

# Water Microdroplets Surrounded by Alcohol Vapor Cause Spontaneous Oxidation of Alcohols to Organic Peroxides

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Cite This: <https://doi.org/10.1021/jacs.4c04092>



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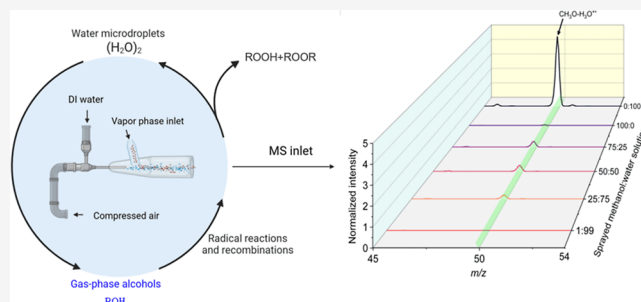


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Supporting Information

**ABSTRACT:** Using real-time mass spectrometric (MS) monitoring, we demonstrate one-step, catalyst-free spontaneous oxidation of various alcohols (ROH) to key reactive intermediates for the formation of ROO<sup>•</sup> compounds on the surface of water microdroplets surrounded by alcohol vapor, carried out under ambient conditions. These organic peroxides (POs) can act as important secondary organic aerosols (SOA). We used hydrogen–deuterium exchange by spraying D<sub>2</sub>O instead of H<sub>2</sub>O to learn about the reaction mechanism, and the results demonstrate the crucial role of the water–air interface in microdroplet chemistry. We find that the formation of POs relies on electron transfer occurring at the microdroplet interface, which generates hydrogen atoms and hydroxyl radicals that lead to a cascade of radical reactions. This electron transfer is believed to be driven by two factors: (1) the emergence of a strong electrostatic potential on the microdroplet's surface; and (2) the partial solvation of ions at the interface. Mass spectra reveal that the formation of POs is dependent on the alcohol structure, with tertiary alcohols showing a higher tendency to form organic peroxides than secondary alcohols, which in turn are more reactive than primary alcohols.



## INTRODUCTION

The extraordinary chemical behavior of sprayed water microdroplets is a subject of intense research interest, with several key factors contributing to the acceleration of reactions in this unique environment. Partial solvation of molecules at the liquid–gas interface of microdroplets may lead to smaller energy barriers for reaching the transition state.<sup>1</sup> Additionally, the emergence of a strong electrostatic potential at the droplet interface can drive electron transfer processes, promoting chemical transformations.<sup>2–4</sup> This may lead to accelerated reactions at the interface rather than inside the microdroplets. Beyond partial solvation and electrostatic potential, other factors can cause rate acceleration at interfaces.<sup>5</sup> Reactants can reach the surface from the bulk or from the gas phase and undergo a chemical transformation, and the products diffuse back into the droplet bulk. Recent studies distinguished reactions at the interface process of water microdroplets from the bulk-phase process. These results underscore the presence of partial solvation at the interface and underscore the intricate interplay between hydrogen bonding and electrostatic potential, which can either facilitate or hinder the polarization of reactants, intermediates, or products at the interface. Understanding and fine-tuning interfacial reactivity hinges upon recognizing these dynamics.<sup>6,7</sup> We previously demonstrated the spontaneous formation of hydrogen peroxide in microdroplets<sup>8</sup> and recently investigated the effect of relative humidity on this process, highlighting the importance of the gas–liquid interface in microdroplet chemistry.<sup>9</sup> Organic

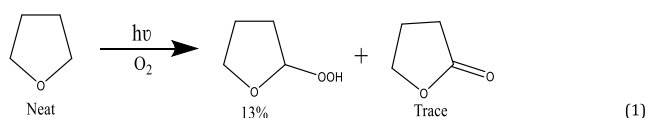
peroxides (POs), consisting of organic compounds featuring peroxide (–O–O–) bonds, are commonly represented by the generic formula ROOR', with R representing an organic group (e.g., alkyl, aryl, or acyl substituent), or R' can be either a hydrogen atom for organic hydroperoxides (ROOH, which is also referred to as an HPO). POs are typically seen as transient products of gas-phase radical reactions, making them temporary repositories for oxidative radicals (HO<sub>x</sub> and RO<sub>x</sub>) within the atmosphere.<sup>10,11</sup> These compounds are key intermediates in the oxidation of organic compounds, playing a significant role in free radical chain termination, oxidant cycling, and the aerosol formation.<sup>12–17</sup> With a relatively weak O–O bond energy (188.3 kJ mol<sup>–1</sup> in the gas phase) compared to the C–O bond energy (347.3 kJ mol<sup>–1</sup>) and the N–O bond energy (221.7 kJ mol<sup>–1</sup>), POs and HPOs readily undergo various chemical transformations (e.g., photolysis, thermolysis, hydrolysis, interaction with sulfite, or transition metal ion-mediated Fenton-like reactions), characterized by short lifetimes in the atmosphere.<sup>18,19</sup> HPOs constitute up to 80% of the total mass of the secondary

