Furan formation pathways exploration in low temperature oxidation of 1,3-butadiene, trans-2-butene, and cis-2-butene

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Abstracts:

Furan is one of the smallest organic compounds with heterocycle ring. With this particular molecular structure, furan is considered as a highly toxic and carcinogenic combustion pollutant, and furan may contribute to the formation of oxygenated soot. In this work, furan formation pathways from 1,3-butadiene, trans-2-butene and cis-2-butene were comprehensively explored. The potential energy surfaces, reaction rate coefficients, and thermodynamics were calculated by quantum chemistry using high level of theories including the CCSD (T) and G3 methods. The proposed reaction pathways were then implemented into the AramcoMech 3.0 model uniformly or independently to examine the model performance with the experimental data. The oxidation experiments of 1,3-butadiene, trans-2-butene and cis-2-butene were performed in a jet stirred reactor (JSR) in the low temperature regime (500-830 K). The JSR is coupled with time-of-flight molecular beam mass spectrometry (ToF-MBMS) using synchrotron radiation as photon ionization source for species identification and quantification. Compared with experiments, both updated models (the independent and uniform model) showed better prediction of furan than the

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base AramcoMech 3.0 model, which highlighted the contribution of the proposed pathways. Reaction pathway analyses reveal that in the proposed reaction pathway, both reactions $C_4H_6 + OH \rightleftharpoons S1-4$ ($H_2C=CH-\dot{C}H-CH_2OH$, but-1-en-3-yl-4-ol) and $C_4H_6 + HO_2 \rightleftharpoons C_4H_61-3OOH4$ ($H_2C=CH-\dot{C}H-CH_2OOH$, but-1-en-3-yl-4-peroxide) not only contribute to furan formation, but also to fuel consumption. Furthermore, the kinetic uncertainty from activation energy calculated by the CCSD series methods, CBS-ANPO, and G4 methods was evaluated for reaction $C_4H_6 + HO_2 \rightleftharpoons C_4H_61-3OOH4$. Instead of developing a new kinetic model, this work aims at proposing and validating new reaction pathways to advance the understanding of furan formation chemistry in low temperature oxidation, and provide guidance for future model development.

Keyword: furan; reaction pathway; low temperature oxidation; pathway analysis; reaction rate coefficients.

1. Introduction

Heterocycles are harmful pollutants that can have detrimental effects on human health and air quality. One of the most common small heterocycles is furan with four carbon atoms and one oxygen atom in the conjugated ring. The furan has low molecular weight of 68 g/mol, a high volatility and a high hydrophobicity, so it can be inhaled and dissolved in the organic tissues [1]. Many medical studies have identified furan to be highly carcinogenic [2, 3]. Some studies on mice showed that furan had a high risk of hepatocellular adenomas and carcinomas [4], and the World Health Organization listed furan as a carcinogenic substance with high priority [5].

Furan is not only harmful to the human health, but also may have a minor effect on climate change. The high amount of furan released from combustion contributes to the formation of oxygenated polycyclic aromatic hydrocarbons (OPAH) [6]. The OPAH molecules with furanic

structures, e.g. dibenzofuran, have relatively low Gibbs free energies due to ring conjugation, so they can survive longer at high flame temperatures [7, 8]. OPAH can be attached to the surface of the soot particles [9-11], hence increasing their hygroscopicity [12]. These hydrophobic soot particles can influence the climate by absorbing large amounts of water vapor before acting as nuclei for cloud condensation [13]. The effect of soot hygroscopicity on cloud condensation and climate change is a large uncertain part in the climate predictions [14, 15].

The attention to furan emission is growing with the prevalence of bio-fuels for engines and power plants [16], especially since the furan derivatives are proposed as promising candidates for the next generation bio-fuels with low carbon footprint [17]. Elevated furan formation is also reported for biomass combustion [18, 19]. In practical engines fueled by gasolines and other hydrocarbons, furan is not a direct major emission pollutant due to short residence time, but it may play a role on the OPAH and oxygenated soot formation. Many previous studies focused on the combustion chemistry of furan and its derivatives [20]. Fundamental studies of furan combustion chemistry include ignition delay time [21], speciation in premixed laminar flames [22, 23], counterflow diffusion flames [24], flow reactors [25, 26], and jet-stirred reactors (JSR) [27]. Although a large amount of work has been reported to study furan combustion, the understanding of furan formation is currently limited. Johansson *et al.* [6] studied the formation chemistry of OPAH with furanic structures at high temperatures in ethylene premixed and diffusion flames. However, studies in the low temperature regime are scarce, and the understanding of furan formation chemistry at low temperatures (< 850 K) needs to be enhanced.

In the latest C_1 - C_4 reaction mechanisms [28, 29], furan formation is described by 1,3-butadiene + $HO_2 \rightleftharpoons$ 2,5-dihydrofuran + OH and 2,5-dihydrofuran $\rightleftharpoons$ furan + H_2 reactions with the estimated kinetic parameters in the high temperature regime [30]. The possible contribution of 1,3-

butadiene + OH reaction to furan formation is not well studied in the low temperature regime. It is also not clear whether furan can be directly produced from cis-2-butene and trans-2-butene. Since cis-2-butene and trans-2-butene are important primary intermediates from low temperature oxidation of gasoline and butanols, detailed furan formation pathways starting from 1,3-butadiene, trans-2-butene, and cis-2-butene were explored and proposed with the consideration of OH and HO₂ radicals as initial adduct reactants in this work. The low temperature chemistry of 1-butene, another important intermediate in gasoline and butanol combustion, was studied in our previous work [31], but furan was not detected, so it is not included in this work.

The remaining part of the paper is composed as follows. Section 2 describes the methodology of quantum chemistry, reaction rate coefficient calculations, JSR experiments and kinetic modeling. Section 3 shows the proposed furan formation pathways starting from trans-2-butene, 2-butenyl radical, 1,3-butadiene and cis-2-butene. These pathways with their calculated rate coefficients were implemented into the base AramcoMech 3.0 model [29] independently or uniformly to test the influence of the base model on furan formation. Section 4 first presents the experimental identification of furan, followed by furan concentration comparison between experiments and simulations using different kinetic models. Pathway analyses were performed to highlight the contribution of the reactions $C_4H_6 + OH \rightleftharpoons S1-4$ ($H_2C=CH-\dot{C}H-CH_2OH$, but-1-en-3-yl-4-ol) and $C_4H_6 + HO_2 \rightleftharpoons C_4H_61-3OOH4$ ($H_2C=CH-\dot{C}H-CH_2OOH$, but-1-en-3-yl-4-peroxide) to furan formation and fuel consumption. The influence of the deviated activation energies of $C_4H_6 + HO_2 \rightleftharpoons C_4H_61-3OOH4$ is revealed. Pressure dependence is examined for the dominant pathway to furan. Section 5 concludes the whole paper.

