

## ARTICLE

# Role of Hydrogen Migrations in Carbonyl Peroxy Radicals in the Atmosphere

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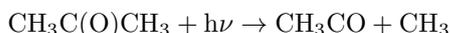
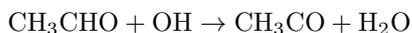
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Carbonyl peroxy radicals (RC(O)O<sub>2</sub>) are the ubiquitous radical intermediates in the atmospheric oxidation of volatile organic compounds. In this work, theoretical studies are carried out to explore the role of the unimolecular H-migration in the carbonyl peroxy radicals by using quantum chemistry and kinetics calculations. The results showed that H-migration could be significant in the atmosphere at least in CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)O<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>C(O)O<sub>2</sub> with rates of ~0.012 and ~0.58 s<sup>-1</sup> at 298 K. Subsequent reactions of CH<sub>3</sub>CHCH<sub>2</sub>C(O)OOH would lead to the products with multi-functional groups, which might affect the aerosol formation process; while (CH<sub>3</sub>)<sub>2</sub>CCH<sub>2</sub>C(O)OOH would transform to formaldehyde and acetone in a few steps. These processes would be important for the atmospheric modelling of volatile organic compounds under low-NO<sub>x</sub> conditions.

**Key words:** Carbonyl peroxy radical, H-migration, Atmospheric oxidation

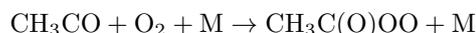
## I. INTRODUCTION

Carbonyl compounds are ubiquitous components in the atmosphere, such as aldehydes and ketones, which are key intermediates in the atmospheric oxidation of volatile organic compounds (VOCs) and play important roles in atmospheric chemistry [1, 2]. The ambient sources of carbonyl compounds include the primary emission from exhausts of motor vehicles, incomplete combustion of hydrocarbons, and particularly the secondary formation in the atmospheric oxidation of hydrocarbons. Photo-oxidation of carbonyl compounds produces intermediate carbonyl radicals (RCO) in the reactions of aldehydes with free radicals such as OH, NO<sub>3</sub>, Cl, and Br, *etc.* or in photolysis of carbonyl compounds:



In the reaction of CH<sub>3</sub>CHO, the formation of CH<sub>3</sub>CO radical accounts for ~97% of the branching ratio; while in the photolysis of acetone, the quantum yield of CH<sub>3</sub>CO is ~20% (the rest ~80% is deactivated by collision) at atmospheric pressure at 300 nm [3, 4]. In

the atmosphere, RCO radical would recombine with O<sub>2</sub> rapidly to form carbonyl peroxy radicals RC(O)O<sub>2</sub>:



The peroxy radical CH<sub>3</sub>C(O)O<sub>2</sub> is also an important intermediate in the low-temperature combustion of fossil fuels where the energetic RO<sub>2</sub>\* could undergo a consecutive unimolecular isomerization and decomposition as RO<sub>2</sub>→QOOH→product+OH [5, 6]. OH radical is recycled in this process.

The reaction of CH<sub>3</sub>CO with O<sub>2</sub> has been the subject of a few studies, covering a range of temperature, pressure, and bath gas [7–15]. These studies have focused on the formation of OH radical at reduced pressures (up to 500 mbar in helium) and elevated temperatures in the interest of fuel combustion. Generally, the OH production increases as temperature increases because of the high barrier for isomerization CH<sub>3</sub>C(O)O<sub>2</sub>→CH<sub>2</sub>C(O)OOH. At room temperatures, the yield of OH radical is well below 1% when extrapolated to the atmospheric pressures [11, 12, 16, 17]. Under the tropospheric conditions, CH<sub>3</sub>C(O)O<sub>2</sub>\* is stabilized by collision and would have significant bimolecular reactions with other trace radicals such as NO, NO<sub>2</sub>, and HO<sub>2</sub>/RO<sub>2</sub> with rate coefficients of ~2.0×10<sup>-11</sup>, ~1.1×10<sup>-11</sup>, and (2.1±0.4)×10<sup>-11</sup> cm<sup>3</sup>·molecule<sup>-1</sup>·s<sup>-1</sup> for NO, NO<sub>2</sub>, and HO<sub>2</sub>, respectively [18]. The reaction with NO<sub>2</sub> is particularly important because of the formation of peroxyacetyl nitrate (PAN), which is

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stable enough to transport from  $\text{NO}_x$ -emission sites to downwind areas, representing a transport of pollution from polluted urban regions to relatively clean suburban regions. Under the low- $\text{NO}_x$  conditions, reaction with  $\text{HO}_2$  radical becomes more important, resulting in the formation of  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  or  $\text{CH}_3\text{C}(\text{O})\text{O}+\text{OH}$ , of which the former would also lead to  $\text{OH}$  formation upon its photolysis in the atmosphere [19].

The unimolecular H-migration  $\text{RO}_2 \rightarrow \text{QOOH}$ , while being important in combustion, is usually ignored in the atmospheric oxidation of VOCs because of its endothermicity and high barriers, *e.g.*, for  $\text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow \text{CH}_2\text{C}(\text{O})\text{OOH}$ , the reaction energy ( $\Delta E_{0\text{K}}$ ) and barrier height ( $\Delta E_{0\text{K}}^\ddagger$ ) were predicted as 11.8 and 125.1 kJ/mol at G3X level [9]. However, the barrier heights for H-migration could be reduced for larger R-groups. In  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO}$ , the barrier height reduces to 113 kJ/mol for the similar H-migration to  $\text{CH}_3\text{CHC}(\text{O})\text{OOH}$  via a five-membered-ring transition state, and the barrier height of 99 kJ/mol for H-migration to  $\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OOH}$  via a six-membered-ring transition state is even lower [17]. Hou and Wang [20] found similar trend in  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO}$ . H-migration via six-membered-ring transition state has a lower barrier because the ring is less constrained. We would reasonably expect the even lower barriers for H-migrations via six-membered-ring transition state with more alkyl substitution in  $\text{RC}(\text{O})\text{O}_2$  radicals, allowing the H-migration to compete with their bimolecular reactions in the atmosphere. Recent laboratory studies have shown that the H-migration in the peroxy radicals could be important in the atmospheric autoxidation of a few important VOCs [21–26]. Field study also suggested the importance of autoxidation via H-migration in urban and suburban atmosphere [26], especially when the concentrations of  $\text{NO}/\text{HO}_2$  are low and the bimolecular reactions no longer dominate the fate of  $\text{RO}_2$  radicals. The elusive  $\text{QOOH}$  radical was also detected experimentally under low oxygen concentrations when the Q-group was resonance-stabilized in  $\text{QOOH}$  radical [27]. However, no information is available so far on the role of H-migration in  $\text{RC}(\text{O})\text{O}_2$  radicals in the atmosphere. A recent study showed that the hydrogen shift (H-shift) reactions could occur in hydroperoxy acylperoxy radicals as  $\text{HOOCH}_2\text{C}(\text{O})\text{OO} \rightarrow \text{OOCH}_2\text{C}(\text{O})\text{OOH}$ , which would be an important reaction pathway in competition with bimolecular reactions [28].

