

Reviewer #2

General comments. This paper presents a study of the kinetics and mechanism of the reaction of OH with peracetic acid ($\text{CH}_3\text{C}(\text{O})\text{OOH}$), including both an absolute experimental investigation (298 – 353 K) and a theoretical investigation (200 - 450 K). The results show that the reaction is considerably slower than reported previously in a published 298 K relative rate investigation, and as a result an unimportant loss process for $\text{CH}_3\text{C}(\text{O})\text{OOH}$ in the atmosphere. Although abstraction of H from the $-\text{C}(=\text{O})\text{OOH}$ group is calculated to be the dominant reaction pathway, this is found to be orders of magnitude slower than for simple $-\text{OOH}$ groups in species such as CH_3OOH . This is an important piece of work, providing the first direct determination of the title reaction, which will help improve representation of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ chemistry (and that of other peroxy-acids) in atmospheric mechanisms. The experimental and theoretical studies are carefully performed, with systematic consideration of possible complications and interferences in the former being carried out and presented. The study is appropriate for publication in ACP, and the authors should consider and address the comments given below in producing an improved version of the manuscript. Although the core work is well described and justified, this paper would generally have benefitted from more careful proof-reading prior to submission – and this is the origin of most of the comments given below.

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

Specific comments

1) Line 27: Should "expected to be" be replaced by "observed to be" or simply deleted?

We now write "observed to be"

2) Line 27: "2nd-most" should be "second-most".

Change made as suggested

3) Line 34: Define PAA (or just use $\text{CH}_3\text{C}(\text{O})\text{OOH}$ consistently throughout), and delete either "atmospheric" or "in the atmosphere".

Change made as suggested

4) Line 38: products should be $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{O} + \text{O}_2$ (or " $\text{OH} + \text{CH}_3 + \text{CO}_2 + \text{O}_2$ " if subsequent decomposition of $\text{CH}_3\text{C}(\text{O})\text{O}$ is included). CH_3O_2 is not a direct product of the reaction.

Change made as suggested

5) Line 46: Again, why not write the actual products of the reaction, $\text{CH}_3\text{C}(\text{O})\text{O} + \text{NO}_2$? Note that you declare $\text{CH}_3\text{C}(\text{O})\text{O}$ as a product of reaction (R10), but seem reluctant to do so for reactions (R1c) and (R3). 6)

Change made as suggested

Lines 49-52: This information seems to tally with IUPAC (2020), but shows little similarity to Atkinson et al. (2006). The IUPAC (2020) citation could also be made less vague. For example, could it link to the specific recommendation, rather than the task group home page?

We now cite only the 2020 (online) IUPAC recommendation.

7) Line 61: The current MCM version is MCM v3.3.1, for which I believe the primary home is now "http://mcm.york.ac.uk/" - although the information is mirrored at <http://mcm.leeds.ac.uk/MCM/> (not "<http://mcm.leeds.ac.uk/MC/>"). However, the described treatment of OH + CH₃C(O)OOH remains the same in MCM v3.3.1.

We now cite only the current MCM version.

8) Lines 80-83: The degree to which the formation of CH₃C(O)OOH from the reaction between HO₂ and CH₃C(O)O₂ represents a loss of oxidation capacity does not depend on whether the CH₃C(O)OOH + OH reaction can compete with deposition. Both OH reaction and deposition are radical neutral (i.e. conserve the number of radicals). Reformation of the lost radicals only results from CH₃C(O)OOH photolysis, so it is the extent to which the other loss processes compete with photolysis that is important.

We now write:

The degree to which the formation of CH₃C(O)OOH from the reaction between HO₂ and CH₃C(O)O₂ represents a permanent sink of peroxy radicals (and thus loss of oxidation capacity) depends on whether the photochemical degradation of CH₃C(O)OOH to reform organic radicals can compete with deposition processes.

9) Line 95: "whereby" would seem to be the wrong adverb here, because the measurement of CH₃C(O)OOH and CH₃C(O)OH by IR absorption is not achieved as a result of either the laser photolysis production or LIF detection of OH. The information should probably be divided into two sentences after "(LIF)".

Change made as suggested

10) Line 245: ".....for the reaction between OH and OD with CH₃C(O)OH" should probably be ".....for the reactions of OH and OD with CH₃C(O)OH."

We now write:

We therefore carried out a set of experiments to measure the rate coefficients for the reactions of OH and OD with CH₃C(O)OH.

11) Line 268: I suggest deleting "the values of".

Change made as suggested

12) Line 273: Again, the IUPAC (2019) citation could link to the specific recommendation for OH + CH₃C(O)OH.

We now reference the current (2020) version.

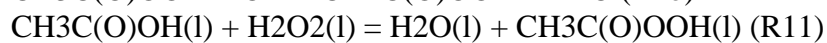
13) Section 4.4.1: Either use PAA (defined somewhere) or CH₃C(O)OOH. This section oscillates between the two.

