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Direct measurements of OH and other product yields from the HO₂ + CH₃C(O)O₂ reaction

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Abstract

The reaction $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{O}_2$ (Reaction R5a), $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{O}_3$ (Reaction R5b), $\text{CH}_3 + \text{CO}_2 + \text{OH} + \text{O}_2$ (Reaction R5c) was studied in a series of experiments conducted at 1000 mbar and (293 ± 2) K in the HIRAC simulation chamber.

5 For the first time, products, $(\text{CH}_3\text{C}(\text{O})\text{OOH}, \text{CH}_3\text{C}(\text{O})\text{OH}, \text{O}_3$ and OH) from all three branching pathways of the reaction have been detected directly and simultaneously. Measurements of radical precursors ($\text{CH}_3\text{OH}, \text{CH}_3\text{CHO}$), HO_2 and some secondary products HCHO and HCOOH further constrained the system. Fitting a comprehensive model to the experimental data, obtained over a range of conditions, determined the
10 branching ratios $\alpha_{(\text{R5a})} = 0.37 \pm 0.10$, $\alpha_{(\text{R5b})} = 0.12 \pm 0.04$ and $\alpha_{(\text{R5c})} = 0.51 \pm 0.12$ (errors at 2σ level). Improved measurement/model agreement was achieved using $k_{(\text{R5})} = (2.4 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is within the large uncertainty of the current IUPAC and JPL recommended rate coefficients for the title reaction. The rate coefficient and branching ratios are in good agreement with a recent study performed by GroB
15 et al. (2014b); taken together, these two studies show that the rate of OH regeneration through Reaction (R5) is more rapid than previously thought. GEOS-Chem has been used to assess the implications of the revised rate coefficients and branching ratios; the modelling shows an enhancement of up to 5% in OH concentrations in tropical rainforest areas and increases of up to 10% at altitudes of 6–8 km above the equator, compared to calculations based on the IUPAC recommended rate coefficient and yield.
20 The enhanced rate of acetylperoxy consumption significantly reduces PAN in remote regions (up to 30%) with commensurate reductions in background NO_x .

1 Introduction

25 Organic peroxy radicals, RO_2 , play a key role in atmospheric chemistry, impacting on the tropospheric HO_x (OH and HO_2) cycle and the O_3 budget. The reaction of OH with volatile organic compounds (VOCs) produces RO_2 radicals which have two main

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destruction pathways: (i) reaction with NO and (ii) reaction with HO₂ or other RO₂ radicals. In areas where reaction with NO dominates the RO₂ loss (typically when [NO] > 100 pptv), RO₂ radicals rapidly react with NO forming NO₂ and recycling OH, through the creation and destruction of HO₂ (Reactions R1–R3). By day, the NO₂ produced in these cycles is converted to O₃, a primary component in photochemical smog.



However, in very low NO_x environments (e.g., remote forested areas or over the marine boundary layer) loss of RO₂ is dominated by reaction with HO₂ and other RO₂ radicals (Reactions R4a–R4c); previously considered as important radical termination processes (Lightfoot et al., 1992; Tyndall et al., 2001) with several possible products depending on the structure of the *R* group. For small alkylperoxy radicals, reaction with HO₂ predominantly produces an organic peroxide (ROOH) through Reaction (R4a). This process is a radical sink in the atmosphere, as a fraction of the water soluble peroxide is lost before radicals are regenerated by photolysis. Observations of ROOH are important as they can be used as an indication of the oxidative capacity of the troposphere (Phillips et al., 2013) and uptake onto aqueous aerosol may influence S(IV) to S(VI) conversion (Lee et al., 2000).



More recent research has shown that radical termination may not be the exclusive reaction pathway for certain RO₂ radicals. Hasson et al. (2004) observed, using chamber studies and measuring stable products, that certain peroxy radical +

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for substituted RO₂ radicals has been put forward as a potential explanation for the shortfall in the [OH] prediction under these conditions (Taraborrelli et al., 2009, 2012; Lelieveld et al., 2008) although at best it merely conserves total HO_x concentrations. Stone et al. (2012) have shown that further amplification of OH in the isoprene mechanism is needed. However, the importance of the kinetics and products of RO₂ + HO₂ chemistry as a radical terminating step under low to moderate NO_x conditions should not be understated. Overall, the kinetics and products of RO₂ + HO₂ is central to the troposphere of the atmosphere especially in the low NO_x environments which are pervasive outside of the industrialized regions of the planet.

A number of studies on the title reaction have taken place with contradictory results as summarised in Jenkin et al. (2007). The results of Jenkin et al. (2007) are in excellent agreement with Hasson et al. (2004) reporting $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$ of $(0.40 \pm 0.16) : (0.20 \pm 0.08) : (0.40 \pm 0.16)$. These indirect observations of channel (Reaction R5c) have been supported by the direct observation of OH using calibrated laser induced fluorescence (LIF), by Dillon and Crowley (2008). Dillon and Crowley also reported smaller but significant OH yields for the reactions of three other carbonyl-containing RO₂. In their most recent work (Groß et al., 2014b), a Transient Absorption Spectroscopy (TAS) detection system was coupled to a calibrated LIF apparatus to enable a more comprehensive study of Reaction (R5). The reactant radicals HO₂ and RO₂, and the channel (Reaction R5b) product O₃ were monitored by TAS, along with OH (or deuterated OD) by LIF. Experiments were conducted over a range of pressures (~ 133 – 667 mbar), with yields of $\alpha_{(R5b)} = 0.16 \pm 0.08$ and $\alpha_{(R5c)} = 0.61 \pm 0.09$ reported, independent of pressure. This is the highest reported OH yield to date, however Groß et al. (2014b) argue that the more comprehensive measurement of reactants and products in an experiment that is not affected by heterogeneous wall losses of organics and radicals (as in the previous chamber based studies), has allowed for a more accurate determination of $\alpha_{(R5c)}$. Groß et al. also reported a higher than recommended (Atkinson et al., 2006) total rate of reaction coefficient for $k_{(R5)} = (2.1 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of pressure. In contrast to the above

work, the combined experimental and theoretical study of Le Crâne et al. (2006) using flash photolysis and monitoring peroxy radicals directly via UV reported no evidence of channel (Reaction R5c) and set an upper limit of 10 % on OH production. Clearly this reaction requires more attention to clarify reaction yields and assess impact on HO_x levels.

Reaction (R5) has been the subject of two theoretical investigations. Firstly, Hasson et al. (2005) calculated the reaction potential energy surface (PES) using CBS-QB3 at the B3LYP/6-311G (2d, d, p) level. The reaction was shown as proceeding either via a triplet surface to CH₃C(O)OOH + O₂ (Reaction R5a) or a singlet surface forming a hydrotetroxide intermediate which can decompose to form either OH + CH₃C(O)O + O₂ (Reaction R5c) via HO₃ formation or CH₃C(O)OH + O₃ (Reaction R5b) through hydrogen exchange. The calculations suggest that channel (Reaction R5c) is considerably less exothermic than the (Reaction R5b) channel (−8.79 and −113.9 kJ mol^{−1} respectively), however, master equation calculations suggested that chemical activation of the initially formed HO₂ – CH₃C(O)O₂ adduct combined with a loose transition state, allowed for the observations to be rationalised. Subsequently, Le Crâne et al. (2006) constructed a similar PES using Density Functional Theory (DFT) at the B3LYP/6-31G(d, p) level. The low exothermicity of the (Reaction R5c) channel (−12.98 kJ mol^{−1}) compared to the Reaction (R5b) channel (−82.9 kJ mol^{−1}) was cited as the dominating factor in the experimentally low OH yields reported (< 0.1). Variations in the thermochemical calculations of the two studies and the interesting enhancement of the OH channel (0.61–0.81) upon deuteration (DO₂) (Groß et al., 2014b) suggest scope for further calculations.

Reported here are the results from the first experiments conducted using free-radical detection (FAGE for OH and HO₂), under simulated ambient conditions. The simultaneous and direct detection of R5 precursors, reactants and products, using FTIR, gas chromatography and an O₃ analyser offered unprecedented, detailed coverage of the key species. This study therefore combined the advantages of the previous chamber studies by Hasson et al. (2004) and Jenkin et al. (2007)

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and the direct OH detection experiments of Dillon and Crowley (2008) and Groß et al. (2014a, b). The implications of the study have been assessed using a global chemical transport model's (GEOS-Chem) predictions of OH, O₃, NO and PAN concentrations with the revised values of rate coefficient and yields compared to those of the IUPAC recommendation.

2 Experimental

2.1 Chamber and instrumentation

Experiments were performed in the HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) chamber at 1000 mbar total pressure of a synthetic air mixture (4 : 1, N₂ : O₂, Zero Grade, BOC) at a constant temperature (293 ± 2 K). HIRAC is a stainless steel chamber with a total volume of 2.25 m³, with multiple access ports used to connect an array of instrumentation and monitoring equipment (pressure gauges, thermocouples, etc.). Further details on the construction can be found in Glowacki et al. (2007a) and Malkin et al. (2010).

Black lamps, housed in eight quartz tubes, were used to initiate photochemistry (Phillips, TL-D 36W/BLB, λ = 350–400 nm). The lamp housings were flushed with N₂ to regulate the temperature and remove photolabile species (Winiberg et al., 2015). The lamps induced a temperature increase of ~ 2 K in the chamber over the course of a typical experiment (< 40 min). Further information on lamp characterisation is available in the Supplement.

