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Butyl Acetate Pyrolysis and Combustion Chemistry: Mechanism Generation and Shock Tube Experiments

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Abstract

The combustion and pyrolysis behavior of light esters and fatty acid methyl esters have been widely studied due to their relevance as biofuel and fuel additives. However, a knowledge gap exists for mid-size alkyl acetates, especially ones with long alkoxy groups. Butyl acetate, in particular, is a promising biofuel with its economic and robust production possibilities and ability to enhance blendstock performance and reduce soot formation. However, it is little studied from both experimental and modeling aspects. This work created detailed oxidation mechanisms for the four butyl acetate isomers (normal-, sec-, tert-, and iso-butyl acetate) at temperatures varying from 650 K to 2000 K and pressures up to 100 atm using the Reaction Mechanism Generator. About 60% of species in each model have thermochemical parameters from published data or in-house quantum calculations, including fuel molecules and intermediate combustion products. Kinetics of essential primary reactions, retro-ene and hydrogen atom abstraction by OH or HO₂, governing the fuel oxidation pathways, were also calculated quantum-mechanically. Simulation of the developed mechanisms indicates that the majority of the fuel will decompose into acetic acid and relevant butenes at elevated temperatures, making their ignition behaviors similar to butenes. The adaptability of the developed models to high-temperature pyrolysis systems was tested against newly collected high-pressure shock experiments; the simulated CO mole fraction time histories have a good agreement with the laser measurement in the shock tube. This work reveals the high-temperature oxidation chemistry of butyl acetates and demonstrates the validity of predictive models for biofuel chemistry established on accurate thermochemical and kinetic parameters.

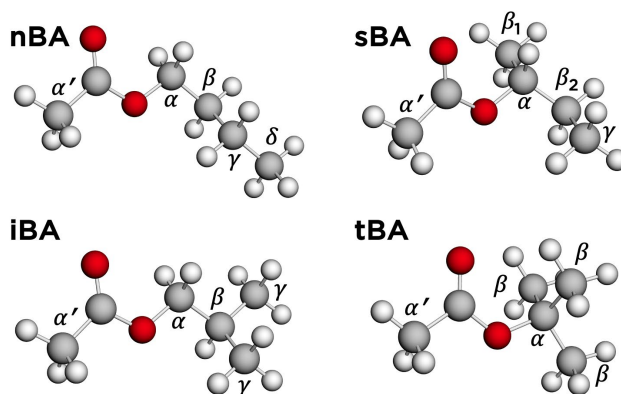
Keywords:

Butyl acetate; Pyrolysis; Combustion chemistry; Reaction mechanism; Shock tube; Biofuels.

1 Introduction

In the last decades, the increased utilization of oxygenated biofuels for the energy supply has promoted the development of comprehensive kinetic mechanisms suitable for accurately representing their combustion chemistry.¹ Numerous studies have been performed to unravel the chemistry of long-chain methyl esters (i.e., fatty acid methyl esters or FAMES).^{2,3} In contrast, the importance of small-chain esters only gained interest recently, incentivizing accurate analysis of

1 their combustion and pyrolysis behaviors.⁴ Indeed, carbon/oxygen bonds in the small-chain esters
2 intrinsically diminish soot formation.⁵ Recently, several studies investigated the oxidation
3 chemistry of methyl formate, methyl acetate, methyl propanoate, and methyl butanoate, either
4 experimentally or computationally.⁶⁻¹¹ However, the chemistry of the homologous **mid-size** alkyl
5 acetate (i.e., **ethyl acetate**, propyl acetate, and butyl acetate) has been poorly studied so far, despite
6 their promising properties for energy supply purposes.¹² In this regard, butyl acetate (BA) has been
7 recognized for its great potential as a sustainable biofuel additive because of its low freezing point,
8 higher flash point, and limited impacts on the cetane number and heat of combustion of the
9 resulting mixture.¹³ Conventionally, a heterogeneous catalyzed reactive distillation of acetic acid
10 with butanol was adopted to produce BA.^{14,15} However, the use of strong acids as catalysts strongly
11 limits this route due to the significant impact on environmental-related key performance indicators
12 of the whole process.¹⁶ In this perspective, alternative bioprocesses based on fermentation have
13 been extensively investigated and successfully tested for environmentally and economically
14 sustainable production of BA.¹⁷ A recent investigation by Wang et al. has characterized the burning
15 properties of droplets of BA.¹⁸ However, to our knowledge, a detailed kinetic mechanism
16 reproducing its chemistry in an oxidative system is still missing, highlighting the need for accurate
17 models to characterize its combustion behavior. In addition, all four isomeric structures of BA (i.e.,
18 normal-, sec-, tert-, and iso-butyl acetate, or nBA, sBA, tBA, and iBA) should be considered, as
19 each may be ruled by different chemistry and overall reactivity. Hence, these structures should be
20 distinguished to properly account for the chemistry of this species.¹⁹ For clarity, **Figure 1** shows
21 their molecular structures and nomenclature considered in this work to distinguish different carbon
22 atoms on the molecule.
23



24
25 *Figure 1. Molecule structures of butyl acetate isomers with carbons adjacent to the ester group labeled by the Greek letters.*

26
27 Understanding the governing reactions is the key to correctly modeling the chemistry of BA
28 isomers. Regardless of the investigated chemical structure, hydrogen atom abstraction reactions
29 by small radicals (e.g., H, OH, and HO₂) play significant roles in combustion chemistry.²⁰ More
30 specifically, the hydrogen atom abstractions from the α and α' positions of an ester group have
31 been reported as dominant primary reactions at low- and intermediate temperatures.²¹⁻²³ Further,
32 recent studies on ethyl acetate showed the dominance of unimolecular decomposition (i.e., retro-
33 ene reaction) at high temperatures.^{3,8} The retro-ene reaction is a concerted pericyclic reaction that
34 involves an intra-molecular hydrogen transfer, a bond break, and a double bond formation via a
35 six-membered ring transition state.²⁴ Undoubtedly, accurate kinetics of the reactions mentioned
36 above is the prerequisite for quantitatively modeling relevant systems. However, the kinetic data

1 for BA-involved reactions are missing in both cases and can only be inferred from the rate rules.²⁵
2 To overcome this problem and increase the accuracy of the resulting model, deriving the kinetics
3 from the *ab initio* calculations is highly desirable.²⁶ This approach has been extensively adopted
4 for estimating the kinetic parameters of elementary reactions,²⁷⁻³⁷ allowing for forming an
5 inclusive and robust kinetic database suitable for sub-mechanisms. Besides, theoretical
6 calculations based on the molecular structure are also useful for obtaining thermochemical data
7 that is usually helpful for inferring reaction reverse rates.³⁸ Among other quantum chemistry
8 methods, the composite method CBS-QB3 developed by Montgomery et al. (1999)³⁹ has been
9 largely suggested for relevant purposes because of its accuracy attested as within ~ 1 kcal/mol of
10 the experimental values and the limited computational costs required.^{40,41}

11 Historically, detailed kinetic models were built in a postdictive manner. A model was usually
12 generated hierarchically, from small intermediate species to the actual fuel-size molecules,
13 according to expert chemistry knowledge. It usually needed to be fit to experimental data to fill
14 the gap caused by missing reactions, inaccurate thermochemical and kinetic parameters, or other
15 issues. However, to our knowledge, BA chemistry cannot be modeled in such a way due to missing
16 data suitable for model validation. Instead, a predictive modeling approach that is embedded in the
17 Reaction Mechanism Generator (RMG) has the potential to generate effective models.^{42,43} RMG
18 creates a mechanism based on accurate thermochemical and kinetic parameters.⁴⁴⁻⁴⁶ Starting from
19 a seed mechanism, it makes reasonable estimations for required parameters, uses those parameters
20 to simulate the systems at the conditions of interest, and picks up the significant species and
21 reactions according to their fluxes to enlarge the model. One of our recent studies also shows that
22 once the most sensitive parameters are refined, the RMG-generated model can even outperform
23 models that are fitted to the experiments.⁴⁷ Therefore, RMG is ideal for modeling BA chemistry.

24 This work was devoted to developing butyl acetate predictive kinetic models for each butyl acetate
25 isomer, which help predict combustion behaviors. A significant amount of theoretical-sound
26 thermochemical and kinetic data was collected from the literature and calculated in-house to
27 enhance the model fidelity. The generated models were used to study the combustion chemistry
28 and predict combustion behaviors at engine-relevant conditions. The adaptability of the produced
29 mechanisms to pyrolysis systems was assessed by validating them with high-pressure shock tube
30 (HPST) experiments collected in this study.

31

32 **2 Computational Methods**

33 In this work, detailed kinetic mechanisms were generated from the first principles for butyl acetate
34 isomers using RMG⁴⁴⁻⁴⁶, simulated using various chemical kinetics simulation software^{48,49}, and
35 validated against measurements collected in pyrolysis conditions through a shock tube. The
36 applied schematic of the model construction is similar to the one reported in our previous work,⁴⁷
37 where mechanisms have been developed and improved iteratively. The kinetics of the primary
38 reaction and potential sub-mechanisms in the oxidation mechanism were calculated using the
39 quantum chemistry approach and collected from the literature, respectively. Additional details on
40 the procedures are provided in the following sections.