Received: March 25, 2024

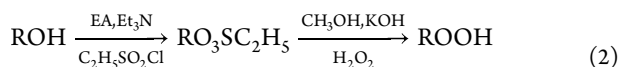
Revised: June 12, 2024

Accepted: June 13, 2024

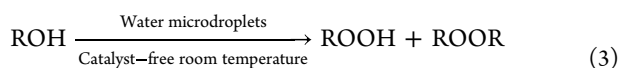
organic aerosols. These aerosols form through atmospheric oxidation of organic substances and contribute, ranging from 10–70%, to the overall mass of particulate matter present in the ambient environment.<sup>19–21</sup> HPOs are also detectable in rainwater at concentrations ranging from 0.1 to 10  $\mu\text{M}$ , likely taken up from the gas phase. The partitioning depends on water solubility for small, volatile POs and on vapor pressure for larger, less water-soluble ones.<sup>22–24</sup> On the other hand, hydroperoxide derivatives are in high demand commercially, with around 90% being utilized by the polymer industry as thermal sources of free radicals in versatile applications.<sup>25</sup> Historically, hydroperoxides were sourced from reactions of hydrogen peroxide with initiators and catalysts, autoxidation with oxygen involving free-radical or nonchain processes, and hydrolysis of metal POs.<sup>26</sup> Now, they are mainly obtained from oxidation of petroleum hydrocarbons in the liquid phase, using air or oxygen in the presence of a catalyst or initiator.<sup>27</sup> While various methods were developed for oxidizing organic substrates using molecular oxygen, achieving efficient, highly selective, and environmentally friendly protocols remains a significant challenge in synthetic chemistry. In this study, we report the one-step, catalyst-free oxidation of alcohols to form HPO (ROOH) and peroxide ether (or dialkyl peroxide) (ROOR). ROOHs and ROORs under ambient conditions, either at the interface of water microdroplets surrounded by alcohol vapor (main emphasis) or alcohol microdroplets surrounded by water vapor. Real-time monitoring of the formation of radical cations by using mass spectrometry (MS) provides compelling evidence for the role of microdroplet interfaces in these reactions. We also present a mechanism for these reactions based on electron transfer at the microdroplet interface. However, the absence of suitable experimental probes complicates the determination of the actual reaction mechanism and the rate constant ( $k$  value) for an intermediate species, leading to the assumption of alternative mechanisms.<sup>28–30</sup> Until now, few approaches have been developed for a mild, catalyst-free, and environmentally friendly synthesis of HPOs. In 2017, Sagadevan et al.<sup>31</sup> developed a method for hydroperoxidation/lactonization of weakly activated C–H bonds in saturated ethereal hydrocarbons using molecular oxygen and red-light excitation under mild conditions. This discovery helped to explain a 35 year-old unresolved mystery regarding the significant variations in the lifetime of singlet  $\text{O}_2$  dependent on the solvent (eq 1).



In 2023, the synthesis of various alkyl hydroperoxides was achieved by OH radical-initiated autoxidation of gas-phase organic compounds (eq 2).<sup>32</sup>



This contrasts with our approach, shown in Eq 3.

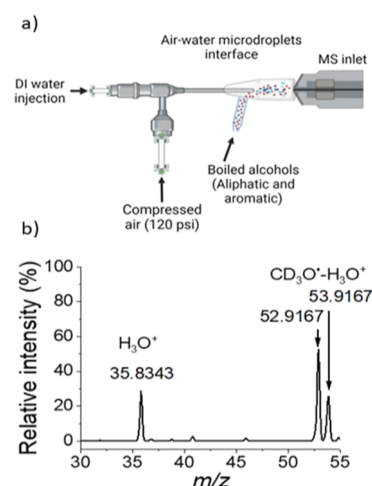


Typical methods for synthesizing hydroperoxides from cyclic and aliphatic alcohols including (a) singlet  $\text{O}_2$ -mediated C–H bond hydroperoxidation of an ethereal hydrocarbon using 765

nm excitation in the presence of  $\text{O}_2$  (1 atm),<sup>31</sup> and (b) gas-phase alcohol dissolved in ethyl acetate (EA) and triethylamine ( $\text{Et}_3\text{N}$ ) in the presence of ethanesulfonyl chloride ( $\text{C}_2\text{H}_5\text{SO}_2\text{Cl}$ ), which converts to  $\text{RO}_3\text{SC}_2\text{H}_5$  and is subsequently transformed to the hydroperoxide by treatment with hydrogen peroxide and base (KOH),<sup>32</sup> have been reported in the literature. To the best of our knowledge, there has been no report involving water microdroplets surrounded by alcohol vapor. The present procedure was performed only on a laboratory scale. One avenue for scaling up might involve releasing microbubbles of alcohol vapor in water. This process could potentially facilitate the translation of our synthetic method into practical industrial applications.