CH₃C(O)OH, CH₃C(O)OOH, HCHO, and HCOOH, along with chemical precursors CH₃CHO, and CH₃OH, were detected using FTIR. The multipass modified Chernin cell was optimised for 72 internal reflections giving an approximate path length of 128.5 m (Glowacki et al., 2007b). Sample IR spectra were recorded as the average of 100 scans (~ 70 s integration period) at 0.5 cm⁻¹ resolution. Reference spectra were taken of the compounds in the HIRAC chamber. Analysis of sample FTIR spectra was conducted

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Appreciable wall loss was observed for the organic acids ($\sim 10^{-4} \text{ s}^{-1}$) and these were characterised and incorporated into the chemical model reaction scheme used (Sect. 2.4). Negligible decay due to photolysis was seen for any species. Trace levels of HO₂ ($\sim 10^8 \text{ molecule cm}^{-3}$) were observed upon illumination of HCHO with all 8 lamps, suggesting some photolysis. However, a negligible decay was observed when monitoring HCHO using FTIR over a 60 min photolysis period (standard experiment time $\sim 10 \text{ min}$).

2.4 Chemical model

Numerical simulation of the chemical system was necessary to gain quantitative information about $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$. Chemical simulations were conducted using the Kintecus numerical integrator package (Ianni, 2002). The comprehensive model mechanism, displayed in Table 2, was constructed from reactions defined in the chamber studies by Hasson et al. (2004) and Jenkin et al. (2007), with updated rate constants where available from IUPAC and JPL (Atkinson et al., 2006; Sander et al., 2011). Simulated rate coefficients $k_{(R5a)} : k_{(R5b)} : k_{(R5c)}$ were optimised automatically using Kintecus, fitted to the experimentally measured products from Reaction (R5). Experimental data were also compared to simulated traces based on the IUPAC recommendation, $k_{(R5)} = (1.4^{+1.4}_{-0.7}) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)} = 0.41 : 0.15 : 0.44$ (Atkinson et al., 2006) and the more recent work by Groß et al. (2014b), $k_{(R5)} = (2.1 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Presented here are two sets of experiments conducted a year apart. There was a decrease in $j(\text{Cl}_2)$ between experiments due to degradation of the lamp with extensive use. Hence, $j(\text{Cl}_2)$ has been determined for each set of experimental data using the measured Cl atom induced decay of the CH₃CHO and CH₃OH reactants. Supporting $j(\text{NO}_2)$ measurements were conducted for all 8 of the black lamps switched on during the later time period, which gave $j(\text{NO}_2) = (2.4 \pm 0.8) \times 10^{-3} \text{ s}^{-1}$. Using IUPAC recommended absorption cross sections for both NO₂ (Atkinson et al.,

2004) and Cl_2 (Atkinson et al., 2007), $j(\text{Cl}_2)$ was estimated at $(3.8 \pm 1.4) \times 10^{-4} \text{ s}^{-1}$, correlating well with the observed reactant decays. The black lamp intensity profiles as a function of time were entered into Kintecus as a constraint for the photolysis rate (as described in Sect. 2.1), allowing accurate modelling of the precursor photolysis. Both the predicted $[\text{OH}]$ and $[\text{HO}_2]$ were observed to better correlate with the measured radical concentrations when using this constraint, compared to starting the model with a constant photolysis rate.

3 Results and discussion

Figure 1 displays typical reactant decay profiles for CH_3CHO and CH_3OH for experiment P11, measured simultaneously using FTIR and GC-FID. The concentrations were determined independently and are in excellent agreement. Similar agreement was observed for experiments P9 and P10 with an overall correlation of $[\text{GC}] : [\text{FTIR}] = (0.97 \pm 0.03)$ and (1.05 ± 0.09) for CH_3CHO and CH_3OH , respectively (uncertainties representative of the standard deviation in repeated measurement to $\pm 2\sigma$).

Figure 2a, b and c show the product profiles of $\text{CH}_3\text{C}(\text{O})\text{OOH}$, $\text{CH}_3\text{C}(\text{O})\text{OH}$ and O_3 respectively as a function of decay in CH_3CHO ($\Delta[\text{CH}_3\text{CHO}]$) for experiments P1–P5, P11 and P12, while Fig. 3 shows OH and HO_2 time profiles for experiment P1, typical of other profiles (see Supplement). For a decrease in $[\text{CH}_3\text{CHO}]$ of $\sim 50\%$, near linear increases in $[\text{CH}_3\text{C}(\text{O})\text{OOH}]$, $[\text{CH}_3\text{C}(\text{O})\text{OH}]$ and $[\text{O}_3]$ were observed, suggesting that the rate of formation of stable products through Reaction (R5) remained constant throughout the $\sim 600 \text{ s}$ reaction period. The monitored prompt increase in $[\text{OH}]$ suggested a primary production channel, maintaining a steady state level of $\sim 10^7 \text{ molecule cm}^{-3}$ throughout the experiment. Concentrations of $[\text{HO}_2]$ were observed to quickly reach a steady state of $\sim 10^{11} \text{ molecule cm}^{-3}$ during each experimental run, providing sufficient HO_2 for reaction with $\text{CH}_3\text{C}(\text{O})\text{O}_2$. No HO_2 data from experiments P4–P6, P10 and P11 were available due to an error with the mass flow controller

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3.1 Assignment of $k_{(R5)}$ and $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$

Table 3 contains assigned yields for all experiments conducted at 1000 mbar and 293 K. Uncertainty in the branching ratios determined here were calculated as a function of the precision error in repeated determinations combined with uncertainties in the FTIR, O₃ analyser and FAGE calibrations and is displayed to $\pm 2\sigma$. Yields from the three branching pathways of CH₃C(O)O₂ + HO₂ were assigned through application and optimisation of the chemical model to each experimental dataset (Sect. 2.4), detailed in Table 3. Displayed in Fig. 5 are the time dependent concentration profiles for CH₃C(O)OOH, CH₃C(O)OH, O₃ and OH for experiment P2, representative of a typical experiment. The results are presented against three modelling scenarios each using the same chemistry but with $k_{(R5)}$ and $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$ based on: Model1 the IUPAC values (1.4×10^{-11} cm³ molecule⁻¹ s⁻¹, 0.41 : 0.15 : 0.44), Model2 the Gros et al. (2014b) values and Model3 values from the best fit to the current experimental data. Model1 matched the data well for channels (Reactions R5a and b) using $\alpha_{(R5a)} = 0.41$, $\alpha_{(R5b)} = 0.15$. However, in general for all datasets except P1, OH was consistently under predicted by the model with $\alpha_{(R5c)} = 0.44$, with modelled [OH] falling outside of the uncertainty of the FAGE measurements ($\pm 38\%$, 2σ). Clearly the rate of production of OH in our system was underestimated.

Using Model2 in our chemical simulation, the [OH] and [O₃] and [CH₃C(O)OH] were reproduced by the model within the uncertainty of the measurements, however the [CH₃C(O)OOH] was systematically under predicted (see Fig. 5). Adjusting the parameters $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$, reasonable agreement between measured and modelled data was observed, well within the uncertainty of the measurements and average yields were determined as $(0.38 \pm 0.08) : (0.12 \pm 0.02) : (0.50 \pm 0.08)$. However, improvement in the measured to modelled agreement for [CH₃C(O)OOH] was typically at the expense of predicted [OH]. Therefore the yields shown here are representative of the best fit to both CH₃C(O)OOH and OH that was possible, weighting the assignment to the larger uncertainty in the [OH] determination.

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Improved correlation between measured and modelled OH was achieved by fitting k_5 and $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$ to the measured data from all three branching pathways from the CH₃C(O)O₂ + HO₂ reaction. A non-linear least squares iterative fitting routine built into the Kintecus package was used to determine the best fit rate coefficients by judging the reduced χ^2 (determined using the Powell method; Press et al., 1992; Ianni, 2002). An increase in the rate coefficients for all channels of Reaction (R5) was observed, whilst the ratio of $k_{(R5a)}$ and $k_{(R5b)}$ ($k_{(R5a)}/k_{(R5b)} = 3.2 \pm 0.2$) remained within uncertainty of the IUPAC recommendation (2.73 ± 0.48), leading to an overall increase in $k_{(R5)} = (2.4 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and average branching ratios of $\alpha_{(R5a)} = 0.37 \pm 0.10$, $\alpha_{(R5b)} = 0.12 \pm 0.04$ and $\alpha_{(R5c)} = 0.51 \pm 0.12$. Uncertainties were taken as the quoted standard errors in the fitting routine to $\pm 2\sigma$. Figure 5 displays the improvement in correlation to the measured data using predicted OH yields from the fitted rate constants.

The OH steady state (SS) concentration ($[\text{OH}]_{\text{ss}}$) in the chemical system was controlled by the production of OH primarily through Reaction (R5) (> 60% for entirety of the ~ 600 s reaction time, Fig. 3) whilst OH loss was controlled by its well characterised reactions with CH₃CHO and CH₃OH at the beginning of the experiment, with HCHO playing an increased role as the experiment progresses (Fig. 3). Reaction of OH with CH₃OH is 10² slower than the analogous reaction with Cl atoms, and so the predicted [CH₃OH] was insensitive to any change in $k_{(R5c)}$. However, the rate coefficient for OH + CH₃CHO was only a factor of ~ 5 slower compared to Cl + CH₃CHO, and so with the $[\text{OH}]_{\text{ss}}$ higher than $[\text{Cl}]_{\text{ss}}$ by a factor of ~ 3, loss of CH₃CHO through reaction with OH starts to become competitive (2 : 1 ratio Cl : OH loss) and so a small sensitivity in [CH₃CHO] to k_{R5c} was observed.

The increase in $k_{(R5)}$, and therefore rate of loss of CH₃CHO, led to an overall reduction in the $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_{\text{ss}}$. The $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_{\text{ss}}$ was controlled primarily through reaction with HO₂ and less so through self-reaction and reaction with CH₃O₂ (Reaction R20) in a ~ 2 : 1 : 1 ratio (for this system). The $[\text{HO}_2]_{\text{ss}}$ remained unaffected by an

increase in $[\text{OH}]_{\text{ss}}$ (minimal change in CH_3OH loss), and the co-product of channel (Reaction R5c) is CH_3O_2 (via Reaction R19), hence the decrease in $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_{\text{ss}}$.

