1   **Atmospheric fate of two relevant unsaturated ketoethers: kinetics, products and**
2   **mechanisms for the reaction of hydroxyl radicals with (*E*)-4-methoxy-3-buten-2-**
3   **one and (1*E*)-1-methoxy-2-methyl-1-penten-3-one.**

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1 **Abstract**

2 The kinetics of the gas-phase reactions of hydroxyl radicals with two unsaturated

3 ~~methoxy-ketones~~ ketoethers (UKE) at (298 ± 3) K and 1 atm of synthetic air have been

4 studied for the first time using the relative rate technique in an environmental reaction

5 chamber by in situ FTIR spectrometry. The rate coefficients obtained using propene and

6 isobutene as reference compounds were (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}) as follows:

7 k_{TMBO}(OH + (*E*)-4-methoxy-3-buten-2-one) = (1.41 ± 0.11), and k_{MMPO}(OH + (1*E*)-1-

8 methoxy-2-methyl-1-penten-3-one) = (3.34 ± 0.43). In addition, quantification of the main

9 oxidation products in the presence of NO$_x$ has been performed and degradation

10 mechanisms for these reactions were developed. ~~The formation products and kinetic data~~

11 ~~confirm that the reactions proceed mainly via an addition of the OH radical to the double~~

12 ~~bond.Gas phase products, identified and quantified from these reactions, are carbonyls~~

13 ~~like~~. Methyl formate, methyl glyoxal, PAN and PPN were identified as main reaction

14 products and quantified for both reactions. The results of the present study provide new

15 insights regarding the contribution of these multifunctional VOCs in the generation of

16 secondary organic aerosols (SOAs) and long-lived nitrogen containing compounds in the

17 atmosphere. Atmospheric lifetimes and ~~the ozone formation potentialhave been estimated~~

18 ~~and possible atmospheric~~ implications are discussed in light of the obtained results.

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1. Introduction

Oxygenated volatile organic compounds (OVOCs) are ubiquitous atmospheric constituents of anthropogenic and natural origin. From those OVOCs, carbonyls have both direct and indirect sources, as a result of biogenic and anthropogenic activities, and because they are formed during chemical degradation processes, which occur in the atmosphere. Unsaturated carbonyls present high reactivity and are easily decomposed throughout chemical reactions into various OVOCs products.

Ketones are one of the dominant groups of carbonyls found in the lower troposphere. They can be emitted into the atmosphere by anthropogenic activities from industry, combustion engine vehicle exhaust and in a large extent are formed as reaction products of other VOCs in the troposphere (Calvert et al., 2011; Jiménez et al., 2014; Mellouki et al., 2015).

More complex unsaturated carbonyls, namely the α, β–unsaturated ketones and α, β-unsaturated ethers are either emitted by plants or are produced as a result of atmospheric oxidation of conjugated dienes (Lv et al., 2018; Mellouki et al., 2015; Zhou et al., 2006). These compounds have been considered as precursors for SOAs secondary organic aerosols (SOAs)(Calvert et al., 2011).

α, β-unsaturated ketoethers (UKE) are compounds with high structural complexity found in the atmosphere. They were detected as reaction products of the atmospheric degradation of furans and unsaturated ethers, compounds, which received substantial interest in the last decade since they are considered promising alternative fuels (Cilek et al., 2011; Li et al., 2018; Villanueva et al., 2009; Zhou et al., 2006). UKEs are also produced during combustion and more specifically in biomass burning (Hatch et al.,
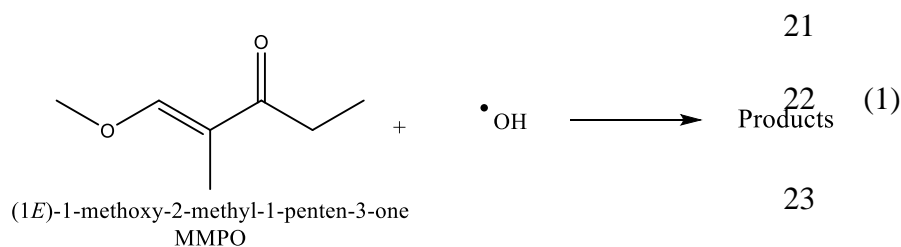
1   2015). They are also of great interest in the pharmaceutical industry since they are often

2   used as precursors and/or intermediates in the production of new anticancer drugs (Gøgsig

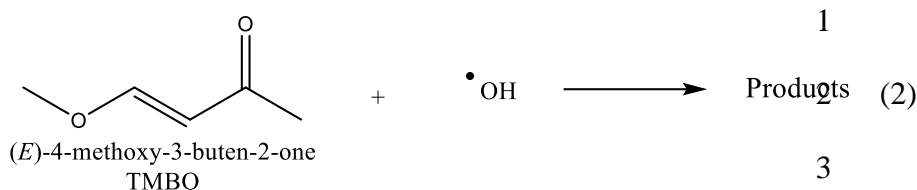3   et al., 2012; Kumar et al., 2016).

4   ~~It is known that the oxidative chemistry of unsaturated VOCs in the troposphere is~~

5   ~~governed mainly by the reaction with hydroxyl radicals (OH) either by addition to a C-C~~

6   ~~double bond or by abstraction of hydrogen atoms from the molecule.~~ α, β -unsaturated

7   ketoethers are a special type of olefins, with an electron rich π system, which makes them

8   more susceptible to rapid oxidation by addition of the OH radical to the double bond.

9   Secondary pollutants, which are formed in such a reaction sequence, could be even more

10   harmful than primary pollutants emitted into the atmosphere. Examples of such secondary

11   harmful pollutants are ~~ozone~~ organic peroxynitrates, ~~in urban areas with high~~

12   ~~concentrations of nitrogen oxides, NO$_x$,~~ highly oxidized molecules and secondary organic

13   aerosols (Atkinson, 2000; Calvert et al., 2015).

14   Accordingly, it is important to study in detail how the OH radical initiated oxidation of

15   these compounds can affect the chemical composition and reactivity of the troposphere

16   and, furthermore, the impact of the secondary pollutants formed during their gas phase

17   chemical degradation.

18   In the present work the OH radical initiated reactions of (1*E*)-1-methoxy-2-methyl-1-

19   penten-3-one and (*E*)-4-methoxy-3-buten-2-one have been investigated:

20

21

(1*E*)-1-methoxy-2-methyl-1-penten-3-one
MMPO

22   (1)

Products

23

4

$$\text{(E)-4-methoxy-3-buten-2-one} \quad + \quad {}^{\bullet}OH \quad \longrightarrow \quad \text{Products} \quad (2)$$

(E)-4-methoxy-3-buten-2-one
TMBO

1
2
3

In addition to the kinetic information, the gaseous reaction products of reactions (1) and (2) have been quantified and reaction mechanisms have been derived for both compounds. The present study represents the first experimental determination of the rate coefficients (k_{TMBO} and k_{MMPO}) and the reaction products formed from the gas phase reactions in the presence of NO_x. The obtained results could be used to generate more complete atmospheric chemical degradation mechanisms, i.e. the master chemical mechanism, which is necessary for a better estimation of the contribution of such compounds to photooxidant and SOAs formation.

2. Experimental

All experiments were performed in a 1080 L quartz-glass reaction chamber at (298 ± 3) K and a total pressure of (760 ± 10) Torr of synthetic air. A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10^{-3} Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40W: 290–480 nm, λ_{max}= 360 nm) and 32 low-pressure mercury vapor lamps (Philips TUV 40W; λ_{max} = 254 nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive in situ long path infrared absorption monitoring of reactants and products in the spectral range 4000 – 700 cm^{-1}. The White system was

1   operated at 82 traverses, giving a total optical path length of (484.7 ± 0.8) m. Infrared

2   spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FTIR

3   spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT)

4   detector.

5   OH radicals were generated by photolysis of CH_3ONO/air mixtures at 360 nm using

6   fluorescent lamps:

7   CH_3ONO +   hν   → CH_3O +   NO   (3)

8   CH_3O + O_2 → CH_2O + HO_2 (4)

9   HO_2 +   NO   →   OH   + NO_2 (5)
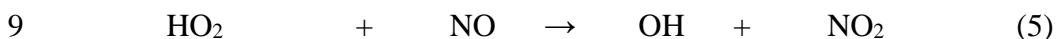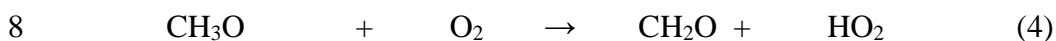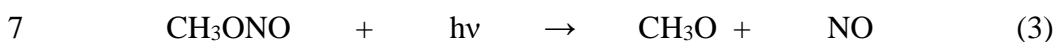
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11   Quantification of TMBO and MMPO ~~reactants~~ and gas phase products was performed by

12   comparison with calibrated reference spectra contained in the IR spectral data bases of

13   the Wuppertal laboratory.