41

1 2.1 Quantum chemistry calculation

2 Quantum chemistry calculations were done on species thermochemical properties and primary
3 reaction kinetics under rigid rotor harmonic oscillator (RRHO) approximation with a 1D hindered
4 rotor correction and transition state theory.⁵⁰ A schematic representation of the procedure,
5 facilitated by using Gaussian^{51,52}, ARC⁵³, and Arkane⁵⁴, is given in Figure 2.

6 Firstly, a rough guess of the species and transition states (TSs) 3D geometry is generated according
7 to the following approach:

- 8 • Species geometries were first created from the ETKDG⁵⁵ algorithm and then optimized by
9 MMFF94s force field;^{56,57} conformers are explored by a torsion mapping algorithm^{53,58}.
- 10 • TSs geometries were manually created, whereas up to five conformers were tried based on
11 the lowest energy reactant and product conformers to account for different conformation.

12 Quantum chemical calculations at the CBS-QB3 level of theory were then applied to the resultant
13 geometries—geometry optimization, harmonic frequencies calculation, and torsional scan were
14 done using the density functional theory at B3LYP/CBSB7, and single point energy was calculated
15 at CBS-QB3 as suggested by Montgomery et al.³⁹ As indicated in Figure 2, several troubleshooting
16 strategies were implemented to monitor the quality of the calculation job and ensure reasonable
17 results. Eventually, the quantum chemistry results were utilized by the software Arkane and
18 converted to thermochemical and kinetic parameters used in the mechanism.

19 Details about the calculation environment, quantum chemistry calculation schemes, utilization of
20 bond additivity correction, etc., can be found in Section 1 of SI.

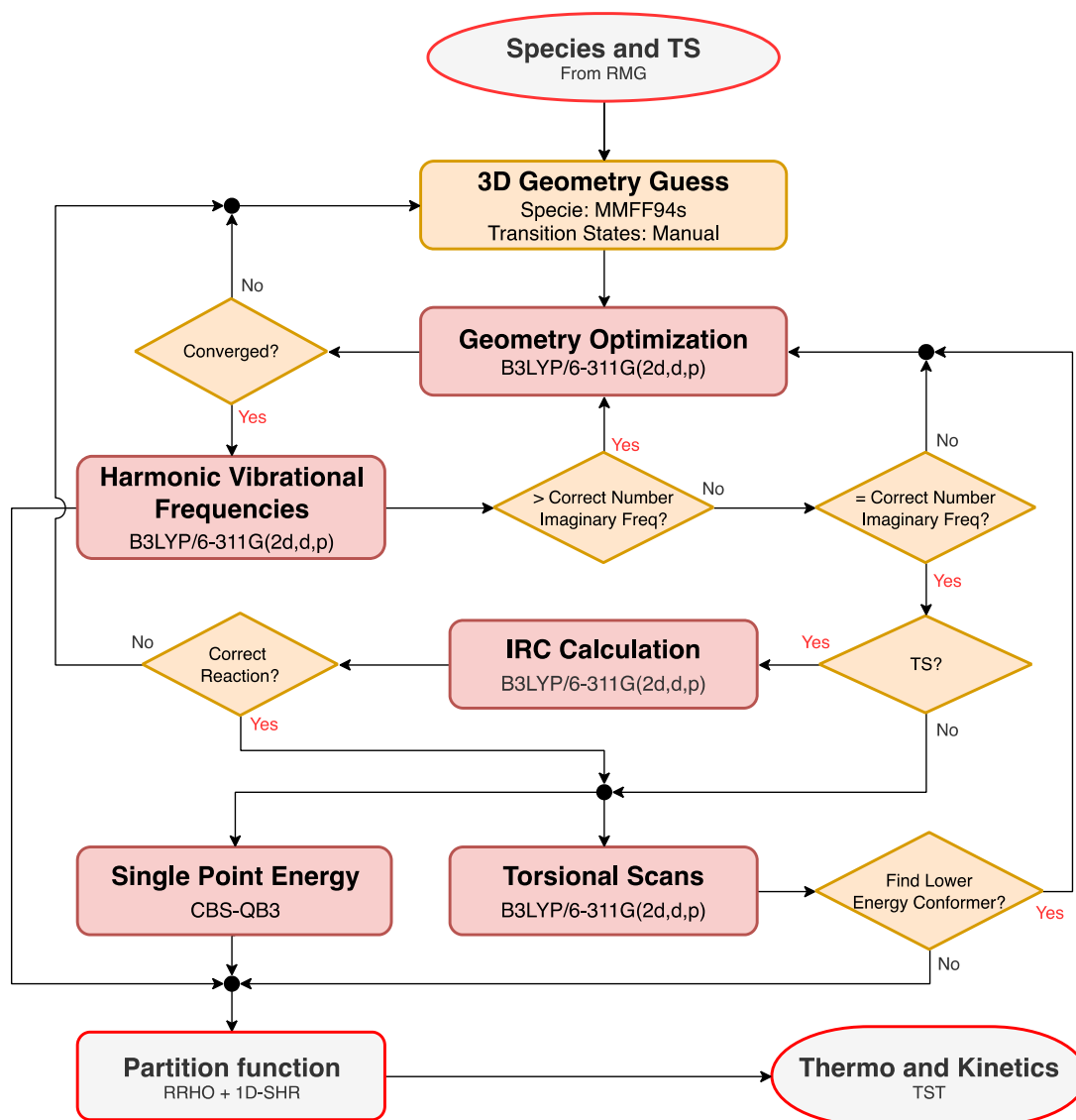


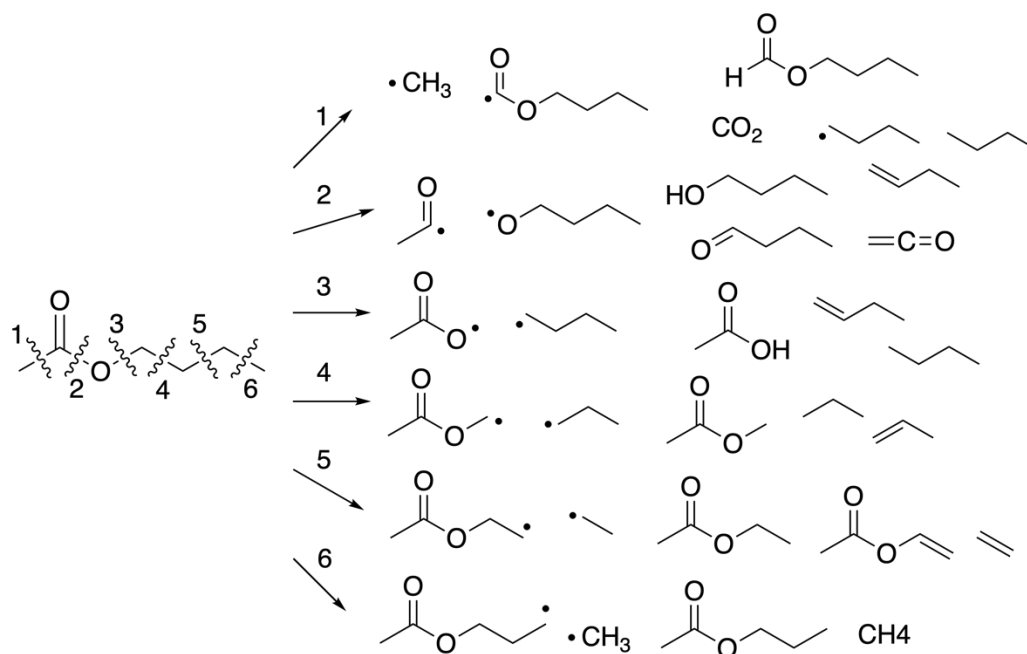
Figure 2. Schematic representation of the workflow used for thermochemical and kinetic properties calculation. Please consider that each color of the nodes corresponds to a different software program applied. Grey boxes: RMG⁴⁴⁻⁴⁶ and Arkane⁵⁴; Orange boxes: ARC⁵³; Red boxes: Gaussian 09⁵¹ or Gaussian 16⁵².