All reference to PAA has been removed.

14) Line 334: Should k₇ be k₅?

Yes, correction made.

15) Line 338: the meaning of "OH regeneration via reactions (R4b + R11)" is not clear, these reactions being:



Reference to R4b and R11 has been removed

16) Line 339: delete first "value".

Change made as suggested

17) Line 355: According to Table S3, the role of reaction (R17b) was not assessed.

We now mention only reaction R17a

18) Lines 375-383. Given that the possible impact of the impurity $\text{H}_2\text{O}_2 + \text{OH}$ reaction is assessed, shouldn't that reaction be included in the mechanism in Table S3, and associated simulations, for completeness?

As we have no in-situ measurement of $[\text{H}_2\text{O}_2]$ measurement and its contribution (if present at the 1% level) can easily be assessed without numerical simulation we did not include it in the reaction scheme.

19) Lines 384-395: This information does not seem to fit in a section entitled "Presence of H_2O_2 impurity".

True. We have generated a new section that deals with the comparison.

4.5 Comparison with the previous determination of k_4 .

20) Line 457: Given the main conclusion of the work, the discussion of the chemistry following the $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OOH}$ reaction almost seems redundant. The description of the chemistry of the product formed from the minor channel, $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$, also seems selective. Although the chemistry of the NO reaction is important, is it really the dominant fate throughout much of the atmosphere?

Although (as we conclude a few sentences later) OH will not be an important sink of $\text{CH}_3\text{C}(\text{O})\text{OOH}$, we prefer to keep this text so as to provide a more complete picture of the role of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ in the atmosphere. We have amended the text regarding the dominant fate of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and have added reactions with HO_2 and RO_2 .

In many regions of the atmosphere (e.g. those impacted by anthropogenic emissions) its dominant fate will be reaction with NO

In air, the minor $\text{CH}_2\text{C}(\text{O})\text{OOH}$ product of reaction (R4b) is expected to add O_2 , forming a peracetic acid peroxy radical, $\text{OOCH}_2\text{C}(\text{O})\text{OOH}$, which will also undergo reactions with NO , RO_2 and HO_2 .



$\text{OCH}_2\text{C}(\text{O})\text{OOH}$ which will quickly decompose to HCHO , CO_2 and OH (Vereecken and Peeters, 2009).



21) Lines 476-478: Given the main message of the work, it is not clear why the discussion in an “atmospheric implications” section returns to a conclusion based on using a high rate coefficient for $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OOH}$ – even though the preceding comments about other loss processes remain relevant. The atmospheric implications of this work are that the $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OOH}$ reaction is unimportant, and that loss is dominated by photolysis and deposition. In my opinion, Section 4.6 could be re-written to state what the atmospheric implications of this work are more clearly and succinctly. In fact, the subsequent conclusions section (section 5) seems to do that very well, and the sections could be merged.

We have removed reference to the high rate coefficient and taken the description of the products formed from $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OOH}$ out of the “atmospheric implications” section and moved them to the “theoretical studies” section.

22) Line 496: The reference here to “other peroxides” should probably more correctly state “other peracids”, as the conclusions specifically relate to the $-\text{C}(\text{O})\text{OOH}$ moiety. In the abstract, this point becomes generalized by the statement “Similar conclusions can be made for other, saturated peroxy-acids”, which may be taken to mean that all saturated peroxy-acids can be regarded as having a one-year lifetime with respect to reaction with OH. Presumably the $-\text{C}(\text{O})\text{OOH}$ moiety deactivates H abstraction from the first carbon in the R group of $\text{RC}(\text{O})\text{OOH}$ compounds, but abstraction from other sites remains significant – particularly if the (saturated) peroxy-acid contains other activating groups (e.g. $-\text{OH}$). The associated comments could therefore be qualified to this effect.

We agree. The statement was too general as has been removed from the abstract.

23) Line 706: Figure 6 caption should state k_5 rather than k_6 . The much larger intercept for k_5 presumably results from the reaction of OD with DONO_2 . This could be stated somewhere.

k_6 replaced with k_5

We also added the text:

The larger intercept for the OD reaction is due to reaction with DONO_2 .

24) Table S2: PAA (still not defined) in rows; $\text{CH}_3\text{C}(\text{O})\text{OOH}$ in columns.

PAA is now defined as $\text{CH}_3\text{C}(\text{O})\text{OH}$ in Table S2.

25) Table S3: Footnote "a" also applies to $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OH}$, $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{O}_2$ and the final channel of $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$. Although not crucial for the simulations, it would be nice if O_2 and CO_2 were declared as products consistently.

Footnote “a” has been added to the appropriate reactions. CO_2 and O_2 have been added where appropriate.