Reactions of organic peroxy radicals, RO$_2$, with substituted and biogenic alkenes at room temperature: unsuspected sinks for some RO$_2$ in the atmosphere?†

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Until now, the reactions of organic peroxy radicals (RO$_2$) with alkenes in the gas phase have been essentially studied at high temperature ($T \approx 360$ K) and in the context of combustion processes, while considered negligible in the Earth’s atmosphere. In this work, the reactions of methyl-, 1-pentyl- and acetylperoxy radicals (CH$_3$O$_2$, C$_5$H$_{11}$O$_2$, and CH$_3$C(O)O$_2$, respectively) with 2-methyl-2-buten, 2,3-dimethyl-2-buten and for the first time the atmospherically relevant isoprene, α-pinene, and limonene were studied at room temperature (298 ± 5 K). Monitoring directly the radicals with chemical ionization mass spectrometry led to rate coefficients larger than expected from previous combustion studies but following similar trends in terms of alkenes, with (in molecule$^{-1}$ cm$^3$ s$^{-1}$) $k_{\text{CH$_3$O$_2$}} = 10^{-16}$ to $10^{-17} \times 2/2$ and $k_{\text{CH$_3$C(O)O$_2$}} = 10^{-14}$ to $10^{-15} \times 5/5$. While these reactions would be negligible for CH$_3$O$_2$ and aliphatic RO$_2$ at room temperature, this might not be the case for acyl-, and perhaps hydroxy-, allyl- and other substituted RO$_2$. Combining our results with the Structure–Activity Relationship (SAR) predicts $k^\text{II}(298 \text{ K}) \sim 10^{-14}$ molecule$^{-1}$ cm$^3$ s$^{-1}$ for hydroxy- and allyl-RO$_2$ from isoprene oxidation, potentially accounting for up to 14% of their sinks in biogenic-rich regions of the atmosphere and much more in laboratory studies.

Introduction

Gas-phase organic peroxy radicals (RO$_2$, where “R” is an organic moiety) play key roles in the chemistry and oxidizing capacity of the lower atmosphere. Atmospheric RO$_2$ displays a wide variety of molecular structures, providing them with very different reactivities and rate coefficients often spanning over several orders of magnitude. Because of the difficulty in monitoring these radicals in the atmosphere, some unknowns remain in the details of their chemistry, which limit the understanding of atmospheric radical cycles. In particular, the measurements of OH and HO$_2$ radical concentrations in the atmosphere have consistently reported discrepancies with models, especially in organic-rich and vegetation-impacted regions, which were attributed to unknown sinks for RO$_2$. Over the last decade, the identification of previously overlooked reactions of RO$_2$ was able to reduce these discrepancies. But recent studies have confirmed the persistence of differences, indicating the occurrence of unknown processes consuming RO$_2$ and producing OH. RO$_2$ can react with a wide range of chemical compounds, including unsaturated organic molecules, such as alkenes, forming the corresponding alkene epoxy as the main product (Scheme 1). Until now, these reactions have been essentially studied for their interest in combustion processes and, with a few exceptions, investigated experimentally at high temperature ($T \approx 360$ K). Extrapolating these results suggest that these reactions are negligible at room temperature, and thus in the Earth’s atmosphere. To our knowledge, they have never been considered in atmospheric chemistry.

Experimental values for the rate coefficients for these reactions, $k^\text{II}$ (molecule$^{-1}$ cm$^3$ s$^{-1}$), are scarce, in particular for CH$_3$O$_2$ [ref. 8] and CH$_3$C(O)O$_2$, Ref. 7 summarizes these data and recommends expressions for $k^\text{II}(T)$, with $T = 360$–800 K.

Scheme 1 General scheme for the reaction of RO$_2$ with unsaturated compounds.

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fitted to the experimental results. For most of the RO₃ listed, extrapolating these expressions to 298 K leads to \( k_{II} \approx 10^{-19} \) molecule \(^{-1}\) cm \(^3\) s \(^{-1}\), thus justifying the omission of these reactions in atmospheric chemistry. But for some RO₂ such as CH₃C(O)O₂, the rate coefficients are 5 to 6 orders of magnitude larger than for CH₃O₂, suggesting that these reactions might not be entirely negligible at room temperature. Extrapolating the expressions in ref. 7 also results in uncertainties on the rate coefficients at 298 K of about \( \pm 10\% \) for CH₃O₂ and \( \pm 30\% \) for CH₃C(O)O₂, further justifying experimental studies. Finally, as previous studies focused exclusively on combustion systems, atmospherically relevant biogenic alkenes such as isoprene or terpenes have never been investigated. To our knowledge, the reaction of RO₂ with conjugated alkenes such as isoprene, prone to allylic rearrangement, has not been studied either. The reactions of RO₂ with biogenic alkenes at room temperature are thus worth investigating as a potential sink for at least some RO₂ in the atmosphere.

