Chlorine Atom-Initiated Low-Temperature Oxidation of Prenol and Isoprenol: The Effect of C=C Double Bonds on the Peroxy Radical Chemistry in Alcohol Oxidation

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1. Abstract

The chlorine atom-initiated oxidation of two unsaturated primary C5 alcohols, prenol (3-methyl-2-buten-1-ol, $(\text{CH}_3)_2\text{CCHCH}_2\text{OH}$) and isoprenol (3-methyl-3-buten-1-ol, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$), is studied at 550 K and low pressure (8 Torr). The time- and isomer-resolved formation of products is probed with multiplexed photoionization mass spectrometry (MPIMS) using tunable vacuum ultraviolet ionizing synchrotron radiation. The peroxy radical chemistry of the unsaturated alcohols appears much less rich than that of saturated C4 and C5 alcohols. The main products observed are the corresponding unsaturated aldehydes – prenal (3-methyl-2-butenal) from prenol oxidation and isoprenal (3-methyl-3-butenal) from isoprenol oxidation. No significant products arising from QOOH chemistry are observed. These results can be qualitatively explained by the formation of resonance stabilized allylic radicals via H-abstraction in the Cl + prenol and Cl + isoprenol initiation reactions. The loss of resonance stabilization upon O_2 addition causes the energies of the intermediate wells, saddle points, and products to increase relative to the energy of the initial radicals and O_2 . These energetic shifts make most product channels observed in the peroxy radical chemistry of saturated alcohols inaccessible for these unsaturated alcohols. The experimental findings are underpinned by quantum-chemical calculations for stationary points on the potential energy surfaces for the reactions of the initial radicals with O_2 . Under our conditions, the dominant channels in prenol and isoprenol oxidation are the chain-terminating HO_2 -forming channels arising from radicals, in which the unpaired electron and the OH group are on the same carbon atom, with stable prenal and isoprenal co-products, respectively. These findings suggest that the presence of C=C double bonds in alcohols will reduce low-temperature reactivity during autoignition.

Keywords: Low-temperature oxidation; autoignition; alcohols; resonance stabilization; peroxy radicals.

2. Introduction

The reaction of O_2 with initial fuel radicals R derived from fuel molecules RH is pivotal for understanding and predicting autoignition in existing and advanced combustion engines, particularly those relying on compression ignition.[1] For the peroxy (RO_2) radicals formed by the $R + O_2$ reaction, chain-terminating formation of HO_2 + unsaturated co-product competes with isomerization to hydroperoxyalkyl ($QOOH$) radicals. These $QOOH$ species can either unimolecularly decompose, principally to OH + cyclic ether for alkane fuels, which is chain-propagating, or react with a second O_2 molecule. The latter reaction constitutes the key chain-branching step in low-temperature autoignition, because it leads to the eventual formation of two OH radicals. The balance among chain termination, chain propagation, and chain branching determines the low-temperature reactivity that influences autoignition properties for any kind of fuel.

Concerns about energy security and climate have stimulated research into liquid fuels derived from biomass. Many different types of biofuels are under consideration, amongst them short- and medium-chain saturated alcohols, particularly ethanol, a currently widely used biofuel, the butanol isomers and isopentanol. Fundamental studies on their low-temperature oxidation chemistry [2-5] have revealed a rich $QOOH$ chemistry and have shown that the alcoholic $-OH$ group significantly alters reactivity when compared to alkane oxidation and introduces new pathways, such as the Waddington mechanism [6,7] or water elimination.[8] Detailed chemical kinetics combustion mechanisms have been developed, which include alcohol-specific low-temperature chemistry and which can successfully model global combustion targets, such as ignition delay time measurements.[9,10]

Very recently, Zheng *et al.*[11] developed a specific and efficient production route of two unsaturated isoprenoid $C_5H_{10}O$ alcohols, prenol (3-methyl-2-buten-1-ol) and isoprenol (3-methyl-3-buten-1-ol), see Fig. 1, as potential biofuels. In contrast to their saturated counterparts, no fundamental studies exist on

low-temperature autoignition chemistry of unsaturated alcohols, and knowledge of their oxidation chemistry is restricted to conditions more relevant to the atmosphere.[12-14]