## METHODS

Figure 1a illustrates the experimental setup for the synthesis of various alkyl and aryl ROORs and ROOHs by spraying

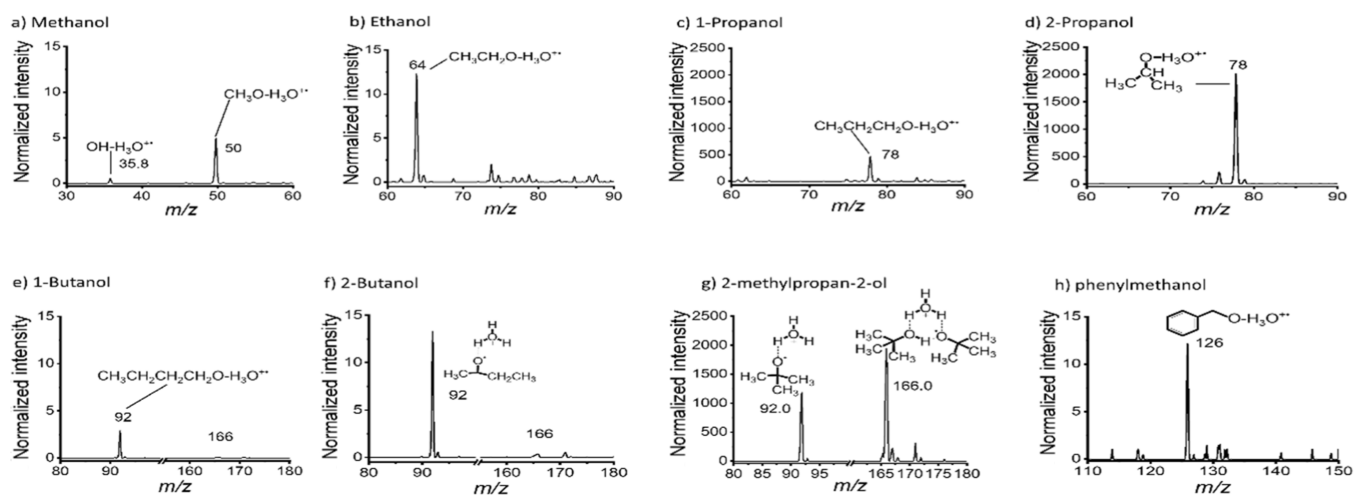


**Figure 1.** Experimental setup is shown in (a) and the resulting mass spectrum in (b) in the presence of deuterated methanol ( $\text{CD}_3\text{OD}$ ).

ultrapure water with a concentric pneumatic nebulizer. Ultrapure deionized (DI) water or deuterated water is fed into the inner core of the sprayer through a silica capillary nozzle (i.d. 70  $\mu\text{m}$ , o.d. 350  $\mu\text{m}$ ) at a flow rate of 10  $\mu\text{L}/\text{min}$ . The liquid water was sprayed under 100 psi compressed air to generate microdroplets. The sprayer is positioned in front of the MS inlet (LTQ XL Orbitrap, Thermo-Fisher, Waltham, MA). Different alcohols are separately introduced to the chamber of sprayed microdroplets by bubbling air in alcohol at room temperature while keeping the alcohol in a boiling water bath. The distance between the nebulizer and MS inlet is approximately 0.4 mm, with the inlet capillary temperature set at 270  $^\circ\text{C}$ . This distance represents the region where oxidation reactions occur between the gas phase and the water microdroplets. Various aliphatic and aromatic alcohols were introduced individually using a stream of compressed air.

## RESULTS AND DISCUSSION

Our setup allows the alcohols to access the air–water interface. They undergo reactions, and the products subsequently diffuse rapidly into the droplet bulk. When deuterated methanol was introduced, multiple new peaks appeared at  $m/z = 53, 54, 55,$  and  $56$ , compared to what is found for  $\text{CH}_3\text{OH}$ , as shown in Figure 1b. These observations signify a hydrogen–deuterium exchange between water and deuterated methanol, resulting in



**Figure 2.** Formation of ROOH and ROOR ions from different alcohol vapors at the interface of air–water microdroplets. Mass spectra of the microdroplets containing (a) methyl hydroperoxide, (b) ethyl hydroperoxide, (c) 1-propyl hydroperoxide, (d) 2-propyl hydroperoxide, (e) 1-butyl hydroperoxide, (f) 2-butyl hydroperoxide, (g) *tert*-butyl hydroperoxide, and (h) benzoyl hydroperoxide.