Clearly the $[\text{CH}_3\text{O}_2]_{\text{ss}}$ played an important role in the determination of Reaction (R5) yields and was defined by primary production in channel (Reaction R5c), and loss through reaction with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ (Reaction R20), HO_2 and itself. The removal of CH_3O_2 via another reaction could also lead to a discrepancy in yield assignment. Recently, Bossolasco et al. (2014) determined the rate coefficient for the rapid reaction of CH_3O_2 with OH radicals ($k = (2.8 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This reaction has been hypothesised to yield a Criegee intermediate as a possible product, and could contribute to significant HCOOH yields in the troposphere in certain environments (Fittschen et al., 2014). Despite the large rate coefficient, this reaction was found to have a negligible effect on the chemical system described here due to the higher concentrations of RO_2 radicals in the system ($\sim 10^{11} \text{ molecule cm}^{-3}$), preferentially reacting with CH_3O_2 . Assuming that every OH + CH_3O_2 reaction leads to HCOOH (used only as an example), only a small effect was observed on the HCOOH yield ($\sim 2\%$), well within the uncertainty in the measurement and model simulation.

Assignment of the yield for channel (Reaction R5c) was found to be insensitive to the ratio of $\alpha_{(\text{R5a})} : \alpha_{(\text{R5b})}$. The ratio of $\alpha_{(\text{R5a})} : \alpha_{(\text{R5c})}$ was observed to affect the $\text{CH}_3\text{C}(\text{O})\text{OH}$ yield, but not that of O_3 , suggesting $\alpha_{(\text{R5b})}$ was also unaffected. Reaction (R5b) was found to be the dominant production channel for $\text{CH}_3\text{C}(\text{O})\text{OH}$ ($\sim 80\%$) with a $\sim 19\%$ yield from the reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ with CH_3O_2 (Reaction R20b). As the dominant production channel for CH_3O_2 in the system was the decomposition of acetylalkoxy radicals (Reaction R19) produced alongside OH in (Reaction R5c) also produced here from Reaction (R20a), a certain sensitivity for $\text{CH}_3\text{C}(\text{O})\text{OH}$ to $\alpha_{(\text{R5c})}$ can be expected. Modelled profiles for both O_3 and $\text{CH}_3\text{C}(\text{O})\text{OH}$ were in good agreement with measurements from two independent techniques, improving confidence in the determination of $\alpha_{(\text{R5b})}$ and suggesting that secondary chemistry was well characterised in the reaction scheme. Predicted concentrations of HCHO and

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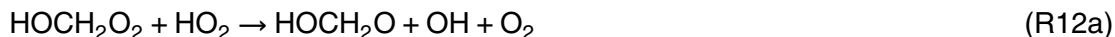
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HCOOH were found to be insensitive to the increased rate constant as their dominant removal was through reaction with Cl radicals ($\sim 10^2$ faster than reaction with OH).

3.2 Secondary OH production

The sum of OH sources from secondary $\text{RO}_2 + \text{HO}_2$ reactions (Fig. 3) showed negligible impact on the measured $[\text{OH}]$ until ~ 200 s, and in total were still the minor production channels even at $t = 600$ s ($\sim 30\%$). Secondary OH was primarily produced through the reaction of Cl with CH_3OOH and HOCH_2O_2 with HO_2 (Reaction R12), the RO_2 radical produced from the association of HO_2 and HCHO (Reaction R11). Reaction (R12) is thought to proceed through three possible channels, producing a hydroxyl-alkoxy radical, HOCH_2O (Reaction R12a), a hydroxyperoxide, HOCH_2OOH (Reaction R12b) and HCOOH (Reaction R12c) in a 0.5:0.3:0.2 ratio (Jenkin et al., 2007).



While Reaction (R11) has received minor attention in the literature (Veyret et al., 1989; Barnes et al., 1985; Rohrer and Berresheim, 2006), to date the subsequent RO_2 reactions with HO_2 have only been studied by Jenkin et al. (2007). During their investigation of the title reaction, photolysis of Cl_2 was used with a CH_3OH /benzene mixture with the aim of detecting any OH produced from Reaction (R12a), using benzene as a chemical tracer for OH. Jenkin et al. (2007) deduced that the chemical model better reproduced the experimentally measured HCHO, HCOOH and OH upon inclusion of the HOCH_2O_2 self-reaction (Reaction R13), the assumed instantaneous

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reaction of HOCH₂O with O₂ (Reaction R14), and the Cl initiated oxidation of HOCH₂OOH (Reactions (R15) and (R16)). At the experimental temperatures, the rates of Reactions (R11) and (R-11) are close to being in equilibrium with only a small amount of HOCH₂O₂ reacting via other pathways (shown as HO₂ + HCHO net loss in HO₂ RODA (rate of destruction analysis) in Fig. 3).



As such, these reactions and their respective rate constants determined by Jenkin et al. (2007) have been included in the chemical model presented here (Table 2). The good agreement between experimental and simulated HCHO and HCOOH (Fig. 4) and the OH at longer times (Fig. 3) show that we are in agreement with the evaluation of OH yields presented by Jenkin et al. (2007). It should be noted, however, that HCOOH showed the largest discrepancy between measured and modelled data overall.

The sensitivity of the uncertainty in the analogous HO₂ association with CH₃CHO (Reaction R17) on the measured products was also investigated. To date, only one study exists into the equilibrium (Tomas et al., 2001), therefore uncertainty in the equilibrium constant could impact on OH and CH₃C(O)OH yields through further reactions of the CH₃CH(OH)O₂ radical with HOCH₂O₂ and CH₃O₂ (see Table 2).



The chemical model showed that the dominating pathway for removal of CH₃CHO was through reaction with HO₂ at ~ 90 %. However, the rate of dissociation from CH₃C(OH)O₂ back to CH₃CHO and HO₂ was > 99 % of the total CH₃C(OH)O₂ loss.

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Hence, negligible $[\text{CH}_3\text{C}(\text{OH})\text{O}_2]_{\text{ss}}$ was formed and the further reaction with other RO_2 species or HO_2 was negligible. Finally, the model was found to be insensitive to the removal of this pathway from the mechanism entirely.

3.3 Sensitivity of the chemical system to initial conditions

3.3.1 Precursor ratio, $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0$

By manipulating the starting ratio of $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0$ it was possible to control the ratio of $\text{HO}_2 : \text{CH}_3\text{C}(\text{O})\text{O}_2$ during a given experiment and $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0$ ratios between 0.0–5.6 were studied. The observed $\text{CH}_3\text{C}(\text{O})\text{OOH}$, $\text{CH}_3\text{C}(\text{O})\text{OH}$ and O_3 experimentally determined product yields were calculated as the gradient from the linear regression of a plot of respective Δ [product] vs. $\Delta[\text{CH}_3\text{CHO}]$. O_3 data were unavailable for experiments P6 and P7 due to a software error. The yields are graphically displayed as a function of $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0$ in Fig. 6. The product yields were observed to remain at a maximum between ratios of 1.2 and 5.6, with yields decreasing towards experiments where no methanol was added (ratio = 0.0). This indicated that for experiments conducted at $[\text{CH}_3\text{CHO}]_0 : [\text{CH}_3\text{OH}]_0 \approx 4$, product yields from Reaction (R5) were still maximised, but interference was minimized from the saturated CH_3OH ν_1 stretch absorption on the surrounding spectrum ($\sim 1000 \text{ cm}^{-1}$).

Each experiment was simulated using Model3. Compared to experiments using a CH_3OH precursor, the chemistry in experiments P8 and P9 was driven by the Cl atom initiated oxidation of CH_3CHO . Hence RO_2 chemistry outside of reaction with HO_2 drives product formation. The initial dominating loss for $\text{CH}_3\text{C}(\text{O})\text{O}_2$ is self-reaction (Reaction R18), followed closely by reaction with CH_3O_2 (Reaction R20), produced through Reaction (R19). The required HO_2 radicals were produced at later times from the Cl initiated oxidation of HCHO (Reaction R21), itself produced from reaction for CH_3O_2 with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ (Reaction R20b). As the HCHO is produced quickly through the abundant $[\text{RO}_2]$, no significant delay in Reaction (R5) product formation was observed on the timescale of the measurements presented here, however the reduced

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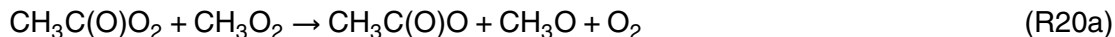
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yields were calculated as there was no excess of HO₂ in the system. This trend has been reported and reproduced in the literature (Jenkin et al., 2007; Hasson et al., 2004).



Displayed in Fig. 7 are the measured and modelled product yields of OH and HO₂, (Fig. 7a), CH₃C(O)OOH and CH₃C(O)OH, (Fig. 7b), O₃, (Fig. 7c) and HCHO, (Fig. 7d), as a function of time for experiment P9 where [CH₃OH]₀ = 0. The simulation was completed using $k_{(\text{R5})} = (2.4 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the branching ratios were optimised to fit the data ($\alpha_{(\text{R5a})} = 0.42 \pm 0.05$, $\alpha_{(\text{R5b})} = 0.14 \pm 0.04$ and $\alpha_{(\text{R5c})} = 0.44 \pm 0.10$) of that experiment. Excellent agreement between the measured and modelled decay of CH₃CHO was observed, which was additionally constrained by measurements from the GC-FID and FTIR, and good agreement between the measured and modelled OH, HO₂, CH₃C(O)OOH and HCHO was also seen (Fig. 7, Model3 data). The model predicted a rapid increase in [OH] at time > 400 s, however in experiment P9, the measured OH appears to remain constant. The simulation suggests that after > 400 s, the OH yield from Reactions (R12a) and (R15)–(R16) start to dominate as the CH₃CHO in the system is depleted, however as no OH and HO₂ data were recorded past ~ 450 s for both experiments P8 and P9, we are unable to comment if the discrepancy from the model 8 increased at later times.