2.2 Relevant kinetic data

Although kinetic data is missing for BA-involved reactions, quantum-mechanically calculated kinetic data for smaller esters or potential intermediates are available, helpful in creating sub-mechanism and improving RMG built-in rate rules. Potentially important reactions are inferred from disconnecting the BA molecules (Figure 3), motivated by the important beta-scission and bond-fission reactions at elevated temperatures. The disconnection analysis reveals that oxidation chemistry involving acetic acid, light alkenes (C₂-C₄), smaller formate/acetate, and C₄

1 alcohol/aldehyde/ketone are potentially significant. In this regard, rate constants for the following
 2 reactions are eventually collected from the literature:

- 3 • H-atom abstraction by OH²³, HO₂²¹ from various esters
- 4 • H-atom abstraction by OH⁵⁹, HO₂⁶⁰ from butanols
- 5 • H-atom abstraction by OH, HO₂, and CH₃ from aldehydes and acids³¹
- 6 • Acetic acid H-atom abstraction and decomposition²⁹
- 7 • Methyl acetate H-atom abstraction⁶¹ and decomposition³³
- 8 • Decomposition of methyl formate³⁶
- 9 • H⁶², OH⁶³ and HO₂⁶⁴ radical addition to light alkenes
- 10 • QOOH decompositions to HO₂ and light alkenes⁶⁴



12
 13 *Figure 3. An illustration of disconnecting butyl acetate molecules. nBA is used as an example.*

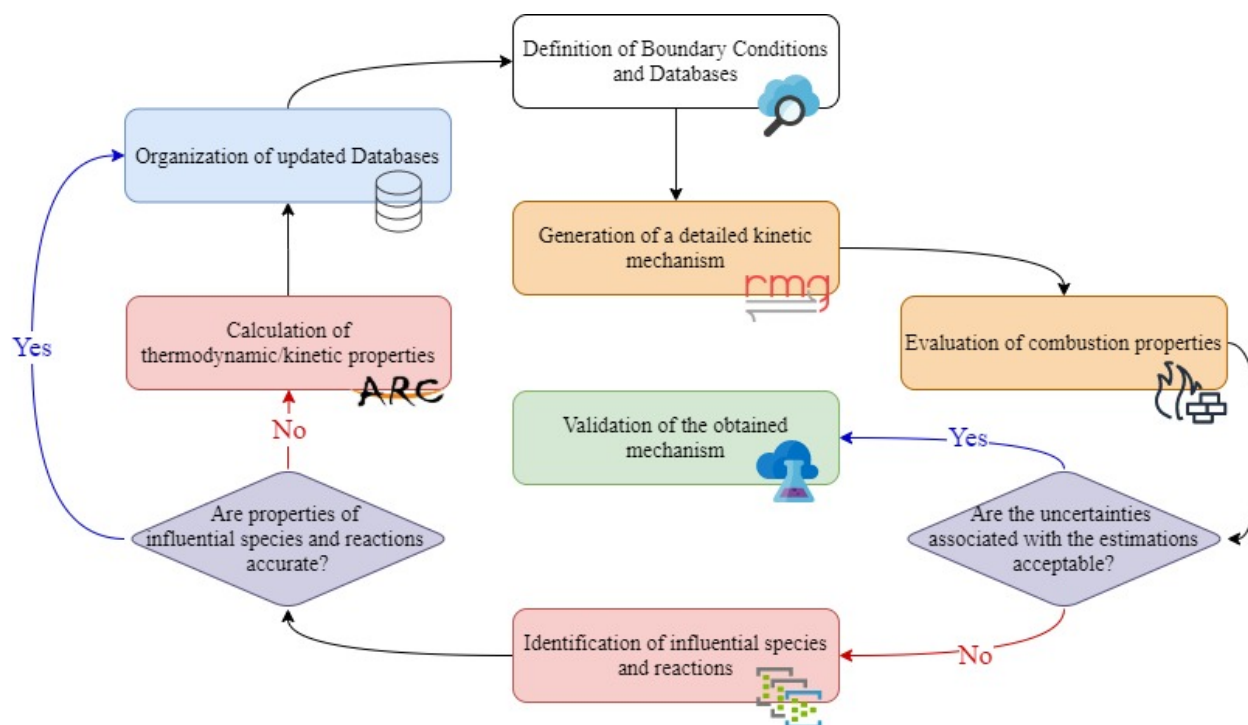
14 Besides, the thermochemistry of species in the C₂-C₄ alkene oxidation sub-mechanisms was
 15 extensively refined in our previous work⁴⁷, and the corresponding data were also used when
 16 building the kinetic model.

18 2.3 Mechanism generation

19 A rate-based method software, above-mentioned as RMG, was implemented for the automatic
 20 generation of reaction mechanisms for the investigated fuels. Details about the network generation
 21 and expansion algorithm can be found in Liu et al.⁴⁴ and Gao et al.⁴⁵, and the choice of parameter
 22 libraries^{41,65-69} and algorithm setup was similar to the light alkene modeling by Pio et al.⁴⁷
 23 Mechanisms were built for each isomer respectively. Considering the molecular structure of the
 24 investigated species, the maximum number of carbon and oxygen atoms allowed in a single
 25 molecule was limited to 15 and 8, respectively. Mono- and bi-radicals, together with the singlet
 26 configuration for oxygen, were permitted. For the sake of simplicity, nitrogen was assumed as an
 27 inert species, and nitrogen oxidation chemistry was neglected. Calculated and collected
 28 thermochemical and kinetic parameters were stored in the RMG database and retrieved whenever

1 needed. Other parameters were estimated through a linear combination of known sub-molecular
2 fragments, following Benson's group additivity method⁷⁰ for the thermochemistry or rate rules
3 based on decision trees distinguishing reaction families for the kinetics.⁴⁶

4 The mechanism refinement was based on identifying the most influential species and reactions to
5 the selected measurable properties via sensitivity and reaction flux analyses (introduced in Section
6 2.4). The impact of a given perturbation of enthalpy of formation H_{f298} on the outcomes of mole
7 fraction of reactants and hydroxyl radicals was evaluated and considered as a sorting score. The
8 ones estimated from the group additivity approach and with the highest scores were refined using
9 the approach described in section 2.1. The later obtained refinements were then introduced into
10 the RMG database, and a new model was generated with the updates. **The database update allows
11 RMG to estimate reaction fluxes more accurately and make better judgments on selecting essential
12 pathways in the following iteration. A more detailed discussion about mechanism changes across
13 iterations can be found in Section 2.5 of SI.** The iterative procedure implemented in this work for
14 the generation and refinement of detailed kinetic mechanisms, as described so far, was schematized
15 in Figure 4.



17
18 *Figure 4. Schematic representation of the workflow used for the generation and refinement of detailed kinetic mechanisms.*

19 20 **2.4 Reactor model simulation**

21 The produced mechanisms were utilized to estimate the ignition delay time (IDT) and generate
22 flux diagrams and sensitivities using the Chemkin⁷¹ and Reaction Mechanism Simulator
23 (RMS)^{49,72}. The time evolution of pressure, temperature, and composition was estimated assuming
24 a closed, isochoric, and adiabatic vessel. The initial temperature and pressure of the simulation
25 were varied within 850 – 1500 K and 5 and 10 atm, respectively. The IDT was identified by the

1 peak of OH concentration time history. The flux diagrams were generated once at 20% and 50%
2 of the IDTs, where time was selected to balance information reported in terms of decomposition
3 and oxidation pathways. Temperature sensitivities were calculated at the ignition delay time
4 defined by the peak of dT/dt , providing good estimates of relative IDT sensitivities as suggested
5 by Ji et al.⁷³ To validate the BA pyrolysis in the HPST, a 0-D reactor under isochoric and adiabatic
6 conditions was modeled to mimic the experimental system adopted in this work. The temperature
7 and the pressure behind the reflected shock (T_5 and P_5) were used as the initial conditions of the
8 simulation. The resulting carbon monoxide (CO) time histories were compared with measurements
9 at first. RMS was also used to analyze the rate of production (ROP) of important intermediates and
10 estimate the branching ratio under combustion-relevant conditions.
11

12 **3 Experiments**

13 **3.1 Shock Tube Facility**

14 Pyrolysis experiments of 4 different isomers of butyl acetate were performed in a stainless-steel,
15 heated shock tube of 14.17 cm inner diameter located at the University of Central Florida. Specific
16 details of the shock tube facility can be found in our previous works⁷⁴⁻⁷⁶. Five piezoelectric
17 pressure transducers, spaced along the last 1.4 m of the shock tube and connected to four time-
18 interval counters, were used to measure the incident shock velocities and the reflected shock
19 pressure. The measured incident shock velocities were linearly extrapolated to obtain the reflected
20 shock velocity at the end wall. Using the measured shock velocity, thermodynamic data of the
21 mixture, and pre-shock temperature and pressure (T_1 , P_1) in normal-shock relations, pressure and
22 temperature behind reflected shock wave (P_5 and T_5) were calculated with the shock condition
23 calculator FROSH⁷⁷. P_5 was also monitored with a Kistler-type 603B1 sensor.
24

25 **3.2 Mixture preparation**

26 BA mixtures were prepared manometrically with two Baratrons from MKS instruments: a 10,000
27 Torr (628D, accuracy of 0.25% of reading) and a 100 Torr (E27D, accuracy of 0.12% of reading).
28 Each isomer of butyl acetate has very low vapor pressure (~1.5-2.5 kPa at room temperature). So,
29 the entire facility, including the mixing tank, filling line, manifold, and shock tube, was heated at
30 80°C to prevent fuel condensation. Also, while preparing the mixture, the partial pressure of the
31 fuel was kept < 75% of the vapor pressure at 80°C to further ensure the gaseous phase of the fuel.
32 Mixtures were prepared with 0.5% fuel loading (research graded, purity > 99%) in an argon bath
33 (> 99.999% purity; nexAir) and were mixed in a 33 L mixing tank. Before starting experiments,
34 each mixture was kept at rest overnight to get homogeneous.
35

36 **3.3 Carbon monoxide (CO) absorbance**

37 Two optical ports, at 2 cm away from the end wall and around the circumference of the tube, were
38 used for the spectroscopic measurements. CO concentrations formed during BA pyrolysis were
39 measured using a continuous-wave distributed feedback quantum cascade laser from Alpes Lasers
40 (TO3-L-50) centered at 2046.277 cm^{-1} . A Bristol 771 Spectrum Analyzer was used to check the
41 wavenumber of the laser beam before each experiment.

