Pressure dependent OH yields in the reactions of CH$_3$CO and HOCH$_2$CO with O$_2$

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OH-formation in the reactions of CH$_3$CO (R1) and HOCH$_2$CO (R4) with O$_2$ was studied in He, N$_2$ and air (27 to 400 mbar) using OH-detection by laser induced fluorescence (LIF). 248 nm laser photolysis of COCl$_2$ in the presence of CH$_3$CHO or HOCH$_2$CHO was used as source of the acyl radicals CH$_3$CO and HOCH$_2$CO. The LIF-system was calibrated in back-to-back experiments by the 248 nm laser photolysis of H$_2$O$_2$ as OH radical precursor. A straight-forward analytical expression was used to derive OH yields ($\alpha$) for both reactions. A Stern–Volmer-analysis results in

$$\frac{a}{\alpha_0} = 1 + \frac{9.4}{C_6} \left(10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \times [M]\right)$$

for N$_2$,

$$\frac{a}{\alpha_0} = 1 + \frac{3.6}{C_6} \left(10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \times [M]\right)$$

for He, and

$$\frac{a}{\alpha_0} = 1 + \frac{1.85}{C_6} \left(10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \times [M]\right)$$

for air. Our results for CH$_3$CO are compared to the previous (divergent) literature values whilst that for HOCH$_2$CO, for which no previous data were available, provide some insight into the factors controlling the yield of OH in these reactions.

1 Introduction

Acetyl radicals (CH$_3$CO) play an important role in atmospheric chemistry. Important sources of acetyl radicals are the photolysis of acetone in the upper troposphere and the reaction of acetaldehyde with OH in the troposphere. The hydroxyl-substituted hydroxy acetyl radicals (HOCH$_2$CO) are formed in the reaction of OH with glycol aldehyde (HOCH$_2$CHO). The only significant reaction of acetyl and hydroxy acetyl radicals in the atmosphere is with O$_2$, forming (mainly) peroxo radicals. Accompanying peroxy radical formation, (R1) displays a second reaction pathway forming OH and an organic by-product. The branching ratio ($\alpha$) for formation of OH increases from small values (<2%) at standard pressure to unity at pressures close to zero.$^{1,2}$

$$\text{CH}_3\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{C(O)O}_2 + \text{M} \quad (\text{R1a})$$

$$\rightarrow \text{OH} + c\text{-CH}_2\text{C(O)O} \quad (\text{R1b})$$

Reaction (R1) is considered to proceed via an excited peroxy radical CH$_3$C(O)O$_2$$^+$ that is either stabilised by collisions with the bath gas molecules M or decomposes to form OH.$^{3-9}$ This is illustrated in reaction Scheme 1 (R = CH$_3$). The pressure dependence of $\alpha$ thus originates from the competition between the pressure- and bath gas-dependent quenching rate $[M] \times k_M$ and the pressure-independent decomposition rate $k_D$. A kinetic

$$\text{Scheme 1 Generalised mechanism for the reactions of CH}_3\text{CO (R = CH}_3\text{)} \text{ and HOCH}_2\text{CO (R = HOCH}_2\text{) with O}_2.$$
For example, in their study of PAN formation, Bridier et al.\textsuperscript{14} generated CH$_3$CO radical in the presence of O$_2$ to examine the kinetics of the reaction of CH$_2$C(O)O$_2$ + NO$_2$ (R2) at pressures down to 20 mbar. As the results of the present publication show, at such pressures 18% of CH$_3$CO reacting with O$_2$ forms OH instead of CH$_3$C(O)O$_2$. Data recorded at low pressure by Bridier et al. might thus be subject to systematic error since reaction channel (R1b) was not known to take place in 1991.

The reaction of CH$_2$C(O)O$_2$ with HO$_2$ (R3), which competes with (R2) at low NO$_x$ levels,\textsuperscript{15} has drawn intense interest in recent years.\textsuperscript{13,16–18} Its main reaction channel (R3a) preserves a HO$_2$ species (HO$_2$ is OH + HO$_2$) and an organic radical and is hence radical-propagating, which helps sustain atmospheric oxidation capacity.

\[
\text{CH}_2\text{C(O)O}_2 + \text{HO}_2 \rightarrow \text{CH}_2\text{C(O)O} + \text{OH} + \text{O}_2 \quad \text{(R3a)}
\]

\[
\rightarrow \text{CH}_2\text{C(O)OH} + \text{O}_2 \quad \text{(R3b)}
\]

\[
\rightarrow \text{CH}_2\text{C(O)OH} + \text{O}_3 \quad \text{(R3c)}
\]

In experiments on (R3), CH$_2$C(O)O$_2$ and HO$_2$ are usually generated by reaction of Cl atoms with CH$_3$CHO and CH$_3$OH in air involving intermediate generation of CH$_3$CO and CH$_3$OH radicals. Therefore, OH-generation influences the initial [CH$_3$C(O)O$_2$]/[HO$_2$]-ratio in these experiments. In product studies that do not allow for an experimental separation between different OH-formation routes, (R1b) must be well known so that discrimination between OH formed in (R1b) and (R3a), respectively, is possible.