The simulation over predicted [CH₃C(O)OH] by a factor of ~ 2 towards the end of the reaction period (~ 600 s) for both experiments P8 and P9. The two main production channels for CH₃C(O)OH are through Reactions (R5b) and (R20b), and in experiment

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P9 the chemical model 12 predicted the flux through both channels was in competition for the first ~ 200 s of the Reaction (R20b) $>$ (Reaction R5b) by $\sim 25\%$. Modifying the branching ratio for Reaction (R20b) in the chemical simulation from 0.1 to 0.03 showed better agreement with measured data in experiment P9 (Fig. 7, Model3a) and kept the branching ratio well within the IUPAC recommended uncertainty of 16 ± 0.1 . Models conducted for $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0 > 1.0$ were found to be insensitive to a change in the $k_{(\text{R}20)}$ branching ratio.

An over-prediction of CH_3O_2 in the chemical model could also increase $\text{CH}_3\text{C}(\text{O})\text{OH}$ through Reaction (R20). However, measurement of HCHO in experiment P9 (Fig. 7d) was well matched by the modelled profile (Fig. 7d, Model3a), calculated through the primary production, Reactions (R20a) and (R23) and self-reaction of CH_3O_2 (Reactions R22 and R23), suggesting the CH_3O chemistry in the system was well understood under these conditions.



These experiments conducted at $[\text{CH}_3\text{OH}]_0 = 0$ have showed that the CH_3CHO and surrounding peroxy chemistry was well characterised by the comprehensive model in Table 2.

3.3.2 Photolysis rate, $j(\text{Cl}_2)$

The target reaction was studied using 2, 4 and 8 photolysis lamps at 1000 mbar and 293 K, preserving $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0 \approx 4$. Photolysis rates for all experiments are displayed in Table 1. Photolysis rates differed between experiments P1–P5 and P6–P12 with the same number of lamps due to the degradation of the lamp emission intensity over time (see Sect. 2). The initial $[\text{Cl}_2]_0$ was lowered in experiments P4, P5

a detailed analysis of the conditions plus appropriate experimental background checks, as detailed in the Supplement, suggests that there negligible interferences to our OH measurements.

3.4 Comparison with literature data

The average branching ratios determined for Reaction (R5) at 1000 mbar and 293 K using the recently reported value for $k_{(R5)}$ from Groß et al. (2014b) as well as those determined using the fitting of the chemical model are presented in Table 4, together with previous reported values. Previous measurements of $k_{(R5)}$ by Moortgat et al. (1989), Crawford et al. (1999), Tomas et al. (2001) and Le Crâne et al. (2006) required measurements of RO₂ by UV absorption spectroscopy. The convoluted UV signal was fit using predetermined absorption cross-sections and a numerical model simulation, which were likely to add uncertainty as no radical recycling channel was considered. Re-evaluation of the data reported by Tomas et al. (2001) and Le Crâne et al. (2006) by Jenkin et al. (2007) suggested this to be the case. The determination of $k_{(R5)}$ by Dillon and Crowley (2008) relied on the more sensitive and specific LIF detection of OH, however, the calibration of the LIF setup, calculation of HO₂ and RO₂ concentrations and chemical modelling of the system all relied on the determination of [Cl]₀ through a Joule meter reading of laser fluence, resulting in the ±30% uncertainty in $k_{(R5)}$ quoted by the authors. This study has been superseded by the determination of $k_{(R5)} = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ – underpinned by direct HO₂ and RO₂ observations, so avoiding this reliance on a Joule meter (Groß et al., 2014a).

3.4.1 Determination of $k_{(R5)}$

Our reported value $k_{(R5)} = (2.4 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is slightly larger than the reported value by Groß et al. (2014a), though within experimental error, and also inside the upper bound quoted in the IUPAC recommendation ($k_{(R5)} = (1.4_{-0.7}^{+1.4}) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Here, $k_{(R5)}$ was determined by measuring all products from

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Reaction (R5) directly and using the chemical simulation outlined in Table 2 to fit to the measured data, summing the individual rate coefficients of branching pathways. This procedure relied on the accurate measurement of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$ by FTIR, O_3 by UV absorption and OH by FAGE, which have been discussed in more detail in Sect. 3.3.3 and the Supplement.

The ratio of the rate coefficients ($k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})}$) can also be used as a metric to compare results. $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})}$ has been estimated as 3.2 ± 0.2 across the all experiments presented here, which is in agreement with the IUPAC recommendation and others all the way back to the first investigation of the reaction by Niki et al. (1985), which was insensitive to channel (Reaction R5c). The high measurement of $k_{(\text{R}5\text{a})}$ by Crawford et al. (1999) was corrected for the $\text{CH}_3\text{C}(\text{O})\text{OOH}$ absorption cross-section by Orlando et al. (2000), calculating $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})} = 2.6$, in line with other reported values. The preservation of this ratio in the work presented here helps substantiate a higher rate coefficient for Reaction (R5c), although this does not correlate with the more recent study by Groß et al. (2014b), where $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})} = 1.44$.

Groß et al. (2014b) mentioned that the discrepancy between their results for $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})}$ and those previously published on longer timescale chamber experiments, insensitive to OH directly, either may have been caused by the relatively large uncertainty on their value of $k_{(\text{R}5\text{b})}$. This uncertainty entered twice in the $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})}$ ratio as $k_{(\text{R}5\text{a})}$ was calculated from $k_{(\text{R}5\text{b})}$ and $k_{(\text{R}5\text{c})}$ assuming only these three reaction channels of Reaction (R5). In fact they could show that their data would, within the experimental uncertainty, also support a $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})}$ ratio of 3 and the effects of this are discussed in the following section. Additionally, Groß et al. pointed out that these discrepancies could as well be due to the fact that in the latter publications $k_{(\text{R}5\text{a})}/k_{(\text{R}5\text{b})}$ ratios are derived from the $\text{CH}_3\text{C}(\text{O})\text{OOH}$ to $\text{CH}_3\text{C}(\text{O})\text{OH}$ or the $\text{CH}_3\text{C}(\text{O})\text{OH}$ to O_3 ratios. These two ratios would not necessarily have to be identical since $\text{CH}_3\text{C}(\text{O})\text{OH}$ production through reactions such as CH_3O_2 with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ (Reaction R20a), could be competitive with (Reaction R5b), as the $\text{CH}_3\text{C}(\text{O})\text{OH}$ yield is still uncertain ($\alpha_{(\text{R}20\text{a})} = 0.1 \pm 0.1$). However, this explanation can now be ruled out since experiments presented

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values. The enhancements here are less dramatic as IUPAC already recommended a significant OH yield, but an increase of up to 5% is observed over parts of the Amazon region.

There is also an increase in OH concentrations at equatorial latitudes at an altitude of 6–8 km (see Supplement) of ~10% compared to the IUPAC recommended rate coefficients and yields. The $\text{RO}_2 + \text{HO}_2$ reaction could therefore play an important role in OH recycling in the upper troposphere, however to date no temperature dependent studies into the OH yield from substituted $\text{RO}_2 + \text{HO}_2$ radical reactions exist. Additional temperature dependent studies would also provide insights into the mechanism of Reaction (R5). The theoretical studies of Le Crâne et al. (2006) and Hasson et al. (2005) suggest that the exothermicity of channel (Reaction R5c) is small and hence one might expect to see significant temperature dependence in the yield distribution.

Only very slight increases in O_3 are observed (see Supplement) as the reaction is only significant when NO concentration are low as so O_3 production is low. The enhanced rate coefficients for Reaction (R5) of this work and of Groß et al. (2014a, b) have a significant effect on PAN concentrations as it leads to faster destruction of the peroxy-acetyl radical in the atmosphere. This leads to up to a 30% reduction in PAN and hence in background NO_x in remote environments as shown in Fig. 9a and b. In these plots the comparison is between the branching ratios and rate coefficients of this work and the IUPAC recommendations. Further comparisons, including vertical profiles, can be found in the Supplement.

The Supplement contains information on: characterisation of HIRAC lamps, further examples of experimental data, details of investigations into possible interferences and outputs from GEOS-Chem modelling.

**The Supplement related to this article is available online at
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Table 1. Experimental conditions and for the investigation into CH₃C(O)O₂ + HO₂ (Reaction R5) conducted in a synthetic air mixture at 1000 mbar and 293 K. Lower $j(\text{Cl}_2)$ for experiments P9–P12 due to degradation of lamps over time in between first P1–P8 experiments. Taken from chemical simulation (Sect. 2.4) at close to $t = 0$ s, units in 10^6 molecule cm⁻³.

Expt ^a	[Cl ₂] ₀ ^b	[CH ₃ OH] ₀ ^b	[CH ₃ CHO] ₀ ^b	Ratio ^c	Lamps	$j(\text{Cl}_2)$ ^d	[Cl] ₀ ^e	Notes
P1	5.89	3.01	0.90	3.3	2	1.25	7.1	
P2	6.51	3.00	0.81	3.7	2	1.25	8.0	
P3	6.08	3.16	0.80	4.0	2	1.25	7.2	
P4	2.21	3.03	0.79	3.8	4	2.50	5.1	No HO ₂
P5	2.47	3.22	0.79	4.1	8	5.00	11.2	No HO ₂
P6	6.36	4.02	0.72	5.6	2	1.25	5.8	No O ₃ , no HO ₂
P7	6.78	0.86	0.56	1.5	2	1.25	11.1	No O ₃
P8	7.00	0.00	0.70	0.0	2	1.25	20.1	
P9	5.59	0.00	0.73	0.0	2	0.80	17.0	GC
P10	5.79	0.72	0.74	1.0	2	0.80	11.4	GC, no HO ₂
P11	5.67	2.37	0.69	3.4	2	0.80	5.6	GC, no HO ₂
P12	2.37	2.65	0.73	3.6	8	3.80	9.9	

^a All experiments performed at 1000 mbar.

^b Precursor concentrations in 10^{14} molecule cm⁻³.

^c Ratio of [CH₃OH]₀ : [CH₃CHO]₀.

^d Photolysis rate units 10^{-4} s⁻¹.

^e Peak initial Cl atom concentration.

