Environmental Science: Atmospheres

ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE

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

Received 14th February 2025
Accepted 6th June 2025

DOI: 10.1039/d5ea00023h

rsc.li/esatmospheres

A perspective on the reactions of organic peroxy radicals with HO_2

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The chemistry of organic peroxy radicals (RO_2) 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 ($RO_2 + RO_2$). Apart from the potential OH production from some oxygenated peroxy radicals, there is less research activity on the reactions of peroxy radicals with HO_2. This article reviews the existing literature data available on $RO_2 + HO_2$ reactions and highlights the gaps where future research is required. To date, limited information has been provided on the reactions of HO_2 with functionalized RO_2, 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 $RO_2 + HO_2$ on the tropospheric HO_x (=OH + HO_2) 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.

Environmental significance

Organic peroxy radicals (RO_2) 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 RO_2 with HO_2, 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 HO_2 in atmospheric chemistry.

Introduction

Organic peroxy radicals (RO_2) are essential intermediates in the atmospheric oxidation of volatile organic compounds (VOCs). These are emitted into the troposphere predominantly from biogenic[1] but also from anthropogenic sources. Besides its central role in the formation of tropospheric ozone and secondary organic aerosol (SOA), RO_2 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

$$RH + OH \rightarrow R + H_2O \tag{R1}$$

$$R + O_2 + M \rightarrow RO_2 + M \tag{R2}$$

or addition (R3) pathways,

$$R_2C{=}CR_2 + OH + M \rightarrow R_2C(OH)CR_2 + M \tag{R3}$$

$$R_2C(OH)CR_2 + O_2 + M \rightarrow R_2C(OH)C(O_2)R_2 + M, \tag{R4}$$

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 NO_2), halogen oxides (ClO, BrO, and IO) or radicals (OH, HO_2, RO_2, and NO_3). The competitiveness of a single process depends heavily on the ambient conditions and the structure of the individual RO_2 species. For instance, NO_x (=NO + NO_2) 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 RO_2 loss in air masses influenced by anthropogenic activities.

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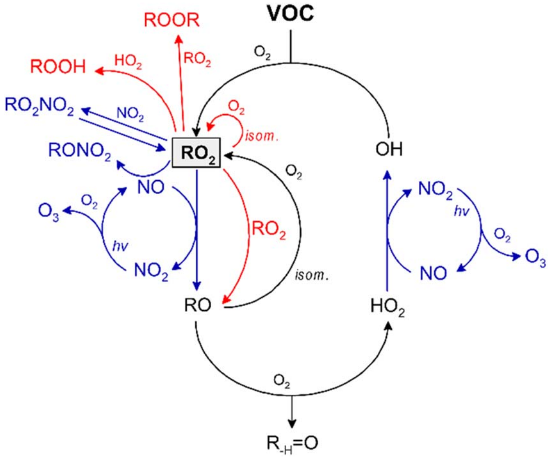

Fig. 1 Simplified, generic scheme for the major paths of RO_2 chemistry under NO_x-dominated conditions (blue) and NO_x-poor conditions, where other pathways become competitive (red).

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 ($=OH + HO_2$) 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 $RO_2 + HO_2$ are being investigated experimentally and, finally, gaps that require further research are identified.

Experimental and analytical approaches

Retrieving information on $RO_2 + HO_2$ 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 $RO_2 + HO_2$ 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 $RO_2 + HO_2$ reactions date back to the work by Cox and Tyndall,[12,13] who investigated the kinetics of $CH_3O_2 + HO_2$ 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 $RO_2 + HO_2$ 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 $RO_2 + HO_2$ reactions when the concentrations of the HO_2 precursor are sufficiently high. In the ideal case, the product branching ratios for $RO_2 + HO_2$ 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 RO_2 + HO_2 chemistry.[36–39] Apart from stable end-products, Winiberg *et al.* were the first to directly quantify OH formation from RO_2 + 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 VOC/Cl_2/HO_2-precursor or VOC/H_2O_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 CH_3O_2 + 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 $CH_3C(O)O_2$ + HO_2 by global modelling of the reaction system. Rate coefficients for all pathways of the $CH_3C(O)O_2$ + 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 CH_4/CH_3OH/Cl_2/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 $CH_3C(O)O_2$ 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 (=RO_2 + RO + HO_2 + 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 $H_3O^+(H_2O)_n$,[97,99,101–103,106–108,113,115] NH_4^+,[114] O_2^+,[92] NO_3^-,[109,110] I^-,[94,111] Br^-,[112,116] 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 $H_3O^+(H_2O)_n$, 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 $H_3O^+(H_2O)_n$ 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] $C_2H_5O_2$,[117,123] hydroxyalkyl peroxy,[119] acetyl peroxy,[124,125] acetonyl peroxy[125] 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 $RO_2 + HO_2$