In the present work we employ a new experimental approach to quantify the pressure-dependence of the OH forming channels (R1b) and (R4b) of the reactions of O$_2$ with CH$_3$CO and its OH-substituted analogue HOCH$_2$CO.

\[
\text{HOCH}_2\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{HOCH}_2\text{C(O)O}_2 + \text{M} \quad \text{(R4a)}
\]

\[
\rightarrow \text{OH} + \cdots \quad \text{(R4b)}
\]

We assume that, for reaction (R4), the same pathways are available as in (R1), i.e. competition between peroxy-radical formation and OH (see Scheme 1, R = HOCH$_2$). The formation of the peroxy radical, its UV-absorption spectrum and its reaction with HO$_2$ will be subject of a future publication from this group.

Throughout this work the branching ratios of the OH-forming reaction channels are defined as follows: $k_{1b}/k_1 = z_{1b}$ and $k_{4b}/k_4 = z_{4b}$.

### 2 Experimental

#### 2.1 Experimental set-up

The experiments detailed in this publication were performed using the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) apparatus that has been described previously\textsuperscript{19,20} and only a short description is given here. Experiments were conducted in a 500 cm$^3$ reactor at room temperature. The pressure was monitored with a capacitance manometer, and gas flow rates were selected such that a fresh gas sample was available for photolysis at each laser pulse. Reactions were performed at pressures between 27 and 400 mbar in nitrogen and helium bath gases with added O$_2$ or N$_2$.

Reactions were initiated by the 248 nm photolysis of H$_2$O$_2$ (8–12 × 10$^{14}$ molecule cm$^{-3}$) or COCl$_2$ (3–11 × 10$^{15}$ molecule cm$^{-3}$) using an excimer laser (Lambda Physik). Laser fluences of 39–55 mJ cm$^{-2}$ per pulse resulted in formation of 0.3–0.5 × 10$^{12}$ OH radicals cm$^{-3}$ or 1–5 × 10$^{12}$ Cl-atoms cm$^{-3}$. Two absorption cells located upstream of the reactor enabled on-line concentration measurements of the reactants at 185 nm and 214 nm. The optical path-lengths of the absorption cells are $l_{185} = 43.8$ cm and $l_{144} = 34.8$ cm.

Fluorescence from OH was detected by a photomultiplier tube shielded by a 309 nm interference filter and a BG 26 glass cut-off filter. The frequency doubled emission from an Nd:YAG-pumped dye laser (Quantel, Lambda Physik) was used to excite the A$^2\Sigma^+(v = 1)$ ← X$^2\Pi(v = 0)$ transition of OH at 281.997 nm.

#### 2.2 Chemicals

Liquid samples of CH$_3$CHO (Roth, ≥ 99.5%) were degassed by repeated evacuation, and stored in a blackened glass bulb as ~1% mixture in N$_2$. HOCH$_2$CHO was prepared during the experiments from its dimer (Sigma-Aldrich) by heating the solid sample to 50–75 °C and eluting gaseous HOCH$_2$CHO by a continuous flow of N$_2$. COCl$_2$ (Fluka, >99%) was stored in a stainless steel canister as ~4% mixture in N$_2$ or He. H$_2$O$_2$ (AppliChem, 50%) was concentrated in vacuum to >80% and used as liquid sample. He (Westfalen, 99.999%), N$_2$ (Westfalen, 99.999%) and O$_2$ (Westfalen, 99.999%) were used as supplied.

### 3 Results

#### 3.1 Experimental approach

We performed back-to-back experiments in reaction mixtures containing either H$_2$O$_2$ or COCl$_2$ as photolytic sources of OH radicals or Cl atoms. Addition of CH$_3$CHO or HOCH$_2$CHO to the COCl$_2$ experiments converted Cl atoms into CH$_3$CO or HOCH$_2$CO, which reacted with O$_2$ to form OH. This allowed us to compare OH formation via title reactions (R1b) and (R4b) directly with OH production from H$_2$O$_2$-photolysis, a well-characterized source of OH radicals. Formation of acyl radicals by the reaction of Cl atoms with CH$_3$CHO ($\Delta H = -58$ kJ mol$^{-1}$)\textsuperscript{18,21} or HOCH$_2$CHO ($\Delta H = -49$ kJ mol$^{-1}$)\textsuperscript{18,21} are exothermic processes and the nascent fragments are expected to be vibrationally and rotationally hot. Assuming an energy transfer efficiency of 300 cm$^{-1}$ per collision with N$_2$, hot CH$_3$CO would be deactivated within 16 collisions, ensuring that, at the high pressures of bath gases used in this study, acetyl should, to a good approximation, be thermalized before reaction with O$_2$ takes place. Experiments in which N$_2$ was mixed with 1% O$_2$ yielded the same results as those with 21% O$_2$, so that no evidence was obtained for reaction of non-thermalised CH$_3$CO with O$_2$. Even in the experiments in He (presumably a less efficient energy transfer medium that N$_2$) no dependence of the OH-yield on O$_2$ partial pressure was obtained. We note also that the existence of a direct channel for OH-formation from excited CH$_3$CO and O$_2$ is considered unlikely.\textsuperscript{9}
3.1.1 Determination of $z$. The OH-LIF system was calibrated by photolyzing $\text{H}_2\text{O}_2$ that, at 248 nm, generates OH radicals with a quantum yield of 2.\textsuperscript{22}