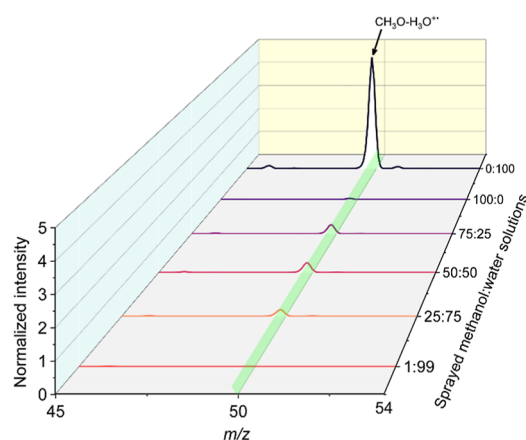
the formation of  $[\text{CD}_3\text{O}-\text{H}_{3-n}\text{D}_n\text{O}]^{+\bullet}$  for  $n \leq 3$ . Furthermore, raising the temperature to the boiling point of water led to an intensification of these peaks, while the peak at  $m/z = 36$  decreased.

Figure 2 presents mass spectra of nebulized water microdroplets enveloped by various alcohols, including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methylpropan-2-ol, and phenylmethanol. To eliminate the influence of temperature, all alcohols were introduced into the chamber while being maintained in a boiling water bath. As reported in our previous studies,<sup>9</sup> sprayed microdroplets exhibit a peak at  $m/z = 36$ , attributed to the formation of  $[\text{OH}-\text{H}_3\text{O}]^{+\bullet}$  (Figure 2a). To assess how the structural variations of alcohols impact the formation of ROORs and ROOHs, the ion current intensities were normalized by dividing them by the peak ion current at  $m/z = 36$ . Introduction of methanol around the microdroplets resulted in a new peak appearing at  $m/z = 50$  (Figure 2a). This peak can be attributed to the formation of  $[\text{CH}_3\text{O}-\text{H}_3\text{O}]^{+\bullet}$ . The appearance of this new peak coincided with a decrease in the intensity of the peak at  $m/z = 36$  (Figure 2a). It is widely recognized that secondary and tertiary alkoxy radical cations exhibit significantly higher stability compared to that of primary alcohols. Our findings align with this well-established trend. Specifically, secondary alcohols such as 2-propanol and 2-butanol exhibit approximately 4-fold stronger peaks at  $m/z = 78$  and 92, respectively, in comparison to their primary isomers, 1-propanol and 1-butanol. In addition, 1-butanol displays only modest solubility, whereas *sec*-butanol demonstrates significantly higher solubility. On the other hand, *t*-butanol is completely miscible with water. The presence of the hydroxyl group in the molecule imparts polarity, enhancing water solubility, while the longer hydrocarbon chain diminishes this polarity and thus decreases solubility (Figure 2e–g). Furthermore, the tertiary alcohol, 2-methylpropan-2-ol (*t*-butanol), displays a robust peak at  $m/z = 92$ , attributed to the formation of  $[\text{t-BuO}-\text{H}_3\text{O}]^{+\bullet}$ . This peak is approximately 80 times more intense than that of its secondary counterpart. Another highly prominent peak at  $m/z = 166$  emerges, indicating the formation of a six-membered cyclic structure through the hydrogen bonding between the hydrogen atoms of the alcohol and the hydronium ion, with the oxygen of the

alkoxy radical, namely,  $[\text{t-BuOH}\cdots\text{t-BuO}\cdots\text{H}_3\text{O}]^{+\bullet}$ . Tandem mass spectrometry (Figure S1) confirms this structure. In the context of aromatic alcohols, they are known to produce highly stable radicals, which would typically lead us to anticipate much more intense peaks in their mass spectra. However, as illustrated in Figure 2h, when examining phenylmethanol, we observe that while a peak does indeed appear at the anticipated  $m/z$  position, its intensity falls short of our expectations. This phenomenon can be attributed to the relatively high boiling point (205 °C) of phenyl methanol. We needed to use heated oil rather than boiling water to obtain a sufficient vapor pressure. Consequently, the presence of this alcohol around the microdroplets is quite restricted, resulting in a limited formation of the radical cation and subsequent detection in mass spectrometric analysis. This approach leads to the formation of hydroperoxide and peroxide from alcohol vapor at the interface of the air–water microdroplets. In this study, we investigated the termination products of alcohol compounds (ROH) at the air–water interface of microdroplets by introducing *t*-butyl alcohol vapor to surround the sprayed water microdroplets and analyzed the collected microdroplets by liquid chromatography using mass spectrometric detection. Our results confirmed the formation of *t*-butyl peroxide and *t*-butyl hydroperoxide (Figure S2a,b). The absence of suitable experimental probes complicates the determination of the actual reaction mechanism and the rate constant ( $k$  value) for an intermediate species, leading to the assumption of alternative mechanisms.<sup>28–30</sup> Similarly, we added alcohol vapors to the sprayed deuterated water microdroplets and generated deuterium peaks as additional features to analyze our previous results in Figure 3. Figure S3 shows the mass spectrum of the observed corresponding formation of  $[\text{RO}-\text{H}_{3-n}\text{D}_n\text{O}]^{+\bullet}$  ions from alcohol vapors (Figure 3a–f). The four suspected deuterium peaks located at  $m/z$  of alcohol vapors represent the hydroperoxide products, respectively. We were able to observe all hydroperoxide products, which indicate the occurrence of electron transfer at the gas–microdroplet interface for the formation of radicals.

