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 and1-(E)-1-methoxy-2-methyl-1-penten-3-one"

by

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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 account 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 notations 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.

Authors reply

The authors express their gratitude to anonymous referee #2 for evaluating and reading the paper carefully and providing thoughtful comments. The comments help to improve the revised version of the manuscript. The authors reply for each comment in blue bellow. The article text body of the manuscript has been amended in red with answers and modifications suggested by referee.

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.

Authors reply

The notations have been unified to k_{UKE} when we consider the two compounds studied and k_{TMBO} and k_{MMPO} when is considered one of the compounds.

The notation was unified with the term "*(E)-*" instead of "trans-"

The notation was unified to "FTIR" instead of "FT-IR"

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.

Authors reply

DONE – the text was modified with reviewer suggestions.

Full chemical name of MMPO was unified to (1*E*)-1-methoxy-2-methyl-1-penten-3-one.

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.

Author's reply

The Abstract was modified taking into account referee suggestions.

The text in the manuscript has been modified adding information about NOx. A new sentence has been added as a concluding remark on the atmospheric implications. The mention about POCP estimated values in the abstract has been removed.

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.

Authors reply

To date there is no information reported on emission rates for TMBO and MMPO. Also, their emission sources and occurrence are not fully identified/understood. These compounds are more likely to be expected in the atmosphere as degradation products of furans and unsaturated ethers (promising alternative fuels), emitted during biomass burning or as atmospheric degradation products of the species emitted during this process (i.e. multifunctional oxygenated aromatics compounds).

The introduction has been modified as referee suggested. The sentences as "It is known that the oxidative chemistry of unsaturated VOCs in the troposphere is governed mainly by the reaction with hydroxyl radicals (OH) either by addition to a C-C double bond or by abstraction of hydrogen atoms from the molecule." and "… in urban areas with high concentrations of nitrogen oxides, NOX…" has been removed from introduction.

Modifications were included in the introduction section as suggested by the referee.

3) Experimental part: The authors refer to UKEs and reference compounds as "reactants". 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).

Authors reply

The referee's comment is correct. OH radical is indeed a reactant but the discussion about reactants monitoring and quantifications should exclude OH as there are different approaches/techniques for OH measurements (e.g. CIMS, LIF, FAGE, etc). We modified the text and specify the reactants when we mentioned them. (e.g. replaced "The reactants were monitored …" with "The TMBO, MMPO and reference compounds were monitored ...")

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 of 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.

Authors reply

In the experiments carried out, NO was generated by the CH3ONO photolysis. There has been added ~ 6 ppmv CH3ONO which will ensure enough OH radicals in the system without supplementary NO addition. However, NO has been present in the reaction mixture from CH3ONO photolysis but in a steady state concentration under detection limit of FTIR instrument (DL(NO) = 50 ppbv). NO has quickly reacted with hydrogen peroxy radicals to form OH radicals in the system. NO_2 has been subtracted from the spectra, his concentration reaching few ppmv since more CH3ONO photolysed. We intend to keep NO concentration low and explore the reaction at middle to low NOx level. There is expected in the presence of NO that peroxy radicals formed during the reaction would lead mainly to 1,2-hydroxyalkoxy radicals formation. When NOx are very low, the peroxy radicals will undergo cross- and self-peroxy reactions which may lead to the formation of multifunctional products with carbonyl, hydroxyl and ester functionalities beside the 1,2-hydroxyalkoxy radicals formed.

We have added the following text in the article:

Page 7 line 11 “Methyl nitrite (6 ppmv) photolysis has been used for OH radical formation. No additional NO has been introduced in the reaction chamber.”

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 analyse the samples to identify the impurities present? Can the impurities affect the measured rate coefficients, since no purification was made?

Authors reply

There was no identification done for the impurities as they are not expected interferences on the measured rate coefficients. However, we performed several freeze-pump-thaw cycles using liquid nitrogen before each set of experiments. In order to avoid the possible following of the IR features attributable to other compounds than main organics investigated in this study (TMBO and MMPO) we have subtracted each ketoether for three different IR bands which are representative for the reference spectrum. This information are stated in the article body. Expected different reactivity if one of these infrared absorption bands will lead to different decay easily identifiable in the subtraction procedure.

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?

Authors reply

Wall loss and photolysis were studied as mentioned in the Experimental section of the article. These represent a negligible contribution of (1-5)x10^{-5} s^{-1} in the presence of OH scavenger (CO) to avoid possible secondary reaction due to the OH contribution from the walls of the chamber.

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 be 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?

Authors reply

Indeed, there were only two kinetic experiments evaluated for each organic compound. We evaluated one more kinetic experiment for the reaction of TMBO with OH radicals using isobutene as reference compound. The rate coefficient value falls in between other existing two values. The slope also changed slightly and even if previously the negative intercept was very small, now is even smaller. We did not force our experimental results to the origin and prefer to keep it as they are, to clearly show that straight line of the slope gives k(UKE)/k(reference) ratio with near zero intercept.

There is indeed a way to obtain rate coefficient ratio from the slope in figure 1 and 2 but we present the results in such manner to prove the linearity of multiple experimental data and also to highlight the values resulted from different experiments.

The addition of new rate coefficient value in the table 1 and the text corrections resulted from this new experimental value of rate coefficient are included in the article body.

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.

Authors reply

The section title was modified as the referee suggests. In addition, the introduction in this section has been removed.

Figures 4 and 6 have to be explained a bit more in the text.

