



Cite this: *Environ. Sci.: Atmos.*, 2025, 5, 737

A perspective on the reactions of organic peroxy radicals with HO₂

Niklas Illmann *

The chemistry of organic peroxy radicals (RO₂) is crucial for ozone and secondary organic aerosol formation in the troposphere. The level of nitrogen monoxide (NO) exerts a major control on further reactions of peroxy radicals. The research on these reactions in the absence of NO has been receiving increasing attention recently. The current studies under these conditions, typically associated with pristine environments, are focused on understanding the formation of highly oxygenated organic molecules (HOMs) *via* autoxidation and generation of accretion products, which supposedly result from peroxy radical permutation reactions (RO₂ + RO₂). Apart from the potential OH production from some oxygenated peroxy radicals, there is less research activity on the reactions of peroxy radicals with HO₂. This article reviews the existing literature data available on RO₂ + HO₂ reactions and highlights the gaps where future research is required. To date, limited information has been provided on the reactions of HO₂ with functionalized RO₂, particularly for β-hydroxyalkyl peroxy radicals, carbonyl-substituted peroxy radicals other than acyl peroxy, and peroxy radicals containing at least two functionalities. In addition, the temperature dependence of product branching ratios is not well established. Future studies targeting the influence of RO₂ + HO₂ on the tropospheric HO_x (=OH + HO₂) budget should ideally enlarge the dataset of OH yields from various peroxy radical structures. This also highlights the need to broaden the investigations on the formed hydroperoxides, whose gas-phase chemistry is not well known.

Received 14th February 2025
Accepted 6th June 2025

DOI: 10.1039/d5ea00023h

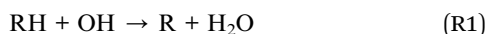
rsc.li/esatmospheres

Environmental significance

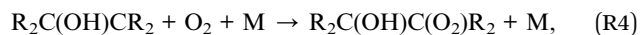
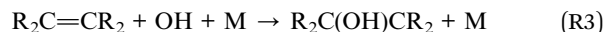
Organic peroxy radicals (RO₂) are key species involved in chain reactions that yield tropospheric ozone and secondary organic aerosols. Emission control strategies, upon international policy agreements, lead to a continuous reduction in nitrogen oxides. Chemical conditions commonly associated with pristine regions are thus expected to become more frequent. Peroxy radical reactions favoured under these conditions, such as unimolecular isomerization, permutation reactions or reactions of RO₂ with HO₂, are complex, and experiments targeting these chemical regimes are challenging. The present work offers an overview of the current state of knowledge and uncovers gaps that need to be addressed to draw a comprehensive picture of the importance of peroxy radical reactions with HO₂ in atmospheric chemistry.

Introduction

Organic peroxy radicals (RO₂) are essential intermediates in the atmospheric oxidation of volatile organic compounds (VOCs). These are emitted into the troposphere predominantly from biogenic¹ but also from anthropogenic sources. Besides its central role in the formation of tropospheric ozone and secondary organic aerosol (SOA), RO₂ chemistry controls the recycling of reactive radicals such as OH (*e.g.* ref. 2 and 3). Once formed through VOC oxidation, *e.g.* in the OH-initiated oxidation either *via* abstraction



or addition (R3) pathways,



the further fate of a specific organic peroxy radical includes unimolecular isomerization (*e.g.* H shift reactions) and bimolecular reactions, such as with nitrogen oxides (NO and NO₂), halogen oxides (ClO, BrO, and IO) or radicals (OH, HO₂, RO₂, and NO₃). The competitiveness of a single process depends heavily on the ambient conditions and the structure of the individual RO₂ species. For instance, NO_x (=NO + NO₂) plays a central role in efficient radical-recycling, including the regeneration of OH and causing the formation of tropospheric ozone (Fig. 1). The reaction with NO typically represents the major RO₂ loss in air masses influenced by anthropogenic activities.

University of Wuppertal, Institute for Atmospheric and Environmental Research, Gaußstraße 20, 42119 Wuppertal, Germany. E-mail: illmann@uni-wuppertal.de



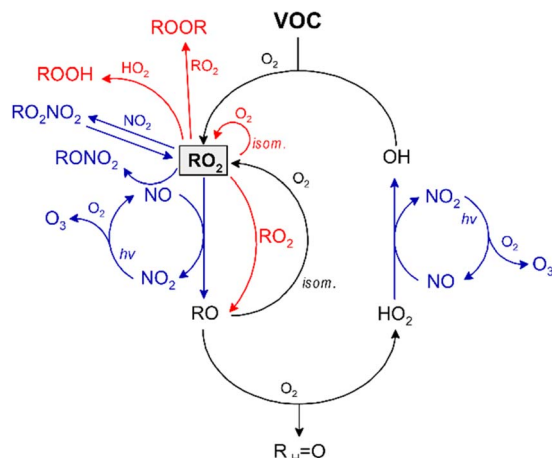


Fig. 1 Simplified, generic scheme for the major paths of RO_2 chemistry under NO_x -dominated conditions (blue) and NO_x -poor conditions, where other pathways become competitive (red).

The knowledge of peroxy radical chemistry, which is incorporated into chemistry-transport models, is crucial for both forecasting local air pollution episodes on regional scale and predicting global earth-climate interactions. Although our understanding of RO_2 chemistry is continuously evolving and has led to improvements in chemistry models, there is always a need to critically review the available chemical mechanisms and experimental set-ups. One of the famous turn-around examples is the unimolecular isomerization of peroxy radicals, which is found to be competitive with bimolecular processes in the troposphere,^{4,5} but, to be observed, requires simulating atmospheric conditions (e.g. concentrations) in the experiment as closely as possible.

Apart from elucidating the HO_x ($=\text{OH} + \text{HO}_2$) budget in forested regions (e.g. ref. 4 and 6), research on the atmospheric oxidation of VOC during the last 15 years has considerably focused on understanding the mechanisms yielding SOA. The detection of highly oxygenated organic molecules (HOMs) formed through a chain of unimolecular isomerization steps called autoxidation initiated the allocation of tremendous research effort in a rapidly growing scientific community (see Bianchi *et al.*⁷ and references therein). However, the formation of low-volatility vapours, which act as aerosol precursors, is not limited to unimolecular processes. Several observations suggest the relevance of accretion products (organic peroxides, ROOR) formation in the permutation reactions (self- and cross-reactions) of (HOM) peroxy radicals, which terminate autoxidation (e.g. ref. 8–10).

In contrast to the increasing number of reports on RO_2 isomerization and permutation reactions, there are very few recent studies on the reactions of peroxy radicals with HO_2 except for some short, renewed interest following the detection of discrepancies in the HO_x budget in forested regions dominated by isoprene emissions (e.g. ref. 6 and 11). The present perspective article reviews the available information on this particular class of organic peroxy radical reactions. In addition, it aims to discuss the challenges that occur when $\text{RO}_2 + \text{HO}_2$ are being investigated experimentally and, finally, gaps that require further research are identified.

Experimental and analytical approaches

Retrieving information on $\text{RO}_2 + \text{HO}_2$ reactions requires experimental approaches and analytical instrumentation that allow the time-resolved detection of either radicals or closed-shell species or both. Although the sections below are spiked with both experimental and analytical information, a brief overview is provided in this section. However, a detailed evaluation and a complete representation of the available methods are beyond the scope of the present work. In addition, there exist a number of developments in radical detection that have not yet been applied to investigate $\text{RO}_2 + \text{HO}_2$ chemistry.

Traditionally, product yields and branching ratios have been determined in static systems, such as simulation chambers, while flow tube applications are commonly used for absolute rate coefficient determination. The first investigations on $\text{RO}_2 + \text{HO}_2$ reactions date back to the work by Cox and Tyndall,^{12,13} who investigated the kinetics of $\text{CH}_3\text{O}_2 + \text{HO}_2$ using molecular modulation spectrometry. In these studies, methyl peroxy radicals were generated by the photolysis of CH_4/Cl_2 mixtures in the presence of oxygen and a relative increase in HO_2 was achieved by the addition of H_2 . This pioneering experimental approach has been adapted ever since in many of the later studies targeting $\text{RO}_2 + \text{HO}_2$ reactions, namely the generation of a specific peroxy radical by the reaction of an organic precursor with Cl atoms and the increase in HO_2 relative to RO_2 by the addition of an HO_2 precursor, such as H_2 , methanol, and formaldehyde. In simulation chamber studies, this approach has been applied to determine product branching ratios by systematically varying the HO_2/RO_2 ratio. This ranges from a system usually dominated by RO_2 permutation reactions, at zero HO_2 precursor, to a system that favours $\text{RO}_2 + \text{HO}_2$ reactions when the concentrations of the HO_2 precursor are sufficiently high. In the ideal case, the product branching ratios for $\text{RO}_2 + \text{HO}_2$ reactions are then obtained from the observed product yields.

In chamber studies, branching ratios were derived from stable end-product analysis of continuously irradiated reaction mixtures mostly by means of Fourier transform infrared spectroscopy (FTIR).^{14–33} In some instances, organic hydroperoxides were measured by the selective reaction of hydroperoxides with peroxidase.^{27,32} The organic hydroperoxides are first trapped in the liquid phase inside a stripping coil attached to the simulation chamber and collected for high performance liquid chromatography (HPLC) analysis. After separation on the column, a reagent consisting of horseradish peroxidase (HRP) and *p*-hydroxyphenylacetic acid is added. The enzyme catalyses a reaction between the hydroperoxide and *p*-hydroxyphenylacetic acid, yielding a dimer whose fluorescence is measured following excitation.³⁴ It is worth noting that the HRP-fluorescence method coupled to HPLC has been applied more regularly to investigations of ozonolysis systems, particularly for detecting H_2O_2 and hydroxyalkyl hydroperoxides (e.g. Hasson *et al.*³⁵ and references therein). The Caltech group has developed a chemical ionisation mass spectrometry (CIMS)



instrument based on clustering with CF_3O^- for detecting hydroperoxides.³⁶ The technique was successfully tested against the HPLC-fluorescence method in the field and subsequently used in numerous investigations, including $\text{RO}_2 + \text{HO}_2$ chemistry.^{36–39} Apart from stable end-products, Winiberg *et al.* were the first to directly quantify OH formation from $\text{RO}_2 + \text{HO}_2$ chemistry in a chamber study through detection with the Fluorescence Assay by Gas Expansion (FAGE) method based on laser-induced fluorescence (LIF).³³

In flow tube applications, peroxy radical generation was commonly initiated by flash^{18,19,40–52} or laser photolysis^{24,53–61} of $\text{VOC}/\text{Cl}_2/\text{HO}_2$ -precursor or $\text{VOC}/\text{H}_2\text{O}_2$ mixtures or, less often, by molecular modulation methods^{12,13,62,63} or discharge flow.^{64,65} Time-resolved ultraviolet (UV) absorption spectroscopy has often been used to monitor peroxy radical species. Rate coefficients are finally obtained by fitting kinetic parameters to the decay rates recorded for the respective species. The UV spectra of small peroxy radicals have been critically reviewed in the literature.⁶⁶ A larger set of absorption cross sections can be found in the Mainz database.⁶⁷

Information on branching ratios was obtained from flow tube experiments in some cases for OH- and O_3 -forming pathways by means of either UV (O_3),^{42,58,60} transient absorption (O_3),⁵⁹ or IR-wavelength-modulated spectroscopy (OH),^{60,61} CIMS (OH, O_3),^{64,65} and LIF (OH).^{56,59} In contrast, there are a few examples of absolute rate coefficient determinations by simulation chamber experiments. Moortgat *et al.*⁶⁸ obtained the rate coefficient for $\text{CH}_3\text{O}_2 + \text{HO}_2$ by the modulated photolysis of acetaldehyde/air mixtures in a 44 L quartz cell. Winiberg *et al.*³³ obtained the absolute rate coefficient for $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ by global modelling of the reaction system. Rate coefficients for all pathways of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction were optimized individually to match the experimental data over a range of conditions. More recently, Østerstrøm *et al.*⁶⁹ redetermined the rate coefficient for the reaction of methyl peroxy with HO_2 . Both CH_3O_2 and HO_2 were detected by FAGE-LIF, and rate coefficients were obtained by applying a numerical model used to fit the temporal decay of both radical species. In contrast to common flash photolysis applications, the authors used a simulation chamber (HIRAC, University of Leeds) to build up steady-state radical concentrations by irradiating $\text{CH}_4/\text{CH}_3\text{OH}/\text{Cl}_2/\text{air}$ mixtures for about 5 min before monitoring the temporal decay of CH_3O_2 and HO_2 after switching off the lamps. This approach has led to substantially lower peroxy radical concentrations than those typically found for kinetic studies in flow tube systems.

Although most kinetic studies relied on UV absorption, a number of methods for peroxy radical detection, including matrix isolation and electron spin resonance spectroscopy (MIESR),^{70,71} laser-induced fluorescence,^{72–78} peroxy radical chemical amplification (PERCA),^{79–91} CIMS^{92–116} and spectroscopic approaches such as cavity ring-down (CRD)^{117–125} or wavelength modulation techniques,^{57,60,61,126–129} were deployed in published works, increasing in the last two decades. These methods differ primarily in the level of chemical speciation of the detected radical species.

The MIESR method is an offline technique that relies on cryofocusing of radicals at 77 K prior to quantifying using electron spin resonance spectroscopy.^{70,71} MIESR can differentiate HO_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ from other RO_2 . The method was developed and predominantly used by the research groups at Forschungszentrum Jülich.

The original FAGE-LIF method is selective for OH but also represents an established method for HO_2 quantification. In essence, HO_2 is detected as OH after titrating the HO_2 with NO. The approach has been expanded for the detection of RO_2 in a second channel (RO_xLIF) by applying a two-stage process that consists of chemical conversion of RO_x ($=\text{RO}_2 + \text{RO} + \text{HO}_2 + \text{OH}$) into OH.⁷⁶ Discrimination between HO_2 and RO_2 is achieved in this set-up by modulating the chemical conversion.⁷⁶ The fundamentals of the FAGE technique and possible interferences have been described in detail in several reviews.^{130–132} More recently, Onel *et al.*⁷⁸ presented an adaptation of FAGE for the sensitive and selective quantification of CH_3O_2 by detecting the off-resonant LIF of CH_3O formed upon the addition of NO.