14   To investigate the mechanism of the OH-radical initiated oxidation of the α,

15   β−unsaturated ketoethers, the mixtures of the compound, CH_3ONO and air were

16   irradiated for periods of 10-30 minutes during which infrared spectra were recorded with

17   the FTIR spectrometer. Typically, up to 128 interferograms were co-added per spectrum

18   over a period of approximately 40 s and 15-20 such spectra were collected. Prior to the

19   reaction initiated by OH radicals, 5 spectra have been collected in dark to check the

20   homogeneity and unexpected dark decay of the compounds under investigations (e.g. wall

21   losses; dark reactions).

22   The TMBO, MMPO and reference compounds ~~reactants~~ were monitored at the following

23   infrared absorption frequencies (in cm^{-1}): TMBO at 958, 1253 and 3020, MMPO at 1245,

24   1653 and 2850, isobutene at 3085 and propene at 3091.

Rate coefficients for the reactions of OH radicals with MMPO and TMBO were determined by comparing their decay rate with that of the corresponding decay of the two reference compounds, isobutene and propene:

OH + UKE → Products (6)

OH + reference → Products (7)
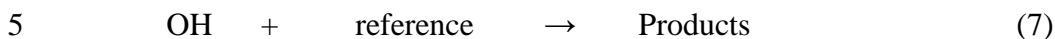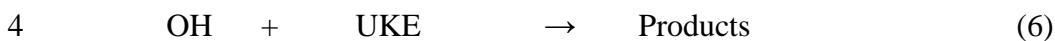
Provided that the reference compound and ~~the reactants~~ TMBO and MMPO are lost only by reactions (6) and (7), it can be shown that:

$$ln\left\{\frac{[UKE]0}{[UKE]t}\right\} = \frac{k_{UKE}}{k_{reference}} ln\left\{\frac{[reference]0}{[reference]t}\right\} \qquad (I)$$

where, $[UKE]_0$, $[reference]_0$, $[UKE]_t$ and $[reference]_t$ are the concentrations of the α, β-unsaturated ketoethers and the reference compound at times t=0 and t, respectively, and k_{UKE} and $k_{reference}$ are the rate coefficients of reactions (6) and (7), respectively.

The initial mixing ratios of the reactants in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K and 1 atm) were TMBO (1-3), MMPO (2-4), isobutene (3-5) and propene (3-5). Methyl nitrite (6 ppmv) photolysis has been used for OH radical formation. No additional NO has been introduced in the reaction chamber.

Possible additional losses due to interferences and/or interactions with the reactor walls could be neglected or corrected. To verify this assumption, mixtures of CH_3ONO/air with the α, β–unsaturated ketoethers and the reference compound were prepared and allowed to stand in the dark for two hours. In all cases, the decay of the organic species in the presence of the OH radical precursor and in the absence of UV light was negligible. Furthermore, to test for a possible photolysis of the compounds, the reactant mixtures without OH radical precursor were irradiated for 30 minutes, using all lamps surrounding the chamber. No significant photolysis of any of the reactants was observed and no additional decay has been monitored due to a possible reaction with interfering radicals.

3. Materials

1   The following chemicals, with purities as stated by the supplier, were used without further

2   purification: synthetic air (Air Liquide, 99.999%), propene (Messer Schweiz AG, 99.5%),

3   isobutene (Messer, 99%), (E)-4-methoxy-3-buten-2-one technical grade (Aldrich, 90%)

4   and (1E)-1-methoxy-2-methyl-1-penten-3-one (Aldrich, > 89.5 %). Methyl nitrite was

5   prepared by the drop-wise addition of 50% sulfuric acid to a saturated solution of sodium

6   nitrite in water and methanol (Taylor et al., 1980). The products were carried by a stream

7   of nitrogen gas through a saturated solution of sodium hydroxide followed by calcium

8   chloride, to remove the excess of acid, water and methanol, respectively. Methyl nitrite

9   was collected and stored at 193 K in dry ice.

10

11   **4. Results and Discussion**

12   *4.1 Rate coefficients for the reaction with OH radicals*

13   Plots of the kinetic data obtained from the experiments of the reaction of OH radicals with

14   TMBO and MMPO using two different reference compounds are shown in Fig. 1 and 2,

15   respectively. At least two experiments have been performed for each reference compound

16   and linear plots were obtained in all cases. For better representation, data for all

17   experiments have been plotted against both references. Rate coefficient ratio

18    $k_{UKE}/k_{Reference}(\pm 2\sigma)$ obtained by combining the experiments results in Fig. 1 and Fig. 2

19   were: for TMBO, $k_{TMBO}/k_{isobutene}= (2.56 \pm 0.13)$ and $k_{TMBO}/k_{propene}= (5.08 \pm 0.16)$. For

20   MMPO, $k_{MMPO}/k_{isobutene}= (6.40 \pm 0.31)$ and $k_{MMPO}/k_{propene}= (11.64 \pm 0.82)$.

21   The linearity of the plots with near-zero intercepts confirms that no interferences have

22   affected the rate coefficient determination. Additionally, the very good agreement of the

23   rate coefficients using the two reference compounds proved the correctness of the

24   investigations.

1   Table 1 lists the values of the rate coefficient ratio $k_{UKE}/k_{Reference}$ obtained in the

2   individual experiments at 298 K and 1 atm for each α, β−unsaturated ketoether. The errors

3   given for the $k_{UKE}/k_{reference}$ ratios are the 2σ statistical errors from the linear regression.

4   The rate coefficients k_{UKE} for reactions 1 and 2 were calculated using the recommended

5   values $k_{propene}$ = $(2.90 \pm 0.10) \times 10^{-11} cm^3$ molecule^{-1} s^1(Atkinson et al., 2006) (OH +

6   propene) and $k_{isobutene}$= $(5.23 \pm 0.24) \times 10^{-11} cm^3$ molecule^{-1} s^1 (OH + isobutene) (Atkinson

7   and Aschmann, 1984).

8   In addition, Table 1 shows the rate coefficients for individual experiments of each

9   reference compound employed in this study as well as the final quoted rate coefficients

10   for the reactions of OH with UKE compounds as an average from all experimental values

11   obtained for the corresponding compound. The error quoted for those final UKE rate

12   coefficients are obtained by using an error propagation approach.

13   To the best of our knowledge rate coefficients for the reactions of OH radicals with (*E*)-

14   4-methoxy-3-buten-2-one and (1*E*)-1-methoxy-2-methyl-1-penten-3-one have not been

15   reported previously in the literature.

16   *4.1.1Reactivity trends*

17   There is a general lack of studies on the reactivity of poly-substituted oxygenated

18   unsaturated compounds, such as the unsaturated ketoethers studied in this work.

19   Only the reactivity of (*E*)-4-methoxy-3-buten-2-one towards ozone was investigated by

20   Grosjean and Grosjean (1999) who reported a rate coefficient k_{O3} of 1.3×10^{-16} cm^3

21   molecule^{-1} s^{-1} (Grosjean and Grosjean, 1999). The authors identified and quantified two

22   main products from the ozonolysis of (*E*)-4-methoxy-3-buten-2-one, namely

23   methylglyoxal $(31.2 \pm 1.9\%)$ and methyl formate $(> 15.7\%)$. These two species are

24   potential products of the OH-initiated oxidation of (*E*)-4-methoxy-3-buten-2-one as well.

It is well known that OH-initiated atmospheric degradation of unsaturated VOCs proceeds mainly through the addition of the OH radical to the double bond (Calvert et al., 2015). Some studies also suggested that the presence of oxygenated functional groups in unsaturated VOCs leads to an increase of k_{OH}, perhaps due to the possibility of hydrogen bonding transition complexes stabilizing the transition states involved in these reactions (Blanco et al., 2012; Gaona-Colmán et al., 2017; Mellouki et al., 2003).

Considering the findings mentioned above, it is interesting to analyze the possible effect on k_{OH} when the ether group (R-O) is directly attached to the C=C bond of the unsaturated ketones and the presence of different substituents in the molecule. For this purpose, Table 2 present two basic structures of unsaturated ketones (I and II) and the OH rate coefficients for different unsaturated ketones obtained experimentally and/or estimated using a SAR method (US EPA. Estimation Programs Interface Suite^{TM} for Microsoft® Windows, 2018).

Starting with the less substituted compound, when the substituents R_1, R_2, and R_3 are all hydrogen atoms (3-buten-2-one), a value of $k_{OH}= 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was experimentally observed (Holloway et al., 2005). Successive replacement of H atoms with methyl groups, for the positions R_2(3-penten2-one) and R_3(4-methyl-3-penten2-one), leads to a considerable increment on the reactivity as shown in Table 2 (Blanco et al., 2012; Gaona-Colmán et al., 2017). Considering the experimental errors of the measurements it is reasonable to conclude that the addition of each methyl group leads to an increase of approximately 4×10^{-11} cm^3 molecule^{-1} s^{-1} in the rate coefficient relative to those of basic structure I.

