Responses to Reviewers' Comments:

We thank the reviewers for the consideration and the constructive comments. The manuscript is revised based on the suggestions made and detailed responses to the reviewers are addressed as follows.

Referee #1

The authors present a detailed study of the aqueous-phase oxidation of methyl ethyl ketone (MEK). Their most significant finding is that this species may be a precursor for methylglyoxal in the aqueous phase. The experiments were carefully performed and a detailed modeling analysis was used to determine the reaction mechanism and rate constants. The paper is suitable for publication in ACP after a few minor points are addressed.

1) My main concern about this paper is that I would like to see a discussion of the relative importance of this source of methylglyoxal as compared to uptake from the gas phase. The Henry’s Law constant of MEK is very low, 2-3 orders of magnitude lower than that of methylglyoxal itself. Considering mass transfer limitations, how significant of a source of methylglyoxal, and by extension, aqueous SOA, is this pathway?

Author`s comment

In Table 1 the Henry constants of MEK and methylglyoxal as well as measured concentrations in the gas, particle and aqueous phase are summarised.

Table 1: Henry constant and concentrations of MEK and methylglyoxal in gas-, particle- and aqueous phase.

<table>
<thead>
<tr>
<th></th>
<th>Henry constant [M atm^{-1}]</th>
<th>Concentration gas phase [ppb]</th>
<th>Concentration particle phase [\mu g m^{-3}]</th>
<th>Concentration aqueous phase [\mu mol L^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEK</td>
<td>7.7 – 50^{abcdefg}</td>
<td>0.02 – 15^{ijklmnop}</td>
<td>0 – 0.1^{1}</td>
<td>0 – 0.65(CW)^{m}; &lt; 0.0005(OW) and 0.00228 (SML)^{v}</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>3.7 × 10^{1h}</td>
<td>≤ 0.05 – 0.09^{op}</td>
<td>0.03 – 270,6^{pqrs}</td>
<td>0.3 – 18(CW)^{vu}</td>
</tr>
<tr>
<td></td>
<td>3.2 × 10^{1d}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CW cloud water, OBW ocean bulk water, SML surface microlayer

a Battery et al., 1969; b Snider and Dawson, 1985; c Ashworth et al., 1988; d Zhou and Mopper, 1990; e Morillon et al., 1999; f Karl et al., 2002; g Schütze and Herrmann 2004; h Betterton and Hoffmann, 1988; i Grosjean et al., 1982, 1983, 2002; j Riemer et al., 1998; k Singh et al., 2004; l Goldan et al., 1995; m Müller et al., 2005; n Feng et al., 2002; o Manger et al., 1995; p Kawamura et al., 2013; q Ortiz et al., 2006; r Matsunaga et al., 2004; s Ieda et al., 2006; t Grosjean and Wright, 1983; u van Pinxteren et al., 2005; v Zhou and Mopper, 1997; w Collett et al., 1990

As it can be seen, MEK has a lower Henry constant with 50 M atm^{-1} as the maximum available value (Schütze and Herrmann, 2004) compared to methylglyoxal (K_H = 3.7 × 10^3 M atm^{-1},
Betterton and Hoffmann, 1988) leading to the conclusion that the transfer from the gas in the aqueous phase is, according to the Henry constant, more important for methylglyoxal than for MEK. Noticeably, van Pinxteren et al. (2005) found higher concentrations of MEK in cloud water as it was expected according to the Henry constant. Thus, phase transfer could be more important than it is known at this moment. Besides it transfer from the gas phase, the formation of MEK in the aqueous phase of clouds and hygroscopic particles should be considered as additional source for aqueous MEK as well. The so-formed aqueous MEK will react to form methylglyoxal with a molar yield of 9.5%.

Methylglyoxal present in the aqueous phase originates from i) uptake from the gas phase and ii) aqueous-phase reactions. The uptake of methylglyoxal from the gas phase in the aqueous phase is not fully understood. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under various relative humidity. It was found, that the uptake was not relevant for methylglyoxal even under high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of $\gamma = 7.6 \times 10^{-3}$ on acidic solution. They found an irreversible uptake, which decrease with increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets $\gamma = 2.9 \times 10^{-3}$, which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be $\gamma = 1.47 - 2.92 \times 10^{-5}$. Overall, $\gamma$ was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) highlighting the discrepancies between the different literature studies.

As the uptake as well as the formation mechanisms of methylglyoxal are not fully understood, it cannot be excluded that the oxidation of MEK represents an important reaction channel for methylglyoxal formation.

Based on the Referee’s comment the following paragraph was added to the manuscript:

Page 31907 Line 1 “4. Atmospheric relevance

*The sources of methylglyoxal in the aqueous phase are thus-far not fully elucidated. Methylglyoxal can originate in the atmospheric aqueous phase through i) uptake from the gas phase, and/or ii) formation in the aqueous phase. The importance of the uptake from the gas into the aqueous phase is discussed in the literature but large discrepancies can be found. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under varying relative humidity. It was found that the uptake was not relevant for methylglyoxal even under*
high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of $\gamma = 7.6 \times 10^{-3}$ on acidic solution. They found an irreversible uptake, which decreases with increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets $\gamma = 2.9 \times 10^{-3}$, which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be $\gamma = 1.47 - 2.92 \times 10^{-5}$. Overall, $\gamma$ was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) showing the discrepancies between the different studies available in literature.

The in-situ formation of methylglyoxal in the aqueous phase could be an important source as well (Blando and Turpin, 2000; Sempere and Kawamura 1994). Within the present study, MEK was found as a new precursor compound for methylglyoxal in the aqueous phase yielding methylglyoxal with a molar yield of 9.5%. Although the Henry constant of MEK (up to $K_H = 50\text{ M atm}^{-1}$, Schütze and Herrmann, 2004) is lower compared to methylglyoxal ($K_H = 3.7 \times 10^3\text{ M atm}^{-1}$, Betterton and Hoffmann, 1988), van Pinxteren et al. (2005) found higher concentrations in cloud water as it was expected. Thus, the phase transfer of MEK from the gas in the aqueous phase could be more important as currently derived from the available Henry constants. Besides the phase transfer, the in-situ formation of MEK in aqueous phase formation might also represents an important source.

As, the oxidation of MEK yielding methylglyoxal has not been studied much before, it should be considered as a formation process of methylglyoxal.”

Minor comments:

1) Methylglyoxal is conventionally one word in English, please change throughout.

Author’s comment
The authors agree with the reviewers comment. The term “methyl glyoxal” was changed to “methylglyoxal” throughout the manuscript.

2) Was there any gas phase in the reactor? Was it in equilibrium with the aqueous phase?

Author’s comment
The bulk reactor was filled with 300 mL of the aqueous solution at the beginning of the experiment containing the precursor compound and $\text{H}_2\text{O}_2$. Over the course of the experiment
samples were taken in steps of 15 minutes (and for some cases 1 hour). Thus, the gas phase increased during the experiment. To take samples, the bulk reactor was opened. Even that the opening time was kept as small as possible the gas phase of the bulk reactor might be mixed with the laboratory air changing the chemical composition. Nevertheless, the Henry constant of methylglyoxal ($K_H \approx 3.7 \times 10^3$ M atm$^{-1}$; Betterton and Hoffmann, 1988) indicates that methylglyoxal will mainly stay in the aqueous phase even when the bulk reactor was opened. Contrary, the Henry constant of MEK was measured to be $K_H = 7.7 \times 50$ M atm$^{-1}$, thus a loss of MEK from the aqueous phase in the gas phase is possible. To proof the hypothesis, the results of blank experiment 2 can be used. As it was mentioned in the manuscript, no loss of MEK was observed. This indicates that MEK stays in the aqueous phase even during opening of the reactor.

3) p. 31898 line 7-8: please elaborate on how the relative photolysis rate constants 'confirm the experimental results’

Author’s comment

Fig. 1 B shows the molar yields of the oxidation products methylglyoxal, hydroxyacetone and 2,3-butanedione over a reaction period of 4 hours. As it can be seen, further reactions are taking place leading to lower molar yields of methylglyoxal, hydroxyacetone and 2,3-butandione towards the end of the experiment.