The presence of C=C double bonds in fuels adds complexity to the initial fuel radical spectrum, because besides abstraction of hydrogen atoms leading to alkyl radicals, H-abstraction forming allylic and vinylic radicals and addition of radicals to double bonds becomes possible.[15] For the simplest allylic radical, allyl (C_3H_5), experimental and computational studies have found that this resonance stabilized radical is rather unreactive towards O_2 , so that allyl reacts mainly via radical-radical reactions at combustion conditions.[16,17] For biodiesel fuels, Westbrook *et al.*[18] recently investigated the influence of C=C double bonds on the ignition properties of methyl esters. They showed that the formation of allylic radicals inhibits low-temperature reactivity because isomerization of the resulting allyl peroxy radicals is disfavored, explaining a reduction in the cetane number with increasing number of double bonds.

This study investigates the influence of C=C double bonds in prenol and isoprenol on the peroxy radical chemistry of the initial fuel radicals when compared to fuel radicals derived from saturated alcohols. We generate Cl atoms by pulsed laser photolysis to initiate the oxidation and probe the time- and isomer-resolved formation of products in a large excess of O_2 using multiplexed synchrotron photoionization mass spectrometry (MPIMS) at 550 K and 8 Torr. The experimental results are supported by quantum-chemical calculations on the potential energy surfaces (PESs) for the reactions of specific initial fuel radicals with O_2 .

3. Experimental Methods

Experiments were performed with the Sandia MPIMS chemical reactor using synchrotron-generated vacuum ultraviolet (VUV) radiation from the Chemical Dynamics Beamline at the Advanced Light Source (ALS). Here we give only a brief description of the experimental setup; more details can be

found in Refs.[19-21]. The reactants (either prenol or isoprenol), Cl_2 , and O_2 , all diluted in helium, are flowed through a quartz tube at 550 K and 8 Torr. Excimer laser photolysis of Cl_2 at 351 nm and 4 Hz generates Cl atoms, which subsequently initiate oxidation of the fuel. A small fraction of the reactive mixture escapes through a pinhole in the sidewall of the reactor, expands into vacuum, is skimmed and crossed with the ionizing VUV radiation. Cations formed are detected in an orthogonal-acceleration time-of flight mass spectrometer. The mass resolution of the spectrometer ($m/\Delta m \approx 1500$) is sufficient to distinguish species with identical nominal mass, but different elemental composition, e.g., C_3H_6 and $\text{C}_2\text{H}_2\text{O}$. Full mass spectra are taken in intervals of 20 μs , and the energy of the ionizing photons is scanned over a range of 8.0 – 11.0 eV in steps of 0.025 eV. The data are normalized to the ALS photon flux using a calibrated photodiode.

The data are acquired as a function of mass-to-charge ratio (m/z), reaction time (defined as kinetic time relative to photolysis), and photoionization energy. The tunability of the ionizing radiation allows isomers to be distinguished based on their ionization energies (IEs) and photoionization spectra. If absolute photoionization cross sections are known, species can be quantified at an isomer-resolved level, as outlined in Refs. [2,4]. In the present work, product yields, defined as $[\text{product}]_{\text{formed}} / [\text{unsaturated alcohol}]_{\text{consumed}}$, are derived by comparing the photoionization signals for the depletion of prenol/isoprenol with those for product formation. We estimate an uncertainty of 20% in the product yields, mainly due to uncertainties in the absolute values of the photoionization cross sections.

Initial number densities (in cm^{-3}) in the experiments were: 5.6×10^{13} (prenol), 6.3×10^{13} (isoprenol), 7.0×10^{16} (O_2), 1.1×10^{14} (Cl_2), $\sim 3 \times 10^{12}$ (Cl), with He added to reach a total number density of $1.4 \times 10^{17} \text{ cm}^{-3}$.