42 The concentration of CO was calculated through the Beer-Lambert Law:

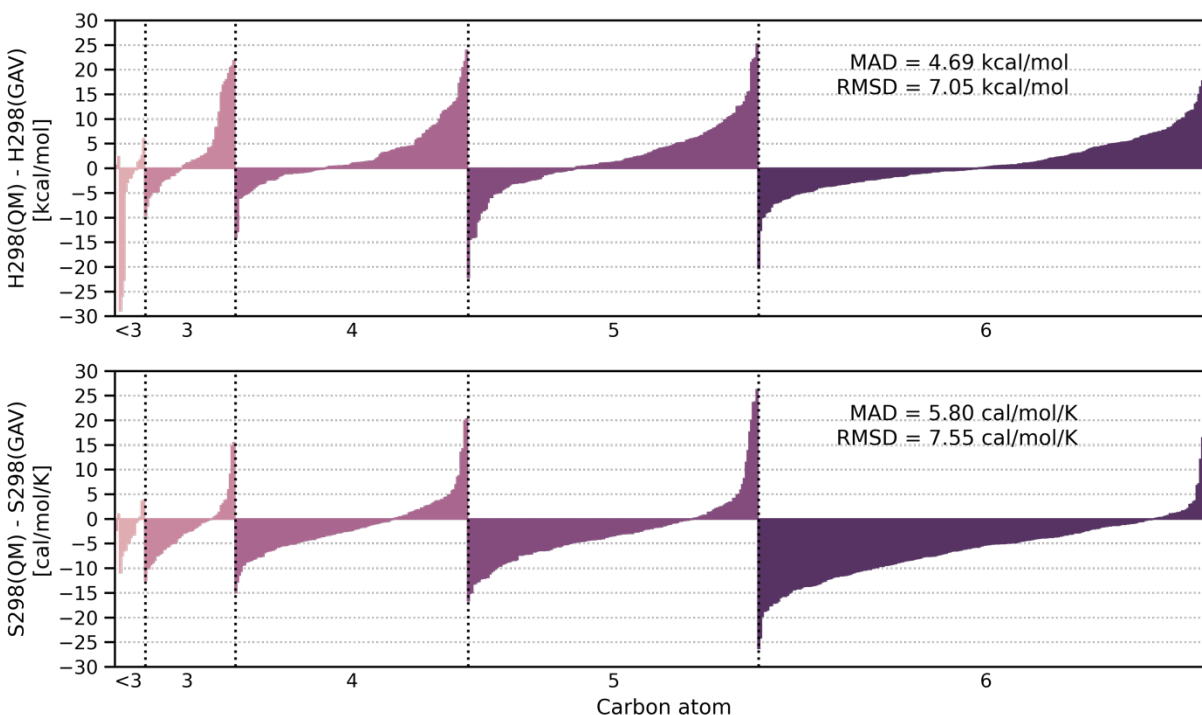
$$X = \frac{\alpha RT}{\sigma PL} \quad (1)$$

where α is the measured absorbance from the laser, P is the time-varying reflected shock pressure of the gas mixture (Pa) found from the Kistler pressure transducer, T is the time-varying temperature of the mixture (K) estimated assuming isentropic condition, L is the path length of the absorbing species (m), R is the universal gas constant ($\frac{J}{mol.K}$), and σ is the absorption cross-section of CO ($\frac{m^2}{mol}$). The time-varying CO cross-section at T_5 , P_5 , and specified wavenumber were taken from the HITEMP database⁷⁸ assuming self-broadening with Voigt profile. The relative uncertainty in the measured concentrations of CO was calculated as a time-varying quantity by the root mean square of the relative uncertainties of the absorbance, pressure, and temperature in Beer's Law (1), which is < 10% for all cases.

4 Results and Discussion

4.1 Quantum chemistry calculation

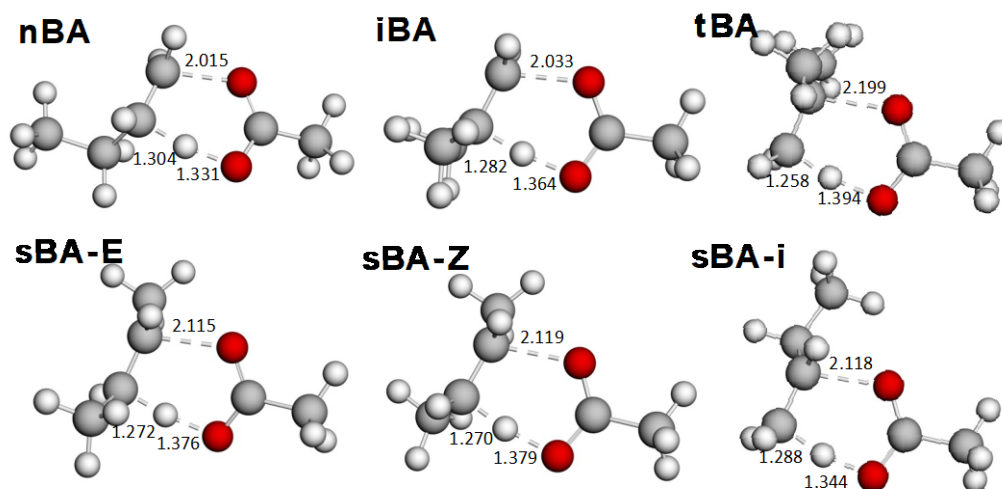
Quantum chemistry calculations conducted in this work include thermochemistry of important fuel, intermediates, and products and rate constants of BA retro-ene reactions and H-atom abstraction reactions. The differences in enthalpy and entropy of formation at 298 K (H_{f298} and S_{f298}) between the group additivity values (GAV) and values from quantum chemistry calculation (QM) (Figure 5) stress the importance of refining these parameters. Eventually, we refined the thermochemistry for around 60% of the species in the final models of this work, and a more detailed analysis can be found in Sections 1.5 and 2.4 of SI.



22

1 *Figure 5. H_{1298} (upper) and S_{1298} (lower) differences between GAV and QM for each species calculated in this work. For better*
2 *visualization, molecules are grouped by the number of carbon atoms and sorted by the deviations in each group. Note, the molecule*
3 *sequence in the two subplots is different.*

4
5 The kinetics of BA retro-ene reactions were calculated in this study. These reactions convert one
6 BA molecule into an acetic acid and a corresponding butene. Considering the different chemical
7 environments of the β -H atoms (the migrating atom) on BA molecules, a single reaction path was
8 identified for nBA, iBA, and tBA, respectively, and three reaction paths were found for sBA. The
9 transition state geometries (of their lowest energy conformer) and calculated rate constants are
10 shown in Figure 6 and Table 1, respectively. Due to the p - π conjugation in the ester functional
11 group, the reaction center in the transition states is nearly planar, contrasting with the geometry in
12 alkene retro-ene transition states. When combining our calculation with published rate coefficients
13 of ethyl, n-propyl, and iso-propyl acetate (i.e., EA⁹, nPA⁷⁹, and iPA¹⁰), we found that a higher
14 degree of substitution at the α -carbon or a lower degree at the β -carbon results in a higher rate
15 coefficient (Figure 7A). The observation coincides with chemical intuition. More alkyl groups at
16 the α -carbon weaken the C-O bond that is to break in the reaction, while more alkyl groups at the
17 β -carbon introduce a stronger steric hindrance. **The rate rules of acetate retro-ene reactions were**
18 **summarized in Table 2.** Besides, the degeneracy varies significantly among BA molecules: tBA
19 has nine accessible β -H atoms, while iBA only has one. Differences in both reactivity and
20 degeneracy of BA molecules accumulate into orders of magnitude differences in retro-ene rate
21 coefficients of different BAs (Figure 7B), potentially affecting the branching in the oxidation.
22
23

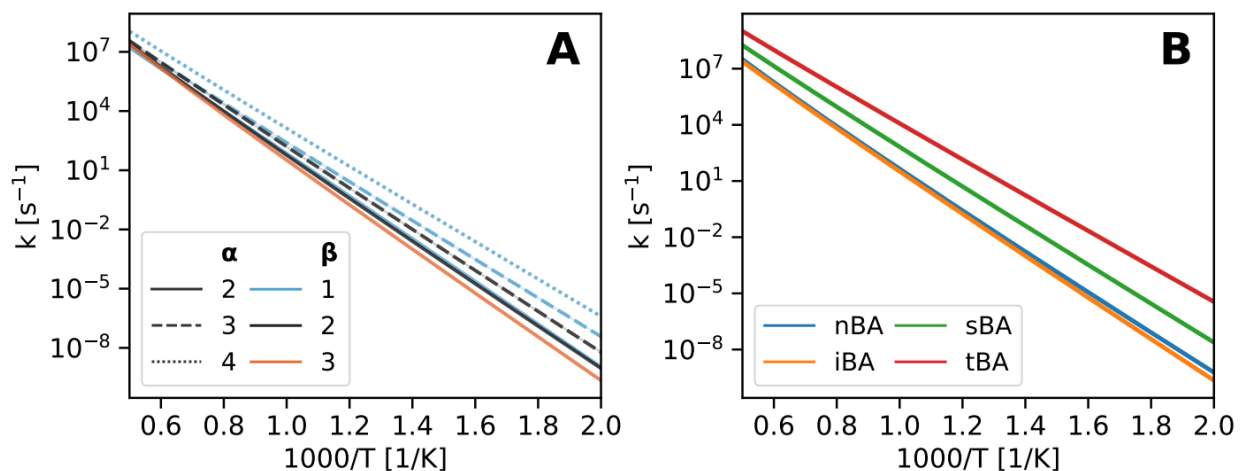


24
25 *Figure 6. Transition states of butyl acetate retro-ene reactions calculated in this work. The distances of bonds that are formed or*
26 *broken during the reaction are noted. The degeneracy of the reaction is marked by highlighting the relevant H atoms.*

1

Table 1. BA retro-ene reaction rate constants in modified Arrhenius formula.