The methyl group added in positions R_2 and R_3 would stabilize the radical formed after the addition of the OH at the C_α for two different effects: (*i*) the positive inductive effect

1   (I+) by the methyl group, which stabilizes the positive charge in the C_β atom and (*ii*) the

2   stabilization due to the hyperconjugation of the carbocation formed at the C_β.

3   Comparing the experimental value $k_{TMBO}= 1.41\times 10^{-10}cm^3$ molecule$^{-1}s^{-1}$ obtained in the

4   present work for (*E*)-4-methoxy-3-buten-2-one with its methylated analogue 3-penten-2-

5   one, one can easily realize the increase by a factor of 2 in the rate coefficient when the *R₃*

6   substituent is a methoxy group. This can be explained by the oxygen's lone pair of

7   electrons, which delocalizes and increases the electron density within the C=C bond. On

8   the other hand, the methoxy group is electron withdrawing through a negative inductive

9   effect (I-) via the σ bonds. However, the mesomeric effect is stronger than the inductive

10   one, which is reflected by an increase of the (*E*)-4-methoxy-3-buten-2-one + OH reaction

11   rate coefficient compared to its mono and bi-methylated analogues that can stabilize the

12   corresponding radical structures only by the inductive effect and hyperconjugation, but

13   not by a mesomeric effect.

14   A similar assessment can be performed considering the basic structure (II). The increasing

15   trend in the reactivity towards OH radicals is quite similar when methyl groups replace H

16   atoms in the structure of 1-pentene-3-one. The experimental rate coefficient $k_{MMPO}=3.34\times$

17   $10^{-10}cm^3$ molecule^{-1} s^{-1} obtained in the present work for the reaction of OH radicals with

18   (1*E*)-1-methoxy-2-methyl-1-penten-3-one is quite high but considering the approximate

19   individual contribution of the substituents on the C=C bond as it was assumed previously

20   for the basic structure (I) reflects entirely the system reactivity.

21

22

23   *4.1.2Structure-activity relationship (SAR) calculations*

1   In the present work, the AOPWIN software included in the EpiSuite 4.1 was used to

2   estimate the rate coefficients of the structures listed in Table 2(US EPA. Estimation

3   Programs Interface Suite[TM] for Microsoft® Windows, 2018).

4   It is worth mentioning that calculated k_{OH} with AOPWIN fit quite well with the

5   experimental values of the simplest structures of the unsaturated ketones shown in Table

6   2, namely 3-buten-2-one and 1-penten-3-one. However, when the hydrogen atoms are

7   replaced by methyl groups in the C=C system for structures (I) and (II), differences

8   between experimental values and those estimated using SAR method become evident by

9   a factor of 1.2 and 1.5, respectively. For structure (I) with two methyl substituents (4-

10   methyl-3-penten-2-one) the difference remains approximately the same (factor 1.3).

11   Comparing the kinetic results obtained in this work for MMPO and TMBO with those

12   predicted by AOPWIN, the differences become substantially larger. In Table 2 it can be

13   seen that for k_{TMBO} the results differ by a factor of two and for k_{MMPO} by a factor of three.

14   This fact highlights the limitations of the AOPWIN-SAR method for predicting the

15   specific site for the addition of the OH radical to each carbon atom of an asymmetrical

16   alkene, ignoring a possible stabilization of the reaction intermediate. The stabilization

17   could generate transition states involving the formation of hydrogen bonding complexes

18   between the OH radical and the oxygenated substituents as it was suggested in previous

19   publications (Blanco et al., 2012; Gaona-Colmán et al., 2017; Mellouki et al., 2003).

20   In conclusion, the AOPWIN-SAR estimation of reaction rate coefficients is a useful tool

21   for simple molecules. However, the OH rate coefficients of the unsaturated ketoethers

22   reported in this work showed significant discrepancies compared with the predicted ones.

23   Probably, as suggested recently by Vereecken et al. (2018) it is not clear if the SAR

24   method can be easily expanded to multifunctional compounds, especially given the small

1 training set available from which to derive cross-substituent parameters or base rate

2 coefficients (Vereecken et al., 2018).

3

4 *4.2 Reaction product distribution and mechanism*

5 ~~It is well known that reactions ofunsaturated compounds will proceed mainly by initial~~

6 ~~addition of OH to the C=C bond leading to the formation of two ß-hydroxyalkyl radicals,~~

7 ~~which in turn rapidly react with oxygen forming β-hydroxyalkyl peroxy~~

8 ~~radicals(Atkinson, 2007).Besides the addition pathway, H atom abstraction also can~~

9 ~~occur in the reaction system. However, based on the structure reactivity relationships~~

10 ~~presentedin table 2, this is expected to contribute no more than 2% to the overall~~

11 ~~reactivity.~~

12 ~~In the presence of NO and O₂, the peroxy radicals formed in the first step of the reaction~~

13 ~~could react further to form mainly 1,2 hydroxyalkoxy radicals. These radicals, oncebeing~~

14 ~~formed, can decompose and/or isomerize. Based on experimental evidence and identified~~

15 ~~reaction products performed in the present study, the potential reactions of the alkoxy~~

16 ~~radicals and the reaction sequence described above are shown in the generalized Schemes~~

17 ~~1 and 2 for each compound studied in the presentwork.~~

18

19 *4.2.1(E)-4-methoxy-3-buten-2-one+ OH radicals*

20 Figure 3 shows an IR spectrum recorded before (trace A) UV irradiation applied for a

21 mixture of ~~(E) 4 methoxy 3 buten 2 one~~ TMBO and CH_3ONO in air. Trace B shows the

22 spectrum recorded after 10 min of UV irradiation of the reaction mixture. Trace D exhibits

23 the product spectrum after subtraction of not reacted TMBO (from the reference spectra

24 trace C), NO, NO_2, CH_3ONO and H_2O. Traces E, F and G show reference spectra of

25 methyl formate, peroxyacetyl nitrate (PAN) and methyl glyoxal, respectively. Trace H

exhibits the residual product spectrum that is obtained after subtraction of known products from the product spectrum in trace D. The absorption from CO_2 has been removed in all traces for clarity since the band was saturated and no information could be obtained from it accordingly. Methyl formate, peroxyacetyl nitrate, and methyl glyoxal were readily identifiable as reaction products. Concentration−time profiles of TMBO and the identified products, methyl formate, PAN, and methyl glyoxal are shown in Fig.4. The concentration−time distribution supports that methyl formate, methyl glyoxal and PAN are primary reaction products. 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.

Depending on the side addition of the OH radical leading to the C_α or C_β, hydroxyalkoxy radicals, A_1 and B_1 will be formed respectively (Scheme 1). Decomposition of the A_1 radical will lead to the formation of methyl formate and methyl glyoxal as primary products. On the other hand, C_3-C_4 bond scission in the B_1 radical will lead to the formation of methyl formate and methyl glyoxal. Additionally, the radical B_1 could decompose through a C_2-C_3 scission generating 2-hydroxy-2-methoxyacetaldehyde and the acetylradical. This route would, beside the formation of 2-hydroxy-2-methoxyacetaldehyde, be responsible for the primary generation of PAN through further reaction of the acetyl radical with O_2/NO_2. In addition, PAN is known to be formed due to the oxidation of methyl glyoxal (Fischer et al., 2014). The reaction of OH radicals with methyl glyoxal occurs exclusively by abstraction of the aldehydic H atom to form $CH_3C(O)CO$ radicals, which have a very short lifetime, dissociating to form CH_3CO +

1 CO (Green et al., 1990). Finally, it is expected that acetyl radicals react, in the presence

2 of O_2, with NO_2 to form PAN (Fischer et al., 2014). Acetyl radicals are of particular

3 importance in atmospheric chemistry as they are key contributors to important pollutants

4 in the atmosphere. PAN (peroxyacetyl nitrate), in high NOx environments, is formed

5 exclusively from acetyl peroxy radicals. However, in low NOx environments, acetyl

6 radicals, in the presence of oxygen, generates acetyl peroxy radicals, which further reacts

7 with HO_2 radicals producing $CH_3C(O)OOH$, $CH_3C(O)OH$, O_3 and OH radicals. These

8 secondary products could have a high impact on the atmospheric chemistry on the global

9 scale (Winiberg et al., 2016).

10 After subtraction of the identified products, the most prominent absorption feature in the

11 IR residual spectra (Fig. 3 trace H) is a carbonyl band at 1730 cm^{-1}, which is more

12 characteristic for an aldehydic than a ketone absorption. This feature suggests the

13 formation of 2-hydroxy-2-methoxyacetaldehyde, which is unfortunately not

14 commercially available. Therefore, direct identification in the residual product spectrum

15 is not possible by using a recorded IR reference spectrum.