2. Methodology

2.1 Quantum chemistry and reaction rate calculations

The local minimum and transition state structures in all proposed reaction pathways were optimized at the DFT/B3LYP/6-311 G+(d,p) level except for 1,3-C₄H₆ + OH barrier-less addition reaction, where the M06-2X/6-311 G+(d,p) method was used to describe the minimum energy pathway (MEP). The frequencies used in reaction rate calculations were obtained using the same method with a correction factor of 0.967 for the DFT/B3LYP/6-311G+(3df,2p) method [32]. To improve the energy accuracy, single-point energies of each structure were further refined using the G3 and CCSD(T)/cc-pvdz methods with geometry optimized at the DFT/B3LYP/6-311/G+(d,p) level. The G3 method was reported to have a mean absolute deviation of 1.07 kcal/mol from experiment based on numerous comparisons [33], and the mean error of the CCSD(T)/cc-pvdz method was estimated to be 1.9 kcal/mol [34]. There were a few reactions where the G3 method failed to converge, so the energy barrier from the CCSD(T)/cc-pvdz method was used in kinetic calculations instead. The contribution to furan formation from most reactions with energy barrier described by CCSD(T)/cc-pvdz method was tested to be negligible in the pathway analysis. Therefore, the accuracy of energy barrier is not an issue to affect the corresponding modelling conclusion. By comparison, the energy barriers evaluated by the G3 and CCSD(T)/cc-pvdz methods match well, and the deviation is within 1.5 kcal/mol for most of the reactions. The biggest energy deviation appears for the 1,3-C₄H₆ + HO₂ ⇌ C₄H₆1-3OOH4 (H₂C=CH-ĊH-CH₂OOH, but-1-en-3-yl-4-peroxide) reaction, where the forward reaction energy barrier calculated using the G3 method is lower than that using the CCSD(T)/cc-pvdz method by 5.3 kcal/mol. Because of the importance of this reaction, the energy barrier was further calculated using the CCSD(T)/complete basis set extrapolation (CBS) [35], CBS-ANPO, and G4 methods for uncertainty analyses in model predictions. All transition states were carefully examined by the intrinsic reaction coordinate (IRC)

calculations to ensure that the transition state connects the reactants and products. All quantum chemistry calculations were performed using Gaussian 09 software package (version D.01) [36].

In this study, most of the reactions are bimolecular reactions. For example, one furan formation pathway starting from 1,3-butadiene mainly consists of $1,3\text{-butadiene} + \text{OH} \rightarrow 2,5\text{-dihydrofuran (P1-8)} + \text{H}$, $1,3\text{-butadiene} + \text{HO}_2 \rightarrow 2,5\text{-dihydrofuran} + \text{OH}$, and $\text{P1-8} + \text{H} \rightarrow \text{S1-14} + \text{H}_2$. The pressure-dependence of reaction rate coefficients in these bimolecular reactions is expected to be ignorable according to previous studies [37]. Moreover, the pressure-dependence of rate coefficients of decomposition reactions becomes weak in the investigated temperature range of 500-900 K, as evidenced by [38, 39]. Therefore, all reaction rate coefficients were initially evaluated at the high-pressure limit and adopted in the kinetic models. Then, the pressure dependence of important reaction pathways filtered by pathway analyses was examined using the RRKM theory by solving the master equation (RRKM-ME) method to investigate if furan formation is pressure dependent in the investigated low-temperature regime. High-pressure limit rate coefficients for reactions with tight transition states were evaluated by transition state theory (TST) based on the frequencies, energy barriers, and molecule information from quantum chemistry calculations. For the barrier-less molecule + radical addition reactions and corresponding dissociation reactions, the reaction rate coefficients were calculated using variational transition state theory (VTST) with the MEP described by the M06-2x/6-311+G(d,p) method. The target C-O bond distance scans were performed with calculation of the optimized structure, energy and vibration frequency at 0.05 Å interval. It was visually confirmed that each point contains a frequency with vibration corresponding to motion along the MEP. The single point energy of each point was further refined using the CCSD(T)/cc-pvdz method. The rate coefficients of H-atom abstraction reactions of trans-2-butene and cis-2-butene by H/OH/OH/HO₂/CH₃

radicals were taken from the 2-butene system [40]. In addition, the rate coefficients of the barrier-less addition reactions, e.g., $n\text{-C}_4\text{H}_5 + \text{HO}_2$ and $n\text{-C}_4\text{H}_5 + \text{OH}$, were chosen by analogy to the benzyl [41] and 1-buten-4-yl [40] systems due to the similarity in the molecular moiety.

The pressure-dependent reaction rate coefficients were calculated in the pressure range of 0.01-10 atm and temperature range of 800-2000 K via RRKM-ME using the MultiWell program suite [42]. The maximum energy was set as $300,000 \text{ cm}^{-1}$. In the Multiwell simulations, the translational and vibrational temperatures were assumed to be the same. To accurately describe the sums and densities of states, an energy grain size of 10 cm^{-1} was used. The collisional energy transfer was described by the temperature-independent exponential-down model ($\Delta E_{\text{down}} = 260 \text{ cm}^{-1}$). It is noteworthy that the reaction rate coefficients in the low temperature regime should be less sensitive to the choice of the collisional energy transfer model, as indicated in our previous study [39] where both temperature-independent exponential-down model ($\Delta E_{\text{down}} = 260 \text{ cm}^{-1}$) and temperature-dependent exponential-down model ($\Delta E_{\text{down}} = 200 \times (T/300 \text{ K})^{0.85} \text{ cm}^{-1}$) [43] were examined. Argon was the bath gas collider with Lennard-Jones parameters σ and ε/k_B of $3.47 \text{ \AA}$ and 114 K . The Lennard-Jones parameters of other species were assumed to be the same as those of furan. In the $1,3\text{-butadiene} + \text{OH} \rightarrow 2,5\text{-dihydrofuran (P1-8)} + \text{H}$ pathway, the loose transition state was utilized to describe the entrance barrier-less $1,3\text{-butadiene} + \text{OH} \rightarrow \text{S1-4 (H}_2\text{C=CH-}\dot{\text{C}}\text{H-CH}_2\text{OH, but-1-en-3-yl-4-ol)}$ reaction, because similar treatment was used by da Silva *et al.* [41]. The yield of product was calculated by initiating the S1-4 with chemical activation energy distribution at different temperatures and pressures. The calculation time was long enough for the bimolecular reaction to reach the equilibrium.

