Supplement of

Fragmentation inside PTR-based mass spectrometers limits the detection of ROOR and ROOH peroxides

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Figure S1. Correlation plot of $C_{10}H_{17}^+$ and the secondary ion cluster $C_{20}H_{33}^+$. 

Figure S2. Time series of kaurene ($C_{20}H_{32}$) and its oxidation products $C_{19}H_{30}O$ and $C_{20}H_{32}O_3$ during the kaurene oxidation experiment.

S1 MESMER simulations.

Once the PES of each model ROOR and ROOH system was obtained, the time-dependent species distribution profile was estimated with MESMER (Master Equation Solver for Multi-Energy Well Reactions) version 6.0 (Glowacki et al., 2012). Together with zero-point corrected energies, vibrational frequencies and rotational constants for each stationary point were used as input. Since the investigated reactions happen in low pressures, and are preceded by an exothermic protonation step ($R_p$), kinetic and collisional relaxation time scales may be of similar magnitude. In such cases, Rice-Ramsperger-Kassel-Marcus (RRKM) theory offers a more appropriate treatment, and was accordingly used to model all isomerization steps in the master equation. The imaginary frequency of each transition state (mode associated with the reaction motion), was provided for calculation of the
Eckart tunnelling factor (Eckart, 1930).\textsuperscript{13} Irreversible dissociation steps were assumed to be barrierless, and were treated with the reverse Inverse Laplace Transformation (ILT) method. The Arrhenius pre-exponential factor was estimated according to a parameterized procedure for obtaining ion-dipole collision rates reported by Su and Chesnavich (1982), giving values in the range of 1–4 x 10\textsuperscript{-9} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. A modified Arrhenius parameter (n°) value of 0.01 was used. The protonation step could not be modelled explicitly, because the treatment of bimolecular exchange reactions in MESMER requires a transition state, which was not found. Thus, the initial charged species (RH\textsuperscript{+}) was modelled as having emerged from a barrierless dissociation reaction, \(A(E_{\text{ex}}) \rightarrow RH^+ + H_2O\), where \(E_{\text{ex}}\) is the excess energy in reactant \(A\), which was assumed to be equal to the zero-point corrected energy of reaction \(R1p\) (\(\Delta E_{zp}\)). This could be done by using the Prior method for the initial distribution of states, where the \(E_{\text{ex}}\) is shared between the dissociation products according to a probability distribution. The probability that \(RH^+\) emerges from the reaction with energy \(E\) is given as described in MESMER’s manual:

\[
p_{ROOH}^+(E, E_{\text{ex}}) = \frac{\rho_{ROOH}^+(E) \cdot [\rho_t \cdot \rho_{H_2O}](E_{\text{ex}} - E)}{[\rho_{ROOH}^+ \cdot \rho_t \cdot \rho_{H_2O}](E_{\text{ex}})}
\]

Where \(\rho_{ROOH}^+(E)\) and \(\rho_{H_2O}\) are the rovibrational density states of \(RH^+\) and \(H_2O\) respectively, and \(\rho_t\) is the relative translational density of states of \(RH^+\) and \(H_2O\). The expression \(\int x \ast y(E)\) is a convolution:

\[
[x \ast y](E) = \int_{0}^{E} x(E - \tau)y(\tau)d\tau
\]

The exponential down model was employed for collisional energy transfer, and the Lennard-Jones potential for estimating collisional frequency. The employed parameters were obtained by fitting MESMER’s simulated collision frequency and collisional relaxation rate to the results from Molecular Dynamics calculations, as described in the next section. The values used for the smaller systems (< 39 atoms) were: \(\langle \Delta E_{\text{down}} \rangle = 145\) cm\textsuperscript{-1}; \(\varepsilon_{LJ} = 200\) K; \(\sigma_{LJ} = 10\) Å. For the larger systems the values \(\langle \Delta E_{\text{down}} \rangle = 185\) cm\textsuperscript{-1}; \(\varepsilon_{LJ} = 550\) K; \(\sigma_{LJ} = 11\) Å were used. \(N_2\) was assigned as bath gas, with Lennard-Jones parameter values \(\varepsilon_{LJ} = 91.85\) K and \(\sigma_{LJ} = 3.919\) Å. Energy grains were set to span values up to 20 k\(h\)T above the highest stationary point and their size was set to 30 cm\textsuperscript{-1}.