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Table 2. Reaction scheme used in the determination of branching ratios for the reaction of CH₃C(O)O₂ with HO₂. RO radical decomposition and reaction with O₂ are assumed instantaneous, indicated by (+O₂) where appropriate. Rate coefficients sourced from IUPAC recommended values unless otherwise stated, all quoted in units = molecule⁻¹ cm³ s⁻¹. (Atkinson et al., 2004). (a) from (Crawford et al., 1999); (b) estimations from (Jenkin et al., 2007), based on reactivity of Cl with other species containing -OOH, -OH, -CHO functional groups; (c) from (Jenkin et al., 2007), estimation based on the reactivity of -OOH in CH₃OOH; (d) taken from Jenkin et al. (2007), estimated based on SAR by (Kwok and Atkinson, 1995) and (Saunders et al., 2003); (e) from (Tomas et al., 2001); (f) estimations from (Jenkin et al., 2007), based on analogous reaction for similar α -hydroxy peroxy radicals; (g) estimations from (Jenkin et al., 2007), assumed equivalent to CH₃C(O)O₂ + CH₃O₂; (h) estimations from (Jenkin et al., 2007), based on the geometric mean of self-reaction rate coefficients and branching ratios of participating RO₂.

	Reaction	Branching Ratio	Rate Coefficient
	Chlorine Initiation		
R6	Cl ₂ + hν → 2Cl		Varied. See text.
R7,8	Cl + CH ₃ OH(+O ₂) → HCHO + HO ₂ + HCl		5.5 × 10 ⁻¹¹
R9,10	Cl + CH ₃ CHO(+O ₂) → CH ₃ C(O)O ₂ + HCl		8.0 × 10 ⁻¹¹
R21	Cl + HCHO(+O ₂) → CO + HO ₂ + HCl		8.1 × 10 ⁻¹¹ exp(-34/T)
	Cl reactions		
	Cl + CH ₃ C(O)OOH → CH ₃ C(O)O ₂ + HCl		4.5 × 10 ⁻¹⁵ (a)
	Cl + CH ₃ C(O)OH(+O ₂) → CH ₃ O ₂ + CO ₂ + HCl		2.65 × 10 ⁻¹⁴
	Cl + H ₂ O ₂ → HO ₂ + HCl		1.1 × 10 ⁻¹¹ exp(-980/T)
	Cl + CH ₃ OOH → HCHO + OH + HCl		5.9 × 10 ⁻¹¹
	Cl + HCOOH(+O ₂) → CO ₂ + HO ₂ + HCl		1.9 × 10 ⁻¹³
R15,R16	Cl + HOCH ₂ OOH → HCOOH + OH + HCl		1.0 × 10 ⁻¹⁰ (b)
	Cl + HOCH ₂ OH(+O ₂) → HCOOH + HO ₂ + HCl		1.0 × 10 ⁻¹⁰ (b)
	Cl + CH ₃ CH(OH)OOH → CH ₃ C(O)OH + OH + HCl		1.0 × 10 ⁻¹⁰ (b)
	Cl + CH ₃ CH(OH) ₂ (+O ₂) → CH ₃ C(O)OH + HO ₂ + HCl		1.0 × 10 ⁻¹⁰ (b)
	Cl + O ₃ → ClO + O ₂		2.8 × 10 ⁻¹¹ exp(-250/T)
	ClO + HO ₂ → HOCl + O ₂		2.2 × 10 ⁻¹² exp(340/T)
	Cl + HO ₂ → HCl + O ₂	0.80	4.4 × 10 ⁻¹¹
	→ ClO + OH	0.20	

Table 2. Continued.

Reaction	Branching Ratio	Rate Coefficient	
OH reactions			
OH + HO ₂ → H ₂ O + O ₂		4.8 × 10 ⁻¹¹ exp(250/T)	
OH + CH ₃ C(O)OH → CH ₃ O ₂ + CO ₂ + H ₂ O		4.2 × 10 ⁻¹⁴ exp(855/T)	
OH + CH ₃ C(O)OOH → CH ₃ C(O)O ₂ + H ₂ O		3.6 × 10 ⁻¹²	(c)
OH + H ₂ O ₂ → HO ₂ + H ₂ O		2.9 × 10 ⁻¹² exp(-160/T)	
OH + CH ₃ OOH → CH ₃ O ₂ + HO ₂	0.65	2.9 × 10 ⁻¹² exp(190/T)	
	→ HCHO + OH + H ₂ O		0.35
OH + HCOOH(+O ₂) → CO ₂ + HO ₂ + H ₂ O		4.5 × 10 ⁻¹³	
OH + HOCH ₂ OOH → HOCH ₂ O ₂ + H ₂ O	0.12	3.1 × 10 ⁻¹¹	(d)
	→ HCOOH + OH + H ₂ O		0.88
OH + HOCH ₂ OH(+O ₂) → HCOOH + OH + H ₂ O		1.1 × 10 ⁻¹¹	(d)
OH + CH ₃ CH(OH)OOH → CH ₃ C(O)OH + OH + H ₂ O		6.0 × 10 ⁻¹¹	(d)
OH + CH ₃ CH(OH) ₂ (+O ₂) → CH ₃ C(O)OH + HO ₂ + H ₂ O		2.4 × 10 ⁻¹¹	(d)
OH + Cl ₂ → Cl + HOCl		3.6 × 10 ⁻¹² exp(-1200/T)	(a)
OH + CO → CO ₂ + HO ₂		1.44 × 10 ⁻¹³ + 3.43 × 10 ⁻³³ [M]	
OH + HCl → Cl + H ₂ O		1.7 × 10 ⁻¹² exp(-230/T)	(a)
OH + O ₃ → HO ₂ + O ₂		1.7 × 10 ⁻¹² exp(-940/T)	
OH + CH ₃ CHO → CH ₃ C(O)O ₂ + H ₂ O		4.4 × 10 ⁻¹² exp(365/T)	
OH + CH ₃ OH → HCHO + HO ₂ + H ₂ O		2.85 × 10 ⁻¹² exp(-345/T)	
OH + HCHO → CO + HO ₂ + H ₂ O		5.4 × 10 ⁻¹² exp(135/T)	
HO₂ reactions			
HO ₂ + O ₃ → OH + O ₂		2.03 × 10 ⁻¹⁶ × (T/300) ^{4.57} exp(693/T)	
R17 HO ₂ + CH ₃ CHO → CH ₃ CH(OH)O ₂		4.4 × 10 ⁻¹⁴	(e)
R-17 CH ₃ CH(OH)O ₂ → HO ₂ + CH ₃ CHO		2.3 × 10 ¹³ exp(-6925/T)	(e)
R11 HO ₂ + HCHO → HOCH ₂ O ₂		9.7 × 10 ⁻¹⁵ exp(625/T)	
R-11 HOCH ₂ O ₂ → HO ₂ + HCHO		2.4 × 10 ¹² exp(-7000/T)	
HO₂ + RO₂ reactions			
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂		2.2 × 10 ⁻¹⁵ exp(600/T) + 1.9 × 10 ⁻³³ [M] exp(980/T)	
R5a CH ₃ C(O)O ₂ + HO ₂ → CH ₃ C(O)OOH + O ₂		5.2 × 10 ⁻¹³ exp(980/T)	
R5b → CH ₃ C(O)OH + O ₃		(see text for branching)	
R5c (+O ₂) → CH ₃ O ₂ + CO ₂ + OH + O ₂			
CH ₃ O ₂ + HO ₂ → CH ₃ OOH + O ₂	0.90	3.8 × 10 ⁻¹³ exp(780/T)	
	→ HCHO + H ₂ O + O ₂		0.10
R12a HOCH ₂ O ₂ + HO ₂ → HOCH ₂ OOH + O ₂	0.50	5.6 × 10 ⁻¹⁵ exp(2300/T)	
R12b → HCOOH + H ₂ O + O ₂	0.30		
R12c (+O ₂) → HCOOH + HO ₂ + OH + O ₂	0.20		
CH ₃ CH(OH)O ₂ + HO ₂ → CH ₃ CH(OH)OOH + O ₂	0.50	5.6 × 10 ⁻¹⁵ exp(2300/T)	(f)
	→ CH ₃ C(O)OH + H ₂ O + O ₂		0.30
(+O ₂) → HCOOH + CH ₃ O ₂ + OH + O ₂	0.20		

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Table 2. Continued.