Reactant	Alkene Product	Degeneracy	A [s^{-1}]	n	Ea [kcal/mol]
nBA	1-C ₄ H ₈	2	3.48E+03	2.72	46.0
iBA	i-C ₄ H ₈	1	3.18E+06	1.87	48.5
sBA	1-C ₄ H ₈	3	3.58E+07	1.65	45.6
sBA	cis-2-C ₄ H ₈	1	1.96E+09	0.97	46.9
sBA	trans-2-C ₄ H ₈	1	2.52E+09	1.01	46.1
tBA	i-C ₄ H ₈	9	1.09E+10	1.08	42.1

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Figure 7. Computed rate coefficients of retro-ene reactions. **A.** The rate rules of the acetate retro-ene reactions on a per H atom basis distinguishing the number of non-H substituents on the α - and β -carbons. Retro-ene rate constants of ethyl⁹, n-propyl⁷⁹, and iso-propyl⁸⁰ acetate along with the 4 butyl acetate isomers are considered. Reactions with the same α and β atom conditions are grouped with mean values. **B.** Overall retro-ene rate constants of each BA isomer.

9
10

Table 2. Acetate retro-ene rate rules in modified Arrhenius formula on a per H atom basis.

Degree of α -carbon	Degree of β -carbon	A [s^{-1}]	n	Ea [kcal/mol]	Discrepancy factor at 1000 K
2	1	4.53E+13	-0.30	49.9	-
2	2	1.19E+07	1.66	47.1	2.6
2	3	3.18E+06	1.87	48.5	-
3	1	1.21E+08	1.25	43.2	2.1
3	2	1.70E+09	1.03	46.3	1.8
4	1	1.21E+09	1.08	42.1	-

11
12
13
* The discrepancy factor measures the largest difference between the rate constant from a fitted rate rule and individual rate constants used to fit the rate rule, providing a rough estimate of the uncertainty.

1

Table 3. Butyl acetate H-atom abstraction rate constants (unit: $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) calculated in this work.

Reaction	A [$\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$]	n	Ea [kcal/mol]
nBA + OH = nBA- α' + H ₂ O	1.66E+03	2.95	0.0640
iBA + OH = iBA- α' + H ₂ O	9.45E+02	3.05	0.0547
sBA + OH = sBA- α' + H ₂ O	9.38E+02	3.07	0.155
tBA + OH = tBA- α' + H ₂ O	1.98E+03	2.97	-0.208
nBA + OH = nBA- α + H ₂ O	8.28E+01	3.18	-3.86
iBA + OH = iBA- α + H ₂ O	1.51E+01	3.40	-4.13
sBA + OH = sBA- α + H ₂ O	9.15E+02	2.79	-4.40
nBA + OH = nBA- β + H ₂ O	6.56E-01	3.81	-4.28
iBA + OH = iBA- β + H ₂ O	2.23E+01	3.27	-4.63
sBA + OH = sBA- β_1 + H ₂ O	1.01E+01	3.61	-2.76
sBA + OH = sBA- β_2 + H ₂ O	5.88E+00	3.58	-3.70
tBA + OH = tBA- β + H ₂ O	2.64E+00	3.91	-2.04
nBA + OH = nBA- γ + H ₂ O	1.48E-05	5.11	-5.70
iBA + OH = iBA- γ + H ₂ O	4.27E-06	5.36	-5.07
sBA + OH = sBA- γ + H ₂ O	9.13E-05	4.97	-5.10
nBA + OH = nBA- δ + H ₂ O	1.06E-07	5.77	-4.47
nBA + HO ₂ = nBA- α + H ₂ O ₂	5.13E-06	5.23	9.50
iBA + HO ₂ = iBA- α + H ₂ O ₂	9.58E-05	4.92	9.95

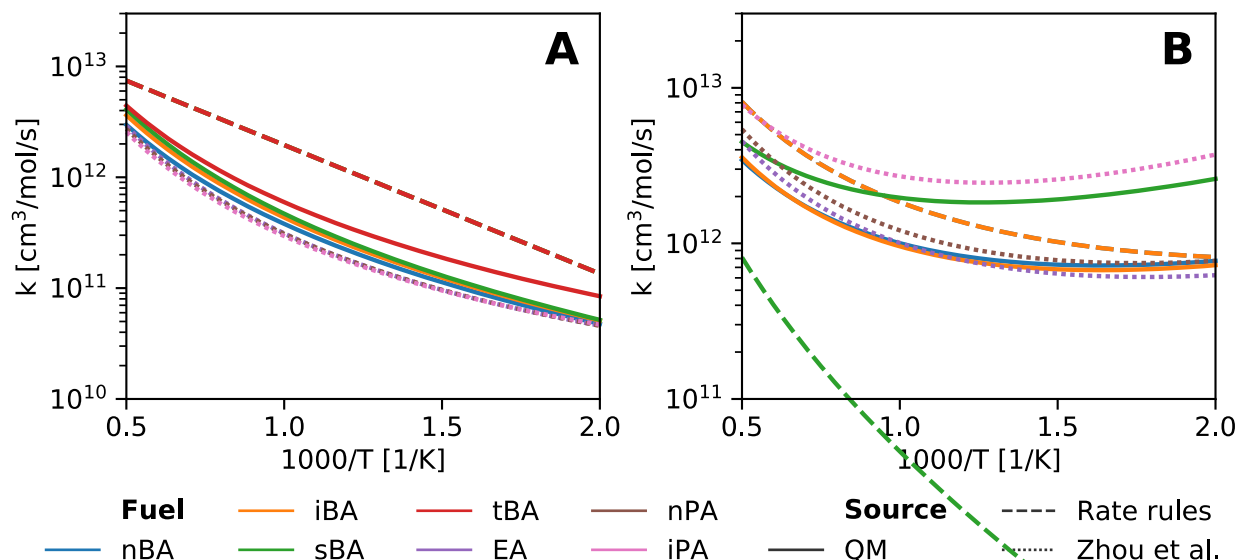
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4 H-atom abstractions by OH radical from BA, as primary competitive reactions with retro-ene
5 reactions, were also calculated, and their rate constants in the modified Arrhenius formula are
6 tabulated in Table 3. Following the chemical structure of the investigated isomers reported in
7 Figure 1, nBA and sBA have hydrogens in five different chemical environments, iBA has four
8 different types of hydrogens, and tBA has two. According to the conformer search, all the lowest
9 energy conformer of the transition states (on the CBS-QB3 potential energy surface) shares the
10 configuration where:

- 11 1. the H atom in the hydroxyl radical points to the acetyl oxygen and forms a hydrogen bond.
- 12 2. at most, one dihedral in the BA fragment is significantly varied from the geometry of the
13 corresponding lowest conformer to fulfill the configuration in item 1.

14 Rate constants were calculated over 500 – 2000 K (Figure 8 and Figures S13-16). As a reference,
15 rate constants for EA, nPA, and iPA from Zhou et al. are plotted alongside. For reactions
16 abstracting α - or α' -hydrogens, rate constants of butyl acetates and ones of lighter acetates have a
17 good agreement (within a factor of two). A slightly larger discrepancy (within a factor of 5) is
18 observed for reactions abstracting β - and γ -hydrogens, where Zhou et al. used a different TS
19 configuration, the H atom in OH pointing to the alkoxy oxygen, in their rate calculation. ~~Whether
20 the difference in configuration is due to using different levels of theory or a lack of conformer
21 search in the previous study is not clear and suggested to be investigated in future study.~~ Whether
22 the difference in configuration is due to using different levels of theory or a lack of conformer
23 search is unclear and suggested to be investigated in a future study. However, the similarity in the
24 investigated acetates still suggests the applicability of rate rules when investigating even larger
25 esters. Besides, the RMG rate rule estimates are also included in Figure 8 and Figure S13-16.
26 While most estimates from the RMG rate rules are reasonably consistent with the calculated values
27 (within an order of magnitude differences), indicating its good generality, significant discrepancies

1 can be found over a few entries (e.g., abstracting sBA's α -H). It emphasizes the necessity of
 2 refining important kinetic parameters during model generation and reveals the irrationalities of the
 3 manually designed RMG rate rules. Worth to note that RMG is in the process of switching from
 4 hand-made rules to rules generated by the substructure isomorphic decision tree algorithm, which
 5 aims to solve similar issues.