\section*{S2 Estimation of thermalization rates with Molecular Dynamics.}

\subsection*{S2.1 Introduction}

During many atmospheric reactions of interest, the product state has a lower total energy than the reactant state. As a result, the initial temperature of the product(s) will be significantly higher than the reactant(s). In the atmosphere, collisions with atmospheric gases (\(N_2, O_2\), etc.) will thermalize the products, bringing the temperature into equilibrium. However, quantifying how this process works is not trivial. Models for the energy transfer processes involved in molecular collisions have certainly been developed (Michael et al., 2002; Miller and Klippenstein, 2006; Pilling and Robertson, 2003; Senosiain et al., 2006), and are included in master equation solving software such as MESMER (Glowacki et al., 2012) used to describe complex gas-phase reaction kinetics. However, these models may be somewhat limited; in particular, they have been developed for and demonstrated to work on rather small molecules and it is unknown how well they may be applied to describe thermalization in larger gas-phase molecules. In this work, we use classical molecular dynamics simulations with empirical force fields to model the thermalization of some of the studied ROOR’ compounds as they undergo collisions in a nitrogen atmosphere. Then, we demonstrate how to use our results to improve the stochastic models for thermalization used in MESMER. In particular, it is apparent that the models used by MESMER significantly
underestimate the collision rate between nitrogen gas and a large gas-phase molecule, and therefore when using the default parameters the rate of thermalization is in turn underestimated.

### S2.2 Potential Models

We used LAMMPS (Plimpton, 1995) to run classical molecular dynamics simulations. OPLS-AA (Jorgensen et al., 1996; Jorgensen and Tirado-Rives, 2005; Kaminski et al., 2001) served as a baseline forcefield for describing a large atmospheric molecule. We used the LigParGen online server (Dodda et al., 2017) to automatically generate a LAMMPS data file for each molecule. In this work, we focus in particular on some molecules which contain peroxide bonds (ROOR’). Since peroxides are not specifically included in the OPLS-AA parameter set we incorporate Lennard-Jones potential parameters, partial charges, bond, and angular terms derived elsewhere for simulations of peroxide and peroxyl groups (Garrec et al., 2014). To model nitrogen molecules, we use a simple model for diatomics, consisting of two Lennard-Jones atoms linked by a rigid bond. No electrostatic interactions are included. The original source for the model is Ref. 12 (Cheung and Powles, 1975). However, we copied the parameters from a later paper (Lee and Kim, 2014), which mistakenly switched the value of \( \varepsilon \) between \( \text{O}_2 \) and \( \text{N}_2 \). As a result, in the model we adopted we had \( \sigma_{\text{N}} = 3.31 \, \text{Å} \), \( \varepsilon_{\text{N}}/k_B = 61.6 \, \text{K} \), with a bond length of 1.1 Å. We did test simulations using the correct value of \( \varepsilon_{\text{N}}/k_B = 37.3 \, \text{K} \) and found no significant difference in the results. Since the energetics of dilute gases are dominated by kinetic energy, it is not surprising that small differences in the potential model would not have a noticeable effect on our findings. It is also worth noting that both the OPLS-AA parameters, and the nitrogen parameters, were derived for simulations of molecules in aqueous environments and liquid nitrogen, respectively, and so it is worth considering whether they can be applied to a gas phase simulation. Recent work has shown that simulations of protein ions in the gas phase are more or less accurate using parameter sets designed for solvated biomolecules, and rather large reductions in the partial charges are needed to cause appreciable effects (Lee et al., 2019). As far as the nitrogen model is concerned, it has been used previously for simulations of gas phase nitrogen and has been shown to perform well (Lee and Kim, 2014; Wang et al., 2020).

### S2.3 Simulation methodology

Our initial simulation box consisted of one analyte molecule in the center of the box, surrounded by randomly placed nitrogen molecules. The cubic box length \( L = 400 \, \text{Å} \), and 1540 \( \text{N}_2 \) molecules were added to give a pressure \( P = 1 \) atm. Other simulations were done with 385 gas molecules, \( P = 0.25 \) atm. We consistently used a timestep of 0.5 fs throughout the work. The SHAKE algorithm was used to hold the \( \text{N}_2 \) bond length constant, as well as any \( \text{OH} \) bonds in the analyte molecules. Systems were equilibrated in the NVT ensemble for 5 ns using two different Nose-Hoover thermostats to separately maintain the temperature of the analyte molecule and the \( \text{N}_2 \) gas. The initial temperature of the analyte \( T_{\text{molec}} \) was set to 800 K, with the nitrogen temperature \( T_{\text{gas}} \) set to 300 K. After equilibration, the thermostats were removed and the remainder of the simulation proceeded using NVE integration. As the simulation proceeded collisions between gas and analyte served to bring the temperature of the gas and the analyte closer together. Simulations were run long enough so that the overall temperature became uniform, typically 25 to 50 ns.

### S2.4 Results and discussion

In Figure S3 we plot \( \Delta T(t) = T_{\text{molec}} - T_{\text{gas}} \) as a function of the simulation time. There is considerable variation in individual simulation runs, so we average over several simulations to reduce the statistical noise.
Figure S3: Temperature difference between analyte molecule and surrounding gas for (EtOOEt)H⁺ (top left), and isomer M3 of the decomposition mechanism of EtOOEt (top right) and ROOR derived from OH oxidation of cyclohexene (bottom). Individual simulation runs are shown in thin black lines, with the average over all simulations in red. The blue line is a fit to an exponential function $\Delta T(t) = Ae^{-Bt}$, with the numerical values of the fit parameters given in the legend.