The enthalpies of formation at 0 K were calculated by the atomization method using the G3 or CCSD(T)/cc-pvdz methods [44] for new species. The temperature-dependent formation enthalpies,

entropies, and heat capacities were evaluated by traditional statistical thermodynamics in the MultiWell program suite [42].

2.2 Jet stirred reactor (JSR) experiments

The JSR experiments were performed at the Chemical Dynamic Beamline of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, California, USA. Detailed descriptions for this setup are available in the literature [45-47], so here is just a brief description. The spherical reactor (volume 33.0 cm³) is made of quartz to minimize the surface reactions. MKS mass flow controllers are used to control the residence time by regulating all the gas flows. The gaseous fuel is mixed with argon as diluent, and then the mixture is introduced to the inlet of the reactor via the inner capillary tube. The capillary tube is preheated to 100 Celsius degrees before admission into the reactor. Oxygen with argon as diluent is introduced through the outer channel to the reactor inlet, so oxygen and fuel cannot meet before the reactor. After admission of the reactants, four opposing nozzles are used to create the jet flows, and the jet flows stir the spherical reactor to achieve a homogeneous reaction environment, so the JSR is considered as 0D perfectly stirred reactor for simple modeling. An electrically heated oven outside the JSR heats up the reactor to the desired reaction temperatures. A K-type thermocouple (uncertainty of 25 K) located on the outside surface of the JSR monitors the reaction temperature, and the temperature inside the reactor was corrected from the measurements following the procedure described by Chen *et al.* [31]. Sample gas is continuously extracted by a quartz sampling nozzle connected to the time-of-flight molecular beam mass spectrometer (ToF-MBMS) at the reactor exit. Two stages of vacuum pumping are applied to create the pressure differences, and generate the molecular beam to quench further reactions, and minimize the loss of reactive radicals and unstable intermediates in the sample gas.

A synchrotron vacuum ultraviolet beam is used as photon ionization source to softly ionize the molecules, and signals on the MS are measured for species quantification. The biggest advantage of photon ionization is that the photon energy can be well controlled within the accuracy of 0.01 eV. This feature brings many benefits for species detection and quantification. First, the photon energies for different species can be carefully chosen to minimize the fragmentations and benefit species quantification. A description of the conversion procedure of species signals to mole fractions is available in the literature [31, 45]. Detected and quantified species with their conversion details are listed in Table S1 in the Supplementary Material-4. The estimated experimental uncertainty of species quantification is 20% for fuel and oxygen, and a factor of 2 for intermediates and products with the measured photon ionization cross sections according to previous literature on the same setup [31]. The photon ionization efficiency (PIE) scans can be performed to identify species by their ionization energies in the database [48]. The experimental uncertainty for photon ionization efficiency (PIE) scan signals is estimated to be 20%. The quantified species at different temperatures from all three experiments account for more than 90% of the carbon atoms, except at 830 K in cis-2-butene experiments, where over 80% is accounted for.

In this work, the JSR experimental conditions are similar among the three fuels: fuel mole fraction of 1.0%, oxygen of 27.5%, argon of 71.5% for 1,3-butadiene; fuel mole fraction of 1.0%, oxygen of 30.0%, and argon of 69.0% for trans-2-butene and cis-2-butene. The reactant compositions are designed to have the same equivalence ratio of 0.2 for all three fuels. The other experimental conditions were residence time of 4.0 seconds, pressure at 700 Torr (≈ 0.933 bar), and temperatures from 500 K to 860 K. The selection of low equivalence ratio and long residence time is to enhance the fuel conversion in the low temperature regime. For safety reason, the argon

concentration needs to be above 50% and the oxygen concentration cannot be too high, so leaner conditions were not pursued. Longer residence time is also not chosen since these may compromise the mixing inside the reactor. The three gaseous fuels, 1,3-butadiene, trans-2-butene, and cis-2-butene from Sigma-Aldrich have the purity above 99%. The oxygen and argon from Praxair have the purity above 99.99%.

2.3 Kinetic modelling

The base model for the numerical simulation in this study is the C₁-C₄ AramcoMech 3.0 model [29]. This model has been validated against the ignition delay time of 1,3-butadiene, trans-2-butene, and cis-2-butene in the low temperature regime. Using the latest NUIGMech model [49] as the base model is not necessary, because its C₄ low temperature chemistry is inherited from the AramcoMech 3.0 model. In this work, the proposed furan formation pathways with reaction rate coefficients, and thermodynamics for the new intermediate species were implemented into the base AramcoMech 3.0 model, as shown in Supplementary Material-1. After the implementation, two different treatments were used to test the base model influence. The first one (referred as uniform model) united a number of species that are the same as those in the AramcoMech 3.0 model. The list of duplicated species is presented in Table S2 in the Supplementary Material-4. In the second one (referred as independent model), the species names were kept different to minimize the influence of the base model. Simulation results using both models and the base model are presented to examine the furan formation.

Simulations were performed by ANSYS Chemkin 19.1 software [50]. The conditions for the perfectly stirred reactor model were the same as the experiments. The end time is set arbitrarily as 50 seconds to ensure converged solutions. The rate of production analysis tool in the software package was used to examine the contribution of the proposed reaction pathways.

3. Proposed furan formation pathways

The goal of this work is to explore the furan formation pathways from C₄ fuels in the low temperature regime. The oxidant radical addition reactions on one of the two central C atom of C₄H_x (x = 5-8) molecules are unlikely to form furan. Therefore, the investigated H-atom abstraction and radical addition reactions are focused on the terminal C atom in this study. The proposed furan formation pathways starting from C₄H₈, C₄H₇, and C₄H₆ molecules are investigated, respectively. All nomenclatures of molecules are included in the pathway network in the following figures (Figs. 1,3,5,6).

