways considered. Wang et al. [41] conducted RRKM/master equation (ME) to obtain the T-P- dependent kinetics of C_4H_6 which were adopted in the widely used models such as USC mech II [42] and Aramco Mech 2.0 [43,44] but their calculation also did not include isomerization paths. To the best of our knowledge, T-P- dependent kinetics on an extensive C_4H_6 PES is not available. As to the H-assisted isomerization of 1,3-butadiene, although it was suggested by several modeling studies [4,36,37], until now no theoretical calculation exists for this reaction and its rate constant is merely an estimation.

Elucidation of the detailed consumption mechanism of 1,3-butadiene is essential for understanding the formation of soot precursors and PAH controls. This paper is concerned with the initiation mechanism of 1,3-butadiene in pyrolysis and oxidation. The ab initio based RRKM/ME method is used to characterize the unimolecular isomerization, H-assisted isomerizations and thermal decompositions of C_4H_6 isomers. Simulations for 1,3-butadiene at both flame and pyrolysis conditions are carried out and comparisons are made between available experimental results and model computations. Rate of Production (ROP) analysis was performed to reveal the initial fuel consumption pathways in 1,3-butadiene pyrolysis and combustion. And it is discussed how the initiation mechanism impacts the formation of important precursors to benzene. The effects of the pressure-dependent kinetics on model prediction ability on soot precursors are also revealed under various pressures.

2. Methodology

2.1. Theoretical calculation

The optimized equilibrium geometries of all stationary points were obtained using the QCISD method [45] with the 6-311++G(2df,2p) basis set. Rovibrational properties of these stationary points are also obtained at the same level, while the vibrational frequencies were scaled by a factor of 0.954 [46]. Single point energies (SPEs) were computed at the level of CCSD(T)-F12/cc-pVTZ-F12 [47]. The minimum energy paths (MEPs) for the below dissociation channels that do not have reverse barriers were constructed with the complete active space self-consistent field theory with second-order perturbation (CASPT2) [48] incorporating with the Dunning-style, double-zeta basis set [49].



For radicals such as methyl or vinyl, which are not resonance-stabilized, a small two-electron, two orbital (2e,2o) active space was sufficient to provide accurate interaction energies (for example R3). In contrast, for resonance-stabilized radicals the (2e,2o)

active space is not adequate to describe the delocalized orbital [50]. Therefore, for reactions (R1) and (R4) (6e,6o) active space was used to include the delocalized π -orbitals. For (R2) we choose the (4e,4o) active space. High-level energies were obtained through the complete basis set (CBS) extrapolation [51] of CASPT2 calculations for the cc-pVTZ and cc-pVQZ bases. An ionization potential-electronic affinity (IPEA) shift of 0.25 was introduced into the CASPT2 calculations [52]. The CCSD(T)-F12 and CASPT2 calculations were performed by the MOLPRO program package [53]. All the other quantum chemical calculations were carried out with the Gaussian 09 program [54].

Rate coefficients for the thermally and chemically activated reactions are obtained by RRKM/ME calculations, with temperature ranging from 800 to 2200 K, and pressure from 0.01 to 100 atm. The vibrational modes corresponding to methyl and ethyl like internal torsions were treated as 1-dimensional hindered rotors with hindrance potentials computed at the level of B3LYP/6-311++G(d,p). For other vibrational modes, harmonic oscillator assumptions were employed to evaluate the densities of states. The barrierless C–C and C–H fission channels were treated with the variational transition state theory (VTST) employing C–C or C–H separations as a distinguished reaction coordinate. The asymmetric Eckart Tunneling corrections [55] were included. For the collisional model used in the master equation simulation, the interaction between the reactant and the bath gas Ar was modeled by the Lennard–Jones (L–J) potential [56]. The L–J parameters were estimated by the method described in [57, 58]. For Ar, $\sigma = 3.47 \text{ \AA}$, $\varepsilon = 79.2 \text{ cm}^{-1}$; for C_4H_6 , $\sigma = 5.30 \text{ \AA}$, $\varepsilon = 225.8 \text{ cm}^{-1}$. The collisional energy transfer function was represented by a single-parameter exponential down model with $\langle \Delta E \rangle_{\text{down}} = 125 \times (T/298)^{0.85} \text{ cm}^{-1}$ which has served as a fairly good model for C3, C4 hydrocarbons [59–61]. The RRKM/ME rate coefficients are computed by using the kinetic code - MESS [62]. The MESS code uses the chemically significant eigenstate approach of Miller and Klippenstein [63] to determine the phenomenological rate coefficients. Details of this method can be found in [64–67], and it has been validated in previous studies on C_3H_7 , C_4H_7 [68,69] to provide accurate results for complex reaction systems. Moreover, this code also provides an automated algorithm for the well-merging phenomenon [70].

2.2. Kinetic modeling

The base models used in the current study is Aramco Mech 2.0 mechanism [43,44]. The new computational results for the initiation reactions of C_4H_6 have been incorporated into the mechanisms. In total 26 reactions were updated or added in the base models, as listed in the Supplementary material. The unimolecular decomposition of C_4H_6 isomers and isomerization among C_4H_6 isomers were calculated in the present work based on the C_4H_6 PES. The previously missing “well-skipping” reactions such as $13C_4H_6 = CH_3 + C_3H_3$ was added into the base models and the sequential reactions that were already included in the original models were updated. The H-addition elimination reaction $H + 13C_4H_6 = C_2H_3 + C_2H_4$ was taken directly from our recent work [69] focusing on the C_4H_7 PES. The H-assisted isomerization of $12C_4H_6$ to $13C_4H_6$ was calculated in this work using the same theoretical method based on an extended C_4H_7 PES [69]. Except for the newly explored channel to $12C_4H_6 + H$, all the other stationary points were taken from [69]. To avoid redundancy, we provide a simplified C_4H_7 PES with the new entrance channel $12C_4H_6 + H$ and major exit channels in Fig. S10. The master equation calculation was performed with the detailed C_4H_7 PES. The H abstraction reactions of C_4H_6 isomers were not changed since they have been used in previous studies on 1,3-butadiene oxidation and have satisfactorily reproduced the experimental observations [16,27]. Detailed discussion on the key initiation reactions will be provided in

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