We find that a single exponential function of the form:

(S1) $\Delta T(t) = Ae^{-Bt}$

fits the temperature difference well in all cases we have studied. The inverse of the constant B in Equation S1 can be interpreted as a characteristic time. For the systems we have studied, and with a gas pressure of 1 atm, this time is on the order of 1 to 10 ns; however, there is considerable variation for different molecules. In the examples we focus on here, we note that the cyclohexene derived ROOR⁺ takes longer to reach the same temperature as the gas compared to the two ethyl peroxide dimers (ca. 5.5 ns vs. 4 ns). By post-processing the trajectories, we obtained more information about the collision events. We define a collision starting if either a nitrogen atom gets closer than 4 Å to one of the atoms in the analyte molecule, and ending when both nitrogen atoms are further away than
4 Å from all of the atoms in the analyte. One complication is the possibility of multiple gas molecules colliding simultaneously; to mitigate against this rare occurrence we ran more simulations with a reduced gas pressure of 0.25 atm. This analysis allows us to compute the gas collision frequency \( f_{\text{coll}} \).

Figure S4: Histogram of the change in the kinetic energy of the colliding gas molecule \( \Delta KE_{\text{coll}} \) during 9 independent simulations with the \((\text{EtOOEt})\text{H}^+\) molecule. The density of N\(_2\) is 0.25 atm.

Table S1: Summary table. \( 1/B \) is the characteristic time decay constant in Equation 1 from the average of several simulations with 1 atm gas pressure. \( f_{\text{coll}} \) and \( \langle KE_{\text{coll}} \rangle \) are the average gas collision rate and kinetic energy transfer from several simulations with 0.25 atm, respectively.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>( 1/B ) (ns)</th>
<th>( f_{\text{coll}} ) (ns(^{-1}))</th>
<th>( \langle KE_{\text{coll}} \rangle ) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 (EtOOEt)</td>
<td>4.0</td>
<td>5.98</td>
<td>0.715</td>
</tr>
<tr>
<td>M3 (EtOOEt)</td>
<td>4.0</td>
<td>6.19</td>
<td>0.519</td>
</tr>
<tr>
<td>M3 (Cyclohexene + OH)</td>
<td>5.6</td>
<td>7.85</td>
<td>0.996</td>
</tr>
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</table>

Another quantity of interest is the energy transfer per collision. We compute the kinetic energy of the gas molecule as an average, using velocities spanning from 3.0 ps to 2.5 ps before/after each collision event. Then we can compute the change in kinetic energy \( \Delta KE_{\text{coll}} = KE_{\text{after}} - KE_{\text{before}} \). There is a large variation in the \( \Delta KE_{\text{coll}} \) measured in each collision. In Figure S4 we show a histogram of the \( \Delta KE_{\text{coll}} \) for all collisions during a series of 9 simulation runs. We see that the probability of collisions which lower the KE of the colliding gas molecule is nearly the same as those which raise the KE. The overall temperature equilibration must therefore arise from the relatively small asymmetry in this histogram, which we see from Figure S4 becomes more symmetric as the simulation proceeds and the temperatures of the gas and analyte become closer. In Table S1 we summarize the values of the temperature decay time constant \( 1/B \), the gas collision frequency \( f_{\text{coll}} \) and the average kinetic energy change per collision \( \langle KE_{\text{coll}} \rangle \) for three different molecules of interest. These quantities will be used in comparison with the MESMER stochastic models to improve the calculations of reaction rates in MESMER.

**S2.4 Fitting MESMER parameters**
Table S2: Selected Lennard-Jones parameters and resulting collision frequency $f_{\text{coll}}$ and fitted $\Delta E_{\text{down}}$ value for MESMER simulations at 1 atm.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>$f_{\text{coll}}$ (ns$^{-1}$)</th>
<th>$\Delta E_{\text{down}}$ (kcal.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 (EtOOEt)</td>
<td>200</td>
<td>10</td>
<td>23.2</td>
<td>0.415</td>
</tr>
<tr>
<td>M3 (Cyclohexene + OH)</td>
<td>550</td>
<td>11</td>
<td>30.0</td>
<td>0.529</td>
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</table>

A series of MESMER simulations were done with EtOOEtH$^+$ and the isomer M3 of the ROOR derived from cyclohexene + OH oxidation, varying Lennard-Jones parameters $\varepsilon$ and $\sigma$ in order to find the combination that yields a value of $f_{\text{coll}}$ at 1 atm that agrees with results from MD calculations. For the smaller molecule, these values were $\varepsilon/k_B = 200$ K and $\sigma = 10$ Å, while for the larger species the selected values were $\varepsilon/k_B = 550$ K and $\sigma = 11$ Å (Table S2). The resulting $f_{\text{coll}}$ values at 1 atm were 23.2 ns$^{-1}$ and 30.0 ns$^{-1}$ for M1 (EtOOEt) and M3 (Cyclohexene + OH) respectively, being very close to the MD values, assuming that the collision frequency is linearly dependent on pressure. The selected parameter values, in special $\sigma$, are much higher than those offered by MESMER as default ($\varepsilon/k_B = 50$ K and $\sigma = 5$ Å) and may represent an unrealistic description of the Lennard-Jones potential well. However, the high values were needed to yield a $f_{\text{coll}}$ that agrees with the MD results, and do not interfere with any other function in MESMER’s model. Having fixed those parameters, another series of MESMER simulations were done where the investigated species starts at a temperature of 800 K, varying the exponential-down model parameter $\langle \Delta E_{\text{down}} \rangle$. The obtained time-dependent internal energy profiles were then compared to the results from MD calculations. The $\langle \Delta E_{\text{down}} \rangle$ value yielding the thermalization curve with closest agreement with results from MD calculations, shown in Table S2 and Figure S5, was selected for use in this study.