16 Carbonyl absorptions in the IR spectra are present in the 1600-1800 cm^{-1} range and 2-

17 hydroxy-2-methoxyacetaldehyde identification in this region of the IR spectrum is not

18 possible. Beside the parent compound, which is presenting features in this carbonyl

19 absorption specific region, many other products formed during the reaction have

20 absorptions in this range. All the products formed in the reaction system have a specific

21 absorption in the carbonyl range (methylglyoxal, methyl formate, PAN and 2-hydroxy-

22 2-methoxyacetaldehyde). However, the later one must have an important pronounced

23 peak in the O-H absorption area; therefore, we may assume the unique absorption at 3550

24 cm^{-1} as being attributed to the O-H absorption of 2-hydroxy-2-methoxyacetaldehyde (SI

1 Fig.S1). This is a strong indication of the 2-hydroxy-2-methoxyacetaldehyde formation,

2 which is in agreement with the proposed mechanism in Scheme 1.

3 Plots of the concentrations of the carbonyls formed vs reacted TMBO give molar

4 formation yields of (65 ± 12) % for methyl formate, (56 ± 16) % for PAN and (69 ± 14)

5 % for methyl glyoxal. The yields have been corrected for secondary reactions with OH

6 radicals as well as for the photolysis and wall deposition processes where necessary

7 (Tuazon et al., 1986). Exemplary plots for the product formation yields are shown in the

8 SI Fig. S2.

9

10 *4.2.2(1E)-1-methoxy-2-methyl-1-penten-3-one+ OH radicals*

11 Figure 5, trace A shows the infrared spectrum for an initial reaction mixture of a ~~(E)-1-~~

12 ~~methoxy-2-methyl-1-penten-3-one~~MMPO/CH_3ONO/air mixture prior to irradiation;

13 trace B exhibits the spectrum recorded after 10 min of irradiation and hence the occurring

14 reaction; trace C shows a reference spectrum of MMPO recorded in a separate experiment

15 in air at 1 atm and 298 K; trace D shows the product spectrum recorded after 10 min of

16 irradiation and after subtraction of not reacted MMPO as well as subtraction of CH_3ONO,

17 NO, H_2O and NO_2 absorption bands; trace E shows a reference spectrum of methyl

18 formate; trace F a reference spectrum of 2,3-pentanedione and trace G a reference

19 spectrum of peroxypropionyl nitrate (PPN). Trace H shows the residual product spectrum

20 after subtraction of the identified reaction products in trace D.

21 The absorption from CO_2 has been removed in all traces for clarity since the band was

22 saturated and no additional information could be obtained, accordingly. Methyl formate

23 and peroxypropionyl nitrate were identified as reaction products. Concentration−time

24 profiles of MMPO, methyl formate and peroxypropionyl nitrate are shown in Fig.6.

25 Figure 6 supports that methyl formate and peroxypropionyl nitrate are primary reaction

products. 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.

After the addition of the OH radical to the double bond of MMPO and subsequent addition of an oxygen molecule followed by reaction with NO, two different hydroxyalkoxy radicals, A_2 and B_2 (scheme 2) could be generated. Unlike for TMBO, the reaction of MMPO with OH radicals at the C_β position could lead to the formation of the more stable tertiary radical A_2 due to the presence of a methyl group in the α position to the carbonyl group.

Scheme 2 shows that both addition channels would lead to the formation of methyl formate and 2,3-pentanedione if the hydroxyalkoxy radical would follow dissociation of bond I in the A_2 radical intermediate and the dissociation of bond II in the B_2 radical intermediate.

The hydroxyalkoxy radical B_2 could lead, beside the formation of 2,3-pentanedione and methyl formate by following scission of bond II, to the formation of 2-hydroxy-2-methyl-3-oxopentanal as product and formaldehyde as reaction co-product as a result of the decomposition of the B2 radical from scission of bond I. Formaldehyde could not be identified as reaction product since it is formed from CH_3ONO photolysis and is present in the reaction spectra. 2-hydroxy-2-methyl-3-oxopentanal is not commercially available and in the absence of a mass spectrometry technique, which could at least identify the mass of this product there, its formation is only an assumption.

Decomposition channel for the A2 radical could follow route I leading to the formation of 2,3-pentanedione and the radical CH_3OCHOH, which could further, in the presence of oxygen, form methyl formate as a co-product. Figure 5 trace E shows a reference

spectrum of methyl formate. The absorption bands at 1210 cm^{-1} and 1755 cm^{-1} were used to identify and quantify the formation of methyl formate.

The formation of 2,3-pentanedioneis confirmed qualitatively by comparison of the product spectrum (Fig.5 trace D) with the existing reference spectrum (Fig.5, trace F). Although there is no doubt in the formation of 2,3-pentanedione, the partial or total overlap of the low intensity absorption bands did not allow us to perform reliable subtraction results to proceed for its quantification. 2,3-pentanedione exists predominantly in the keto form with the enol form being present to a few percent, at the most, in the gas phase at room temperature (Kung, 1974; Szabó et al., 2011). The predominance of the keto form for this compound makes its reactivity toward OH radicals much lower. Furthermore, in comparison with 2,4-pentanedione, a dicarbonyl compound having the enolic form predominantly and thus being more reactive toward OH radicals (9.05× 10^{-11} cm^3 molecule^{-1} s^1) (Zhou et al., 2008), 2,3-pentanedione, with a rate coefficient for the reaction with OH radicals of 2.25× 10^{-12} cm^3 molecule^{-1} s^1 (Szabó et al., 2011) is 40 times less reactive and consequently the secondary reaction with OH radicals could be of less importance (Messaadia et al., 2015).

On the other hand, photolysis quantum yields for 2,3-pentanedione using XeF laser radiation and UV lamps at room temperature in 1000 mbar of air were studied by Szabó et al., 2011. The results obtained in their work suggest that 2,3-pentanedione would suffer significant photochemical changes even at relatively long wavelengths involving short photolysis lifetime in the troposphere. If we consider these facts, it would be possible to expect a non-negligible photolysis of the compound in our experimental system under the conditions used for this study.

Decomposition of the A2 hydroxyalkoxy radical could follow the scission on route II leading to 1-hydroxy-1-methoxypropan-2-one and propionyl radical. 1-hydroxy-1-

methoxypropan-2-oneis not commercially available and thus is not possible to identify this compound by comparison with an infrared reference spectrum. However, the absorption band with the maximum at 3512 cm^{-1} could be assumed to the OH stretching band of 1-hydroxy-1-methoxypropan-2-one.(see SI Fig.S3). The infrared spectrum in Fig.S3 presents one main absorption feature that could be attributed to the O-H stretching of 1-hydroxy-1-methoxypropan-2-one produced by the more stable tertiary radical (A$_2$).

The propionyl radical could further form peroxypropionyl nitrate (PPN) (Fig. 5 trace G) in the presence of O$_2$ and NO$_2$.

Plots of the concentrations of methyl formate and PPN formed against reacted MMPO in the OH radical reaction give molar formation yields of (40 ± 12)% and (17 ± 6) % respectively. The yields have been corrected for secondary reactions with OH radicals using the method outlined by Tuazón et al., 1986. Exemplary plots of the product formation yields are shown in the SI Fig. S4.

5. Atmospheric Implications and Conclusions

Once emitted into the atmosphere, it is expected that unsaturated ketoethers such as TMBO and MMPO will follow gas phase degradation processes initiated by the main tropospheric oxidants (OH radicals, ozone, chlorine atoms and NO$_3$ radicals). Rate coefficients obtained in this work for the reaction of TMBO and MMPO with OH radicals were used to calculate their tropospheric lifetimes using the expression $\tau_x = 1/k_{ox}[\text{Ox}]$ where [Ox] is the typical atmospheric concentration of the oxidant in the troposphere and k_{ox} is the rate coefficient for thereaction of the TMBO and MMPO towards the oxidants. Considering 12-h day-time average OH radical concentration of 2×10^6 molecule cm^{-3} (global weighted-average concentration) (Bloss et al., 2005) an average lifetime of 0.98 and 0.42 hours were estimated for TMBO and MMPO, respectively. As mentioned before, in the literature there is only one experimental determination for the TMBO

reaction rate coefficient with O_3 performed by Grosjean et al. (1999). By using $k_{O3}=1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and a 24-h average O_3 concentration of 7×10^{11} molecule cm^{-3} (Logan, 1985) an estimated tropospheric residence time of 3.1 hours was calculated. A similar tropospheric lifetime is expected for MMPO towards ozone but due to the lack of kinetic data, no exact value could be calculated for MMPO. Unfortunately, no kinetic data are available for the reactions of TMBO and MMPO with Cl atoms and NO_3 radicals. However, it is ~~possible~~ reasonable to conclude that reaction with OH radicals is the main tropospheric removal pathway during daytime for the two ketoethers studied due to the short lifetimes calculated in this work. For ethers it is known that photodissociation quantum yields are relatively low and the photolysis of ketones becomes important only at high altitudes (Mellouki et al., 2015). Thus, it is reasonable to assume that photolysis of the studied compounds is only of minor importance for their atmospheric removal.