In this work, we carried out a systematic theoretical study on carbonyl peroxy chemistry using quantum chemistry and kinetics calculations. H-migrations in a few short-chain  $\text{RC}(\text{O})\text{O}_2$  radicals were investigated to examine the effect of alkyl substitution. An additional reaction pathway was suggested for  $\text{RC}(\text{O})\text{O}_2$  radicals in the atmosphere.

## II. THEORETICAL METHODS

All the molecular structures were optimized at the DFT-M06-2X/6-311++G(2df,2p) level, which was found to be adequate for thermochemical and kinetics study [29]. Each transition state has one imaginary frequency associating with the reaction coordinate. The optimized structures were submitted to single-point energy calculation using the complete basis set model chemistry with restricted (ROCBS-QB3) [30] and unrestricted (UCBS-QB3) [31] wave functions and explicitly correlated coupled-cluster theory at RHF-RCCSD(T)/F-12a/cc-pVDZ-F12 level (F12) [32, 33]. The calculations based on RHF-wavefunction in ROCBS-QB3 eliminate the empirical correction term due to spin contamination appearing in UCBS-QB3 calculations for open-shell species. This is important for the calculations of a few transition states. The quality of electron correlation of F12 here is better than that in standard CCSD(T)/cc-pVQZ [34]. The values of  $T_1$ -diagnostic in CCSD calculations were checked for the multi-reference nature of the wavefunction and for the validity of CCSD(T) calculations using single-reference wavefunctions [35]. The M06-2X and CBS calculations were carried out using the Gaussian 09 package [36] and F12 ones using Molpro 2015 package [37, 38].

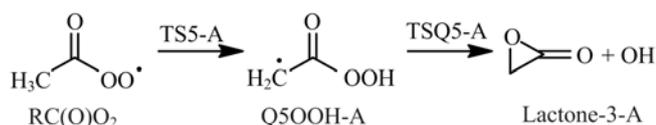
The reaction kinetics and pressure dependence of rate coefficients were obtained by calculations coupling the unimolecular rate theory and collisional energy transfer through the master equation (RRKM-ME) [39]. The calculations were carried out using the MESMER code [40], in which the RRKM theory was used for  $E$ -resolved microcanonical rate  $k(E)$  for processes with ‘well-defined’ transition states, and the inverse Laplace transform (ILT) method was used for the microcanonical rate  $k(E)$  for the barrierless dissociation of  $\text{RC}(\text{O})\text{O}_2$  to  $\text{RCO}+\text{O}_2$  with a fixed recombination rate coefficient [39, 41]. A high-pressure limit rate coefficient of  $6 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  was used for all  $\text{RCO}+\text{O}_2$  reactions. The single exponential-down model was used to approximate the collisional energy transfer. The collisional parameters of radicals were estimated by the method of Gilbert and Smith [42] and the tunneling correction factors were included to  $k(E)$  by the method of Miller [43]. Collisional parameters  $\sigma$  and  $\epsilon$  were: 2.55 Å and  $10.2 \text{ cm}^{-1}$  for helium, 3.9 Å and  $48.0 \text{ cm}^{-1}$  for  $\text{N}_2$ , 5.6 Å and  $500 \text{ cm}^{-1}$  for  $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2$  and  $\text{QOOHs}$ , 6.0 Å and  $530 \text{ cm}^{-1}$  for  $\text{C}_3\text{H}_7\text{C}(\text{O})\text{O}_2$  and  $\text{QOOHs}$ , and 6.33 Å and  $545 \text{ cm}^{-1}$  for  $\text{C}_4\text{H}_9\text{C}(\text{O})\text{O}_2$  and  $\text{QOOHs}$ . Internal rotations, when free in reactant and frozen in transition state, were treated as hindered rotors. Potential energy profiles for the internal rotations were fitted to truncated cosine and sine functions. As being implemented in MESMER, the energy levels of the internal rotations were obtained by numerically solving their Schrödinger equations using the Fourier Grid Hamiltonian (FGH) method [44], and were then used for the calculation of density/sum of state of the

species in RRKM calculations.

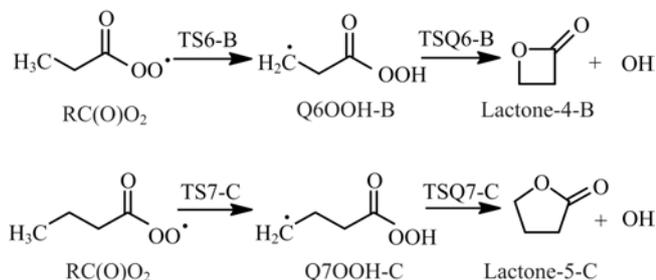
### III. RESULTS AND DISCUSSION

#### A. Potential energy surfaces and prompt OH formation

The reaction of  $\text{CH}_3\text{CO}$  and  $\text{O}_2$  has been studied extensively for the interest of fuel combustion. The reaction proceeds by addition and H-migration from  $\text{C}_\alpha$  through a five-membered-ring transition state (TS5-A) to form Q5OOH-A, and then decomposition through a transition state TSQ5-A to a lactone-3-A product (3 is the number of the lactone ring members) and an OH radical as:



Under low pressures and high temperatures,  $\text{RC(O)O}_2$  from the recombination contains high enough energy to isomerize and decompose promptly before being thermalized by collisions. For larger  $\text{RC(O)O}_2$ , the  $-\text{OO}$  group might also take an H-atom from the  $\text{C}_\beta/\text{C}_\gamma$ -position through a six/seven-membered-ring transition state (TS6/TS7), forming a radical denoted as Q6OOH/Q7OOH. The Q6OOH/Q7OOH would further isomerize and decompose to (substituted) propio-/butyro-lactone (lactone-4/-5) and an OH radical through transition states TSQ6/TSQ7,