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 $(0.5–2) \times 10^{-11}$ cm^3 $molecule^{-1}$ 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 HO_2 for specific substitution patterns (Table 1). Overall, $RO_2 + HO_2$ 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 RO_2 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 acetonyl 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 + HO_2. 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 HO_2. For example, the rate coefficients for both neopentyl and cyclopentyl peroxy (C_5) 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 $RO_2 + HO_2$ rate coefficients. The concept by King *et al.*[141] relies on perturbation frontier molecular orbital (PFMO) theory, and $RO_2 + HO_2$ 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 $R–CH{=}CH_2$, where R corresponds to the same organic substituent present in the peroxy radical.

As discussed in several studies, $RO_2 + HO_2$ 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 RO_2 + NO reactions, with NO being an electrophile, the HO_2 radical acts rather as a nucleophile in $RO_2 + HO_2$ 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.

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \quad (R5a)$$

$$RO_2 + HO_2 \rightarrow ROH + O_3 \quad (R5b)$$

$$RO_2 + HO_2 \rightarrow RO + OH + O_2 \quad (R5c)$$

$$RO_2 + HO_2 \rightarrow R_{-H}{=}O + OH + HO_2 \quad (R5d)$$

$$RO_2 + HO_2 \rightarrow R_{-H}{=}O + H_2O + O_2 \quad (R5e)$$

Interestingly, the first product study focusing on $RO_2 + HO_2$ investigated the acetyl peroxy radical and not the simpler CH_3O_2, as might be intuitively expected.[14] In the early 1980s, information on $CH_3O_2 + HO_2$ was obtained as an offshoot of investigations targeting the CH_3O_2 self-reaction.[143,144] In fact, Calvert and co-workers had already observed methyl hydroperoxide formation from CH_3O_2 radicals generated by the photolysis of azomethane in the early 1960s.[145,146] However, at that time, the occurrence and participation of HO_2 in the reaction system were not yet known, and methyl hydroperoxide was postulated to occur through either the CH_3O_2 self-reaction, the reaction of CH_3O_2 with CH_3O, or H atom abstraction from an organic species by excited CH_3O_2.[145,146]

In 1985, Niki *et al.* investigated the oxidation of acetaldehyde by irradiating CH_3CHO/Cl_2/air mixtures at atmospheric pressure and room temperature.[14] In these experiments, the HO_2 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 HO_2 must proceed *via* at least two channels yielding either peracetic acid (≈75%) or O_3 (≈25%).

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (R6a)$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3 \quad (R6b)$$

Table 1 Rate coefficients for $RO_2 + HO_2$ reactions. Temperature-dependence follows the Arrhenius expression $k(T) = A \times \exp(-E_a/RT)$