Chemical amplification techniques rely on efficient radical recycling in the presence of NO. In the original PERCA approach, pioneered by Cantrell and Stedman,^{79,80} amplified NO_2 formed upon the addition of NO and CO is used for peroxy radical quantification. Several techniques have been applied to quantify the resultant amplified NO_2 , including luminol-chemiluminescence,^{79–83,85,87} laser-induced fluorescence,⁸⁶ cavity-enhanced absorption spectroscopy (CEAS)⁹⁰ and cavity ring-down spectroscopy (CRDS).^{88,89} PERCA instruments consequently yield a sum parameter RO_x . Wood *et al.*⁹¹ presented a chemical amplification technique (ECHAMP) based on ethane instead of carbon monoxide. In the approach presented by Reiner *et al.*,⁸⁴ carbon monoxide is replaced by SO_2 and the resultant H_2SO_4 is detected by CIMS. A separation between HO_2 and RO_2 is achieved by modulating the NO/O_2 ratio.¹³³

CIMS is applied to detect peroxy radicals using various reagent ions, such as $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$,^{97,99,101–103,106–108,113,115} NH_4^+ ,¹¹⁴ O_2^+ ,⁹² NO_3^- ,^{109,110} I^- ,^{94,111} Br^- ,^{112,116} $\text{O}_2^{-95,96}$ or SF_6^- .^{64,65,93,94,98,104,106,107} These ionisation schemes differ primarily in the resulting ions and their ability to detect specific classes of peroxy radicals. For instance, although $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, NH_4^+ and NO_3^- result in cluster ions, RO_2 were detected as parent ions in O_2^- and SF_6^- mode.^{93–96,98,100} Exceptions to the SF_6^- mode are HO_2 and CH_3O_2 , which are detected as SF_4O_2^- and FO_2^- , respectively.^{64,65,106,107}

A number of studies have provided evidence that $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ can detect different alkyl peroxy^{97,99,101–103,106–108,113,115} and bicyclic peroxy radicals.^{106–108} Both I^- and SF_6^- were found to be suitable for measuring acyl peroxy radicals, particularly acetyl peroxy.^{93,94,98} HO_2 detection has been successfully proven by clustering with I^- (ref. 111) or Br^- ,^{112,116} while the detection of highly oxidized RO_2 has been reported by clustering with NO_3^- .^{109,110} CRD approaches have been developed in the near-infrared and used for the detection of CH_3O_2 ,^{117,121,124,125} $\text{C}_2\text{H}_5\text{O}_2$,^{117,123} hydroxyalkyl peroxy,¹¹⁹ acetyl peroxy,^{124,125} acetyl peroxy¹²⁵ and particularly HO_2 .^{118,120,122,123,125}

The applicability of these techniques to pulsed photolysis/flow tube applications and chamber experiments depends on



the respective detection limits, time resolution and the chemical speciation of radical species. For example, flow tube experiments require a high time resolution to enable monitoring of the temporal decay of radicals but result in radical concentrations that are typically orders of magnitude larger than those in simulation chambers.

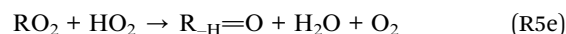
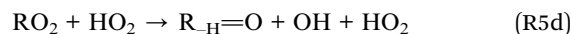
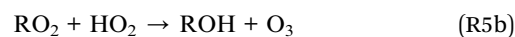
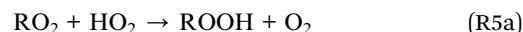
An overview of RO₂ + HO₂

Based on the body of kinetic data published since those of Cox and Tyndall^{12,13} (Table 1), it is established that rate coefficients for the title reactions should lie in the range of $(0.5\text{--}2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at room temperature. They tend to be larger in the case of β -hydroxy-substituted peroxy radicals, such as those resulting from the addition of OH to an unsaturated organic compound, while substitution with halogen atoms appears to slow down the reactivity towards HO₂ for specific substitution patterns (Table 1). Overall, RO₂ + HO₂ reactions are thus rather rapid. The variation in the rate coefficient values spans a factor of roughly only 4–5 and is obviously significantly less pronounced than that of RO₂ permutation reactions, whose rate coefficients span several orders of magnitude (e.g. ref. 135 and 136). The reader should note that in all instances, the values recommended by the International Union of Pure and Applied Chemistry (IUPAC) for room temperature rate coefficients are uncertain by a factor of 1.6–2.¹³⁴ These recommended uncertainty ranges reflect either a limited number of determinations or significant variation in the available data. In the case of methyl and acetyl peroxy, the IUPAC recommendation is identical to the values of the Jet Propulsion Laboratory (JPL).¹³⁷ In contrast, although within the large error limits, the IUPAC and JPL recommendations differ by about 30% for the room temperature rate coefficient for acetyl peroxy + HO₂. Nevertheless, it is well established that room temperature rate coefficients appear to increase with size in the case of the reaction of alkyl peroxy radicals with HO₂. For example, the rate coefficients for both neopentyl and cyclopentyl peroxy (C₅) are almost identical while being a factor of about three larger than that for methyl peroxy (Table 1).

This observation led to the construction of expressions relating the rate coefficient k to the number of carbon atoms.^{55,138,139} For example, Boyd *et al.*⁵⁵ presented a relationship of the form $k = 2.2 \times 10^{-11} \times [1 - \exp(-0.26 \times n)]$ for the room temperature rate coefficients, where n is the number of carbon atoms. Subsequently, this equation was updated by Calvert *et al.*¹⁴⁰ The more recent estimation method by Jenkin *et al.*¹³⁶ introduced a modified expression by relating the rate coefficient to a newly developed parameter n_{CON} , which is the number of carbon, oxygen and nitrogen atoms of the organic group R without counting the peroxy radical oxygen atoms. This approach resulted in two parameterisations that differentiate between acyl peroxy and non-acyl peroxy radicals, considering the fact that the rate coefficients of acyl peroxy radicals appear to be larger than their alkyl analogues. For completeness, it is worth mentioning that two other correlation-type structure–activity relationships have been reported for the prediction of RO₂ + HO₂ rate coefficients. The concept by King *et al.*¹⁴¹ relies

on perturbation frontier molecular orbital (PFMO) theory, and RO₂ + HO₂ rate coefficients are correlated with the single occupied molecular orbital (SOMO) energy of the peroxy radical. Johnson *et al.*¹⁴² proposed a correlation between the logarithm of k and the (calculated) ionisation potential of a structural analogue R–CH=CH₂, where R corresponds to the same organic substituent present in the peroxy radical.

As discussed in several studies, RO₂ + HO₂ reactions exhibit a negative temperature-dependence (with rather large negative activation energies, Table 1), suggesting that these reactions proceed *via* an intermediate complex. In contrast to RO₂ + NO reactions, with NO being an electrophile, the HO₂ radical acts rather as a nucleophile in RO₂ + HO₂ reactions according to frontier molecular orbital theory.¹⁴¹ In a simplified manner, these reactions are often described as occurring through a single channel yielding quantitatively a hydroperoxide although this turned out to be merely true for alkyl peroxy radicals (e.g. ref. 3 and 135). Meanwhile, product studies have shown the occurrence of other reaction channels, where the accessibility of some of the pathways depends on the peroxy radical structure.



Interestingly, the first product study focusing on RO₂ + HO₂ investigated the acetyl peroxy radical and not the simpler CH₃O₂, as might be intuitively expected.¹⁴ In the early 1980s, information on CH₃O₂ + HO₂ was obtained as an offshoot of investigations targeting the CH₃O₂ self-reaction.^{143,144} In fact, Calvert and co-workers had already observed methyl hydroperoxide formation from CH₃O₂ radicals generated by the photolysis of azomethane in the early 1960s.^{145,146} However, at that time, the occurrence and participation of HO₂ in the reaction system were not yet known, and methyl hydroperoxide was postulated to occur through either the CH₃O₂ self-reaction, the reaction of CH₃O₂ with CH₃O, or H atom abstraction from an organic species by excited CH₃O₂.^{145,146}

In 1985, Niki *et al.* investigated the oxidation of acetaldehyde by irradiating CH₃CHO/Cl₂/air mixtures at atmospheric pressure and room temperature.¹⁴ In these experiments, the HO₂ radical concentrations were increased by the addition of formaldehyde, and the reaction mixtures were monitored by Fourier-transform infrared (FTIR) spectroscopy. Based on the product analysis, the authors showed that the reaction of acetyl peroxy with HO₂ must proceed *via* at least two channels yielding either peracetic acid ($\approx 75\%$) or O₃ ($\approx 25\%$).

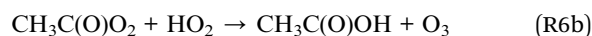
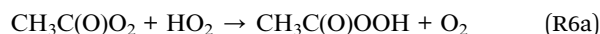


Table 1 Rate coefficients for RO₂ + HO₂ reactions. Temperature-dependence follows the Arrhenius expression $k(T) = A \times \exp(-E_a/RT)$

| Peroxy radical | $k_{298\text{ K}} \times 10^{12} (\text{cm}^3 \text{ s}^{-1})$ | $A \times 10^{13} (\text{cm}^3 \text{ s}^{-1})$ | $E_a/R (\text{K})$ | Ref. |
|--|--|---|--------------------|-----------|
| Alkyl peroxy | | | | |
| CH ₃ O ₂ | 5.2 | 3.8 | −780 | 134 |
| CH ₃ CH ₂ O ₂ | 6.9 | 6.4 | −710 | 134 |
| neo-C ₅ H ₁₁ O ₂ | 15 | 1.4 | −1380 | 18 and 55 |
| cyclo-C ₅ H ₉ O ₂ | 18 | 2.1 | −1320 | 19 |
| cyclo-C ₆ H ₁₁ O ₂ | 17 | 2.6 | −1250 | 19 |
| C ₁₀ H ₂₁ O ₂ ^a | 20 | | | 55 |
| C ₁₄ H ₂₉ O ₂ ^b | 21 | | | 55 |
| Haloalkyl peroxy | | | | |
| CH ₂ ClO ₂ | 5.0 | 3.2 | −820 | 48 |
| CHCl ₂ O ₂ | 5.9 | 5.6 | −700 | 22 |
| CCl ₃ O ₂ | 5.1 | 4.8 | −706 | 22 |
| CF ₂ ClO ₂ | 3.4 | | | 50 |
| CF ₂ ClCH ₂ O ₂ | 6.8 | | | 50 |
| CFCl ₂ CH ₂ O ₂ | 9.2 | | | 50 |
| CF ₃ CCl ₂ O ₂ | 1.9 | | | 49 |
| CF ₃ CHFO ₂ | 4.3 | 2.0 | −910 | 134 |
| CF ₃ CF ₂ O ₂ | 1.2 | | | 50 |
| CF ₂ ClCF ₂ O ₂ | 1.2 | | | 50 |
| β-Aryl peroxy | | | | |
| C ₆ H ₅ CH ₂ O ₂ | 12 | 1.5 | −1310 | 134 |
| Alkoxyalkyl peroxy | | | | |
| CH ₃ OCH ₂ O ₂ | 12 | | | 134 |
| Acyl peroxy | | | | |
| CH ₃ C(O)O ₂ | 20 | 1.73 | −730 | 134 |
| C ₆ H ₅ C(O)O ₂ | 38 | 110 | −364 | 58 |
| Carbonyl-containing peroxy | | | | |
| CH ₃ C(O)CH ₂ O ₂ | 9.0 | | | 134 |
| α-Hydroxyalkyl peroxy | | | | |
| HOCH ₂ O ₂ | 12 | 0.056 | −2300 | 134 |
| β-Hydroxyalkyl peroxy | | | | |
| HOCH ₂ CH ₂ O ₂ | 13 | | | 134 |
| HO-(1,2-C ₂ H ₂ Cl ₂)-O ₂ | 6 | | | 55 |
| (CH ₃) ₂ C(OH)CH ₂ O ₂ | 14 | 0.56 | −1650 | 134 |
| CH ₃ CH(OH)CH(O ₂)CH ₃ | 15 | | | 54 |
| (CH ₃) ₂ C(OH)C(O ₂)(CH ₃) ₂ | 15 | | | 55 |
| HO-(cyclohexene)-O ₂ ^c | 22 | | | 55 |
| HO-(α-pinene)-O ₂ ^c | 21 | | | 55 |
| HO-(γ-terpinene)-O ₂ ^c | 20 | | | 55 |
| HO-(D-limonene)-O ₂ ^c | 21 | | | 55 |
| Hydroxyalkenyl peroxy | | | | |
| HO-(isoprene)-O ₂ ^d | 17 | | | 55 |

^a Represents the mixture of peroxy radicals generated from decane + OH. ^b Represents the mixture of peroxy radicals generated from tetradecane + OH. ^c Peroxy radicals generated from the reaction of the parent VOC with OH. The β-hydroxyalkyl peroxy radical isomers are the predominant RO₂ in the system. ^d Represents the mixture of HOC₅H₈O₂ isomers formed from isoprene + OH.

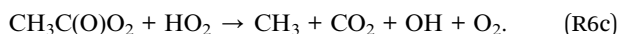
As pointed out by Calvert *et al.*,³ channel (R6b) is intriguing in the sense that it represents one of the few known chemical reactions yielding ozone directly, even though its contribution to tropospheric ozone is, however, rather small. In essence, this early investigation has already drawn a more complex picture of RO₂ + HO₂ reactions.

Subsequently, these results were confirmed by Moortgat *et al.*⁴² who generated the target radicals by the flash photolysis of Cl₂/CH₃CHO/CH₃OH/N₂/O₂ mixtures and detected the species by time-resolved UV spectroscopy. Based on this analysis, they obtained the rate coefficient for the target reaction (over the temperature range 253–368 K) and the branching ratio



for channel (R6b). They suggested that an H-bond in the tetroxide intermediate (ROOOOH), possible only due to the carbonyl group, allows for decomposition into $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{O}_3$.⁴²

The occurrence of a third reaction channel, producing OH, was first reported for a perfluorinated acyl peroxy radical.²⁶ The branching ratio obtained in this study has been corrected in follow-up work.²⁸ This observation, together with a revised infrared cross section for peracetic acid¹⁴⁷ and thermochemical considerations, has motivated Hasson *et al.*²⁷ to undertake a reinvestigation of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ system. Based essentially on two observations, they did prove the existence of channel (R6c):



First, using the updated infrared cross section reduced the peracetic yield and led to a carbon balance well below 100% when considering only the well-established reaction products (peracetic acid + acetic acid). Second, the change observed for both the methyl hydroperoxide and the CO_2 yield while transitioning from an RO_2 -dominated to an HO_2 -dominated system was inconsistent with a reaction scheme that considered only channels (R6a) and (R6b) for $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$.