4. Theoretical Methods

We performed quantum-chemical calculations on the PESs of the reactions of O₂ with the initial radicals derived from Cl + prenol and Cl + isoprenol H-abstraction reactions. Minima and first-order saddle points were calculated at the RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) [22-24] and CBS-QB3[25, 26] levels of theory. Minimum-energy conformers were systematically searched for at either B3LYP/6-31G(d) or B3LYP/6-31G levels of theory.

The entrance channels for the O₂ addition to allylic radicals were not explicitly characterized. RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) calculations on the entrance barrier for the allyl radical + O₂ addition gave a large T1 diagnostic[27] of 0.042, suggesting that multireference calculations might be necessary for an adequate description of this barrier, which exceeds the scope of this work.

In addition, we performed calculations on adiabatic ionization energies (AIEs) of selected products using the CBS-QB3 method. The RCCSD(T)-F12a/VDZ-F12 calculations were performed with Molpro 2010.[28] All other calculations were performed with Gaussian09.[29] The energies of all minima, saddle points, and products considered, including a comparison of the results from RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) and CBS-QB3 calculations, are presented in Tables S1-S4.

5. Results and Discussion

Studies of the reaction of Cl with alkenes revealed a temperature- and pressure dependent competition between addition of Cl to the double bond and allylic H-abstraction. At atmospheric conditions, addition to the double bond dominates, whereas at higher temperature and/or lower pressure allylic H-abstraction increasingly dominates.[30,31] No studies exist on the reaction of Cl with prenol and isoprenol under the conditions of our study (550 K and 8 Torr). Nevertheless, the Cl + C₂H₄ and Cl + C₃H₆ reactions mainly proceed via abstraction reactions at conditions close to the present experiments,[30,32]

suggesting that H-abstraction reactions dominate for Cl + prenol and Cl + isoprenol under our conditions. As will be discussed below, our experimental results support this hypothesis.

Fig. 1 shows the initial radicals created by H-abstraction from prenol/isoprenol by Cl atoms. Abstraction of alcoholic[33] and vinylic[32] hydrogen atoms by Cl is endothermic and thus unimportant under our conditions. H-abstraction from prenol by Cl therefore produces exclusively allylic radicals: One with radical character on the α - and γ -C atoms relative to the $-\text{OH}$ group (denoted as $\alpha/\gamma\text{-R}$), and one with radical character on the β and δ -C atoms (denoted as $\beta/\delta\text{-R}$). For isoprenol, the allylic radicals $\beta/\delta\text{-R}$ and $\delta/\delta\text{-R}$ can be formed, along with the alkyl radical $\alpha\text{-R}_{\text{IP}}$. Note that Cl + prenol and Cl + isoprenol produce the same allylic $\beta/\delta\text{-R}$ radical.

Fig. 2a shows the product mass spectrum for prenol oxidation. The dominant product signal occurs at $m/z = 84$ ($\text{C}_5\text{H}_8\text{O}$), two mass units below the mass of prenol ($m/z = 86$). The agreement of the $\text{C}_5\text{H}_8\text{O}$ photoionization spectrum with a prenal calibration spectrum (Fig. 3a) identifies prenal (3-methyl-2-butenal) as the major carrier of the $\text{C}_5\text{H}_8\text{O}$ signal. The onset at 8.1 eV in the product spectrum might indicate minor formation of 3-methyl-1,3-butadienol (AIE = 8.16 eV). Comparing the $\text{C}_5\text{H}_8\text{O}$ product signal with the depletion signal of prenol reveals that 60% of the prenol consumed forms prenal. This result establishes prenal as the main product of prenol oxidation under our conditions. The time profile for prenal formation (Fig. 3c) is in reasonable agreement with the time profile for prenol removal, suggesting that prenal is a primary product. Other products identified based on their photoionization spectra are methacrolein ($m/z = 70$, product yield: 2%), acetone ($m/z = 58$, 14%; in Fig. 2a the acetone product signal is masked by dissociative ionization of prenol), and formaldehyde ($m/z = 30$, 14%). The signal-to-noise ratio of their time profiles prevents us from assigning them as primary or secondary products based on their formation kinetics.