The following rate constants for the OH radical reaction are reported in the literature: $k_{OH} = 5.3 \times 10^8 - 1.1 \times 10^9$ M$^{-1}$ s$^{-1}$ (Monod et al., 2005; Ervens et al., 2003; Herrmann et al., 2005; Tan et al., 2010) for methylglyoxal, $k_{OH} = 0.8 - 1.2 \times 10^9$ M$^{-1}$ s$^{-1}$ (Stefan and Bolton, 1999; Herrmann et al., 2005) for hydroxyacetone and $k_{OH} = 1.4 - 1.8 \times 10^8$ M$^{-1}$ s$^{-1}$ (Gligorovski and Herrmann, 2004, Lilie et al., 1968) for 2,3-butanedione. Additionally, photolysis rates were determined in the present study to be $k_p = 3 \times 10^5$ s$^{-1}$, $2 \times 10^5$ s$^{-1}$ and $9 \times 10^6$ s$^{-1}$ for methylglyoxal, hydroxyacetone and 2,3-butandione, respectively.

According to the rate constants for the OH radical reaction reported in the literature and the measured photolysis rates, a faster consumption of methylglyoxal and hydroxyacetone can be expected than for 2,3-butanedione. Such a faster consumption can be clearly seen form Figure 1B because methylglyoxal and hydroxylacetone are completely consumed at the end of the experiment whereas 2,3-butanedione was still present. This might be caused by the smaller rate constant as well as by the lower photolysis rate.
According to the Referees´ comment, the following sentence was added to the manuscript:
Page 31898 Line 7-9 was changed to: "This indicates a faster decomposition compared to 2,3-butanedione of methylglyoxal and hydroxyacetone, which showed a complete consumption at the end of the experiment (Fig. 1). 2,3-Butanedione was not completely consumed during the reaction time of 4 hours, which might be a result of the lower photolysis rate constants."

Referee #2

These authors offer an alternative pathway of methylglyoxal formation in the atmospheric aqueous phase. Namely, the authors have investigated the aqueous phase oxidation of methyl ethyl ketone (MEK) by highly reactive hydroxyl radicals (OH). Few reaction products of atmospheric relevance were detected and identified i.e. 2,3-butanedione, hydroxyacetone and methylglyoxal. A reaction mechanism has been proposed for the formation of methylglyoxal and evaluated with a model study. The experiments are very well done and the authors have carefully addressed all issues regarding the application of these results to atmospheric aqueous phase. The paper is concise and nicely written, with no excess information. ACP is an appropriate journal for the paper on this topic. It can therefore be published in ACP after minor revisions.

1) How relevant are the used concentrations of 0.1 mmol l\(^{-1}\) of MEK in these experiments compared to the concentrations of MEK in cloud water ranging between 70 and 650 nmol l\(^{-1}\) (van Pinxteren et al., 2005)? How the concentrations of MEK would impact the experiments?

Author´s comment

The authors agree on the referees comment that the MEK concentration was much higher in the experiment than found in ambient measurements. Such a high MEK concentration of 0.1 mmol L\(^{-1}\) was necessary for the experiment to ensure the traceability of the reaction and in particular the formation of formed products.

With higher MEK concentrations, side reactions like photolysis of MEK will increase. In particular, more alkyld peroxo radicals (RO\(_2\)) will be present in the system and this will change the ratio of RO\(_2\) to hydroperoxy radicals (HO\(_2\)). The [RO\(_2\)]/[HO\(_2\)] is a critical issue in terms of product distribution (e.g. Keywood et al., 2004; Docherty and Ziemann, 2003). As it can be seen in Figure 4, the reaction of RO\(_2\) radicals with HO\(_2\) radicals leads to the formation of organic peroxides (R14/R25), whereas the recombination of RO\(_2\) radicals leads to the formation of carbonyl compounds and alcohols. Thus, with higher RO\(_2\) radical concentration and a larger
[RO₂]/[HO₂] the formation of organic peroxides might become of minor importance. In addition, if RO₂ radical concentration is not sufficient side reactions like recombination of HO₂ radicals (R5) or the reaction of HO₂ radicals with OH radicals (R4) and H₂O₂ (R6) get more importance. This will lead to additional sinks for OH and HO₂ radicals. Furthermore, if the concentrations of MEK or H₂O₂ are too high the bulk reactor will not be completely penetrated by light. For that reason, a concentration of 0.1 mmol L⁻¹ ensure a good balance to detect the formed products, to have a complete illuminated reactor and to avoid strong photolysis of MEK during the oxidation.

2) The authors did not precise at what temperature were performed the experiments? I suppose at ambient temperature (298K).

Author’s comment
The experiments were conducted at a temperature of 298 K.

Based on the referees’ comment the following sentence was added:
Page 31895, Line 8: The sentence “The experiments were conducted at a temperature of 298 K.” was included in the manuscript.

How important is this pathway of methyl glyoxal formation in comparison to the other sources? Reactions of carbonyl compounds in tropospheric clouds produce organic aerosol mass through in-cloud oxidation and during post-cloud evaporation. To get a clearer picture about the impact of these processes on the SOA formation one has to compare the OH radical reactivity in the aqueous phase with the evaporation post-cloud processes at lower temperatures, at the range between 5 and 15 °C relevant for the tropospheric clouds. I would like to see discussion on this issue.

Author’s comment
Methylglyoxal can be originated in the aqueous phase through i) uptake from the gas phase, and ii) aqueous-phase reactions as it is discussed in comment 1 for referee #1. The uptake of methylglyoxal from the gas phase in the aqueous phase is not fully understood, thus the formation of methylglyoxal through aqueous phase reaction, in particular through oxidation of MEK might represent an important formation process for methylglyoxal. The temperature dependency was not the focus of this study and thus it was not investigated.
However, an increasing rate constant for the OH radical oxidation of MEK at higher temperature was found by Mezyk (1994). The rate constant increase from $k = 0.490 \pm 0.005 \times 10^{-9} \text{M}^{-1} \text{s}^{-1}$ at 1.5 °C to $k = 1.35 \pm 0.07 \times 10^{-9} \text{M}^{-1} \text{s}^{-1}$ at 66.5 °C (Table 2).

Table 2: Rate constants and Henry constants for MEK at different temperatures.

<table>
<thead>
<tr>
<th>Henry constant $[\text{M atm}^{-1}]^a$</th>
<th>Temperature [°C]</th>
<th>Rate constant $\times 10^{-9}$ $[\text{M}^{-1} \text{s}^{-1}]^b$</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.0 ± 0.8</td>
<td>10</td>
<td>0.490 ± 0.005</td>
<td>1.5</td>
</tr>
<tr>
<td>19.8 ± 1.4</td>
<td>25</td>
<td>0.590 ± 0.001</td>
<td>13.5</td>
</tr>
<tr>
<td>14.1 ± 0.2</td>
<td>30</td>
<td>0.734 ± 0.008</td>
<td>24.4</td>
</tr>
<tr>
<td>10.9 ± 0.5</td>
<td>35</td>
<td>0.936 ± 0.009</td>
<td>41.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.35 ± 0.07</td>
<td>66.5</td>
</tr>
</tbody>
</table>

a: Zhou and Mopper (1990), b: Mezyk (1994)

This indicates a faster OH radical oxidation at higher temperatures and hence a faster formation of methylglyoxal can be expected. On the other hand, it was found by Zhou and Mopper (1990), that the Henry constant decrease from $K_H = 49 \pm 0.8 \text{ M atm}^{-1}$ at 0°C to $K_H = 7.1 \pm 0.7 \text{ M atm}^{-1}$ at 45°C (Table 2), which shows a stronger partitioning of MEK from the gas phase in the aqueous phase with decreasing temperature. Thus, higher concentrations of MEK should be found in the aqueous phase at lower temperatures.

In summary, the influence of the temperature cannot be finally estimated because of the contrary dependency of the Henry constant and the rate constant for the OH radical oxidation.

Minor comments:

1) Perhaps a right axis can be added in Figure 1 with different scaling than the left axis in order to better present the molar yield of hydroxyacetone. In figure 3 you either describe MEK (black) and 2,3 butanediol (red) in the caption or in the legend. The same applies for Figure 6.

Author’s comment
A right axis was included in Figure 1 for the molar yield of hydroxyacetone.
In Figure 1, 3, 6, 7, S2 and S3 the description in the figure caption “black” for MEK, “green” for methylglyoxal, “blue” for hydroxyacetone and “red” for 2,3-butanedione was deleted.

References:


Grosjean, D., and Wright, B.: Carbonyls in urban fog, ice fog, cloudwater and rainwater, Atmospheric Environment, 17, 2093-2096, 10.1016/0004-6981(83)90368-2, 1983.


The following changes were made to the manuscript

The term “methyl glyoxal” was changed to “methylglyoxal” in the manuscript text as well as in Fig. 1 and 4 and Table 1 and 2.

Page 31895 Line 8: The sentence “The experiments were conducted at a temperature of 298 K.” was included in the manuscript.