In these first investigations, the OH-forming channel was identified by closed-shell co-products. Meanwhile, OH formation is quantified by both direct and indirect measurements and, as presented in the section below, is also reported for other $\text{RO}_2 + \text{HO}_2$ reactions. One of the established methods to scavenge OH in systems where organic precursor/ Cl_2 mixtures are irradiated is the addition of excess benzene. The reaction of benzene with Cl atoms is extremely slow ($k_{\text{Cl}} < 2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),²⁰ while benzene is reasonably reactive towards OH radicals ($k_{\text{OH}} \approx 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)¹⁴⁸ and consequently allows scavenging of OH without representing a significant sink for Cl atoms. Jenkin *et al.*²⁹ adapted this technique for investigations on $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ and used phenol formation (from benzene + OH) to diagnose OH. It was previously found that, under these conditions, the phenol yield is about $53\% \pm 7\%$.¹⁴⁹ The authors performed a detailed analysis showing that benzene chemistry does not affect the removal of acetyl peroxy radicals under HO_2 -dominated conditions. In later studies, direct measurements of OH were performed by laser-induced fluorescence or mid-infrared wavelength modulation spectroscopy, resulting in branching ratios consistent with the former indirect measurements within the assigned uncertainties.^{33,56,59,60}

The apparent differences between the reactions of alkyl peroxy radicals and functionalized peroxy radicals with HO_2 were addressed in several theoretical studies.^{52,150–154} Although it was initially believed that $\text{RO}_2 + \text{HO}_2$ reactions proceed *via* a tetroxide intermediate (ROOOOH) similar to RO_2 permutation reactions, it was found that hydroperoxide formation occurs *via* a hydrogen-bonded pre-reactive complex ($\text{ROO} \cdots \text{HOO}$) on a triplet potential energy surface (PES).^{150,151,153} Other reaction channels, such as the formation of OH or O_3 , proceed through the tetroxide intermediate on a singlet PES (Fig. 2).^{52,150,152} As

pointed out by Vereecken and Francisco,¹⁵⁵ the hydrogen bonding results in a submerged barrier for H migration (on the triplet surface); consequently, the accessibility of pathways other than hydroperoxide formation depends on the barriers for the decomposition of the tetroxide intermediate (formed on the singlet surface). In the case of simple alkyl peroxy radicals, these barriers cause all pathways proceeding *via* the ROOOOH intermediate to appear uncompetitive. However, for oxygenated peroxy radicals, such as those containing a carbonyl group, several theoretical calculations suggest lower energy barriers owing to strong hydrogen bonding in the tetroxide intermediate, hence facilitating decomposition towards other reaction products.^{52,150,154}

Interestingly, the number of alkyl peroxy radicals investigated in experimental product studies is rather small; so far, such studies have mainly addressed methyl^{15,17,156} and ethyl peroxy,^{16,25,27,65} followed by single investigations on neopentyl,¹⁸ cyclopentyl¹⁹ and cyclohexyl¹⁹ peroxy, and at least for the methyl peroxy radical, the occurrence of a second channel, yielding a carbonyl + H_2O (R5e), has been postulated. Jenkin *et al.*⁶² reported significant HDO formation from the photolysis of $\text{Cl}_2/\text{CD}_4/\text{CH}_3\text{OH}/\text{O}_2$ mixtures analysed by UV and infrared diode laser spectroscopy. Although the authors presented a detailed error analysis and identified potentially interfering processes yielding HDO, they were able to explain their results only by HDO formation (about 40%) from $\text{CD}_3\text{O}_2 + \text{HO}_2$. Subsequently, Wallington and Japar¹⁵ investigated $\text{CH}_3\text{O}_2 + \text{HO}_2$ by FTIR spectroscopy and concluded, based on the quantification of methyl hydroperoxide, that this reaction produces only a hydroperoxide. In their preceding work, the authors presented similar results on ethyl peroxy.¹⁶ In contrast, Elrod *et al.*¹⁵⁶



Fig. 2 Pathways of $\text{RO}_2 + \text{HO}_2$ reactions illustrated by $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$. The pathway yielding the hydroperoxide (peracid) proceeds over a triplet potential energy surface, while tetroxide formation proceeds over a singlet surface. The acetoxy radical formed in the OH channel immediately decomposes and yields $\text{CO}_2 + \text{CH}_3\text{O}_2$ under atmospheric conditions.



reported an 11% contribution of the carbonyl + H₂O channel from CH₃O₂ + HO₂ at 298 K, increasing to about 31% at 218 K.

Theoretical work on CH₃O₂ + HO₂ has been performed by applying different computational methods.^{151,153,157,158} Although most of these studies found methyl hydroperoxide formation to be the only reaction channel,^{151,157} Drougas¹⁵⁸ concluded that formaldehyde formation is also accessible, particularly at lower temperatures. At present, IUPAC recommends a branching ratio for HCHO formation of 0.1 ± 0.1 at 298 K, while JPL continues to recommend a 100% yield for methyl hydroperoxide.^{134,137} Owing to the ubiquity of methyl peroxy radicals throughout the troposphere, further studies on this subject, particularly on the temperature-dependence, would be very valuable.

Similarly, carbonyl formation of 71–100% has been reported for the reactions of halogenated alkyl peroxy radicals, such as CH_{3–n}Cl_nO₂ (*n* = 1–3) or CH₂FO₂ with HO₂.^{21–23} The co-product of this pathway was originally proposed to be H₂O. Meanwhile, theoretical work has shown that the channel proceeds over a singlet PES *via* a five-membered ring intermediate with the halogen atom exhibiting a stabilizing effect that lowers energy barriers.^{151,152} The expected co-products are then OH + HO₂. These calculations reproduce the experimental data for CH₂FO₂ and CH₂ClO₂ radicals. Interestingly, no hydroperoxide was detected in the experiments on CHCl₂O₂ and CCl₃O₂ + HO₂.²² However, as pointed out by Hou *et al.*,¹⁵² these observations might rely on chemical activation in the nascent hydroperoxide product. Subsequent decomposition of the hydroperoxide yields carbonyl products, which will add to the carbonyl yield of the carbonyl + OH + HO₂ channel (R5d).¹⁵² Clearly, halogenated alkyl peroxy radicals behave differently from alkyl peroxy in their reaction with hydroperoxy radicals.

How relevant are RO₂ + HO₂ reactions to tropospheric chemistry?

Based on the reports of various field campaigns, it has been established that tropospheric HO₂ is of the order of 10⁸ cm^{–3} with peak daytime concentrations of up to 1 × 10⁹ cm^{–3} (*e.g.* Stone *et al.*¹³² and references therein). Since the rate coefficients for the reactions of organic peroxy radicals with HO₂ are close to those with NO ($\approx 9 \times 10^{-12}$ cm³ molecule^{–1} s^{–1} at 298 K), RO₂ + HO₂ becomes thus competitive to RO₂ + NO once NO concentrations are close to HO₂. Before it was discovered that unimolecular isomerization of peroxy radicals is competitive under atmospheric conditions, RO₂ + HO₂ reactions were generally considered to be one of the major loss processes in so-called “low NO” environments. One should note that, although the term “low NO” is insufficient to define a chemical regime, it is used here for simplicity and represents the conditions under which the reaction of peroxy radicals with NO no longer represents the major peroxy radical loss process.

H migration was found to be particularly rapid, *e.g.* for allylic peroxy radicals or migration of aldehydic H atoms.⁵ For example, unimolecular isomerisation was shown to account for about 50% of the loss of isoprene peroxy radicals at NO levels below 200 pptv.¹⁵⁹ Overall, rate coefficients for H migration

depend heavily on the peroxy radical structure and thus span several orders of magnitude in contrast to rate coefficients for reactions of organic peroxy radicals with HO₂.⁵ As a rule of thumb, RO₂ + HO₂ appears competitive to unimolecular isomerisation at room temperature once H migration is <0.01 s^{–1}.

Low concentrations of NO, which are essential for the occurrence of RO₂ + HO₂ reactions, are commonly found in air masses that are not impacted by anthropogenic activities; for example, those found over tropical and boreal forests. However, this traditional perspective appears to change, *e.g.* as a consequence of changing emission profiles, and examples of “low NO” chemistry are also reported for urban areas. Praske *et al.* concluded that autoxidation becomes increasingly competitive to RO₂ + NO chemistry in urban and suburban areas of the United States owing to the overall reduction in NO_x emissions.¹⁶⁰ Although the authors have shown this effect mainly for peroxy radicals exhibiting large H-shift rate coefficients, the competitiveness of RO₂ + HO₂ reactions is also supposed to increase if NO_x emissions are further declining. Newland *et al.* provided evidence for traditional “low NO” chemistry in the polluted air masses of central Beijing in the afternoon when high levels of photochemically produced O₃ limit the availability of NO.¹⁶¹ Products of peroxy radical reactions with HO₂, namely hydrogen peroxide (HO₂ + HO₂) and peracetic acid (acetyl peroxy + HO₂), have also been identified in biomass burning plumes. Yokelson *et al.* observed initial fire emissions of both these peroxide species from biomass burning in the Yucatán; however, the authors highlighted that fast initial photochemistry may account partly for the significant amounts present in the young smoke.¹⁶² Indeed, according to current emission inventories, peracetic acid is not emitted directly from biomass burning,¹⁶³ yet elevated levels of both hydrogen peroxide and peracetic acid are observed when air masses are influenced by biomass burning plumes.¹⁶⁴ In essence, the occurrence of chemical conditions allowing for RO₂ + HO₂ appears to be less limited to typical pristine conditions and becomes more frequently encountered.

Role of RO₂ + HO₂ in the tropospheric HO_x budget

The reactions of peroxy radicals with HO₂ are primarily considered a sink for HO_x owing to the formation of an organic hydroperoxide, which (supposedly) terminates radical-chain reactions. This perspective appears simplified since OH formation was discovered for some RO₂ + HO₂ reactions. After model-to-measurement discrepancies indicated that significant unidentified HO_x recycling must occur in regions dominated by isoprene emissions (*e.g.* ref. 6, 11 and 165–167), it has been initially hypothesized that this might be the effect of peroxy radical reactions with HO₂.^{6,11} However, following tremendous research activities during the last 15 years, there seems now to be a consensus that the efficient OH recycling emerges primarily from unimolecular isomerization of isoprene peroxy radicals (*e.g.* ref. 4, 159 and 168–170). Simultaneously, these radicals were shown to yield predominantly isoprene



hydroperoxides (ISOPPOOHs) when reacting with HO_2 .¹⁷¹ The reader should note that this is different for peroxy radicals resulting from the major isoprene oxidation products, methacrolein and methyl vinyl ketone. Both methacrolein and methyl vinyl ketone peroxy radicals synthesized by the photolysis of VOC/alcohol/ $\text{Cl}_2/\text{O}_2/\text{N}_2$ mixtures were shown to generate OH with yields of about $80\% \pm 20\%$.³² Praske *et al.*³⁹ confirmed significant OH formation from methyl vinyl ketone + OH under HO_2 -dominated conditions, which consequently adds to the OH recycling by unimolecular isomerization.

Table 2 summarizes OH yields reported for reactions of HO_2 with different organic peroxy radicals. These were mostly determined for carbonyl-substituted, particularly acyl peroxy radicals. However, in addition to these data, some outstanding observations should be considered. Significant OH formation was reported to occur from the reaction of HO_2 with the β -hydroxy peroxy radicals of α -pinene (Fig. 3), following the observation of substantial pinonaldehyde formation under HO_2 -dominated conditions, which is in contrast to the very low OH yield for simple β -hydroxy peroxy radicals, such as $\text{HOCH}_2\text{CH}_2\text{O}_2$.^{37,56} One should note that, although a computational study showed that OH production appears thermodynamically accessible, at least for some of the α -pinene-derived peroxy radical isomers, a more recent experimental study

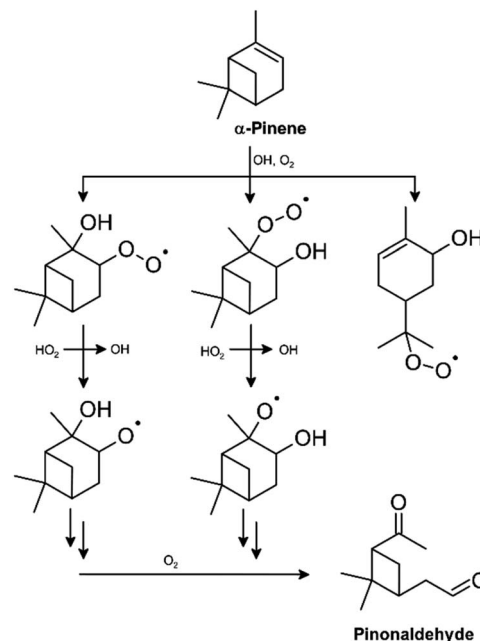


Fig. 3 OH production via the reaction of α -pinene-derived peroxy radicals with HO_2 , as suggested by Eddingsaas *et al.*³⁷

Table 2 OH yields reported for different $\text{RO}_2 + \text{HO}_2$ reactions at room temperature

| Peroxy radical | OH yield (%) | Reference |
|--|--------------|-----------|
| $\text{CH}_3\text{C}(\text{O})\text{O}_2$ | 40 ± 16 | 27 |
| | <10 | 52 |
| | 43 ± 10 | 29 |
| | 50 ± 20 | 56 |
| | 61 ± 9 | 59 |
| | 51 ± 12 | 33 |
| | 48 ± 9 | 60 |
| $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2$ | 40 ± 10 | 32 |
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}_2$ | 47 ± 15 | 32 |
| $\text{CF}_3\text{C}(\text{O})\text{O}_2$ | 52 ± 5 | 28 |
| $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{O}_2$ | 50 ± 8 | 28 |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{O}_2$ | 47 ± 11 | 28 |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{O}_2$ | 27 ± 18 | 28 |
| $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2^a$ | ≈ 20 | 56 |
| | 20 ± 5 | 58 |
| $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ | 67 ± 20 | 27 |
| | ≈ 15 | 56 |
| | 15 ± 8 | 30 |
| | 25 ± 13 | 32 |
| | 30 ± 4 | 61 |
| $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{O}_2)\text{CH}_3$ | ≈ 20 | 56 |
| | 58 ± 10 | 32 |
| $\text{CH}_2\text{ClC}(\text{CH}_3)(\text{O}_2)\text{CHO}^b$ | 80 ± 20 | 32 |
| $\text{CH}_2\text{ClCH}(\text{O}_2)\text{C}(\text{O})\text{CH}_3^c$ | 80 ± 20 | 32 |
| $\text{CH}_2\text{OHCH}(\text{O}_2)\text{C}(\text{O})\text{CH}_3$ | 48 | 39 |
| HOCH_2O_2 | 20 ± 5 | 29 |
| $\text{HOCH}_2\text{CH}_2\text{O}_2$ | <4 | 56 |
| $\text{CH}_3\text{OCH}_2\text{O}_2$ | 19 ± 8 | 31 |
| $\text{O}_2\text{NO}-(\text{isoprene})-\text{O}_2$ | 53 | 38 |

^a Benzoyl peroxy. ^b Surrogate for $\text{OH}-(\text{methacrolein})-\text{O}_2$. ^c Surrogate for $\text{OH}-(\text{methyl vinyl ketone})-\text{O}_2$.

performed under “low NO” conditions determined a substantially lower pinonaldehyde yield.^{172,173} This stresses the need to extend the studies on OH recycling to other monoterpenes. Rollins *et al.* argued that the carbonyl/hydroperoxide ratio observed in their experiments suggests pathways other than hydroperoxide formation for the reaction of HO_2 with peroxy radicals formed in the isoprene + NO_3 system; subsequently, OH formation was reported for different nitrooxy alkylperoxy radicals derived from isoprene.^{38,174} In addition, Birdsall and co-workers found OH regeneration in the oxidation of aromatics under HO_2 -dominated conditions and proposed the reaction of bicyclic peroxy radicals with HO_2 to produce OH.^{106,107}

It appears that two pathways define the role of the reactions of organic peroxy radicals with HO_2 in the HO_x budget. One is obviously OH production in the radical-propagating channel (R5c), which seems accessible for various oxygenated peroxy radicals and hence reduces the strength of acting as a HO_x sink. However, it is worth mentioning that, apart from the reaction of acyl peroxy radicals with HO_2 , the further chemistry of the alkoxy co-product also recycles HO_2 as long as alkoxy isomerization is unimportant. The second major control for the HO_x budget is organic hydroperoxide formation, as mentioned earlier. Classifying the reactions of organic peroxy radicals with HO_2 as a HO_x sink relies purely on the fact that organic hydroperoxides supposedly act as temporary HO_x reservoirs on a significant timescale before possibly regenerating OH by photolysis. In addition, when gas-phase photochemical and photophysical processes are slow, the removal of organic hydroperoxides is likely dominated by heterogeneous losses. For example, the atmospheric lifetime of the most abundant organic hydroperoxide, methyl hydroperoxide, is on the order of 1 day; although its solubility is comparatively low, it was found



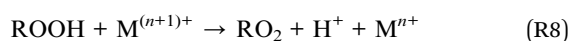
in water droplets.^{175–177} It was already demonstrated that dissolved organic hydroperoxides are still able to act as a source of HO_x and initiate photochemistry in the liquid phase.^{178,179} The overall picture might change when considering more complex or multi-functional hydroperoxides. It is intriguing that, although formed through unimolecular processes, rapid photolysis of hydroperoxy aldehydes (HPALDs) is one of the key routes of OH recycling in isoprene chemistry.^{159,180,181} In addition, Praske *et al.*³⁹ observed rapid photolysis of a multifunctional hydroperoxide formed in the reaction of HO₂ with a peroxy radical resulting from OH addition to methyl vinyl ketone. These results indicate that HO_x recycling from the reactions of organic peroxy radicals with HO₂ may also depend strongly on the identity of the organic hydroperoxide, and further studies on a larger set of species can help refine the role of RO₂ + HO₂ reactions in the tropospheric HO_x budget.