The yields of prompt OH formation in reactions of  $\text{CH}_3\text{CO}$  and  $\text{CH}_3\text{CH}_2\text{CO}$  with  $\text{O}_2$  under reduced pressures (up to  $\sim 0.5$  bar in helium) and elevated temperatures have been measured in previous studies [7–16]; however, it was also found that the OH yields approached zero at room temperature and atmospheric pressure for both  $\text{CH}_3\text{CO}$  and  $\text{CH}_3\text{CH}_2\text{CO}$  radicals. No previous information is available for the OH formation in the reaction of other RCO radicals. Here we examined several RCO radicals using theoretical calculations. Table S1 (see supplementary materials) lists the relative energies of intermediates, transition states, and products at UCBS-QB3, ROCBS-QB3, and F12 levels for the reactions. Generally, UCBS-QB3 and F12 agreed within 4 kJ/mol, while ROCBS-QB3 predicted

lower barrier heights. In this study, we used energies at F12 level for discussion and for kinetics calculations if not otherwise stated, because the CCSD calculations in F12 usually have their values of  $T_1$ -diagnostic less than 0.025 for the transition states (Table S1 in supplementary materials). Conversely, the values of  $T_1$ -diagnostic in those of U/ROCBS-QB3 were usually higher than 0.03 for TSQ5 and TSQ6. FIG. 1 shows the potential energy surfaces for H-migrations and subsequent decomposition to lactone and OH radical for the reactions of  $\text{CH}_3\text{CO}$ ,  $\text{CH}_3\text{CH}_2\text{CO}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}$ , and  $(\text{CH}_3)_2\text{CHCH}_2\text{CO}$  with  $\text{O}_2$  at F12 level.

The alkyl substitution in R-group might affect the kinetics of reactions between RCO radicals and  $\text{O}_2$  by lowering the barrier heights for the intramolecular H-migrations. Upon successive methyl substitution, the barrier height for H-migrations in  $\text{RC(O)O}_2$  radicals decreases gradually, *e.g.*, from 122.2 kJ/mol via 108.7 kJ/mol to 93.2 kJ/mol for H-migration from  $\text{C}_\alpha$  in  $\text{CH}_3\text{C(O)O}_2$ ,  $\text{CH}_3\text{CH}_2\text{C(O)O}_2$ , and  $(\text{CH}_3)_2\text{CHC(O)O}_2$ , or from 99.6 kJ/mol via 84.6 kJ/mol to 73.4 kJ/mol for H-migration from  $\text{C}_\beta$  in  $\text{CH}_3\text{CH}_2\text{C(O)O}_2$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)O}_2$ , and  $(\text{CH}_3)_2\text{CHCH}_2\text{C(O)O}_2$ . For H-migrations from  $\text{C}_\alpha$  via  $\text{C}_\beta$  to  $\text{C}_\gamma$  through five-, six- and seven-membered-ring transition states, their barrier heights decrease gradually due to the decreased ring strain energy, *e.g.*, from 109.2 kJ/mol via 86.7 kJ/mol to 79.8 kJ/mol in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C(O)O}_2$  for H-abstractions from  $\text{C}_\alpha$ ,  $\text{C}_\beta$ , and  $\text{C}_\gamma$  which are all secondary carbons, even though the Q5OOH radicals are resonance stabilized (Table S1 in supplementary materials). For the decompositions  $\text{QnOOH} \rightarrow \text{lactone} + \text{OH}$ , alkyl substitution to the carbon radical center also reduces the barrier height (TSQn, relative to QnOOH), *e.g.*, from 95.4 kJ/mol via 89.7 kJ/mol to 82.5 kJ/mol in Q5OOH for Q5= $-\text{CH}_2\text{C(O)}$ ,  $-\text{CH}(\text{CH}_3)\text{C(O)}$ , and  $-\text{C}(\text{CH}_3)_2\text{C(O)}$ , and from 81.9 kJ/mol via 69.5 kJ/mol to 59.7 kJ/mol in Q6OOH for Q6= $-\text{CH}_2\text{CH}_2\text{C(O)}$ ,  $-\text{CH}(\text{CH}_3)\text{CH}_2\text{C(O)}$ , and  $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{C(O)}$ , respectively.

Prompt OH formation depends obviously on some parameters including reaction energies and barrier heights, the  $\langle \Delta E \rangle_{\text{Down}}$  in modeling of collisional energy transfer, and the internal rotations *etc.* FIG. S1 (see supplementary materials) shows the OH formation yield in the reaction of  $\text{CH}_3\text{CH}_2\text{CO}$  and  $\text{O}_2$  at 298 K and at low pressures using helium or  $\text{N}_2$  as buffer gas from RRKM-ME calculations with different values for  $\langle \Delta E \rangle_{\text{Down}}$ , along with the available experimental values. The predicted OH yields, in helium buffer with  $\langle \Delta E \rangle_{\text{Down}} = 100 \text{ cm}^{-1}$ , agree excellently with the experimental values by Zügner *et al.* [11] while being much lower than the values by Baeza-Romero *et al.* [16]. Increasing  $\langle \Delta E \rangle_{\text{Down}}$  to  $200 \text{ cm}^{-1}$  for helium buffer gas resulted in underestimation of OH yields. A  $\langle \Delta E \rangle_{\text{Down}}$  of  $100 \text{ cm}^{-1}$  for helium is likely an optimal value for reaction  $\text{C}_2\text{H}_5\text{CO} + \text{O}_2$  in fitting the OH yields. However,

