



Larger than expected organic acid yields from the multi-generation oxidation of petrochemical alkenes

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Abstract. Alkenes are primary pollutants in petrochemical source atmospheres, and their atmospheric chemistry is of great importance for tropospheric ozone and secondary organic aerosol formation. Hence, combining quantum chemical calculations and kinetic modelling, we investigated the oxidation mechanism and kinetics of 2-butene (BU), as one of the most important alkenes, and its impact on the environment. The mechanism results show that OH addition is the dominant pathway for *cis*- and *trans*-isomers of BU, and then the corresponding OH-adducts are attacked by O₂ to produce peroxy radicals, which further react with NO to form acetaldehyde and hydroxyalkyl radicals. Different from the one adopted in current atmospheric models, addition of hydroxyalkyl radicals by O₂ and NO to form acetic acid proceeds with a smaller barrier than that for H-abstraction by O₂ to form acetaldehyde. A lifetime of less than a few hours (< 4 h) for BU is estimated in the petrochemical regions. Kinetic modelling demonstrates that oxidation of BU is predicted to yield significant amounts of organic acids (> 56 %) in the petrochemical areas, larger than those are currently recognized, even in environments with low NO concentrations. Our results reveal that the OH-initiated oxidation of BU contributes importantly to organic acid budgets, particularly in the petrochemical regions, bridging the gap in organic acid budgets.

1 Introduction

Anthropogenic volatile organic compounds (AVOCs) have been associated with climate change, air quality, and environmental impacts via exposure to primary emissions and/or after their photochemical behaviors and multi-generation oxidation (Srivastava et al., 2022; Brook et al., 2010; Chen et al., 2024; Li et al., 2024). The latter leads to secondary air pollution, including secondary organic aerosol (SOA), tropospheric ozone, secondary organic acid, and so on (Peng et al., 2021; Yang et al., 2024; Tan et al., 2019). Automotive emissions of AVOCs have steadily decreased from efforts to control tailpipe emissions in China, and as a result, other

sources of AVOC emissions are growing in relative importance. Among them, petrochemical emissions are appreciable quantities with proportions for 7 %–26 % of total AVOC emissions. Furthermore, petrochemical emissions exhibit the largest potential of SOA formation (~ 23.7 %) among all industrial emission processes (Wu and Xie, 2018). However, owing to the complex atmospheric chemistry of AVOCs from petrochemical emissions, their reaction mechanisms are uncharacterized, hindering the accurate assessment of their role in air quality and global climate.

Alkenes represent a significant proportion of AVOCs in petrochemical industrial areas (Guo et al., 2022b, a; Henderson et al., 2010; Yang et al., 2023). A field observation re-

vealed that alkenes accounted for $53.7 \pm 8.5 \%$ of the total VOCs in the Lanzhou petrochemical area, with an average daily concentration of 82.3 ± 13.1 ppb (Yang et al., 2024). Previous studies have shown that multi-generation oxidation of biogenic and anthropogenic alkenes is important to the formation of local free radicals, tropospheric ozone, and SOA (Wu et al., 2021; Wang et al., 2022; Yang et al., 2023; Tan et al., 2024; Huang et al., 2025). For example, the reaction of biogenic alkene, isoprene, with nitrate radicals (NO_3) produces some N-containing monomers and dimers, leading to an estimated yield of organic aerosol mass of approximately $(5 \pm 2) \%$ (Wu et al., 2021). The gas-phase oxidation of biogenic alkenes (isoprene and monoterpenes) produces abundant semi-volatile organic products, whose second- or later-generation products are major contributors to SOA (Wang et al., 2018). Recent studies have pointed out that multi-generation oxidation of anthropogenic alkenes contribute to 8%–20% of SOA mass (Lee et al., 2022) and about 89% of O_3 formation (Yang et al., 2024) in the petrochemical regions. Hence, the atmospheric chemistry of alkenes causes significantly secondary pollution to the petrochemical regions. Given the ubiquity of anthropogenic alkenes in petrochemical areas, understanding the multi-generation oxidation mechanisms of anthropogenic alkenes is crucial for accurately predicting their impacts on air quality.

Although multi-generation oxidation of alkenes is believed to be important to SOA and O_3 formation, some studies have highlighted an unignorable source of the multi-generation oxidation for alkenes to secondary organic acids in the troposphere (Link et al., 2021; Srivastava et al., 2023; Wang et al., 2020; Isaacman-Vanwertz et al., 2018; Friedman and Farmer, 2018; Larsen et al., 2001). For example, a previous experimental study has revealed that organic acids obtained by the oxidation of isoprene and α -pinene account for about 28% of the initial organic carbon (Link et al., 2021). However, a global chemistry-climate model simulation has shown that formic acid, an important class of organic acids in the atmosphere, was underestimated by 2 to 5 times relative to that of satellite observations (Franco et al., 2021). Therefore, current models still highly underestimate ambient concentrations of these acids, indicating that significant sources of organic acid in the atmosphere remain unidentified. Previous studies have identified several missing sources, including primarily from combustion emissions, biogenic emissions, aqueous-phase chemistry of oxygenated VOCs, and photochemical reactions of alkenes (Paulot et al., 2011; Müller et al., 2019; Shaw et al., 2018; Chaliyakunnel et al., 2016; Franco et al., 2021; Link et al., 2021; Parandaman et al., 2018). Therefore, it is interesting to investigate the impact of their photochemistry on the formation of organic acids, to narrow the gap between observed and modelled organic acid concentrations, especially in typical petrochemical areas.