Peroxy radical	$k_{298\ K} \times 10^{12}$ ($cm^3\ s^{-1}$)	$A \times 10^{13}$ ($cm^3\ s^{-1}$)	E_a/R (K)	Ref.
Alkyl peroxy				
CH_3O_2	5.2	3.8	−780	134
$CH_3CH_2O_2$	6.9	6.4	−710	134
neo-$C_5H_{11}O_2$	15	1.4	−1380	18 and 55
cyclo-$C_5H_9O_2$	18	2.1	−1320	19
cyclo-$C_6H_{11}O_2$	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_2ClO_2	5.0	3.2	−820	48
$CHCl_2O_2$	5.9	5.6	−700	22
CCl_3O_2	5.1	4.8	−706	22
CF_2ClO_2	3.4			50
$CF_2ClCH_2O_2$	6.8			50
$CFCl_2CH_2O_2$	9.2			50
$CF_3CCl_2O_2$	1.9			49
CF_3CHFO_2	4.3	2.0	−910	134
$CF_3CF_2O_2$	1.2			50
$CF_2ClCF_2O_2$	1.2			50
β-Aryl peroxy				
$C_6H_5CH_2O_2$	12	1.5	−1310	134
Alkoxyalkyl peroxy				
$CH_3OCH_2O_2$	12			134
Acyl peroxy				
$CH_3C(O)O_2$	20	1.73	−730	134
$C_6H_5C(O)O_2$	38	110	−364	58
Carbonyl-containing peroxy				
$CH_3C(O)CH_2O_2$	9.0			134
α-Hydroxyalkyl peroxy				
$HOCH_2O_2$	12	0.056	−2300	134
β-Hydroxyalkyl peroxy				
$HOCH_2CH_2O_2$	13			134
HO–(1,2-$C_2H_2Cl_2$)–O_2	6			55
$(CH_3)_2C(OH)CH_2O_2$	14	0.56	−1650	134
$CH_3CH(OH)CH(O_2)CH_3$	15			54
$(CH_3)_2C(OH)C(O_2)(CH_3)_2$	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 RO_2 in the system. [d] Represents the mixture of $HOC_5H_8O_2$ 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 $RO_2 + HO_2$ reactions.

Subsequently, these results were confirmed by Moortgat *et al.*[42] who generated the target radicals by the flash photolysis of $Cl_2/CH_3CHO/CH_3OH/N_2/O_2$ 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 $CH_3C(O)OH + O_3$.[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 acid[147] and thermochemical considerations, has motivated Hasson *et al.*[27] to undertake a reinvestigation of the $CH_3C(O)O_2 + HO_2$ system. Based essentially on two observations, they did prove the existence of channel (R6c):

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3 + CO_2 + OH + O_2. \qquad \text{(R6c)}$$

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 $CH_3C(O)O_2 + HO_2$.

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 $RO_2 + HO_2$ 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 ($k_{Cl} < 2 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}),[20] while benzene is reasonably reactive towards OH radicals ($k_{OH} \approx 1 \times 10^{-12}$ cm^3 molecule^{-1} 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 $CH_3C(O)O_2 + HO_2$ and used phenol formation (from benzene + OH) to diagnose OH. It was previously found that, under these conditions, the phenol yield is about 53% ± 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 $RO_2 + HO_2$ 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 (ROO··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] cyclopentyl[19] and cyclohexyl[19] 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 Cl_2/CD_4/CH_3OH/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 $CD_3O_2 + HO_2$. Subsequently, Wallington and Japar[15] investigated $CH_3O_2 + HO_2$ 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]

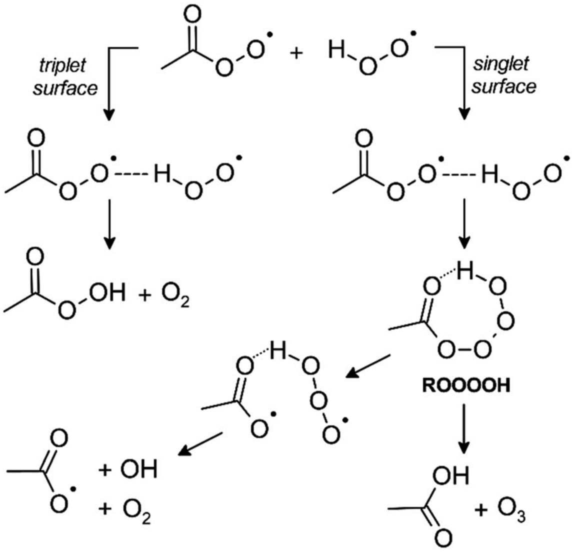

Fig. 2 Pathways of $RO_2 + HO_2$ reactions illustrated by $CH_3C(O)O_2 + HO_2$. The pathway yielding the hydroperoxide (peracid) proceeds over a triplet potential energy surface, while tetroxide formation proceeds over a singlet surface. The acetoxy radical formed in the OH channel immediately decomposes and yields $CO_2 + CH_3O_2$ under atmospheric conditions.

reported an 11% contribution of the carbonyl + H_2O channel from CH_3O_2 + HO_2 at 298 K, increasing to about 31% at 218 K.