![Collisional relaxation curves obtained from MD and MESMER calculations for EtOOEtH$^+$ (a) and isomer M3 of the cyclohexene + OH oxidation derived ROOR (b), at 298.15 K and 1 atm. In both methods the starting temperature of the analyte is 800 K. Fitted Lennard-Jones parameters and exponential-down values are: a) $\langle \Delta E_{\text{down}} \rangle = 145$ cm$^{-1}$; $\varepsilon_{\text{LJ}} = 200$ K; $\sigma_{\text{LJ}} = 10$ Å; b) $\langle \Delta E_{\text{down}} \rangle = 185$ cm$^{-1}$; $\varepsilon_{\text{LJ}} = 550$ K; $\sigma_{\text{LJ}} = 11$ Å.](image)

**S3 Reaction Mechanism and Energetics.**

The general mechanism for fragmentation of ROOR’ and ROOH are shown in Scheme 2 and 3 respectively. The calculated Potential Energy Surfaces are depicted in Figures S6-13. Important values for structure and reactivity analysis, such as protonation energies, initial step barrier heights and direct dissociation energies, are shown in Table S3.

**S3.1 Model ROOR.**
The calculations revealed that the rate-determining step, i.e. the step with the highest barrier on the most favourable reaction pathway, is \( \text{R1a} \) for the MeOOOMe system and \( \text{R1c} \) for HOEtOOOMe and O=EtOOOMe. For the EtOOEt and iPrOOiPr systems, these two steps share a very similar reaction barrier height, and both should be rate-determining. \( \text{R1a} \) involves the cleavage of the peroxo O-O bond with a concerted H migration to the unprotonated peroxy O from its adjacent carbon (1,2 shift), leading to the formation of a proton-bridged alcohol-aldehyde/ketone (M2). In step \( \text{R1c} \), the O-O bond cleavage occurs alongside the 1,2 shift of an organic substituent instead. In most cases, the two fragments formed, an alcohol and a carboxonium ion, rapidly undergo addition to form a protonated acetal/ketal (M6). IRC calculations indicate that with O=EtOOOMe, this addition does not occur, and \( \text{R1c} \) yields a product complex. Nevertheless, the constituting fragments of the product from \( \text{R1c} \), either covalently bound or complexed, may suffer barrierless dissociation into P6. A third initial step (\( \text{R1b} \)) was found, where the peroxy O-O bond cleavage occurs with concerted H2 elimination from the C(OO)C carbon atoms, via a ring-like transition state. This channel leads to the formation of a proton-bridged pair of aldehydes/ketones (P4), but it was not found to be competitive. The key branching point in the reaction mechanism following \( \text{R1a} \) appears to be the not-so-loosely bound species M2. Reaction channels available for M2 include: nucleophilic attack on the carbonyl C by the alcohol O (\( \text{R2a} \)), producing a protonated hemiacetal/hemiketal (M3); H2 elimination (\( \text{R2b} \)), producing the proton-bridged pair of aldehydes/ketones (P4); barrierless dissociation (\( \text{R2c} \) or \( \text{R2d} \)) into alcohol + protonated aldehyde/ketone (P1) or protonated alcohol + aldehyde/ketone (P2). Species M3 may further react by a 1,3-H transfer to the hydroxyl O, concerted with a C-OH bond cleavage (\( \text{R3a} \)), yielding a H2O:carboxonium ion complex (M4). Complex M4 fragments may in turn fly apart into P3 + H2O (\( \text{R4b} \)), or react with each other producing P2 (\( \text{R4a} \)). The proton-bridged pair of aldehydes/ketones (P4) can also dissociate (R5) into its constituting fragments (P5). Three channels involving direct dissociation of the initial reactant without rearrangement are available, but none was observed to be competitive for the model ROOR’ systems: Heterolytic C-O bond cleavage yielding a hydroperoxide R’OOH and the corresponding carbocation R’ (R9); Homolytic O-O bond cleavage yielding an alkoxy radical R’O and an alcohol radical cation ROH’’ (R10); and a homolytic analogue of R9, yielding a hydroperoxide radical cation R’OOH’’ and a carbon centered radical R’ (R11).