$$\text{H}_2\text{O}_2 + h\nu (248 \text{ nm}) \rightarrow 2\text{OH}$$  \hspace{1cm} (R5)

Quasi-instantaneous photolytic OH-formation and subsequent OH loss via (R6) result in a mono-exponential decay of [OH] that was recorded by OH-LIF.

$$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (R6)

The LIF-signal is proportional to [OH] and was fitted by eqn (2) where $f_{\text{cal}}$ is a calibration factor that quantifies the sensitivity of the LIF-system:

$$\text{LIF}(t) = f_{\text{cal}} \times [\text{OH}](t) = s_{\text{OH}} \times e^{-a_{\text{OH}}t}$$  \hspace{1cm} (2)

where $a_{\text{OH}}$ and $s_{\text{OH}}$ represent the fitted parameters. Due to the low conversion of $\text{H}_2\text{O}_2$ ($<0.1\%$) its concentration, $[\text{H}_2\text{O}_2]$, can be considered constant over the course of the reaction. With $k'_a = k_a \times [\text{H}_2\text{O}_2]$ and $[\text{OH}]_a$ as the initial OH concentration, the temporal evolution of [OH] can be described by the integrated rate law for first-order kinetics:

$$[\text{OH}](t) = [\text{OH}]_0 \times e^{-k_a't} \hspace{1cm} (3)$$

Combining eqn (2) and (3) we get:

$$f_{\text{cal}} [\text{OH}]_0 = s_{\text{OH}}$$  \hspace{1cm} (4)

In back-to-back experiments, $\text{H}_2\text{O}_2$ was replaced by $\text{COCl}_2$ and an acyl radical source (CH$_3$CHO or HOCH$_2$CHO). Photolysis of $\text{COCl}_2$ generates Cl atoms with a quantum yield of 2.\textsuperscript{23,24}

$$\text{COCl}_2 + h\nu (248 \text{ nm}) \rightarrow 2\text{Cl} + \text{CO}$$  \hspace{1cm} (R7)

Reaction of Cl with CH$_3$CHO (R8) forms CH$_3$CO with a yield very close to unity ($k_8 = 8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).\textsuperscript{17}

$$\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{HCl}$$  \hspace{1cm} (R8)

OH formation in reaction (R1b) and its main loss via reaction (R9) are both resolved on the time-scale of our experiments and a bi-exponential time-dependence of the LIF-signal is observed ($k_9 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).\textsuperscript{17,18}

$$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CO} + \text{H}_2\text{O}$$  \hspace{1cm} (R9a)

$$\hspace{2cm} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$$  \hspace{1cm} (R9b)

Reaction with OH generates mainly CH$_3$CO ($x_{a0} = 0.95$) which is accounted for in the analytical expression of the [OH] time evolution presented below. Only 5% of the OH formed in (R1) is thus converted via (R9b) into CH$_3$CHO. Even if CH$_3$CHO were converted with unity yield into OH radicals, this would result in a maximum overestimation of no more than 5% in the value of $z_{1b}$.

Measured LIF-profiles were analysed using eqn (5).

$$\text{LIF}(t) = f_{\text{cal}} \times [\text{OH}](t) = s_{\text{Cl}} \times \frac{a_{\text{Cl}}}{a_{\text{Cl}}-a_{\text{Cl}}} (e^{-a_{\text{Cl}}t} - e^{-a_{\text{Cl}}t'})$$  \hspace{1cm} (5)

where $a_{\text{Cl}}$, $a_{\text{Cl}}$, and $s_{\text{Cl}}$ represent the fitted parameters. Under the assumptions that (R1) is fast compared to (R8) and (R9) and that [CH$_3$CHO] remains constant on the experimental time-scale, an analytical expression for the temporal evolution of [OH] can be derived.

$$[\text{OH}](t) = \frac{z_{1b}[\text{Cl}]_0/k_s}{(1-z_{1b}[\text{Cl}]_0/k_s)} \left( e^{-k'_a't} - e^{-(1-z_{1b}[\text{Cl}]_0/k_s)t'} \right) \hspace{1cm} (6)$$