3.1 Pathways starting from H-atom abstraction of trans-2-butene

The furan (P1-9) formation pathway network starting from H-atom abstraction of trans-2-butene (R1-1) is shown in Fig. 1. The H-atom abstraction reactions $R1-1 + H \rightleftharpoons S1-2 + H_2$, $R1-1 + O \rightleftharpoons S1-2 + OH$, $R1-1 + OH \rightleftharpoons S1-2 + H_2O$, $R1-1 + HO_2 \rightleftharpoons S1-2 + H_2O_2$, and $R1-1 + CH_3 \rightleftharpoons S1-2 + CH_4$ are considered in this study. Many previous studies indicate that HO₂ and OH are the most important radical oxidants at low to intermediate temperatures [41, 51, 52]. Here, the addition of HO₂ is considered, followed by H₂O elimination reaction. The addition reaction of HO₂ and S1-2 radical is barrier-less, which is confirmed by the relaxed scan calculation. The calculated energy monotonically increases with the bond distance between the O atom of HO₂ and the unsaturated C atom on S1-2, which is similar to the MEP in benzyl + HO₂ system [41]. The H₂O eliminates from the adduct S1-10 with the energy barrier of 43.6 kcal/mol ($S1-10 \rightarrow S1-11 + H_2O$). The 2,5-dihydrofuran (P1-8) is formed via the pathway of $S1-11 \rightarrow S1-12 \rightarrow S1-13 \rightarrow P1-8$. This pathway is featured by H-atom transfer ($S1-11 \rightarrow S1-12$, 80.1 kcal/mol), C-C rotation ($S1-12 \rightarrow S1-13$, 1.9 kcal/mol), and cyclization ($S1-13 \rightarrow P1-8$, 67.4 kcal/mol). In the cyclization reaction $S1-13 \rightarrow P1-$

8, it was observed that the H-atom transfer happens prior to the cyclization (see Fig. 2). Furan (P1-9) is formed via the dehydrogenation reactions of 2,5-dihydrofuran (P1-8) by either H₂ elimination (P1-8 → P1-9 + H₂, 48.6 kcal/mol) or H-atom abstraction from H, OH, and HO₂ radicals (e.g., P1-8 + H → S1-14 + H₂, 5.4 kcal/mol; S1-14 → P1-9 + H, 32.1 kcal/mol).

3.2 Pathways starting from H-atom abstraction of 2-butenyl radical

Instead of the OH/HO₂ addition reactions, the alternative H-atom abstraction reaction of 2-butenyl (S1-2) produces 1,3-butadiene (S1-3). Here, the following reactions of OH and HO₂ radical addition to 1,3-butadiene are considered (see Fig. 3). The OH radical addition reaction is barrier-less (see Fig. 4a), but HO₂ addition reaction has tight transition state (see Fig. 4b). Once S1-4 is yielded from OH radical addition reaction, the furan precursor P1-8 is produced via the pathway of S1-4 → S1-5 → S1-6 → S1-7 → P1-8 + H. Reaction S1-4 → S1-5 involves H-atom transfer from OH moiety to the adjacent C atom with the energy barrier of 40.3 kcal/mol. The reaction S1-5 → S1-6 (2.9 kcal/mol) is featured by C-C rotation to facilitate the subsequent cyclization (S1-6 → S1-7). The energy barrier of S1-6 → S1-7 reaction is 19.3 kcal/mol, much lower than that of S1-13 → P1-8 (67.6 kcal/mol). S1-7 → P1-8 + H is an H-atom elimination reaction with the energy barrier of 36.9 kcal/mol. This value is close to the energy barrier in typical H-atom elimination reaction in hydrogen-abstraction/acetylene-addition pathway (~ 38 kcal/mol) [37]. The subsequent pathway of furan formation from P1-8 was discussed before.

If the entrance channel is HO₂ addition reaction (S1-3 + HO₂ → S1-18, 11.2 kcal/mol), there are two pathways leading to furan. They are S1-3 + HO₂ → S1-18 → S1-20 → S1-21 → S1-13 → P1-8 → P1-9, and S1-3 + HO₂ → S1-18 → S1-24 → P1-8 → P1-9 as shown in Fig. 3. The following kinetic analysis indicates that the former pathway is less competitive due to the high energy barrier of S1-13 → P1-8 (67.4 kcal/mol), so the latter pathway is dominant. S1-18 → S1-

24 is a C-C rotation reaction with the energy barrier of 16.2 kcal/mol in the pathway of S1-3 + HO₂ → S1-18 → S1-24 → P1-8 + OH → P1-9 + OH + H₂. The following step S1-24 → P1-8 (24.6 kcal/mol) eliminates OH radical first, and then forms 5-member ring as shown in Fig. 4c. Please note that S1-24 can also be formed if the C-C rotation of S1-3 happens prior to the HO₂ addition reaction, which will be included in the pathway network starting from H-atom abstraction of cis-2-butene in section 3.4.

3.3 Pathways starting from H-atom abstraction of 1,3-butadiene

The further H-atom abstraction reactions of 1,3-butadiene produce S1-15, which rapidly converts to S1-16 and S1-22 respectively via the barrier-less addition reactions as shown in Fig. 5. Starting from S1-16, there are two pathways (S1-16 → S1-17 → S1-19 → S1-14 → P1-9 + H and S1-16 → S1-17 → S1-13 → P1-8 → P1-9 + H₂) that contribute to furan formation. The main features of the first pathway include C-C rotation (S1-16 → S1-17, 5.8 kcal/mol), H-atom abstraction (S1-17 + H → S1-19 + H₂, 8.0 kcal/mol), cyclization (S1-19 → S1-14, 26.7 kcal/mol), and H-atom elimination (S1-14 → P1-9 + H, 33.8 kcal/mol). The reaction step S1-17 + H → S1-19 + H₂ in the second pathway has lower energy barrier than the one of S1-17 → S1-13 (63.4 kcal/mol) in the first pathway, but the requirement for an extra H radical undermines its contribution.

For the pathway of S1-15 + HO₂ → S1-22 → S1-23 → S1-14 + OH → P1-9 + OH + H with HO₂ addition as entrance channel, the main features are similar to that of S1-3 + HO₂ → S1-18 → S1-24 → P1-8 + OH with cyclization reaction as the rate-determining step. It is also noteworthy that the low concentration of S1-15 in low temperature regime limits its contribution to furan formation. For example, the calculated mole fraction of S1-15 in 1,3-butadiene case is only 1.07×10^{-11} at 800 K.

3.4 Pathways starting from cis-2-butene

To complete the reaction network for furan formation, some possible reaction pathways starting from cis-2-butene (S2-1) to furan are proposed, investigated, and shown in Fig. 6. Generally, once the rotation of the middle C-C bond happens ($S2-2 \rightarrow S1-2$, $S2-3 \rightarrow S1-3$), the growth network of S2-1 is similar to that of trans-2-butene as discussed before.