Page 31898 Line 7-9: “This indicates a faster decomposition of methyl glyoxal and hydroxyacetone and confirms the experimental results.” was changed to “This indicates a faster decomposition compared to 2,3-butanedione of methylglyoxal and hydroxyacetone, which showed a complete consumption at the end of the experiment (Fig. 1). 2,3-Butanedione was not completely consumed during the reaction time of 4 hours, which might be a result of the lower photolysis rate constants.”

Page 31898 Line 24-25: “This is in good agreement with the experimental results obtained in the the present study.” was changed to “This is in good agreement with the experimental results obtained in the present study.”

Page 31906 Line 1: The paragraph “4. Atmospheric relevance
The sources of methylglyoxal in the aqueous phase are thus far not fully elucidated. Methylglyoxal can originate in the atmospheric aqueous phase through i) uptake from the gas phase, and/or ii) formation in the aqueous phase. The importance of the uptake from the gas into the aqueous phase is discussed in the literature but large discrepancies can be found. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under varying relative humidity. It was found that the uptake was not relevant for methylglyoxal even under
high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of $\gamma = 7.6 \times 10^{-3}$ on acidic solution. They found an irreversible uptake, which decreases with increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets $\gamma = 2.9 \times 10^{-3}$, which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be $\gamma = 1.47 - 2.92 \times 10^{-5}$. Overall, $\gamma$ was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) showing the discrepancies between the different studies available in literature.

The in-situ formation of methylglyoxal in the aqueous phase could be an important source as well (Blando and Turpin, 2000; Sempere and Kawamura 1994). Within the present study, MEK was found as a new precursor compound for methylglyoxal in the aqueous phase yielding methylglyoxal with a molar yield of 9.5%. Although the Henry constant of MEK (up to $K_H = 50 \text{ M atm}^{-1}$, Schütze and Herrmann, 2004) is lower compared to methylglyoxal ($K_H = 3.7 \times 10^3 \text{ M atm}^{-1}$, Betterton and Hoffmann, 1988), van Pinxteren et al. (2005) found higher concentrations in cloud water as it was expected. Thus, the phase transfer of MEK from the gas in the aqueous phase could be more important as currently derived from the available Henry constants. Besides the phase transfer, the in-situ formation of MEK in aqueous phase formation might also represents an important source.

As, the oxidation of MEK yielding methylglyoxal has not been studied much before, it should be considered as a formation process of methylglyoxal.” was included in the manuscript.

Page 31906 Line 1: “4. Summary” was changed to “5. Summary”


Page 31911 Line 16: The reference “Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H., Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res, 110, 1-10, 2005.” was added to the manuscript.


Page 31912 Line 31: The reference “Sempere, R., and Kawamura K.: Comparative distribution of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban, Atmos. Environ., 28, 449-459, 1994.” was included in the manuscript.


Page 31918: The figure caption “Figure 1: Consumption of MEK (black; A) during the oxidation with OH radicals and time-resolved formation of the products methylglyoxal (green; B), 2,3-butanedione (red; B), and hydroxyacetone (blue; B)” was changed to “Figure 1: Consumption of MEK (A) during the oxidation with OH radicals and time-resolved formation of the products methylglyoxal (B), 2,3-butanedione (B), and hydroxyacetone (B).”

Page 31920: The figure caption “Figure 3: Photolysis of MEK (black) and time-resolved formation of 2,3-butanedione (red).” was changed to “Figure 3: Photolysis of MEK and time-resolved formation of 2,3-butanedione.”

Page 31923: The figure caption “Figure 6: Comparison of the molar yields of 2,3-butanedione (A, red) and methylglyoxal (B, green) for the model and experimental results using different branching ratios of the primary/secondary H-atom abstraction varied between 60/40 up to 10/90.” was changed to “Figure 6: Comparison of the molar yields of 2,3-butanedione (A) and methylglyoxal (B) for the model and experimental results using different branching ratios of the primary/secondary H-atom abstraction varied between 60/40 up to 10/90.”

Page 31924: The figure caption “Figure 7: Comparison of the model and experimental results for MEK (A, black), 2,3-butanedione (B, red), and methylglyoxal (C, green).” was changed to
“Figure 7: Comparison of the model and experimental results for MEK (A), 2,3-butanedione (B), and methylglyoxal (C).”

**General changes made to the supplement**

The term “methyl glyoxal” was changed to “methylglyoxal” in the supplement text and Fig, S1, S2 and S3.

Page 2: The figure caption “Figure S2: Formation of methylglyoxal (green) due to the photolysis of hydroxyacetone (blue) and 2,3-butanedione (red).” was changed to “Figure S2: Formation of methylglyoxal due to the photolysis of hydroxyacetone and 2,3-butanedione.”

Page 3: The figure caption “Figure S3: Oxidation of hydroxyacetone (blue) and formation of methylglyoxal (green).” was changed to “Figure S3: Oxidation of hydroxyacetone and formation of methylglyoxal.”
A new source of methylglyoxal in the aqueous phase

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Abstract

Carbonyl compounds are ubiquitous in atmospheric multiphase system participating in gas, particle, and aqueous-phase chemistry. One important compound is methyl ethyl ketone (MEK), as it is detected in significant amounts in the gas phase as well as in cloud water, ice, and rain. Consequently, it can be expected that MEK influences the liquid phase chemistry. Therefore, the oxidation of MEK and the formation of corresponding oxidation products were investigated in the aqueous phase. Several oxidation products were identified from the oxidation with OH radicals, including 2,3-butanedione, hydroxyacetone, and methylglyoxal. The molar yields were 29.5% for 2,3-butanedione, 3.0% for hydroxyacetone, and 9.5% for methylglyoxal. Since methylglyoxal is often related to the formation of organics in the aqueous phase, MEK should be considered for the formation of aqueous secondary organic aerosol (aqSOA). Based on the experimentally obtained data, a reaction mechanism for the formation of methylglyoxal has been developed and evaluated with a model study. Besides known rate constants, the model contains measured photolysis rate constants for MEK ($k_p = 5 \times 10^{-5} \text{ s}^{-1}$), 2,3-butanedione ($k_p = 9 \times 10^{-6} \text{ s}^{-1}$), methylglyoxal ($k_p = 3 \times 10^{-5} \text{ s}^{-1}$), and hydroxyacetone ($k_p = 2 \times 10^{-5} \text{ s}^{-1}$). From the model predictions, a branching ratio of 60/40 for primary/secondary H-atom abstraction at the MEK skeleton was found. This branching ratio reproduces the experiment results very well, especially the methylglyoxal formation, which showed excellent agreement. Overall, this study demonstrates MEK as a methylglyoxal precursor compound for the first time.
1. Introduction

In the last decades, carbonyl compounds have been a subject of intense research due to their ubiquitous abundance and their effect on atmospheric chemistry and human health. They are emitted directly from biogenic and anthropogenic sources or formed through the oxidation of hydrocarbons (e.g., Atkinson, 1997; Matthews and Howell, 1981; Lipari et al., 1984; Ciccioli et al., 1993; Mopper and Stahovec, 1986; Carlier et al., 1986; Hallquist et al., 2009). One carbonyl compound that is emitted from numerous and mainly biological sources is methyl ethyl ketone (MEK). It is released from grass, clover (Kirstine et al., 1998; de Gouw et al., 1999), different types of forests, and biomass burning processes (Khalil and Rasmussen, 1992; Warneke et al., 1999; Isidorov et al., 1985). Anthropogenic emissions are also important MEK sources, such as artificial biomass burning (Andreae and Merlet, 2001; Akagi et al., 2011; Yokelson et al., 2013; Brilli et al., 2014) and tobacco smoke (Buyske et al., 1956; Yokelson et al., 2013). In addition, MEK is emitted into the atmosphere through the application as solvent for the production of glue, resins, cellulose, rubber, paraffin wax and lacquer (Ware, 1988).

Tropospheric MEK gas-phase concentration was found to be in the range of 0.02 – 15 ppbv, depending on the region (Grosjean et al., 2002; Riemer et al., 1998; Singh et al., 2004; Snider and Dawson, 1985; Goldan et al., 1995; Grosjean et al., 1983; Grosjean, 1982; Müller et al., 2005; Feng et al., 2004). Singh et al. (2004) measured a concentration in a remote region of 0.02 ppbv, whereas Grosjean et al. (1983) observed a MEK concentration of 11.3 ppbv in Los Angeles. Brown et al. (1994) concluded that MEK is one of the major volatile organic compounds (VOCs) in indoor air.