8
 9 Figure 8. Rate constants comparisons of H-atom abstraction reactions on a per H atom basis at α' site (A) and α site (B). Solid
 10 lines are calculated in this work, dashed lines are estimated using RMG rate rules, and dotted lines are adapted from Zhou et
 11 al.²³

12
 13 Figure 9 shows branching ratios of H-atom abstractions by OH with respect to different carbon
 14 atoms and BA isomers. At lower temperatures, the most dominant pathways are the ones
 15 abstracting α - and β -hydrogens. At increasing temperatures, the reactivity of each pathway
 16 becomes more even, and the contribution sequence becomes more consistent with the order of
 17 reaction degeneracy. Regardless of the reactivity complexity at different sites of different BAs, the
 18 total H-atom abstraction rate constants are close among BAs and barely variable across the
 19 temperature of interest (Figure 10). Larger differences are observed at lower temperatures, mainly
 20 due to tBA missing reactive α -H atoms.

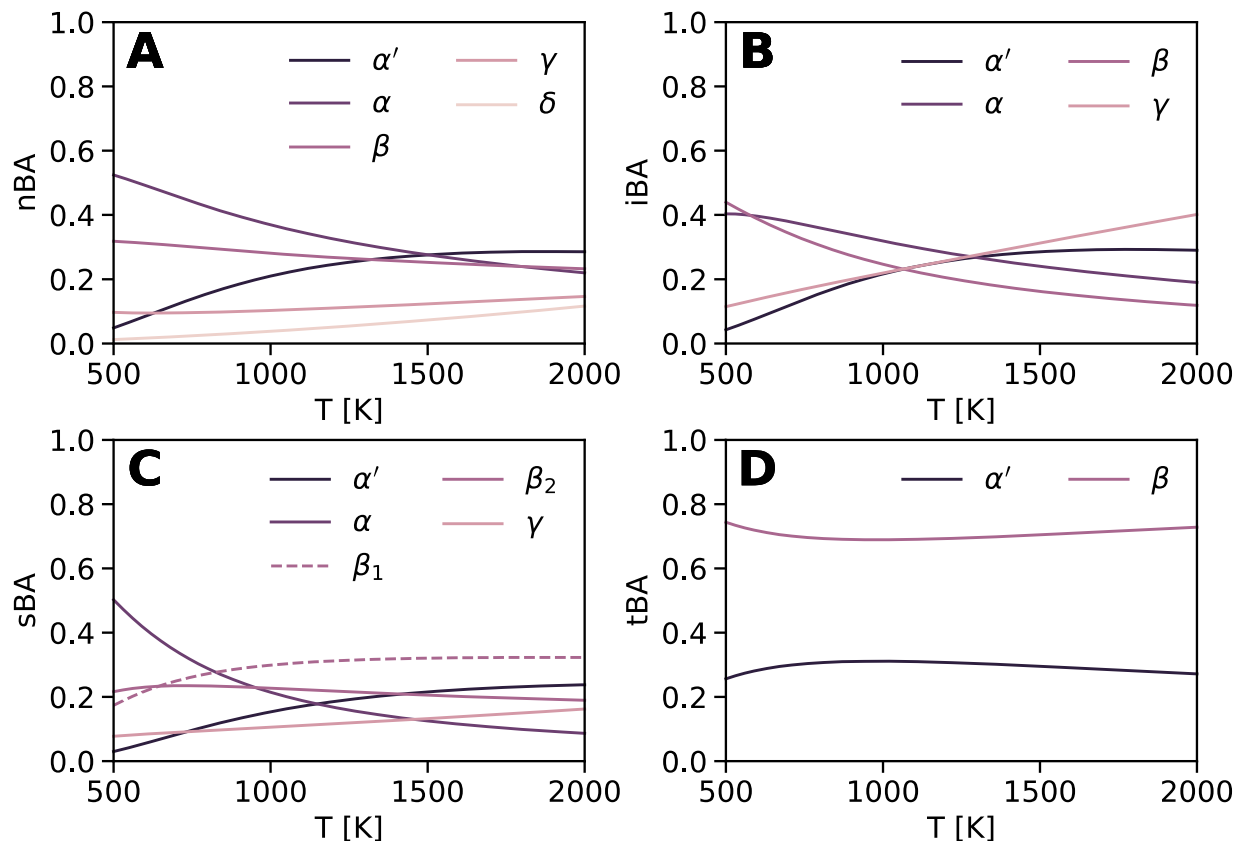


Figure 9. Branching ratios of the H-atom abstraction by OH in the temperature range from 500–2000 K for BAs studied in this work. (A) nBA, (B) iBA, (C) sBA, and (D) tBA.

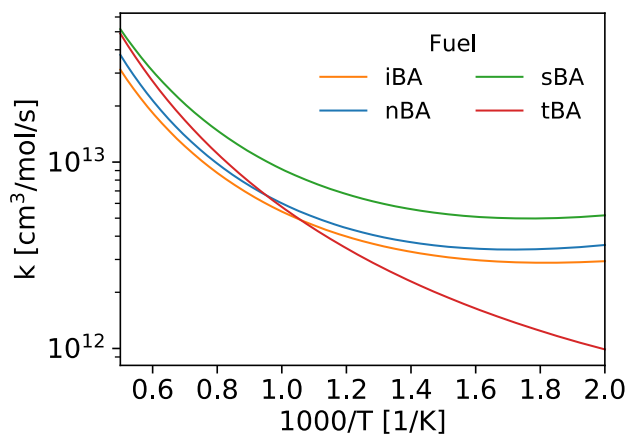


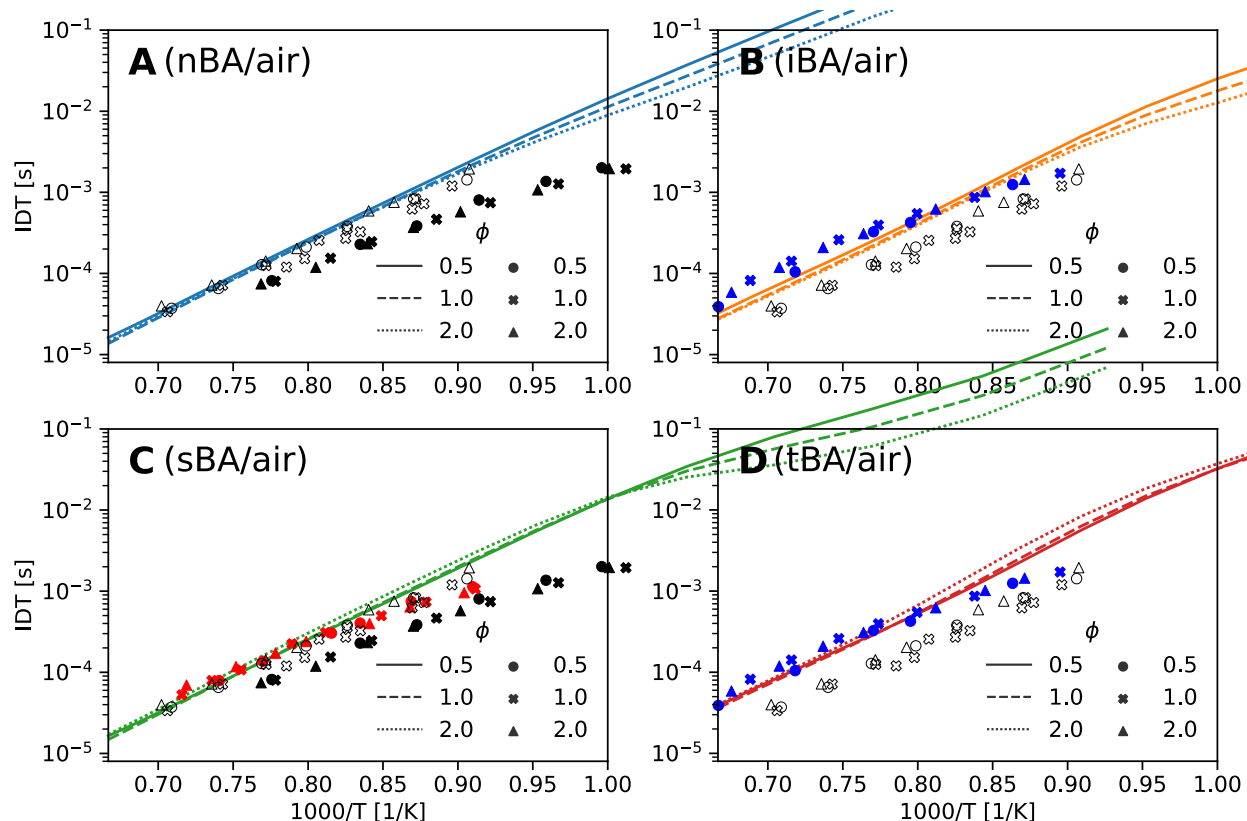
Figure 10. The total rate constants of BA H-atom abstraction reactions.

