The following contains the comments of the referee (black), our replies (blue) indicating changes that will be made to the revised document (red).

Reviewer #1

GENERAL COMMENTS

This manuscript revisits the gas-phase kinetics of the OH+CH3C(O)OOH (PAA) reaction as a function of temperature (298-353 K) by an absolute kinetic method. Several additional experiments were performed to check for a potential interference of the OH-reformation (via the study of OD + PAA reaction) and a kinetic numerical simulation was also carried out to quantify the role of secondary OH-reactions. The very low rate coefficient measured experimentally for the OH+CH3C(O)OOH reaction is confirmed theoretically in this work, by using the multiconformer canonical transition state theory. The disagreement of more than two orders of magnitude with the results from the relative kinetic study by Wu et al. (2017) is discussed. The theoretical temperature-dependence of the rate coefficient of the tittle reaction shows a significant curvature in the Arrhenius plots which is not seen experimentally due to the large uncertainties in k. Despite the calculated negative Tdependence of k, the contribution of the title reaction to the atmospheric removal of CH3C(O)OOH above the boundary layer is not significant with respect to its photolysis in the actinic region, but with a longer lifetime of CH3C(O)OOH (around weeks in the free and upper troposphere) than previously assumed. Finally, the reaction mechanism is investigated theoretically concluding that the importance of CH3C(O)O radical formation. The present comprehensive kinetic study remarks the kinetic complexity of the acetic/peracetic system and the experimental efforts that have to be done to get a reliable rate coefficient. The combination of experimental studies with computation is of great aid to elucidate observed discrepancies or to get deep insights into the reaction mechanisms. Both the experiments and calculations are carefully performed and the paper is generally well structured. In my opinion, the results from this study are of high interest for improving the atmospheric chemical models. Thus, I recommend the publication of this manuscript in the Atmospheric Chemistry and Physics journal after addressing the specific comments/ suggested changes that, in my opinion, need to be included for improving it.

We thank the reviewer for the careful review and the positive assessment of our manuscript.

SPECIFIC COMMENTS/SUGGESTIONS

1) Introduction It is said that the branching ratio (BR = k1a / k1) is 0.37 ± 0.09 at 298 K, while it is 0.31 at 240 K temperatures, stating that the branching ratio to form CH3C(O)OOH decreases with temperature. Well, as no uncertainties are given for the BR at 240 K, I think that it lies within the uncertainties of BR at 298 K.

The IUPAC panel recommend a temperature dependence, which is what we quote. We have amended the text to:

Laboratory studies, summarised by IUPAC, indicate that the overall rate coefficient (k_1) for reaction R1 (at 298 K) is $(2 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and that $CH_3C(O)OOH$ is formed with a branching ratio (k_{1a} / k_1) of 0.37 ± 0.09 at this temperature. At lower temperatures, such as those found in the upper troposphere, the rate coefficient increases (k_1 (240 K) = 3.7×10^{-11} cm^3 molecule^{-1} s^{-1}) while the branching ratio to $CH_3C(O)OOH$ decreases: k_{1a} / k_1 (240 K) = 0.31 (Atkinson et al., 2006; IUPAC, 2020).

2) Experimental section The pressure in the reactor was monitored with 10, 100 and 1000 Torr capacitance manometers. Can you provide in the text (and in Tables S1 and S2) the pressure range in the kinetic experiments?
We have added this information to the methods section and the Tables of results in the SI.
The pressure in the reactor, generally between ~50 and 100 Torr N_2 was monitored with 100 and 1000 Torr capacitance manometers (1 Torr = 1.333 HPa).
In section 4.2 we write:
k_6 was determined at a total pressure (N_2) of 57 and 102 Torr, k_7 was examined at 66 Torr (N_2).
In section 4.3 we write:
The experiments were conducted at a total pressure of ~100 Torr (N_2).
In section 4.4.2 we write:
The results of experiments (at ~57 Torr N_2) in which…….

The sentence "The CH3C(O)OH-dimer spectrum was measured in the small cell (pathlength 15 cm) using a similar procedure but using higher pressures of CH3C(O)OH + CH3C(O)OH-dimer (up to 1.36 Torr) to favour dimer formation" is not clear. What is the highest pressure of the mixture acetic acid/dimer? 1.36 Torr in 700 Torr of N2? At the beginning of the section it is stated that "in total typically 3-18 Torr". Please confirm this.
The 1.36 Torr was the pressure in the small optical absorption cell. The 3-18 Torr pressures refer to the mixing line. We have modified the text to avoid confusion.
The $CH_3C(O)OH$-dimer spectrum was measured in the small optical absorption cell (l = 15 cm) using up to 1.36 Torr (dosed directly into the cell) of the $CH_3C(O)OH$ / $CH_3C(O)OH$-dimer mixture to favour dimer formation.