In the present study, we investigated the multi-generation oxidation mechanism and kinetics of 2-butene (BU) initiated by hydroxyl radical (OH) using a combination of quantum

chemical calculations and kinetic modelling. BU is a representative alkene in the petrochemical regions, with the concentrations range from 0.5 to 11.4 ppb (Li et al., 2017; Ren et al., 2024; Wang et al., 2022; Zeng et al., 2022). Based on the mechanisms and kinetics, we also applied photochemical box model simulations to study the yields of organic acids from BU. The effects of OH and NO on the reaction mechanisms of BU were evaluated, and the implications of organic acids formation were discussed.

2 Methods

All geometries of the reactants (Rs), pre-reactive complexes, transition states (TSs), intermediates (IMs) and products in this study were fully optimized at the M06-2X/6-311+G(2df,2p) level (Zhao and Truhlar, 2008). Harmonic vibrational frequencies were performed at the same level to check all stationary points either a TS (with only one imaginary frequency) or the minima (without any imaginary frequencies), and to provide zero-point vibrational energy (ZPVE), which is scaled by a factor of 0.967. Intrinsic reaction coordinate (IRC) calculations were carried out at the M06-2X/6-311+G(2df,2p) level to verify that each TS is connected to the desired Rs and products (Fukui, 1981). The single-point energy (SPE) calculations were further refined by the DLPNO-CCSD(T)/aug-cc-pVTZ level (Riplinger et al., 2013) with normal pair natural orbital (NormalPNO) criteria (Liakos et al., 2015) to yield more accurate energetics. T_1 diagnostic values in the DLPNO-CCSD(T) calculations for the IMs and TSs involved in the key reaction pathways were checked for multi-reference character. The T_1 diagnostic values for all checked important species in this work are lower than the threshold value of 0.045, indicating the reliability of applied single reference methods. In all cases, the energies were calculated relative to the corresponding reactants including ZPVE corrections. $\Delta E_a^\#$ is defined as the activation energy ($\Delta E_a^\# = E_{\text{TS}} - E_{\text{Reactant}}$), while ΔE_r is defined as the reaction energy ($\Delta E_r = E_{\text{Product}} - E_{\text{Reactant}}$). All above calculations were performed within Gaussian 09 and ORCA 5.0.0 program (Frisch et al., 2009; Neese, 2012). The Multiwfn program and Visual Molecular Dynamics (VMD) were utilized to analyze and visualize the molecular orbitals of relevant species (Humphrey et al., 1996; Lu and Chen, 2012).

The combination of single-conformer and multi-conformers approximation was adopted to investigate the reaction mechanism in a cost-effective way of considering the effect of multiple conformers of the reactants and TSs. Based on the single-conformer calculations, the effect of multiple conformers was considered for the crucial reaction step of H-shift reaction of RO_2 . The systematic structure scanning method was employed to produce the conformers by the Molclus program (Lu, 2020). The systematic structure scanning was performed by regularly rotating the dihedral angle that determines the conformers of the target

molecules. For the target molecules, it yielded 4–256 conformers depending on the complexity of the system. Initial geometry optimizations and single-point electronic energy calculations were performed at the B3LYP/6-31+G(d) level. Subsequently, conformers with electronic energies within 2 kcal mol^{-1} relative to the lowest-energy conformer were further considered for geometry optimization at the M06-2X/6-311+G(2df,2p) level. On the lowest electronic energy R, intermediate, TS, and product geometries at the M06-2X/6-311+G(2df,2p) level, single-point calculation at the DLPNO-CCSD(T)/aug-cc-pVTZ level was carried out.

The rate constants for the reactions with TSs were calculated using the variational transition state theory (VTST) along with one-dimensional asymmetric Eckart tunnelling correction (Bao and Truhlar, 2017; Eckart, 1930). Besides, the rate constants for the barrierless reactions were calculated by employing the variable-reaction-coordinate variational transition state theory (VRC-VTST) (Bao and Truhlar, 2017). For pathways involving multiple conformers, the rate constants were calculated using multi-conformer transition state theory (MC-TST) (Møller et al., 2016), incorporating data for all conformers obtained from the Molclus program (Lu, 2020). All the kinetics calculations were performed with the KiSTheP 2021 and Polyrate 2017-C programs (Canneaux et al., 2014; Zheng, 2018).

A box-model was used to investigate the formation of organic acids, built using AtChem2 Program (Sommariva et al., 2020) with a chemical mechanism taken from the Master Chemical Mechanism (MCM v3.3.1) (Jenkin et al., 1997; Saunders et al., 2003). The box model was constrained by the initial concentrations of NO, NO₂, BU, and OH as listed in Table S1 in the Supplement (Yang et al., 2024, 2023). The concentration of OH ([OH]) was kept constant throughout the simulation over a 2 h period. More details about the box model simulation are shown in the Supplement.

3 Results and discussion

3.1 OH-Initiated reactions of *cis*- and *trans*-BU

In the atmosphere, there exists two stable isomers of BU, i.e., *cis*-2-butene (*cis*-BU) and *trans*-2-butene (*trans*-BU), which are proven to be ubiquitous and difficult to interconvert (Tuzon et al., 1998; Wang et al., 2022; Mo et al., 2022). Hence, to systematically assess the photochemistry of BU, we considered the OH-initiated reactions of *cis*-BU and *trans*-BU. Figure S1 in the Supplement displays the optimized structure for all stationary points (SPs) involved in these two reactions at the M06-2X/6-311+G(2df,2p) level. For comparison, other levels, including the B3LYP, MPW1PW91, and ω B97X-D/6-311+G(2df,2p) levels, were performed to calculate the geometries (Fig. S2). The structural parameters of all SPs obtained by the four levels are similar, with the largest discrepancies of less than 0.01 Å in bond lengths and 1.70° in bond angles. Hence, the M06-2X level of theory can accu-

ately describe the geometrical information of OH-initiated reactions of *cis*-BU and *trans*-BU.