**Table S3.** Protonation energy, initial step barrier heights and direct dissociation energies calculated at the RHF-RCCSD(T)-F12/aVDZ-F12 // oB97XD/aug-cc-pVTZ level of theory for ROOR and ROOH decomposition. All values correspond to zero-point corrected energies, given in kcal.mol\(^{-1}\), relative to the lowest energy protonation isomer of the initial charged species. Species structures are given in Scheme 2 and 3.

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<th>(ROOR')H*</th>
<th>ROOR' + H2O - H2O</th>
<th>TS 1a</th>
<th>TS 1b</th>
<th>TS 1c</th>
<th>TS 1d</th>
<th>P9</th>
<th>P10</th>
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</tbody>
</table>

Considering the alky-substituted ROOR’ systems, faster fragmentation rates were observed with increasing degree of substitution (R = Me < R = Et < R = iPr). The reason behind this trend is an increasing exothermicity of protonation by H₂O⁺ and decreasing barrier heights for rate-determining steps R₁a and R₁c. The first of these factors may be explained by the greater electronic density introduced into the peroxy oxygens by methyl groups via inductive effects, increasing the proton affinity of the peroxide. The second factor can be understood by examining the part of the molecule where a 1,2-migration occurs during steps R₁a and R₁c when, en route to the transition state, the α-carbon atom increasingly becomes electron-deficient and assumes a sp² character. The C-H σ-bonds present in an adjacent methyl group may interact with this C atom’s partially empty p-orbital, stabilizing the transition state by hyperconjugation. Thus, in comparison to the MeOOMe system, the presence of one methyl group (EtOOEt) lowers the R₁a reaction barrier by 5.7 kcal.mol⁻¹; and a second methyl group (iPrOOiPr) lowers this barrier by an additional 3.1 kcal.mol⁻¹. In reaction step R₁c, the group undergoing 1,2-shift to the oxygen atom is one of these methyl groups, which cannot participate in hyperconjugative stabilization of the transition state. Yet within the same reacting system, steps R₁a and R₁c have very similar barrier heights. Additional insight into the energetics of these competing channels is brought by analysing the kinetics of Baeyer-Villiger reactions (Clayden et al., 2012). During the rearrangement, a part of the positive charge may be allocated on the group being transferred, and therefore groups that better accommodate this charge stabilize the transition state to a greater degree. The importance of such factor is evidenced by the dissociative character of the rearrangement in the transition states of R₁a and R₁c, where the shifting group sits closer to the C than to the O atom. Methyl cation is a better leaving group than H⁺, and therefore as far as the migrating group is concerned, a 1,2-shift involving the former (R₁c) is more favourable than with the latter (R₁a).

Figure S6. Potential energy surface calculated at the RHF-RCCSD(T)-F12a/VDZ-F12// oB97XD/aug-cc-pVTZ level of theory, for decomposition of Me-OO-Me (green), Et-OO-Et (red) and iPr-OO-iPr (blue) following protonation in the gas phase. Molecular structures for stationary points are shown in Scheme 2. Values given are relative zero-point corrected energies in kcal.mol⁻¹.
At the lower limit of excess energy, significant decomposition of MeOOMe occurs only after ~1 s, the major products being protonated methanol + formaldehyde (P2) and protonated formaldehyde + methanol (P1) with a branching ratio of 0.92 and 0.08 respectively. End products and respective branching ratios for decomposition of EtOOEt are P6 (0.62), P2 (0.31), P1 (0.06) and P3 (0.01); while those for iPrOOiPr are P6 (0.55), P2 (0.32) and P1 (0.13). Species M3 is not a stable minimum in the PES of iPrOOiPr, since geometry optimizations lead to a different structure. This result makes sense considering the high steric strain present in such a molecule. A transition state for R2a was also not found for iPrOOiPr, so this step and all those that would follow it are assumed to be unavailable for this ROOR. Observing the PES for the channels available for intermediate M2, shown in Figure S6, it would be expected that most of MeOOMe and EtOOEt reacting through R1a would subsequently follow R4a, the most energetically favourable dissociation route. However, reaction dynamics simulations revealed that P3 is only a minor fragmentation product. The reason behind this result may be that, upon reaching M2, the reacting system accumulates considerable excess internal energy, enough to promote immediate dissociation into P1 or P2 before a significant fraction of species can further react to yield M4 (Schalley et al., 1997).