Measurement of H2O, H2O2 and DONO2 concentrations: It is clear that acetic and peracetic acids were quantified by FTIR spectroscopy and that H2O was measured by IR relative to VUV spectroscopy at 185 nm, but what about H2O2 and DONO2? Were they measured by IR spectroscopy too?
We made no attempt to measure the concentrations of H_2O_2 and $DONO_2$ optically as these parameters are not required in our analysis.

3) IR absorption cross sections As the authors known, the absorption cross sections in the IR region are usually expressed in base 10, that is that the absorbance is defined as the log10 of the intensities ratio at a certain wavenumber. In contrast, in the UV region the absorption cross sections are usually expressed in base e, that is that the absorbance is defined as ln of the intensities ratio. Please state in the text.
We have added text in section 4.1 (Infrared absorption cross-sections).
Note that all IR-cross sections we quote are "base e".

The authors comment that the IR absorption spectra of H2O in the PAA samples was obtained relative to its VUV-absorption 185 nm. What is the contribution of H2O2 to the total absorption at 185 nm? Is it negligible?
The reference IR spectra were obtained using pure H_2O samples and monitoring absorption at 185 nm and in the IR. There is thus no contribution from H_2O_2.

4) Kinetics of OH/OD + CH3C(O)OH reactions The title of section 4.2 is not only "OH + CH3C(O)OH". I suggest this change: "4.2 OH/OD + CH3C(O)OH:

Change made:

4.2 OH/OD + $CH_3C(O)OH$: Determination of k_6 and k_7 at 298 K

Determination of k6 and k7 at 298 K". In some parts of this section refer only a reference to the OH+acetic acid reaction exclusively is made. For example, in equations (1) and (2) or in the sentence "Typically, the values of [CH3C(O)OH] varied by < 3% during the time required to measure the OH-decay". Please complete or revise.

To avoid repeating almost identical equations we now write:

Similar expressions (switch OD for OH and k_7 for k_6) apply to the OD experiments.

during the time required to measure the OH or OD-decay,

5) Kinetics of OH + CH3C(O)OOH reactions Please, include what ki' is to clarify the relationship with ki. It is far from this section.

We already write: "Where k_6' and k_4' are the pseudo-first order rate constants for loss of OH via reaction (R6) and (R4), respectively."

Can the authors provide a bit more detail on how the concentration of CH3C(O)OOH is corrected by decomposition of the dimer at high temperatures?

There is no known dimer formation for $CH_3C(O)OOH$, so the reviewer probably refers to acetic acid dimer. We now write:

When the reactor is operated at high temperatures some of the $CH_3C(O)OH$-dimer present in the IR-absorption cell is converted to $CH_3C(O)OH$ in the reactor and correction was made to account for this using the temperature dependent equilibrium constant.

Temperature dependence of k4: Why did not the authors measure k4 at temperatures lower than 298 K of interest in the upper troposphere?

The decay of OH which we measure is largely due to reaction with $CH_3C(O)OH$ and we have no significant contribution from OH reacting with $CH_3C(O)OOH$. As the rate constant for reaction between OH and $CH_3C(O)OH$ increases at lower temperatures it made little sense to conduct experiments at temperatures appropriate for e.g. the upper troposphere.

Theory: It is stated that the rate coefficient k4 is calculated in the high-pressure limit. The measured k are also in the HPL? What is the total pressure in the reactor?

We had omitted to mention the pressure and have added text to section 2.1

The pressure in the reactor, generally between ~50 and 100 Torr N_2 was monitored with 100 and 1000 Torr capacitance manometers (1 Torr = 1.333 HPa).

We have also added text to section 4.5:

Given the slow product formation rate, the protruding reaction barriers, and the fast formation and decomposition of the complex, k_4 is not expected to show a pressure-dependence and should be at the high-pressure limit under the experimental conditions (50-100 Torr N_2).

Secondary OH-reactions: The OH+CH3 reaction is the main loss process in the system. In the text, a reference to Baulch et al. (2005) is made, while in Table S2 the rate coefficient for this reaction is taken from Sangwan et al. (2012). As the OH+CH3 reaction is pressure dependent, the total pressure of the bath gas used has to be stated to derive k given in Table S3 from Sangwan et al.

We have removed the citation to Bauch 2005. The termolecular reaction between OH and CH_3 is in fact independent of pressure (of He) between ~8 and 680 Torr (Pereira, 1997) and is thus at the high-pressure limit under our experimental conditions. We have chosen to take the rate constant (in He) from the latest work on this reaction for our simulations. We now cite (Table S3) the Pereira et al study (which covers our pressure range) as well as Sangwan et al.

The rate coefficient for reaction of OH with CH_3 is at the high-pressure-limit, with a value close to 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Pereira et al., 1997; Sangwan et al., 2012) under our experimental conditions.