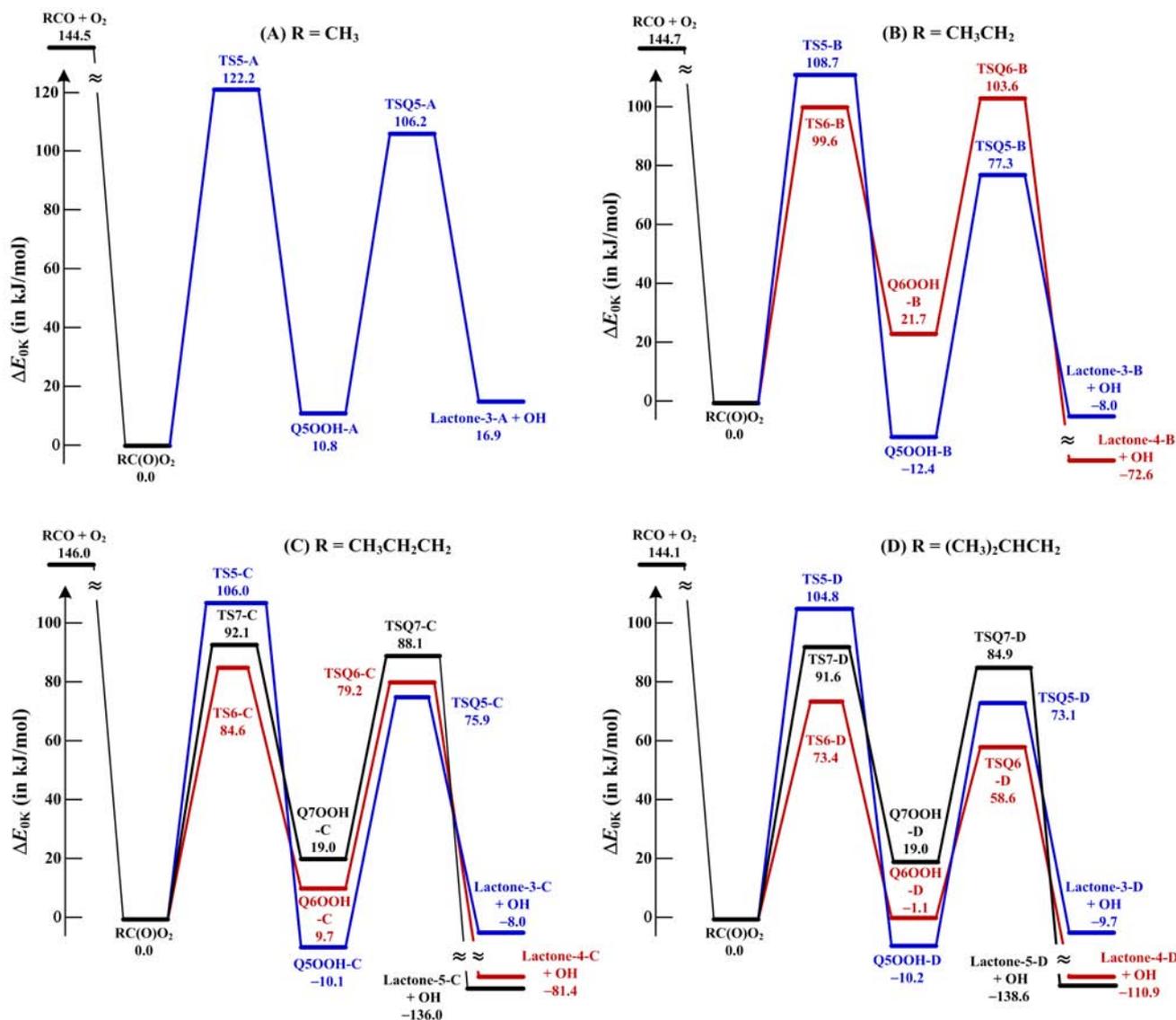


FIG. 1 Potential energy surfaces at RHF-RCCSD(T)-F12a/cc-pVDZ-F12 level for reactions of O<sub>2</sub> with RCO radical for CH<sub>3</sub>CO (A), CH<sub>3</sub>CH<sub>2</sub>CO (B), CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO (C), and (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CO (D).

obtaining an 'exact' value for  $\langle \Delta E \rangle_{\text{Down}}$  is difficult both experimentally and theoretically. Generally,  $\langle \Delta E \rangle_{\text{Down}}$  depends on energy, density of states, and temperature (average collisional energy), *etc.* Collision with larger colliders usually has larger energy transfer. For simplicity, we adopted  $\langle \Delta E \rangle_{\text{Down}}$  values of 250 cm<sup>-1</sup> for reactions of RCO + O<sub>2</sub> in N<sub>2</sub> buffer gas in current study. It is also necessary to treat the internal rotations as hindered rotors (see FIG. S2 in supplementary materials for potential energy profiles) because treating the internal rotations as harmonic oscillators would over-estimate the OH yield (FIG. S1 in supplementary materials). Treating the internal rotations as harmonic oscillator, Zügner *et al.* fitted their experimental results in helium buffer gas and obtained a  $\langle \Delta E \rangle_{\text{Down}}$  value of 20 cm<sup>-1</sup>, which is obviously too small.

FIG. 2 shows the typical yield profiles of intermediate radical RC(O)O<sub>2</sub> and the product channels via Q5OOH and Q6OOH at two different pressures for R = CH<sub>3</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>. With increased pressure, fraction of the collisionally stabilized CH<sub>3</sub>CH<sub>2</sub>C(O)O<sub>2</sub> increases drastically and OH formation yield decreases drastically. Note that OH formation via Q5OOH-B for R = CH<sub>3</sub>CH<sub>2</sub> is higher than that via Q6OOH-B because of the high barriers of TSQ6 for Q6OOH decomposition (FIG. 1(B)); while for R = (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>, OH formation via Q6OOH-D is virtually the sole channel. Clearly, the OH radical is formed promptly at both pressures, *e.g.*, within  $\sim 5 \times 10^{-6}$  s of the reaction time at 3.8 torr or within  $5 \times 10^{-7}$  s of the reaction time at 38 torr. The decay rates of CH<sub>3</sub>CH<sub>2</sub>C(O)O<sub>2</sub>\* or the equivalent rates of OH forma-