4.2 Combustion chemistry at elevated temperatures

Ignition delay time (IDT) was evaluated as an alternative measure of the overall reactivity. Figure 11 includes the IDTs at 10 atm across high initial temperatures (i.e., within 1000–1500 K) and different fuel-to-air ratios (0.5, 1.0, and 2.0), along with the HPST IDTs of relevant butenes^{35,81,82} from the retro-ene reactions at the same conditions. Since butene isomers are major intermediates

1 during BA oxidation and decomposition, their IDTs are expected to be relevant to BA ignition.
 2 Moreover, HPST IDTs of EA^{8,11} under similar conditions but at higher pressures (15 and 20 bar)
 3 are also included as references. Indeed, IDTs of EA have been proved to be insensitive to pressure
 4 under the investigated conditions (Figure S17). Comparing EA and BA IDTs provides additional
 5 hints about the influence of the retro-ene reactions and acetic acid sub-mechanism on IDTs, which
 6 are identified as significant according to Morsch et al.¹¹ and Figure S18. In addition, IDTs of BAs
 7 at intermediate temperatures are compared to IDTs simulated with the same assumption using
 8 well-validated models of butenes^{35,81,82} and EA¹¹ (Figure S19). BA IDTs comparison between 5
 9 and 10 atm can be found in Figure S20.

10



11
 12 *Figure 11. The estimated ignition delay time of butyl acetate isomers in air at 10 atm as a function of ~~initial~~ temperature and*
 13 *equivalence ratio. (A) nBA, (B) iBA, (C) sBA, and (D) tBA. HPST IDTs of relevant butenes at the same conditions are plotted as*
 14 *solid markers: black - 1-butene⁸¹, red - 2-butene⁸², and blue - iso-butene³⁵. HPST IDTs of ethyl acetate at 15 (adapted from*
 15 *Ahmed et al.⁸) and 20 bar (adapted from Morsch et al.¹¹) are plotted as hollow markers.*

16
 17 It is worth mentioning that the simulated IDTs for butyl acetate isomers at high temperatures are
 18 close to the measured IDTs for butene isomers and ethyl acetate under similar conditions.
 19 Specifically, IDTs for nBA and sBA are in line with 1-butene and 2-butene, whereas estimated
 20 values for iBA and tBA match the i-butene IDTs. **In addition, the BA IDTs show little dependence**
 21 **on ϕ and pressure at elevated temperatures, similar to the behavior of butenes and EA.** Over 1000
 22 K, retro-ene reactions are fast enough to become the dominant primary reactions. Hence, either the
 23 retro-ene reaction or the activation of the butene isomer produced by the retro-ene reaction is the
 24 rate-determining step for butyl acetate oxidation at these temperatures. As an example, the flux
 25 diagram of sBA oxidation at 1300 K is shown in Figure 12A, where over 98% of the sBA

1 undergoes retro-ene reaction, and most of the diagram is about butene chemistry. The dominance
2 of the retro-ene pathway is consistent with the observations reported by Ahmed et al.⁸ about ethyl
3 acetate. At lower temperatures, the contribution of H-atom abstraction increases. The resultant fuel
4 radicals may undergo beta-scission reactions or O₂ addition and the subsequent
5 isomerization/chain branching pathways (as the lower half in Figure 12B). These reactions convert
6 BAs into smaller fragments or unsaturated acetates resembling the butene oxidation intermediates.
7 However, as kinetics of the above-mentioned beta-scission, isomerization, and other reactions
8 were estimated by rate rules in the developed mechanisms, larger uncertainties at lower
9 temperature IDTs are expected. This observation suggests that investigating these reactions is
10 needed for more reliable results at lower temperatures.

11 Figure 13 shows the temperature sensitivities at ignition delay time (defined by the peak of dT/dt),
12 900 K, 10 atm, and stoichiometric composition with air. Sensitivities at other fuel-to-air ratios and
13 temperatures can be found in Section 6 of SI. According to Ji et al.⁷³, temperature sensitivity at the
14 ignition delay state has almost the same direction as the IDT sensitivity. Therefore, it can be used
15 as an alternative to the latter. As shown in Figure 13, nBA, iBA, and sBA share a similar trend in
16 the list of sensitive reactions. Besides the essential C₀ and C₁ chemistry, H-atom abstraction from
17 BAs by HO₂ and OH radicals, retro-ene reactions, beta-scission reactions, and butene chemistry
18 also top the list. The significance of HO₂ chain branching reactions is as expected and similar to
19 observations by Morsch et al. about EA at 850 K. Among them, the most sensitive abstraction
20 reactions take away the hydrogen atom at the α -carbon and are also the most dominant abstraction
21 reactions. On the other hand, retro-ene reactions, as competitors of the abstraction reactions, reduce
22 the reactivity. For tBA, iso-butene oxidation reactions instead of tBA-involved reactions are
23 significant, e.g., O₂, OH, and HO₂ addition and H-atom abstraction. The difference in sensitive
24 reactions is mainly due to the decomposition of tBA much faster than other isomers, resulting in
25 tBA almost fully decomposed to acetic acid and iso-butene before the radical pool becomes large
26 enough to make H-atom abstraction reactions competitive. As evidence, the 20% fuel consumption
27 time for tBA is about three orders of magnitude smaller than its IDT at 900 K, while the time
28 difference of other BAs is within an order of magnitude.

29

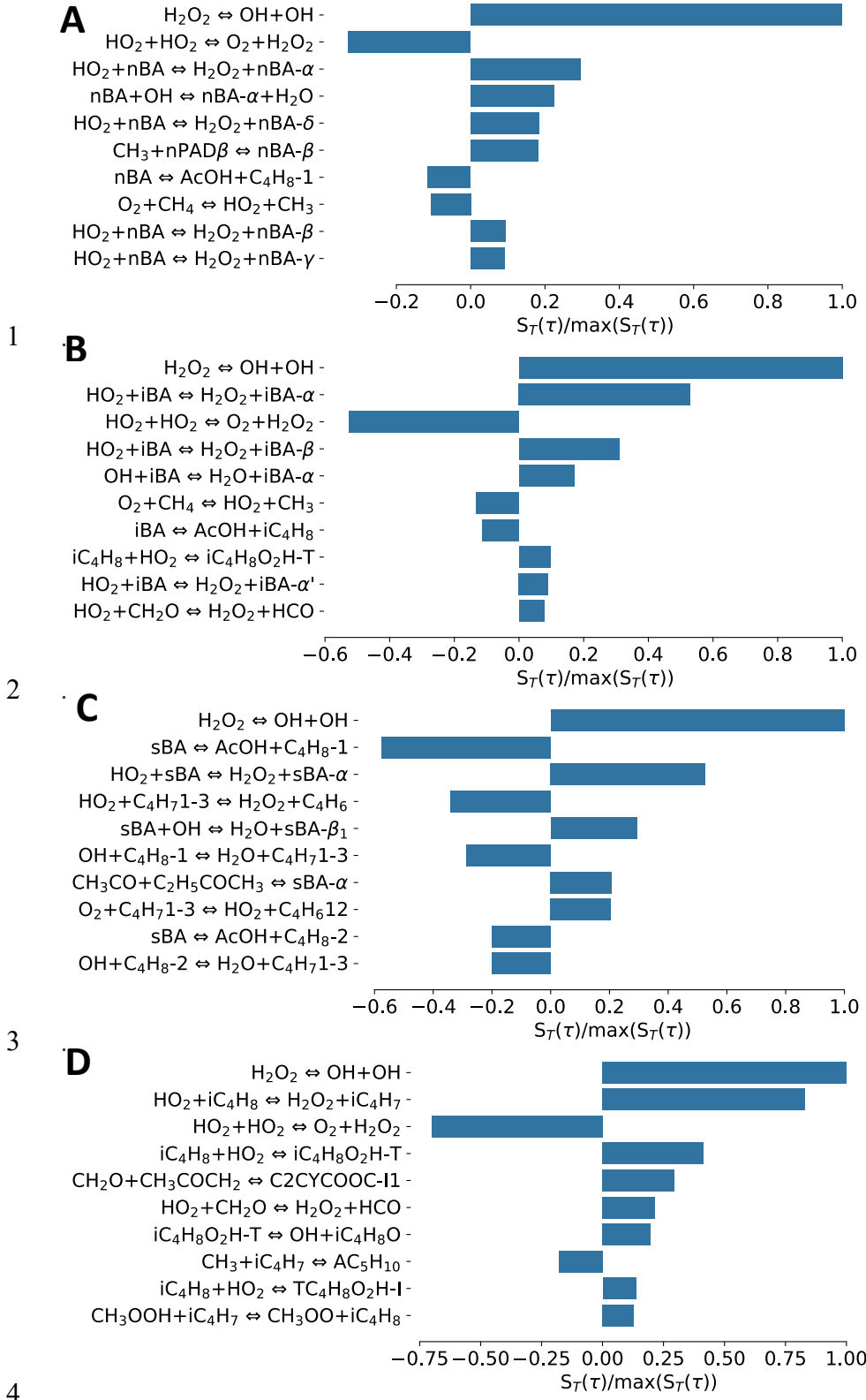


Figure 13. Normalized temperature sensitivity analysis at ignition delay time, 900 K, 10 atm, and stoichiometric composition with air. (A) nBA, (B) iBA, (C) sBA, and (D) tBA.