The reaction products of the OH radical initiated degradation of MMPO and TMBO ~~together with kinetic results obtained in this study,~~ confirm that the main degradation mechanisms follow the addition pathways to the double bonds. Products, identified and quantified from these reactions, are carbonyls like methyl formate, methyl glyoxal and 2,3-pentanedione and long-lived nitrogen containing compounds such as PAN and PPN. Both type of these oxygenated products could have further impact on atmospheric processes. The present study proposes new gas phase contributors to the total budget of methyl glyoxal in the atmosphere a well known precursor for SOAs formation (Fu et al., 2008). Even more this study becomes important since MMPO and TMBO are VOCspossibly released from open biomass burning events whose emissions factors for methyl glyoxal are not well established (Zarzana et al., 2018). PAN and PPN, quantified also as reaction products, are phytotoxic air pollutants, which act as NOx reservoir in remote areas (Taylor, 1969). Beside a large number of PAN measurement campaigns,

most recent chemical transport models still unsolved the PANs global distributions due to the lack of understanding of the PAN source attribution in the atmosphere (Fischer et al., 2014). Although the acetyl radical is intermediary in the formation of PAN in this study, by its acetyl peroxy radical formed in the presence of oxygen, this radical it could play an important role in the HO_x balance over the low NO_x environment. The acetyl peroxy radical is a well known precursor of OH radicals as a result of the reaction with HO_2 in the remote atmosphere (Winiberg et al., 2016). Therefore, the gas phase mechanism proposed in this study could be of importance for understanding atmospheric processes at the global scale, either in the atmosphere with low NO_x levels or in the atmosphere with increased NO_x. The results of the present study provide improved insights regarding the important contribution of multifunctional VOCs in the chemistry of atmosphere.

6. Competing interests

The authors declare that they have no conflict of interest.

7. Author contribution

RG, IB, IGB, PW designed experimental setup, RG conducted the measurements, RG and IGB processed the data, RG, IGB and PW prepared the manuscript with contribution from all the co-authors on different stages of writing process.

8. Acknowledgements

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1 **Figure Captions**

2 **Figure 1:** Relative rate data for the reaction of OH radicals with (*E*)-4-methoxy-3-buten-2-one

3 using propene (■) and isobutene (●) as reference compounds at 298 K and atmospheric pressure

4 of air.

5

6 **Figure 2:** Relative rate data for the reaction of OH radicals with (1*E*)-1-methoxy-2-methyl-1-

7 penten-3-one using propene (■) and isobutene (●) as reference compounds at 298 K and

8 atmospheric pressure of air.

9

10 **Figure 3:** Infrared spectral data: trace A infrared spectrum of a TMBO/CH$_3$ONO/air reaction

11 mixture before irradiation; trace B mixture after 10 min irradiation; trace C reference spectrum of

12 TMBO; trace D product spectrum; trace E reference spectrum of methyl formate; trace F reference

13 spectrum of peroxyacetyl nitrate; trace G reference spectrum of methyl glyoxal; trace H residual

14 spectrum after subtraction of the identified reaction products in trace D.

15 **Figure 4:** Concentration−time dependencies for the reaction of TMBO (■) + OH radicals and the

16 quantified products, methyl formate (♦MF), peroxyacetyl nitrate (●PAN), and methyl glyoxal

17 (▲MG).

18 **Figure 5:** Infrared spectral data: trace A infrared spectrum of a MMPO/CH$_3$ONO/air reaction

19 mixture before irradiation; trace B mixture after 10 min irradiation; trace C reference spectrum of

20 MMPO; traced product spectrum; trace E reference spectrum of methyl formate; trace F reference

21 spectrum of 2, 3-pentanedione; trace G reference spectrum of PPN; trace H residual spectrum

22 after subtraction of the identified reaction products in trace D.

23 **Figure 6:** Concentration−time profiles for the reaction of MMPO (■)+ OH radicals and

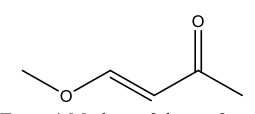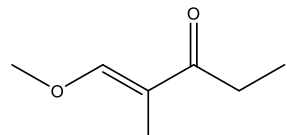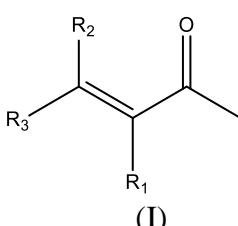24 the quantified product methyl formate (♦MF) and peroxypropionyl nitrate (●PPN).
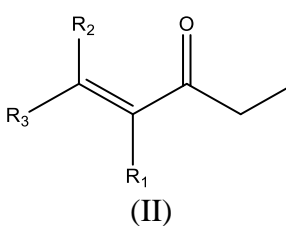
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1 **Table 1.** Rate coefficient ratios $k_{UKE}/k_{Reference}$ and rate coefficients for the reaction of OH radicals
2 with (*E*)-4-methoxy-3-buten-2-one and (1*E*)-1-methoxy-2-methyl-1-penten-3-one at (298 ± 3) K
3 in 1 atm of air.
4

Compound	Reference	$k_{UKE}/k_{Reference}$	k_{UKE} (10^{-10} cm^3 molecule^{-1}s^{-1})
	Isobutene	2.41 ± 0.02	1.26 ± 0.06
	Isobutene	2.74 ± 0.04	1.43 ± 0.07
Trans-4-Methoxy-3-buten-2-one	Isobutene	2.67 ± 0.09	1.40 ± 0.10
	Propene	5.02 ± 0.06	1.46 ± 0.05
	Propene	5.20 ± 0.07	1.51 ± 0.06
	Average		**1.41 ± 0.11**
	Isobutene	6.30± 0.12	3.30 ± 0.16
	Isobutene	6.54± 0.38	3.42 ± 0.25
	Propene	11.00 ± 0.77	3.19 ± 0.25
(E)-1-methoxy-2-methyl-1-penten-3-one	Propene	11.88 ± 0.49	3.45 ± 0.19
	Average		**3.34 ± 0.43**

5

1 **Table 2.** OH rate coefficients for different unsaturated ketones obtained experimentally
2 and predicted using a SAR method.
3

Basic structure	Substituent -R	Compound name	Experimental k_{OH} (cm³ molecule⁻¹s⁻¹)	SAR calculated k_{OH}^{f} (cm³ molecule⁻¹s⁻¹)
(I)	$R_1=R_2=R_3=H$	3-buten-2-one	$(2.0 \pm 0.3) \times 10^{-11a}$	$H_{abs}= 1.02 \times 10^{-13}$ $OH_{Add}= 2.37 \times 10^{-11}$ **Overall= 2.38 × 10⁻¹¹**
	$R_1=H$, $R_2=H$, $R_3=CH_3$	3-penten-2-one	$(7.22 \pm 1.74) \times 10^{-11b}$	*(E)-isomer* $H_{abs}= 2.38 \times 10^{-13}$ $OH_{Add}= 5.76 \times 10^{-11}$ **Overall=5.78 × 10⁻¹¹**
	$R_1=H, R_2=CH_3, R_3=CH_3$	4-methyl-3-penten-2-one	$(1.02 \pm 0.20) \times 10^{-10c}$	$H_{abs}=3.74 \times 10^{-13}$ $OH_{Add}= 7.82 \times 10^{-11}$ **Overall=7.86× 10⁻¹¹**
	$R_1=H$, $R_2=H$, $R_3=OCH_3$	(E)-4-methoxy-3-buten-2-one	$(1.42 \pm 0.12) \times 10^{-10d}$	$H_{abs}=9.32 \times 10^{-13}$ $OH_{Add}= 7.49 \times 10^{-11}$ **Overall=7.58 × 10⁻¹¹**
(II)	$R_1=R_2=R_3=H$	1-penten-3-one	$(2.90 \pm 0.79) \times 10^{-11e}$	$H_{abs}=1.23 \times 10^{-12}$ $OH_{Add}= 2.37 \times 10^{-11}$ **Overall=2.49× 10⁻¹¹**
	$R_1=H$, $R_2=H$, $R_3=CH_3$	(E)-4-hexen-3-one	$(9.04 \pm 2.12) \times 10^{-11b}$	*(E)-isomer* $H_{abs}=1.37 \times 10^{-12}$ $OH_{Add}= 5.76× 10^{-11}$ **Overall=5.90 × 10⁻¹¹**
	$R_1=H, R_2=CH_3, R_3=CH_3$	5-methyl-4-hexen-3-one	-	$H_{abs}=1.50 \times 10^{-12}$ $OH_{Add}=7.82 \times 10^{-11}$ **Overall=7.97 × 10⁻¹¹**
	$R_1=CH_3, R_2=H, R_3=OCH_3$	(1E)-1-methoxy-2-methyl-1-penten-3-one	$(3.34 \pm 0.43) \times 10^{-10d}$	$H_{abs}= 2.20 \times 10^{-12}$ $OH_{Add}= 1.02 \times 10^{-10}$ **Overall=1.04 × 10⁻¹⁰**