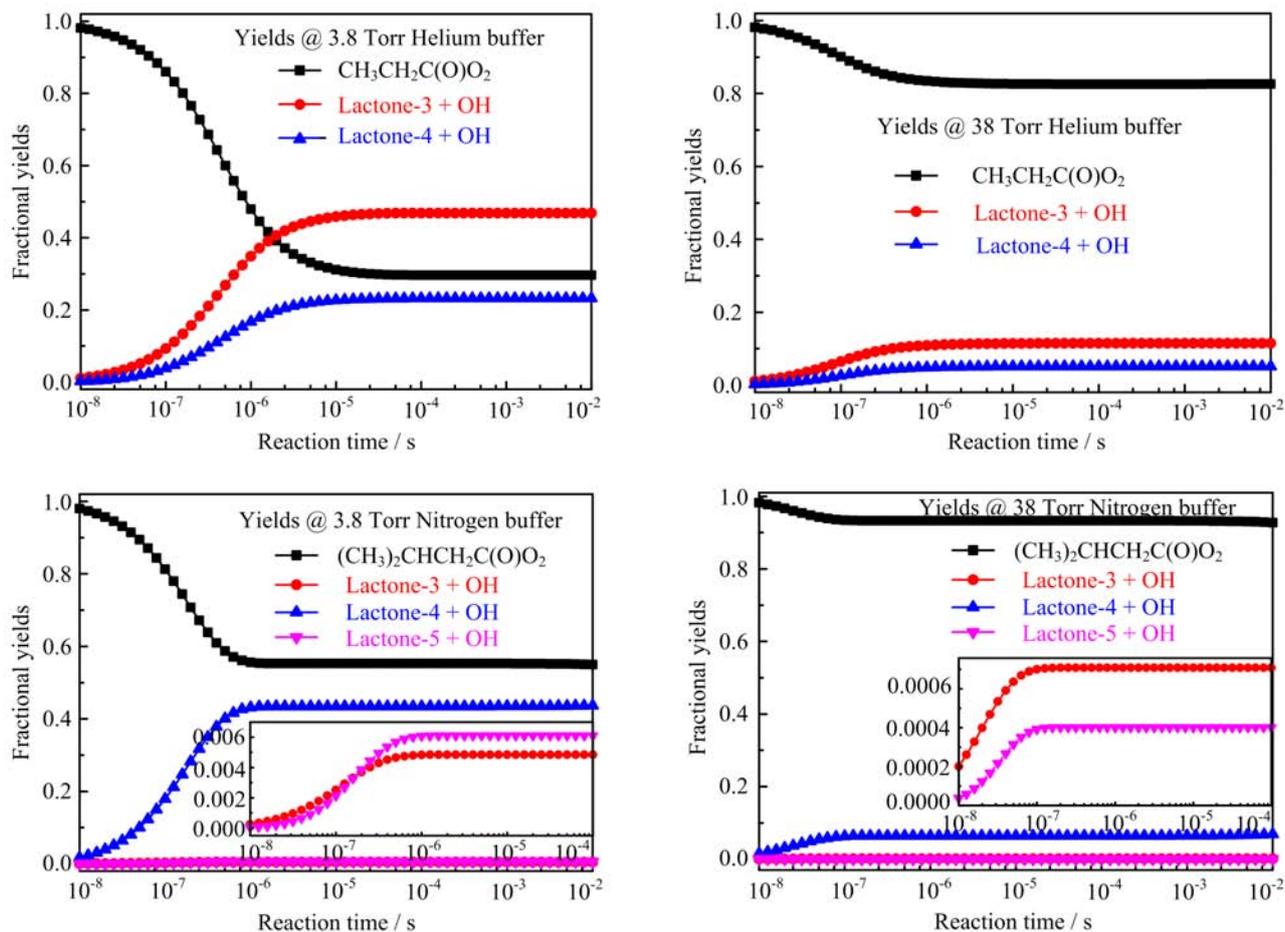


FIG. 2 Fractional yield profiles of intermediate radicals and end products from RRKM-ME calculations at 298 K and different pressures based on potential energy surfaces at RHF-RCCSD(T)-F12a/cc-pVDZ-F12 level.

tion from Q5OOH-B/Q6OOH-B\*, obtained by fitting its profiles within the first reaction time of  $10^{-5}$  s, are all higher than  $10^6$  s $^{-1}$  at both pressures. Therefore we could ignore the recombination of QOOH with O<sub>2</sub> in the RRKM-ME calculations when comparing the OH yields from theoretical prediction to the experimental measurements. In those experiments, with low [O<sub>2</sub>] (usually less than  $10^{15}$  molecule/cm<sup>3</sup>) and low pressures, the effective rates of recombination were usually less than  $10^4$  s $^{-1}$  in previous measurements if assuming a rate coefficient of  $<5 \times 10^{-12}$  cm<sup>3</sup>·molecule $^{-1}$ ·s $^{-1}$ . In the atmosphere, OH formation would become negligible due to the relatively high reaction pressure and high concentration of O<sub>2</sub>. High reaction pressure would result in the deactivation of RCO\* by collision, and high [O<sub>2</sub>] would rapidly deplete Q5OOH and Q6OOH by recombining to OOQ5OOH and OOQ6OOH.

Prompt OH formation is also expected in the reactions of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO and (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CO with O<sub>2</sub>. FIG. 3 shows the predicted OH yields from RRKM-ME calculations. The prompt OH formation within  $10^{-4}$  s of reaction time is significant at low pressures but decreases rapidly with the increased pressure to

about zero at atmospheric pressure and temperatures up to 343 K, *e.g.*,  $\sim 0.005$  only at 380 torr and 343 K. Values with N<sub>2</sub> buffer gas and of 250 cm $^{-1}$  are recommended for the scenarios in the troposphere. Prompt formation of QnOOH radical is also negligible ( $<0.01$  of fractional yield) at atmospheric pressure. Therefore, the reaction of RCO and O<sub>2</sub> in the atmosphere would form RC(O)O<sub>2</sub> as the sole first-generation intermediate radicals.

Prompt OH formation in reactions of RCO with O<sub>2</sub> is different from those in alkyl peroxy radicals, in which isomerizations from ROO to QOOH are much more endothermic and therefore highly reversible, resulting in negligible OH formation at room temperatures [5, 6]. Savee *et al.* [27] also directly observed resonance stabilized QOOH radical intermediate in oxidation of 1,3-cycloheptadiene, in which the resonance stabilized QOOH radical is formed from its corresponding RO<sub>2</sub> radical with a low barrier of  $\sim 50$  kJ/mol but is confined by a high barrier of  $\sim 104$  kJ/mol for its decomposition. In reactions of RCO+O<sub>2</sub>, all Q5OOH intermediates are also resonance stabilized but the kinetics is much different. The Q5OOH radicals could be un-

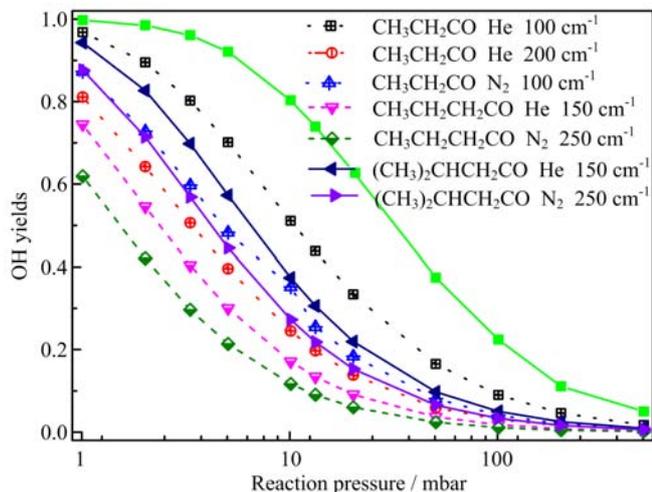
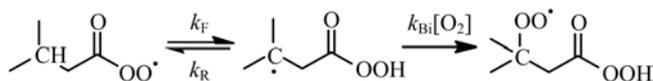


FIG. 3 Prompt formation of OH from RRKM-ME calculations based on electronic energies at RHF-RCCSD(T)-F12a/cc-pVDZ-F12 level in the reactions of  $O_2$  with RCO radical for  $CH_3CH_2CO$ ,  $CH_3CH_2CH_2CO$ , and  $(CH_3)_2CHCH_2CO$  using different  $\langle \Delta E \rangle_{Down}$  for collisional energy transfer.

likely captured due to the high barriers ( $>100$  kJ/mol) from  $RC(O)O_2$  to  $Q_5OOH$  and relatively low barriers ( $<95$  kJ/mol) for decompositions of  $Q_5OOH$  to 3-lactone+OH.