MINOR SUGGESTED CHANGES

When mentioning a range, please use parenthesis. For example, in (6.17 - 38.5) × 1014 molecule cm-3.

Changes made as suggested

Use “rate coefficient” or “rate constant” through the manuscript, but not a mixture of both.

We now use “rate coefficient” throughout

Unify “Pseudo-first-order” or “pseudo first-order”;

We now use pseudo-first-order throughout

“peracetic” or “per-acetic”; “CH3C(O)OOH” or “CH3C(=O)OOH”; “CH2O” or “HCHO”.

We now use peracetic, $CH_3C(O)OOH$ and HCHO throughout

Line 13: Include units of k in “ ~6 × 10-14 in the cold upper troposphere”.

Change made as suggested

Line 18: Replace “dry-deposition” by “dry deposition”

Change made as suggested

Line 19: Replace “peroxy-acids” by “peroxy acids”

Change made as suggested

Line 24-28: This sentence is too long. It can be re-written as: “Despite the acidic peroxide, peracetic acid (CH3C(O)OOH, PAA), is expected to be the 2nd-most abundant organic peroxide (after CH3OOH) in the troposphere, ambient measurements are relatively scarce. Several atmospheric measurements of PAA were reported in the boundary layer (Crowley et al., 2018; Fels and Junkermann, 1994; He et al., 2010; Liang et al., 2013; Phillips et al., 2013; Walker et al., 2006; Zhang et al., 2010) and from aircraft (Crounse et al., 2006; Wang et al., 2019), indicating that it is present throughout the troposphere.”

The sentence has been modified

Line 61: Replace k2 by k4.

Change made as suggested

Line 74: peroxy radical chemistry
Change made as suggested

Line 96: infrared is more common than infra-red.
We now use infrared throughout

Line 105: The sentence is confusing, since OH is not generated from DONO2. I suggest to change it: Laser pulses at 248 nm (â´Lij20 ns), provided at 10 Hz by an excimer laser (Compex 205F, Coherent) operated using KrF, were used for generating OH and OD radicals. In particular, H2O2 was used as the photochemical precursor of OH radicals in the study of the OH+CH3C(O)OH reaction, while DONO2 and PAA were used in the study of OD+PAA and OH+PAA reactions, respectively”. It is true that this is specified further in next sections.
Text changed, we now write:
Pulses of 248 nm laser light (~20 ns) for OH generation from H_2O_2 and $CH_3C(O)OOH$ or OD generation from $DONO_2$ were provided…..

Line 125: 45-cm long
Text changed, we now write:
…by flowing the sample through an absorption cell ($l = 45$ cm) made of glass,

Line 211: a quantitative IR spectrum
Change made as suggested

Line 217: 45-cm path-length absorption cell
Change made as suggested

Line 277: Parenthesis are missing in the value of k7.
Change made as suggested

Line 287-288: “. . .by scaling a reference spectrum of. . .”
Change made as suggested

Line 333: Change k7 by k5.
Change made as suggested

Line 338: This sentence is not clear“. . .and we conclude that OH-reformation via Reactions (R4b + R11). . .” In reaction 4b, the CH2C(O)OOH radical is formed and R11 is the equilibrium between CH3C(O)OH(l) and CH3C(O)OOH(l). Are these reactions the ones you refer?
The reactions were wrongly numbered. We now simply state
…and we conclude that OH-reformation is not responsible for the divergence….

Line 354: R17 will also have a rate coefficient close
Change made as suggested

Line 376: Delete “using methods” in “Analysis of head-space samples of CH3C(O)OOH and H2O2 using methods. . .”

Change made as suggested

Tables and Figures

Tables S1 and S2: Please order the values of k’ and k4’ increasing the concentration of acetic and peracetic acids for ease of presentation.
Change made as suggested

In Table S2, I would list the values of k’6+kd instead of k’4+kd, since from them k4 are obtained.
k_4 is obtained from plots of $k_4' + k_d$ versus [$CH_3C(O)OOH$], this is why we list this parameter.
Table S3: Replace the = by an arrow in the reaction OH + CH3C(O)O2 = HO2 + CH3
Change made as suggested

Figure 5a: Decays are better to be normalized as in Figure 5b or Fig 4.
In Figure 5b, the photolysis of $DONO_2$ is used as OH source and thus the initial amount of OD does not change. In Figure 5a, the amount of OH is variable (as its precursor was $CH_3C(O)OOH$.

Figure 9, caption: “as upper limits OF the rate coefficient”
Text modified

Figure S2: The legend of y-axis is not correct. It is not “integrated band strength”, it is plotted the “integrated absorbance” with units of cm-1. “Absorbance” is not a physical unit, but a dimensionless parameter.
This comment refers to S1.
We have corrected the y-axis labelling

Figure S3: The legend of y-axis is not correct. “Absorbance” is a dimensionless parameter by definition, so “arbitrary units” has to be deleted.
Change made as suggested