The potential energy surfaces (PESs) for all possible pathways of the OH-initiated reactions of *cis*- and *trans*-BU are presented in Fig. 1. There are two kinds of pathways, i.e., OH-addition (R_{add}) and H-abstraction (R_{abs}). Each pathway has a pre-reactive complex prior to the corresponding TS, which is more stable than the corresponding reactants. As shown in Fig. S1, the C_{2v} symmetry of *cis*-/*trans*-BU suggests one OH-addition (*cis*-/*trans*- R_{add}) and two H-abstraction (*cis*-/*trans*- R_{abs}) pathways in the *cis*-/*trans*-BU reaction systems. For *cis*-BU, the pathway of H-abstraction from $-\text{CH}_3$ (*cis*- R_{abs1}) possesses a lower $\Delta E_{\text{a}}^{\#}$ value of $2.36 \text{ kcal mol}^{-1}$ and a more negative exothermicity of $-30.96 \text{ kcal mol}^{-1}$ than H-abstraction from $-\text{CH=}$ group (*cis*- R_{abs2}). It is attributed to the smaller bond dissociation energy of C–H bond ($D_{298}^0(\text{C–H})$) at the $-\text{CH}_3$ groups relative to that at the $-\text{CH=}$ groups in *cis*-BU (Tables S2 and S3). It suggests that the H-abstraction from the $-\text{CH}_3$ group is more favorable than that from the $-\text{CH=}$ group. However, OH-addition to C=C double bond (*cis*- R_{add1}) proceeds via a negative $\Delta E_{\text{a}}^{\#}$ value of $-0.97 \text{ kcal mol}^{-1}$, which is at least 3 kcal mol^{-1} smaller than those of H-abstraction pathways, indicating favorable formation of the OH-adduct intermediate (*cis*-IM_{add1}). Similarly, OH-addition to *trans*-BU (*trans*- R_{add1}) is also a dominant pathway, but it possesses a more negative $\Delta E_{\text{a}}^{\#}$ value of $-1.33 \text{ kcal mol}^{-1}$ than the *cis*- R_{add1} pathway. The interaction region indicator listed in Fig. S3 reveals that OH-addition to the C=C bond of *cis*-BU exhibits a stronger steric hindrance compared to that of *trans*-BU, attributed to the van der Waals and steric hindrance interactions between the two $-\text{CH}_3$ groups in *cis*-TS_{add1}. The larger Mayer bond order of the forming C–O bond in *trans*-TS_{add1} (0.251) relative to that in *cis*-TS (0.192) suggests stronger electronic interactions in the *trans*-TS_{add1}. This difference, combined with steric hindrance, primarily influences the reactivity of the C=C bond in both *cis*-BU and *trans*-BU, leading to the formation of stable OH-adduct intermediates (*cis*- and *trans*-IM_{add1}).

The rate constant of each pathway and the total rate constants (k_{total}) of the OH-initial reactions of *cis*- and *trans*-BU were calculated and are summarized in Fig. 2 and Tables S4 and S5, along with comparisons with the available experimental data (Atkinson, 2000; Ohta, 1984). The rate constants were calculated over the temperature range of 240–340 K, considered from the surface of the earth to the lower troposphere. The total rate constant of each reaction system is obtained by the sum of calculated rate constants for all pathways. There is a negative correlation between k_{total} and temperatures in the temperature range of 240–340 K, attributable to the presence of the pre-reactive complexes (Chen et al., 2022; Giri et al., 2022) and the submerged TSs ($\Delta E_{\text{a}}^{\#} < 0$) (Zádor et al., 2009) in the OH-addition pathways. Our calculated rate constants at the DLPNO/aug-cc-pVTZ//M06-2X/6-311+G(2df,2p) level also compare favor-

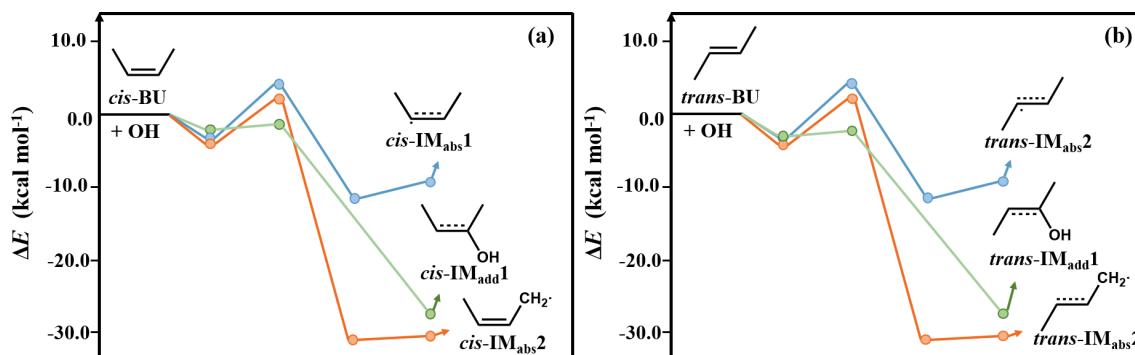


Figure 1. Potential energy surfaces (PESs) for the OH-initiated reactions of (a) *cis*-BU and (b) *trans*-BU with OH (unit: kcal mol⁻¹).