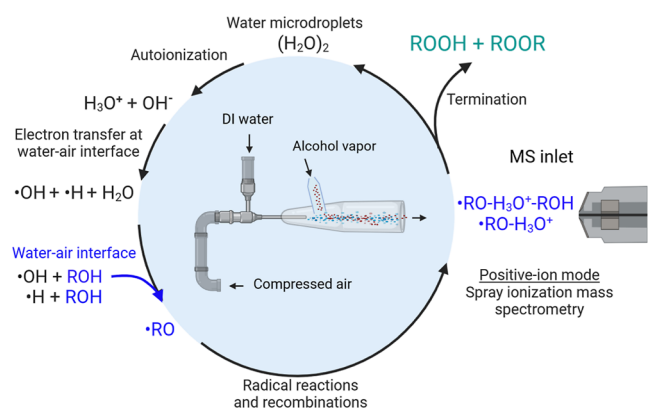
To investigate the mechanisms of hydroxyl formation and alcohol oxidation at the surface of microdroplets, we also conducted a study involving spraying microdroplets of different methanol–water mixtures with air in the presence





**Figure 3.** Formation of  $\text{CH}_3\text{O}-\text{H}_3\text{O}^{+\bullet}$  from various sprayed ratios of methanol/water mixtures. 1:99 up to 100:0 mixtures are sprayed in air at 50% relative humidity. For comparison, the 0:100 water microdroplets are sprayed in the presence of methanol vapor in air at 50% relative humidity.

of 50% relative humidity. This was compared to the results with pure water microdroplets in the presence of methanol vapor in air. We were intrigued by these oxidations, considering that alcohol lacks readily available sites for oxygen atom transfer, unlike water, which forms  $\text{H}_3\text{O}^+$  as demonstrated in Figure 4. The absence of  $\text{H}_3\text{O}^+$  formation in



**Figure 4.** Proposed chemistry cycle for the formation of hydroperoxides from alcohol vapors in contact with water microdroplets.

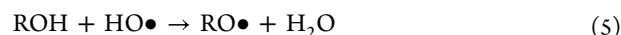
methanol sprayed microdroplets provides a strong barrier for the formation of ROORs and ROOHs. Figure 3 illustrates a small portion of hydroperoxide formation through alcohol oxidation, showing that the radical formation mechanism starts at the air–water interface of the water microdroplets. This raises the question of the significance of hydroperoxide formation-dependent alcohol oxidation at the gas–water interface. However, in the absence of methanol within water microdroplets during the water oxidation step in Figure 4, we observed and characterized the highest hydroperoxide ions at the gas–water interface in the presence of alcohol vapors. The intrinsic surface potential of water microdroplets may drive asymmetric charge separation during microdroplet fission, contact electrification, and the oxidation of water,<sup>7,8</sup> possibly serving as a key factor in the oxidation of alcohols at the gas–water microdroplet interface. Based on the experimental results, primary and secondary alcohols contribute to the formation of both ROOH and ROOR, whereas tertiary