In this work, RO₂ + alkene reactions were investigated experimentally for the methyl peroxy radical, CH₃O₂, 1-pentyl peroxy radical, hereafter referred to as C₅H₁₁O₂, and peroxy acyl radical, CH₃C(O)O₂, with 2-methyl-2-butene, 2,3-dimethylbutene, isoprene, α-pinene, and limonene at 298 ± 5 K.

**Experimental section**

**Experimental conditions**

The complete list of experiments is given in Section S1 of the ESI† The experiments were performed in a vertical quartz reactor of length \( L = 120 \) cm and internal diameter \( d = 5 \) cm, previously described in ref. 10 (Fig. 1) and operated in a continuous flow. The bath gas (synthetic air, 3–4 sLM, standard temperature = 273 K and pressure = 1 atm) and the radical precursors (CH₄, CH₃I, C₅H₁₁I, CH₃CHO and, where necessary, Cl₂) were introduced at the top of the reactor. Under these conditions, the gas flow was well in the laminar regime, with a Reynolds number of about 150. At the bottom of the reactor (\( z = 120 \) cm in Fig. 1), 1–4% of the flow mixture was sampled into a Chemical Ionization Mass Spectrometer (CIMS) using proton transfer as the ionization method.† The CIMS monitored continuously the RO₂ and stable compounds in the reactions at a residence time of 17 s and recorded their changes as alkenes were periodically added to the reactor (Fig. 2A), which were then used in the kinetic analysis.

The temperature and relative humidity inside the reactor were determined in separate sets of experiments, but under the same conditions of pressure, flow, and UV-light irradiation, by placing an infrared hygrometer (Extech 101) inside the reactor. The uncertainties of ±5 K attributed to the temperature include

![Fig. 1 Schematics of the reactor used for the experiments.](image)

![Fig. 2 Typical experimental profiles and kinetic analysis for the reaction CH₂O₂ + isoprene (experiment Alk03 in Table S1†): (A) real-time evolution of CH₂O₂ concentration (red line, \( m/z = 84 \)), isoprene (green line, \( m/z = 69 \)) and production of isoprene epoxy (blue line, \( m/z = 121 \)). The areas shaded in blue correspond to the periodic addition of isoprene; (B) corresponding first-order variation of the ratio \( S_{RO₂}^c/S_{RO₂} \) as a function of isoprene concentration providing \( k_{II} \)(298 K).](image)
both the variabilities during the experiments and over the entire
time span of the study.

The RO₂ were produced photochemically by irradiating the
reactor over the wavelengths 280–400 nm with four fluorescent
lights (Philips TL12, 40 W). For CH₃O₂ and CH₃C(O)O₂, the
radical was produced by photolyzing chlorine, Cl₂, in the pres-
ence of an organic precursor (CH₄, and CH₃CHO, respectively)
as in ref. 11. For CH₂O, the sequence was:

\[
\text{Cl}_2 + \text{hv} \rightarrow 2\text{Cl}
\]
\[
\text{Cl} + \text{CH}_2 \rightarrow \text{CH}_3 + \text{HCl}
\]
\[
\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_2\text{O}_2 + \text{M}
\]

And for CH₃C(O)O₂:

\[
\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{C(O)} + \text{HCl}
\]
\[
\text{CH}_3\text{C(O)} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{C(O)O}_2 + \text{M}
\]

Irradiation tests were performed and confirmed that
CH₃CHO was not photolyzed by the UV lights in the reactor and
that its only fate was reaction.³

CH₂O and C₅H₁₁O₂ were also produced by photolyzing
directly their iodinated precursors, CH₃I and C₅H₁₁I, respec-
tively, as in ref. 10. For CH₂O:

\[
\text{CH}_3\text{l} + \text{hv} \rightarrow \text{CH}_3 + \text{I}
\]

Followed by reaction.⁴ For C₅H₁₁O₂:

\[
\text{C}_5\text{H}_{11}\text{I} + \text{hv} \rightarrow \text{C}_5\text{H}_{11} + \text{I}
\]
\[
\text{C}_5\text{H}_{11} + \text{O}_2 + \text{M} \rightarrow \text{C}_5\text{H}_{11}\text{O}_2 + \text{M}
\]

CH₂O was produced from two different precursors, CH₄ +
Cl₂ and CH₃I, to rule out potential artefacts due to side-chem-
istry due to Cl₂/Cl or I atoms. Table S1† in the ESI provides the
range of concentrations used for the different precursors. Only
a small fraction of Cl₂ was photolyzed, leading to [Cl] in the
range 10¹¹ to 10¹² molecule cm⁻³. In the systems using the
photolysis of iodinated compounds, the number of radicals produced
(thus I atoms) was in the same range, based on the
initial concentrations of RO₂ observed in this and previous
studies.¹⁰–¹¹ In this study, the maximum RO₂ concentrations in the
reactor were in the range 5 × 10¹⁰ to 5 × 10¹¹ molecule cm⁻³ for
CH₂O, 1–2 × 10¹¹ molecule cm⁻³ for C₅H₁₁O₂, and 1–3 ×
10¹⁰ molecule cm⁻³ for CH₃C(O)O₂.