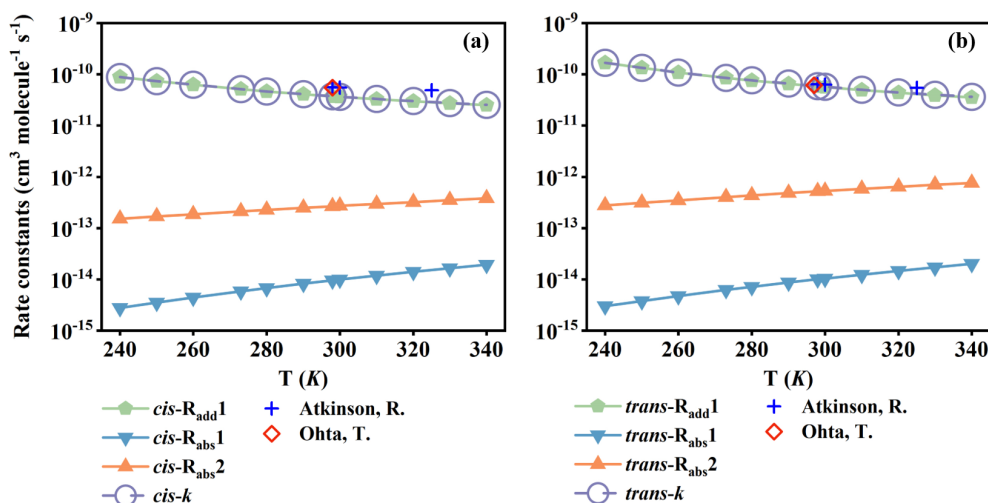


Figure 2. The rate constants (cm³ molecule⁻¹ s⁻¹) of (a) *cis*-BU and (b) *trans*-BU with OH against the temperature range of 240–340 K. The experimental rate constants are from Atkinson (2000) and Ohta (1984), respectively.

ably with the available experimental data. For example, the rate constant of the *trans*-BU + OH reaction at 298 K is 5.85×10^{-11} cm³ molecule⁻¹ s⁻¹, in lines with the experimental values of $(5.40 \pm 0.02) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ reported by Atkinson (2000) and $(6.09 \pm 0.3) \times 10^{-11}$ obtained by Ohta (1984). Hence, the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2df,2p) method provides a reliable description for the kinetics of the OH-initial reactions of *cis*-BU and *trans*-BU.

Tables S4 and S5 list the temperature dependences of the branching ratios (Γ) over the temperature range from 240 to 340 K. For *cis*-BU, the rate constant of OH-addition pathway is at least two orders of magnitude higher than those of the corresponding H-abstraction pathways. At 340 K, the OH-addition pathway accounts for 98.4 % of the total reaction, this fraction increases to 99.8 % when the temperature is lowered to 240 K. The contribution of OH-addition pathway to the total rate constant is more than 99 % in the whole measured temperature ranges. Similarly, for *trans*-BU, the OH-addition pathway is also of major importance. Ar-

rehenius expressions are derived to be $k_{\text{total}}(\textit{cis}\text{-BU} + \text{OH}) = 1.23 \times 10^{-12} \exp(1021.32/T)$ and $k_{\text{total}}(\textit{trans}\text{-BU} + \text{OH}) = 8.90 \times 10^{-13} \exp(1251.48/T)$ over the temperature range of 240–340 K. From the calculated Arrhenius expressions, the activation energies of the *cis*- and *trans*-BU reaction systems are deduced to be -2.03 and -2.49 kcal mol⁻¹, respectively. These negative activation energy values indicate that the OH-initiated reactions of *cis*- and *trans*-BU are kinetically favored in the troposphere, to rapidly form the OH-adduct intermediates.

3.2 Subsequent reactions of the OH-adduct intermediates

The OH-adduct intermediates, i.e., *cis*- and *trans*-IM_{add}1, proceed via three competitive pathways including reaction with O₂ (R3), isomerization (R4), and decomposition (R5). A Schematic PES presented in Fig. S4 reveals that the TSs of *cis*- and *trans*-R3 are not identified, but there are TSs for R4 and R5 pathways with the $\Delta E_a^\ddagger$ values more than