What are the challenges?

The (mainly historical) overview presented above, in particular on the reaction of the acetyl peroxy radical with HO₂, highlights that the quantification of organic hydroperoxides is not only key for understanding RO₂ + HO₂ reactions but certainly represents one of the major experimental challenges. Quantifying organic hydroperoxides is demanding for three reasons: the behaviour of organic hydroperoxides under experimental conditions, the accessibility of standards, and the rather limited number of analytical methods for gaseous organic hydroperoxides.

It is well known that hydroperoxides decompose readily; for example, they are thermally sensitive in general. However, two observations illustrate another feature besides thermal decomposition. Conversion processes of hydroperoxides into the corresponding carbonyl were reported to occur inside analytical instrumentation, such as GC systems or PTR-MS, leading to bias in both atmospheric and experimental observations if they remain unrecognized.¹⁸² Similar observations have been made in atmospheric simulation chamber experiments. Bernhammer *et al.*¹⁸³ investigated the formation and loss processes of isoprene oxidation products under low NO_x conditions. The authors showed that isoprene hydroperoxides (ISOPOOHs) are partly converted into methyl vinyl ketone and methacrolein on the stainless steel surface of the simulation chamber. Hence, a quantitative description of isoprene hydroperoxides was achieved indirectly by considering the larger-than-expected methyl vinyl ketone and methacrolein yields observed in the oxidation experiments.

Both observations rely on the same chemical principle: metal ions, such as copper, iron, and manganese, can initiate hydroperoxide decomposition by electron-transfer (*e.g.* Sanchez and Myers¹⁸⁴ and references therein):



If both reactions are accessible, that is both valence states can react as is the case for most transition metals, this results in

the catalytic destruction of the hydroperoxide, which affects the experimental results.

The accessibility and usage of hydroperoxide standards are twofold challenging. First, it is obvious that special care must be taken in the preparation and handling of pure hydroperoxide samples, owing to the explosive nature of organic hydroperoxides, at least for hydroperoxides with a high peroxide oxygen content, such as methyl and ethyl hydroperoxide. An option to overcome this issue is the handling of diluted solutions, which, to a certain extent, limits their application to analytical methods quantifying hydroperoxides in the liquid phase. Although various synthesis routes exist, *e.g.* methylation of H₂O₂ by dimethyl sulphate for the preparation of methyl hydroperoxide,¹⁸⁵ the reaction of alkyl methanesulfonates (mesylates) with H₂O₂ for larger and branched alkyl hydroperoxides,^{186,187} and the reaction of tertiary alcohols with H₂O₂ for tertiary alkyl hydroperoxides, the preparation of higher functionalized hydroperoxides is demanding. However, it should be mentioned that research efforts in the last decade have made accessible, for example, the preparation of isoprene hydroperoxides.^{182,188,189}

Additionally, achieving a quantitative conversion of a precursor compound into the desired hydroperoxide is not always possible. For example, peracids are easily synthesized by mixing concentrated H₂O₂ solutions with the corresponding acid often in the presence of an acidic catalyst (commonly sulphuric acid).¹⁹⁰ In the case of peracetic acid, this results in equilibrium mixtures containing a peracid fraction on the order of 40%. The determination of infrared absorption cross sections based on the vaporization of these samples requires scrupulously accounting for other volatilized components, such as H₂O, acetic acid and the acetic acid dimer, which hence represents a potential source of error. As pointed out by Orlando *et al.*,¹⁴⁷ this might have been one of the reasons for the low absorption cross section reported for peracetic acid by Crawford *et al.*²⁴ FTIR spectroscopy is one of the workhorses for analysing gaseous reaction systems in atmospheric simulation chamber experiments and has consequently been used regularly for the quantification of organic hydroperoxides. However, as discussed above, the reliability of the retrieved information depends on well-established absorption cross sections and hence on well-characterized procedures for vaporizing samples with known organic hydroperoxide content.

As presented in the overview section, the product study of Hasson *et al.*²⁷ was the first to use the revised absorption cross section for peracetic acid. However, the authors validated the FTIR data against the HPLC-fluorescence method. In separate experiments, by preparing gas phase mixtures of peracetic acid in the chamber, Hasson *et al.*²⁷ showed that FTIR and HPLC analyses agree within a factor of about 1.2. Based on the reported product yields in different experiments, both methods agreed on average within a factor of 1.2, 1.1 and 1.5 for methyl hydroperoxide, ethyl hydroperoxide and peracetic acid, respectively, in the oxidation experiments. There is no doubt about these experimental results, yet these data highlight that the quantification of organic hydroperoxides remains a challenging task. Hasson *et al.*³⁵ pointed out that hydroperoxide yields



obtained from different ozonolysis systems (where $\text{RO}_2 + \text{HO}_2$ reactions occur) in several studies vary considerably although both experimental methodologies and analytical instrumentation were similar. The authors presumed that this might be due to the complexity of applying the HPLC-fluorescence technique to simulation chamber experiments. In addition, the selectivity of horseradish peroxidase (HRP) limits the detectability of organic hydroperoxides. Although linear *n*-alkyl hydroperoxides up to C_{18} were found to react with HRP with similar efficiencies, secondary and tertiary hydroperoxides exhibit either significantly lower responses or are undetectable.^{191,192}

Overall, there is a need for additional analytical methods preferably preserving the chemical integrity of the sample. Chemical ionisation mass spectrometry (CIMS), which is increasingly used in atmospheric science, is certainly one of these methods. Generally, the number of ionisation schemes used in CIMS instruments is increasing; particularly, reagent ions, such as NH_4^+ or I^- , are promising. It is realistic to estimate that a large body of work will be necessary to reduce overall uncertainties and that the lack of hydroperoxide standards might remain a limiting factor.

Another major experimental challenge relies on the procedures used for peroxy radical generation and the subsequent radical chemistry. Most of the data on reaction products and branching ratios were obtained from atmospheric simulation chamber experiments by either Cl atom reactions of an organic precursor or VOC + OH oxidation experiments performed under HO_2 -dominated conditions. It is obvious that the generation of (almost exclusively) a single peroxy radical in the initial step is limited in these approaches to small organics such as methane (for methyl peroxy), ethane (for ethyl peroxy), acetaldehyde (for acetyl peroxy), acetone (for acetonyl peroxy) or unsubstituted cycloalkanes (for cycloalkyl peroxy). For larger molecules, the reaction with Cl, and even OH, concurrently generates several different peroxy radicals, initiating a series of RO_2 permutation reactions. As illustrated by the reaction sequence of the acetyl peroxy radical (Fig. 4), even the generation of a single RO_2

species results in a cascade of reactions producing additional RO_2 species. Moreover, this is complicated by the fact that further oxidation of closed-shell first-generation products adds to the radical pool by generating peroxy radicals and possibly OH. Advances in the understanding of site-specific chemistry (e.g. ref. 193) and refined structure–activity relationships (e.g. ref. 194) will help at least to determine the relative ratio of peroxy radicals initially formed in oxidation systems more accurately; however, as pointed out by Ervens *et al.*,¹⁹⁵ further experimental work on this subject is highly required. In addition, there is a growing number of reports on the generation of specific peroxy radicals from photolytic precursors, such as iodine-containing organic compounds.^{63,196–200}

The addition of an HO_2 precursor aims at shifting the reaction system towards conditions where the reaction of RO_2 with HO_2 is favoured, and in the limiting case, RO_2 reacts almost exclusively with HO_2 . However, both the experimental set-up and the chemistry often impede the attainment of this rather ideal case. The amount of HO_2 precursor is often limited by the deployed analytical instrumentation; for example, high concentrations of methanol complicate the analysis of FTIR spectra or might deplete the reagent ions in CIMS instruments. In addition, when increasing the HO_2 concentration, the self-reaction and the reaction with aldehydes, particularly with formaldehyde, become significant loss processes for HO_2 .

The overall consequence is that the kinetic information on $\text{RO}_2 + \text{HO}_2$ reactions is mostly obtained from the modelling of a complex chemical reaction system. This not only requires accurate analytics data but also information on rate coefficients and branching ratios of all involved reactions. Missing or incomplete data add uncertainty to the branching ratio determination for the target reaction. For instance, acetic acid is formed from $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$, as discussed above, but it also appears to arise from the cross-reaction of acetyl peroxy with methyl peroxy (Fig. 4). According to the currently recommended values, this channel accounts for about 10% of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$ reaction.¹³⁴ However, the relative error is 100%. Recently, Assali and Fittschen¹²⁴ reported a rate coefficient for the cross-reaction, which is a factor of two larger than the current recommendations. Simultaneously, they obtained a lower contribution from the radical-propagating channel.

The above-discussed challenges, partly or entirely, also apply to the absolute rate coefficient determination work. Most of the kinetic data presented in Table 1 were obtained from flash photolysis or pulsed laser photolysis experiments combined with UV absorption spectroscopy in the 1990s and early 2000s. Accordingly, accurate absorption cross sections of the radical species present in the system and a successful separation of overlapping absorption bands are crucial for the determination of rate coefficients. Since rate coefficients are finally obtained by fitting kinetic parameters to the decay rates recorded for the respective species, the uncertainty of the rate coefficient depends on the accuracy of the available kinetic mechanism. For example, by trend smaller rate coefficients and stronger temperature dependence were reported for $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ before the radical-propagating channel was discovered and included in the analysis.^{24,33,42,52,56,59,60}

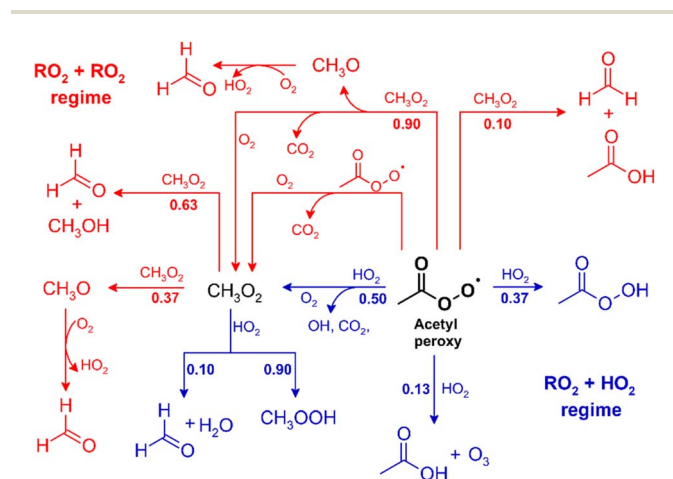


Fig. 4 Reaction sequence for $\text{CH}_3\text{C}(\text{O})\text{O}_2$ in the absence of NO. The co-product O_2 is omitted for readability reasons. Branching ratios (in bold) represent the current IUPAC recommendations.¹³⁴

Some of these issues were minimized by Boyd *et al.*⁵⁵ by determining the rate coefficients under a large excess of HO₂. The authors employed nearly pseudo-first order conditions using an excess of H₂O₂, hence suppressing RO₂ self-reactions and subsequent chemistry. However, this approach is limited to reaction systems without significant radical recycling. Østerstrøm *et al.*⁶⁹ reduced the uncertainties in the CH₃O₂ + HO₂ rate coefficient significantly by detecting methyl peroxy and HO₂ using the FAGE-LIF method and applying an updated kinetic model, which uses a revised rate coefficient for the CH₃O₂ self-reaction they have obtained in preceding work.²⁰¹ The authors determined temperature-dependent rate coefficients of about 15% lower than current recommendations.

The progress made in the detection of peroxy radicals and possibly the rethinking of experimental designs will help reduce uncertainties. For example, Zuraski *et al.*⁶¹ investigated the kinetics and OH production from the acetonyl peroxy + HO₂ reaction by monitoring the three radical species independently using a combination of IR and UV measurements. However, further advances in the detection of radicals, particularly with respect to chemical speciation, are still desirable.

Gaps in knowledge

Substantial progress has been made over the last approximately 25 years in understanding the reactions of organic peroxy radicals with HO₂, particularly with respect to the occurrence of pathways other than organic hydroperoxide formation. However, there remain several areas that require further research as a consequence of either a lack of data or significant uncertainties and divergence in existing data:

(1) Rate coefficients

Currently, there are few recommended values (assigned with large uncertainty ranges) for the rate coefficients of the title reactions, which are insufficient to cover the variety of peroxy radicals that are potentially produced in the troposphere.

(2) OH formation

As evident from Table 2, significant scattering is found for the OH yield of some RO₂ + HO₂ reactions, and additional measurements are required to reduce overall uncertainties. Thus far, most data on acyl peroxy radicals have been reported. Systematic investigations of a broader range of peroxy radicals would help draw a more comprehensive picture of OH formation from RO₂ + HO₂ and, more specifically, assess the influence of functional groups and structures on OH yield.

(3) β-Hydroxy peroxy radicals

The dataset on β-hydroxy peroxy radicals is scarce. Given the importance of this class of peroxy radicals in the atmosphere (they are formed following the addition of OH to nearly all unsaturated VOC) and the apparent discrepancies reported in the literature (*e.g.* ethene-derived *vs.* α-pinene-derived peroxy radicals), there is a need for systematic investigations on β-hydroxy peroxy radicals with respect to structural variation.