alcohols just make a contribution to ROOH formation, as shown in Figure S2c. The introduction of methanol into water microdroplets forms  $m/z$  peaks at 45, 46, 61, and 62, which can be attributed to methyl hydroperoxide and dimethyl peroxide formation. These observations in the negative mode confirm the radical pathway ( $\text{CH}_3\text{O}^{\bullet-}$ ). Similarly, when ethanol is introduced under similar conditions,  $m/z$  peaks at 61, 62, 89, and 90 emerge, indicating the formation of ethyl hydroperoxide and diethyl peroxide. By introducing 2-propanol into a splash of sprayed water microdroplets, we observed an  $m/z$  peak at 75, corresponding to the formation of the isopropyl peroxy anion ( $\text{C}_3\text{H}_7\text{OO}^{\bullet-}$ ). A peak at  $m/z$  117 is also detected, indicative of di-isopropyl peroxide. On the other hand, mass spectrometry in negative mode for tertiary alcohols predominantly indicates the formation of HPOs. For example, the introduction of *t*-butyl alcohol vapor to sprayed water microdroplets elicits a peak at  $m/z = 89$ , which can be attributed to the formation of *t*-butyl peroxy anions in the gas phase, as depicted in Figure S2c. Notably, we do not observe peaks that would confirm the formation of di-*t*-butyl peroxide. These findings confirm that the mechanism for secondary and tertiary alcohols involves the carbocation form. This result confirms the peroxy radical anions ( $\text{RO}_2^{\bullet-}$ ) pathway in our experimental setup. Therefore, the production of peroxy radical anions ( $\text{RO}_2^{\bullet-}$ ) implies that the introduction of vapor alcohols to the sprayed water microdroplets must be an alternative pathway to  $\text{RO}_2$  formation at room temperature. The mechanism of hydroxyl formation and alcohol oxidation at the surface of microdroplets provides insights into the role of spontaneously formed radicals on water microdroplet surfaces in the oxidation of alcohols. This approach aims to contribute to our understanding of organic peroxide synthesis, particularly in atmospheric aerosols. The typical reactions for the formation of pathways of atmospheric organic peroxides are stabilized Criegee intermediates and organic peroxy radicals at lower temperatures.<sup>33–35</sup> Our methods show the potential of our findings to develop a novel synthetic method that leverages the insights gained from our investigation. Additionally, we explore the implications of our results for understanding the sources of organic peroxides in the atmosphere, particularly through the oxidation of alcohols at the gas–water microdroplet interface. A few plausible mechanisms have been proposed to account for the conversion of alcohol vapor into organic peroxides by water microdroplets. Our recent studies have clearly provided strong evidence for the formation of  $\text{H}\bullet$ ,  $\text{HO}\bullet$ , and  $\text{O}_2^{\bullet-}$  radicals on the air–water interface of a microdroplet using the electron paramagnetic resonance technique.<sup>9,36</sup>

These intermediate radicals can react with ROH to produce  $\text{RO}\bullet$  by means of chemical transformations



and

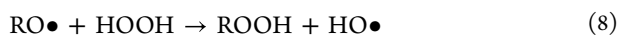


It might be questioned what evidence we have for the existence of  $\text{RO}\bullet$ . As shown in Figure S4, we were able to trap this alkoxy radical using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), which was detected using a mass spectrometric technique. It is also expected that  $\text{RO}\bullet$  will go on to form organic peroxides and hydroperoxides by such reactions as





and



The hydrogen peroxide is already known to be spontaneously formed in water microdroplets, and the presence of  $\text{O}_2^{\bullet-}$  can further increase its concentration by the following reaction



We summarize this process in Figure 4. Many more related reactions can be presented and further experimental studies for the formation of organic peroxides and hydroperoxides are needed.

## CONCLUSIONS

We have found that water microdroplets surrounded by alcohol vapor (ROH) readily transform into hydroperoxide ROOH and peroxide ROOR molecules. This process happens at the surface of water microdroplets in which different radical species react with ROH to make alkoxy radicals  $\text{RO}\bullet$ . Further work needs to be carried out to establish the reaction rate for this process, but preliminary data suggest that this reaction occurs rapidly. These reactions are expected to be an important source of organic peroxides in atmospheric aerosols.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c04092>.

MS<sup>2</sup> spectrum of the peak at  $m/z$  of 166; evaluation of the (a) LC-ESI-MS of *t*-butyl peroxide, (b) LC-ESI-MS of *t*-butyl hydroperoxide, and (c) negative mode MS of alcohol vapors introduced to sprayed water microdroplets; evaluation of the HDX-MS of multiple alcohol vapors with deuterated water microdroplets; and mass spectra of water microdroplets spiked with DMPO (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We acknowledge the financial support from the Air Force Office of Scientific Research through the Multidisciplinary

University Research Initiative (MURI) Program (AFOSR FA9550-21-1-0170). We are deeply indebted to Abbas Rahmati (University of Isfahan), who provided us with many suggestions concerning the mechanism for the formation of organic peroxides from water microdroplets.