3.5 Calculated rate coefficients of reactions in the pathway network

Based on the results and discussions in previous sections, the rate coefficients of reactions in the pathway network were calculated and presented in Table 1 in the form of Arrhenius coefficients. The rate validations using the RRKM-ME method were done for the thermal decomposition reaction of phenol and those using the TST method were done for addition reactions of C_2H_2 +phenyl and phenyl+ phenylacetylene in our previous studies [39, 53, 54]. Here, the reaction rate coefficients of the $C_4H_6 + OH$ addition reaction using VTST is tested against the values by Bai *et al.* [55]. As shown in Fig. 7, our results match well with the reported data and the deviation is within 30%. BH&HLYP/6-311++G(d,p) level of theory is used by Bai *et al.* [55] to describe the vibrational frequencies, while the M06-2X/6-311G+(d,p) method is used in this study. The rate deviation is likely resulting from the different choice of the calculation method. The updated reaction rate coefficients for H-atom abstraction are listed in Table S3 in the Supplementary Material-4. The Chemkin format of species thermodynamics is provided in the Supplementary Material-2.

Table 1: Reaction rate coefficients of the proposed reaction pathways (Units of E: kcal/mol).

Nomenclatures of molecules are included in Figs. 1,3,5,6.

No.	Reaction	A	n	E	Comments
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Pathways starting from 1,3-C ₄ H ₆					
1	S1-3+OH → S1-4	4.2 x 10 ⁶	1.911	-3.232	This study
-1	S1-4 → S1-3+OH	1.7 x 10 ¹⁵	-0.244	36.80	This study
2	S1-4 → S1-5	1.7 x 10 ¹¹	0.3909	35.98	This study
-2	S1-5 → S1-4	3.3 x 10 ¹¹	0.3106	27.36	This study
3	S1-5 → S1-6	2.4 x 10 ¹²	-0.0022	2.89	This study
-3	S1-6 → S1-5	6.7 x 10 ¹²	0.045	2	This study
4	S1-6 → S1-7	2.5 x 10 ¹²	-0.06	19.3	This study
-4	S1-7 → S1-6	6.1 x 10 ¹²	0.131	32.74	This study
5	S1-7 → P1-8+H	3.1 x 10 ¹¹	0.7598	37.92	This study
-5	P1-8+H → S1-7	3.4 x 10 ⁸	1.508	4.22	This study
6	P1-8 → P1-9+H ₂	3.5 x 10 ⁷	1.475	41.86	This study
-6	P1-9+H ₂ → P1-8	2.9 x 10 ¹	2.926	40.84	This study
7	P1-8+H → S1-14+H ₂	6.0 x 10 ⁷	1.753	3.23	This study
-7	S1-14+H ₂ → P1-8+H	2.8 x 10 ⁴	2.462	26.02	This study
8	S1-14 → P1-9+H	2.4 x 10 ¹¹	0.7632	28.42	This study
-8	P1-9+H → S1-14	7.8 x 10 ⁸	1.434	4.42	This study
9	P1-8+O ₂ → S1-14+HO ₂	2.4 x 10 ¹	3.207	4.46	This study
-9	S1-14+HO ₂ → P1-8+O ₂	6.8 x 10 ⁻²	3.403	15.3	This study
10	P1-8+HO ₂ ⇌ S1-14+H ₂ O ₂	6.3 x 10 ¹	3.37	13.72	Analogy to C ₃ H ₈ +HO ₂ ⇌ C ₃ H ₇ +H ₂ O ₂ [40]
11	P1-8+OH ⇌ S1-14+H ₂ O	4.7 x 10 ⁷	1.61	-0.035	Analogy to C ₃ H ₈ +OH ⇌ C ₃ H ₇ +H ₂ O [40]
12	S1-3+ HO ₂ → S1-18	1.1 x 10 ²	3.047	11.2	This study
-12	S1-18 → S1-3+ HO ₂	2.5 x 10 ¹³	0.085	21.8	This study
13	S1-18 → S1-20+OH	5.6 x 10 ¹²	0.2055	12.95	This study
-13	S1-20+OH → S1-18	2.9 x 10 ⁴	2.588	25.1	This study
14	S1-20 → S1-21	1.7 x 10 ¹²	0.41	33.58	This study
-14	S1-21 → S1-20	1.8 x 10 ¹¹	0.4216	59.58	This study
15	S1-21 → S1-13	3.7 x 10 ¹²	-0.0259	2.198	This study
-15	S1-13 → S1-21	5.0 x 10 ¹²	-0.0465	0.712	This study
16	S1-18 → S1-24	1.9 x 10 ¹³	-0.011	9.0	This study
-16	S1-24 → S1-18	9.9 x 10 ¹²	-0.0003	13.13	This study
17	S1-24 → P1-8+OH	8.0 x 10 ¹¹	0.3419	23.12	This study
-17	P1-8+OH → S1-24	2.9 x 10 ⁴	2.8	46.7	This study
Pathway starting from tran-2-C ₄ H ₇					
18	S1-2+HO ₂ ⇌ S1-10	8.2 x 10 ⁴	2.2	-5.13	Analogy to benzyl+HO ₂ ⇌ benzylhydroperoxide [41]
18	S1-10 → S1-11+H ₂ O	7.0 x 10 ⁹	1.026	37.2	This study
-19	S1-11+H ₂ O → S1-10	5.1 x 10 ⁻²⁶	3.888	97.44	This study
19	S1-11 → S1-12	6.6 x 10 ⁷	1.465	74.1	This study
-20	S1-12 → S1-11	7.5 x 10 ⁷	1.405	69.52	This study
20	S1-12 → S1-13	4.1 x 10 ¹⁰	0.037	1.4	This study
-21	S1-13 → S1-12	1.7 x 10 ¹³	-0.204	1.02	This study
21	S1-13 → P1-8	6.7 x 10 ¹⁰	0.402	66.1	This study
-22	P1-8 → S1-13	1.6 x 10 ¹²	0.511	56.8	This study
Pathways starting from N-C ₄ H ₅					
22	S1-15+OH ⇌ S1-16	3.0 x 10 ¹³	0	0	Analogy to IC ₄ H ₇ +OH ⇌ IC ₄ H ₇ OH [40]
23	S1-16 → S1-17	3.2 x 10 ¹²	0.0615	5.7	This study
-23	S1-17 → S1-16	2.6 x 10 ¹²	0.125	3.1	This study
24	S1-17 → S1-13	1.9 x 10 ¹⁰	0.7917	58.9	This study
-24	S1-13 → S1-17	1.5 x 10 ¹⁰	0.771	70.2	This study