Because the radicals studied had very different reactivities,
different set-ups were used to study their reactions. CH₂O was
produced in the top half of the reactor (z ≤ 54 cm in Fig. 1) and
reacted with alkenes in the dark in the lower half (z ≥ 56 cm),
the alkenes being introduced at z = 56 cm (Fig. 1). This was not
possible with C₅H₁₁O₂ and CH₃C(O)O₂, as producing them in the
top half of the reactor resulted in non-measurable concen-
trations at the bottom (z = 120 cm). These radicals were thus
produced in the bottom half of the reactor, the alkenes being
still introduced at z = 56 cm. Thus, for these radicals,
photochemical production and reactions with alkenes occurred
simultaneously in the lower half of the reactor. A separate series
of experiments were performed and showed that the photolysis of
RO₂ in the reactor was negligible, as was that of the stable
reaction products (peroxides and aldehydes).

To avoid potential artefacts due to varying flow rate or
pressure in the reactor when injecting the alkenes, the total flow
through the alkenes inlet was maintained continuous
throughout the experiments using a flow controller toggled
between pure N₂ and mixtures of alkenes in N₂. The existence of
potential artefacts due to insufficient mixing of the alkenes in
the reactor was also examined for CH₂O by varying the total
flow rate through the alkenes inlet from 5 to 200 sccm, while
maintaining the same alken concentrations (using different
dilution factors). The same results were obtained with all flow
rates, indicating that such mixing effects were negligible under
these conditions.

Chemicals

Gases. Synthetic air, 99.999%, CH₄, 1% in N₂, and Cl₂, 1% in
N₂, all Air Products. A standard mixture of CH₃CHO 2950 ppm
in N₂ was prepared by injecting 2 mL of the pure liquid in an
evacuated 6 L cylinder and completing with high pressure N₂.

Liquids. CH₃CHO, ≥ 99.5%, Aldrich; CH₃I, 99% stabilized,
Acros Organics; C₅H₁₁I, 97%, Acros; isoprene, 99%, Aldrich; α-
pinene, 98%, Sigma; limonene, 97%, Aldrich; 2,3-dimethyl-2-
butene, 98%, Acros. These liquids were placed in glass bubblers
and introduced into the reactor by sending controlled flows of
synthetic air or N₂ through the liquids. The gas-phase concen-
trations of these compounds in the reactor were then deter-
mined from the ratio of the alkene flow to the total flow and
from the vapor pressure of the liquids at 298 K given in Table S2
of the ESI.†

Detection of RO₂, alkenes, and reaction products. The
Chemical Ionization Mass Spectrometer (CIMS) used in this
study employs proton transfer as the ionization method.¹⁰–¹¹ A
compound A was thus detected by undergoing proton transfer
with the parent ions H₂O⁺ and its water clusters, H₂O⁺(H₂O)ₙ
(with n = 1–5), following the reaction:

\[
\text{A} + \text{H}_2\text{O}^+(\text{H}_2\text{O})_n \rightarrow \text{AH}^+(\text{H}_2\text{O})_n + (n - m + 1)\text{H}_2\text{O}
\]

A compound of molecular mass M was thus detected by its
ion products at m/z = M + 1, M + 19, M + 37, M + 55, M + 73, etc.
Previous studies have shown that a CIMS instru ment operating
on this principle can detect volatile RO₂ in addition to stable
molecules.¹⁰–¹² As in our previous studies,¹⁰¹¹ the potential
contribution of other compounds than RO₂ at their expected m/
z was investigated by adding an excess of NO in the reactor,
before or after the series of RO₂ + alkene experiments. These
tests showed that less than 10% of the signals came from other
compounds than RO₂, which was attributed to impurities in the
system. These constant contributions to the RO₂ signals
however cancelled out in the first-order kinetic analysis used in
this work. In the presence of alkenes, the contribution of other
compounds to the RO₂ m/z was not expected because the latter
have even values while stable C₆H₄O₂ compounds have odd m/z values with proton transfer.