As for the systems containing oxygenated substituents, HOEtOOMe and O=EtOOME, relatively less fragmentation was observed within relevant time scales. At 1.023 mbar, ~68.2% of HOEtOOME and ~24.6% of O=EtOOME are left intact after 100 μs, the major fragmentation product being P6 in both cases. As described in the beginning of this section, interconversion between the initial protonation isomers was found to be fast. Very low-lying transition states were found for steps R0b in the PES of HOEtOOME, whereas no transition states were found for the O=EtOOME counterparts. Thus, for the sake of analysis of the rate of decomposition of these two peroxides, all of their initial reaction step transition states can be assumed to be connected to their most stable protonation isomer, HOEtOOHMe* and HO=EtOOME*, shown in Figure S7. Both species have an intramolecular H-bond between a peroxy group’s and the substituent’s oxygen atom, in a six-member ring-like conformation. This factor grants extra stability to these protonation isomers, as seen by the larger exothermicity of reaction of the parent peroxides with H3O+, compared to EtOOEt (Table S3). Calculations with O=EtOOHMe* indicate that the most favourable conformation of this species is not a minimum in the PES, since the proton is transferred to the carbonyl-oxygen during geometry optimisation. By having the carbonyl as the protonation site, reactant HO=EtOOME* is further stabilised by resonance. Higher energy protonation isomers HOEtHOOOME* and O=EtHOOME* also make an intramolecular H-bond, but in a more rigid five-member ring-like conformation, which is weaker due to the less then optimal O---H-O angles. No such H-bond is present in the R1c and the two R1a transition states available in the PES of HOEtOOME (Figure S7), which partly explains the higher barriers, and therefore the lower reaction rates. The same is true for the R1c and the lowest energy R1a transition state in the PES of O=EtOOME. IRC calculation with the TS1a connected to isomer HOEtOOHMe* revealed that this reaction step would produce the protonated hemiacetal (M3) instead of M2, even though the latter is lower in energy.
Figure S7. Potential energy surface calculated at the RHF-RCCSD(T)-F12a/VDZ-F12//oB97XD/aug-cc-pVTZ level of theory for the initial steps in the decomposition of HOCH2CH2OOMe (left) and OCHCH2OOMe (right) following protonation in the gas phase. Molecular structures carrying the double-dagger symbol ‡ are transition states. Values given in purple are relative zero-point corrected energies in kcal.mol⁻¹.

The absence of H-bonds in transition states described above results from a stereochemical constraint of such reactions (Clayden et al., 2012), where the migrating group has to be anti-periplanar to the leaving (alcohol) group. During the rearrangement, the electrons in the breaking C-C (or C-H) σ orbital gradually move into the empty O-O σ* orbital. Optimal overlap between these orbitals is achieved with an anti-periplanar conformation between the two involved moieties. Different to alkyl-substituted systems, HOEtOOMe and O=EtOOMe react only through the channel starting with R1c, as a result of the much lower reaction barrier of this step relative to R1a (Table S3). Due to resonance, both -CH₂OH and -CHO can accommodate a partial positive charge better than a methyl group, thus stabilizing the R1c transition state to a greater degree when taking part in the 1,2-shift. However, -CH₂OH is not as effective in stabilizing an adjacent carbocationic center, having C-H bonds available for hyperconjugation, but also an electron-withdrawing OH group. As a result, the R1a transition encountered by HOEtOOHMe⁺ is not stabilized to the same extent as R1c. The -CHO group is moderately electron-withdrawing by induction, producing instead a destabilizing effect on the R1a transition state encountered by HO=EtOOME⁺, yielding the largest barrier for this step (36.5 kcal.mol⁻¹) among the studied model ROOR’ systems.

The reaction of protonated AcOOAc, which follows a different mechanism, is shown through its PES in Figure S8. Initial reaction with H₂O⁺ can occur with protonation of a carbonyl-oxygen or a peroxyl-oxygen. Since a protonated carbonyl favors a planar geometry, the former may produce two isomers (E and Z), depending on which “side” of the functional group the proton is transferred to. However, the torsional barrier between the two isomers is relatively low (~11 kcal.mol⁻¹) and interconversion occurs at time scales shorter than other reaction pathways. The peroxyl-oxygen protonated AcOOAc was not found to be a stable minimum, since geometry optimization leads instead to a dissociation product complex, where the fragments are an acylium ion (Ac⁺) and peracetic acid (AcOOH). This result is similar to what was obtained for calculations with protonated acetic acid by Shi et al. (2015), where protonation at the hydroxyl-oxygen leads to a H₂O : acylium ion complex. The charged AcOOH:Ac⁺ complex is however strongly bound, and reassociation with concerted H transfer to the carbonyl-oxygen has a very low barrier (1.37 kcal.mol⁻¹), producing the more stable Z-isomer of the carbonyl-protonated AcOOAc. The only reaction pathway left to consider is a rearrangement available for the E and Z isomers, leading to a protonated acetic methylcarbonic anhydride (AMCAH⁺). The barrier for this reaction is low compared to the energy released during protonation and the produced anhydride is stable. Reaction dynamics simulations revealed
that after 100 μs, at 1.023 mbar and 298.15 K, about 18% of protonated AcOOAc is converted to AMCAH$^+$ and only ~1% yields the fragmentation products (AcOOH + Ac$^+$).

[S3.2 Model ROOH.]