25	$S1-17+H \rightarrow S1-19+H_2$	8.0×10^6	1.941	4.6	This study
-25	$S1-19+H_2 \rightarrow S1-17+H$	2.0×10^3	2.812	37.1	This study
26	$S1-19 \rightarrow S1-14$	5.2×10^{11}	0.091	23.96	This study
-26	$S1-14 \rightarrow S1-19$	5.8×10^{12}	0.15	19.05	This study
27	$S1-15+HO_2 \rightleftharpoons S1-22$	8.2×10^4	2.2	-5.13	Analogy to benzyl+HO ₂ $\rightleftharpoons$ benzylhydroperoxide [41]
28	$S1-22 \rightarrow S1-23$	7.2×10^{12}	-0.0068	5.06	This study
-28	$S1-23 \rightarrow S1-22$	3.3×10^{12}	0.0561	7.91	This study
29	$S1-23 \rightarrow S1-14$	3.0×10^{11}	0.3345	33.1	This study
-29	$S1-14 \rightarrow S1-23$	4.8×10^3	2.446	22.9	This study
Pathways starting from cis-2-C₄H₇					
30	$S2-2+HO_2 \rightleftharpoons S2-5$	8.2×10^4	2.2	-5.13	Analogy to benzyl+HO ₂ $\rightleftharpoons$ benzylhydroperoxide [41]
31	$S2-5 \rightarrow S2-6+H_2O$	6.8×10^7	1.218	41.58	This study
-31	$S2-6+H_2O \rightarrow S2-5$	4.9×10^3	3.98	74.8	This study
32	$S2-5 \rightarrow S2-7+H_2O$	1.3×10^{10}	0.991	36.4	This study
-32	$S2-7+H_2O \rightarrow S2-5$	5.2×10^{-2}	3.799	97.9	This study
33	$S2-6 \rightarrow S2-7$	3.8×10^{10}	0.811	56.2	This study
-33	$S2-7 \rightarrow S2-6$	2.1×10^9	0.8576	84.8	This study
34	$S2-3 \rightarrow S2-4$	3.5×10^{11}	0.234	41.6	This study
-34	$S2-4 \rightarrow S2-3$	3.9×10^{12}	0.276	32.42	This study
35	$S1-2 \rightarrow S2-2$	1.4×10^{13}	0.0519	14.4	This study
-35	$S2-2 \rightarrow S1-2$	4.9×10^{12}	0.0663	13.1	This study
36	$S2-2+HO_2 \rightarrow S1-24$	1.7×10^2	3.007	11.5	This study
-36	$S1-24 \rightarrow S2-2+HO_2$	9.1×10^{12}	0.1938	22.57	This study
37	$S2-3 \rightarrow S1-3$	1.1×10^{13}	-0.1003	2.794	This study
-37	$S1-3 \rightarrow S2-3$	1.5×10^{13}	-0.1	5.704	This study

4. Examination of furan formation pathways

In this section, experimental identification of furan is presented first, followed by the concentration profiles comparison between experiments and simulations using the AramcoMech 3.0 model, the independent model and the uniform model. Please note that the temperatures were shifted 30 K lower to compensate the effect of cooling water on the sampling probe and probe perturbation, which follows the procedure in the literature on the same experimental setup [31, 56]. Pathway analyses are presented later to indicate their contribution to fuel consumption and furan formation. Furthermore, the influence of uncertainty originating from rate coefficient calculations of the key reaction $C_4H_6 + HO_2 \rightleftharpoons S1-18$ (C_4H_6 -3OOH4) on model prediction is discussed in the

uniform model. All of the speciation data from experiments are available in Supplementary Material-3.

4.1 Furan identification and quantification by experiments, and predictions by simulations

4.1.1 Experimental identification of furan

To identify furan, PIE scans were performed in 1,3-butadiene and trans-2-butene experiments as shown in Fig. 8, but not for cis-2-butene experiment because of the low signals of C₄H₄O. The PIE scan was performed from 8.50 eV to 10.50 eV with 0.05 eV per step at a reaction temperature of 830 K to achieve large signals of C₄H₄O. It is observed that the onset in both 1,3-butadiene and trans-2-butene experiments is 8.85 eV. The match of this onset with the ionization energy of furan (onset: 8.88 eV [57]), and the fitting curves of furan photon ionization cross section in the database [57] both identify C₄H₄O as furan. Other isomers with molecular formula of C₄H₄O are less probable than furan, because their molecular structures are too difficult to be formed, and they have different ionization energies. Table S4 in the Supplementary Material-2 lists a few conceivable isomers with the molecular formula of C₄H₄O.

4.1.2 Predictions of furan in 1,3-butadiene, cis-2-butene, and trans-2-butene experiments

The examination of the proposed furan formation pathways is described in this section. Mole fraction profiles of furan vs temperature were compared and presented in Fig. 9 for all three fuels. Scattered points are from experiments, and lines with different colors and styles represent different kinetic models. Among the three fuels, 1,3-butadiene produces the highest furan concentrations, which is followed by trans-2-butene. Cis-2-butene has lowest furan formation by both experiments and simulations in the low temperature regime. The differences of furan formation among the three fuels suggest that most of the furan is originated from 1,3-butadiene, and the furan formation from

trans-2-butene and cis-2-butene is minor. Both predictions by the uniform model and the independent model show good agreement for furan formation in the 1,3-butadiene case with some minor differences, but the AramcoMech 3.0 model did not. Note that in the 1,3-butadiene case, the trends of profiles using both updated models differ between experiment and simulation. However, the simulation results fall into the experimental uncertainty range, which means major furan formation pathways are covered. For the trans-2-butene case, the experimental data have higher values than simulations, although the quantified furan concentration is low. The concentrations of furan are near the detection limit of the device (10 ppm), which may be responsible for the mismatch.

The dominant furan formation pathway in the AramcoMech 3.0 model is dehydrogenation of 2,5-dihydrofuran ($C_4H_6O_2$). The 2,5-dihydrofuran is produced from cyclization of but-1-en-3-yl-4-peroxide ($C_4H_6O_2$), which can be traced back to but-3-en-1-yl radical (C_4H_7) and C_4H_6 . The under-prediction of the 2,5-dihydrofuran mole fraction causes under-prediction of furan in the AramcoMech 3.0 model. In the independent and uniform models, more complete furan formation networks (see Figs. 1, 3, 5, 6) are proposed, and the improvements substantiate the importance of the proposed furan formation pathways.