The CIMS allowed monitoring continuously, with a time resolution of ~1 s, the evolution of RO₂, alkenes, and stable reaction products as the alkenes were periodically added to the reactor (Fig. 2A). Table S3 of the ESI† gives the complete list of the ion masses at which these compounds were detected. Although knowing the absolute concentrations of RO₂ in the reactor was not necessary for the first-order kinetic analysis in this work (cf. “Kinetic analysis” below), they were determined in order to constrain the simulations that were used to validate these analyses (see “Kinetic simulations” below). For this, the detection sensitivities determined for these radicals in previous studies were used: $S_{CH_3O_2} = 5000 \text{ Hz ppb}^{-1} \text{, } 10^{18}$ and $S_{CH_3C(O)O_2} = 2000 \text{ Hz ppb}^{-1}$, and $S_{CH_3O_2} = 200 \text{ Hz ppb}^{-1}$, and $S_{CH_3C(O)O_2} = 2000 \text{ Hz ppb}^{-1}$).

For each reaction investigated, the occurrence of the reaction was confirmed by observing both the decrease of the RO₂ signal, $S_{RO_2}$ (thus of RO₂ concentration) upon alkene addition and by the build-up of stable products at the expected ion masses for the alkene epoxy (Fig. 2A).

Kinetic analysis

The rate coefficients, $k^I$ (molecule$^{-1}$ cm$^{-3}$ s$^{-1}$), for the reactions RO$_2$ + alkene were determined experimentally from the ratios of the RO₂ signal between the absence and the presence of alkene, measured with the CIMS at the bottom of the reactor, and a simple first-order expression.

For radicals produced in the top half of the reactor and reacting in the dark in the bottom half (CH$_3$O₂ in this study), the maximum radical concentration, $[RO_2]_i$, is reached near mid-reactor ($z \approx 54 \text{ cm}$ in Fig. 1), and then decreases as a result of second-order sinks (self-reaction) and first-order sinks (wall losses, reactions with HO$_2$, potential isomerization... see Section S4 of the ESI† for the different RO₂) to reach $[RO_2]_f$ at $z = 120 \text{ cm}$. Assuming that the second-order sinks are negligible, $[RO_2]$ and $[RO_2]$ are linked by a simple first-order expression:

$$\ln \left( \frac{[RO_2]}{[RO_2]} \right) = -k^I \times t_{res} \quad (11)$$

where $k^I$ = sum of 1st order sinks and $t_{res} = $ residence time between $z = 56$ and $120 \text{ cm}$ ($\approx 17 \text{ s}$ in this study). In the presence of alkenes, the reaction RO₂ + alkene adds another first-order term, further reducing $[RO_2]_f$ to $[RO_2]_f$ at $z = 120 \text{ cm}$:

$$\ln \left( \frac{[RO_2]}{[RO_2]} \right) = -(k^I + k^{\text{alkene}}) \times t_{res} \quad (12)$$

with $k^{\text{alkene}} = k^I \times [\text{alkene}]$. Subtracting eqn (11) from eqn (12) thus gives:

$$\ln \left( \frac{[RO_2]}{[RO_2]} \right) = \ln \left( \frac{[SRO_2]}{[SRO_2]} \right) = -k^I_{\text{alkene}} \times [\text{alkene}] \times t_{res} \quad (13a)$$

thus:

$$k^I_{\text{alkene}} = -\frac{1}{[\text{alkene}]} \times \frac{1}{t_{res}} \times \ln \left( \frac{[SRO_2]}{[SRO_2]} \right) \quad (13b)$$

The rate coefficient $k^I$ was then determined by applying eqn (13b) to the RO₂ signals measured in the absence and in the presence of alkenes with the CIMS. Eqn (13b) is, however, only an approximation of the kinetics for CH$_3$O₂ because of the potential contributions of second-order sinks, and even more so for C$_6$H$_4$O₂ and CH$_2$C(O)O$_2$ as these radicals were simultaneously produced and consumed in the reactor (Fig. 3 bottom).

In addition, for all the radicals, the first-order sinks were not necessarily identical in the absence and in the presence of alkenes, as the concentrations of HO₂ (and of CH$_3$O₂ in the CH$_3$C(O)O$_2$ system) varied. Thus, kinetic simulations were run (next section) to determine the correction factors to apply to eqn (13b) to determine $k^I$ in each series of experiments.

The correction factors for the reactions of CH$_3$O₂ were small (see below), implying only small uncertainties in the kinetic results, but larger for C$_6$H$_4$O₂ and CH$_2$C(O)O$_2$, implying larger uncertainties. The uncertainties in the values of $k^I$ obtained from these analyses were thus estimated to be $\times 2/2$, for CH$_3$O₂, mostly based on the statistical dispersion, and $\times 5/5$ for the reactions of C$_6$H$_4$O₂ and CH$_2$C(O)O$_2$ because of the larger uncertainties in the correction factors and of the limited range of alkene concentrations that could be used in these experiments.
Kinetic simulations

Kinetic simulations using Chemsimul (V3.90, 2018) were performed to validate our kinetic analysis and to quantify the correction factors to apply to eqn (13b) to determine \( k^\text{II} \) from the experimental data. Complete details on these simulations, including the chemical equations, rate coefficients, and numerical results, are given in Section S4 of the ESL. Briefly, they consisted of calculating first the concentration profiles in the reactor with \([\text{alkene}] = 0\) and constraining \([\text{RO}_2]_0\) with the experimental \text{RO}_2 signals. Then, they were run again using alkene concentrations typical of the experiments to determine \([\text{RO}_2]_0\) (Fig. 3). Eqn (13b) was then applied to determine \( k^\text{II} \).