Theoretical work on CH_3O_2 + HO_2 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] Drougas[158] 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 $CH_{3-n}Cl_nO_2$ ($n = 1$–3) or CH_2FO_2 with HO_2.[21–23] The co-product of this pathway was originally proposed to be H_2O. 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 + HO_2. These calculations reproduce the experimental data for CH_2FO_2 and CH_2ClO_2 radicals. Interestingly, no hydroperoxide was detected in the experiments on $CHCl_2O_2$ and CCl_3O_2 + HO_2.[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 + HO_2 channel (R5d).[152] Clearly, halogenated alkyl peroxy radicals behave differently from alkyl peroxy in their reaction with hydroperoxy radicals.

How relevant are RO_2 + HO_2 reactions to tropospheric chemistry?

Based on the reports of various field campaigns, it has been established that tropospheric HO_2 is of the order of 10^8 cm^{-3} with peak daytime concentrations of up to 1×10^9 cm^{-3} (*e.g.* Stone *et al.*[132] and references therein). Since the rate coefficients for the reactions of organic peroxy radicals with HO_2 are close to those with NO ($\approx 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K), RO_2 + HO_2 becomes thus competitive to RO_2 + NO once NO concentrations are close to HO_2. Before it was discovered that unimolecular isomerization of peroxy radicals is competitive under atmospheric conditions, RO_2 + HO_2 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 HO_2.[5] As a rule of thumb, RO_2 + HO_2 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 RO_2 + HO_2 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 RO_2 + 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 RO_2 + HO_2 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 O_3 limit the availability of NO.[161] Products of peroxy radical reactions with HO_2, namely hydrogen peroxide (HO_2 + HO_2) and peracetic acid (acetyl peroxy + HO_2), 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 RO_2 + HO_2 appears to be less limited to typical pristine conditions and becomes more frequently encountered.

Role of RO_2 + HO_2 in the tropospheric HO_x budget

The reactions of peroxy radicals with HO_2 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 RO_2 + HO_2 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 HO_2.[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 (ISOPOOHs) 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/Cl_2/O_2/N_2 mixtures were shown to generate OH with yields of about 80% ± 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 $HOCH_2CH_2O_2$.[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 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 coworkers 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]

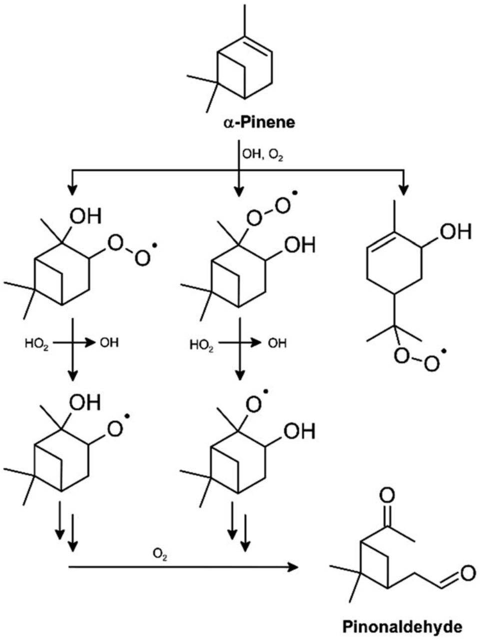

Fig. 3 OH production *via* the reaction of α-pinene-derived peroxy radicals with HO_2, as suggested by Eddingsaas *et al.*[37]

Table 2 OH yields reported for different RO_2 + HO_2 reactions at room temperature