4.3 High-temperature pyrolysis

Although the models were not originally developed to predict pyrolysis systems, it is possible to use them for simulating pyrolysis, as the model includes the following essential chemistry:

- the retro-ene reactions that are also the primary reactions in the pyrolysis system
- H-atom abstractions by H and CH₃ for BA isomers and butenes
- relevant beta scissions of BA and butene radicals
- acetic acid decomposition chemistry

Carbon monoxide (CO) mole fraction time histories from shock tube experiments and simulations were compared in Figure 14. For figure clarity, only half of the measurements are included, whereas the remaining data can be found in Figures S29-S36.

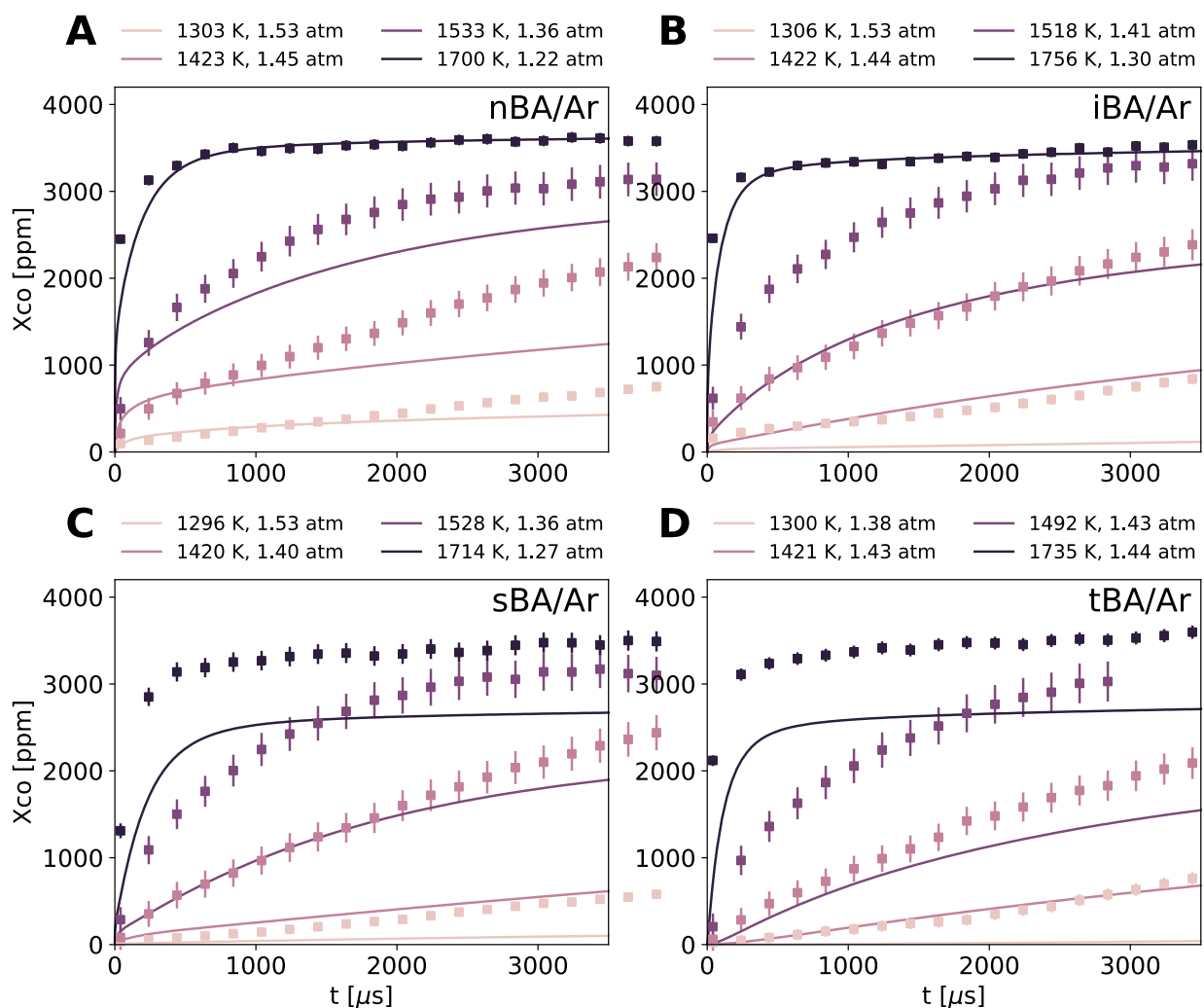


Figure 14. CO mole fraction time histories in the BA pyrolysis systems. (A) nBA, (B) iBA, (C) sBA, and (D) tBA. The lines are predictions from the simulation, and the markers are the measurements from the experiments.

Generally speaking, the pyrolysis of different BA isomers shows a negligible difference in CO profile according to the experiments. The models can capture the CO generation time history to some extent but generally underpredict CO production rate.

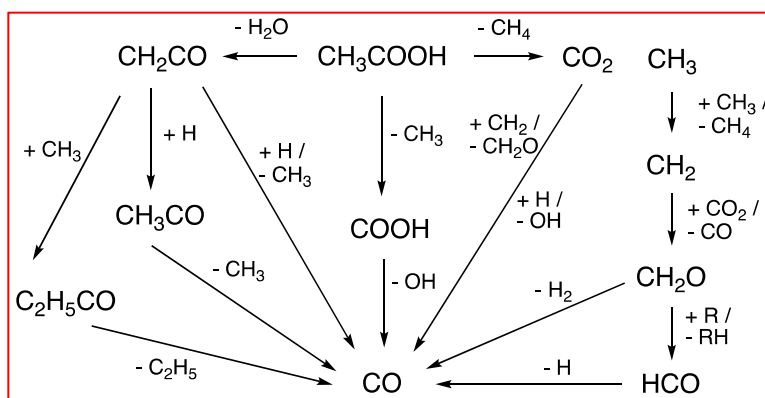


Figure 15. Major pathways in the BA pyrolysis system producing CO between 1200-1700 K.

Figure 15 shows the dominant pathways producing CO from butyl acetates at high temperatures according to the kinetic models. Thermochemistry of all involved species and kinetics of all pathways show in Fig. 15, except $\text{CO}_2 + \text{CH}_2 \rightleftharpoons \text{CO} + \text{CH}_2\text{O}$ and a few $\text{CH}_2\text{O} + \text{R} \rightleftharpoons \text{HCO} + \text{R}$ reactions, are from either RMG libraries or published databases, and are expected to have reasonable accuracy. All the important pathways start from the acetic acid formed from the butyl acetate, and involve radical intermediates, indicating the relevance of the radical pool growth on CO production rate. Indeed, the actual branching of a system depends on the abundance and distribution of each radical species. Sensitivities of CO concentration at 1500 K, 1 atm, and 1 ms from each BA isomer can be found in Section 8 of SI. The results highlight the significance of acetic acid sub-mechanism, C1 - C2 chemistry, a few alkene reactions, retro-ene reactions, and fuel fission reactions for predicting CO production (Table S2). Among them, fuel fission reactions are critical to the radical accumulation, but their exact rate coefficients at these reaction conditions are unknown; here they are all estimated by RMG rate rules.

5 Conclusions

This work presents butyl acetate oxidation models created using a predictive modeling approach. Their predictive capability is achieved by gathering accurate parameters for species and reactions in the potential sub-mechanism, calculating primary reactions with a decent quantum chemistry method, implementing a rate-based algorithm to build the kinetic mechanism in the RMG, and iteratively refining the thermochemistry of critical species. The generated models are for qualitatively and semi-quantitatively predicting oxidation systems, especially at elevated temperatures. Even though no data is available for straightforwardly validating the proposed models, careful comparison and investigation were made to illustrate the rationale of the calculated parameters, reveal the dominant chemistry in the oxidation systems, and demonstrate the adaptability of the model to the pyrolysis predictions. The major weakness of the models is the kinetic parameters of sensitive low-temperature oxidation pathways, e.g., BA peroxide isomerization, still derived from rate rules and with large uncertainties, limiting the accuracy of the model performance at lower temperatures. Other than the generated models, this work makes the following data available:

- QM-based kinetics of H-atom abstraction and retro-ene reactions for BA isomers
- Thermochemical data of over 600 species relevant to the oxidation and decomposition of oxygenated species at the CBS-QB3 level of theory

1 • CO mole fraction time histories of shock tube BA pyrolysis at 1300-1700 K
2 These data are valuable for creating ester-specific rate rules, building kinetic mechanisms for
3 oxygenated species, and validating BA pyrolysis models. As a stepstone, this work yields the
4 fundamentals necessary for creating a better BA model in future work and facilitates the evaluation
5 of BA molecules as useful biofuels computationally.
6

7 **Supporting Information**

8 Supporting Information associated with this article includes the newly generated mechanism in
9 various formats, the quantum chemical calculation detail, data visualization of the model statistics,
10 complementary results for shock tube experiments, and supplementary mechanism analysis in
11 terms of ignition delay time, flux diagram, and sensitivities.
12

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17
18

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