(4) Multifunctional peroxy radicals

Investigations reported in the literature are limited to peroxy radicals containing very few different functional groups. Given the partial focus on acyl peroxy radicals, additional systematic studies on the different functional groups of oxygenated peroxy radicals would be valuable for refining our understanding of RO₂ + HO₂ reactions. In particular, it is entirely unknown at present how reactivity and product branching ratios are affected by a combination of different functionalities.

(5) Temperature-dependence

Although the temperature-dependence was reported for the absolute rate coefficients of a range of peroxy radicals (Table 1), the temperature-dependence of product branching ratios, in particular for oxygenated peroxy radicals, is not well established. Dedicated temperature-dependent product studies were, to the best of the author's knowledge, reported only for ethyl peroxy²⁵ and acetyl peroxy.⁶⁰ There is a clear need for further research to assess the relative change in branching ratios with temperature.

(6) Hydroperoxides

As discussed above, the atmospheric fate of an organic hydroperoxide is crucial for the HO_x budget related to a specific RO₂ + HO₂ reaction. Accordingly, organic hydroperoxides may be regarded as an additional area of research, particularly in the case of multifunctional hydroperoxides, which are potentially more sensitive to photolysis.

(7) Theoretical investigations

Few studies have applied computational methods to RO₂ + HO₂ reactions. As with experimental data, further theoretical studies, particularly on the accessibility of pathways other than hydroperoxide formation for different peroxy radical structures, are desirable.

Conclusions

The present work highlights that despite the progress made in understanding RO₂ + HO₂ reactions, there are several areas requiring further research activities. Although H-shift isomerization is now accepted to represent a significant peroxy radical loss process for certain peroxy radical classes, it might be less competitive for others. Thus, under pristine-like conditions, the reaction with HO₂ still represents one of the major loss processes for a large range of peroxy radicals formed in the atmosphere. This, together with the observed increased incidence of low NO_x tropospheric conditions, indicates that the systematic scrutiny of the title reaction is essential to draw a comprehensive image of the peroxy radical chemistry.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this perspective.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

NI gratefully acknowledges Iulia Patroescu-Klotz for proof-reading this manuscript.

References

- 1 A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor and P. Zimmerman, A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, 1995, **100**, 8873–8892.
- 2 R. Atkinson and J. Arey, Atmospheric Degradation of Volatile Organic Compounds, *Chem. Rev.*, 2003, **103**, 4605–4638.
- 3 J. G. Calvert, J. J. Orlando, W. R. Stockwell and T. J. Wallington, *The Mechanisms of Reactions Influencing Atmospheric Ozone*, Oxford University Press, Oxford, 2015.
- 4 H. Fuchs, A. Hofzumahaus, F. Rohrer, B. Bohn, T. Brauers, H.-P. Dorn, R. Häseler, F. Holland, M. Kaminski, X. Li, S. Nehr, R. Tillmann, R. Wegener and A. Wahner, Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, *Nat. Geosci.*, 2013, **6**, 1023–1026.
- 5 L. Vereecken and B. Nozière, H migration in peroxy radicals under atmospheric conditions, *Atmos. Chem. Phys.*, 2020, **20**, 7429–7458.
- 6 J. Lelieveld, T. M. Butler, J. N. Crowley, T. J. Dillon, H. Fischer, L. Ganzeveld, H. Harder, M. G. Lawrence, M. Martinez, D. Taraborrelli and J. Williams, Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 2008, **452**, 737–740.
- 7 F. Bianchi, T. Kurtén, M. Riva, C. Mohr, M. P. Rissanen, P. Roldin, T. Berndt, J. D. Crounse, P. O. Wennberg, T. F. Mentel, J. Wildt, H. Junninen, T. Jokinen, M. Kulmala, D. R. Worsnop, J. A. Thornton, N. Donahue, H. G. Kjaergaard and M. Ehn, Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, *Chem. Rev.*, 2019, **119**, 3472–3509.
- 8 M. Ehn, J. A. Thornton, E. Kleist, M. Sipilä, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, S. Andres, I.-H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurtén, L. B. Nielsen, S. Jørgensen, H. G. Kjaergaard, M. Canagaratna, M. Dal Maso, T. Berndt, T. Petäjä, A. Wahner, V.-M. Kerminen, M. Kulmala, D. R. Worsnop, J. Wildt and T. F. Mentel, A large source of low-volatility secondary organic aerosol, *Nature*, 2014, **506**, 476–479.
- 9 T. F. Mentel, M. Springer, M. Ehn, E. Kleist, I. Pullinen, T. Kurtén, M. Rissanen, A. Wahner and J. Wildt, Formation of highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the ozonolysis of alkenes – deduced from structure–product relationships, *Atmos. Chem. Phys.*, 2015, **15**, 6745–6765.
- 10 T. Berndt, W. Scholz, B. Mentler, L. Fischer, H. Herrmann, M. Kulmala and A. Hansel, Accretion Product Formation from Self- and Cross-Reactions of RO₂ Radicals in the Atmosphere, *Angew. Chem., Int. Ed.*, 2018, **57**, 3820–3824.
- 11 J. A. Thornton, P. J. Wooldridge, R. C. Cohen, M. Martinez, H. Harder, W. H. Brune, E. J. Williams, J. M. Roberts, F. C. Fehsenfeld, S. R. Hall, R. E. Shetter, B. P. Wert and A. Fried, Ozone production rates as a function of NO_x abundances and HO_x productions rates in the Nashville urban plume, *J. Geophys. Res.*, 2002, **107**, 4146.
- 12 R. A. Cox and G. S. Tyndall, Rate constants for the reactions of CH₃O₂ in the gas phase, *Chem. Phys. Lett.*, 1979, **65**, 357–360.
- 13 R. A. Cox and G. S. Tyndall, Rate constants for the reactions of CH₃O₂ with HO₂, NO and NO₂ using molecular modulation spectrometry, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 153–163.
- 14 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, FTIR Study of the Kinetics and Mechanism for Cl-Atom-Initiated Reactions of Acetaldehyde, *J. Phys. Chem.*, 1985, **89**, 588–591.
- 15 T. J. Wallington and S. M. Japar, Reaction of CH₃O₂ + HO₂ in air at 295 K: a product study, *Chem. Phys. Lett.*, 1990, **167**, 513–518.
- 16 T. J. Wallington and S. M. Japar, FTIR product study of the reaction of C₂H₅O₂ + HO₂ in air at 295 K, *Chem. Phys. Lett.*, 1990, **166**, 495–499.
- 17 T. J. Wallington, Fourier-transform Infrared Product Study of the Reaction of CH₃O₂ + HO₂ over the Pressure Range 15–700 Torr at 295 K, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2379–2382.
- 18 D. M. Rowley, R. Lesclaux, P. D. Lightfoot, K. Hughes, M. D. Hurley, S. Rudy and T. J. Wallington, A Kinetic and Mechanistic Study of the Reaction of Neopentylperoxy Radicals with HO₂, *J. Phys. Chem.*, 1992, **96**, 7043–7048.
- 19 D. M. Rowley, R. Lesclaux, P. D. Lightfoot, B. Nozière, T. J. Wallington and M. D. Hurly, Kinetic and Mechanistic Studies of the Reactions of Cyclopentylperoxy and Cyclohexylperoxy Radicals with HO₂, *J. Phys. Chem.*, 1992, **96**, 4889–4894.
- 20 B. Nozière, R. Lesclaux, M. D. Hurley, M. A. Dearth and T. J. Wallington, A Kinetic and Mechanistic Study of the Self-Reaction and Reaction with HO₂ of the Benzylperoxy Radical, *J. Phys. Chem.*, 1994, **98**, 2864–2873.
- 21 T. J. Wallington, M. D. Hurley, W. F. Schneider, J. Sehested and O. J. Nielsen, Mechanistic study of the gas-phase reaction of CH₂FO₂ radicals with HO₂, *Chem. Phys. Lett.*, 1994, **218**, 34–42.
- 22 V. Catoire, R. Lesclaux, W. F. Schneider and T. J. Wallington, Kinetics and Mechanisms of the Self-Reactions of CCl₃O₂ and CHCl₂O₂ Radicals and Their Reactions with HO₂, *J. Phys. Chem.*, 1996, **100**, 14356–14371.



- 23 T. J. Wallington, M. D. Hurley and W. F. Schneider, Atmospheric chemistry of CH_3Cl : mechanistic study of the reaction of CH_2ClO_2 radicals with HO_2 , *Chem. Phys. Lett.*, 1996, **251**, 164–173.
- 24 M. A. Crawford, T. J. Wallington, J. J. Szente, M. M. Maricq and J. S. Francisco, Kinetics and Mechanism of the Acetylperoxy + HO_2 Reaction, *J. Phys. Chem. A*, 1999, **103**, 365–378.
- 25 M. Spittler, I. Barnes, K. H. Becker and T. J. Wallington, Product study of the $\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2$ reaction in 760 Torr of air at 284–312 K, *Chem. Phys. Lett.*, 2000, **321**, 57–61.
- 26 M. P. S. Andersen, M. D. Hurley, T. J. Wallington, J. C. Ball, J. W. Martin, D. A. Ellis and S. A. Mabury, Atmospheric chemistry of $\text{C}_2\text{F}_5\text{CHO}$: mechanism of the $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction, *Chem. Phys. Lett.*, 2003, **381**, 14–21.
- 27 A. S. Hasson, G. S. Tyndall and J. J. Orlando, A Product Yield Study of the Reaction of HO_2 Radicals with Ethyl Peroxy ($\text{C}_2\text{H}_5\text{O}_2$), Acetyl Peroxy ($\text{CH}_3\text{C}(\text{O})\text{O}_2$), and Acetyl Peroxy ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$) Radicals, *J. Phys. Chem. A*, 2004, **108**, 5979–5989.
- 28 M. D. Hurley, J. C. Ball, T. J. Wallington, M. P. S. Andersen, O. J. Nielsen, D. A. Ellis, J. W. Martin and S. A. Mabury, Atmospheric Chemistry of $n\text{-C}_x\text{F}_{2x+1}\text{CHO}$ ($x = 1, 2, 3, 4$): Fate of $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})$ Radicals, *J. Phys. Chem. A*, 2006, **110**, 12443–12447.
- 29 M. E. Jenkin, M. D. Hurley and T. J. Wallington, Investigation of the radical product channel of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction in the gas phase, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3149–3162.
- 30 M. E. Jenkin, M. D. Hurley and T. J. Wallington, Investigation of the radical product channel of the $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{HO}_2$ reaction in the gas phase, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4274–4280.
- 31 M. E. Jenkin, M. D. Hurley and T. J. Wallington, Investigation of the radical product channel of the $\text{CH}_3\text{OCH}_2\text{O}_2 + \text{HO}_2$ reaction in the gas phase, *J. Phys. Chem. A*, 2010, **114**, 408–416.
- 32 A. L. Hasson, G. S. Tyndall, J. J. Orlando, S. Singh, S. Q. Hernandez, S. Campbell and Y. Ibarra, Branching Ratios for the Reaction of Selected Carbonyl-Containing Peroxy Radicals with Hydroperoxy Radicals, *J. Phys. Chem. A*, 2012, **116**, 6264–6281.
- 33 F. A. F. Winiberg, T. J. Dillon, S. C. Orr, C. B. M. Groß, I. Bejan, C. A. Brumby, M. J. Evans, S. C. Smith, D. E. Heard and P. W. Seakins, Direct measurements of OH and other product yields from the $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ reaction, *Atmos. Chem. Phys.*, 2016, **16**, 4023–4042.
- 34 G. G. Guilbault, P. J. Brignac Jr and M. Juneau, New Substrates for the Fluorometric Determination of Oxidative Enzymes, *Anal. Chem.*, 1968, **40**, 1256–1263.
- 35 A. S. Hasson, G. Orzechowska and S. E. Paulson, Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 1. ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene, *J. Geophys. Res.*, 2001, **106**, 34131–34142.
- 36 J. D. Crounse, K. A. McKinney, A. J. Kwan and P. O. Wennberg, Measurement of Gas-Phase Hydroperoxides by Chemical Ionization Mass Spectrometry, *Anal. Chem.*, 2006, **78**, 6726–6732.
- 37 N. C. Eddingsaas, C. L. Loza, L. D. Yee, J. H. Seinfeld and P. O. Wennberg, α -pinene photooxidation under controlled chemical conditions – part 1: gas-phase composition in low- and high- NO_x environments, *Atmos. Chem. Phys.*, 2012, **12**, 6489–6504.
- 38 R. H. Schwantes, A. P. Teng, T. B. Nguyen, M. M. Coggon, J. D. Crounse, J. M. St. Clair, X. Zhang, K. A. Schilling, J. H. Seinfeld and P. O. Wennberg, Isoprene NO_3 Oxidation Products from the $\text{RO}_2 + \text{HO}_2$ Pathway, *J. Phys. Chem. A*, 2015, **119**, 10158–10171.
- 39 E. Praske, J. D. Crounse, K. H. Bates, T. Kurtén, H. G. Kjaergaard and P. O. Wennberg, Atmospheric Fate of Methyl Vinyl Ketone: Peroxy Radical Reactions with NO and HO_2 , *J. Phys. Chem. A*, 2015, **119**, 4562–4572.
- 40 P. Dagaut, T. J. Wallington and M. J. Kurylo, Temperature Dependence of the Rate Constant for the $\text{HO}_2 + \text{CH}_3\text{O}_2$ Gas-Phase Reaction, *J. Phys. Chem.*, 1988, **92**, 3833–3836.
- 41 P. Dagaut, T. J. Wallington and M. J. Kurylo, Flash Photolysis Kinetic Absorption Spectroscopy Study of the Gas-Phase Reaction $\text{HO}_2 + \text{C}_2\text{H}_5\text{O}_2$ over the Temperature Range 228 – 380 K, *J. Phys. Chem.*, 1988, **92**, 3836–3839.
- 42 G. K. Moortgat, B. Veyret and R. Lesclaux, Kinetics of the reaction of HO_2 with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ in the temperature range 253–368 K, *Chem. Phys. Lett.*, 1989, **160**, 443–447.
- 43 B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox and G. K. Moortgat, Kinetics and Mechanism of the Photooxidation of Formaldehyde. 1. Flash Photolysis Study, *J. Phys. Chem.*, 1989, **93**, 2368–2374.
- 44 P. D. Lightfoot, B. Veyret and R. Lesclaux, Flash Photolysis Study of the $\text{CH}_3\text{O}_2 + \text{HO}_2$ Reaction between 248 and 573 K, *J. Phys. Chem.*, 1990, **94**, 708–714.
- 45 F. F. Fenter, V. Catoire, R. Lesclaux and P. D. Lightfoot, The Ethylperoxy Radical: Its Ultraviolet Spectrum, Self-Reaction, and Reaction with HO_2 , Each Studied as a Function of Temperature, *J. Phys. Chem.*, 1993, **97**, 3530–3538.
- 46 I. Bridier, B. Veyret, R. Lesclaux and M. E. Jenkin, Flash Photolysis Study of the UV Spectrum and Kinetics of Reactions of the Acetylperoxy Radical, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2993–2997.
- 47 M. M. Maricq and J. J. Szente, A Kinetic Study of the Reaction between Ethylperoxy and HO_2 , *J. Phys. Chem.*, 1994, **98**, 2078–2082.
- 48 V. Catoire, R. Lesclaux, P. D. Lightfoot and M.-T. Rayez, Kinetic Study of the Reactions of CH_2ClO_2 with Itself and with HO_2 , and Theoretical Study of the Reactions of CH_2ClO_2 between 251 and 600 K, *J. Phys. Chem.*, 1994, **98**, 2889–2898.
- 49 G. D. Hayman, M. E. Jenkin, T. P. Murrels and C. E. Johnson, Tropospheric degradation chemistry of HCFC-123 (CF_3CHCl_2): a proposed replacement chlorofluorocarbon, *Atmos. Environ.*, 1994, **28**, 421–437.
- 50 G. D. Hayman and F. Battin-Leclerc, Kinetic of the Reactions of the HO_2 Radical with Peroxyl Radicals derived from Hydrochlorofluorocarbons and