In this expression, $k'_a = [\text{CH}_3\text{CHO}] \times k_a$, $k'_a = [\text{CH}_3\text{CHO}] \times k_a$ and $[\text{Cl}]_0$ is the Cl-concentration initially formed by photolysis. Conditions were chosen such that reaction (R1) was 5.2–250 times faster than (R8), and 28–1300 times faster than (R9) and thus fast on the experimental time-scale of $\sim 1$ ms. Combining eqn (5) and (6) we get:

$$z_{1b}f_{\text{cal}} [\text{Cl}]_0 = s_{\text{Cl}}$$  \hspace{1cm} (7)

$f_{\text{cal}}$ can be eliminated from eqn (7) by insertion of eqn (4) because experiments were conducted back-to-back.

$$z_{1b} = \frac{s_{\text{Cl}}}{[\text{OH}]_0 / [\text{Cl}]_0}$$  \hspace{1cm} (8)

This assumes that fluorescence quenching is dominated by the bath gas and that the contribution of reactants is negligible so that switching between $\text{H}_2\text{O}_2$ and $\text{COCl}_2$/aldehyde does not change the detection sensitivity to OH. The experiments performed in He, which is a weak quencher of OH-fluorescence, are the most likely to be influenced, should this not be the case. In Section 3.3 we show however that such quenching effects did not have a measurable effect on the results obtained.

The initial concentrations $[\text{OH}]_0$ and $[\text{Cl}]_0$ were calculated from $[\text{H}_2\text{O}_2]$ and $[\text{COCl}_2]$, the respective 248 nm cross sections and the number of photons per photolysis pulse $n_{\text{Phot}}$. We then derive:

$$z_{1b} = \frac{s_{\text{Cl}}}{[\text{OH}]_0 / [\text{Cl}]_0} \times \frac{\phi_{248}^{\text{H}_2\text{O}_2} n_{\text{Phot}}}{1 - e^{-248 [\text{H}_2\text{O}_2] / (\sigma_{\text{laser}} \cdot k_s)}} \times \frac{\phi_{248}^{\text{COCl}_2} n_{\text{Phot}}}{1 - e^{-248 [\text{COCl}_2] / (\sigma_{\text{laser}} \cdot k_s)}}$$

$$= \frac{s_{\text{Cl}}}{[\text{OH}]_0 / [\text{Cl}]_0} \times \frac{1 - e^{-248 [\text{H}_2\text{O}_2] / (\sigma_{\text{laser}} \cdot k_s)}}{1 - e^{-248 [\text{COCl}_2] / (\sigma_{\text{laser}} \cdot k_s)}}$$  \hspace{1cm} (9)

Since the laser intensity remained stable (within $\sim 1\%$) during back-to back experiments, $n_{\text{Phot}}$ cancels out as do the quantum yields of OH formation ($\phi_{248}^{\text{H}_2\text{O}_2}$) and Cl formation ($\phi_{248}^{\text{COCl}_2}$) that both equal 2. The precursor concentrations $[\text{H}_2\text{O}_2]$ and $[\text{COCl}_2]$ were calculated from the respective optical depths $\sigma_{214}^{\text{H}_2\text{O}_2}$ and $\sigma_{214}^{\text{COCl}_2}$ measured at 214 nm in a separate absorption cell (see Section 2.1).

$$[\text{precursor}] = \frac{OD_{214}^{\text{precursor}}}{\sigma_{214}^{\text{precursor}}}$$  \hspace{1cm} (10)

HOCH$_2$CHO was used as acyl radical precursor in experiments for the determination of $z_{4b}$. Reaction of Cl atoms with HOCH$_2$CHO (R10) forms HOCH$_2$CO with a yield of
\[ s_{10a} = 0.65 \left( k_{10} = 7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \right) \]. \(^{25,26}\) Reaction of HOCHCHO with \( O_2 \) (R11), is not known to form OH. \(^{25,26}\)

\[
\begin{align*}
\text{Cl} + \text{HOCH}_2\text{CHO} & \rightarrow \text{HOCH}_2\text{CO} + \text{HCl} \quad \text{(R10a)} \\
\text{HOCHCHO} + \text{O}_2 & \rightarrow \text{HC(O)CHO} + \text{HO}_2 \quad \text{(R11)} \\
\end{align*}
\]

Reaction with HOCH_2CHO (R12) is the main OH loss channel in these experiments.

\[
\begin{align*}
\text{OH} + \text{HOCH}_2\text{CHO} & \rightarrow \text{HOCH}_2\text{CO} + \text{H}_2\text{O} \quad \text{(R12a)} \\
\text{HOCHCHO} + \text{H}_2\text{O} & \rightarrow \text{HOCH}_2\text{CO} + \text{H}_2\text{O} \quad \text{(R12b)} \\
\end{align*}
\]

Reaction with OH generates HOCH_2CO with a higher yield \((s_{12a} = 0.80)\) than reaction with Cl. Based on this kinetic scheme, one again expects a bi-exponential time profile of [OH] that can be analysed by eqn (5). The temporal evolution of [OH] is described by the integrated rate law (11) which was derived analytically assuming reaction (R4) to be fast compared to reactions (R10) and (R12) and that [HOCH_2CHO] was not significantly depleted during the experiments.

\[
[\text{OH}](t) = \frac{s_{10a}k_{10a}k_{10b}[\text{Cl}]}{k_{10a} - k_{10b}} \left( e^{-k_{10a}t} - e^{-(1-s_{12a}k_{12})t} \right) \tag{11}
\]

with \( k_{10} = [\text{HOCH}_2\text{CHO}] \times k_{10} \) and \( k_{10} = [\text{HOCH}_2\text{CHO}] \times k_{12} \).