For ROOH$^+$ the initial step with the lowest barrier is of the R1a type for R=Me and R1c type for R=Et, iPr or tBut, analogous to the ones found for ROOR, but in this case the molecule dissociates into a proton-bridged aldehyde/ketone : water complex (M2) or a carboxonium ion : water complex (M6). The trend in energetics for protonation exothermicity and initial step barrier height is the same as for the ROOR analogues, where the former increases and the latter decreases with larger substituents (R = Me < R = Et < R = iPr), likely due to the same factors discussed in the ROOR section. However, the energy released during protonation by H$_3$O$^+$ is considerably smaller for ROOH systems, which could reduce the proportion of molecules that react at non-thermal rates. On the other hand, the barrier heights for the (rate limiting) step R1a are also much lower for the alkyl-substituted ROOH systems, meaning thermal reaction rates are faster. Given that any of the considered R groups have a greater electron-donating effect than a hydrogen, a ROOH system has a smaller proton affinity and its O-O bond is more polarized compared to a ROOR.

Reaction dynamics simulations for MeOOH$_2^+$ revealed that this species decomposes only at thermal rates, which is evidenced by the single, pressure dependent decay curve (Figure 5). At 1.023 mbar, about ~17% of MeOOH$_2^+$ is decomposed after 100 μs, opposed to ~0% observed for MeOOHMe$^+$ in the same conditions. EtOOH$_2^+$, iPrOOH$_2^+$ and tButOOH$_2^+$ show very low barriers for step R1c (3.08, 1.21 and 0.12 kcal.mol$^{-1}$ respectively), and all three species are entirely (>99%) fragmented within ~1 μs. The final products of MeOOH$_2^+$ decomposition are protonated formaldehyde + H$_2$O (P1, 9.3%) and formaldehyde + H$_3$O$^+$ (P2, 7.7%). Water addition to the protonated carbonyl in M2 is also possible for the MeOOH system, but it was not found to be an important reaction channel since the product is higher in energy and subsequent H$_2$ elimination (R3b) has a very high barrier. The major fragmentation products of all other alkyl-substituted ROOH$_2^+$ are a carboxonium ion + H$_2$O (P3). Complex M6’s constituting fragments can react with each other via nucleophilic substitution producing a protonated alcohol : aldehyde/ketone complex (M7), which can also undergo barrierless dissociation, yielding P7. However, this route was not observed to be competitive.
In contrast, protonation isomer ROOH+ is rather inert. Apart from isomerization into ROOH2+, only the three direct dissociation channels are available these: Heterolytic C-O bond cleavage yielding H2O2 and the corresponding carbocation R’ (R8); Homolytic O-O bond cleavage yielding OH radical and a ROH+ radical cation (R9); and a homolytic analogue of R8, yielding H2O2+ radical cation and a carbon centered radical R’ (R10). Each of these channels was investigated for the other ROOH systems but, except for R8 with tButOOH+, none were observed to contribute to decomposition within significant timescales, under the lower limit of excess energy scenario. For MeOHOH+, the most favorable of these channels is R9, but the required energy is so high that the system would rather react through R0a to give MeOOH2+. R8 dissociation energy decreases fast with increasing alkyl-substituent size, as the electron donating methyl groups stabilize the formed carbocation, and this step becomes the most favorable for the other ROOH+ systems. At 1.023 mbar, about 89.8% of tButOOH+ fragments into tert-butyl cation + H2O2 within 100 μs, while other ROOH+ remain unreacted.

Figure S9. Potential energy surface calculated at the RHF-RCCSD(T)-F12a/VDZ-F12//ωB97XD/aug-cc-pVTZ level of theory, for decomposition of MeOOH (green), EtOOH (red), iPrOOH (blue) and tButOOH (yellow) following protonation in the gas phase. Molecular structures for stationary points are shown in Scheme 3. Values given are relative zero-point corrected energies in kcal.mol−1.
Figure S10. Potential energy surface calculated at the RHF-RCCSD(T)-F12a/VDZ-F12//ωB97XD/aug-cc-pVTZ level of theory for the initial steps in the decomposition of HOEtOOH (left) and O=EtOOH (right) following protonation in the gas phase. Molecular structures carrying the double-dagger symbol ‡ are transition states. Values given in purple are relative zero-point corrected energies in kcal.mol\(^{-1}\).

The calculations revealed that following protonation, HOEtOOH and O=EtOOH undergo little to no fragmentation within relevant time scales. Like with HOEtOOMe and O=EtOOMe, initial step R1c is favored over R1a. After 100 μs at 1.023 mbar, about 14.6% of HOEtOOH has fragmented into P3, while no significant amount of O=EtOOH has reacted. The underlying reason for the lower reactivities of these ROOH is the same as described previously for their ROOR' analogues: The intramolecular H-bond which stabilizes the protonated reactant is absent in the transition state of the initial steps R1c and R1a, resulting in higher reaction barriers (Figure S10). Furthermore, geometry optimizations indicate that the lowest energy conformation of the ROOH\(_2^+\) isomer of these systems is not stable, undergoing barrierless H transfer to the alcohol/carbonyl group’s oxygen, producing the more stable H\(_2\)OEtOOH\(^+\) and HO=EtOOH\(^+\) isomers. The ROOH\(^+\) isomers are possible but C-O or O-O scissions (R8-10) are unfavorable, and H-shift leading to the hydroxyl/carbonyl-protonated isomers (R0c) is very fast.