- Hydrofluorocarbons, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1313–1323.
- 51 A. Tomas, E. Villenave and R. Lesclaux, Reactions of the HO₂ Radical with CH₃CHO and CH₃C(O)O₂ in the Gas Phase, *J. Phys. Chem.*, 2001, **105**, 3505–3514.
 - 52 J.-P. Le Crâne, M.-T. Rayez, J.-C. Rayez and E. Villenave, A reinvestigation of the kinetics and the mechanism of the CH₃C(O)O₂ + HO₂ reaction using both experimental and theoretical approaches, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2163–2171.
 - 53 T. P. Murrells, M. E. Jenkin, S. J. Shalliker and G. D. Hayman, Laser Flash Photolysis of the UV Spectrum and Kinetics of Reactions of HOCH₂CH₂O₂ Radicals, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2351–2360.
 - 54 M. E. Jenkin and G. D. Hayman, Kinetics of Reactions of Primary, Secondary and Tertiary β-Hydroxy Peroxyl Radicals, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1911–1922.
 - 55 A. A. Boyd, P.-M. Flaud, N. Daugey and R. Lesclaux, Rate Constants for RO₂ + HO₂ Reactions Measured under a Large Excess of HO₂, *J. Phys. Chem. A*, 2003, **107**, 818–821.
 - 56 T. J. Dillon and J. N. Crowley, Direct detection of OH formation in the reactions of HO₂ with CH₃C(O)O₂ and other substituted peroxy radicals, *Atmos. Chem. Phys.*, 2008, **8**, 4877–4889.
 - 57 A. C. Noell, L. S. Alconel, D. J. Robichaud, M. Okumura and S. P. Sander, Near-Infrared Kinetic Spectroscopy of the HO₂ and C₂H₅O₂ Self-Reactions and Cross Reactions, *J. Phys. Chem. A*, 2010, **114**, 6983–6995.
 - 58 E. Roth, A. Chakir and A. Ferhati, Study of a Benzoylperoxy Radical in the Gas Phase: Ultraviolet Spectrum and C₆H₅C(O)O₂ + HO₂ Reaction between 295 and 357 K, *J. Phys. Chem. A*, 2010, **114**, 10367–10379.
 - 59 C. B. M. Groß, T. J. Dillon, G. Schuster, J. Lelieveld and J. N. Crowley, Direct Kinetic Study of OH and O₃ Formation in the Reaction of CH₃C(O)O₂ with HO₂, *J. Phys. Chem. A*, 2014, **118**, 974–985.
 - 60 A. O. Hui, M. Fradet, M. Okumura and S. P. Sander, Temperature Dependence Study of the Kinetics and Product Yields of the HO₂ + CH₃C(O)O₂ Reaction by Direct Detection of OH and HO₂ Radicals Using 2f-IR Wavelength Modulation Spectroscopy, *J. Phys. Chem. A*, 2019, **123**, 3655–3671.
 - 61 K. Zuraski, A. O. Hui, F. J. Grieman, E. Darby, K. H. Möller, F. A. F. Winiberg, C. J. Percival, M. D. Smarte, M. Okumura, H. G. Kjaergaard and S. P. Sander, Acetonyl Peroxy and Hydro Peroxy Self- and Cross-Reactions: Kinetics, Mechanism, and Chaperone Enhancement from the Perspective of the Hydroxyl Radical Product, *J. Phys. Chem. A*, 2020, **124**, 8128–8143.
 - 62 M. E. Jenkin, R. A. Cox, G. D. Hayman and L. J. Whyte, Kinetic study of the reactions CH₃O₂ + CH₃O₂ and CH₃O₂ + HO₂ using molecular modulation spectroscopy, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 913–930.
 - 63 M. E. Jenkin and R. A. Cox, Kinetics of Reactions of CH₃O₂ and HOCH₂CH₂O₂ Radicals Produced by the Photolysis of Iodomethane and 2-Iodoethanol, *J. Phys. Chem.*, 1991, **95**, 3229–3237.
 - 64 M. T. Raventós-Duran, M. McGillen, C. J. Percival, P. D. Hamer and D. E. Shallcross, Kinetics of the CH₃O₂ + HO₂ Reaction: A Temperature and Pressure Dependence Study Using Chemical Ionization Mass Spectrometry, *Int. J. Chem. Kinet.*, 2007, **39**, 571–579.
 - 65 M. T. Raventós-Duran, C. J. Percival, M. R. McGillen, P. D. Hamer and D. E. Shallcross, Kinetics and branching ratio studies of the reaction of C₂H₅O₂ + HO₂ using chemical ionisation mass spectrometry, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4338–4348.
 - 66 G. S. Tyndall, R. A. Cox, C. Granier, R. Lesclaux, G. K. Moortgat, M. J. Pilling, A. R. Ravishankara and T. J. Wallington, Atmospheric chemistry of small organic peroxy radicals, *J. Geophys. Res.*, 2001, **106**, 12157–12182.
 - 67 H. Keller-Rudek, G. K. Moortgat, R. Sander and R. Sörensen, The MPI-Mainz UV/VIS spectral atlas of gaseous molecules of atmospheric interest, *Earth Syst. Sci. Data*, 2013, **5**, 365–373.
 - 68 G. K. Moortgat, R. A. Cox, G. Schuster, J. P. Burrows and G. S. Tyndall, Peroxy Radical Reactions in the Photo-oxidation of CH₃CHO, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 809–829.
 - 69 F. F. Østerstrøm, L. Onel, A. Brennan, J. M. Parr, L. K. Whalley, P. W. Seakins and D. E. Heard, Kinetics of the Cross-reaction of CH₃O₂ + HO₂ in the Highly Instrumented Reactor for Atmospheric Chemistry, *Int. J. Chem. Kinet.*, 2023, **55**, 489–500.
 - 70 D. Mihelcic, P. Müsgen and D. H. Ehhalt, An Improved Method of Measuring Tropospheric NO₂ and RO₂ by Matrix Isolation and Electron Spin Resonance, *J. Atmos. Chem.*, 1985, **3**, 341–361.
 - 71 D. Mihelcic, A. Volz-Thomas, H. W. Pätz, D. Kley and M. Mihelcic, Numerical Analysis of ESR Spectra from Atmospheric Samples, *J. Atmos. Chem.*, 1990, **11**, 271–297.
 - 72 T. M. Hard, R. J. O'Brien, C. Y. Chan and A. A. Mehrabzadeh, Tropospheric free radical determination by fluorescence assay with gas expansion, *Environ. Sci. Technol.*, 1984, **18**, 768–777.
 - 73 P. S. Stevens, J. H. Mather and W. H. Brune, Measurement of tropospheric OH and HO₂ by laser-induced fluorescence at low pressure, *J. Geophys. Res.*, 1994, **99**, 3543–3557.
 - 74 W. H. Brune, P. S. Stevens and J. H. Mather, Measuring OH and HO₂ in the Troposphere by Laser-Induced Fluorescence at Low Pressure, *J. Atmos. Sci.*, 1995, **52**, 3328–3336.
 - 75 D. J. Creasey, P. A. Halford-Maw, D. E. Heard, M. J. Pilling and B. J. Whitaker, Implementation and initial deployment of a field instrument for measurement of OH and HO₂ in the troposphere by laser-induced fluorescence, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2907–2913.
 - 76 H. Fuchs, F. Holland and A. Hofzumahaus, Measurement of tropospheric RO₂ and HO₂ radicals by a laser-induced fluorescence instrument, *Rev. Sci. Instrum.*, 2008, **79**, 084104.
 - 77 L. Whalley, M. A. Blitz, M. Desservettaz, P. W. Seakins and D. E. Heard, Reporting the sensitivity of laser-induced fluorescence instruments used for HO₂ detection to an



- interference from RO_2 radicals and introducing a novel approach that enables HO_2 and certain RO_2 types to be selectively measured, *Atmos. Meas. Tech.*, 2013, **6**, 3425–3440.
- 78 L. Onel, A. Brennan, P. W. Seakins, L. Whalley and D. E. Heard, A new method for atmospheric detection of the CH_3O_2 radical, *Atmos. Meas. Tech.*, 2017, **10**, 3985–4000.
 - 79 C. A. Cantrell and D. H. Stedman, A possible technique for the measurement of atmospheric peroxy radicals, *Geophys. Res. Lett.*, 1982, **9**, 846–849.
 - 80 C. A. Cantrell, D. H. Stedman and G. J. Wendel, Measurement of Atmospheric Peroxy Radicals by Chemical Amplification, *Anal. Chem.*, 1984, **56**, 1496–1502.
 - 81 D. R. Hastie, M. Weissenmayer, J. P. Burrows and G. W. Harris, Calibrated Chemical Amplifier for Atmospheric RO_x Measurements, *Anal. Chem.*, 1991, **63**, 2048–2057.
 - 82 C. A. Cantrell, R. E. Shetter, J. A. Lind, A. H. McDaniel and J. G. Calvert, An Improved Chemical Amplifier Technique for Peroxy Radical Measurements, *J. Geophys. Res.*, 1993, **98**, 2897–2909.
 - 83 C. A. Cantrell, R. E. Shetter and J. G. Calvert, Dual-Inlet Chemical Amplifier for Atmospheric Peroxy Radical Measurements, *Anal. Chem.*, 1996, **68**, 4194–4199.
 - 84 T. Reiner, M. Hanke and F. Arnold, Atmospheric peroxy radical measurements by ion molecule reaction-mass spectrometry: a novel analytical method using amplifying chemical conversion to sulphuric acid, *J. Geophys. Res.*, 1997, **102**, 1311–1326.
 - 85 T. J. Green, C. E. Reeves, N. Brough, G. D. Edwards, P. S. Monks and S. A. Penkett, Airborne measurements of peroxy radicals using the PERCA technique, *J. Environ. Monit.*, 2003, **5**, 75–83.
 - 86 Y. Sadanaga, J. Matsumoto, K. Sakurai, R. Isozaki, S. Kato, T. Nomaguchi, H. Bandow and Y. Kajii, Development of a measurement system of peroxy radicals using a chemical amplification/laser-induced fluorescence technique, *Rev. Sci. Instrum.*, 2004, **75**, 864–872.
 - 87 D. Kartal, M. D. Andrés-Hernández, L. Reichert, H. Schlager and J. P. Burrows, Technical note: characterisation of a DUALER instrument for the airborne measurement of peroxy radicals during AMMA 2006, *Atmos. Chem. Phys.*, 2010, **10**, 3047–3062.
 - 88 M. Horstjann, M. D. Andrés Hernández, V. Nenakhov, A. Chrobry and J. P. Burrows, Peroxy radical detection for airborne atmospheric measurements using absorption spectroscopy of NO_2 , *Atmos. Meas. Tech.*, 2014, **7**, 1245–1257.
 - 89 Y. Liu and J. Zhang, Atmospheric Peroxy Radical Measurements Using Dual-Channel Chemical Amplification Cavity Ringdown Spectroscopy, *Anal. Chem.*, 2014, **86**, 5391–5398.
 - 90 Y. Chen, C. Yang, W. Zhao, B. Fang, X. Xu, Y. Gai, X. Lin, W. Chen and W. Zhang, Ultra-sensitive measurement of peroxy radicals by chemical amplification broadband cavity-enhanced spectroscopy, *Analyst*, 2016, **141**, 5870–5878.
 - 91 E. C. Wood, B. L. Deming and S. Kundu, Ethane-Based Chemical Amplification Measurement Techniques for Atmospheric Peroxy Radicals, *Environ. Sci. Technol. Lett.*, 2017, **4**, 15–19.
 - 92 P. W. Villalta, L. G. Huey and C. J. Howard, A Temperature-Dependent Kinetics Study of the $\text{CH}_3\text{O}_2 + \text{NO}$ Reaction Using Chemical Ionization Mass Spectrometry, *J. Phys. Chem.*, 1995, **99**, 12829–12834.
 - 93 P. W. Villalta and C. J. Howard, Direct Kinetics Study of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}$ Reaction Using Chemical Ionization Mass Spectrometry, *J. Phys. Chem.*, 1996, **100**, 13624–13628.
 - 94 P. W. Villalta, E. R. Lovejoy and D. R. Hanson, Reaction probability of peroxyacetyl radical on aqueous surfaces, *Geophys. Res. Lett.*, 1996, **23**, 1765–1768.
 - 95 J. Eberhard, P. W. Villalta and C. J. Howard, Reaction of Isopropyl Peroxy Radicals with NO over the Temperature Range 201–410 K, *J. Phys. Chem.*, 1996, **100**, 993–997.
 - 96 J. Eberhard and C. J. Howard, Rate Coefficients for the Reactions of Some C_3 to C_5 Hydrocarbon Peroxy Radicals with NO, *J. Phys. Chem. A*, 1997, **101**, 3360–3366.
 - 97 K. W. Scholtens, B. M. Messer, C. D. Cappa and M. J. Elrod, Kinetics of the $\text{CH}_3\text{O}_2 + \text{NO}$ Reaction: Temperature Dependence of the Overall Rate Constant and an Improved Upper Limit for the CH_3ONO_2 Branching Channel, *J. Phys. Chem. A*, 1999, **103**, 4378–4384.
 - 98 T. Moise, W. Denzer and Y. Rudich, Direct Kinetics of the Reaction of Peroxyacetyl Radical with NO between 218 and 370 K, *J. Phys. Chem. A*, 1999, **103**, 6766–6771.
 - 99 D. L. Ranschaert, N. J. Schneider and M. J. Elrod, Kinetics of the $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}$ Reactions: Temperature Dependence of the Overall Rate Constant and the $\text{C}_2\text{H}_5\text{ONO}_2$ Branching Channel of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}$, *J. Phys. Chem. A*, 2000, **104**, 5758–5765.
 - 100 D. Zhang, R. Zhang, C. Church and S. W. North, Experimental study of hydroxyalkyl peroxy radicals from OH-initiated reactions of isoprene, *Chem. Phys. Lett.*, 2001, **343**, 49–54.
 - 101 J. M. Chow, A. M. Miller and M. J. Elrod, Kinetics of the $\text{C}_3\text{H}_7\text{O}_2 + \text{NO}$ Reaction: Temperature Dependence of the Overall Rate Constant and the $\text{i-C}_3\text{H}_7\text{ONO}_2$ Branching Channel, *J. Phys. Chem. A*, 2003, **107**, 3040–3047.
 - 102 A. M. Miller, L. Y. Yeung, A. C. Kiep and M. J. Elrod, Overall rate constant measurements of the reactions of alkene-derived hydroxyalkylperoxy radicals with nitric oxide, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3402–3407.
 - 103 D. Hanson, J. Orlando, B. Noziere and E. Kosciuch, Proton transfer mass spectrometry studies of peroxy radicals, *Int. J. Mass Spectrom.*, 2004, **239**, 147–159.
 - 104 A. Bacak, M. W. Bardwell, M. T. Raventos, C. J. Percival, G. Sanchez-Reyna and D. E. Shallcross, Kinetics of the Reaction of $\text{CH}_3\text{O}_2 + \text{NO}$: A Temperature and Pressure Dependence Study with Chemical Ionization Mass Spectrometry, *J. Phys. Chem. A*, 2004, **108**, 10681–10687.
 - 105 A. K. Patchen, M. J. Pennino and M. J. Elrod, Overall Rate Constant Measurements of the Reaction of Chloroalkylperoxy Radicals with Nitric oxide, *J. Phys. Chem. A*, 2005, **109**, 5865–5871.