4.2 Influence of proposed pathways on fuel consumption

The fuel reactivity is sensitive to OH and HO_2 radical concentrations in the low temperature regime, where the OH and HO_2 radicals trigger the chain reactions. The furan formation is also initiated by OH and HO_2 radicals, which might influence the radical pool and hence the fuel consumption. Therefore, the influence of proposed pathways on fuel consumption rates is examined in this section. Figure 10 shows the comparison among experiments and three model predictions for the fuels in all three cases. The AramcoMech 3.0 model over-predicted the fuel

consumption rates in the low temperature regime, and it is improved in the uniform model and the independent model. The over-prediction of fuel reactivity is also observed in the ignition delay time measurements at 10 bar for 1,3-butadiene [29], trans-2-butene, and cis-2-butene [40] in the low temperature regime. The fuel consumption is higher for the uniform model than for the independent model, but furan concentrations only have minor differences as shown in Fig. 9. Therefore, it can be suggested that the influence of fuel consumption rates on furan formation is minor, and the fuel is dominantly consumed by other pathways instead of the proposed furan formation pathways. Additional support for this statement is provided in product profiles and pathway analyses in the later sections.

The main reason for the reduced fuel consumption could be the separate treatment and updated rate constants for H-atom abstraction of trans-2-butene and cis-2-butene in the uniform and independent models, and the competitive OH and HO₂ addition reactions in the proposed pathway may have minor effects in the 1,3-butadiene case. Further investigations on the fuel consumption reaction rates are necessary for better predictions of 1,3-butadiene, trans-2-butene and cis-2-butene consumption in the low temperature regime.

4.3 Influence of the proposed pathways on main products and intermediates predictions

In this section, the influence of the proposed pathway on main products and intermediates is examined. The comparison of experiments and three model simulations for the main products, e.g. H₂O, CO, and CO₂ are presented in Fig. 11, and key intermediates, e.g. formaldehyde and acetaldehyde are presented in Fig. 12. Ethylene, propene, and 1,3-butadiene are presented in Figs. S1 and S2 in Supplementary Material-4. In general, the independent model and the uniform model both have better predictions for most of the species than the AramcoMech 3.0 model, except that CO₂ in the trans-2-butene case is under-predicted. For the main products and intermediates, one

possible reason is the reduced fuel consumption. For some intermediates like acetaldehyde, another possible reason is the competitiveness of the proposed OH and HO₂ addition pathways. For example, the Waddington pathway [58] to produce acetaldehyde in trans-2-butene and cis-2-butene cases is undermined by the proposed OH addition reactions, so the acetaldehyde production is reduced. Further investigations are necessary for model optimization.

4.4 Pathway analyses

In this section, pathway analyses are performed to indicate the contribution of the proposed pathways to furan formation and fuel consumption. From the pathway analysis for furan, the main production pathway is the barrier-less OH addition pathway to produce S1-4, and HO₂ addition pathway with high energy barrier only has a minor effect. It is also found that the equilibrium constant for $C_4H_6 + OH \rightleftharpoons S1-4$ is critical for furan formation, which is determined by the calculated forward and reverse reaction rates in this work.

To examine the contribution of the proposed pathway to fuel consumption, pathway analysis is performed for 1,3-butadiene. The results are presented in Fig. 13 for the top five consumption pathways. It can be found that the OH addition reaction at 800 K only consumes 2.4% and 2.6% in the uniform model and the independent model, respectively, and HO₂ addition reaction has lower contribution. This observation further supports the previous statement that the influence of the base model is minor on furan formation, but the reactions of $C_4H_6 + OH \rightleftharpoons S1-4$ and $C_4H_6 + HO_2 \rightleftharpoons S1-18$ may have minor effects on the fuel consumption. Similar observations are obtained in the recent studies of OH and HO₂ addition on 1,3-butadiene [55, 59]. It is noteworthy that since only 10% of fuel is consumed in experiments, the actual effect on furan emission could be minor.

The rate of $\text{C}_4\text{H}_6 + \text{HO}_2 \rightleftharpoons \text{S1-18}$ reaction is sensitive to the energy barrier in the low temperature regime. For example, a deviation of 2.0 kcal/mol in the energy barrier results in the uncertainty of rate coefficient by a factor of 4.2 at 700 K. Motivated by the big deviation (5.3 kcal/mol) of the forward reaction energy barriers calculated by the CCSD(T)/cc-pvdz and G3 methods, other high-level methods including the CCSD(T)/CBS, CBS-ANPO, and G4 methods were applied to re-evaluate the energy barrier, and the results are shown in Table 2. The energy barrier of forward reaction predicted by the G4 method is 11.2 kcal/mol, which is close to the value predicted by the CCSD(T)/CBS method (11.8 kcal/mol). Given that the G4 and CCSD(T)/CBS methods are generally considered as benchmark methods in energy calculations [60], the value of 11.2 kcal/mol by the G4 method is adopted in this study. The influence of different energy barrier calculated by different methods in both forward and reverse reactions is presented in Fig. 14 for furan and 1,3-butadiene to reveal the influence of the uncertainty using the uniform model. If the energy barrier is 8.1 kcal/mol predicted by the G3 and DFT/B3LYP/6-311+G(d,p) methods, the furan formation is enhanced with over-predicted fuel consumption rate in the temperature range of 700-800 K. On the contrary, the fuel consumption rate prediction slightly improves at the cost of furan prediction if the energy barrier is 13.4 kcal/mol calculated by the CCSD(T)/cc-pvdz method. The energy barrier calculated by the G4 method has the best predictions for both furan and fuel predictions (see Fig. 14).

Table 2. Comparisons of the calculated energy barriers (kcal/mol) using different methods for forward reaction of $\text{C}_4\text{H}_6 + \text{HO}_2 \rightleftharpoons \text{S1-18}$.