	Reaction	Branching Ratio	Rate Coefficient	
	RO ₂ self-reactions			
R18,R19	2CH ₃ C(O)O ₂ (+O ₂) → 2CH ₃ O ₂ + O ₂ + CO ₂		2.9 × 10 ⁻¹² exp(500/T)	
R22b	2CH ₃ O ₂ → HCHO + CH ₃ OH + O ₂	0.63	1.03 × 10 ⁻¹³ exp(365/T)	
R22a,R23	(+2O ₂) → 2HCHO + 2HO ₂ + O ₂	0.37		
R13a,R14	2HOCH ₂ O ₂ (+2O ₂) → 2HCOOH + 2HO ₂ + O ₂	0.88	5.7 × 10 ⁻¹²	
R13b	→ HCOOH + HOCH ₂ OH + O ₂	0.12		
	2CH ₃ CH(OH)O ₂ → CH ₃ C(O)OH + CH ₃ CH(OH) ₂ + O ₂	0.12	5.7 × 10 ⁻¹²	(f)
	(+2O ₂) → 2HCOOH + 2CH ₃ O ₂ + O ₂	0.88		
	RO ₂ + RO ₂ reactions			
R20b	CH ₃ C(O)O ₂ + CH ₃ O ₂ → CH ₃ C(O)OH + HCHO + O ₂	0.10	2.0 × 10 ⁻¹² exp(500/T)	
R20a	(+2O ₂) → CH ₃ O ₂ + CO ₂ + HCHO + HO ₂ + O ₂	0.90		
	CH ₃ C(O)O ₂ + HOCH ₂ O ₂ → CH ₃ C(O)OH + HCOOH + O ₂	0.10	2.0 × 10 ⁻¹² exp(500/T)	(g)
	(+2O ₂) → CH ₃ O ₂ + CO ₂ + HCOOH + HO ₂ + O ₂	0.90		
	CH ₃ C(O)O ₂ + CH ₃ CH(OH)O ₂ → 2CH ₃ C(O)OH + O ₂	0.90	2.0 × 10 ⁻¹² exp(500/T)	(g)
	(+2O ₂) → CH ₃ O ₂ + CO ₂ + HCOOH + CH ₃ O ₂ + O ₂	0.10		
	CH ₃ O ₂ + HOCH ₂ O ₂ → HCHO + HOCH ₂ OH + O ₂	0.19	1.4 × 10 ⁻¹²	(h)
	→ CH ₃ OH + HCOOH + O ₂	0.19		
	(+2O ₂) → HCHO + HCOOH + 2HO ₂ + O ₂	0.62		
	CH ₃ O ₂ + CH ₃ CH(OH)O ₂ → HCHO + CH ₃ CH(OH) ₂ + O ₂	0.19	1.4 × 10 ⁻¹²	(h)
	→ CH ₃ OH + CH ₃ C(O)OH + O ₂	0.19		
	(+2O ₂) → HCHO + HO ₂ + HCOOH + CH ₃ O ₂ + O ₂	0.62		
	HOCH ₂ O ₂ + CH ₃ CH(OH)O ₂ → HCOOH + CH ₃ CH(OH) ₂ + O ₂	0.06	5.7 × 10 ⁻¹²	(h)
	→ HOCH ₂ OH + CH ₃ C(O)OH + O ₂	0.06		
	(+2O ₂) → HCOOH + HO ₂ + HCOOH + CH ₃ O ₂ + O ₂	0.88		

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Table 3. Branching ratios for Reaction (R5) determined by fitting the chemical model to the experimental data, allowing the chemical simulation to optimise $k_{(R5a)}$, $k_{(R5b)}$ and $k_{(R5c)}$ independently. The total rate coefficient was determined from the fitting procedure also listed $k_{(R5)}$. The bottom row displays average values and calculated standard deviations ($\pm 2\sigma$). All other experiments conducted using 2 photolysis lamps.

Expt	$\alpha_{(R5a)}$	$\alpha_{(R5b)}$	$\alpha_{(R5c)}$	$k_{(R5a)}$	$k_{(R5b)}$	$k_{(R5c)}$ ^a	$k_{(R5)}$ ^a
P1	0.41	0.13	0.45	7.22	2.30	7.94	17.5
P2	0.35	0.10	0.55	8.58	2.48	13.3	24.3
P3	0.33	0.11	0.56	9.19	3.05	15.3	27.5
P4 ^b	0.32	0.10	0.58	9.09	2.87	16.3	28.3
P5 ^c	0.34	0.11	0.55	8.48	2.62	13.8	24.9
P11 ^b	0.38	0.11	0.50	8.99	2.69	11.8	23.5
P12 ^b	0.45	0.15	0.41	8.41	2.79	7.63	18.8
	0.37 ± 0.10	0.12 ± 0.04	0.51 ± 0.12	8.57	2.69	1.23	24 ± 8

^a Rate coefficient units in $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b Experiment conducted using 4 photolysis lamps.

^c Experiment conducted using 8 photolysis lamps.

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Table 4. Comparison of the results determined in this study with those present in the literature. Authors are referenced as they appear in the bibliography and tilde symbols indicate where a value was not measured directly. Data previous to (Hasson et al., 2004) had not considered a third branching pathway ($\alpha_{(R5c)}$) but are included here to compare the ratio of $k_{(R5a)}$ and $k_{(R5b)}$ as well as the overall rate constant for CH₃C(O)O₂ + HO₂ ($k_{(R5)}$).

Author	$\alpha_{(R5a)}$	$\alpha_{(R5b)}$	$\alpha_{(R5c)}$	$k_{(R5a)}/k_{(R5b)}$	$k_{(R5)}^a$
This work	0.38±0.08	0.12±0.02	0.50±0.08	3.1 ± 0.33.2 ± 0.2	2.1 ^b
fitted $k_{(R5)}$	0.37 ± 0.10	0.12 ± 0.04	0.51 ± 0.12		2.4 ± 0.4
Groß et al. (2014b)	0.23 ± 0.12	0.16 ± 0.08	0.61 ± 0.09	1.44	2.1 ± 0.4
Dillon and Crowley (2008)	–	–	0.50 ± 0.20	–	1.4 ± 0.5
Jenkin et al. (2007)	0.38 ± 0.13	0.12 ± 0.04	0.43 ± 0.10	3.16 ± 0.48	(1.4 ^c)
Le Crâne et al. (2006)	–	0.20 ± 0.01	< 0.1	–	1.50 ± 0.08
Hasson et al. (2004)	0.40 ± 0.16	0.20 ± 0.08	0.40 ± 0.16	2.00 ± 0.57	2.2
Tomas et al. (2001)	–	0.20 ± 0.02	–	–	1.51 ± 0.07
Crawford et al. (1999)	(0.72) ^c	0.12 ± 0.04	–	7.3 (2.6) ^d	4.4 ± 1.6
Horie and Moortgat (1992)	–	–	–	2.7	–
Moortgat et al. (1989)	–	0.33 ± 0.07	–	–	1.3 ± 0.3
Niki et al. (1985)	~ 0.75	~ 0.25	–	~ 3	–
IUPAC (Atkinson et al., 2006)	0.41 ± 0.20	0.15 ± 0.10	0.44 ± 0.20	2.7	1.4 ^{+1.4} _{-0.7}

^a Units for $k_{(R5)}$, molecule⁻¹ cm³ s⁻¹.

^b Analysis conducted using recently reported value for $k_{(R5)}$ from Gross et al., 2014.

^c Jenkin et al., 2007 assumed k_{R5} as that recommended by IUPAC.

^d Bracketed data from (Crawford et al., 1999) corrected for erroneous absorption cross section for CH₃C(O)OOH by (Orlando et al., 2000).

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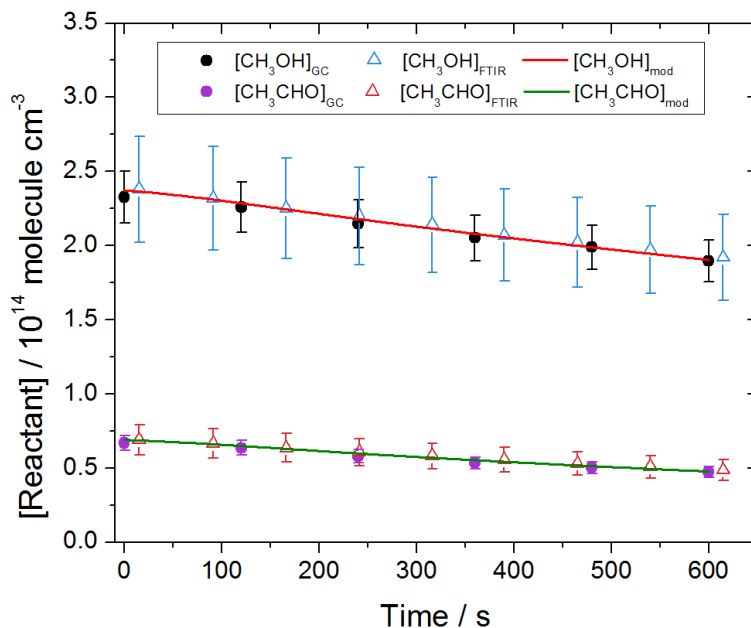


Figure 1. Decay of reactants CH₃CHO and CH₃OH from experiment P11 measured simultaneously using FTIR and GC-FID conducted at 1000 mbar and 298 K. Error bars are representative of the uncertainty in the calibration of the FTIR and GC-FID ($\pm 2\sigma$). Measurements are in excellent agreement within their respective uncertainties. Chemical simulation was conducted using the reaction scheme outlined in Table 2 using $k_{(R5)} = 2.35 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)} = 0.38 : 0.11 : 0.5$. Model concentrations for CH₃CHO and CH₃OH was observed to agree well with the experimental data, confirming accurate prediction of the reactant decays, and therefore the $j(\text{Cl}_2)$ photolysis rate ($= (8 \pm 1) \times 10^{-5} \text{ s}^{-1}$).

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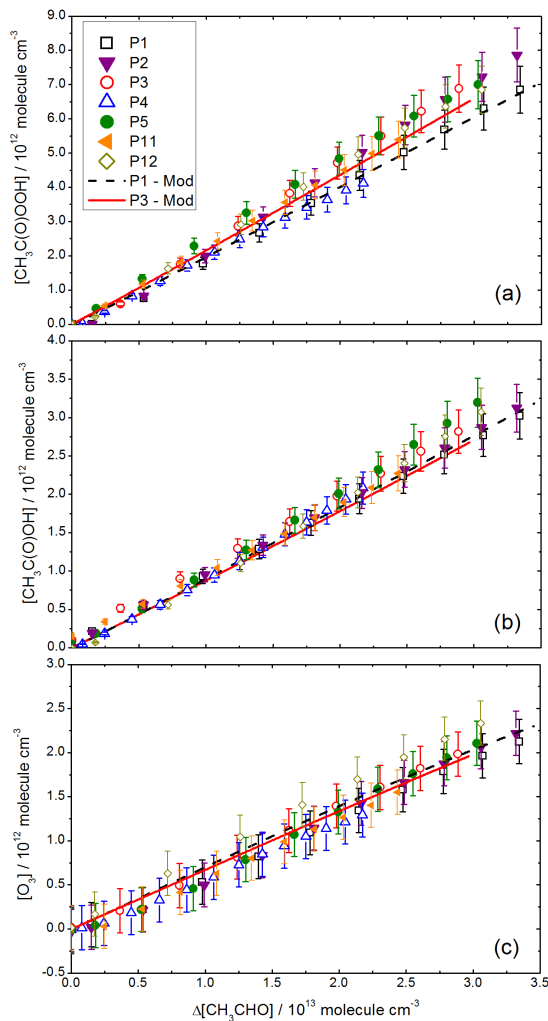

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Figure 2. Products $\text{CH}_3\text{C}(\text{O})\text{OOH}$, **(a)**, $\text{CH}_3\text{C}(\text{O})\text{OH}$, **(b)**, and O_3 , **(c)**, as a function of $\Delta[\text{CH}_3\text{CHO}]$ for $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0 \approx 4$ in air at 1000 mbar and 293 K for runs P1–P5, P11 and P12. Good agreement was observed between experimental data and the chemical model for all datasets with $k_{(\text{R5})} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and average determined yields of $\alpha_{(\text{R5a})} = 0.37 \pm 0.10$, $\alpha_{(\text{R5b})} = 0.12 \pm 0.04$ and $\alpha_{(\text{R5c})} = 0.51 \pm 0.12$. Only model runs for experiments P1 and P3 are shown as examples, the optimised branching ratios for which are shown in Table 1. All uncertainties quoted to $\pm 1\sigma$.