- 106 A. W. Birdsall, J. F. Andreoni and M. J. Elrod, Investigation of the Role of Bicyclic Peroxy Radicals in the Oxidation Mechanism of Toluene, *J. Phys. Chem. A*, 2010, **114**, 10655–10663.
- 107 A. W. Birdsall and M. J. Elrod, Comprehensive NO-Dependent Study of the Products of the Oxidation of Atmospherically Relevant Aromatic Compounds, *J. Phys. Chem. A*, 2011, **115**, 5397–5407.
- 108 M. J. Elrod, Kinetics Study of the Aromatic Bicyclic Peroxy Radical + NO Reaction: Overall Rate Constant and Nitrate Product Yield Measurements, *J. Phys. Chem. A*, 2011, **115**, 8125–8130.
- 109 T. Jokinen, M. Sipilä, S. Richters, V.-M. Kerminen, P. Paasonen, F. Stratmann, D. Worsnop, M. Kulmala, M. Ehn, H. Herrmann and T. Berndt, Rapid Measurements Forms Highly Oxidized RO₂ Radicals in the Atmosphere, *Angew. Chem., Int. Ed.*, 2014, **53**, 14596–14600.
- 110 T. Berndt, S. Richters, R. Kaethner, J. Voigtländer, F. Stratmann, M. Sipilä, M. Kulmala and H. Herrmann, Gas-Phase Ozonolysis of Cycloalkenes: Formation of Highly Oxidized RO₂ Radicals and Their Reactions with NO, NO₂, SO₂, and Other RO₂ Radicals, *J. Phys. Chem. A*, 2015, **119**, 10336–10348.
- 111 P. R. Veres, J. M. Roberts, R. J. Wild, P. M. Edwards, S. S. Brown, T. S. Bates, P. K. Quinn, J. E. Johnson, R. J. Zamora and J. de Gouw, Peroxynitric acid (HO₂NO₂) measurements during the UBWOS 2013 and 2014 studies using iodide ion chemical ionization mass spectrometry, *Atmos. Chem. Phys.*, 2015, **15**, 8101–8114.
- 112 J. Sanchez, D. J. Tanner, D. Chen, L. G. Huey and N. L. Ng, A new technique for the direct detection of HO₂ radicals using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization, *Atmos. Meas. Tech.*, 2016, **9**, 3851–3861.
- 113 B. Nozière and D. R. Hanson, Speciated Monitoring of Gas-Phase Organic Peroxy Radicals by Chemical Ionization Mass Spectrometry: Cross-Reactions between CH₃O₂, CH₃(CO)O₂, (CH₃)₃CO₂, and c-C₆H₁₁O₂, *J. Phys. Chem. A*, 2017, **121**, 8453–8464.
- 114 A. Hansel, W. Scholz, B. Mentler, L. Fischer and T. Berndt, Detection of RO₂ radicals and other products from cyclohexene ozonolysis with NH₄⁺ and acetate chemical ionization mass spectrometry, *Atmos. Environ.*, 2018, **186**, 248–255.
- 115 B. Nozière and L. Vereecken, Direct Observation of Aliphatic Peroxy Radical Autoxidation and Water Effects: An Experimental and Theoretical Study, *Angew. Chem., Int. Ed.*, 2019, **58**, 13976–13982.
- 116 S. R. Albrecht, A. Novelli, A. Hofzumahaus, S. Kang, Y. Baker, T. Mentel, A. Wahner and H. Fuchs, Measurements of hydroperoxy radicals (HO₂) at atmospheric concentrations using bromide chemical ionisation mass spectrometry, *Atmos. Meas. Tech.*, 2019, **12**, 891–902.
- 117 D. B. Atkinson and J. L. Spillman, Alkyl Peroxy Radical Kinetics Measured using Near-infrared CW-Cavity Ring-down Spectroscopy, *J. Phys. Chem. A*, 2002, **106**, 8891–8902.
- 118 J. Thiébaud and C. Fittschen, Near infrared cw-CRDS coupled to laser photolysis: spectroscopy and kinetics of the HO₂ radical, *Appl. Phys. B*, 2006, **85**, 383–389.
- 119 M. K. Sprague, E. R. Garland, A. K. Mollner, C. Bloss, B. D. Bean, M. L. Weichman, L. A. Mertens, M. Okumura and S. P. Sander, Kinetics of n-Butoxy and 2-Pentoxo Isomerization and Detection of Primary Products by Infrared Cavity Ringdown Spectroscopy, *J. Phys. Chem. A*, 2012, **116**, 6327–6340.
- 120 L. Onel, A. Brennan, M. Gianella, G. Ronnie, A. L. Aguila, G. Hancock, L. Whalley, P. W. Seakins, G. A. Ritchie and D. E. Heard, An intercomparison of HO₂ measurements by fluorescence assay by gas expansion and cavity ring-down spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry), *Atmos. Meas. Tech.*, 2017, **10**, 4877–4894.
- 121 L. Onel, A. Brennan, M. Gianella, J. Hooper, N. Ng, G. Hancock, L. Whalley, P. W. Seakins, G. A. Ritchie and D. E. Heard, An intercomparison of CH₃O₂ measurements by fluorescence assay by gas expansion and cavity ring-down spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry), *Atmos. Meas. Tech.*, 2020, **13**, 2441–2456.
- 122 C. Wang, W. Zhao, B. Fang, N. Yang, F. Cheng, X. Hu, Y. Chen, W. Zhang, C. Fittschen and W. Chen, Portable cavity ring-down spectrometer for an HO₂ radical measurement: instrument's performance and potential improvement using a narrow linewidth laser, *Opt. Express*, 2022, **30**, 37446–37456.
- 123 M. Shamas, M. Assali, C. Zhang, X. Tang, W. Zhang, L. Pillier, C. Schoemaeker and C. Fittschen, Rate Constant and Branching Ratio for the Reactions of the Ethyl Peroxy Radical with Itself and with the Ethoxy Radical, *ACS Earth Space Chem.*, 2022, **6**, 181–188.
- 124 M. Assali and C. Fittschen, Rate Constants and Branching Ratios for the Self-Reaction of Acetyl Peroxy (CH₃C(O)O₂·) and its Reaction with CH₃O₂, *Atmosphere*, 2022, **13**, 186.
- 125 M. Assali and C. Fittschen, Self-Reaction of Acetyl Peroxy Radicals and Their Reaction with Cl Atoms, *J. Phys. Chem. A*, 2022, **126**, 4585–4597.
- 126 T. J. Johnson, F. G. Wienhold, J. P. Burrows, G. W. Harris and H. Burkhard, Measurements of Line Strengths in the HO₂ ν₁ Overtone Band at 1.5 μm Using an InGaAsP laser, *J. Phys. Chem.*, 1991, **95**, 6499–6502.
- 127 C. A. Taatjes and D. B. Oh, Time-resolved wavelength modulation spectroscopy measurements of HO₂ kinetics, *Appl. Opt.*, 1997, **36**, 5817–5821.
- 128 L. E. Christensen, M. Okumura, S. P. Sander, R. R. Friedl, C. E. Miller and J. J. Sloan, Measurements of the Rate Constant of HO₂ + NO₂ + N₂ → HO₂NO₂ + N₂ Using Near-Infrared Wavelength-Modulation Spectroscopy and UV-Visible Absorption Spectroscopy, *J. Phys. Chem. A*, 2004, **108**, 80–91.



- 129 F. J. Grieman, A. C. Noell, C. Davis-Van Atta, M. Okumura and S. P. Sander, Determination of Equilibrium Constants for the Reaction between Acetone and HO₂ Using Infrared Kinetic Spectroscopy, *J. Phys. Chem. A*, 2011, **115**, 10527–10538.
- 130 D. E. Heard and M. J. Pilling, Measurement of OH and HO₂ in the Troposphere, *Chem. Rev.*, 2003, **103**, 5163–5198.
- 131 D. E. Heard, Atmospheric field measurements of the hydroxyl radical using laser-induced fluorescence spectroscopy, *Annu. Rev. Phys. Chem.*, 2006, **57**, 191–216.
- 132 D. Stone, L. K. Whalley and D. E. Heard, Tropospheric OH and HO₂ radicals: field measurements and model comparisons, *Chem. Soc. Rev.*, 2012, **41**, 6348–6404.
- 133 R. S. Hornbrook, J. H. Crawford, G. D. Edwards, O. Goyea, R. L. Mauldin III, J. S. Olson and C. A. Cantrell, Measurements of tropospheric HO₂ and RO₂ by oxygen dilution modulation and chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 2011, **4**, 735–756.
- 134 IUPAC Datasheet for Gas Phase Reactions, retrieved from <https://iupac.aeris-data.fr/>.
- 135 J. J. Orlando and G. F. Tyndall, Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chem. Soc. Rev.*, 2012, **41**, 6294–6317.
- 136 M. E. Jenkin, R. Valorso, B. Aumont and A. R. Rickard, Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction, *Atmos. Chem. Phys.*, 2019, **19**, 7691–7717.
- 137 J. B. Burkholder, S. P. Sander, J. Abbatt, J. R. Barker, C. Cappa, J. D. Crounse, T. S. Dibble, R. E. Huie, C. E. Kolb, M. J. Kurylo, V. L. Orkin, C. J. Percival, D. M. Wilmouth and P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*, Evaluation No. 19, JPL Publication 19-5, Jet Propulsion Laboratory, Pasadena, 2019, <https://jpldataeval.jpl.nasa.gov>.
- 138 M. E. Jenkin, S. M. Saunders and M. J. Pilling, The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, *Atmos. Environ.*, 1997, **31**, 81–104.
- 139 S. M. Saunders, M. E. Jenkin, R. G. Derwent and M. J. Pilling, Protocol for the development of the Master Chemical Mechanism, MCM v3 (part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 2003, **3**, 161–180.
- 140 J. G. Calvert, R. G. Derwent, J. J. Orlando, G. S. Tyndall and T. J. Wallington, *Mechanisms of Atmospheric Oxidation of the Alkanes*, Oxford University Press, Oxford, 2008.
- 141 M. D. King, C. E. Canosa-Mas and R. P. Wayne, Gas-phase reactions between RO₂ and NO, HO₂ or CH₃O₂: correlations between rate constants and the SOMO energy of the peroxy (RO₂) radical, *Atmos. Environ.*, 2001, **35**, 2081–2088.
- 142 D. Johnson, D. W. Price and G. Marston, Correlation-type structure activity relationships for the kinetics of gas-phase RO₂ self-reactions and reaction with HO₂, *Atmos. Environ.*, 2004, **38**, 1447–1458.
- 143 C. S. Kan, J. G. Calvert and J. H. Shaw, Reactive Channels of the CH₃O₃–CH₃O₂ Reaction, *J. Phys. Chem.*, 1980, **84**, 3411–3417.
- 144 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, Fourier Transform Infrared Studies of the Self-Reaction of CH₃O₂ Radicals, *J. Phys. Chem.*, 1981, **85**, 877–881.
- 145 N. R. Subbaratnam and J. G. Calvert, The Mechanism of Methyl Hydroperoxide Formation in the Photooxidation of Azomethane at 25°, *J. Am. Chem. Soc.*, 1962, **84**, 1113–1118.
- 146 D. F. Dever and J. G. Calvert, Rate Studies of the Oxidation of Methyl Radicals in Oxygen-rich Media at 25°, *J. Am. Chem. Soc.*, 1962, **84**, 1362–1368.
- 147 J. J. Orlando, G. S. Tyndall, L. Vereecken and J. Peeters, The Atmospheric Chemistry of the Acetoxyl Radical, *J. Phys. Chem. A*, 2000, **104**, 11578–11588.
- 148 A. Mellouki, M. Ammann, R. A. Cox, J. N. Crowley, H. Herrmann, M. E. Jenkin, V. F. McNeill, J. Troe and T. J. Wallington, Evaluated kinetic and photochemical data for atmospheric chemistry: volume VIII – gas-phase reactions of organic species with four, or more, carbon atoms (≥C₄), *Atmos. Chem. Phys.*, 2021, **21**, 4797–4808.
- 149 R. Volkamer, B. Klotz, I. Barnes, T. Imamura, K. Wirtz, N. Washida, K. H. Becker and U. Platt, OH-initiated oxidation of benzene part I. Phenol formation under atmospheric conditions, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1598–1610.
- 150 A. S. Hasson, K. T. Kuwata, M. C. Arroyo and E. B. Petersen, Theoretical studies of the reaction of hydroperoxy radicals (HO₂) with ethyl peroxy (CH₃CH₂O₂), acetyl peroxy (CH₃C(O)O₂), and acetonyl peroxy (CH₃C(O)CH₂O₂) radicals, *J. Photochem. Photobiol., A*, 2005, **176**, 218–230.
- 151 H. Hou and B. Wang, A Systematic Computational Study on the Reactions of HO₂ with RO₂: The HO₂ + CH₃O₂(CD₃O₂) and HO₂ + CH₂FO₂ Reactions, *J. Phys. Chem. A*, 2005, **109**, 451–460.
- 152 H. Hou, L. Deng, J. Li and B. Wang, A Systematic Computational Study of the Reactions of HO₂ with RO₂: The HO₂ + CH₂ClO₂, CHCl₂O₂, and CCl₃O₂ Reactions, *J. Phys. Chem. A*, 2005, **109**, 9299–9309.
- 153 J. P. Anglada, S. Olivella and A. Solé, Mechanistic Study of the HO₂ + CH₃O₂ → CH₃O₂H + O₂ Reaction in the Gas Phase. Computational Evidence for the Formation of a Hydrogen-Bonded Diradical Complex, *J. Phys. Chem. A*, 2006, **110**, 6073–6082.
- 154 T. L. Nguyen, L. Vereecken and J. Peeters, Theoretical Study of the HOCH₂OO + HO₂ Reaction: Detailed Molecular Mechanisms of the Three Reaction Channels, *Z. Phys. Chem.*, 2010, **210**, 1081–1093.
- 155 L. Vereecken and J. S. Francisco, Theoretical studies of atmospheric reaction mechanisms in the troposphere, *Chem. Soc. Rev.*, 2012, **41**, 6259–6293.
- 156 M. J. Elrod, D. L. Ranschaert and N. J. Schneider, Direct Kinetics Study of the Temperature Dependence of the