Authors reply

There has been added a text at page 14 line 11:

"There is also easily to observe the constant concentrations of TMBO prior to reaction begin. This is accountable for homogeneity of the reaction mixture. Five spectra have been collected before switching on the light which corresponds to 240 s. No decay of TMBO is present in this time suggesting missing dark interference in the reaction system. From Fig. 4 could be observed a conversion of up to 80% of TMBO in 10 min of reaction time."

We added a text in the article body at page 17 line 2

"MMPO concentration is constant during 5 spectra recorded in dark which consist of 120 s mixing time. Perfect homogeneity and no dark interferences could be observed. From Fig. 6 could be observed a total conversion of MMPO in 10 min of reaction time."

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.

Authors reply

Indeed, the reaction has been initiated after a collection of 5 spectra in dark to prove that reaction mixture is homogeneous and no wall losses or dark reaction occurs. This is in agreement with very low wall deposition occurring in the reaction system. There is an obvious reaction time zero in the Figure 4 and 6 when the TMBO/MMPO concentrations decay.

However, to express referee suggestion the text has been amended at page 6 with the addition of:

"Typically, up to 128 interferograms were co-added per spectrum over a period of approximately 40 s and 15-20 such spectra were collected. Prior to the reaction initiated by OH radicals, 5 spectra have been collected in dark to check the homogeneity and unexpected dark decay of the compounds under investigations (e.g. wall losses; dark reactions)."

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?

Authors reply

The article has discussed in detail the reactions mechanisms. However, there was not possible to qualitatively extend the contribution of each addition sites. There are few reasons which do not allow us to discuss quantitatively in detail the contribution of each addition site:

- There are similar products which are formed by addition of OH on different sites and could not allow us to attribute exclusively the reaction products to a specific addition site;
- Some products as PAN it is formed not exclusively as primary product but could also be a secondary product from further oxidation of methyl glyoxal;
- The molar yields are different indeed for the reaction of OH radicals with TMBO and MMPO, respectively. However, instead of the sum of molar yields we assume the carbon balance which may have better importance in terms of quantitative judgement. The carbon balance is solved around 80-85% for TMBO + OH reaction while up to 20 % for MMPO reaction could be quantified. As referee stated there are coproducts as 2,3-pentanedione which are not identified and could be responsible for missing carbon balance.

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 life- time 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 concluded 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?

Authors reply

Actually the lifetime is calculated as $\tau_x=1/k_{ox}[Ox]$ where [Ox] is the typical atmospheric concentration of the oxidant, in our case OH radicals. This is a decay calculated for a second order reaction. There is difficult to calculate tropospheric lifetime of one species with respect to one oxidant without assuming a well mixing in the atmosphere. Lifetime is a more intuitive meaningful parameter to help understand a reaction rate coefficient. For more accurate lifetime calculation should be considered the processes which could lead to removal of organic species in the troposphere, reaction with ozone, hydroxyl and nitrate radical, chlorine atoms, photolysis, dry and wet deposition, etc., to mention only few of them.

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?

Authors reply

Indeed, there are many studies providing information for SOA formation from methylglyoxal. As reviewer stated, could be an evidence for SOA formation the appearance of broad band at larger wavenumbers in

IR spectra. However, we consider improper to attribute such band to SOA formation from methylglyoxal as there could be other precursor for SOA (e.g. TMBO itself or it's oxidation products). In our experiments we have not used a Scanning Mobility Particle Sizer or other proper instruments to evidence the SOA formation and we cannot explore further this assumption.

C. Some minor suggested changes:

Page 3, line 17: (SOAs).

- SOA was changed for SOAs

Page 3, line 18: "... (UKE) are compounds with high structural complexity. . . Page 3, line 19: "..detected as reaction products of the atmospheric. . ."

- DONE

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

- DONE

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

- DONE

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

- DONE

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

- DONE

Page 4, line 15: Revise sentence "and reactivity of the troposphere?" What do you mean?

- REVISED

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

- DONE

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

- DONE

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

- DONE

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

- DONE ($k_{propene}$ and $k_{isobutene}$)

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

- DONE

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

- DONE

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

- DONE

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

- DONE

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

- DONE

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

- DONE

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

- DONE

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

- DONE, Rephrased.

"The infrared spectrum in Fig. S3 presents one main absorption feature that could be attributed to the O-H stretching of1-hydroxy-1-methoxypropan-2-one produced by the more stable tertiary radical (A_2)."

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

- DONE

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

- Revised. We prefer to report lifetimes in hours for ozone and OH radicals for consistency.

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

- DONE

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

- DONE

D. Tables and Figures

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

Authors reply

We tried to modified figure 1 and 2 and merge them in one figure. The result was not a better figure representing the data since both of the plots have same scale on y axis. The scale up for one of the compounds do not satisfied also. We prefer to keep both figures and to have separate tracks along papers for the results coming from each of the investigated compounds.

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 " " in the experimental k for 4-methyl-3-penten-2-one. Format of the references in the footnote needs revision.

- DONE

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.

Authors reply

As referee advises, we added the following clarification in the legend of scheme 1 and 2: Quantified products appear in the boxes and the identified products are rounded by a dashed rectangle.

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

- DONE. Penten-2,3-dione was placed in a dashed rectangle following the referee's recommendation.
- DONE. legend of y-axis in Figures 3 and 5 was changed.

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.

- Caption of Figure S1 and S3: "3800 cm-1". DONE
- DONE: Legend of y- and x-axis of Figures S2 and S4 was changed.
- Y-axis should start in zero. DONE
- legend of x-axis in Figures S1 and S2 should be "Wavenumber (cm-1). And for y-axis it should be "Absorbance". DONE.