The results showed that, for CH\(_3\)O\(_2\) reactions, the correction factor was 0.76, mostly compensating for neglecting the self-reaction and for the differences in the first-order sinks in the absence and presence of alkenes. For the reactions of C\(_5\)H\(_{11}\)O\(_2\) and CH\(_3\)C(O)O\(_2\), these factors were larger, \( \sim 5 \) and \( \sim 19 \), respectively, compensating for a number of contributions detailed in Section S4 of the ESL.

Results and discussion

The rate coefficients, \( k^\text{II}(298 \text{ K}) \), obtained in this work are summarized in Fig. 4 and listed in Table S5 of the ESL. For the alkenes studied in this work they varied between about 2 and 7 \( \times 10^{-18} \) molecule\(^{-1}\) \( \text{cm}^3 \text{s}^{-1} \) for CH\(_3\)O\(_2\), 8 to 160 \( \times 10^{-18} \) molecule\(^{-1}\) \( \text{cm}^3 \text{s}^{-1} \) for C\(_5\)H\(_{11}\)O\(_2\) and 2 to 12 \( \times 10^{-14} \) molecule\(^{-1}\) \( \text{cm}^3 \text{s}^{-1} \) for CH\(_3\)C(O)O\(_2\). For all radicals, the rate coefficients followed similar trends in terms of alkene structure, the smallest coefficients being for isoprene and the largest for 2,3-dimethyl-2-butene. These results show that these reactions would be slow at room temperature for CH\(_3\)O\(_2\), C\(_5\)H\(_{11}\)O\(_2\), and probably other aliphatic RO\(_2\) but not necessarily for CH\(_3\)C(O)O\(_2\). These results also implied that, at room temperature, CH\(_3\)O\(_2\) reacts about 18 times faster than HO\(_2\), based on the rate coefficients for HO\(_2\) + alkenes in ref. 7.

Comparison with high-temperature data and the Structure–Activity Relationship (SAR)

In Fig. 4, the rate coefficients obtained in this work are compared with those extrapolated from previous high-temperature studies (for those available).\(^7\)\(^9\) The rate coefficients were also calculated for CH\(_3\)O\(_2\), CH\(_3\)C(O)O\(_2\) and the alkenes studied in this work using the Structure–Activity Relationship (SAR) recommended in ref. 7. For C\(_5\)H\(_{11}\)O\(_2\), this could not be done because the required parameters were not available in the literature. For CH\(_3\)O\(_2\) and CH\(_3\)C(O)O\(_2\), the activation energy of each reaction, \( E \) (kJ mol\(^{-1}\)), was calculated from the charge-transfer energy, \( \Delta E_c \) (kJ mol\(^{-1}\)), using an equation recommended in ref. 7.

\[
E = 83.0 - 1.82 \times \Delta E_c
\]  

(14)

\( \Delta E_c \) was itself determined from the absolute electronegativity, \( \chi \), and absolute hardness, \( \eta \), of the radical and alkene involved, each determined from their ionization energy, \( I \), and electron affinity \( A \):

\[
\Delta E_c = -(\chi_{\text{RO}_2} - \chi_{\text{alkene}})^2/4 \times (\eta_{\text{RO}_2} - \eta_{\text{alkene}})
\]  

(15)

with

\[
\chi = (I + A)/2
\]  

(16)

\[
\eta = (I - A)/2
\]  

(17)

The pre-exponential factor for the rate coefficients, \( A_0 \), used in these SAR calculations was the one recommended in ref. 7 and obtained from empirically fitting the combustion data: \( A_0 = 2.09 \times 10^{-14} \) molecule\(^{-1}\) \( \text{cm}^3 \text{s}^{-1} \). The ionization energies, \( I \), and electron affinities, \( A \), used in these calculations and the values predicted for \( k^\text{II}(298 \text{ K}) \) are presented in Table 1.

Fig. 4 clearly shows that the \( k^\text{II}(298 \text{ K}) \) obtained in this work is larger than expected from the combustion data, by about a factor 60 for CH\(_3\)C(O)O\(_2\) and 100 to 300 for CH\(_3\)O\(_2\), and by factors 20 and 250 to 1000, respectively, from the SAR predictions. In addition, while the present results indicate that CH\(_3\)O\(_2\) reacts 18 times faster than HO\(_2\) (with 2,3-dimethyl-2-butene) the
high-temperature data predicted it to react 6 times slower than H2O2.