Because α/γ -R (β/δ -R) has radical character at both the α - and γ - (β - and δ -) carbon atoms, O_2 can add to either site, leading to substituted allylic peroxy radicals. Figs. 4 and 5 show relevant stationary points on the PESs for the α/γ -R + O_2 and β/δ -R + O_2 reactions. In these figures, energetically higher-lying channels are excluded for clarity.

A central theme in the α/γ -R + O_2 and β/δ -R + O_2 reactions is the loss of resonance stabilization upon addition of O_2 , leading to substantially shallower RO_2 wells and higher exit barriers when compared to the reaction of O_2 with initial fuel radicals derived from saturated alcohols. For instance, α - RO_2 in ethanol[5] and butanol[4] oxidation is stabilized relative to α -R + O_2 by $\sim 160 \text{ kJ mol}^{-1}$. In contrast, the stabilization energy of the α - RO_2 well in prenyl oxidation relative to α/γ -R + O_2 is only 98 kJ mol^{-1} , $\sim 60 \text{ kJ mol}^{-1}$ less than in the saturated system. Similarly, the barrier heights for the exit channels in the α/γ -R + O_2 and β/δ -R + O_2 reactions in prenyl oxidation increase substantially when compared to the exit channels in the saturated systems, making most product channels inaccessible under low-temperature conditions (see Figs. 4 and 5). However, the alcoholic $-OH$ group favors HO_2 elimination from α - RO_2 to prenyl + HO_2 to such an extent that the barrier for HO_2 -elimination is 63 kJ mol^{-1} below the energy of the reactants, low enough to make this channel readily accessible despite the loss of resonance stabilization. *Cis*-/*trans*- isomers exist for γ - RO_2 , and the only channel with a barrier below the α/γ -R + O_2 reactant energies is again formation of prenyl + HO_2 , in this case via isomerization of *cis*- γ - RO_2 to a vinoxy-type QOOH radical and subsequent loss of HO_2 . An analogous channel is not possible for *trans*- γ - RO_2 for steric reasons. Because its exit barriers are above the reactants energy and entropically disfavored compared to backdissociation, the major fate of *trans*- γ - RO_2 will be backdissociation to α/γ -R + O_2 or secondary reactions. As for other initial fuel radicals whose fate will be discussed below, these secondary reactions are reactions of R with species other than O_2 and can for example be radical-radical in nature ($R + R$, $R + RO_2$, or $R + Cl$).

Based on these arguments, prenal + HO₂ is the major product channel from α/γ -R + O₂, which qualitatively rationalizes the high yield of prenal observed in our experiments. Making the reasonable assumption that pathways to prenal other than via α/γ -R + O₂ are absent (see discussion of β/δ -R pathways below) places a lower limit of 60% on the yield of α/γ -R from the Cl + prenal reaction at 550 K and 8 Torr. This result corroborates the dominance of allylic H-abstraction from prenal by Cl atoms at these conditions.

Whereas the dominance of HO₂ elimination from α -RO₂ is a similarity in the oxidation of saturated and unsaturated alcohols, the reactivity of the β , γ , and δ -RO₂ is greatly altered. For instance, in the low-temperature oxidation of *n*-butanol[4] and isopentanol[2,8] the most favored reaction of γ -RO₂ is H-atom abstraction from the carbon atom connected to the alcoholic –OH group, forming the QOOH radical γ -Q₁. The γ -RO₂ $\leftrightarrow$ γ -Q₁ isomerization barrier in these systems is over 70 kJ mol⁻¹ below the γ -R + O₂ energy.[4,8] In contrast, the *cis*- γ -RO₂ $\leftrightarrow$ γ -Q₁ isomerization barrier in prenal oxidation is over 30 kJ mol⁻¹ above α/γ -R + O₂, making γ -Q₁ unimportant in prenal oxidation. The loss of resonance stabilization upon O₂ addition to α/γ -R, the necessity of abstraction of a vinylic H atom in *cis*- γ -RO₂, and increased ring strain due to the presence of a double bond in the cyclic saddle-point structure all contribute to this increase in barrier height.