Peroxy radical	OH yield (%)	Reference
$CH_3C(O)O_2$	40 ± 16	27
	<10	52
	43 ± 10	29
	50 ± 20	56
	61 ± 9	59
	51 ± 12	33
	48 ± 9	60
$CH_3CH_2C(O)O_2$	40 ± 10	32
$CH_3CH_2CH_2C(O)O_2$	47 ± 15	32
$CF_3C(O)O_2$	52 ± 5	28
$CF_3CF_2C(O)O_2$	50 ± 8	28
$CF_3CF_2CF_2C(O)O_2$	47 ± 11	28
$CF_3CF_2CF_2CF_2C(O)O_2$	27 ± 18	28
$C_6H_5C(O)O_2$[a]	≈20	56
	20 ± 5	58
$CH_3C(O)CH_2O_2$	67 ± 20	27
	≈15	56
	15 ± 8	30
	25 ± 13	32
	30 ± 4	61
$CH_3C(O)CH(O_2)CH_3$	≈20	56
	58 ± 10	32
$CH_2ClC(CH_3)(O_2)CHO$[b]	80 ± 20	32
$CH_2ClCH(O_2)C(O)CH_3$[c]	80 ± 20	32
$CH_2OHCH(O_2)C(O)CH_3$	48	39
$HOCH_2O_2$	20 ± 5	29
$HOCH_2CH_2O_2$	<4	56
$CH_3OCH_2O_2$	19 ± 8	31
O_2NO–(isoprene)–O_2	53	38

[a] Benzoyl peroxy. [b] Surrogate for OH–(methacrolein)–O_2. [c] Surrogate for OH–(methyl vinyl ketone)–O_2.

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 HO_2 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 HO_2 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 $RO_2 + HO_2$ 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 HO_2, highlights that the quantification of organic hydroperoxides is not only key for understanding $RO_2 + HO_2$ 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 Myers[184] and references therein):

$$ROOH + M^{n+} \rightarrow RO + OH^- + M^{(n+1)+} \tag{R7}$$

$$ROOH + M^{(n+1)+} \rightarrow RO_2 + H^+ + M^{n+} \tag{R8}$$

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 H_2O_2 by dimethyl sulphate for the preparation of methyl hydroperoxide,[185] the reaction of alkyl methanesulfonates (mesylates) with H_2O_2 for larger and branched alkyl hydroperoxides,[186,187] and the reaction of tertiary alcohols with H_2O_2 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 H_2O_2 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 H_2O, 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 $RO_2 + HO_2$ 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]

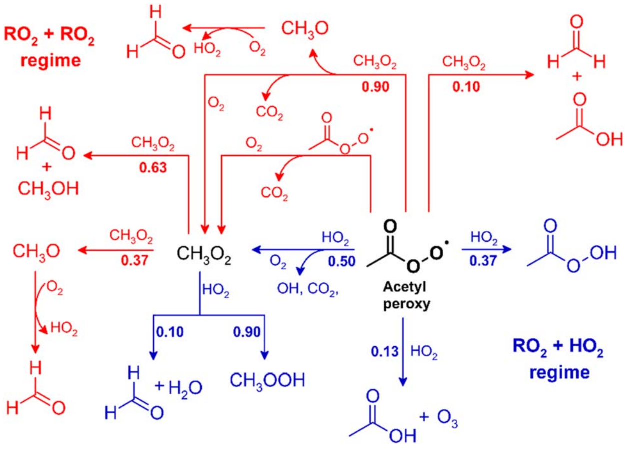

Fig. 4 Reaction sequence for $CH_3C(O)O_2$ in the absence of NO. The co-product O_2 is omitted for readability reasons. Branching ratios (in bold) represent the current IUPAC recommendations.[134]

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 $RO_2 + HO_2$ 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 $CH_3C(O)O_2 + HO_2$, 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 $CH_3C(O)O_2 + CH_3O_2$ reaction.[134] However, the relative error is 100%. Recently, Assali and Fittschen[124] 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 $CH_3C(O)O_2 + HO_2$ before the radical-propagating channel was discovered and included in the analysis.[24,33,42,52,56,59,60]

Some of these issues were minimized by Boyd *et al.*[55] by determining the rate coefficients under a large excess of HO_2. The authors employed nearly pseudo-first order conditions using an excess of H_2O_2, hence suppressing RO_2 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 CH_3O_2 + HO_2 rate coefficient significantly by detecting methyl peroxy and HO_2 using the FAGE-LIF method and applying an updated kinetic model, which uses a revised rate coefficient for the CH_3O_2 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 + HO_2 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 HO_2, 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 RO_2 + HO_2 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 RO_2 + HO_2 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 RO_2 + HO_2 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 peroxy[25] 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 RO_2 + HO_2 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 RO_2 + HO_2 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 RO_2 + HO_2 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 HO_2 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 proofreading this manuscript.

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