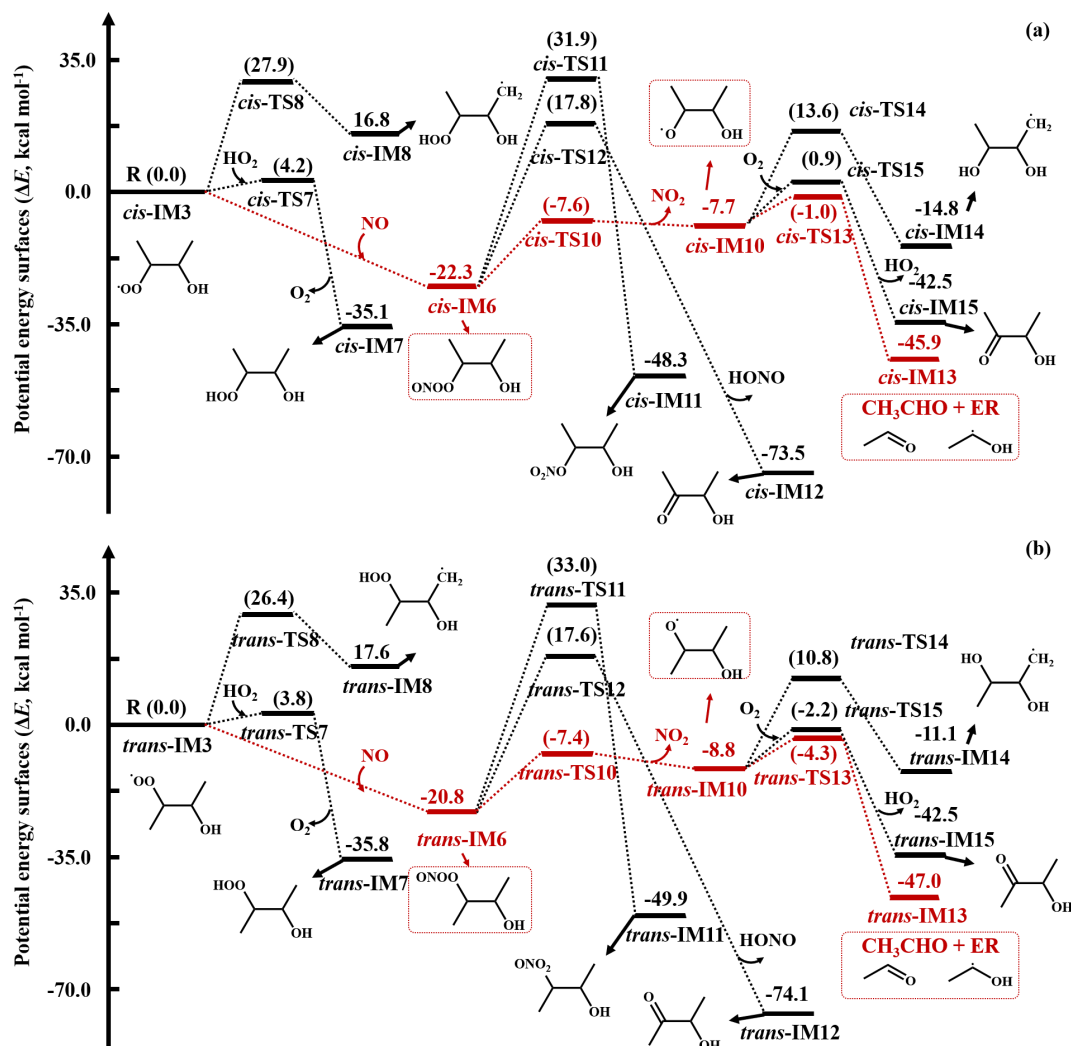


Figure 3. PESs of the reaction of (a) *cis*-IM3 and (b) *trans*-IM3. The number denotes the $\Delta E_a^\ddagger$ and ΔE_r for each reaction step.

30.0 kcal mol⁻¹. The calculated rate constants of R4 and R5 pathways are 7.3×10^{-13} and 2.6×10^{-11} s⁻¹ in the *cis*- and *trans*-BU reaction systems (Table S6), which are 18–20 orders of magnitude smaller than that of R3 (6.0×10^{-11} cm³ molecule⁻¹ s⁻¹, corresponding to an equivalent first-order rate constant of 3.0×10^7 s⁻¹). Considering the branching ratios among the three pathways, about 99 % of both *cis*- and *trans*-IM_{add} 1 react with O₂ to form peroxy radicals (*cis*-/*trans*-RO₂), which further propagate the oxidation.

For *cis*-RO₂, attacked by NO (*cis*-R6) or HO₂ radical (*cis*-R7) forms the peroxy nitrite (*cis*-RO₂NO) or the hydroperoxide (*cis*-ROOH). Alternatively, there exists the autoxidation of *cis*-RO₂, which proceeds via two-step reactions, i.e., a H-shift reaction (*cis*-R8) followed by an O₂-addition (*cis*-R9), with the high $\Delta E_a^\ddagger$ value and the small rate constant (Figs. S7 and S8). Similarly, the reaction with HO₂ radical also proceeds via a TS with the $\Delta E_a^\ddagger$ value of 4.20 kcal mol⁻¹ (Fig. S6). However, the association reaction of *cis*-RO₂ with

NO is barrierless and exothermic (Figs. 3 and S5), and the corresponding equivalent first-order rate constant is 1.1 s⁻¹, which is at least five orders of magnitude higher than those of *cis*-R7 and *cis*-R8 pathways (Tables S7–S11).

As shown in Fig. S8, the reaction of *cis*-RO₂ with HO₂ is competitive in the troposphere only if HO₂ concentration exceeds 40 ppt, which is the maximum atmospheric concentration. It implies that the *cis*-RO₂NO is the dominant product from *cis*-RO₂. Subsequently, there are three reaction pathways of *cis*-RO₂NO, i.e., NO₂-elimination (*cis*-R10), intramolecular isomerization (*cis*-R11), and dissociation (*cis*-R12). The $\Delta E_a^\ddagger$ values of *cis*-R11 and *cis*-R12 are 54.23 and 38.35 kcal mol⁻¹ (Fig. 3), respectively, which are 26.36 kcal mol⁻¹ larger than that of *cis*-R10. It indicates that the formation of organic nitrates (*cis*-ON), acetoin (CH₃CH(OH)C(=O)CH₃), and HONO is of minor importance. The calculated HONO yield is < 1 %, indicating the negligible formation, in contrast to the

yield of 50 % for 1-butene under high- NO_x conditions reported by Chen et al. (Chen et al., 2021). The discrepancy is attributed to the characteristic of structure, i.e., the distinct β -hydrogen availability of the two alkenes. As shown in Fig. 3, the favorably produced alkoxy radical (*cis*-RO) via *cis*-R10 then undergoes dissociation (*cis*-R13), isomerization (*cis*-R14), and H-abstraction (*cis*-R15) to yield acetaldehyde (CH_3CHO) and hydroxyalkyl radicals (CH_3CHOH), $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2$ radical, and acetoin ($\text{CH}_3\text{C}(=\text{O})\text{CH}(\text{OH})\text{CH}_3$), respectively. The *cis*-R13 pathway possesses a smaller $\Delta E_a^\ddagger$ value of $6.51 \text{ kcal mol}^{-1}$ and a larger rate constant of $1.10 \times 10^8 \text{ s}^{-1}$ at 298 K relative to the *cis*-R14 and *cis*-R15 pathways (Table S12), indicating a major importance to form CH_3CHO and CH_3CHOH .