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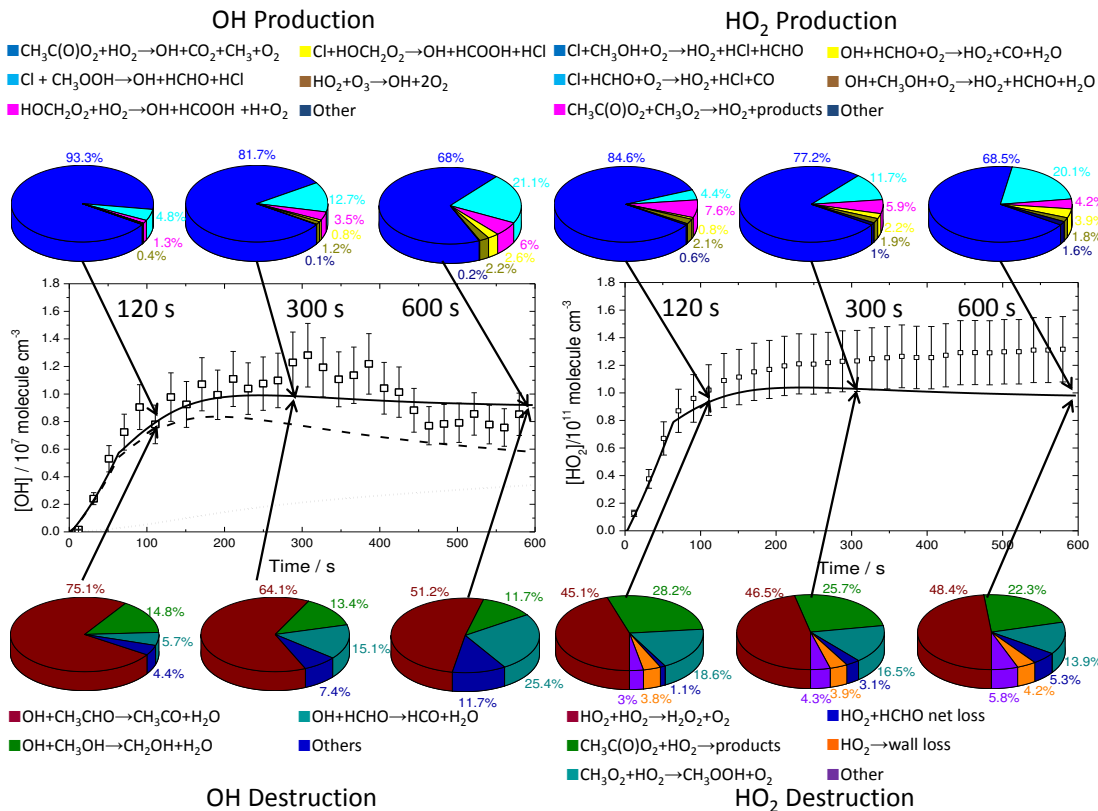
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Figure 3. The OH and HO₂ time profiles during experiment P1, [CH₃OH]₀ : [CH₃CHO]₀ ≈ 4, 1000 mbar in air and 293 K, where photolysis was initiated at $t = 0$ s. Chemical model predictions also shown (solid lines) calculated using optimised branching ratios (P1) $\alpha_{(R5c)} = 0.45 \pm 0.08$ calculated using the fitted $k_{(R5)} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Contribution to total [OH] from Reaction (R5c) and all other secondary sources are shown as dashed and dotted traces respectively. Error bars represent uncertainty to $\pm 1\sigma$ in the FAGE calibration procedure. Above and below each profile are shown rate of production and rate of destruction analyses at 120, 300 and 600 s. OH production is dominated by the title reaction and OH loss processes are predominantly controlled by well-characterised reactions. HO₂ production and loss is controlled by more reactions, but these too are well-characterised.

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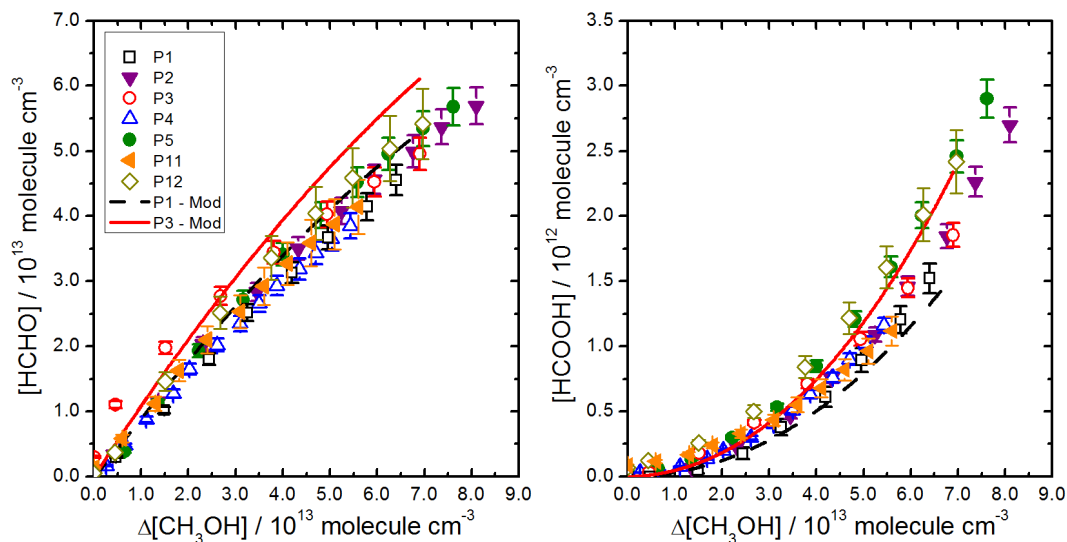


Figure 4. The [HCHO] (left) and [HCOOH] (right) profiles as a function of $\Delta[\text{CH}_3\text{OH}]$ for experiments P1–P5, P11 and P12, for $[\text{CH}_3\text{OH}]_0 : [\text{CH}_3\text{CHO}]_0 \approx 3.8$ at 1000 mbar and 293 K. Good agreement was observed between experimental data and the chemical model for all datasets with $k_{(\text{R}5)} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and average determined yields of $\alpha_{(\text{R}5\text{a})} = 0.37 \pm 0.10$, $\alpha_{(\text{R}5\text{b})} = 0.12 \pm 0.04$ and $\alpha_{(\text{R}5\text{c})} = 0.51 \pm 0.12$. Only model runs for experiments P1 and P3 are plotted as examples, the optimised (R5) branching ratios for which are shown in Table 1. All uncertainties quoted to $\pm 1\sigma$.

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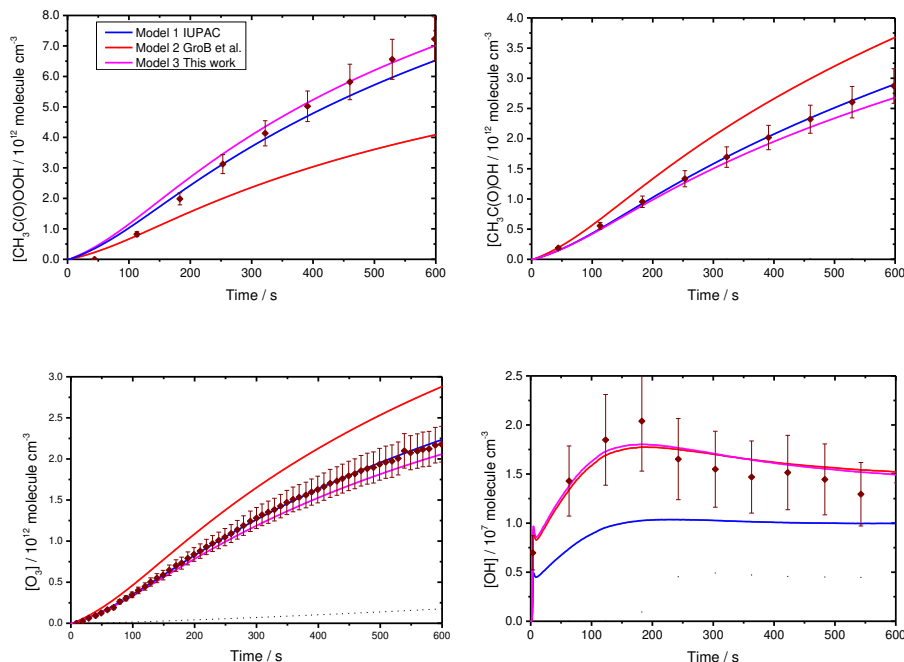


Figure 5. Comparison of the measured CH₃C(O)OOH, **(a)**, CH₃C(O)OH, **(b)**, O₃, **(c)**, and OH **(d)** with various modelling scenarios, displayed as a function of time for experiment P2 conducted at 1000 mbar and 293 K. Error bars are representative of the uncertainty in the FTIR (for **(a)** – **(c)**) and FAGE **(d)** measurement techniques to $\pm 2\sigma$. Chemical simulations were conducted with different $k_{(R5)}$ and branching ratios $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)}$. Model 1 (IUPAC): $k_{(R5)} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)} = 0.44 : 0.15 : 0.41$. Model 2 (GroB et al., 2014b): $k_{(R5)} = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)} = 0.23 : 0.16 : 0.61$. Model 3 (this work, 2015): $k_{(R5)} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $\alpha_{(R5a)} : \alpha_{(R5b)} : \alpha_{(R5c)} = 0.35 : 0.10 : 0.55$.