### B. Thermal H-migrations in $RC(O)O_2$ radicals

In the atmosphere, the prompt OH formation in  $RCO+O_2$  is quenched by collisional deactivation of  $RC(O)O_2^*$  radicals. However, the thermalized  $RC(O)O_2$  radicals might be able to undergo the unimolecular isomerizations shown above. Such H-migrations in  $RC(O)O_2$  radicals was usually ignored in the atmospheric oxidation of VOCs. However, with low barrier heights for substituted R-groups, the H-migration in  $RC(O)O_2$  could become fast enough to compete with or even dominate over their bimolecular reactions in the atmosphere. Instead of decomposing to lactone and OH radical, the  $QOOH$  radicals would recombine rapidly with  $O_2$  such as for  $(CH_3)_2CHCH_2C(O)O_2$ ,

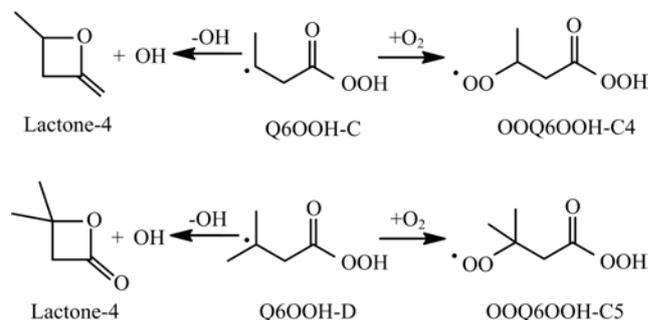


where the intermediate  $Q_6OOH$  radical is depleted by reversed H-migration and rapid recombination with  $O_2$ . Table I lists the reaction energies, barrier heights, and the rates for the forward processes. Under the atmospheric conditions, values of  $k_{Bi}[O_2]$ , at  $\sim 5 \times 10^7$  s $^{-1}$ , are orders of magnitude larger than those of  $k_F$  or  $k_R$  for all  $RC(O)O_2$  radicals exam-

ined here (Table I). Assuming steady-state for  $QOOH$ , the effective rate from  $RC(O)O_2$  to  $O_2QOOH$  is  $k_{eff} = k_F k_{Bi}[O_2] / (k_R + k_{Bi}[O_2]) \approx k_F$ .

We have carried out RRKM-ME calculations and obtained  $k_F$  values of  $1.38 \times 10^{-4}$ ,  $1.20 \times 10^{-2}$ , and  $0.58$  s $^{-1}$  for H-migrations via six-membered-ring transition state in  $CH_3CH_2C(O)O_2$ ,  $CH_3CH_2CH_2C(O)O_2$ , and  $(CH_3)_2CHCH_2C(O)O_2$ , respectively, at 298 K and atmospheric pressure. The overall tunneling correction factors for the thermal distribution of  $RC(O)O_2$  radicals were 131, 75, and 33, respectively. The rates from  $CH_3CH_2CH_2C(O)O_2$  and  $(CH_3)_2CHCH_2C(O)O_2$  to their  $Q_6OOH$ s are comparable to the effective bimolecular rates from  $10^{-2}$  s $^{-1}$  to  $10$  s $^{-1}$  in the atmosphere with NO in the range of 40 pptv to 40 ppbv if assuming rate coefficients of  $10^{-11}$  cm $^3$ ·molecule $^{-1}$ ·s $^{-1}$  for reactions between  $RC(O)O_2$  and NO [18]. Isomerizations via five- or seven-membered-ring transition states are comparatively too slow for all  $RC(O)O_2$  radicals. Obviously, the H-migration would be faster and therefore more important with the increase of reaction temperature. Table I lists the temperature dependences for several H-migration processes. In  $CH_3CH_2C(O)O_2$ , the transition state to  $CH_3CHC(O)OOH$  is tighter than the six-membered-ring one to  $CH_2CH_2C(O)OOH$ , resulting a larger pre-exponential  $A$  factor but with a higher barrier.

The  $Q_6OOH$  radicals formed from H-migration in  $RC(O)O_2$  would either decompose as discussed above or recombine with  $O_2$  as:



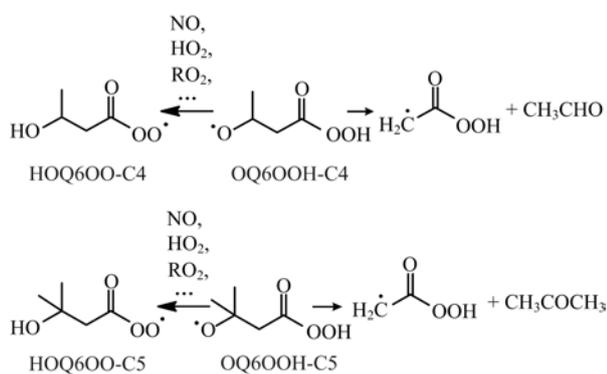
For both  $Q_6OOH$  radicals, the decomposition, at rate of 7.8 s $^{-1}$  or 280 s $^{-1}$  at 298 K (Table I), is too slow to compete with their recombination with the atmospheric  $O_2$ . Schemes 1 and 2 show further transformation of peroxy radicals  $OOQ_6OOH$  formed from recombination with  $O_2$ . Unimolecular isomerization in the two  $OOQ_6OOH$  radicals should be negligible due to their high barriers, *e.g.*,  $\sim 139$  kJ/mol for H-migration of  $OOCH_2CH_2C(O)OOH \rightarrow HOCH_2CH_2C(O)O_2$  at ROCBS-QB3 level. Therefore, they would react with other atmospheric trace radicals such as NO,  $HO_2$ , and  $RO_2$  *etc.* Reaction of  $OOQ_6OOH$  with NO/ $HO_2$  would result in formation of nitrates, hydroperoxides, and alkoxy radical  $OQ_6OOH+OH$  [18]. The alkoxy radical  $OQ_6OOH$  would decompose or isomerize rapidly as:

TABLE I Reaction energies and barrier heights ( $\Delta E_{0K}$  and  $\Delta E_{0K}^\ddagger$ , in kJ/mol) at F12 level, the rates at 298 K ( $k_{F,298K}$ , in  $s^{-1}$ ) and temperature dependent rate coefficients of unimolecular reactions<sup>a</sup>.