In addition to the gas-phase measurements, the concentrations measured in bulk water samples collected at an open station near the Bahamas reached a concentration of < 0.5 nmol L\(^{-1}\) (Zhou and Mopper, 1997). Furthermore, an enrichment of MEK in the surface micro layer was found with concentrations up to 2.28 nmol L\(^{-1}\) (Zhou and Mopper, 1997). MEK was also investigated in ice, fog, and rain samples (Grosjean and Wright, 1983). It was not found in fog but there were traces in rain water. In cloud water, a concentration of up to 650 nmol L\(^{-1}\) was measured. This is supported by van Pinxteren et al. (2005), who measured a concentration of 70 to 300 nmol L\(^{-1}\) in cloud water. These studies concluded that the liquid-phase fraction of MEK is higher than the expected fraction calculated according to the Henry constant.

The Henry constants at a temperature of 25 °C were found to vary between 7.7 and 21 M atm\(^{-1}\) in numerous studies (Buttery et al., 1969; Snider and Dawson, 1985; Ashworth et al., 1988; Zhou and Mopper, 1990; Morillon et al., 1999; Karl et al., 2002). However, Schütze and Herrmann (2004) estimated the Henry constant to be between 23 and 50 M atm\(^{-1}\), which is higher than the previous measured values found in the literature. This higher Henry constant supports the conclusion from van Pinxteren et al. (2005) and tends to support the investigation of MEK in the liquid phase as aqSOA precursor compound. AqSOA is formed through the oxidation of organic compounds in the aqueous particle phase and is often related to missing SOA sources. These missing sources are most likely responsible for the huge discrepancies between measured and calculated SOA burden. As model results usually underestimate the SOA burden (Kanakidou et al., 2005; Goldstein and Galbally, 2007), missing SOA sources have to be considered in such models to close this gap (Ervens et al., 2011; Herrmann et al., 1999; Herrmann et al., 2015).

In the present study, the reaction of MEK with OH radicals in water was investigated. Based on the experimentally obtained data, a reaction mechanism was developed to explain methylglyoxal formation. The
2. Experimental

2.1 Chemicals and standards

Cyclohexanone-2,2,6,6-d4 (98%), hydrochloric acid, and catalase from bovine liver (40000-60000 units mg\(^{-1}\) protein) were obtained from Sigma-Aldrich (Hamburg, Germany). \(\text{O}-(2,3,4,5,6\)-pentafluorobenzyl)hydroxylamine hydrochloride (≥99%), 2,3-butanedione (99%), hydroxyacetone (90%), and methylglyoxal (40% in water) were purchased from Fluka (Hamburg, Germany). Dichloromethane (Chromasolv 99.8%) and methyl ethyl ketone (99.7%) were obtained from Riedel de Haen (Seelze, Germany), and hydrogen peroxide (30% Suprapur®) was obtained from Merck KGaA (Darmstadt, Germany). Ultrapure water was used to prepare the reaction solutions for the bulk reactor experiments and the stock solutions of the authentic standard compounds (Milli-Q gradient A 10, 18.2 MΩ cm\(^{-1}\), 3 ppb TOC, Millipore, USA).

2.2 Bulk reactor experiments

The aqueous-photolysis phase of MEK was conducted in a 300 mL batch reactor using the photolysis of hydrogen peroxide (\(\text{H}_2\text{O}_2\)) as an OH radical source (Set 1). The experiments were conducted at a temperature of 298 K. For the experiments, 0.1 mmol L\(^{-1}\) of the precursor compound was mixed with 2 mmol L\(^{-1}\) of \(\text{H}_2\text{O}_2\). The solution was then irradiated at \(\lambda = 254\) nm for 4 hours to continuously generate OH radicals (500 W xenon-mercury lamp, Andover Corporation Optical bandpass filter: L.O.T. - Oriel GmbH & Co. KG, Darmstadt, Germany). To obtain time-resolved data, samples were taken once per hour (0 – 4 hours; number of repetitions \(n = 3\)) or in steps of 15 minutes (\(n = 1\)) and analyzed after derivatization using GC/MS. To avoid further reactions of the organics present in the sample with remaining \(\text{H}_2\text{O}_2\), 100 µL of catalase (4 mg mL\(^{-1}\) in water) were added to each sample. Furthermore, a set of blank experiments was conducted to exclude that (a) MEK reacts with \(\text{H}_2\text{O}_2\) (Set 2), (b) identified oxidation products originate from photolysis (Set 3), (c) the photolysis of contaminants in the \(\text{H}_2\text{O}_2\) solution results in the formation of organics (Set 4), and (d) oxidation of 2,3-butanedione or hydroxyacetone also forms methylglyoxal (Set 5/6). To determine the photolysis rate constants of 2,3-butanedione, methylglyoxal, and hydroxyacetone, the photolysis of these products was investigated as well with the setup used (Set 7). A complete overview of the experiments conducted is given in Table 1.

2.3 Sample preparation

Two types of samples were taken over a period of 4 hours. For the first type of samples, 60 µL of the reaction mixture were diluted with 2940 µL of water to avoid saturation of the GC/MS detector during the quantification of MEK, 2,3-butanedione or hydroxyacetone. For the second type of samples, 3 mL of the reaction mixture were taken and injected without any dilution to enable the identification and quantification of the formed carbonyl compounds.

Samples of all sets were derivatized with 300 µL of \(\text{o}-(2,3,4,5,6\)-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, 5 mg mL\(^{-1}\)) at room temperature (Rodigast et al., 2015). Cyclohexanone-2,2,6,6-d4 was used as an internal standard (150 µL, 100 µmol L\(^{-1}\)), and after 24 hours, a pH value of 1 was adjusted by adding hydrochloric acid (37%) to the reaction mixture. The target compounds were extracted for 30 minutes with 250 µL of dichloromethane using an orbital shaker (1500 rpm, revolutions per minutes). Finally, 1 µL of the organic phase
was used for GC/MS analysis. A 5-point calibration was performed for each chromatographic run using a series of the standard solutions (MEK, methylglyoxal, 2,3-butanedione, and hydroxyacetone) with concentrations ranging from 1 to 50 μmol L⁻¹.

2.4 Instrumentation
Derivatized carbonyl compounds were analyzed using a GC System (6890 Series Agilent Technologies, Frankfurt, Germany) coupled with an electron ionization quadrupole mass spectrometer in splitless mode at a temperature of 250 °C (Agilent 5973 Network mass selective detector, Frankfurt, Germany). They were separated with an HP-5MS UI column (Agilent J & W GC columns, 30 m × 0.25 mm × 0.25 μm) using the following temperature program: 50 °C isothermal for 2 minutes and elevated to 230 °C with 10 °C minute⁻¹. The temperature of 230 °C was held for 1 minute, and the temperature gradient ended with 320 °C, which was held constant for 10 minutes.

3. Results
3.1 Experimental results from bulk reactor
MEK was oxidized with OH radicals, and the decay of MEK was monitored by GC/MS. Fig. 1A shows the consumption of the precursor compound MEK. As can be seen, MEK was almost consumed after 180 minutes of reaction time. From the analysis of the collected samples, 2,3-butanedione, hydroxyacetone, and methylglyoxal were observed as the most dominating oxidation products. The formation of methylglyoxal from the oxidation of MEK was unexpected as it has not been reported in the literature before. Due to the relevance of methylglyoxal for aqSOA formation, its formation was comprehensively characterized in the present study.

Nevertheless, in Fig. 1B, 2,3-butanedione was found as the main oxidation product of MEK reaching a maximum yield of ≈ 29.5 ± 6.0% after 60 minutes. The small variations of the molar yields over the course of the experiment might result from slight temperature changes during the experiment despite the reactor temperature being controlled. However, the curve shape shows that the concentration of 2,3-butanedione starts to decrease after 60 minutes, indicating further reactions of 2,3-butanedione. This decrease results in a molar yield of 18.9 ± 3.9% at the end of the experiment (240 minutes).