- CH₂O Branching Channel for the CH₃O₂ + HO₂ Reaction, *Int. J. Chem. Kinet.*, 2001, **33**, 363–376.
- 157 X.-M. Zhou, Z.-Y. Zhou, Q.-Y. Wu, A. F. Jalbout and N. Zhang, Reaction of CH₃O₂ and HO₂: ab initio characterization of dimer structure and vibrational mode analysis for reaction mechanisms, *Int. J. Quantum Chem.*, 2006, **106**, 514–525.
- 158 E. Drougas, Quantum mechanical studies of the CH₃O₂ + HO₂ reaction, *Comput. Theor. Chem.*, 2016, **1093**, 98–103.
- 159 A. Novelli, L. Vereecken, B. Bohn, H.-P. Dorn, G. I. Gkatzelis, A. Hofzumahaus, F. Holland, D. Reimer, F. Rohrer, S. Rosanka, D. Taraborrelli, R. Tillmann, R. Wegener, Z. Yu, A. Kiendler-Scharr, A. Wahner and H. Fuchs, Importance of isomerization reactions for OH radical regeneration from the photo-oxidation of isoprene investigated in the atmospheric simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 2020, **20**, 3333–3355.
- 160 E. Praske, R. V. Otkjaer, J. D. Crounse, J. C. Hethcox, B. M. Stoltz, H. G. Kjaergaard and P. O. Wennberg, Atmospheric autoxidation is increasingly important in urban and suburban North America, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 64–69.
- 161 M. J. Newland, D. J. Bryant, R. E. Dunmore, T. J. Bannan, W. J. F. Acton, B. Langford, J. R. Hopkins, F. A. Squires, W. Dixon, W. S. Drysdale, P. D. Ivatt, M. J. Evans, P. M. Edwards, L. K. Whalley, D. E. Heard, E. J. Slater, R. Woodward-Massey, C. Ye, A. Mehra, S. D. Worrall, A. Bacak, H. Coe, C. J. Percival, C. N. Hewitt, J. D. Lee, T. Cui, J. D. Surratt, X. Wang, A. C. Lewis, A. R. Rickard and J. F. Hamilton, Low-NO atmospheric oxidation pathways in a polluted megacity, *Atmos. Chem. Phys.*, 2021, **21**, 1613–1625.
- 162 R. J. Yokelson, J. D. Crounse, P. F. DeCarlo, T. Karl, S. Urbanski, E. Atlas, T. Campos, Y. Shinozuka, V. Kapustin, A. D. Clarke, A. Weinheimer, D. J. Knapp, D. D. Montzka, J. Holloway, P. Weibring, F. Flocke, W. Zheng, D. Toohey, P. O. Wennberg, C. Wiedinmyer, L. Mauldin, A. Fried, D. Richter, J. Walega, J. L. Jimenez, K. Adachi, P. R. Buseck, S. R. Hall and R. Shetter, Emissions from biomass burning in the Yucatan, *Atmos. Chem. Phys.*, 2009, **9**, 5785–5812.
- 163 M. O. Andreae, Emission of trace gases and aerosols from biomass burning – an updated assessment, *Atmos. Chem. Phys.*, 2019, **19**, 8523–8546.
- 164 J. N. Crowley, N. Pouvesle, G. J. Phillips, R. Axinte, H. Fischer, T. Petäjä, A. Nölscher, J. Williams, K. Hens, H. Harder, M. Martinez-Harder, A. Novelli, D. Kubistin, B. Bohn and J. Lelieveld, Insights into HO_x and RO_x chemistry in the boreal forest via measurement of peroxyacetic acid, peroxyacetic nitric anhydride (PAN) and hydrogen peroxide, *Atmos. Chem. Phys.*, 2018, **18**, 13457–13479.
- 165 D. Tan, I. Faloon, J. B. Simpas, W. Brune, P. B. Shepson, T. L. Couch, A. L. Sumner, M. A. Carroll, T. Thornberry, E. Apel, D. Riemer and W. Stockwell, HO_x budgets in a deciduous forest: results from the PROPHET summer 1998 campaign, *J. Geophys. Res.*, 2001, **106**, 24407–24427.
- 166 A. Hofzumahaus, F. Rohrer, K. Lu, B. Bohn, T. Brauers, C.-C. Chang, H. Fuchs, F. Holland, K. Kita, Y. Kondo, X. Li, S. Lou, M. Shao, L. Zeng, A. Wahner and Y. Zhang, Amplified Trace Gas Removal in the Troposphere, *Science*, 2009, **324**, 1702–1704.
- 167 D. Kubistin, H. Harder, M. Martinez, M. Rudolf, R. Sander, H. Bozem, G. Eerdekens, H. Fischer, C. Gurk, T. Klüpfel, R. Königsstedt, U. Parchatka, C. L. Schiller, A. Stickler, D. Taraborrelli, J. Willimas and J. Lelieveld, Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA, *Atmos. Chem. Phys.*, 2010, **10**, 9705–9728.
- 168 J. Peeters, T. L. Nguyen and L. Vereecken, HO_x radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5935–5939.
- 169 J. Peeters, J.-F. Müller, T. Stavrou and V. S. Nguyen, Hydroxyl Radical Recycling in Isoprene Oxidation Driven by Hydrogen Bonding and Hydrogen Tunneling: The Upgraded LIM1 Mechanism, *J. Phys. Chem. A*, 2014, **118**, 8625–8643.
- 170 D. J. Medeiros, M. A. Blitz, P. W. Seakins and L. K. Whalley, Direct Measurements of Isoprene Autoxidation: Pinpointing Atmospheric Oxidation in Tropical Forests, *JACS Au*, 2022, **2**, 809–818.
- 171 F. Paulot, J. D. Crounse, H. G. Kjaergaard, A. Kürten, J. M. S. Clair, J. H. Seinfeld and P. O. Wennberg, Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, *Science*, 2009, **325**, 730–733.
- 172 S. Iyer, H. Reiman, K. H. Möller, M. P. Rissanen, H. G. Kjaergaard and T. Kurtén, Computational Investigation of RO₂ + HO₂ and RO₂ + RO₂ Reactions of Monoterpene Derived First-Generation Peroxy Radicals Leading to Radical Recycling, *J. Phys. Chem. A*, 2018, **122**, 9542–9552.
- 173 M. Rolletter, M. Kaminski, I.-H. Acir, B. Bohn, H.-P. Dorn, X. Li, A. Lutz, S. Nehr, F. Rohrer, R. Tillmann, R. Wegener, A. Hofzumahaus, A. Kiendler-Scharr, A. Wahner and H. Fuchs, Investigation of the α -pinene photooxidation by OH in the atmospheric simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 2019, **19**, 11635–11649.
- 174 A. W. Rollins, A. Kiendler-Scharr, J. L. Fry, T. Brauers, S. S. Brown, H.-P. Dorn, W. P. Dubé, H. Fuchs, A. Mensah, T. F. Mentel, F. Rohrer, R. Tillmann, R. Wegener, P. J. Wooldridge and R. C. Cohen, Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yield, *Atmos. Chem. Phys.*, 2009, **9**, 6685–6703.
- 175 E. Hellpointner and S. Gäh, Detection of methyl, hydroxymethyl and hydroxyethyl hydroperoxides in air and precipitation, *Nature*, 1989, **337**, 631–634.
- 176 A. V. Jackson and C. N. Hewitt, Atmosphere Hydrogen Peroxide and Organic Hydroperoxides: A Review, *Crit. Rev. Environ. Sci. Technol.*, 1999, **29**, 175–228.
- 177 M. Lee, B. G. Heikes and D. W. O'Sullivan, Hydrogen peroxide and organic hydroperoxide in the troposphere, *Atmos. Environ.*, 2000, **34**, 3475–3494.



- 178 A. Monod, E. Chevallier, R. D. Jolibois, J. F. Doussin, B. Picquet-Varrault and P. Carlier, Photooxidation of methylhydroperoxide and ethylhydroperoxide in the aqueous phase under simulated cloud droplet conditions, *Atmos. Environ.*, 2007, **41**, 2412–2426.
- 179 S. A. Epstein, D. Shemesh, V. T. Tran, S. A. Nizkorodov and R. B. Gerber, Absorption Spectra and Photolysis of Methyl Peroxide in Liquid and Frozen Water, *J. Phys. Chem. A*, 2012, **116**, 6068–6077.
- 180 J. Peeters and J.-F. Müller, HO_x radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14227–14235.
- 181 G. M. Wolfe, J. D. Crounse, J. D. Parrish, J. M. St. Clair, M. R. Beaver, F. Paulot, T. P. Yoon, P. O. Wennberg and F. N. Keutsch, Photolysis, OH reactivity and ozone reactivity of a proxy for isoprene-derived hydroperoxyenals (HPALDs), *Phys. Chem. Chem. Phys.*, 2012, **14**, 7276–7286.
- 182 J. C. Rivera-Rios, T. B. Nguyen, J. D. Crounse, W. Jud, J. M. S. Clair, T. Mikoviny, J. B. Gilman, B. M. Lerner, J. B. Kaiser, J. de Gouw, A. Wisthaler, A. Hansel, P. O. Wennberg, J. H. Seinfeld and F. N. Keutsch, Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation: observational bias in diagnosing pristine versus anthropogenically controlled atmospheric chemistry, *Geophys. Res. Lett.*, 2014, **41**, 8645–8651.
- 183 A.-K. Bernhammer, M. Breitenlechner, F. N. Keutsch and A. Hansel, Technical note: conversion of isoprene hydroxy hydroperoxides (ISOPOOHs) on metal environmental simulation chamber walls, *Atmos. Chem. Phys.*, 2017, **17**, 4053–4062.
- 184 J. Sanchez and T. N. Myers, Peroxides and Peroxide Compounds, Organic Peroxides, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, 1st edn, 2000.
- 185 G. L. Vaghjiani and A. R. Ravishankara, Kinetics and Mechanism of OH Reaction with CH₃OOH, *J. Phys. Chem. A*, 1989, **93**, 1948–1959.
- 186 H. R. Williams and H. S. Mosher, Peroxides. I. n-Alkyl Hydroperoxides, *J. Am. Chem. Soc.*, 1954, **76**, 2984–2987.
- 187 H. R. Williams and H. S. Mosher, Organic Peroxides. II. Secondary Alkyl Hydroperoxides, *J. Am. Chem. Soc.*, 1954, **76**, 2987–2990.
- 188 M. Riva, S. H. Budisulistiorini, Y. Chen, Z. Zhang, E. L. D'Ambro, X. Zhang, A. Gold, B. J. Turpin, J. A. Thornton, M. R. Canagaratna and J. D. Surratt, Chemical Characterization of Secondary Organic Aerosol from Oxidation of Isoprene Hydroxy Hydroperoxides, *Environ. Sci. Technol.*, 2016, **50**, 9889–9899.
- 189 P. Mettke, A. Mutzel, O. Böge and H. Herrmann, Synthesis and Characterization of Atmospherically Relevant Hydroxy Hydroperoxides, *Atmosphere*, 2022, **13**, 507.
- 190 X. Zhao, T. Zhang, Y. Zhou and D. Liu, Preparation of peracetic acid from hydrogen peroxide part I: kinetics for peracetic acid synthesis and hydrolysis, *J. Mol. Catal. A: Chem.*, 2007, **271**, 246–252.
- 191 P. Heinmöller, H.-H. Kurth, R. Rabong, W. V. Turner, A. Kettrup and S. Gäb, Selective HPLC Analysis of n-Alkyl Hydroperoxides up to C₁₈H₃₈O₂, *Anal. Chem.*, 1998, **70**, 1437–1439.
- 192 K. G. Paul, P. I. Ohlsson and S. Wold, Formation of Horseradish Peroxidase Compound I with Alkyl Hydroperoxides, *Acta Chem. Scand., Ser. B*, 1979, **33**, 747–754.
- 193 M. R. McGillen, G. S. Tyndall, J. J. Orlando, A. S. Pimentel, D. J. Medeiros and J. B. Burkholder, Experimentally Determined Site-Specific Reactivity of the Gas-Phase OH and Cl + i-Butanol Reactions Between 251 and 340 K, *J. Phys. Chem. A*, 2016, **120**, 9968–9981.
- 194 M. R. McGillen, L. Michelat, J. J. Orlando and W. P. L. Carter, The use of the electrotopological state as a basis for predicting hydrogen abstraction rate coefficients: a proof of principle for the reactions of alkanes and haloalkanes with OH, *Environ. Sci.: Atmos.*, 2024, **4**, 18–34.
- 195 B. Ervens, A. Rickard, B. Aumont, W. P. L. Carter, M. McGillen, A. Mellouki, J. Orlando, B. Picquet-Varrault, P. Seakins, W. R. Stockwell, L. Vereecken and T. J. Wallington, Opinion: challenges and needs of tropospheric chemical mechanism development, *Atmos. Chem. Phys.*, 2024, **24**, 13317–13339.
- 196 I. Barnes, K. H. Becker and L. Ruppert, FTIR product study of the self-reaction of β-hydroxyethyl peroxy radicals, *Chem. Phys. Lett.*, 1993, **203**, 295–301.
- 197 B. Nozière and L. Vereecken, Direct Observation of Aliphatic Peroxy Radical Autoxidation and Water Effects: An Experimental and Theoretical Study, *Angew. Chem., Int. Ed.*, 2019, **58**, 13976–13982.
- 198 B. Nozière and L. Vereecken, H-shift and cyclization reactions in unsaturated alkylperoxy radicals near room temperature: propagating or terminating autoxidation?, *Phys. Chem. Chem. Phys.*, 2024, **26**, 25373–25384.
- 199 B. Nozière and F. Fache, Reactions of organic peroxy radicals, RO₂, with substituted and biogenic alkenes at room temperature: unsuspected sinks for some RO₂ in the atmosphere?, *Chem. Sci.*, 2021, **12**, 11676–11683.
- 200 B. Nozière, O. Durif, E. Dubus, S. Kyllington, A. Emmer, F. Fache, F. Piel and A. Wisthaler, The reaction of organic peroxy radicals with unsaturated compounds controlled by a non-epoxide pathway under atmospheric conditions, *Phys. Chem. Chem. Phys.*, 2023, **25**, 7772–7782.
- 201 L. Onel, A. Brennan, F. F. Østerstrøm, E. Cooke, L. Whalley, P. W. Seakins and D. E. Heard, Kinetics and Product Branching Ratio Study of the CH₃O₂ Self-Reaction in the Highly Instrumented Reactor for Atmospheric Chemistry, *J. Phys. Chem. A*, 2022, **126**, 7639–7649.