Methacrolein + CH₂O + OH are the expected products of the Waddington mechanism in the β/δ -R + O₂ reaction via β -RO₂ (see Fig. 5). The observed 2% yield of methacrolein suggests an only minor role of the Waddington mechanism in prenal oxidation, considering that the yield of β/δ -R from Cl + prenal might be as high as 40%. This observation marks another difference from the oxidation of saturated alcohols, where the Waddington mechanism is the major product channel in β -R + O₂ reactions.[2-4] Our calculations suggest that the saddle point for the H-transfer in the β -RO₂ $\leftrightarrow$ β -Q₀ reaction is close to the energy of the β/δ -R + O₂ reactants. However, like β -R + O₂ reactions in ethanol[5] and *n*-butanol[4] oxidation, the β -RO₂ $\leftrightarrow$ β -Q₀ saddle point has a large T1 diagnostic (0.047), suggesting multireference

calculations might be necessary to obtain a more reliable saddle-point energy. Interestingly, β -Q_O is not a minimum on the ZPE-corrected PES in the β/δ -R + O₂ reaction, so that β -RO₂ $\leftrightarrow$ β -Q_O directly forms methacrolein + CH₂O + OH via β -CC bond fission of β -Q_O. As apparent in Fig. 5, other product channels from β -RO₂ are also disfavored.

For *cis*- δ -RO₂, the only barrier below the β/δ -R + O₂ asymptote is isomerization to the QOOH radical *cis*- δ -Q_{1/3} (-8 kJ mol⁻¹ relative to β/δ -R + O₂). *Cis*- δ -Q_{1/3} benefits from allylic resonance stabilization, making it energetically more favorable than δ -RO₂. The lowest-lying exit channel from *cis*- δ -Q_{1/3} is a concerted H-transfer/OH-loss to 4-hydroxy-3-methyl-2-butenal; an analogous channel was recently characterized in γ - and δ -hydroxybutyl + O₂ reactions.[4] Attempts to locate a saddle point for water elimination from *cis*- δ -Q_{1/3} were unsuccessful at both B3LYP/6-311G(d,p) and M06-2X/6-311++G(d,p) levels of theory and instead led to the saddle point for H-transfer/OH-loss. Ring-strain effects from unsaturation in the cyclic saddle-point structure might explain this effect. In our experiments, we observe weak ion signal at $m/z = 100$ (C₅H₈O₂), the parent mass of the stable coproduct from H-shift/OH-loss, 4-hydroxy-3-methyl-2-butenal. However, the experimental onset in the photoionization spectrum occurs at ~ 9.2 eV, below the calculated AIE for this species of 9.56 eV, and no distinct onset at 9.56 eV exists (see Fig. S1). These results do not support formation of 4-hydroxy-3-methyl-2-butenal and might indicate that the *cis*- δ -RO₂ $\leftrightarrow$ *cis*- δ -Q_{1/3} isomerization is unimportant. Other products that might arise from unimolecular β -RO₂ and δ -RO₂ chemistry were not observed. For instance, the AIEs of the possible three- (8.56 eV) and five-membered ring (9.37 eV) cyclic ether products are in disagreement with the observed onset in the $m/z = 100$ spectrum (see Table S5 and Fig. S1). These results suggest that β/δ -R principally reacts via secondary chemistry.