A similar trend was observed for hydroxyacetone and methylglyoxal, as the concentration of methylglyoxal was the highest after 15 minutes (≈ 9.5%) and started to decrease afterwards. In comparison, hydroxyacetone reached the highest concentration after 60 minutes with a molar yield of 3.0 ± 2.6%. The standard deviation of the determined molar yields of hydroxyacetone was high, and therefore, only after reaction times of 60 and 120 minutes could a molar yield of hydroxyacetone be determined.
Methylglyoxal and hydroxyacetone were completely consumed at the end of the experiment. The strong decrease of the concentrations of the detected carbonyl compounds might result from the reaction with OH radicals and/or from photolysis. Both mechanisms are most likely, as it has been demonstrated that the detected carbonyl compounds react quickly with OH radicals (Lilie et al., 1968; Gligorovski and Herrmann, 2004; Doussin and Monod, 2013; Monod et al., 2005; Ervens et al., 2003; Herrmann et al., 2005; Tan et al., 2010; Stefan and Bolton, 1999) and they are prone to photolysis (Faust et al., 1997; Tan et al., 2010). The photolysis rate constants of the detected carbonyl compounds were determined in the present study because of the dependency on the setup used (Set 7; see supplement S2 for more details). Methylglyoxal and hydroxyacetone showed higher photolysis rate constants of \( k_p = 3 \times 10^{5} \text{s}^{-1} \) and \( k_p = 2 \times 10^{3} \text{s}^{-1} \) in comparison to 2,3-butanedione \( (k_p = 9 \times 10^{5} \text{s}^{-1}) \). This indicates a faster decomposition compared to 2,3-butanedione of methylglyoxal and hydroxyacetone, which showed a complete consumption at the end of the experiment (Fig. 1). 2,3-Butanedione was not completely consumed during the reaction time of 4 hours, which might be a result of the lower photolysis rate constants.

Furthermore, during the photolysis of 2,3-butanedione and hydroxyacetone, methylglyoxal was found with molar yields of \( \approx 17\% \) and \( \approx 19\% \), respectively (see Fig. S2, supplement S2). Due to the low molar yield of hydroxyacetone during the oxidation of MEK \( (\approx 3\%) \) and the slow photolysis rate constant of 2,3-butanedione, these processes are of minor importance for the methylglyoxal yield.

For 2,3-butanedione, a huge discrepancy of the rate constants for the OH radical oxidation can be found between the different literature studies. They vary by one order of magnitude in a range of \( k = 1.4 \times 10^{8} \text{M}^{-1} \text{s}^{-1} \) (Gligorovski and Herrmann, 2004) up to \( k = 1.86 \times 10^{9} \text{M}^{-1} \text{s}^{-1} \) (Doussin and Monod, 2013). Rate constants were determined between \( k = 5.3 \times 10^{8} \text{M}^{-1} \text{s}^{-1} \) and \( k = 1.1 \times 10^{9} \text{M}^{-1} \text{s}^{-1} \) for methylglyoxal (Monod et al., 2005; Ervens et al., 2003; Herrmann et al., 2005; Tan et al., 2010) and between \( k = 0.8 \times 10^{9} \text{M}^{-1} \text{s}^{-1} \) and \( k = 1.2 \times 10^{9} \text{M}^{-1} \text{s}^{-1} \) for hydroxyacetone (Stefan and Bolton, 1999; Herrmann et al., 2005). In consideration of the similar rate constant for 2,3-butanedione determined by Lilie et al. (1968) \( (k = 1.8 \times 10^{8} \text{M}^{-1} \text{s}^{-1}) \) and Gligorovski and Herrmann (2004) \( (k = 1.4 \times 10^{8} \text{M}^{-1} \text{s}^{-1}) \), 2,3-butanedione revealed a slower OH radical reaction than methylglyoxal and hydroxyacetone. This is in good agreement with the experimental results obtained in the present study.

Since 2,3-butanedione is the main oxidation product, it was necessary to investigate the contribution of 2,3-butanedione to the product distribution, especially for the formation of methylglyoxal. In the oxidation of 2,3-butanedione (Set 5), no methylglyoxal was detected in the GC/MS chromatogram over a reaction period of 240 min (Fig. 2). Consequently, a contribution of 2,3-butanedione to the methylglyoxal formation could be excluded.

Despite the low molar yield of hydroxyacetone during MEK oxidation, the oxidation of hydroxyacetone was investigated for methylglyoxal formation as well (Herrmann et al., 2005; Schaefer et al., 2012; Set 6). During the oxidation, a molar yield of 100% was found after a reaction time of 60 minutes (see supplement S3, Fig. S3). After 60 minutes of reaction time, the molar yield of methylglyoxal decreases through further reactions, as was observed during MEK oxidation. However, due to the low molar yield of hydroxyacetone \( (3.0\%) \), the oxidation has only minor importance for the observed molar yield of methylglyoxal.

To ensure methylglyoxal was only formed during the oxidation of MEK, an experiment was conducted to investigate the non-radical reaction of MEK with \( \text{H}_2\text{O}_2 \) in the dark (Set 2). During this experiment, no decomposition of MEK was observed, excluding the non-radical reaction of MEK with \( \text{H}_2\text{O}_2 \) as a source of methylglyoxal. Furthermore, the photolysis of MEK has to be considered as a source for methylglyoxal. Hence,
the photolysis of MEK was studied at \( \lambda = 254 \) nm (Set 3). As can be seen in Fig. 3, the photolysis of MEK leads to the formation of 2,3-butanedione with a molar yield of \( \approx 2.2\% \) indicating that the photolysis of MEK is an additional source. No further carbonyl compounds were detected from the photolysis of MEK, and thus, the photolysis of MEK can be excluded as a methylglyoxal source. The blank experiment (Set 4) indicated the absence of methylglyoxal as well.

In summary, the oxidation of MEK constitutes a source for methylglyoxal, and due to the high concentration of MEK in cloud water (70 – 650 nmol L\(^{-1}\); Grosjean and Wright, 1983; van Pinxteren et al., 2005), this source is of atmospheric relevance. Due to the molar yields of 9.5\% for methylglyoxal, 29.5\% for 2,3-butanedione, and 3.0\% for hydroxyacetone, \( \approx 42\% \) of the oxidation products of MEK could be elucidated in the present study with only these carbonyl compounds (Table 2). This highlights the importance of carbonyl compounds for the aqueous phase chemistry. Based on the experimental findings, a reaction mechanism was developed to describe the formation of methylglyoxal (Fig. 4).

### 3.2 Oxidation mechanism and model description

According to the structure of MEK, the OH radical attack can proceed at three different positions (Fig. 4; H-atoms at carbons 1, 3, and 4). For the present study, only the attack at carbons 3 and 4 is considered because these processes lead to the formation of the observed products (Fig. 4). Note that the abstraction of a hydrogen atom at carbon 3 leads to a secondary alkyl radical (A), whereas at the terminal carbon, a primary alkyl radical is formed (B). The branching ratios for the formation of the primary and secondary alkyl radicals will be discussed in detail in the next section (Sect. 3.2.1).

The primary and secondary alkyl radicals react rapidly with oxygen to form alkylperoxy radicals. The alkylperoxy radical recombines to a tetroxide and reacts further in three different ways, including the formation of an carbonyl compound and an alcohol (i), the formation of two carbonyl compounds and \( \text{H}_2\text{O}_2 \) (ii), and the decomposition into an alkoxy radical (iii) (von Sonntag and Schuchmann, 1991). The decomposition of the tetroxide into a peroxide and oxygen was not considered further due to the minor importance of this process (von Sonntag and Schuchmann, 1997). The secondary and primary alkylperoxy radicals can react with \( \text{HO}_2 \) forming organic hydroperoxides. The organic peroxyxides react with OH radicals or photolyze, resulting in the formation of an alkyl radical or tetroxide that can react further, as described before through pathways i–iii. The described mechanism was included in a COPASI model to examine the developed oxidation mechanism, the decomposition of the precursor compound, and the formation of the observed products. Table 3 shows the considered reactions, the rate constants, and their references. Only the reactions leading to the formation of the products identified are discussed in detail.

Surprisingly, the products 3-oxobutanal and hydroxybutanone were not observed during the experiments. Since 3-oxobutanal contains two carbonyl groups, two derivatives can be formed, including one (mass to charge ratio \( m/z \) 281; \( \text{M}^+ \)) or two (\( m/z \) 476; \( \text{M}^+ \)) derivatized groups. Hydroxybutanone has one carbonyl group with a derivatized \( m/z \) 283 (\( \text{M}^+ \)). As can be seen in Fig. 5, \( m/z \) 283 was not found in the extracted ion chromatogram (EIC). Furthermore, \( m/z \) 281 and 476 can be detected in the EIC of the bulk reactor samples, but they can also be found in the EIC of the authentic standard compounds. The sample of the authentic standard compounds does not contain hydroxybutanone and 3-oxobutanal. According to the comparison of the EIC of the bulk reactor samples and the authentic standard, it can be assumed that \( m/z \) 281 and 476 are fragments of the internal standard and 2,3-butandione. No additional signals in the EIC of the samples were detected at \( m/z \) 281, 283, and 476, and thus, 3-
oxobutanal and hydroxybutanone are not formed during the experiment. Hence, their formation pathways were excluded from the model.