Besides these discrepancies, the rate coefficients obtained in this work followed similar trends to the high-temperature experimental data and SAR predictions in terms of alkene substitution and RO2 structure. In particular, for all the RO2, kII(298 K) increased with alkene substitution, including for the alkenes studied here for the first time, in the sequence isoprene < 2-methyl-2-butene < α-pinene < limonene < 2,3-dimethyl-2-butene. As explained in ref. 7 for an electrophilic addition of a RO2 radical onto a double bond the activation energy, E, is expected to vary proportionally with the alkene ionization energy, which is implicit in eqn (14)−(17). In this work, kII was indeed found to increase with alkene ionization energies (Table 1): isoprene, 8.86;13 2-methyl-2-butene, 8.68;7 limonene, 8.30;11 2,3-dimethyl-2-butene, 8.27. Only for α-pinene the ionization energy of 8.07 eV found in the literature did not seem consistent with that of the similar molecule limonene. α-pinene was thus arbitrarily assigned an ionization energy of 8.5 eV in Fig. 4 and in the SAR calculations. With this, linear regressions (on the In scale) were performed on the results, but excluding the data for isoprene (see discussion below).

These linear regressions (dashed lines in Fig. 4) allowed the estimation of kII(298 K) for reactions that had not been studied. For instance, kII(298 K) for CH3C(O)O2 + terpenes was estimated to be in the range 0.5−1 × 10−13 molecule−1 cm3 s−1 (blue line in Fig. 4).

Leaving out the RO2 + isoprene data from the linear regressions revealed that the kII(298 K) for these reactions was systematically larger than the regressions (Fig. 4). These deviations corresponded to a factor 2.8 in average, thus providing an estimate for the excess reactivity due to allylic rearrangement in the RO2 + isoprene reactions.

As explained in ref. 7 and implicit in the SAR calculations, kII for RO2 + alkene also varies strongly with the RO2 structure. In the present work, for the same alkene, CH3C(O)O2 reacts 9000 to 18 000 times faster than CH3O2, while the combustion data predicted a ratio of 36 000 between these radicals with 2-methyl-2-butene. The SAR predicted even larger ratios, between 400 000 and 1 000 000, but the large discrepancies with the experimental data are likely due to the empirical determination of the preexponential factors.

The rate coefficients measured for C6H11O2 in this work indicate that this radical reacts about 14 times faster than CH3O2 in average. This seems reasonable as the rate coefficients for other radicals (for instance i-C3H7O2 in Table 1) indicate that kII increases only by a small factor for each additional carbon atom. However, as no other experimental data were available for this radical and its ionization energy and electron affinity were not available, no further comparison could be made with these rate coefficients.

The large discrepancies between the rate coefficients obtained in this work and those reported at high temperature7−9 seem difficult to reconcile, suggesting experimental or analytical artefacts in at least one of the data sets. In the present work,

Table 1 Parameters and SAR predictions for kII(298 K) for various RO2 and alkenes

