Atmospheric
Chemistry
and Physics

Discussions

Interactive comment on "Atmospheric fate of two relevant unsaturated ketoethers: kinetics, products and mechanisms for the reaction of hydroxyl radicals with (E)-4-methoxy-3-buten-2-one and 1-(E)-1-methoxy-2-methyl-1-penten-3-one" *by* **Rodrigo Gastón Gibilisco et al.**

Anonymous Referee #2

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A. General Comments

This manuscript reports the first kinetic and product study for the OH-reaction of two unsaturated ketoethers (UKE) in the presence of NOx at room temperature and atmospheric pressure. A FTIR spectrometer coupled to a smog chamber was used to measure the relative decay of the UKE in the presence of a reference compound. One of

the goals of this work is its contribution to the knowledge of the rate coefficients (kOH) for these reactions. Many atmospheric modellers use structure-activity relationships to derive an unknown OH-rate coefficient, nevertheless as highlighted in this paper, for some reactions with multifunctionalized organic compounds, such as (E)-4-methoxy-3-buten-2-one (TMBO) and 1-(E)-1-methoxy-2-methyl-1-penten-3-one (MMPO), the estimations are far from "reality", i.e. the experimental results. It is true that the kinetic results can also be affected by experimental problems, but in this case the experiments seem to be carefully performed and tests to check for dark reactions and other reactions were carried out to report a reliable kOH. The determined kOH for the titled reactions are reported to be very fast, on the order of 10-10 cm3 molecule-1 s-1, implying that the tropospheric degradation of TMBO and MMPO occurs at a local scale and as a consequence the degradation products can affect the local air quality. In a polluted atmosphere (where NOx are present), the expected gaseous products of the OH+TMBO and OH+MMPO reactions are carbonyl compounds (methyl formate (MF) for both and methyl glyoxal (MG) for TMBO) and peroxynitrates (PAN and peroxypropionyl nitrate (PPN), respectively). MF and MG are the main reaction products of the OH+TMBO reaction with molar yields of ca. 65%, while the molar yield of MF in the OH+MMPO is ca. 40%. PAN and PPN molar yields accounts for 56% and 17%, respectively. In addition and based on the features of the residual IR spectra, a hydroxymethoxy aldehydes are expected to be produced in both reactions, however no quantification was possible because they are not commercially available. The proposed mechanisms are in agreement with the general reaction mechanism for unsaturated carbonyls, where the addition of OH radicals to the double bond is the main reaction pathway. The impact of the title reactions through the primary reaction products on the MG and PAN atmospheric budgets is also discussed. The manuscript is in general well-structured and it is written in such a way that it is easy to follow. However, it lacks of homogeneity in the format of figures and in the nomenclature of the unsaturated ketoethers (UKE, alfa,beta-unsaturated keto ethers, etc) and notatios of kinetic parameters. The kinetic data and the product distribution presented in this work are reliable, as stated above,

and the derived conclusions are relevant to better understand the fate of UKE in the atmosphere.

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.

B. Specific comments/suggestions

Please unify notation: k1 and k2 (abstract), kUKE (equations), kUKE+OH (Table 1), k6 (text) or kOH (text, Table 2), k6/k7 (text) or kUKE/kreference (Table 1), trans- or (E)-, FTIR or FT-IR, etc.

Avoid duplication of spelt acronyms (e.g., TMBO, PAN appear spelt twice in the text).

Revise the format of chemical names (hyphens), chemical formulas, etc.

1) Abstract: An initial sentence of the importance of these compounds is worth including it as well as a concluding remark on the atmospheric implications. In the sentence "The product formation and kinetic data confirm that reaction proceeds mainly via OH-addition...", how can a rate coefficient itself give information on the reaction mechanism? It should be stated that the experiments are performed in the presence of NOx (see below). Finally, it is mentioned that POCP values are estimated and I could not see those estimations in the manuscript. Modify the abstract or include those calculations.

2) Additional information of the investigated UKEs: Please include (if available) emission rates or atmospheric concentrations of TMBO and MMPO in the introduction section. The way of presenting the importance of this investigation needs some refining or reorganization. I would center the introduction on the potential role of TMBO and MMPO in the atmosphere. General information that can be found in Atmospheric Chemistry books has to be reduced or deleted.

3) Experimental part: The authors refer to UKEs and reference compounds as "reac-

tants". Note that the OH radical is also a reactant, so sentences using "reactant" have to be rephrased to be more specific (for example, last paragraph on Page 6). Does NOx come from photolysis of CH3ONO exclusively? If NO was not added, NO and NO2 concentrations are expected to be low (depending on the initial concentration con CH3ONO). What is the NO concentration in the experiments? Can you assume that your results are extrapolated to a clean or a polluted atmosphere? The NO concentration has to be included in the text.

4) Potential interferences in the kinetic data: Impurity levels of the investigated UKEs are 10% for TMBO and 10.5% for MMPO. Did the authors analyze the samples to identify the impurities present? Can the impurities affect the measured rate coefficients, since no purification was made? Were the wall losses and photolysis of TMBO and MMPO and the reference compounds measured? The authors say these losses are negligible. What is the order of magnitude of the first order rate coefficients for these processes?

5) Kinetic results and discussion: On page 8, the authors claim that "at least" two experiment were carried out per reference compound used, while in Table 1 the number of experiments seem to be exactly 2. Please, change it. On the other hand, when using isobutene as reference compound for the TMBO, the first rate constant ratio slightly differs in both experiments. When the error propagation is applied k can hardly lies within the error limits. In Figure 1 and 2, all experiments are plotted together for each reference compound, however then the individual plots are used to derive the rate coefficient ratio. Is this just to show the reproducibility? The rate coefficient ratio could also been obtained from the slope of plots in Fig. 1 and 2. In these plots, a slight negative intercept is shown when isobutene is used as reference compound. Any justification?

