Review of "Atmospheric breakdown kinetics and air quality impact of potential "green" solvents the oxymethylene ethers OME3 and OME4"

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This study is relevant to the field of atmospheric chemistry, as it provides the first experimental rate coefficients for reactions of interest. These data are important for the development of improved structure–activity relationships or other predictive tools for kinetic parameters describing OH + VOC reactions.

I recommend publication after addressing the comments below.

The text lacks clarity at times, and the language should be improved in several places. The experiments and theoretical work require further elaboration, particularly to demonstrate that appropriate validation tests have been performed. Additionally, the discussion of the results needs to be more thoroughly developed.

The manuscript also lacks a single, well-structured document titled *Supplementary Information*, which should include clearly defined subsections detailing the computational methods, as well as the experimental and theoretical results. Currently, the supporting information is spread across multiple files that are not described and some of them are not easily accessible. A dedicated section at the end of the main manuscript should summarize the contents of the Supplementary Information.

Specific comments

- line 62: It should be added that the R1 – R4 reactions are hydrogen abstraction reactions.

- line 71: The year for Moriarty et al is missing.

- line 77: Please add the acronym used in reaction R5 in the text, i.e. "2,2,5,5-tetramethyloxolane (TMO)". Suggest mentioning that this compound is a substituted tetrahydrofuran to explain why it has been chosen as an example and adding the values for the rate coefficients predicted by SAR and found experimentally.

- line 80: replace "lab-based" with "laboratory-based"

- line 83: "further indication into the atmospheric fate of…" Please replace "indication" with "insight".

- line 98: Please add the name of the compound labelled with OME5.

- line 100 (Figure 1): Some of the trace colours are very similar, making it difficult to identify which compound they correspond to. Please choose more distinct colours to improve clarity.

Please add the OME4 spectrum to the figure.

- line 102 (capture of Figure 1): "(OME3)" is missing after 989 cm-1, this wavenumber is not attributed to any compound.

- line 105-106: I think it is necessary that the authors comment about the possible losses of OME3 and especially OME4 in liquid form on the walls of septum/chamber during injection as those compounds have low vapour pressure. Were any tests performed to verify whether the gas phase concentrations of the OMEs matched those calculated based on the volume of liquid injected into the chamber? Such tests could involve injecting different volumes of the OME3/OME4 and checking whether the resulting optical absorbance ratios correspond to the volume ratios.

- line 107: Please replace C2O2Cl2 with (COCl)2

- line 113 (reaction R9): A small fraction of COCl is formed. Please comment if there are any issues about sequential decomposition of COCl.

- line 117: There is a partial overlap between the absorption features of OME3 and C3H6 (figure 1). OME3 was measured at 989 cm-1 where there is some absorption of C3H6. Can the author clarify how this was taken into account when determining the 989 cm-1 absorbance of OME3?

The errors in the determination of concentrations caused by spectral overlap can be avoided by fitting reference spectra to the measured spectra in a range of wavenumbers. Could the authors comment on their choice of determining concentrations from A_{max} instead of using the fitting method?

- line 126: Citations are missing after "from literature". Why OME spectra predicted through DFT calculations were used instead of experimental spectra, determined by the authors?

- line 132 (table 1): It is unclear what is meant by "Fitted or manually entered data from multiple sources" in the Source of recommended values column.

-line 146: What is the estimated concentration of H_2O_2 that led to the stated approximate concentration of OH?

- lines 158-171: Although line 93 mentions that kinetic parameters were determined via computational methods, Section 2.4 does not provide an explanation of the procedure.

- line 185 (Figure 2 caption): As it is the first time when the notation k_{3RR} is used it should be mentioned that it represents the rate coefficient obtained by the relative rate method. Please replace "exemplar plot" with "example of a plot" or "typical/representative plot", which are more widely used alternatives; the same for figures 3 and 5.

- line 205 (Figure 4): Please provide a plot with the entire decays, showing their baselines at later times. I suggest showing the current Figure 4 as an inset of this figure. Fitting the entire experimental decays will show whether they follow a single exponential behaviour as assumed.

- line 206: I suggest delete the word "Displays" and change "each was …" with "each decay was"

- line 207: The typical notation is "k_{obs}", not "B" as the meaning is the observed rate coefficient.

- lines 217-218: Suggest adding "(see below)" after "Systematic errors from unintended radical side-reactions were considered unlikely."

- line 247: Please add "(equation 4)" after "modified Arrhenius expression".

- lines 262-263: The absolute knowledge of [OME] is required by the rate relative method too, not only by the PLP-LIF method.

- line 265: This line states that there are significant uncertainties in reference rate coefficient values. However, according to table 1 the errors are typically 10-20%.

- line 271: An error of about 40% is recommended for k4. Can the authors elaborate on the methodology used for this estimation? The same for the conservative errors of the other rate coefficients.

- line 275: The authors states that "There is a clear trend whereby the larger compounds react with OH faster than those with fewer CH2 groups". However, table 4 shows that while the OH + OME1 reaction is nearly twice as fast as the OH + CH_3OCH_3 reaction, OME3 and OME4 react with OH at similar rates. Can the authors comment on this?

- line 288: The values for CH3OCH3, OME1 and OME2 determined by McGillen's method are needed in order to conclude if this method gives overall better predictions than the SAR of Jenkin et al. (2018). Table 4 shows that the Jenkin et al.'s prediction of k(OH+CH3OCH3) is close to the experimental value. The authors should comment on that. The comparison given in table 4 would benefit if calculations using different SARs would be included.

- line 289: Can the authors explain the principle of the COSMO-RS method? The text states that "the pre-reaction complex formation assumed for all oxygenates by the model". Please explain what pre-reaction complex formation was assumed as a number of publications are cited (Klamt, 1993, 1996, 2018).

- line 309: "Also" at the beginning of the sentence should be replaced by "In addition" or "Additionally"

- lines 314-315: Please see the comment about line 271 above.

- line 320: The sections Atmospheric Implications and Conclusions need to be separated

- line 321: Equation 5 is not given

- line 334: I think VOOC is a typo and it should be VOC

- lines 339-340: Can the authors specify which traditional solvents are being referred to? Please re-phrase "fuel atmospheric oxidation cycles."