4 a-(Holloway et al., 2005); b-(Blanco et al., 2012); c-(Gaona-Colmán et al., 2017); d- This work; e-(Blanco
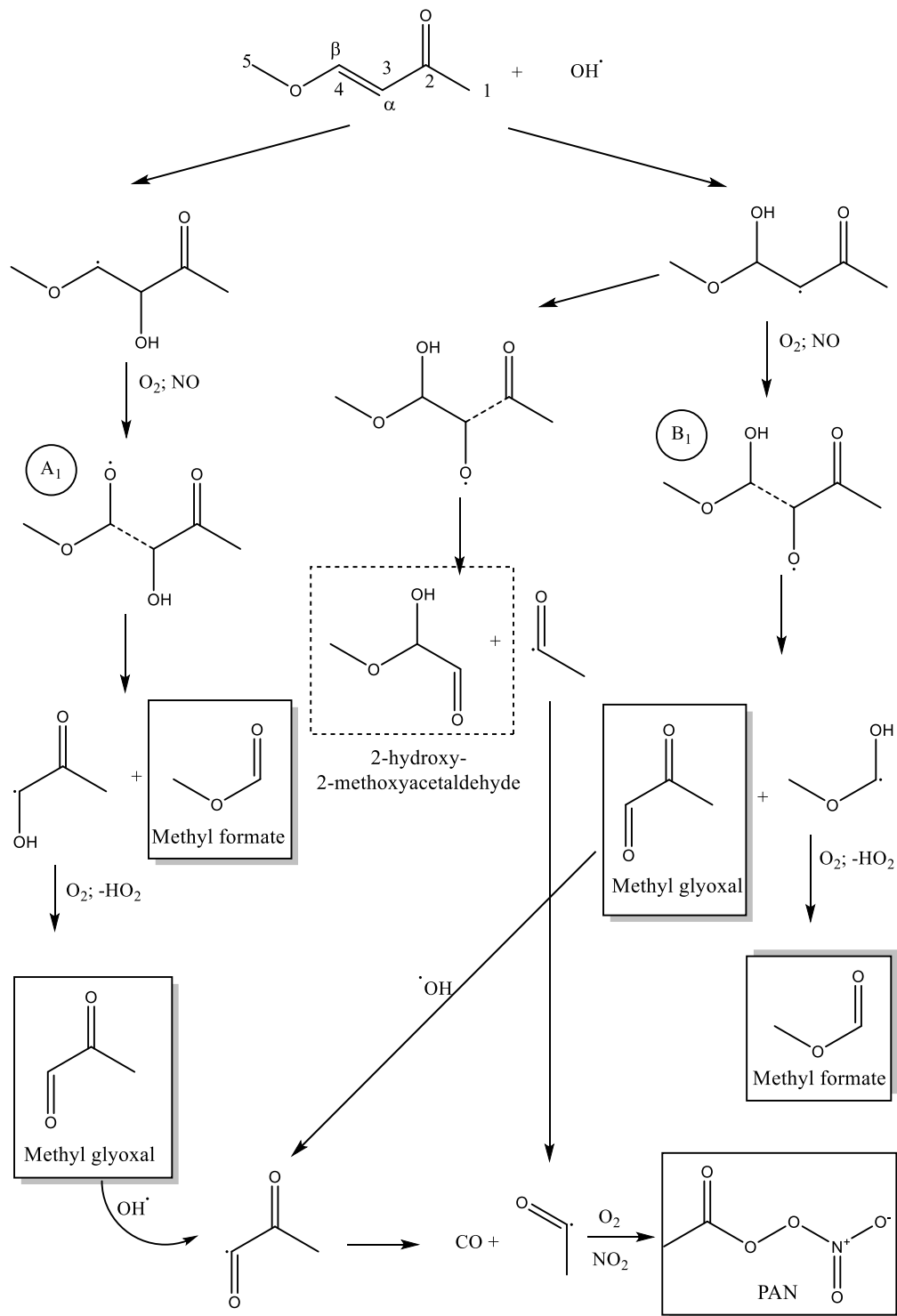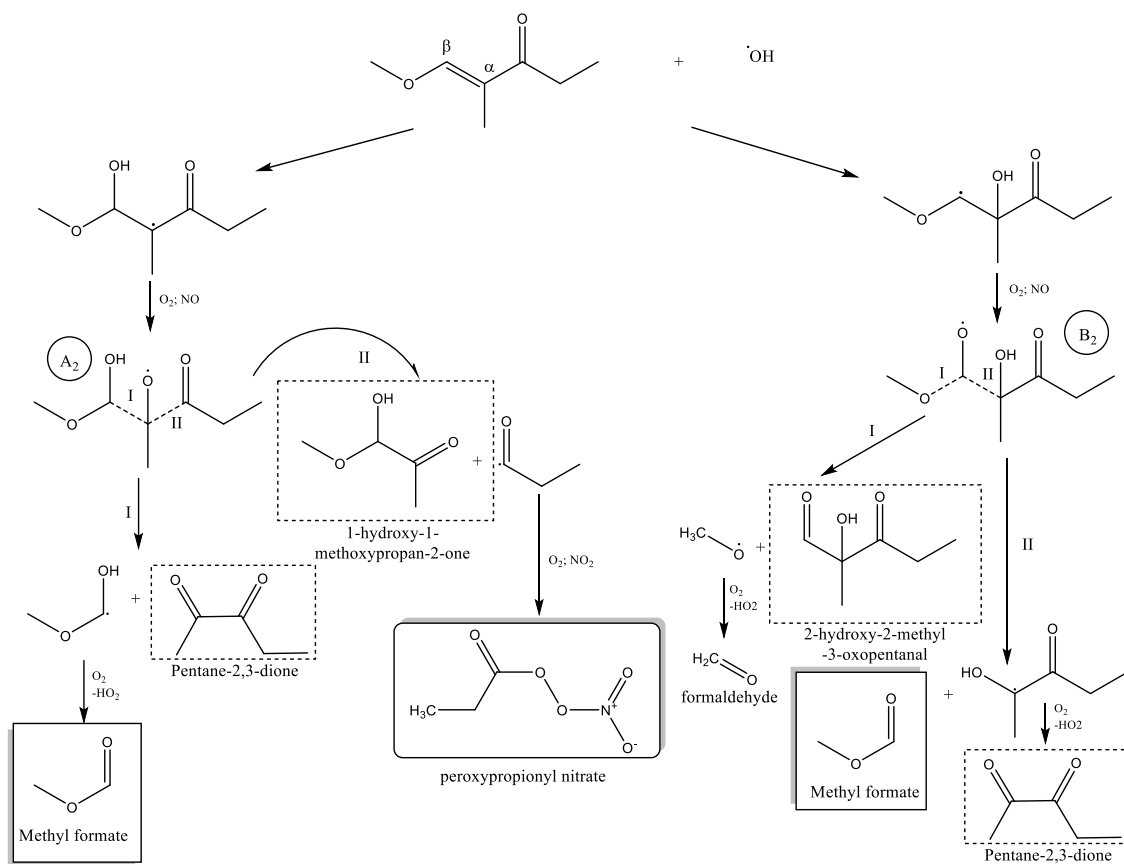5 and Teruel, 2011)
6
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1 **Scheme 1.** Simplified reaction mechanism for the addition channel in the OH-radical initiated
2 oxidation of the(*E*)-4-methoxy-3-buten-2-one. Quantified products appear in the boxes and the