Under the experimental conditions applied in this work and assuming the rate coefficients of (R1) and (R4) to be equal, (R4) was 12 to 280 times faster than (R10) and 110 to 2700 times faster than (R12) and, thus, fast on the experimental time-scale of \( \sim 1 \text{ ms} \). As for the CH_3CO + O_2 system we can derive an analytical expression for \( z_{4b} \) from eqn (4) and (11).

\[
\begin{align*}
214 & 214 \\
\text{OD} & = \frac{1}{z_{10a}} \frac{s_{10} \text{H}_2\text{O}_2 \cdot \sigma_{214} \text{COCl}_2 \cdot \sigma_{214} \text{H}_2\text{O}_2}{s_{\text{OH}} \cdot \sigma_{214} \text{COCl}_2 \cdot \sigma_{214} \text{H}_2\text{O}_2} \quad \text{(12)}
\end{align*}
\]

\( z_{4b} \) can thus be derived from measurement of \( \text{OD}^{214} \text{H}_2\text{O}_2 \), \( \text{OD}^{214} \text{COCl}_2 \), \( s_{\text{OH}} \) and \( s_{10} \), the absorption cross sections of COCl_2 and H_2O_2 at 214 nm and 248 nm and the branching ratio \( z_{10a} \).

### 3.1.2 Error estimation

The exponents in eqn (9) and (12) can be expanded in a Taylor series that is stopped after the second term. By insertion of eqn (9) and (10) thus becomes

\[
\begin{align*}
214 & 214 \\
\text{OD} & = \frac{s_{10} k_{10} s_{\text{OH}} k_{12}}{1 - e^{-k_{10a}t} - e^{-(1-s_{12}k_{12})t}} \quad \text{(13)}
\end{align*}
\]

Similarly, eqn (12) becomes

\[
\begin{align*}
214 & 214 \\
\text{OD} & = \frac{s_{10} k_{10} s_{\text{OH}} k_{12}}{1 - e^{-k_{10a}t} - e^{-(1-s_{12}k_{12})t}} \quad \text{(14)}
\end{align*}
\]

This allows us to separate statistical errors, i.e. reading errors or uncertainties in the determinations of \( s_{\text{OH}} \) and \( s_{10} \) which are small, from the systematic errors originating from uncertainties in literature values of the absorption cross sections and, in the case of \( z_{4b} \), the branching ratio \( z_{10a} = 0.65 \pm 0.05 \).\(^{25}\) To reduce systematic error, absorption cross sections were taken from literature sources that specify values for both wavelengths used in this work. Values for H_2O_2 were taken from Vaghjiani et al.,\(^{27}\) values for COCl_2 were taken from Meller et al. whose data are published in the MPI-Mainz UV/VIS Spectral Atlas\(^{28}\). \( \sigma_{214}^{\text{H}_2\text{O}_2} = 33.0 \pm 2.2 \), \( \sigma_{214}^{\text{H}_2\text{O}_2} = 9.25 \pm 0.70 \), \( \sigma_{248}^{\text{COCl}_2} = 11.3 \pm 1.1 \) and \( \sigma_{248}^{\text{COCl}_2} = 8.96 \pm 0.90 \) all values given in units of \( 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \).
We note that the data show no dependence on the O₂ concentration and that values of \( k_{1b} \) determined in air would be higher if CH₃CO were not thermalized and if there were an additional OH-formation route via CH₃COO⁻ + O₂. This observation rules out a significant contribution of hot acetyl radicals.

3.3 CH₃CO + O₂ (He)

Back-to-back PLP-LIF-experiments on (R1) were performed at pressures between 33 and 400 mbar of He. From the fit-parameters and the respective [CH₃CHO] we derived \( k_a = (7.6 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k_b = (1.9 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) where the uncertainties represent statistical errors (2σ) in the fit-parameters, only. As described above, [CH₃CHO] was determined from barometric and mass flow readings and carries an additional uncertainty of \( \sim 20\% \). These values are, within combined uncertainties, in accordance with the currently recommended literature values.