## REFERENCES

- (1) Ghosh, J.; Mendoza, J.; Cooks, R. G. Accelerated and Concerted Aza-Michael Addition and SuFEx Reaction in Microdroplets in Unitary and High-Throughput Formats. *Angew. Chem., Int. Ed.* **2022**, *61* (50), No. e202214090.
- (2) Xiong, H.; Lee, J. K.; Zare, R. N.; Min, W. Strong Electric Field Observed at the Interface of Aqueous Microdroplets. *J. Phys. Chem. Lett.* **2020**, *11* (17), 7423–7428.
- (3) Hao, H.; Leven, I.; Head-Gordon, T. Can electric fields drive chemistry for an aqueous microdroplet? *Nat. Commun.* **2022**, *13* (1), 280.
- (4) Martins-Costa, M. T. C.; Ruiz-López, M. F. Electrostatics and Chemical Reactivity at the Air-Water Interface. *J. Am. Chem. Soc.* **2023**, *145* (2), 1400–1406.
- (5) Ruiz-Lopez, M. F.; Francisco, J. S.; Martins-Costa, M. T. C.; Anglada, J. M. Molecular reactions at aqueous interfaces. *Nat. Rev. Chem.* **2020**, *4* (9), 459–475.
- (6) Judd, K. D.; Parsons, S. W.; Eremin, D. B.; Fokin, V. V.; Dawlaty, J. M. Visualizing partial solvation at the air-water interface. *Chem. Sci.* **2024**, *15*, 8346–8354.
- (7) Lee, J. K.; Walker, K. L.; Han, H. S.; Kang, J.; Prinz, F. B.; Waymouth, R. M.; Nam, H. G.; Zare, R. N. Spontaneous generation of hydrogen peroxide from aqueous microdroplets. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116* (39), 19294–19298.
- (8) Mehrgardi, M. A.; Mofidfar, M.; Zare, R. N. Sprayed Water Microdroplets Are Able to Generate Hydrogen Peroxide Spontaneously. *J. Am. Chem. Soc.* **2022**, *144* (17), 7606–7609.
- (9) Mofidfar, M.; Mehrgardi, M. A.; Xia, Y.; Zare, R. N. Dependence on relative humidity in the formation of reactive oxygen species in water droplets. *Proc. Natl. Acad. Sci. U.S.A.* **2024**, *121* (12), No. e2315940121.
- (10) Wang, S.; Zhao, Y.; Chan, A. W. H.; Yao, M.; Chen, Z.; Abbott, J. P. D. Organic Peroxides in Aerosol: Key Reactive Intermediates for Multiphase Processes in the Atmosphere. *Chem. Rev.* **2023**, *123* (4), 1635–1679.
- (11) Jackson, A. V.; Hewitt, C. N. Atmosphere Hydrogen Peroxide and Organic Hydroperoxides: A Review. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29* (2), 175–228.
- (12) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103* (12), 4605–4638.
- (13) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I.-H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma, J.; Kontkanen, J.; Nieminen, T.; Kurtén, T.; Nielsen, L. B.; Jørgensen, S.; Kjaergaard, H. G.; Canagaratna, M.; Maso, M. D.; Berndt, T.; Petäjä, T.; Wahner, A.; Kerminen, V.-M.; Kulmala, M.; Worsnop, D. R.; Wildt, J.; Mentel, T. F. A large source of low-volatility secondary organic aerosol. *Nature* **2014**, *506* (7489), 476–479.
- (14) Tröstl, J.; Chuang, W. K.; Gordon, H.; Heinritzi, M.; Yan, C.; Molteni, U.; Ahlm, L.; Frege, C.; Bianchi, F.; Wagner, R.; et al. The role of low-volatility organic compounds in initial particle growth in the atmosphere. *Nature* **2016**, *533* (7604), 527–531.
- (15) Bianchi, F.; Kurtén, T.; Riva, M.; Mohr, C.; Rissanen, M. P.; Roldin, P.; Berndt, T.; Crouse, J. D.; Wennberg, P. O.; Mentel, T. F.; et al. Highly oxygenated organic molecules (HOM) from gas-phase autoxidation involving peroxy radicals: A key contributor to atmospheric aerosol. *Chem. Rev.* **2019**, *119* (6), 3472–3509.
- (16) Lee, M.; Heikes, B. G.; O'Sullivan, D. W. Hydrogen peroxide and organic hydroperoxide in the troposphere: a review. *Atmos. Environ.* **2000**, *34* (21), 3475–3494.