Figure S11. Potential energy surface calculated at the RHF-RCCSD(T)-F12a/VDZ-F12//ωB97XD/aug-cc-pVTZ level of theory for the reaction of peracetic acid (right) and performic acid (left) following protonation in the gas phase. Molecular structures carrying the double-dagger symbol ‡ are transition states. Values given in purple are relative zero-point corrected energies in kcal.mol\(^{-1}\).

Decomposition of the protonated peroxy acids follow a different mechanism than that shown in Scheme 3. Their potential energy surface is presented in Figure S11. Two protonation products were found for peracetic acid, the most stable being the carbonyl-oxygen protonated species (HAcOOH\(^+\)). Protonation of the peroxy-oxygen atom adjacent to the acyl carbon occurs with concomitant C-O(OH) bond scission, leading to formation of an acylium ion (Ac\(^+\)) and H\(_2\)O\(_2\) complex. The energy required for dissociation of this complex is higher than the excess energy released during protonation, and only ~0.6% of it fragments after 100 μs at 1.023 mbar. Interconversion between the Ac\(^+\):H\(_2\)O\(_2\) complex and HAcOOH\(^+\) is possible but very unfavorable given the high reaction barrier involved (55.3 kcal.mol\(^{-1}\)). Species AcOOH\(_2^+\) is not stable, being rapidly converted into HAcOOH\(^+\). Protonation of any oxygen atom in performic acid may result in a stable product, however the only exothermic channel produces the carbonyl-protonated isomer (HOCHOOC\(^+\)). No transition state was found for proton transfer from the carbonyl to the terminal peroxy-oxygen, indicating this step should have a very low barrier. The produced isomer OCHOOC\(_2^+\) has a decomposition reaction channel available that leads to the formation of protonated carbonic acid, however the overall barrier is too high (32.5 kcal.mol\(^{-1}\)) and it doesn’t happen at relevant time scales. Nevertheless, the elemental composition would be retained, and the mass spectrum signal would not be impacted. Similar to
peracetic acid, protonation of the oxygen adjacent to the acyl carbon in performic acid would lead to formation of a formyl cation (HCO\(^+\)) and H\(_2\)O\(_2\) complex.

**S3.3 Cyclohexene oxidation products**

A new reaction pathway (R1d) was found to be available for the ROOR and ROOH derived from ozonolysis of cyclohexene, depicted in Scheme S1. In it, instead of a 1,2-rearrangement of a H or an organyl group like in R1a or R1c, a more favorable 1,6 H-transfer occurs alongside the O-O bond scission. This reaction step is possible due to the presence of a carbonyl group situated at a further distance from the peroxide group and, for the ROOR system, it was observed to be dominant among decomposition steps involving rearrangement.

![Figure S12. Initial decomposition step R1d, found for ROOR and ROOH derived from cyclohexene ozonolysis.](image1)

![Figure S13. Potential energy surface calculated at the oB97XD/aug-cc-pVTZ level of theory for reaction following protonation in the gas phase, for the ROOR (left) and ROOH (right) derived from cyclohexene oxidation by OH. Molecular structures carrying the double-dagger symbol \(‡\) are transition states. Values given in purple are relative zero-point corrected energies in kcal.mol\(^{-1}\).](image2)
Figure S14. Potential energy surface calculated at the oB97XD/aug-cc-pVTZ level of theory for reaction following protonation in the gas phase, for the ROOR (left) and ROOH (right) derived from cyclohexene oxidation by O₃. Molecular structures carrying the double-dagger symbol ‡ are transition states. Values given in purple are relative zero-point corrected energies in kcal.mol⁻¹.

S3.4 High Energy Collisions.

Figure S15. Potential energy surface calculated at the RHF-RCCSD(T)-F12a/VDZ-F12 // oB97XD/aug-cc-pVTZ level of theory for reaction following protonation in the gas phase, for n-butanol. Molecular structures carrying the double-dagger symbol ‡ are transition states. Values given in purple are relative zero-point corrected energies in kcal.mol⁻¹.
Figure S16. Reaction dynamics simulation results for n-butanol following protonation, under three excess energy scenarios. Graphs represent the time evolution profile of fragmentation, at 298.15 K and 1.013 mbar.

Figure S17. Reaction dynamics simulation results for n-butanol and the investigated ROOR systems, under two excess internal energy scenarios: Protonation energy only (orange) and protonation energy + 0.5 eV (red). Graphs represent the time evolution profile for reaction of initial protonated reactants, at 298.15 K and 1.013 mbar.
Figure S18. Reaction dynamics simulation results for the investigated ROOR systems, under two excess internal energy scenarios: Protonation energy only (orange) and protonation energy + 0.5 eV (red). Graphs represent the time evolution profile for reaction of initial protonated reactants, at 298.15 K and 1.013 mbar.

References