| RO2 + Alkene                                         | I (eV) | A (eV) | α (eV) | η (eV) | ΔEc (kJ mol−1) | E (kJ mol−1) | kII(298 K) (molecule−1 cm3 s−1) |
|------------------------------------------------------|--------|--------|--------|--------|----------------|--------------|--------------------------------|
| CH3C(O)O2 + 2,3-dimethyl-2-butene                    | 8.27   | −2.27  | 3.0    | 5.3    | 43.2           | 4.39         | 3.6 × 10−14                     |
| Limonene                                             | 8.30   | −2.10  | 3.1    | 5.2    | 38.0           | 13.85        | 4.1 × 10−15                     |
| α-pinene                                             | 8.07   | −2.10  | 3.2    | 5.3    | 30.3           | 9.73         | 4.1 × 10−15                     |
| 2-Methyl-2-butene                                    | 8.68   | −2.24  | 3.2    | 5.5    | 24.5           | 38.37        | 3.9 × 10−14                     |
| Isoprene                                             | 8.86   | −2.80  | 3.0    | 5.8    | 11.58          | 2.75         | 4.4 × 10−15                     |
| CH3C(O)O2                                            | 11.18  | 1.21   | 6.2    | 5.0    | 11.00          | 1.40         | 4.8 × 10−15                     |
| i-C5H7O2(H3C−CHO2−CH3)                               | 11.86  | 2.02   | 6.4    | 4.4    | 11.44          | 1.60         | 4.8 × 10−15                     |
| CH2C(O)O2 + 2,3-dimethyl-2-butene                    | 43.2   | 4.39   | 3.6 × 10−14 |      |                |              |                                |
| CH3C(O)O2 + limonene                                 | 41.5   | 7.55   | 9.9 × 10−15 |     |                |              |                                |
| CH3C(O)O2 + α-pinene                                 | 39.0   | 11.95  | 1.7 × 10−15 |     |                |              |                                |
| CH3C(O)O2 + 2-methyl-2-butene                        | 38.0   | 13.85  | 7.8 × 10−16 |     |                |              |                                |
| CH3C(O)O2 + isoprene                                 | 40.3   | 9.73   | 4.1 × 10−15 |     |                |              |                                |
| CH3O2 + α-pinene                                     | 24.0   | 39.31  | 2.7 × 10−20 |     |                |              |                                |
| CH3O2 + isoprene                                     | 22.7   | 41.71  | 1.0 × 10−20 |     |                |              |                                |
| CH3O2 + α-pinene                                     | 21.0   | 44.71  | 3.0 × 10−21 |     |                |              |                                |
| CH3O2 + 2-methyl-2-butene                            | 20.4   | 43.83  | 1.9 × 10−21 |     |                |              |                                |
| CH3O2 + isoprene                                     | 22.3   | 42.34  | 7.9 × 10−21 |     |                |              |                                |
| i-C5H7O2 + 2,3-dimethyl-2-butene                     | 24.5   | 38.37  | 3.9 × 10−20 |     |                |              |                                |
| HOC3H7O2 + HOCH2−CHO2−CH3                            | 29.4   | 29.40  | 1.5 × 10−18 |     |                |              |                                |
| CH3O2 + α-pinene                                     | 27.3   | 33.36  | 3.0 × 10−19 |     |                |              |                                |
| CH3O2 + CH2O2(=CH−CH2−O)                            | 11.58  | 2.75   | 4.4 × 10−15 |     |                |              |                                |
| CH3O2 + limonene                                     | 11.18  | 1.21   | 5.0 × 10−15 |     |                |              |                                |
| CH3O2 + α-pinene                                     | 11.00  | 1.40   | 4.8 × 10−15 |     |                |              |                                |
| HOC3H7O2 + HOCH2−CHO2−CH3                            | 11.86  | 2.02   | 4.4 × 10−15 |     |                |              |                                |
| C6H11O2 + 2,3-dimethyl-2-butene                      | 11.44  | 1.60   | 4.8 × 10−15 |     |                |              |                                |

* Ref. 14. ** Ref. 15. *** Ref. 13. **** Based on cyclohexene in ref. 15 but corrected by −0.03 eV for each methyl group. ****** From ref. 15 but for two double bonds. Ref. 16. ******* Ref. 7.
monitoring directly RO₂ with only minor potential interference from other compounds should be more selective than monitoring the overall epoxide formation in previous studies.⁸⁻¹⁹ And using a relative kinetic approach (“alkene off”/“alkene on”) should limit the artefacts in the results by cancelling out a large part of the RO₂ sinks other than alkenes. The potential role of side-reactions involving OH radicals or Cl atoms was also investigated and ruled out by performing kinetic simulations (Section S4 of the ESI†). This was further confirmed by the fact that large discrepancies with the high-temperature results were obtained in this work with all types of precursors (Cl₂, iodinated compounds) and set-ups. One potential artefact that could account for the large rate coefficients in this work would be insufficient mixing, leading to large underestimations of the alkene concentrations. But, besides the fact that such mixing effects were ruled out by varying the total alkene flow rate (Experimental section), they should affect equally all the rate coefficients, while the discrepancies with the high-temperature data are much larger for CH₂O₂ than for CH₃C(O)O₂ reactions (by almost a factor of 5). As a further confirmation, the kinetic simulations showed that such large alkene concentrations would entirely consume RO₂, making it impossible to observe profiles such as that in Fig. 2B. While no obvious artefact accounting for the large discrepancies with the high-temperature data can be found in our work, identifying such an artefact in these previous studies⁸⁻¹⁹ is not easy, especially as little information was provided on their kinetic analysis. In these previous studies, the rate coefficients were determined from the overall formation of the epoxy product. Thus, underestimating the contribution of HO₂ to this formation or overestimating the RO₂ concentrations, for instance by overlooking side-reactions, could have potentially underestimated the RO₂ + alkene rate coefficients.

Other RO₂ and alkenes leading to significant reactions at room temperature

Beyond CH₃C(O)O₂ and the substituted alkenes studied in this work, it would be interesting to identify other alkenes and RO₂ leading to significant reaction rates at room temperature. First, previous studies have shown that oxygenated substituents such as carbonyl groups further enhance the reactivity of unsaturated compounds compared to their alkene analogues. In particular the rate coefficient for the reaction of CH₃C(O)O₂ with C₂H₅CHO (acrolein)⁷⁷ was reported to be about 3 times the one with propane. This suggests that oxidation products from isoprene, such as methacrolein and methyl vinyl ketone, or from terpenes, or even unsaturated alcohols such as the biogenic compound 2-methyl-3-buten-2-ol, might react faster with RO₂ than isoprene or terpenes themselves.