No obvious channels from unimolecular peroxy radical chemistry exist for acetone and only the Waddington mechanism forms formaldehyde, suggesting that acetone and the excess of formaldehyde over methacrolein likely arise from secondary reactions. We observe significant product signal at $m/z =$

82 (C_5H_6O). Fig. S2 shows the photoionization spectrum and the time profile of this mass channel, which is tentatively assigned as 3-methylfuran. Its slow rise suggests formation via secondary chemistry and its yield is positively correlated to $[O_2]$. Interestingly, in isoprenol oxidation we observe the same product, with a similarly slow rise time and a yield also enhanced by increasing $[O_2]$. This agreement suggests a common precursor in both systems, which we are unable to identify.

H-abstraction from isoprenol by Cl atoms can produce three different initial fuel radicals: An α -hydroxyalkyl radical (α - R_{IP}), or the resonance stabilized radicals β/δ -R and δ/δ -R (see Fig. 1). Based on the calculated PES presented in Fig. 6a, the reaction of α - R_{IP} with O_2 is expected to favor HO_2 elimination forming isoprenal (C_5H_8O ; 3-methyl-3-butenal) + HO_2 ; an analogous channel dominates for other α -hydroxyalkyl + O_2 reactions. The experimental product mass spectrum of Cl-initiated isoprenol oxidation (Fig. 2b) indeed shows fairly strong C_5H_8O signal. Fig. 3b shows the photoionization spectrum of the C_5H_8O product. Isoprenal was not commercially available, nor did we attempt to synthesize it. Therefore an experimental photoionization spectrum is unavailable preventing the unambiguous identification of the observed C_5H_8O signal as isoprenal and its quantification.

Nevertheless, the calculated AIE of isoprenal of 9.29 eV is in reasonable agreement with the observed experimental onset. In addition, we found a low-lying dissociative ionization pathway from $C_5H_8O^+$ to $CH_3 + C_4H_5O^+$ ($m/z = 69$) (see Fig. S3). The calculated appearance energy (AE) of 9.79 eV is in reasonable agreement with the experimental onset of the C_4H_5O signal of ~ 9.6 eV, suggesting that the strong $m/z = 69$ signal arises at least in part from dissociative ionization of isoprenal. Based on the assumption that the *partial* photoionization cross sections of prenal and isoprenal at $m/z = 84$ are identical at 11.0 eV, $\sim 35\%$ of the isoprenol consumed forms isoprenal. Under the alternative assumption that the *total* photoionization cross sections of prenal and isoprenal are identical at 11.0 eV and that $m/z = 69$ signal in isoprenol oxidation arises solely from dissociative ionization of isoprenal, an isoprenal

yield of ~75% would result. Both scenarios suggest that isoprenal is a major product from Cl-initiated isoprenol oxidation.

We find a ~ 4% yield of methacrolein in the isoprenol oxidation experiments, corroborating an only minor role of the Waddington channel that proceeds from the β/δ -R + O₂ reaction. An observed CH₂O yield of 30% suggests secondary reactions as its main source. Signal in the product mass spectrum at m/z = 90, 92, 102, and 104 is caused by species containing one chlorine atom, suggesting they are formed from secondary chlorine chemistry. In addition to contributions from products originating from β/δ -R, these products may partly originate from the δ/δ -R radical unique to isoprenol oxidation, although we cannot rule out potential contributions from product formation initiated by Cl addition to the C=C double bond of isoprenol. The absence of low-lying exit channels in the δ/δ -R + O₂ reaction (Fig. 6b) supports the hypothesis that δ/δ -R reacts principally via secondary chemistry under our conditions.

6. Conclusions

We have measured products from Cl-initiated oxidation of prenol and isoprenol at 550 K and 8 Torr using time- and isomer-resolved MPIMS detection. The formation of resonance stabilized allylic radicals in the Cl + prenol/isoprenol reactions leads to shallow RO₂ wells that enhance the importance of backdissociation to R + O₂. Our observations, supported by quantum-chemical calculations, show that most of the product channels that are accessible in reactions of hydroxyalkyl + O₂ reactions derived from saturated alcohols have prohibitively high barriers for unsaturated alcohols. An exception is HO₂ + prenal formation from the α/γ -R + O₂ reaction, which is still energetically accessible. Formation of QOOH in the reaction of the resonance stabilized initial fuel radicals with O₂ is greatly suppressed. As a consequence, pathways associated with chain-propagating or chain-branching OH formation are not readily available, likely limiting low-temperature reactivity during autoignition. However, the main chain carrier under low-temperature conditions is the OH radical, which, if present, can readily add to the C=C double bond in prenol and isoprenol. The resulting dihydroxyalkyl radicals will have a different

reactivity towards O₂, and further studies are necessary to elucidate their peroxy radical chemistry under low-temperature conditions.