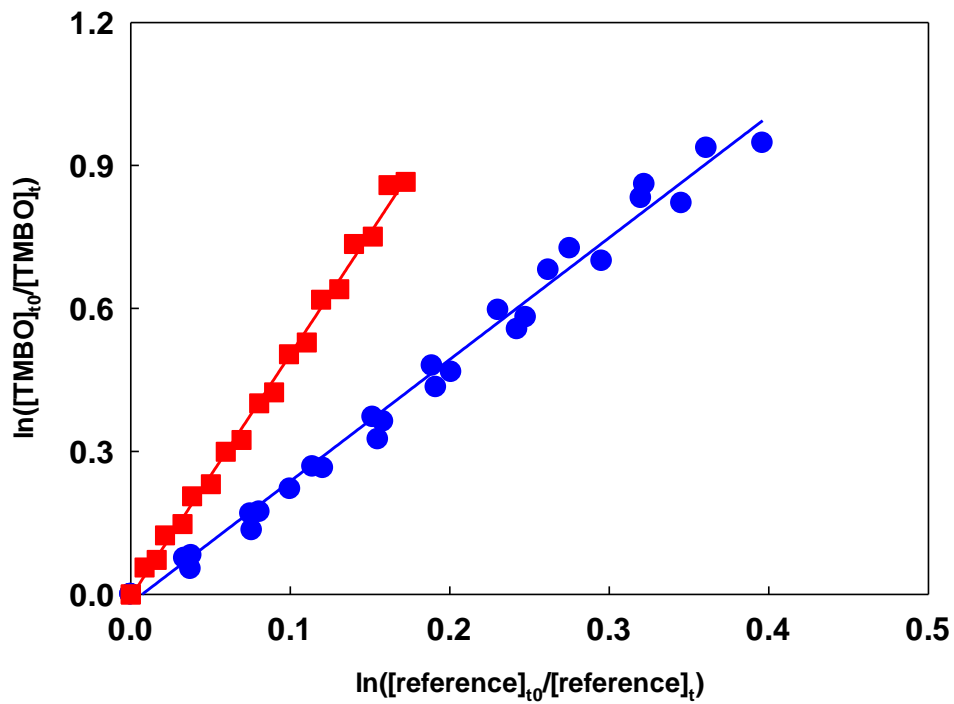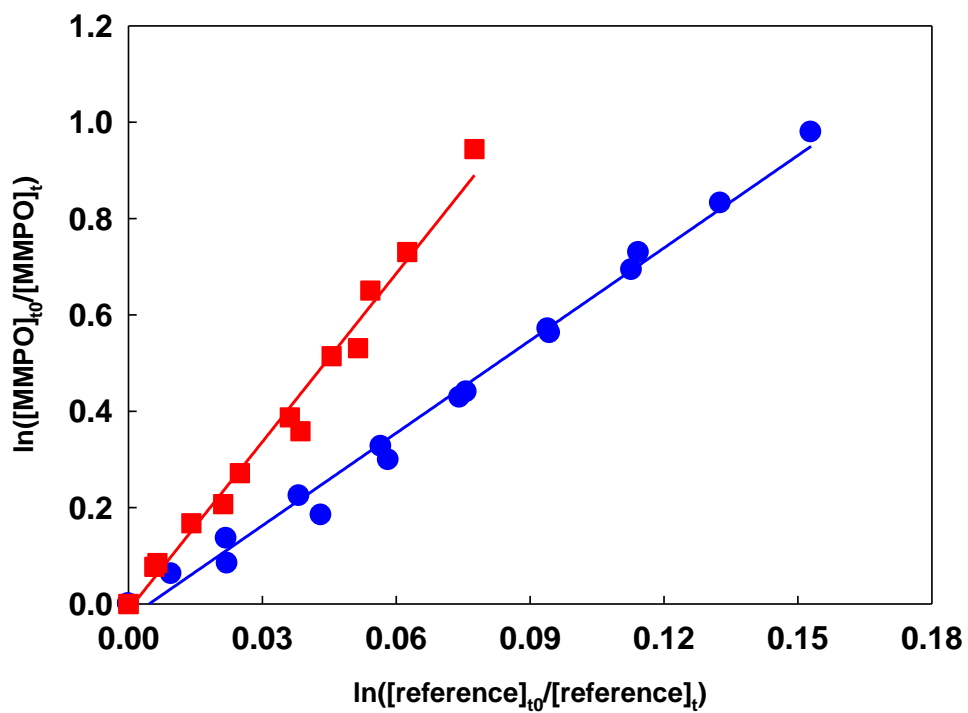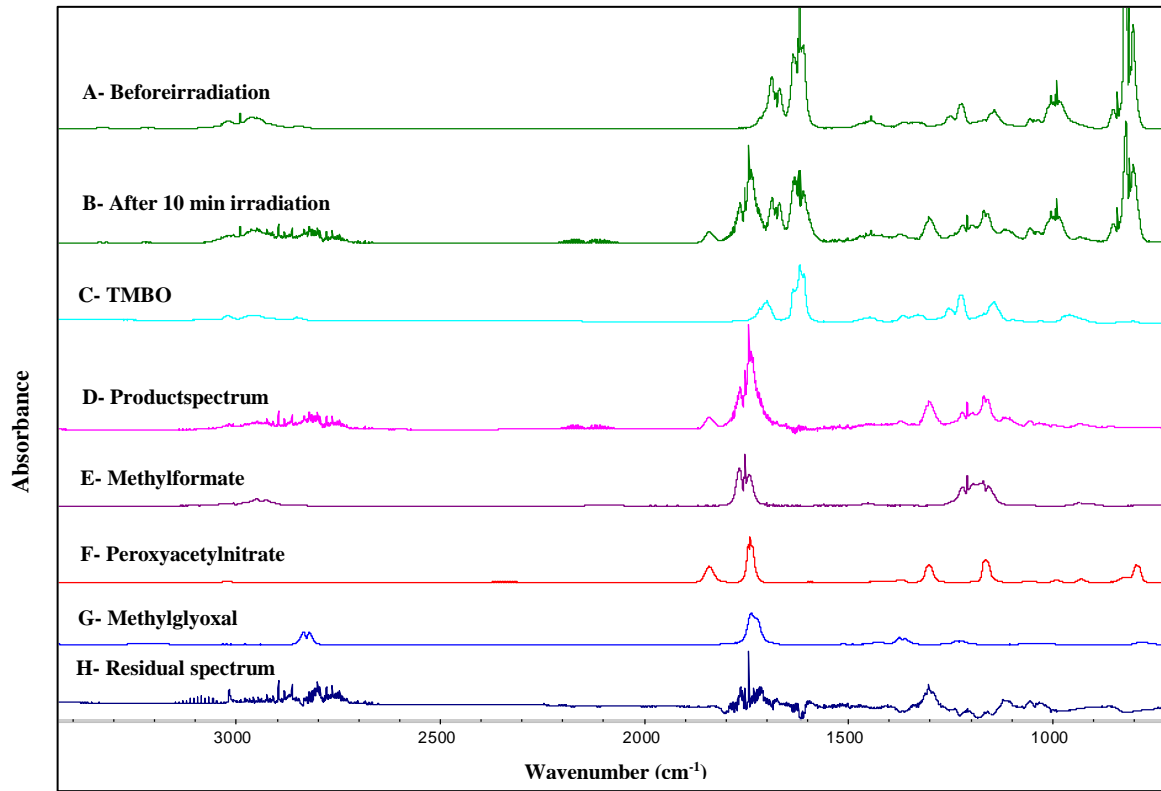3 identified products are rounded by a dashed rectangle.
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1 **Scheme 2.** Simplified reaction mechanism for the addition channel in the OH-radical
2 initiated oxidation of (1E)-1-methoxy-2-methyl-1-penten-3-one. Quantified products appear
3 in the boxes and the identified products are rounded by a dashed rectangle.
4
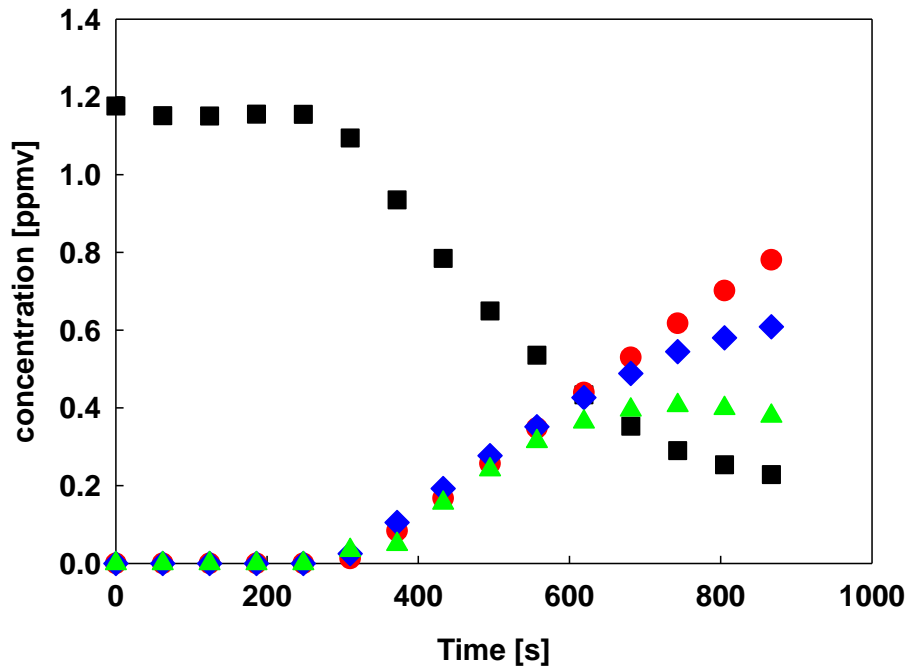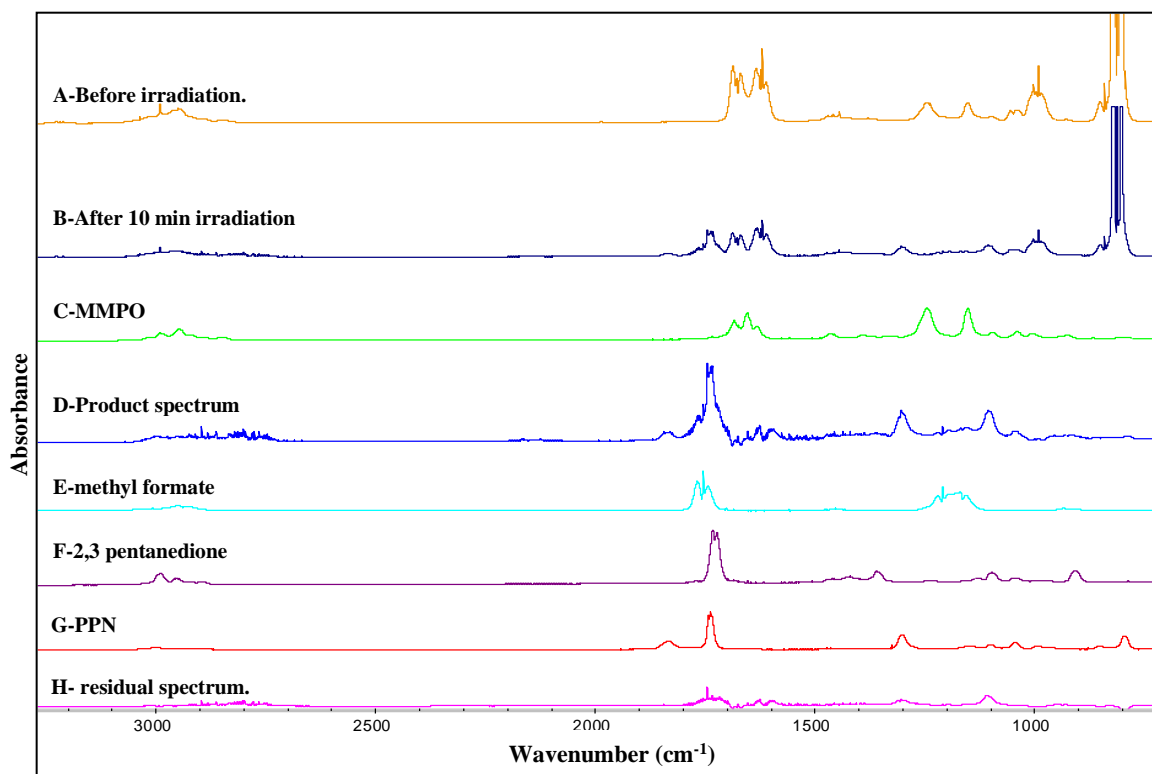