Similarly, as shown in Fig. S5, the subsequent reactions of *trans*-RO₂ involve three essential steps: (i) the association with NO to form *trans*-RO₂NO, (ii) the NO₂-elimination of *trans*-RO₂NO to produce *trans*-RO, and (iii) the dissociation of *trans*-RO to yield CH_3CHO and CH_3CHOH radical. However, the differences between the subsequent reactions of *cis*-IM_{add}1 and *trans*-IM_{add}1 are reflected in the lower reaction energy barriers and the larger rate constants of *trans*-IM_{add}1. For example, the $\Delta E_a^\ddagger$ value of *trans*-R12 pathway is $11.99 \text{ kcal mol}^{-1}$, which is $2.6 \text{ kcal mol}^{-1}$ lower than that of *cis*-R12 pathway, and the corresponding rate constant of *trans*-R12 pathway is six times larger than that of *cis*-R12 pathway. It is attributed to a stronger steric hindrance in subsequent reactions of *cis*-IM_{add}1 relative to *trans*-IM_{add}1. Therefore, CH_3CHO and CH_3CHOH radicals are more rapidly produced from *trans*-BU relative to *cis*-BU in the atmosphere.

3.3 The fate of BU

According to the previous study (Da Silva et al., 2009; Zádor et al., 2009), $\text{CH}_3\text{CHOH}\cdot$ radical (ER) undergoes a step-wise O₂-addition/HO₂-elimination mechanism (R16) via ER-O₂ formation, to form CH_3CHO and HO₂ radical. The formation of ER-O₂ is an exothermic process with the ΔE_r of $-34.11 \text{ kcal mol}^{-1}$, which supports to overcome the $\Delta E_a^\ddagger$ value of $11.27 \text{ kcal mol}^{-1}$ (Figs. 4 and S9). However, under the petrochemical conditions, ER-O₂ readily react with NO, which is abundant in polluted areas, forming ER-O₂NO, because this reaction is a barrierless and largely exothermic with the $\Delta E_a^\ddagger$ value of $-24.16 \text{ kcal mol}^{-1}$ (R17). Subsequent decomposition of ER-O₂NO (R19) possesses a $\Delta E_a^\ddagger$ value of $13.69 \text{ kcal mol}^{-1}$, which can be overcome because the excess energy ($-24.16 \text{ kcal mol}^{-1}$) from ER-O₂NO formation, leading to the formation of alkoxy radical (ER-O) and NO₂. ER-O reacts with O₂ (R20) to produce acetic acid (CH_3COOH) and HO₂ radical, with the $\Delta E_a^\ddagger$ and ΔE_r values of 5.40 and $-48.13 \text{ kcal mol}^{-1}$, respectively. To elucidate the significance of acid formation pathway in petrochemical regions, the kinetic data were investigated and listed in Table S13. The rate constant for CH_3CHO

and HO₂ formation is $2.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, which is slightly smaller than that for ER-O and NO₂ formation ($4.79 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Furthermore, the predicted branching ratios forming CH_3CHO and CH_3COOH are 29.7 % and 69.4 %, respectively, which requires to further assess the contribution of BU to organic acids in the atmosphere. Furthermore, we predict a minor pathway via RO₂ + NO reaction to form organic nitrate, consistent with the work by Muthuramu et al. (1993) for a small yield for the formation of organic nitrate from *cis*-BU ($3.7 \% \pm 0.9 \%$). In addition, we also evaluate the tropospheric lifetimes (τ) for *cis*-BU and *trans*-BU at different [OH] levels. The gas-phase OH oxidation lifetimes were estimated using $\tau = 1/(k_{\text{total}}[\text{OH}])$, where k_{total} and [OH] are the total rate constant and OH concentration, respectively. As shown in Table S14, the τ values are 9.29 and 5.93 h for *cis*-BU and *trans*-BU, respectively, under the remote areas with the [OH] of $8 \times 10^5 \text{ molecule cm}^{-3}$, which are higher than those of the corresponding lifetimes under the petrochemical regions with the [OH] of $1 \times 10^7 \text{ molecule cm}^{-3}$. The short τ value of BUs in the petrochemical regions indicate that they are more readily oxidized, implying a more significant environmental impact in these regions compared to urban regions. The τ values of *cis*- and *trans*-BU are further shortened to be 2.70 and 1.62 h as the temperature drops to 273 K in the petrochemical regions. Given that organic acids are more conducive to atmospheric new particle formation and growth under low-temperature conditions (Peng et al., 2021), it is essential to focus on the contribution of the BU oxidation in the petrochemical regions to the formation of organic acids at low temperatures.

3.4 Rate of CH₃COOH formation

To evaluate the impact of our established mechanisms on the formation of organic acids in the petrochemical regions, a box model simulation was performed to quantify the production rate ($r_{\text{CH}_3\text{COOH}}$) and yield ($Y_{\text{CH}_3\text{COOH}}$) of CH_3COOH by using the MCM v3.3.1 coupled with the AtChem2 box model. For comparison, the corresponding simulation under the traditional mechanism of CH_3COOH formation in MCM v3.3.1 was also carried out. All the simulations were conducted using the measured mixing ratios of BUs, OH, and NO in a typical petrochemical industrial region, and all the settings were posted in Table S1 (Yang et al., 2024). It is evident from Figs. 5 and S10 that the $r_{\text{CH}_3\text{COOH}}$ values corrected with our proposed mechanism exhibit a significant increase of more than ten times under typical petrochemical conditions, where the concentrations of [OH] and NO ([NO]) are $2 \times 10^6 \text{ molecule cm}^{-3}$ and 10 ppb ($2.5 \times 10^{11} \text{ molecule cm}^{-3}$), respectively. Even when [OH] and [NO] decrease, the $r_{\text{CH}_3\text{COOH}}$ values are also increased by more than five times. Large production rates of CH_3COOH correspond to the high $Y_{\text{CH}_3\text{COOH}}$ values, for example, the $Y_{\text{CH}_3\text{COOH}}$ value in *cis*-BU + OH reaction with