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9. Figures

Figure 1: Initial radicals formed via H-abstraction by Cl atoms from prenol and isoprenol.

Figure 2: Mass spectra for oxidation of (a) prenol and (b) isoprenol. The spectra are obtained by integrating over photon energies from 8.0 – 11.0 eV and over a reaction time from 0 – 30 ms. The spectra show the difference between the average pre-photolysis signal and product formation initiated by photolysis. Negative parent ($m/z = 86$) and daughter ion peaks caused by reactive removal of prenol and isoprenol are cut for clarity.

Figure 3: (a) C_5H_8O ($m/z = 84$) photoionization product spectrum from prenal oxidation, compared to a calibration spectrum of prenal. (b) C_5H_8O and C_4H_5O ($m/z = 69$) photoionization product spectra from isoprenol oxidation. C_4H_5O is most likely a daughter ion from isoprenal (calculated AIE: 9.29 eV). (c) Time profiles of prenal and isoprenal (both at $m/z = 69$ and $m/z = 84$). The photoionization spectra were obtained by integrating over a reaction time of 0 – 30 ms, and the time profiles were obtained by integrating over photon energies from 8.0 – 11.0 eV.

Figure 5: PES for the reaction of $\beta/\delta\text{-R} + \text{O}_2$. Energies are at 0 K relative to the more stable of the two $\beta/\delta\text{-R}$ conformers shown at the RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) level of theory.

Figure 6: PES for the reaction of (a) $\alpha\text{-R}_{\text{IP}} + \text{O}_2$ and (b) $\delta/\delta\text{-R} + \text{O}_2$. Energies are at 0 K relative to the $\text{R} + \text{O}_2$ reactants at the RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) level of theory. The $\alpha\text{-R}_{\text{IP}}\text{O}_2 \leftrightarrow \alpha\text{-Q}_{\text{IP},\text{O}}$ saddle point was not found with the M06-2X/6-311++G(d,p) method. Instead, its energy relative to $\alpha\text{-R}_{\text{IP}}\text{O}_2$ at the CBS-QB3 level is shown. Energetically low-lying channels are highlighted.

10. Separate List of Figure Captions

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Figure 4: PES for the reaction of α/γ -R + O₂. Energies are at 0 K relative to the more stable of the two α/γ -R conformers shown at the RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) level of theory. The α -RO₂ $\leftrightarrow$ α -Q_O saddle point was not found with the M06-2X/6-311++G(d,p) method. Instead its energy relative to α -RO₂ at the CBS-QB3 level is shown. Energetically low-lying channels are highlighted.

Figure 5: PES for the reaction of β/δ -R + O₂. Energies are at 0 K relative to the more stable of the two β/δ -R conformers shown at the RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) level of theory.

Figure 6: PES for the reaction of (a) α -R_{IP} + O₂ and (b) δ/δ -R + O₂. Energies are at 0 K relative to the R + O₂ reactants at the RCCSD(T)-F12a/VDZ-F12//M06-2X/6-311++G(d,p) level of theory. The α -R_{IP}O₂

$\leftrightarrow \alpha\text{-Q}_{\text{IP}, \text{O}}$ saddle point was not found with the M06-2X/6-311++G(d,p) method. Instead, its energy relative to $\alpha\text{-R}_{\text{IP}}\text{O}_2$ at the CBS-QB3 level is shown. Energetically low-lying channels are highlighted.