

# ***Interactive comment on “Reaction between CH<sub>3</sub>C(O)OOH (peracetic acid) and OH in the gas-phase: A combined experimental and theoretical study of the kinetics and mechanism” by Matias Berasategui et al.***

## **Anonymous Referee #1**

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GENERAL COMMENTS This manuscript revisits the gas-phase kinetics of the OH+CH<sub>3</sub>C(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+CH<sub>3</sub>C(O)OOH reaction is confirmed theoretically in this work, by using the multi-conformer canonical transition state theory. The disagreement of more than two or-

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ders 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 title 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  $T$ -dependence of  $k$ , the contribution of the title reaction to the atmospheric removal of  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  above the boundary layer is not significant with respect to its photolysis in the actinic region, but with a longer lifetime of  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  (around weeks in the free and upper troposphere) than previously assumed. Finally, the reaction mechanism is investigated theoretically concluding that the importance of  $\text{CH}_3\text{C}(\text{O})\text{O}$  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.

**SPECIFIC COMMENTS/SUGGESTIONS** 1) Introduction It is said that the branching ratio ( $\text{BR} = k_{1a} / k_1$ ) is  $0.37 \pm 0.09$  at 298 K, while it is 0.31 at 240 K temperatures, stating that the branching ratio to form  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  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.

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?

The sentence "The  $\text{CH}_3\text{C}(\text{O})\text{OH}$ -dimer spectrum was measured in the small cell (path-

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length 15 cm) using a similar procedure but using higher pressures of  $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OH}$ -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  $\text{N}_2$ ? At the beginning of the section it is stated that “in total typically 3-18 Torr”. Please confirm this.

Measurement of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{DONO}_2$  concentrations: It is clear that acetic and peracetic acids were quantified by FTIR spectroscopy and that  $\text{H}_2\text{O}$  was measured by IR relative to VUV spectroscopy at 185 nm, but what about  $\text{H}_2\text{O}_2$  and  $\text{DONO}_2$ ? Were they measured by IR spectroscopy too?

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  $\log_{10}$  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.

The authors comment that the IR absorption spectra of  $\text{H}_2\text{O}$  in the PAA samples was obtained relative to its VUV-absorption 185 nm. What is the contribution of  $\text{H}_2\text{O}_2$  to the total absorption at 185 nm? Is it negligible?

4) Kinetics of  $\text{OH}/\text{OD} + \text{CH}_3\text{C}(\text{O})\text{OH}$  reactions The title of section 4.2 is not only “ $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OH}$ ”. I suggest this change: “4.2  $\text{OH}/\text{OD} + \text{CH}_3\text{C}(\text{O})\text{OH}$ : Determination of  $k_6$  and  $k_7$  at 298 K”. In some parts of this section refer only a reference to the  $\text{OH}$ +acetic acid reaction exclusively is made. For example, in equations (1) and (2) or in the sentence “Typically, the values of  $[\text{CH}_3\text{C}(\text{O})\text{OH}]$  varied by  $< 3\%$  during the time required to measure the  $\text{OH}$ -decay”. Please complete or revise.

5) Kinetics of  $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OOH}$  reactions Please, include what  $k_i'$  is to clarify the relationship with  $k_i$ . It is far from this section. Can the authors provide a bit more detail on how the concentration of  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  is corrected by decomposition of the dimer at high temperatures?

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Temperature dependence of  $k_4$ : Why did not the authors measure  $k_4$  at temperatures lower than 298 K of interest in the upper troposphere?

Theory: It is stated that the rate coefficient  $k_4$  is calculated in the high-pressure limit. The measured  $k$  are also in the HPL? What is the total pressure in the reactor?

Secondary OH-reactions: The OH+CH<sub>3</sub> 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+CH<sub>3</sub> 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.

MINOR SUGGESTED CHANGES When mentioning a range, please use parenthesis. For example, in  $(6.17 - 38.5) \times 10^{14}$  molecule cm<sup>-3</sup>. Use “rate coefficient” or “rate constant” through the manuscript, but not a mixture of both. Unify “Pseudo-first-order” or “pseudo first-order”; “peracetic” or “per-acetic”; “CH<sub>3</sub>C(O)OOH” or “CH<sub>3</sub>C(=O)OOH”; “CH<sub>2</sub>O” or “HCHO”.

Line 13: Include units of  $k$  in “ $\sim 6 \times 10^{-14}$  in the cold upper troposphere”. Line 18: Replace “dry-deposition” by “dry deposition” Line 19: Replace “peroxy-acids” by “peroxy acids” Line 24-28: This sentence is too long. It can be re-written as: “Despite the acidic peroxide, peracetic acid (CH<sub>3</sub>C(O)OOH, PAA), is expected to be the 2nd-most abundant organic peroxide (after CH<sub>3</sub>OOH) 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 (Crouse et al., 2006; Wang et al., 2019), indicating that it is present throughout the troposphere.” Line 61: Replace  $k_2$  by  $k_4$ . Line 74: peroxy radical chemistry Line 96: infrared is more common than infra-red. Line 105: The sentence is confusing, since OH is not generated from DONO<sub>2</sub>. I suggest to change it: Laser pulses at 248 nm (ÅLij20 ns), provided at 10 Hz by an excimer laser (Compex 205

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F, Coherent) operated using KrF, were used for generating OH and OD radicals. In particular, H<sub>2</sub>O<sub>2</sub> was used as the photochemical precursor of OH radicals in the study of the OH+CH<sub>3</sub>C(O)OH reaction, while DONO<sub>2</sub> 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. Line 125: 45-cm long Line 211: a quantitative IR spectrum Line 217: 45-cm path-length absorption cell Line 277: Parenthesis are missing in the value of k<sub>7</sub>. Line 287-288: "...by scaling a reference spectrum of..." Line 333: Change k<sub>7</sub> by k<sub>5</sub>. Line 338: This sentence is not clear "...and we conclude that OH-reformation via Reactions (R<sub>4b</sub> + R<sub>11</sub>)..." In reaction 4b, the CH<sub>2</sub>C(O)OOH radical is formed and R<sub>11</sub> is the equilibrium between CH<sub>3</sub>C(O)OH(l) and CH<sub>3</sub>C(O)OOH(l). Are these reactions the ones you refer? Line 354: R<sub>17</sub> will also have a rate coefficient close Line 376: Delete "using methods" in "Analysis of head-space samples of CH<sub>3</sub>C(O)OOH and H<sub>2</sub>O<sub>2</sub> using methods..."

#### Tables and Figures

Tables S1 and S2: Please order the values of k' and k<sub>4</sub>' increasing the concentration of acetic and peracetic acids for ease of presentation. In Table S2, I would list the values of k'<sub>6</sub>+k<sub>d</sub> instead of k'<sub>4</sub>+k<sub>d</sub>, since from them k<sub>4</sub> are obtained.

Table S3: Replace the = by an arrow in the reaction OH + CH<sub>3</sub>C(O)O<sub>2</sub> = HO<sub>2</sub> + CH<sub>3</sub>

Figure 5a: Decays are better to be normalized as in Figure 5b or Fig 4.

Figure 9, caption: "as upper limits OF the rate coefficient"

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<sup>-1</sup>. "Absorbance" is not a physical unit, but a dimensionless parameter.

Figure S3: The legend of y-axis is not correct. "Absorbance" is a dimensionless parameter by definition, so "arbitrary units" has to be deleted.

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