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Fig. 1

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Fig.2

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Fig. 3

A- Beforeirradiation

B- After 10 min irradiation

C- TMBO

D- Productspectrum

E- Methylformate

F- Peroxyacetylnitrate

G- Methylglyoxal

H- Residual spectrum

Absorbance

Wavenumber (cm^{-1})

Fig. 4

concentration [ppmv]

Time [s]

1

Fig. 5

A-Before irradiation.

B-After 10 min irradiation

C-MMPO

D-Product spectrum

E-methyl formate

F-2,3 pentanedione

G-PPN

H- residual spectrum.

Absorbance

Wavenumber (cm⁻¹)

2

3

4

Fig. 6
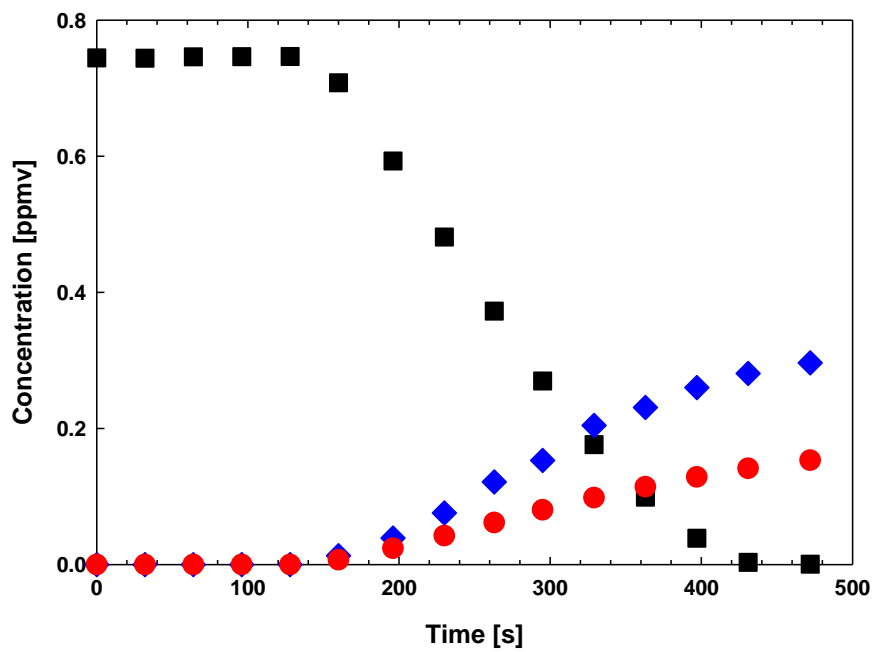
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1 **Interactive comment on:**

2 **"Atmospheric fate of two relevant unsaturated ketoethers:**

3 **kinetics, products and mechanisms for the reaction of hydroxyl**

4 **radicals with(E)-4-methoxy-3-buten-2-one and1-(E)-1-methoxy-2-**

5 **methyl-1-penten-3-one"**

6 **by**

7 **Rodrigo Gastón Gibilisco et al.**

8 **Anonymous Referee #1**

9 **Received and published: 11 March 2020**

10

11 The first reviewer has done a good job of summarizing the goals and results of the paper.
12 I fully concur with everything they presented, and will not repeat those general comments.
13 Overall, this is a clear paper that describes high quality gas-phase kinetics results for the
14 OH oxidation of some multifunctional oxygenates. To provide validation of models like
15 MCM, there is the need for the type of kinetics and product information presented in the
16 paper. The relative rate technique is very well established, two reference compounds were
17 used, and the group performing the measurements has a strong reputation. My overall
18 impression is that the results are solid. The paper goes into considerable depth on the
19 oxidation mechanism and comparison to results of estimation methods.

20 Overall, I recommend publication. I have no substantive comments to make. Minor
21 comments:

22 The authors express their gratitude to anonymous referee #1 for evaluating and reading
23 the paper carefully and providing thoughtful comments. The comments help to improve
24 the revised version of the manuscript. The authors reply in blue for each comment bellow.
25 The article text body of the manuscript has been amended in red with answers and
26 modifications suggested by referee.

27 Page 3, line 12 – check reference format
28- DONE

29 Page 10, line 9 – substituents
30- DONE

31 Page 11, line 8 – change deducting to withdrawing
32- DONE

33 Page 19, line 13 – space needed
34- DONE

35 Figure 1 – missing line of best fit
36- DONE

37 Scheme 1 – explain the meaning of the dashed line in the structure
38- DONE

39 My main comment is that I would like a bit more information on how the product yields
40 were calculated, especially their associated uncertainties. Was a multivariate fitting
41 performed? In particular, the residual spectrum is quite large with intensity at some
42 frequencies where products are identified.

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44

45

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
Rodrigo Gastón Gibilisco et al.
Anonymous Referee #2
Received and published: 28 February 2020

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 $(1-5) \times 10^{-5}$ 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:

3- 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;

6- 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;

8- 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 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 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 $\tau_x = 1/k_{ox}[\text{Ox}]$ 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.

1

2 Scheme 2: Pentane-2,3-dione was not able to be quantified. Maybe it can be distinguished
3 from the quantified products. Note that "Absorbances" are unitless by definition (-
4 log(I/I0)) where I and I0 is the transmitted light in the presence and absence of absorber,
5 respectively. Please, change legend of y-axis in Figures 3 and 5. In addition, the legend
6 in x-axis in these figures covers part of the axis and it is a bit cut.

7- DONE. Penten-2,3-dione was placed in a dashed rectangle following the referee's
8 recommendation.

9- DONE. legend of y-axis in Figures 3 and 5 was changed.

10

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

17- Caption of Figure S1 and S3: "3800 cm-1". DONE

18- DONE: Legend of y- and x-axis of Figures S2 and S4 was changed.

19- Y-axis should start in zero. DONE

20- legend of x-axis in Figures S1 and S2 should be "Wavenumber (cm-1). And for y-axis it
21 should be "Absorbance". DONE.

22