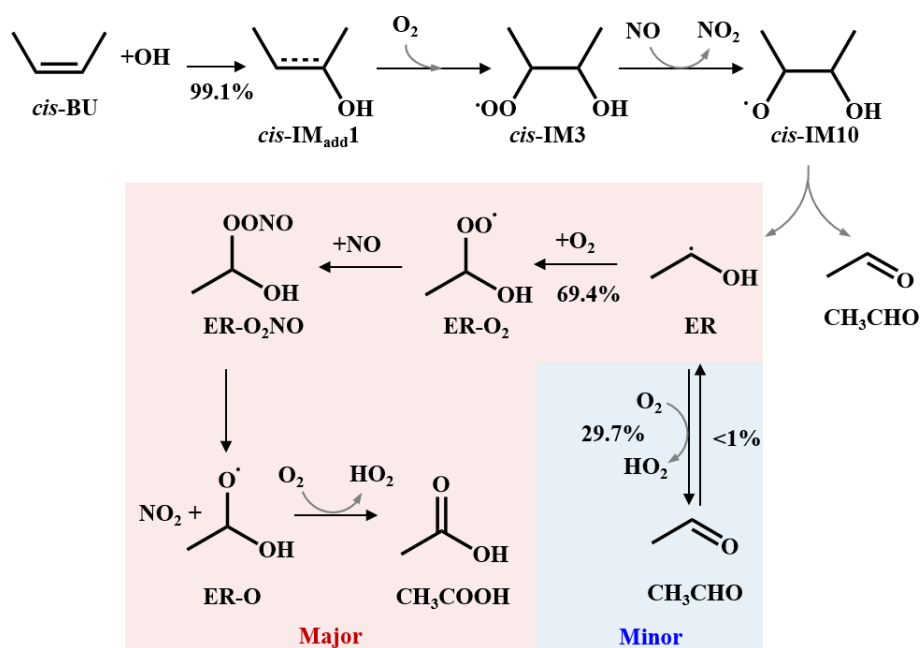


Figure 4. Schematic representation of the preferred pathways of the *cis*-BU + OH reactions leading to formation of acetaldehyde (CH_3CHO) and acetic acid (CH_3COOH). Values of branching ratio are shown in black.

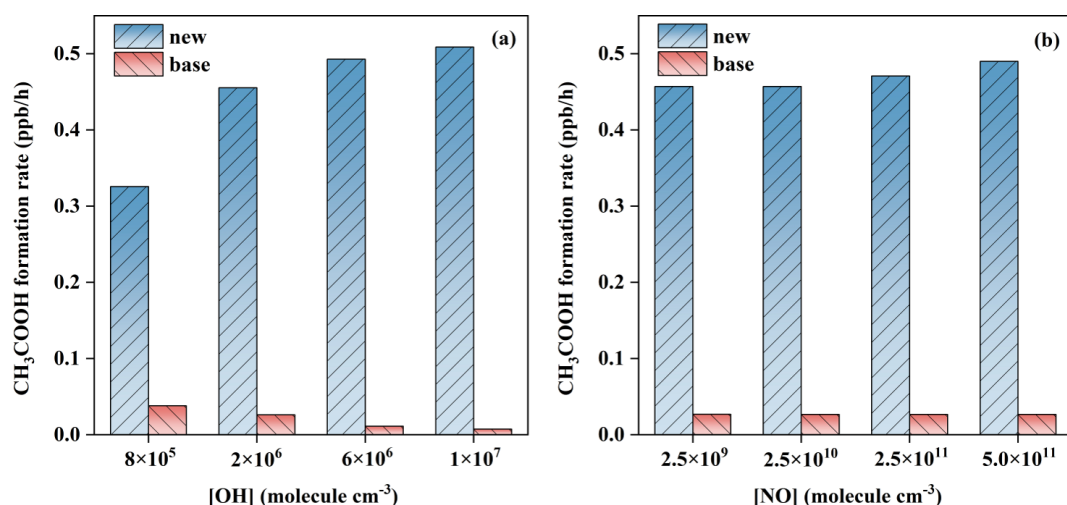


Figure 5. Mean formation rate of CH_3COOH (unit: ppb h^{-1}) from the *cis*-BU + OH reactions as a function of (a) OH concentration ($[\text{OH}]$) and (b) NO concentration ($[\text{NO}]$) under the petrochemical region conditions. The comparison is made between the MCMv3.3.1 and the new mechanism.

57 % is more than ten times higher than that without our proposed mechanism under the typical petrochemical conditions. Hence, the photooxidation of *cis*-/*trans*-BU corrected by our proposed mechanisms has a significant impact on the formation of organic acids in the petrochemical source regions, with particularly pronounced effects on the formation of small-molecule gaseous organic acids.

To further assess the atmospheric regions where the photochemistry of BU will have significance, we also calculated the $r_{\text{CH}_3\text{COOH}}$ values under the varying $[\text{OH}]$ and $[\text{NO}]$

corresponding to the atmospheric conditions (Figs. 5 and S10) (Tan et al., 2019). In a high $[\text{NO}]$ condition of $4.9 \times 10^{10} \text{ molecule cm}^{-3}$ with the $[\text{OH}]$ of $6 \times 10^6 \text{ molecule cm}^{-3}$, the $r_{\text{CH}_3\text{COOH}}$ values are 0.51 and 0.47 ppb h^{-1} in *cis*-BU + OH and *trans*-BU + OH reactions, which are at least 55 % larger than those with the $[\text{OH}]$ of $8 \times 10^5 \text{ molecule cm}^{-3}$, respectively. Even in a low $[\text{NO}]$ condition of $2.5 \times 10^9 \text{ molecule cm}^{-3}$, the $r_{\text{CH}_3\text{COOH}}$ values in two reactions are also significantly regulated by the atmospheric $[\text{OH}]$. However, there is little effect of $[\text{NO}]$ on the $r_{\text{CH}_3\text{COOH}}$ values.