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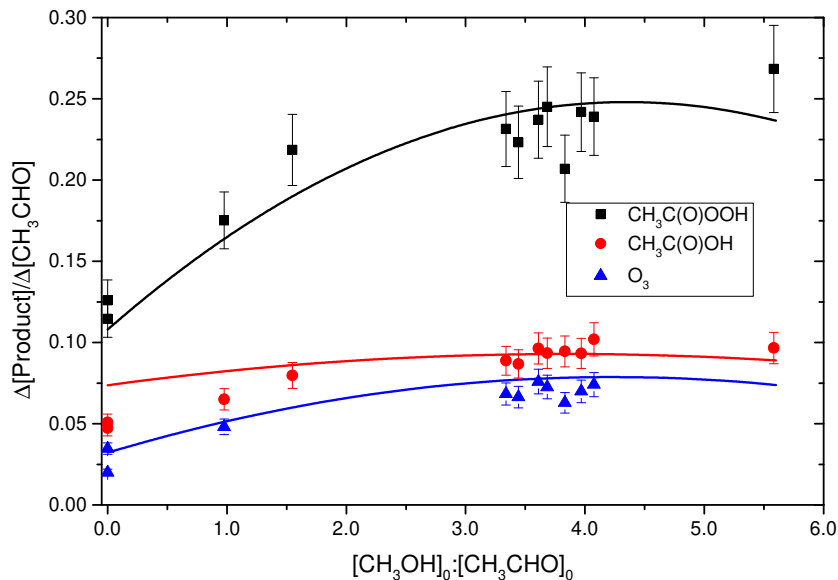


Figure 6. Experimentally determined product yields (relative to decay in CH₃CHO) for CH₃C(O)OOH, CH₃C(O)OH and O₃ as a function of the [CH₃OH]₀ : [CH₃CHO]₀ ratio where each point represents one experiment. Model3 predictions for each species yield also displayed for comparison (solid lines of corresponding colour). Uncertainties calculated to 2σ from linear regression of respective [product] vs. Δ[CH₃CHO] plot.

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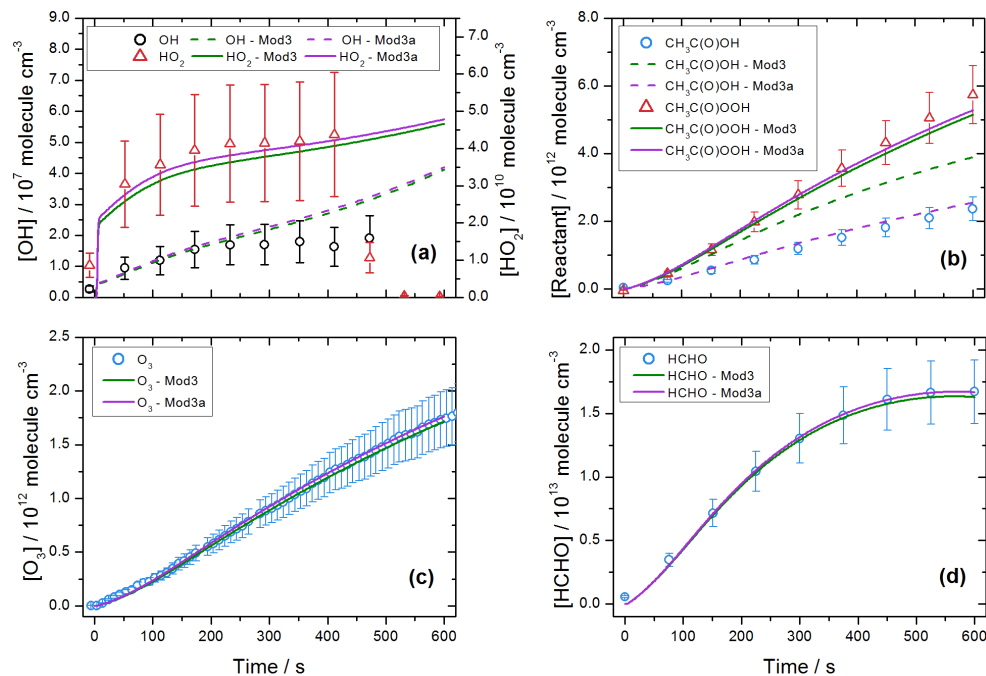


Figure 7. Experimental results for OH and HO₂, **(a)**, CH₃C(O)OOH and CH₃C(O)OH, **(b)**, O₃, **(c)** and HCHO, **(d)**, as a function of time for experiment P9 where [CH₃OH]₀ : [CH₃CHO]₀ = 0.0, 1000 mbar and 293 K. Yields for Reaction (R5) were modelled using the base model reaction scheme shown in Table 2 and varied to fit the measurements, using $k_{(R5)} = (2.4 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $\alpha_{(R5a)} = 0.42 \pm 0.05$, $\alpha_{(R5b)} = 0.14 \pm 0.04$ and $\alpha_{(R5c)} = 0.44 \pm 0.10$ (Model3). Model agreement to measured CH₃C(O)OH was improved by varying the modelled branching ratios of Reactions (R20a) and (R20b) are shown in trace Model3a. All uncertainties quoted to $\pm 2\sigma$.

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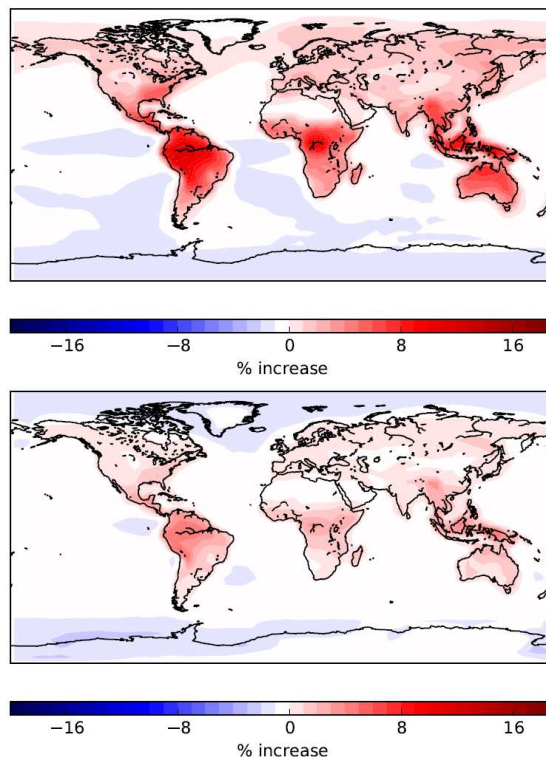


Figure 8. Percentage increase of surface OH concentrations calculated from rate constant and yields from this study ($\alpha_{(R5a)} = 0.37$, $\alpha_{(R5b)} = 0.12$, $\alpha_{(R5c)} = 0.51$, $k_{(R5)} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) compared to **(a)** the same overall rate coefficient but with the OH channel set to zero ($\alpha_{(R5a)} = 0.75$, $\alpha_{(R5b)} = 0.25$, $\alpha_{(R5c)} = 0$) and with **(b)** the IUPAC recommendation ($\alpha_{(R5a)} = 0.41$, $\alpha_{(R5b)} = 0.15$, $\alpha_{(R5c)} = 0.44$, $k_{(R5)} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

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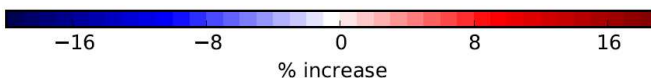
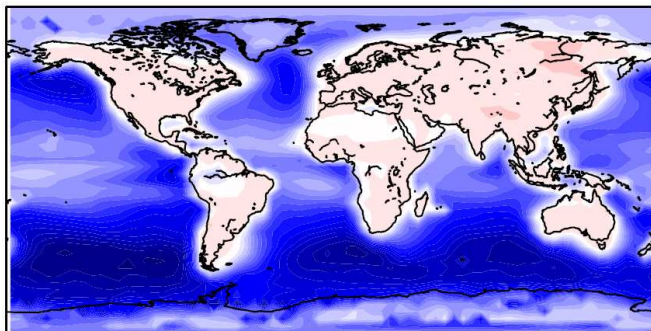
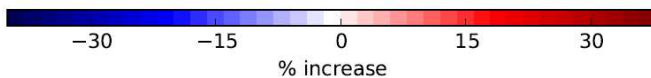
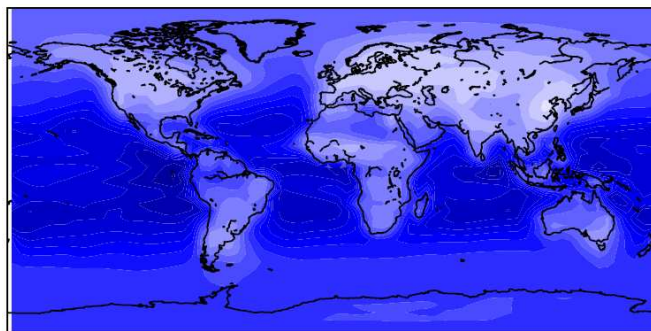


Figure 9. Percentage increase in (a) [PAN] and (b) [NO] of varying $k_{(R5)}$ from the IUPAC value ($k_{(R5)} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) to that of the current study ($k_{(R5)} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

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