Fig. 3 shows the results of all experiments performed in He with an addition of 2.7 (or 1.3) mbar of O₂ as a plot of the reciprocal of \( k_{1b} \) against He number density [M]. For the experiments with 2.7 mbar O₂, a linear regression of the data resulted in (all errors statistical, 2σ)

\[
\frac{1}{k_{1b}}(\text{He}) = (2.13 \pm 0.35) + (3.52 \pm 0.19) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} [\text{M}]
\]

The two data points obtained using 1.3 mbar of O₂ reveal the expected trend, slightly enhanced yields (but a similar slope) due to the quenching effect of O₂. With 2.7 mbar of O₂ we expect \( k_{1b}^{-1} \) to approach 1.6 ± 0.11 (the value we derive from \( \frac{k_M}{k_D} \)-value for N₂ and air) at zero pressure. Within the statistical uncertainties the intercept (2.13 ± 0.35) is however slightly higher than this. In the experiments in He, the main contribution to OH-fluorescence quenching is O₂ and not the H₂O₂ and CH₃CHO and Cl₂CO reactants. The fact that the two datasets obtained with different O₂ concentrations are in good agreement, supports this.

We therefore re-fitted the data using eqn (1), i.e. we performed another linear regression with the intercept being fixed to 1.6 (thick solid line in Fig. 3). From this we derived

\[
\frac{k_M}{k_D} = (3.62 \pm 0.05) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ (error statistical only, 2σ)}
\]

We applied eqn (13) to incorporate the systematic uncertainties (2σ) and derived a final value of

\[
\frac{k_M}{k_D} = (3.6 \pm 0.6) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}
\]

In Fig. 3 these error margins are represented by thin solid lines.

3.4 HOCH₂CO + O₂ (N₂/O₂)

Back-to-back PLP-LIF-experiments using HOCH₂CHO as acyl radical precursor were performed at pressures between 33 and 269 mbar in N₂ or air. Fig. 4 shows a pair of OH-LIF time profiles recorded at 133 mbar in N₂ which were fitted using eqn (2) or (5), respectively. As a check for possible error sources

\[
\text{OH-LIF signal / arb. units}
\]

\[
\text{1/} t \text{ (s)}
\]

Fig. 4 OH-LIF profiles measured in back-to-back experiments at 133 mbar of N₂ bath gas containing 2.7 mbar of O₂. The solid lines are fits using equations (2) and (5).
of our experimental approach, we derived the rate-coefficients of reactions (R10) and (R12) from the fit-parameters and the respective [HOCH₂CHO], we get \( k_{10} = (6.6 \pm 0.3) \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹, and \( k_{12} = (1.0 \pm 0.2) \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹ where the uncertainties represent statistical errors (2\( \sigma \)) in the fit-parameters, only. [HOCH₂CHO] was derived by measuring its absorption at 185 nm using a literature value for the absorption cross section of HOCH₂CHO (\( \sigma \) is \( 3.85 \pm 0.20 \times 10^{-18} \) cm² molecule⁻¹) and carries an additional uncertainty of \( \sim 10\% \). Our values are, within combined uncertainties, in accordance with the currently recommended literature values of \( k_{10, \text{Lit}} = (7.6 \pm 1.5) \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹ and \( k_{12, \text{Lit}} = (0.80^{0.33}_{-0.23}) \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹.

Fig. 5 shows the results of all single determinations of \( x_{4b}^{-1} \) plotted as \( x_{4b}^{-1} \) versus bath gas number density [M] or pressure, respectively.

\[
\frac{k_M}{k_D} = (1.85 \pm 0.16) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \quad \text{(solid black line in Fig. 5) for the data recorded in nitrogen and}
\]
\[
\frac{k_M}{k_D} = (1.62 \pm 0.14) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \quad \text{(dashed black line) for the data recorded in air.}
\]

Within combined uncertainties measurements in nitrogen and air resulted in the same values of \( \frac{k_M}{k_D} \) and, accordingly, \( x_{4b}^{-1} \).

The slightly larger \( x_{4b}^{-1} \) values observed at higher pressures in air are potentially due to experimental scatter. Our data do not however allow us to completely rule out the existence of an additional, \( \text{O}_2 \)-dependent OH-source as the cause. Therefore, we decided to rely exclusively on the data recorded in \( \text{N}_2 \) (with 1–10\% of \( \text{O}_2 \) added) which would be less impacted by such an additional OH-source. Doing so we commit a maximum error of 7\% in \( x_{4b}^{-1} \) compared to values derived from all data. The fact that the data obtained at a fixed \( \text{O}_2 \)-to-\( \text{N}_2 \) ratio of 21\%, but at various pressures (and thus at different \( \text{O}_2 \) concentrations), display no significant deviation from the expected behaviour, suggests that an additional OH forming channel that is dependent on the \( \text{O}_2 \) partial pressure is not significant. Incorporation of systematic uncertainties (2\( \sigma \)), results in a final value of \( \frac{k_M}{k_D} = (1.85 \pm 0.38) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \). The error margins that also enclose the data recorded in air are presented in Fig. 5 by thin solid lines.