DFT/B3LYP/ 6-311+G(d,p)	CCSD(T)				CBS-ANPO	G3	G4
	cc-pVDZ	pVTZ	cc-pVQZ	CBS			
8.1	13.4	12.3	11.9	11.8	9.5	8.1	11.2

The high-pressure limit reaction rate coefficients were used in the above analyses, where the results indicate that C_4H_6 (S1-3) + OH $\rightarrow$ S1-4 $\rightarrow$ S1-5 $\rightarrow$ S1-6 $\rightarrow$ S1-7 $\rightarrow$ P1-8 $\rightarrow$ furan (P1-9) is the dominant pathway for furan formation. The pressure dependence for this pathway is investigated here in the temperature range of 800-2000 K. The pressure dependence at lower temperature is not pursued, since the calculations become time-consuming due to low reaction rates. The results shown in Fig. 15 suggest that the furan formation is pressure independent when the temperature is below 1000 K. The yield of P1-8 in the bimolecular reaction S1-3 + OH $\rightarrow$ P1-8 + H system linearly increases with temperature, but are independent with pressure, as shown in Fig. 15a. For the H_2 elimination reaction P1-8 $\rightarrow$ P1-9 + H_2 , its reaction rate is pressure dependent in the temperature range of 1100-2000 K and becomes insensitive at lower temperatures. The conclusion from Fig. 15 indicates that the above analyses using high-pressure limit reaction rate are valid at different pressures in the low temperature regime.

5. Conclusions

In this work, furan formation pathways originated from 1,3-butadiene, trans-2-butene, and cis-2-butene are proposed. Potential energy surfaces, reaction rate coefficients of the proposed pathways, and the thermodynamics of new species were evaluated by high level theories of quantum chemistry. The proposed reaction pathways were implemented into the latest AramcoMech 3.0 model to evaluate the prediction performance with the experimental data. Two treatments (uniform model and independent model) were applied to test the base model influence on furan formation predictions.

The experiments were performed in a JSR coupled with ToF-MBMS using synchrotron ultra violet radiation as photon ionization source, which allows *in-situ* species identification and

quantification. Furan was identified by its ionization energy onset and PIE curve. The temperature versus mole fraction profiles of furan were well captured and improved by both uniform and independent models compared to the AramcoMech 3.0 base model. The improvement of furan predictions is mainly attributed to the updated H-atom abstraction rate, and the addition of the proposed reaction pathways, e.g. OH and HO₂ addition to 1,3-butadiene. The comparison between the simulation results using the uniform and the independent model indicates that furan formation is less influenced by the base model.

The pathway analysis for furan in the 1,3-butadiene case indicates that furan formation mainly comes from the barrier-less OH addition reactions to 1,3-butadiene in the proposed pathways. Pathway analysis for the fuel indicates that both 1,3-butadiene + OH and 1,3-butadiene + HO₂ addition pathways have some effects on fuel consumption. Further analyses were performed with the energy barrier of the 1,3-butadiene + HO₂ addition reaction by different level of theories in quantum chemistry to reveal the influence of calculated rate-coefficient uncertainty on model predictions. Calculations under different pressures indicate the pressure independence of the proposed pathways in the low temperature regime. Instead of proposing a new model, this work aims at proposing and examining furan formation pathways to further the understanding of furan formation chemistry in low temperature regime.

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Figure 1: The furan formation from H-atom abstraction of trans-2-butene (R1-1 reaction network), green values are from the G3 method and black values are from the CCSD(T)/cc-pvdz method.

Figure 2: The MEP for TS138.

Figure 3: The furan formation from H-atom abstraction of 2-butenyl (R1-1 reaction network), green values are from the G3 method and black values are from the CCSD(T)/cc-pvdz method.

Figure 4: The MEP for (a) S1-3 + OH, (b) TS318, (c) TS248.

Figure 5: The furan formation from 1,3-butadiene (R1-1 reaction network) green values are from the G3 method and black values are from the CCSD(T)/cc-pvdz method.

Figure 6: The furan formation pathway starting from cis-2-C₄H₈ (R2-1 reaction network) green values are from the G3 method and black values are from the CCSD(T)/cc-pvdz method.

Figure 7: High pressure limits reaction rate coefficients of $\text{C}_4\text{H}_6 + \text{OH}$ addition reaction.

Figure 8: PIE curves of $\text{C}_4\text{H}_4\text{O}$. JSR conditions: 1.0% fuel (left: 1,3-butadiene case; right: trans-2-butene case), $\phi=0.2$, $\tau=4$ s, $T=830$ K. Scattered points are measurements; lines are fits from cross sections in the database [57]; shaded areas indicate the experimental error.

Figure 9: Temperature versus mole fraction profiles of furan by the experiments (open points) and numerical simulations using different kinetic models (lines) for (a) 1,3-butadiene case; (b) trans-2-butene case; (c) cis-2-butene case. JSR conditions: 1.0% fuel, $\phi=0.2$, $\tau=4$ s, $T=590-830$ K. The shaded area indicates the experimental error.

Figure 10: Temperature versus mole fraction profiles of the fuels by the experiments (open points) and numerical simulations using different kinetic models (lines). Left: 1,3-butadiene case; Middle: trans-2-butene case; Right: cis-2-butene case. JSR conditions: 1.0% fuel, $\phi=0.2$, $\tau=4$ s, $T=590-830$ K. The shaded area indicates the experimental error.

Figure 11: Temperature versus mole fraction profiles of the main products from the experiments (open points) and numerical simulations using different kinetic models (lines). Left: 1,3-butadiene case; Middle: trans-2-butene case; Right: cis-2-butene case. JSR conditions: 1.0% fuel, $\phi=0.2$, $\tau=4$ s, $T=590\text{-}830$ K. The shaded areas indicate the experimental error.

Figure 12: Temperature versus mole fraction profiles of the formaldehyde and acetaldehyde from the experiments (open points) and numerical simulations using different kinetic models (lines). Left: 1,3-butadiene case; Middle: trans-2-butene case; Right: cis-2-butene case. JSR conditions: 1.0% fuel, $\phi=0.2$, $\tau=4$ s, $T=590-830$ K. The shaded areas indicate the experimental error.

Figure 13: Rate of production analysis of fuel consumption in 1,3-butadiene case. Simulation conditions: 1.0% fuel, $\phi=0.2$, $\tau=4$ s, $T=550-860$ K.

Figure 14: The temperature versus mole fraction profiles of furan by the experiments and numerical simulations using the variation of energy barrier from different quantum chemistry methods in reaction $C_4H_6 + HO_2 \rightleftharpoons S1-18$ in the uniform model. JSR conditions: 1.0% of 1,3-butadiene, $\phi=0.2$, $\tau=4$ s, $T=550-860$ K. The shaded area indicates the experimental error.

Figure 15: Pressure dependence for the main furan formation pathway by RRKM-ME calculation.

(a) The yield of P1-8 in $S1-3+OH \rightarrow S1-4 \rightarrow S1-5 \rightarrow S1-6 \rightarrow S1-7 \rightarrow P1-8 + H$ pathway. (b) The decomposition reaction rate coefficient of $P1-8 \rightarrow P1-9 + H_2$.