3.2.1 HO\textsubscript{0} chemistry and OH radical attack

The relevant reactions for HO\textsubscript{0} chemistry according to R1-R6 are included in the mechanism. OH radicals were formed through the photolysis of H\textsubscript{2}O\textsubscript{2} at $\lambda = 254$ nm with measured photolysis rate constants of $k_0 = 7.6 \times 10^{-6}$ s\textsuperscript{-1} (R1, see supplement S1). The formed OH radicals react further with MEK in a first oxidation step, leading to the formation of a primary (R7) and secondary alkyl radical (R8). The rate constants were postulated by Herrmann et al. (2005) to be $k = 1.17 \times 10^8$ M\textsuperscript{-1} s\textsuperscript{-1} and $k = 1.3 \times 10^8$ M\textsuperscript{-1} s\textsuperscript{-1} for the formation of the primary and secondary alkyl radicals, respectively. This is in good agreement with the model study by Sebbar et al., who postulated that the H-atom abstraction most likely proceeds at the secondary carbon of MEK (Sebbar et al., 2014; Sebbar et al., 2011) due to the lower C-H bond dissociation energy ($\approx 377$ kJ mol\textsuperscript{-1}, C4) in comparison to the primary carbon atom ($\approx 423$ kJ mol\textsuperscript{-1}, C3). In the present study, a rate constant $k = 1.5 \times 10^8$ M\textsuperscript{-1} s\textsuperscript{-1} (Gligorovski and Herrmann, 2004) was used, and the branching ratio was varied from 60/40 to 10/90 for the primary/secondary H-atom abstraction.

The results are shown in Fig. 6 and discussed based on the molar yields of the products. As can be seen for 2,3-butanedione (Fig. 6A), a branching ratio of 60% for the primary H-atom abstraction and 40% for the secondary H-atom abstraction leads to lower molar yields, whereas the molar yields start to increase with an increasing fraction of secondary H-atom abstraction. According to the mechanism (Fig. 4), 2,3-butanedione is only formed via secondary H-atom abstraction, and thus, it is feasible to reach higher molar yields with a higher fraction of secondary H-atom abstraction. However, with an increasing secondary H-atom abstraction, the experimentally determined concentration was increasingly overestimated, especially at the beginning of the experiment. After 60 minutes of reaction time, the highest experimentally determined molar yield (29.5 ± 6.0%) was overestimated by a factor of $\approx 2$ with a ratio of 10/90 for primary/secondary H-atom abstraction (molar yield $\approx 49.9\%$), whereas a ratio of 60/40 resulted in reasonably good agreement (molar yield $\approx 23.7\%$). Based on this, a branching ratio of 60/40 for primary/secondary H-atom abstraction was used in the present model.

In contrast, methylglyoxal molar yields were increasingly underestimated with an increasing fraction of secondary H-atom abstraction (Fig. 6B). Thus, after 15 minutes of reaction time, the experimental molar yield ($\approx 9.5\%$) was underestimated by a factor of $\approx 5$ with a higher fraction of the secondary H-atom abstraction (molar yield $\approx 2\%$). In comparison with a ratio of 60/40 for primary/secondary H-atom abstraction, a molar yield of $\approx 11.4\%$ was observed, which is in good agreement with the experiment. Overall, the branching ratio of 60/40 (primary/secondary H-atom abstraction) resulted in reasonable agreement for 2,3-butanedione and in an excellent conformity to the methylglyoxal molar yields. This shows the importance of the primary H-atom abstraction as the main decomposition pathway of MEK and thus for methylglyoxal formation.

The primary and secondary alkyl radicals react further with oxygen (R9/R21) with a rate constant of $k = 3.1 \times 10^9$ M\textsuperscript{-1} s\textsuperscript{-1} (Zegota et al., 1986; Glowa et al., 2000), which was reported for the formation of acetonylperoxy radicals. The rate constants of the acetonylperoxy radical were used for the formation of the primary alkylperoxy radical (R9) and further reactions of the alkylperoxy radical because of their structural similarity. They were also applied by Glowa et al. (2000) for the formation of the secondary alkylperoxy radical of MEK. Further reactions of the primary and secondary alkylperoxy radicals resulting in different oxidation products will be discussed in detail in the following section (Sect. 3.2.2 and 3.2.3).
3.2.2 Oxidation of MEK leading to the formation of methylglyoxal and hydroxyacetone

Only the formation of the alkoxy radical (iii; R10) leads to the formation of methylglyoxal. The alkoxy radical further reacts rapidly with oxygen into an acetoxyperoxy radical under elimination of formaldehyde. The acetoxyperoxy radicals can recombine again to form a tetroxide (Schaefer et al., 2012). The latter is able to decompose through pathways i–iii, which are illustrated in R11–R13. Consequently, the decomposition of the tetroxide can explain the formation of hydroxyacetone and methylglyoxal (R11; \( k = 2 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \); Zegota et al., 1986), methylglyoxal (R12; \( k = 4 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \); Zegota et al., 1986), and methylglyoxal and hydrogen peroxide

(R13; \( k = 4 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \); Zegota et al., 1986; Schaefer et al., 2012).

In addition to the discussed pathway, the primary alkylperoxy radical has the opportunity to react with HO\(_2\) instead of the recombination, forming an organic hydroperoxide (R14). The rate constant was reported by von Sonntag and Schuchmann (1991) to be from \( 10^7 \text{ M}^{-1} \text{s}^{-1} \) up to \( 10^9 \text{ M}^{-1} \text{s}^{-1} \). For the primary alkylperoxy radical, \( k = 1 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \) was used as it led to the best agreement of the experimental data and the model results. The formed peroxide can react with OH radicals (R15) or photolyze (R16). The same rate constant \( (k = 2.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1}) \) as that for the OH radical oxidation of H\(_2\)O\(_2\) was used for R15 due to a lack of literature data. According to the assumption by Monod et al. (2007), the rate constant for the photolysis of the formed peroxide (R16) was defined to be 1/10 of the photolysis rate constants of hydrogen peroxide. Thus, a photolysis rate constant of \( k_p = 7.6 \times 10^{-7} \text{ s}^{-1} \) was included in the model. This was used as a first approximation due to a lack of literature data for the formed hydroperoxides. The photolysis of the organic peroxide leads to the formation of formaldehyde, OH radicals, and an acetonyl radical, which reacts further with oxygen (R17) to form an acetoxyperoxy radical \( (k = 3.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}) \); Zegota et al., 1986; R19) and subsequently methylglyoxal (R18 – 20).

3.2.3 Oxidation of MEK leading to the formation of methylglyoxal and 2,3-butanedione

As described for the primary alkylperoxy radical, the secondary alkylperoxy radical recombines and forms a tetroxide. This reacts to form either (i) 2,3-butanedione and acetoin (R22) or (ii) 2,3-butanedione and hydrogen peroxide (R23) and is considered with rate constants of \( k = 2.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) and \( k = 4.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) (Glowa et al., 2000). The tetroxide can decompose into an alkoxy radical as well (iii) and react further to form 2,3-butanedione, methylglyoxal, a methyl radical, and HO\(_2\) (R24; \( k = 5 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \); Glowa et al., 2000). The rate constants postulated by Glowa et al. (2000) are derived from the branching ratios determined by Zegota et al. (1986) for acetone. Glowa et al. (2000) simulated the concentration profiles of MEK and the corresponding products and postulated the rate coefficient used in the present model study. The secondary alkylperoxy radical also has the opportunity to react with HO\(_2\) to form an organic peroxide (R25), which photolyzes (R26; \( k = 7.6 \times 10^{-7} \text{ s}^{-1} \)) or reacts further with OH radicals (R28; \( k = 2.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \)). Through the photolysis, an alkoxy radical was formed that leads to methylglyoxal, 2,3-butanedione, a methyl group, and HO\(_2\) radicals (R27; \( k = 4 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \)).

3.2.4 Further reactions and photolysis of formed oxidation products and MEK

The products 2,3-butanedione, methylglyoxal, and hydroxyacetone positively identified by GC/MS analysis might also react further, forming a variety of oxidation products. The rate constant of methylglyoxal with OH radicals is given in the range of \( k = 5.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) to \( k = 1.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) (Monod et al., 2005; Ervens et al., 2003; Herrmann et al., 2005; Tan et al., 2010), whereas a rate constant of \( k = 5.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) (R29; Monod et al., 2005)

21
leads to the best agreement between the experimental data and the model results. In comparison, the rate constants
determined by Ervens et al. (2003), Herrmann et al. (2005), and Tan et al. (2010) resulted in an underestimation
of the molar yield. Methylglyoxal also has the opportunity to photolyze. The photolysis is included with
\( k_p = 3 \times 10^{-5} \text{ s}^{-1} \) (R30) in the present model.