Our studies on OH formation in the reactions of \( \text{CH}_3\text{CO} \) (R1) and \( \text{HOCH}_2\text{CO} \) (R4) with \( \text{O}_2 \) reveal a strong dependence of the yield on substituents, with \( \frac{k_M}{k_D} \) for (R4) a factor of 5 smaller than for (R1). Under the assumption that the collisional quenching of both activated peroxy radicals proceeds at a similar rate this large difference can be attributed to a more efficient decomposition of \( \text{HOCH}_2\text{C(O)}\text{OO}_2 \) compared to \( \text{CH}_3\text{C(O)}\text{OO}_2 \). This may be rationalized in terms of a more favourable reaction pathway in which the hydroxyl group of \( \text{HOCH}_2\text{C(O)}\text{OO}_2 \) enables formation of a six-membered transition state as illustrated in Scheme 2 in which highly stable products (formaldehyde and \( \text{CO}_2 \)) are formed along with OH.

4 Comparison with literature

4.1 \( \text{CH}_3\text{CO} + \text{O}_2 \)

Several experimental studies have reported OH formation via (R1b) in \( \text{N}_2 \), \( \text{O}_2 \) and \( \text{He} \). Table 1 and Fig. 2 and 3 summarise
Table 1  Summary of results (all room temperature) and comparison with literature

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<tbody>
<tr>
<td>CH3CO kM/kD</td>
<td>N2</td>
<td>9.4 ± 1.7</td>
<td>(5.9)</td>
<td>11.0 ± 2.5</td>
<td>3.59 ± 0.60</td>
<td>2.67 ± 1.40</td>
<td>(9)</td>
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<tr>
<td>CH3CO kM/kD</td>
<td>He</td>
<td>3.6 ± 0.6</td>
<td>1.06 ± 0.05</td>
<td>4.3 ± 1.0</td>
<td>3.9 ± 0.6</td>
<td>1.31 ± 0.51</td>
<td>1.63 ± 0.54</td>
<td>1.6</td>
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<tr>
<td>Ratio N2/He</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.7</td>
<td>2.7</td>
<td>1.6</td>
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<td></td>
</tr>
<tr>
<td>HOCH2CO kM/kD</td>
<td>N2</td>
<td>1.85 ± 0.38</td>
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The k_M/k_D values from these studies as well as those from our work. Note that in Fig. 3 the literature data are plotted with an intercept of 1.6 to take into account the presence of O_2 in our experiments at extrapolated zero mbar of He.

Tyndall et al.\(^5\) studied the reaction of Cl atoms with CH_3CHO by irradiation of Cl_2-CH_3CHO-mixtures in N_2 or O_2 in environmental chambers and analysed the reaction mixtures by infra-red absorption spectroscopy. They found a pressure-dependence of the apparent rate coefficient of (R8) when the experiments were performed in O_2 but not for the measurements in N_2. The value measured in O_2 increased if the experimental pressure was decreased; at 1.6 mbar the apparent rate coefficient was 2.7 times higher than that derived in N_2. The authors attributed these findings to OH formation in (R1b). Thus, they did not directly detect OH, but their kinetic and product studies provided strong evidence for OH formation. The k_M-values shown in Table 1 was derived by Carr et al.\(^3\) based on a personal communication with Tyndall et al.\(^5\).

Blitz et al.\(^4\) used the 248 nm pulsed laser photolysis of CH_3C(O)OH in He to generate CH_3CO and used OH-LIF for the detection of hydroxyl radicals formed in (R1b) at pressures between 13–533 mbar. Calibration of the LIF-system was achieved by fixing x_{1b} at zero pressure to unity, which neglects to take into account the fact that the acetyl radical yield is pressure dependent as a significant (but variable) fraction thermally decomposes to CH_3 and CO, at least in nitrogen bath gas.\(^31–33\) Blitz et al. could thus have underestimated the value of k_M/k_D by about 16%.\(^3\)

Talukdar et al.\(^34\) used different photolytic schemes (photolysis of acetone, Cl + CH_3CHO and OH + CH_3CHO) for CH_3CO generation coupled to OH-LIF to investigate OH-formation or modification of OH kinetics due to (R1) at experimental pressures between 27–800 mbar in He, N_2 and O_2. The resulting k_M/k_D values are in good agreement with our results.

Kovács et al.\(^6\) used two low-pressure fast discharge flow tubes (operated at pressures between 1.3 and 11 mbar in helium) that were equipped with LIF or resonance fluorescence detection of OH radicals. CH_3CO was formed by reacting CH_3CHO with OH that was generated from H and NO_2, or from F and H_2O. The authors compared decay rates of OH radicals with or without O_2 present in the reaction mixture. We applied eqn (1) to the z_{1b} data provided by Kovács et al. to derive a value of k_M/k_D that is in good agreement with those presented by Talukdar et al. and this work.