Reactions	$\Delta E_{0K}$	$\Delta E_{0K}^\ddagger$	$k_{F,298K}$
$CH_3CH_2C(O)O_2 \rightarrow CH_3CHC(O)OOH$	-12.4	108.7	$1.38 \times 10^{-5}$
			$\ln k_F = 36.542 - 21.466 \times 10^3/T + 2.1605 \times 10^6/T^2$
$CH_3CH_2C(O)O_2 \rightarrow CH_2CH_2C(O)OOH$	21.7	99.6	$1.56 \times 10^{-4}$
			$\ln k_F = 28.033 - 15.523 \times 10^3/T + 1.3596 \times 10^6/T^2$
$CH_3CH_2C(O)O_2 \rightarrow \text{lactone-4} + OH$	-94.3	81.9	$7.06 \times 10^{-4}$
$CH_3CH_2CH_2C(O)O_2 \rightarrow CH_3CH_2CHC(O)OOH$	-10.1	106.0	$1.10 \times 10^{-5}$
$CH_3CH_2CH_2C(O)O_2 \rightarrow CH_3CHCH_2C(O)OOH$	9.7	84.6	$1.20 \times 10^{-2}$
			$\ln k_F = 27.839 - 14.059 \times 10^3/T + 1.3332 \times 10^6/T^2$
$CH_3CH_2CH_2C(O)O_2 \rightarrow CH_2CH_2CH_2C(O)OOH$	19.0	92.1	$9.54 \times 10^{-4}$
			$\ln k_F = 24.289 - 13.242 \times 10^3/T + 2.4289 \times 10^6/T^2$
$CH_3CHCH_2C(O)OOH \rightarrow \text{lactone-4} + OH$		69.5	7.84
$CH_3CH(O)CH_2C(O)OOH \rightarrow CH_3CHO + CH_2C(O)OOH^a$		50.0	$1.25 \times 10^4$
$CH_3CH(O)CH_2C(O)OOH \rightarrow CH_3 + HC(O)CH_2C(O)OOH^a$		61.1	$1.73 \times 10^2$
$CH_3CH(O)CH_2C(O)OOH \rightarrow CH_3CH(OH)CH_2C(O)OO^a$		52.7	$1.15 \times 10^6$
			$\ln k_F = 23.2592 - 4.2718 \times 10^3/T + 0.4475 \times 10^6/T^2$
$CH_3CH(OH)CH_2C(O)OO \rightarrow CH_3C(OH)CH_2C(O)OOH$		77.7	$\sim 0.90$
$(CH_3)_2CHCH_2C(O)OO \rightarrow (CH_3)_2CHCHC(O)OOH$	-10.2	104.8	$1.65 \times 10^{-5}$
$(CH_3)_2CHCH_2C(O)OO \rightarrow (CH_3)_2CCH_2C(O)OOH$	-1.1	73.4	0.58
			$\ln k_F = 30.3451 - 13.7169 \times 10^3/T + 1.3448 \times 10^6/T^2$
$(CH_3)_2CHCH_2C(O)OO \rightarrow CH_2CH(CH_3)CH_2C(O)OOH$	18.0	91.6	$1.18 \times 10^{-3}$
$(CH_3)_2CCH_2C(O)OOH \rightarrow \text{lactone-4} + OH$	-109.7	59.7	$2.80 \times 10^2$
			$\ln k_F = 32.3211 - 9.7906 \times 10^3/T + 0.5471 \times 10^6/T^2$
$(CH_3)_2C(O)CH_2C(O)OOH \rightarrow CH_3COCH_3 + CH_2C(O)OOH^b$		45.46	$5.97 \times 10^4$
$(CH_3)_2C(O)CH_2C(O)OOH \rightarrow CH_3 + CH_3C(O)CH_2C(O)OOH^b$		58.51	$4.59 \times 10^2$
$(CH_3)_2C(O)CH_2C(O)OOH \rightarrow (CH_3)_2C(OH)CH_2C(O)OO^b$		53.16	$1.15 \times 10^6$

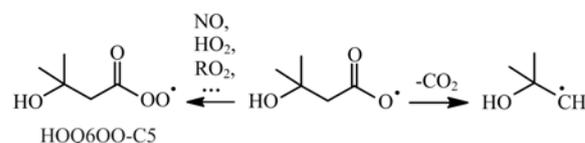
<sup>a</sup> All energies are at RHF-RCCSD(T)-F12a/cc-pVDZ-F12//M06-2X/6-311++G(2df,2p) level.

<sup>b</sup> Energies are at ROCBS-QB3 level with M06-2X/6-311++G(2df,2p) geometries.

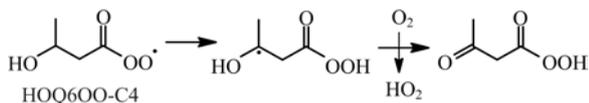


The OQ6OOH radical could also react with  $O_2$  at effective rates of  $0.5 \times 10^4 - 5 \times 10^4 s^{-1}$  with rate coefficients of  $10^{-15} - 10^{-14} cm^3 \cdot molecules^{-1} \cdot s^{-1}$  [45]. We have identified the transition states for the H-migration and C-C bond scission of OQ6OOH-C4 and OQ6OOH-C5 at M06-2X level, obtained their barrier heights at ROCBS-QB3 level, and predicted their rates using RRKM-ME calculations (Table I). For both OQ6OOH radicals,

the barriers for the H-migrations are slightly higher than those for the C-C bond scissions; however, the H-migrations are greatly enhanced by tunneling effect with imaginary vibrational frequency of  $\sim 2200i cm^{-1}$  (M06-2X). Then, the main fate of OQ6OOH radical becomes the formation of HOQ6OO at rates of  $\sim 10^6 s^{-1}$  at 298 K. In the atmosphere, radical HOQ6OO-C5 would again react with NO,  $HO_2$ , and other  $RO_2$  radicals as:

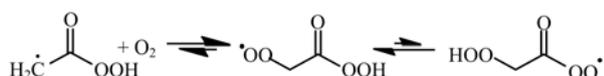


Reaction with NO would also form organic nitrates, and reactions with  $HO_2/R'O_2$  would also form  $HOC(CH_3)_2CH_2C(O)OOH$  and  $HOC(CH_3)_2CH_2C(O)OH$  [18]. On the other hand, the HOQ6OO-C4 might undergo another intramolecular H-migration as:



A barrier height of 77.7 kJ/mol was obtained at F12 level, resulting in a rate of  $\sim 0.9 \text{ s}^{-1}$  at 298 K. The process is expected to dominate under the atmospheric conditions when the slower H-migration in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}_2$ , with a rate of  $0.012 \text{ s}^{-1}$  only, is significant.