2,3-Butanedione is also prone to OH radical oxidation and photolysis. As discussed, a huge discrepancy
exists in the rate constants for the reaction of OH radicals with 2,3-butanedione (Lilie et al., 1968; Doussin and
Monod 2013; Gligorovski and Herrmann, 2004). In the present study, the value of \( k = 1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) (R31)
determined by Gligorovski and Herrmann (2004) was used. The higher rate constants reported by Lilie et al.
(1968) and Doussin and Monod (2013) resulted in consumption that was too fast. The photolysis was included
with a rate constant of \( k_p = 9 \times 10^8 \text{ s}^{-1} \) in the COPASI model (R32). It should be mentioned that methylglyoxal
was formed during the photolysis of 2,3-butanedione. However, the photolysis was too small to contribute
significantly to methylglyoxal formation. For more details, see supplement S2.

The oxidation of hydroxyacetone with OH radicals was also considered in the model study with a rate
constant of \( k = 8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) (R33; Stefan and Bolton, 1999). During the experiment, methylglyoxal was formed
with 100% molar yield. Thus, the reaction of hydroxyacetone to methylglyoxal was included in the model study.
The photolysis of hydroxyacetone was measured with a rate of \( k_p = 2 \times 10^5 \text{ s}^{-1} \), leading to methylglyoxal with a
molar yield of \( \approx 19\% \) (R34). The photolysis rate constant of MEK was measured as \( k_p = 5 \times 10^5 \text{ s}^{-1} \) (see
supplement S2, Fig. S1). During the experiment, 2,3-butanedione was found with a molar yield of 2.2%. Thus,
the reaction of MEK leading to 2,3-butanedione was included in the model study (R35).

### 3.3 Model results and comparison with the experimental dataset

The described reactions are included in a model, and the decomposition of MEK and molar yields of
formed products were compared to the experimentally obtained data (Fig. 7). The model was not validated with
the time course of hydroxyacetone due to the high standard deviation of the experimental results. The comparison
of the model study and the experiment showed very good agreement for the consumption of MEK (Fig. 7A).
There is also good agreement for the formation of methylglyoxal and limited agreement for the molar yields of
2,3-butanedione. The initial high molar yield of 2,3-butanedione is reflected well (Fig. 7B). Thus, after 60 minutes
of reaction time, molar yields of 23.7% in the model study and 29.5 ± 6.0% in the experiment were reached. Under
consideration of the standard deviation, this is in good agreement with the COPASI model.

The determined molar yields up to a reaction time of 120 minutes showed very good conformity with the
experiment (18.2% and 22.1 ± 9.0%). The temporal behavior shows that the determined molar yield in the model
study is somewhat lower towards the end of the experiment. Hence, it is possible that there are other reaction
pathways that lead to higher molar yields of 2,3-butanedione at the end of the experiment, which are not
considered in the model study as of now. Good agreement between the model results and experiment was observed
for methylglyoxal (Fig. 7C). The curve shapes are very similar, and hence, fast formation and decomposition of
methylglyoxal were found in the model study and in the experiment. After 15 minutes of reaction time, a molar
yield of 9.5% was found in the experiment. In comparison, the model study resulted in a molar yield of 11.4%,
which is in good agreement with the experiment and validates the COPASI model.
4. Atmospheric relevance

The sources of methylglyoxal in the aqueous phase are thus-far not fully elucidated. Methylglyoxal can originate in the atmospheric aqueous phase through i) uptake from the gas phase, and/or ii) formation in the aqueous phase. The importance of the uptake from the gas into the aqueous phase is discussed in the literature but large discrepancies can be found. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under varying relative humidity. It was found that the uptake was not relevant for methylglyoxal even under high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of $\gamma = 7.6 \times 10^{-3}$ on acidic solution. They found an irreversible uptake, which decreases with increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets $\gamma = 2.9 \times 10^{-3}$, which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be $\gamma = 1.47 - 2.92 \times 10^{-3}$. Overall, $\gamma$ was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) showing the discrepancies between the different studies available in literature.

The in-situ formation of methylglyoxal in the aqueous phase could be an important source as well (Blando and Turpin, 2000; Sempere and Kawamura 1994). Within the present study, MEK was found as a new precursor compound for methylglyoxal in the aqueous phase yielding methylglyoxal with a molar yield of 9.5%. Although the Henry constant of MEK (up to $K_H = 50$ M atm$^{-1}$, Schütze and Herrmann, 2004) is lower compared to methylglyoxal ($K_H = 3.7 \times 10^4$ M atm$^{-1}$, Betterton and Hoffmann, 1988), van Pinxteren et al. (2005) found higher concentrations in cloud water as it was expected. Thus, the phase transfer of MEK from the gas in the aqueous phase could be more important as currently derived from the available Henry constants. Besides the phase transfer, the in-situ formation of MEK in aqueous phase formation might also represents an important source.

As, the oxidation of MEK yielding methylglyoxal has not been studied much before, it should be considered as a formation process of methylglyoxal.

5. Summary

In the present study, MEK was identified as a new source for methylglyoxal in the aqueous phase. It was demonstrated that methylglyoxal originates directly from MEK oxidation and not from side reactions such as photolysis or non-radical reactions. A molar yield of $\approx 9.5\%$ was determined during the oxidation. Based on the experimental results, a reaction mechanism could be developed. The calculations with a COPASI model supported the experimental results and confirm MEK as a precursor compound for methylglyoxal in aqueous medium.

Further carbonyl compounds could be identified and quantified. 2,3-Butanedione was found as the main oxidation product (molar yield $\approx 29.5\%$) and was formed during the photolysis of MEK as well. As a further oxidation product, hydroxyacetone was identified and was formed with a molar yield of $\approx 3.0\%$ during the oxidation of MEK.

The oxidation mechanism of MEK in aqueous solution was elucidated, and MEK was demonstrated to be as a precursor compound for methylglyoxal in the aqueous phase. Regarding the important role of methylglyoxal for the aqSOA formation, MEK has to be considered for aqSOA as well, which could be a next step in reducing the underestimation of the SOA burden by model studies.
5. Acknowledgements

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References


Grosjean, D., and Wright, B.: Carbonyls in urban fog, ice fog, cloudwater and rainwater, Atmospheric Environment, 17, 2093-2096, 10.1016/0004-6981(83)90368-2, 1983.


Sebbar, N., Bozzelli, J. W., and Bockhorn, H.: Reactivity, thermochemistry and kinetics of 2-butane radicals: CH2C(=O)CHCH3, CH3C(=O)CHCH3 and CH3C(=O)CH2CH3, 2011.


Ware, G. W.: Methyl ethyl ketone, Reviews of Environmental Contamination and Toxicology, 106, 165-174, 1988.


Table 1: Conducted experiments in the bulk reactor.

<table>
<thead>
<tr>
<th>Number of experiment</th>
<th>Type of experiment</th>
<th>Concentration precursor compound [mmol L(^{-1})]</th>
<th>Concentration H(_2)O(_2) [mmol L(^{-1})]</th>
<th>UV light ((\lambda = 254) nm)</th>
<th>Reaction time [hours]</th>
<th>Number of repetition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxidation of MEK</td>
<td>0.1</td>
<td>2</td>
<td>✓</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Reaction of H(_2)O(_2) with MEK</td>
<td>0.1</td>
<td>2</td>
<td>-</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Photolysis of MEK</td>
<td>0.1</td>
<td>-</td>
<td>✓</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Photolysis of H(_2)O(_2)</td>
<td>-</td>
<td>2</td>
<td>✓</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Oxidation of 2,3-butanedione</td>
<td>0.1</td>
<td>2</td>
<td>✓</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>Oxidation of hydroxyacetone</td>
<td>0.1</td>
<td>2</td>
<td>✓</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>Photolysis of 2,3-butanedione, hydroxyacetone, methylglyoxal</td>
<td>0.1</td>
<td>-</td>
<td>✓</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

MEK: Methyl ethyl ketone

Figure 1: Consumption of MEK (A) during the oxidation with OH radicals and time-resolved formation of the products methylglyoxal (B), 2,3-butanedione (B), and hydroxyacetone (B).
Figure 2: GC/MS chromatogram of oxidation of 2,3-butanedione (a,b,c) and the authentic standard compounds 2,3-butanedione (a,b,c) and methylglyoxal (d,e).

Figure 3: Photolysis of MEK and time-resolved formation of 2,3-butanedione.
Table 2: Maximal molar yields of the oxidation products.