6) Product distribution and reaction mechanism: This section starts with a comment on the general mechanism for unsaturated compounds. I think it is not necessary. I would change the title of the section to "Reaction product distribution and mechanism",

since the identification of the gaseous products allows the proposition of the reaction mechanism. Figures 4 and 6 have to be explained a bit more in the text. UV lights seem to be switched on at ca. 250 s and 120 s. Before that time no lights are on, for that reason the concentration of TMBO and MMPO are constant. So, t=0 in the figures is not the reaction time zero. Maybe this can be confusing for a non-expert reader and it would be better to start with t=0 just before the disappearance of UKE and formation of products. In light of the reported molar yields, can you comment on the contribution of each addition sites? For TMBO the sum of molar yields is around 200%, while for MMPO is much lower. Is this only due to the unquantified 2,3-pentanedione or some other reasons?

7) Lifetime estimation: When using indistinctly "lifetime" and "residence time", the authors assume that the UKE removal is described by a first order decay. Is that right? Lifetime refers to the time it takes for an excess amount of the gas in the atmosphere to decay to a fraction 1/e. This is not the same as the mathematical "residence time" (= average time for a trace gas until it exits the atmosphere). In the calculation of the lifetime of TMBO and MMPO, it is implicitly considered that these species are well-mixed in the atmosphere; however they react very fast to be well-mixed. How can it be calculated in a more accurate way? It is conclude that the OH-reaction is the main diurnal degradation pathway for TMBO and MMPO. What would happen if these species are emitted in a marine area? As no measurement of the rate coefficient for the corresponding Cl-reactions, is there any way to estimate the potential contribution of these reaction to the overall removal of TMBO and MMPO?

8) Potential formation of SOAs: In the conclusion section, it is pointed out that MG is a source of secondary organic aerosols. Usually, the formation of aerosols can be evidenced in the IR spectrum by a change in the baseline or the appearance of broad bands at certain wavenumbers. In Figure S1 a slight change in the baseline at wavenumbers between 3400 and 3800 cm-1 is observed. Can this be an indication of SOA formation as MG is one of the major reaction products of the OH+TMBO reaction?

C. Some minor suggested changes:

Page 3, line 17: (SOAs).

Page 3, line 18: "...(UKE) are compounds with high structural complexity..."

Page 3, line 19: "..detected as reaction products of the atmospheric..."

Page 3, line 22-23: "UKEs are also produced during combustion and more specifically in biomass burning..."

Page 4, line 3: "chemistry of unsaturated VOCs..."

Page 4, line 11: Highly oxidized molecules are not used further in the text. Acronym can be deleted.

Page 4, line 12: Remove authors from reference Calvert et al. (2015).

Page 4, line 5: Revise sentence "and reactivity of the troposphere?" What do you mean?

Page 5, line 5: "...information, the gaseous reaction products of reactions (1) and (2)..."

Page 7, Eq. I: Revise subscripts and notation.

Page 8, line 9: "...to remove the excess of acid..."

Page 9, lines 5-6: k is k7. See first comment about notation (choose the one you consider the clearest).

Page 10, line 8: "...the ether group (R-O)..". R-O-R' is an ether, not an ether group.

Page 11, line 7: "...increases the electron density..."

Page 14, line 15: "...of the aldehydic H atom..."

Page 14, line 21: Delete "in the presence of NOx". It is already said in the previous

line.

Page 17, line 6: "Formaldehyde (no comma) could not be..."

Page 17, line 10: "…..this product there, its formation is only an assumption."

Page 17, line 23: "…makes its reactivity toward OH radicals..."

Page 18, lines 18-20: This sentence is hard to understand. Rephrase it, please.

Page 19, line 13: Add a space between Bloss et al. (2005) and "an".

Page 19, line 14: "…0.42 hours (comment: maybe better in minutes) were estimated..."

Page 19, line 22: Avoid the use of contractions.

Page 19, line 23: "…..removal pathway during daytime..."

D. Tables and Figures

Figure 1 and Figure 2 can be merged in one. In Figure 1 one fit of the plot is missing.

Table 1. A missing space between "…-penten-3-one and at". Parenthesis inside the table are not necessary. In Tables 1 and 2, units of k in the heading of the table are in a smaller font. In Table 2, a "+" has to be replaced by "$\pm$" in the experimental k for 4-methyl-3-penten-2-one. Format of the references in the footnote needs revision.

Scheme 1: Even it is obvious when reading, it would be worth indicating in the text that the quantified products appear in the boxes and the identified, but not quantified, products are rounded by a dashed rectangle. To refer the consecutive reactions of the first radical, after OH addition to the double bond, with O2 and afterwards with NO, I suggest to write "1) O2 2) NO" or "+O2, +NO" instead of "O2; NO". And "+O2, -HO2" to form MF. For ease of presentation, radical B1 can be presented once and from it two arrows for the two different degradation routes.

Scheme 2: Pentane-2,3-dione was not able to be quantified. Maybe it can be distin-

guished from the quantified products. Note that "Absorbances" are unitless by definition (- log(I/I0)) where I and I0 is the transmitted light in the presence and absence of absorber, respectively. Please, change legend of y-axis in Figures 3 and 5. In addition, the legend in x-axis in these figures covers part of the axis and it is a bit cut.

E. Supplementary information:

Caption of Figure S1 and S3: "3800 cm-1". In legend of y- and x-axis of Figures S2 and S4, the units of delta[ ] have to be included. Y-axis should start in zero. The format of these plots is not the same as the rest of figures. The legend of x-axis in Figures S1 and S2 should be "Wavenumber (cm-1)" and for y-axis it should be "Absorbance", for consistency with the rest of IR spectra of the manuscript.