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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Reaction between $CH_3C(O)OOH$ (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 #2

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General comments

This paper presents a study of the kinetics and mechanism of the reaction of OH with peracetic acid (CH3C(O)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 CH3C(O)OOH in the atmosphere. Although abstraction of H from the -C(=O)OOH group is calculated to be the dominant reaction pathway, this is found to be orders of magnitude slower than for

simple -OOH groups in species such as CH3OOH.

This is an important piece of work, providing the first direct determination of the title reaction, which will help improve representation of CH3C(O)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.

Specific comments

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

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

3) Line 34: Define PAA (or just use CH3C(O)OOH consistently throughout), and delete either "atmospheric" or "in the atmosphere".

4) Line 38: products should be OH + CH3C(O)O + O2 (or "OH + CH3 + CO2 + O2" if subsequent decomposition of CH3C(O)O is included). CH3O2 is not a direct product of the reaction.

5) Line 46: Again, why not write the actual products of the reaction, CH3C(O)O + NO2? Note that you declare CH3C(O)O as a product of reaction (R10), but seem reluctant to do so for reactions (R1c) and (R3).

6) 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?

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.

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.

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)".

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."

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

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

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

14) Line 334: Should k7 be k5?

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

CH3C(O)OOH + OH = CH2C(O)OOH + H2O (R4b)

CH3C(O)OH(l) + H2O2(l) = H2O(l) + CH3C(O)OOH(l) (R11)

16) Line 339: delete first “value”.

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

18) Lines 375-383. Given that the possible impact of the impurity H2O2 + OH reaction is assessed, shouldn’t that reaction be included in the mechanism in Table S3, and associated simulations, for completeness?

19) Lines 384-395: This information does not seem to fit in a section entitled "Presence of H2O2 impurity".

20) Line 457: Given the main conclusion of the work, the discussion of the chemistry following the OH + CH3C(O)OOH reaction almost seems redundant. The description of the chemistry of the product formed from the minor channel, OOCH2C(O)OOH, also seems selective. Although the chemistry of the NO reaction is important, is its really the dominant fate throughout much of the atmosphere?

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 OH + CH3C(O)OOH – even though the preceding comments about other loss processes remain relevant. The atmospheric implications of this work are that the OH + CH3C(O)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.

22) Line 496: The reference here to “other peroxides” should probably more correctly state “other peracids”, as the conclusions specifically relate to the -C(O)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 -C(O)OOH moiety deactivates H abstraction from the first carbon in the R group of RC(O)OOH compounds, but abstraction from other sites remains significant – particularly if the (saturated) peroxy-acid contains other activating groups (e.g. -OH). The associated comments could therefore be qualified to this effect.

23) Line 706: Figure 6 caption should state k5 rather than k6. The much larger intercept for k5 presumably results from the reaction of OD with DONO2. This could be stated somewhere.

24) Table S2: PAA (still not defined) in rows; CH3C(O)OOH in columns.

25) Table S3: Footnote "a" also applies to OH + CH3C(O)OH, OH + CH3C(O)O2 and the final channel of HO2 + CH3C(O)O2. Although not crucial for the simulations, it would be nice if O2 and CO2 were declared as products consistently.

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