Carr et al.\(^3\) used the 248 nm pulsed laser photolysis of CH_3C(O)OH to generate prompt OH and CH_3CO radicals in equal amounts. Detection of OH radicals was achieved by OH-LIF. Experiments were restricted to pressures of <138 mbar of He, or <34 mbar of N_2. The approach is self-calibrated since it allows comparison of prompt OH formed in the photolysis step to OH formed from acetyl + O_2 and thus requires only separation of the LIF signal into prompt and slow components. Errors in the separation of prompt and slow OH contributions would thus affect z_{1b} two-fold and would be manifest at higher pressures of N_2 where the yield of OH is small. The resulting value for k_M/k_D agrees well with the previous one of Blitz et al. from the same lab but accordingly differs by a factor of \sim 3 from our values.

Carr et al.\(^2\) photolysed acetone at 248 nm to form CH_3CO and used OH-LIF detection. The resulting OH time profiles were fitted by a bi-exponential equation similar to the one presented here. Relative values of z_{1b} were measured in the pressure range of 7–400 mbar and based on an absolute scale by setting z_{1b} at 0 mbar to unity. Data were corrected by 25–35% for a pressure-dependence\(^31,33\) in the CH_3CO yield of acetone photolysis. In their N_2-experiments the authors needed to make an additional correction since they observed a decrease of LIF-sensitivity at elevated pressures. The correction factors were derived in separate experiments by measuring OH-formation from 248 nm photolysis of t-butylhydroperoxide at the same pressure.

Although not a detailed study of the OH yield in the title reaction, we recently published data on OH formation in the reaction of HO_2 with CH_3C(O)OH (ref. 13) and also observed (in this case “unwanted”) OH-formation via (R1b). This work was conducted in a different apparatus and used a different CH_3CO-formation scheme (355 nm-pulsed photolysis of CH_3CHO-CH_3OH-Cl_2-O_2-N_2-mixtures). OH was detected by an OH-LIF-unit that was calibrated by measuring OH from the reaction of HO_2 with NO. In spite of the different experimental approach we could accurately simulate the OH signals due to reaction (R1b) with the OH yield presented in the current work (see Fig. 8 in Groß et al.\(^5\)). Use of z from the more recent publication of Carr et al.\(^2\) would have resulted in an overestimation of initial OH-formation by a factor of 3.
Our results are in good agreement with those of Talukdar et al.\textsuperscript{4,6} and Kovács.\textsuperscript{6} We cannot explain the differences between our work and that of Blitz et al.\textsuperscript{4} and Carr et al.\textsuperscript{2,5} but we highlight the fact that no correction needs to be applied to our data.

In Table 1 we also show the ratio of the respective values in N\textsubscript{2} and He bath gases. From our data we derive a value of 2.6 which is in agreement with those of Talukdar et al.\textsuperscript{(2.7) and the 2007 study of Carr et al.\textsuperscript{2.6}. From the 2011 dataset of Carr et al. we derive a lower value of 1.6.

4.2 HOC\textsubscript{2}CHO + O\textsubscript{2}

Butkovskaya et al.\textsuperscript{35} investigated the OH-initiated oxidation of HOC\textsubscript{2}CHO in a turbulent flow reactor at 267 mbar of N\textsubscript{2}. A chemical ionisation mass spectrometer was used to detect OH and derive a yield of $x_{ab} = 22\%$. This high yield may reflect the fact that Butkovskaya et al.\textsuperscript{35} were unaware that the reaction of HOC\textsubscript{2}C(O)O\textsubscript{2} with HO\textsubscript{2} (formed at a yield of 20\% from OH + HOC\textsubscript{2}CHO in the presence of O\textsubscript{2}) forms OH with a yield of $\sim 70\%$.\textsuperscript{16,36}

OH formation has also been observed\textsuperscript{37} in the reaction of O\textsubscript{2} with CH\textsubscript{3}COO, which is isomeric with HOC\textsubscript{2}CHO. Similar to (R4), OH-formation is accompanied by CH\textsubscript{2}O and CO\textsubscript{2} by-products. The value of $k_M/k_D$ reported, $(7.4 \pm 1.9) \times 10^{-18}$ cm$^3$ molecule$^{-1}$, is four times larger than our value for HOC\textsubscript{2}CHO. Given that the products of decomposition are identical the difference must be related to energetic differences in the transition state leading to dissociation.

5 Conclusion

We determined the pressure-dependence of the OH-forming branching ratios $x_{1b}$ of reaction (R1a) and $x_{ab}$ reaction (R4b) using a novel experimental approach. The values for $x_{ab}$ are in accordance with some earlier studies\textsuperscript{6,34} but clearly differ from those from the Leeds group\textsuperscript{14,17} that derive much higher OH yields. Our data for $x_{ab}$ show that hydroxylation of CH\textsubscript{3}CO enhances OH-formation in the reaction with O\textsubscript{2} by approximately a factor of five.

Acknowledgements

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References