- (17) Walker, J.; Philip, S.; Martin, R.; Seinfeld, J. Simulation of nitrate, sulfate, and ammonium aerosols over the United States. *Atmos. Chem. Phys.* **2012**, *12* (22), 11213–11227.
- (18) Glowacki, D. R.; Pilling, M. J. Unimolecular Reactions of Peroxy Radicals in Atmospheric Chemistry and Combustion. *ChemPhysChem* **2010**, *11* (18), 3836–3843.
- (19) Wang, S.; Zhao, Y.; Chan, A. W.; Yao, M.; Chen, Z.; Abbatt, J. P. Organic peroxides in aerosol: key reactive intermediates for multiphase processes in the atmosphere. *Chem. Rev.* **2023**, *123* (4), 1635–1679.
- (20) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N.; George, C.; Goldstein, A.; et al. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, *9* (14), 5155–5236.
- (21) Jimenez, J. L.; Canagaratna, M.; Donahue, N.; Prevot, A.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N.; et al. Evolution of organic aerosols in the atmosphere. *science* **2009**, *326* (5959), 1525–1529.
- (22) Liang, H.; Chen, Z.; Huang, D.; Zhao, Y.; Li, Z. Impacts of aerosols on the chemistry of atmospheric trace gases: a case study of peroxides and HO<sub>2</sub> radicals. *Atmos. Chem. Phys.* **2013**, *13* (22), 11259–11276.
- (23) Hellpointner, E.; Gäb, S. Detection of methyl, hydroxymethyl and hydroxyethyl hydroperoxides in air and precipitation. *Nature* **1989**, *337* (6208), 631–634.
- (24) O'Sullivan, D. W.; Lee, M.; Noone, B. C.; Heikes, B. G. Henry's Law Constant Determinations for Hydrogen Peroxide, Methyl Hydroperoxide, Hydroxymethyl Hydroperoxide, Ethyl Hydroperoxide, and Peroxyacetic Acid. *J. Phys. Chem.* **1996**, *100* (8), 3241–3247.
- (25) Sanchez, J.; Myers, T. N. Peroxides and Peroxide Compounds, Organic Peroxides. *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley, 2000.
- (26) Alexandrov, Y. A. Preparation, Properties and Applications of Organo-Silicon Peroxides. *J. Organomet. Chem.* **1982**, *238* (1), 1–78.
- (27) Suresh, A. K.; Sharma, M. M.; Sridhar, T. Engineering Aspects of Industrial Liquid-Phase Air Oxidation of Hydrocarbons. *Ind. Eng. Chem. Res.* **2000**, *39* (11), 3958–3997.
- (28) Fishbein, J. C.; Jencks, W. P. Elimination reactions of beta-cyano thioethers: evidence for a carbanion intermediate and a change in rate-limiting step. *J. Am. Chem. Soc.* **1988**, *110* (15), 5075–5086.
- (29) Jencks, W. P. Ingold Lecture. How does a reaction choose its mechanism? *Chem. Soc. Rev.* **1981**, *10* (3), 345–375.
- (30) Kumar, A.; Mondal, S.; Mofidfar, M.; Zare, R. N.; Banerjee, S. Capturing Reactive Carbanions by Microdroplets. *J. Am. Chem. Soc.* **2022**, *144* (17), 7573–7577.
- (31) Sagadevan, A.; Hwang, K. C.; Su, M.-D. Singlet oxygen-mediated selective C-H bond hydroperoxidation of etheral hydrocarbons. *Nat. Commun.* **2017**, *8* (1), 1812.
- (32) Hu, Z.; Di, Q.; Liu, B.; Li, Y.; He, Y.; Zhu, Q.; Xu, Q.; Dagaut, P.; Hansen, N.; Sarathy, S. M.; Xing, L.; Truhlar, D. G.; Wang, Z. Elucidating the photodissociation fingerprint and quantifying the determination of organic hydroperoxides in gas-phase autoxidation. *Proc. Natl. Acad. Sci. U.S.A.* **2023**, *120* (10), No. e2220131120.
- (33) Dai, Y.; Chen, Z.; Qin, X.; Dong, P.; Xu, J.; Hu, J.; Gu, L.; Chen, S. Hydrolysis reactivity reveals significant seasonal variation in the composition of organic peroxides in ambient PM<sub>2.5</sub>. *Sci. Total Environ.* **2024**, *927*, 172143.
- (34) Chhantyal-Pun, R.; Khan, M. A. H.; Zachhuber, N.; Percival, C. J.; Shallcross, D. E.; Orr-Ewing, A. J. Impact of Criegee Intermediate Reactions with Peroxy Radicals on Tropospheric Organic Aerosol. *ACS Earth Space Chem.* **2020**, *4* (10), 1743–1755.
- (35) Orlando, J. J.; Tyndall, G. S.; Wallington, T. J. The Atmospheric Chemistry of Alkoxy Radicals. *Chem. Rev.* **2003**, *103* (12), 4657–4690.
- (36) Chen, X.; Xia, Y.; Zhang, Z.; Hua, L.; Jia, X.; Wang, F.; Zare, R. N. Hydrocarbon Degradation by Contact with Anoxic Water Microdroplets. *J. Am. Chem. Soc.* **2023**, *145* (39), 21538–21545.