The SAR, ionization energies and electron affinities in ref. 7 were also used to estimate the rate coefficients with 2,3-dimethyl-2-butene at 298 K for other RO₂ than those studied experimentally: isopropylperoxy, i-C₃H₇O₂ or H₂C–CH₂O₂–CH₃, 1-hydroxy-2-propylperoxy, HOCH₂H₂O₂ or HOCH₂–CHO–CH₂, and allylperoxy, C₃H₅O₂ or H₂C=CH–CH₂O₂. The ionization energies, electron affinities, and results for these radicals are presented in Table 1. They show that, at 298 K, HOC₃H₅O₂ reacts about 40 times faster than its aliphatic analogue i-C₃H₇O₂. Allylperoxy, C₃H₅O₂, was predicted to react about 8 times faster than i-C₃H₇O₂, which was assumed to be a typical factor for allyl-substituents, in the absence of ionization energies and electron affinities allowing a comparison with the primary aliphatic analogue 1-C₃H₇O₂. Some RO₂ produced by the OH oxidation of isoprene contains both HO- and allyl-substituents, and thus their rate coefficients with alkenes might combine the above factors and be significant at room temperature. The rate coefficient with 2,3-dimethyl-2-butene for such C₅-RO₂ can be roughly estimated from that of 1-C₃H₇O₂, measured in this work, kII ≈1.5 × 10⁻¹⁶ molecule⁻¹ cm³ s⁻¹, and the factors × 40 and × 8 for the HO- and allyl substituents, leading to 5 × 10⁻¹⁴ molecule⁻¹ cm³ s⁻¹. This estimate has for only purpose to make a first assessment of the importance of these reactions in the laboratory and in the atmosphere, and would obviously need to be confirmed by experimental studies.

Conclusions and atmospheric implications

The rate coefficients for RO₂ + alkene reactions at room temperature measured in this work were larger than expected from previous combustion studies. While those for many RO₂, in particular aliphatic ones, would still be small (≤10⁻¹⁵ molecule⁻¹ cm³ s⁻¹), those for acyl-substituted RO₂ could be as large as 10⁻¹⁴ to 10⁻¹³ molecule⁻¹ cm³ s⁻¹. SAR predictions indicate that other substituents, such as HO- or allyl-, would also contribute to enhance the reactivity of RO₂ towards alkenes, especially when combined as for the RO₂ produced by the OH-oxidation of multi-unsaturated alkenes (isoprene, terpenes, …).

While these estimates await confirmation from further experimental studies, the importance of these reactions in the atmosphere and laboratory for the RO₂ produced by the OH-oxidation of isoprene can be determined from the rate coefficient estimated above. Assuming kII (RO₂ + isoprene) ≈1/5 × kII (RO₂ + 2,3-dimethyl-2-butene) = 10⁻¹⁴ molecule⁻¹ cm³ s⁻¹ and typical isoprene concentrations of 10¹² molecule cm⁻³ in the laboratory or smog chamber would correspond to RO₂ sinks of 0.01 s⁻¹. Note that, while some of these RO₂ radicals would rapidly undergo H-migration reactions,¹³⁻¹⁹ their HOOQO₂ isomers would also carry HO- and allyl-groups, and thus have similar rate coefficients to alkenes. In the absence of NO, the main other sink for the RO₂ would be their reactions with HO₂.

Typical HO₂ concentrations of 10⁷ molecule cm⁻³ and a rate coefficient of 10⁻¹¹ molecule⁻¹ cm³ s⁻¹ also correspond to a sink of 0.01 s⁻¹, implying that the reactions with isoprene could represent as much as half of the RO₂ sinks under such conditions. If so, they should lead to measurable concentrations of isoprene epoxies, which might have been overlooked or mis-attributed in previous isoprene oxidation studies.¹⁹ In the atmosphere, the concentrations reported (for instance in ref. 1) in vegetation-impacted regions, isoprene = 5 × 10¹⁰; NO = 5 × 10⁸; HO₂ = 10⁷ molecule cm⁻³, correspond to sinks for
isoprene-RO$_2$ (and HOOQO$_2$) of 0.0005, 0.002, and 0.001 s$^{-1}$, respectively. Reactions with isoprene could thus represent as much as 14% of the sinks for these RO$_2$ radicals, to which their reactions with methacrolein and methyl vinyl ketone would probably have to be added. Thus, for some RO$_2$, RO$_2$ + alkene reactions might not be negligible even in the atmosphere, which emphasizes the need for further experimental investigations at room temperature.

**Data availability**

Most of the data is presented in the ESI.$^\dagger$

**Author contributions**

BN: conceptualization; methodology; investigation; visualization; writing – original draft; FF: conceptualization; visualization; writing – original draft.

**Conflicts of interest**

The authors have no conflicts to declare.

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