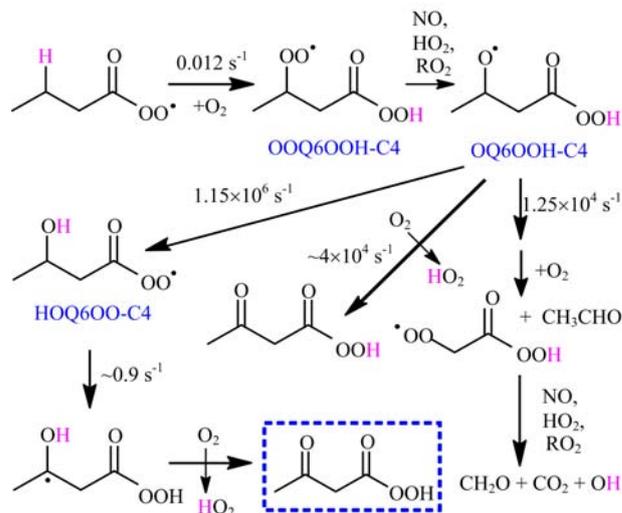
The  $\text{CH}_2\text{C}(\text{O})\text{O}_2\text{H}$  radical, as a minor product from the decomposition of  $\text{OQ6OOH-C4/C5}$ , would recombine with  $\text{O}_2$  to  $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$  in the atmosphere (see Schemes 1 and 2 for details):



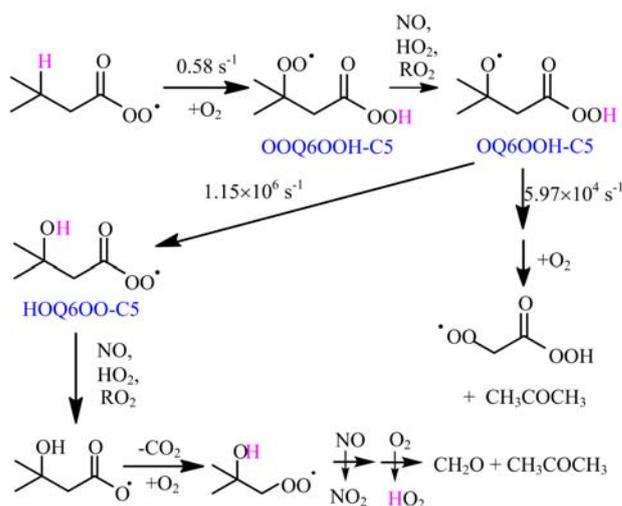
The  $\text{O}_2$  addition to  $\text{CH}_2\text{C}(\text{O})\text{OOH}$  is exothermic with  $\Delta E_{0\text{K}}$  of  $-90.3 \text{ kJ/mol}$  at F12 level ( $\Delta G_{298\text{K}} = -51.9 \text{ kJ/mol}$ ). In the atmosphere, with  $[\text{O}_2]$  of  $\sim 5 \times 10^{18} \text{ molecules/cm}^3$  and a rate coefficient of  $\sim 1.9 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  as for  $\text{O}_2$  addition to  $\text{CH}_2\text{CHO}$  or of  $\sim 1.2 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  as for  $\text{O}_2$  addition to  $\text{CH}_2\text{C}(\text{O})\text{CH}_3$  [46, 47], the back-decomposition of  $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$  radical could be estimated as  $\sim 7.6 \times 10^{-4}$  or  $\sim 4.8 \times 10^{-3} \text{ s}^{-1}$  at 298 K from the equilibrium constant. Further intramolecular H-migration in  $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$ , according to Knap and Jørgensen, is endothermic and highly reversible ( $k_{\text{R}} \approx 5 \times 10^3 \text{ s}^{-1}$ ) and therefore negligibly slow [28]. Thus in the atmosphere,  $\text{CH}_2\text{C}(\text{O})\text{OOH}$  would be transformed to  $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$ , which would react with  $\text{NO}/\text{HO}_2$ , forming  $\text{OCH}_2\text{C}(\text{O})\text{OOH}$ , and then be converted to  $\text{HC}(\text{O})\text{C}(\text{O})\text{OOH}$  by reacting with  $\text{O}_2$ . Decomposition of  $\text{OCH}_2\text{C}(\text{O})\text{OOH}$  to  $\text{CH}_2\text{O} + \text{CO}_2 + \text{OH}$ , with a barrier of 65 kJ/mol (ROCBS-QB3) and a rate of  $\sim 10^2 \text{ s}^{-1}$  at 298 K, is negligible compared to its reaction with  $\text{O}_2$ .

#### IV. CONCLUSION

Theoretical studies are carried out here to explore the role of the unimolecular H-migration in the carbonyl peroxy radicals by using quantum chemistry and RRKM-ME calculations. While prompt OH formation with high yields is found in the reactions of RCO radicals with  $\text{O}_2$  under the conditions of reduced pressures ( $< 0.5 \text{ bar}$ ), low  $\text{O}_2$  concentrations, and elevated temperatures, it is negligible under atmospheric conditions. Reaction of RCO and  $\text{O}_2$  would form  $\text{RC}(\text{O})\text{O}_2$  radical in the atmosphere. In the atmosphere, H-migration could be significant at least in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}_2$  and  $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{O})\text{O}_2$ , *e.g.*, with rates of  $\sim 0.012$  and  $\sim 0.58 \text{ s}^{-1}$  at 298 K and atmospheric pressure. After the H-migration, subsequent re-



Scheme 1 New pathways of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}_2$  radical after H-migration.



Scheme 2 New pathways of  $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{O})\text{O}_2$  radical after H-migration.

actions of  $\text{Q6OOH-C4}$  would lead to the products with multi-functional groups, which might affect the aerosol formation process; while  $\text{Q6OOH-C5}$  would transform to formaldehyde, acetone, and  $\text{HO}_2$  radical in a few steps. Schemes 1 and 2 summarize the predicted new pathways of the two radicals after H-migration. This additional degradation pathway of  $\text{RC}(\text{O})\text{O}_2$  radicals would affect the formation of carbonyl peroxy nitrates ( $\text{RC}(\text{O})\text{OONO}_2$ ) and ozone. Adding such processes to the atmospheric oxidation mechanism of VOCs might be necessary for properly modeling the fate and effect of VOCs in the atmosphere.

Note that we have used the reaction energies and barrier heights at RHF-RCCSD(T)-F12a/cc-pVDZ-F12 (F12) level for the calculations of rates or rate coeffi-

cients for most cases. Comparing the three methods for electronic energies (Table S1 in supplementary materials), we can see that the F12 method usually predicts higher energy barriers than U/ROCBS-QB3. Therefore, the role of H-migration in RC(O)O<sub>2</sub> radicals would be more pronounced if using energies and barrier heights at U/ROCBS-QB3 levels. Nevertheless, our calculations here suggested the role of H-migrations in the atmospheric fate of long-chain and substituted carbonyl peroxy radicals.

**Supplementary materials:** Table containing relative energies in reactions of RCO and O<sub>2</sub> at various levels of theory (Table S1), and figures for fractional OH yields in reaction of CH<sub>3</sub>CH<sub>2</sub>CO and O<sub>2</sub> from RRKM-ME calculations (FIG. S1) and potential energy profiles for internal rotations in RC(O)O<sub>2</sub> radicals (FIG. S2) are given.

## V. ACKNOWLEDGMENTS

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