For example, at the same $[\text{OH}]$ of $2 \times 10^6 \text{ molecule cm}^{-3}$, the $r_{\text{CH}_3\text{COOH}}$ value in *cis*-BU + OH reaction is 0.49 ppb h^{-1} at the $[\text{NO}]$ of $5.0 \times 10^{11} \text{ molecule cm}^{-3}$, while in the $[\text{NO}]$ of $2.5 \times 10^9 \text{ molecule cm}^{-3}$, the $r_{\text{CH}_3\text{COOH}}$ value is only decreased by 7 %. Combined with the mechanism results, the yield of organic acid from the BU + OH reaction is regulated by the atmospheric OH concentration. Therefore, under both typical petrochemical source region conditions and general atmospheric conditions, *cis*-BU + OH and *trans*-BU + OH reactions can form CH_3COOH through the subsequent oxidation of CH_3CHOH radicals, exhibiting unexpectedly high formation rates during daylight hours.

4 Conclusions and atmospheric implications

AVOCs have profound impacts on air quality, human health and climate, and BU is the major AVOCs emitted from the petrochemical regions. Hence, from combined quantum chemical calculations and photochemical box model simulations, this study provides a systematic insight into the multi-generation oxidation mechanisms, kinetics, and atmospheric fate of BU and its contribution to the formation of organic acid. The initial reactions of both the *cis*- and *trans*-isomers of BU readily involve OH addition to the C=C double bond, yielding the corresponding OH-adducts. Subsequent reactions proceed via O_2 addition, NO-association, NO_2 -elimination, and further decomposition to produce CH_3CHO and CH_3CHOH radical. CH_3CHOH radical is converted into CH_3COOH and HO_2 radical, facilitated by O_2 and NO through the pathways of O_2 addition, NO-association, NO_2 -elimination, and H-abstraction. Our mechanism highlights that the rapid and irreversible reaction of $\text{CH}_3\text{CHOH}\cdot$ with O_2 and NO is a key mechanistic step in the formation of CH_3COOH , which is one of the most favorable products, with a yield of 57 %. However, previous experimental studies on the OH-initiated oxidation of BU obtained a low yield of CH_3COOH (< 10 %) (Atkinson, 1997; Muthuramu et al., 1993). Given the rapid partitioning of gas CH_3COOH into the liquid phase in the experimental environment (Franco et al., 2021), the measured yield likely corresponds to the lower experimental limit.

This study further reveals that the multi-generation oxidation of BU in the petrochemical environment, may be particularly important for organic acid formation. Using our calculated kinetics data, we estimate a lifetime of less than 4 h for BU in the petrochemical environment, indicating that BU are rapidly oxidized following the local emission. By adding our established mechanisms to the photochemical box model simulations, our calculated formation rates and yields of CH_3COOH are at least 10 times higher than those from the traditional mechanism. Besides, the impact of OH concentrations on the formation rate of CH_3COOH is greater than that of NO concentrations. That is, the formation rate of CH_3COOH rapidly drops, as OH concentrations decrease.

This highlights the dominant role of OH radicals in the initial oxidation steps of multi-step oxidation processes. With the increasing oxidative capacity and decreasing nitrogen oxides (NO_x) abundance in polluted areas (Newland et al., 2021), further study is needed to explore the impacts of these factors on the multi-generation oxidation reactions of alkenes.

Contrary to the consensus that the complex multi-generation oxidation of alkenes primarily contributes to the formation of low-volatility products, we discovered that the multi-generation oxidation of BU can unexpectedly contribute to the formation of organic acids. The unexpected production of organic acids can not only help to explain the missing source of organic acids but also affect the acidity of atmospheric precipitation, especially for the petrochemical region atmosphere. In the atmosphere, we predict that the multi-generation oxidation of alkenes during the daytime will produce CH_3COOH at a rate of 10.4 ppb h^{-1} (Fig. S10), which can be comparable with the simulated source from the photochemical reaction of biogenic alkenes (Paulot et al., 2011). Therefore, the mechanism for the formation of organic acids from BU isomers established by this study is more significant than previously recognized, particularly in the petrochemical regions with the high emissions of BU isomers. Further investigation is warranted into the multi-generation oxidation of AVOCs, as well as their impacts on the formation of organic acids and the environment.

Data availability. The data are accessible by contacting the corresponding author (jiym@gdut.edu.cn).

Supplement. The following information is provided in the Supplement: the comparison of the geometries of *cis*- and *trans*-isomers of BU calculated at the M06-2X/6-311+G(2df,2p) level of theory and other levels including B3LYP/6-311+G(2df,2p), MPW1PW91/6-311+G(2df,2p), and $\omega\text{B97X-D}/6-311+G(2df,2p)$; the interaction region indicator analyses of *cis*-TS_{add1} and *trans*-TS_{add1}; rate constants of each elementary pathway involved in the reaction of *cis*-BU + OH and *trans*-BU + OH; PESs for the subsequent reactions of *cis*- and *trans*-isomers of OH adduct, involving the bimolecular reactions with O_2 , NO, and HO_2 , and the unimolecular reactions of isomerization and dissociation; geometries of all stationary points; mean formation rate of CH_3COOH from the *trans*-BU + OH reactions; parameter settings and simulation results of the AtChem2 model. The supplement related to this article is available online at <https://doi.org/10.5194/acp-25-16041-2025-supplement>.

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Competing interests. The contact author has declared that none of the authors has any competing interests.

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