<table>
<thead>
<tr>
<th>Oxidation product</th>
<th>Maximal molar yield (± standard deviation) in %</th>
<th>Reaction time in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-Butanedione</td>
<td>29.5 ± 6.0</td>
<td>60</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>9.5</td>
<td>15</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>3.0 ± 2.6</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 4: Recommendation of an oxidation mechanism of MEK for the formation of 2,3-butanedione, hydroxyacetone and methylglyoxal.
Table 3: Reaction mechanism and rate constants for the modelling of the experiment with COPASI.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant $k$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$H_2O_2 + H_2O \rightarrow 2 OH$</td>
<td>$7.6 \times 10^9 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R2</td>
<td>$2 OH \rightarrow H_2O_2$</td>
<td>$3.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R3</td>
<td>$OH + H_2O_2 \rightarrow HO_2 + H_2O$</td>
<td>$2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R4</td>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
<td>$6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R5</td>
<td>$2 HO_2 \rightarrow H_2O_2 + O_2$</td>
<td>$9.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R6</td>
<td>$H_2O_2 + OH \rightarrow OH + H_2O$</td>
<td>$0.5 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R7</td>
<td>$CH_3C(O)CH_2 + OH \rightarrow CH_3C(O)CHCH_3 + H_2O$</td>
<td>$9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R8</td>
<td>$CH_3C(O)CH_2 + OH \rightarrow CH_3C(O)CHCH_3 + H_2O$</td>
<td>$6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R9</td>
<td>$CH_3C(O)CH_2 + O_2 \rightarrow CH_3C(O)CH(OH)CH_2$</td>
<td>$3.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R10</td>
<td>$2 CH_3C(O)CHCHO + O_2 \rightarrow 2 CH_3C(O)CH_2O_2 + 2 HCHO$</td>
<td>$4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R11</td>
<td>$2 CH_3C(O)CHCHO \rightarrow CH_3C(O)CH_2O_2 + CH_3C(O)CH(OH) + O_2$</td>
<td>$2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R12</td>
<td>$2 CH_3C(O)CHCHO \rightarrow 2 HO_2 + 2 CH_3C(O)C(O)H$</td>
<td>$4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R13</td>
<td>$2 CH_3C(O)CHCHO \rightarrow 2 CH_3C(O)C(O)H + H_2O_2$</td>
<td>$4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R14</td>
<td>$CH_3C(O)CH_2O_2 + HO_2 \rightarrow CH_3C(O)CHCH_2O_2 + O_2$</td>
<td>$1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R15</td>
<td>$CH_3C(O)CHCHOOH + OH \rightarrow Product$</td>
<td>$2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R16</td>
<td>$CH_3C(O)CHCHOOH \rightarrow OH + HCHO + CH_3C(O)CH_2$</td>
<td>$7.6 \times 10^7 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R17</td>
<td>$CH_3C(O)CHCHO + O_2 \rightarrow CH_3C(O)CH_2O_2$</td>
<td>$3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R18</td>
<td>$2 CH_3C(O)CHCHO \rightarrow CH_3C(O)CH_2O_2 + CH_3C(O)C(O)H + O_2$</td>
<td>$2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R19</td>
<td>$2 CH_3C(O)CHCHO \rightarrow H_2O_2 + 2 CH_3C(O)C(O)H$</td>
<td>$4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R20</td>
<td>$2 CH_3C(O)CHCHO \rightarrow 2 CH_3C(O)C(O)H + HO_2$</td>
<td>$4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R21</td>
<td>$2 CH_3C(O)CHCHO \rightarrow CH_3C(O)CHCHO + O_2$</td>
<td>$3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R22</td>
<td>$2 CH_3C(O)CHCHO \rightarrow 2 CH_3C(O)CHCHO + 2 CH_3C(O)C(O)H$</td>
<td>$2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R23</td>
<td>$2 CH_3C(O)CHCHO \rightarrow H_2O_2 + 2 CH_3C(O)C(O)H$</td>
<td>$4.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R24</td>
<td>$2 CH_3C(O)CHCHO \rightarrow CH_3C(O)CHCHO + 2 CH_3C(O)C(O)H + CH_3 + HO_2$</td>
<td>$5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R25</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)CH_2 + O_2$</td>
<td>$1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R26</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)CH_2 + OH$</td>
<td>$7.6 \times 10^7 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R27</td>
<td>$2 CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)CH_2 + CH_3 + HO_2$</td>
<td>$4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R28</td>
<td>$CH_3C(O)CHOOOHCH_3 + O_2 \rightarrow CH_3C(O)CH_2 + CH_3 + HO_2$</td>
<td>$2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R29</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow Product$</td>
<td>$5.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R30</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow Product$</td>
<td>$3 \times 10^7 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R31</td>
<td>$CH_3C(O)CH_2 + OH \rightarrow Product$</td>
<td>$1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R32</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)$</td>
<td>$9 \times 10^6 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R33</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)$</td>
<td>$8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R34</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)$</td>
<td>$2 \times 10^6 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>R35</td>
<td>$CH_3C(O)CH_2 + HO \rightarrow CH_3C(O)CH(OH)$</td>
<td>$5 \times 10^6 \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>
Figure 5: Extracted ion chromatogram (EIC) of m/z 281 M⁺, m/z 476 M⁺ and m/z 283 M⁺ during the oxidation of MEK and EIC of the authentic standard compounds.

Figure 6: Comparison of the molar yields of 2,3-butanedione (A) and methylglyoxal (B) for the model and experimental results using different branching ratios of the primary/secondary H-atom abstraction varied between 60/40 up to 10/90.
Figure 7: Comparison of the model and experimental results for MEK (A), 2,3-butanedione (B), and methylglyoxal (C).
Supplement

S1 Determination of photon flux of Xe/Hg lamp and the photolysis rate constants of H$_2$O$_2$

The photon flux of the 500-W Xe/Hg lamp used in the experimental setup was determined with ferrioxalate actinometry (Hatchard and Parker, 1956). For this method, two types of solutions were prepared. Solution 1 contained 0.006 mol L$^{-1}$ of K$_3$Fe(C$_2$O$_4$)$_3$ in 0.05 mol L$^{-1}$ of H$_2$SO$_4$ and was made under red light in the absence of oxygen to avoid Fe$^{2+}$ formation. Solution 2 contained 7.5 mL of phenanthroline (5 × 10$^{-3}$ mol L$^{-1}$) and 1 mL of acetate solution. The acetate solution was made of 0.6 mol L$^{-1}$ of sodium acetate trihydrate and 0.17 mol L$^{-1}$ of H$_2$SO$_4$ in water. To determine the photon flux, 300 mL of solution 1 was filled in the bulk reactor and illuminated ($\lambda = 254$ nm). In steps of 5 minutes, 2 mL of the solution were collected from the bulk reactor and mixed with solution 2. This mixture was allowed to react for 30 minutes. The absorption was measured with UV/Vis spectroscopy at $\lambda = 510$ nm. Based on the absorption, the photon flux was calculated with $q = 4.94 \times 10^{-9}$ mol s$^{-1}$ (q = 2.96 molecules s$^{-1}$). Using the photon flux, the decomposition rate of H$_2$O$_2$ was calculated according to Eq. (S1):

$$\frac{d[H_2O_2]}{dt} = \frac{q \times \theta}{V \times N_A} \times (1 - 10^e \times c \times d) \quad \text{Eq. (1)}$$

$q$  Photon flux [molecules s$^{-1}$]
$\theta$  Quantum yield H$_2$O$_2$ (Kwon and Kwon, 2010)
$V$  Reaction volume [L]
$N_A$  Avogadro constant [molecules mol$^{-1}$]
$e$  Extinction coefficient H$_2$O$_2$ [L mol$^{-1}$ cm$^{-1}$]
$c$  Concentration H$_2$O$_2$ [mol L$^{-1}$]
$d$  Optical path length [cm]

Based on the decay of H$_2$O$_2$, a photolysis rate constant of $k_{PH2O2} = 7.6 \times 10^{-6}$ s$^{-1}$ was calculated according to Eq. (S2):

$$k_{PH2O2} = \frac{d[H_2O_2]}{c dt} \quad \text{Eq. (2)}$$
Photolysis rate constants were determined using the decay of the respective precursor compound (MEK, 2,3-butanedione, hydroxyacetone, and methylglyoxal). The photolysis rate constants were determined by plotting the logarithmic concentration of the precursor compound against the reaction time in seconds. According to the linear regression \(y = mx + n\), the photolysis rate constants correspond to the slope of the linear fit \(m\). The results are illustrated in Fig. S1.

For MEK, 2,3-butanedione, methylglyoxal, and hydroxyacetone, the photolysis rate constants were determined with \(k_{p,\text{MEK}} = 5 \times 10^{-5} \text{ s}^{-1}\), \(k_{p,\text{Methylglyoxal}} = 3 \times 10^{-5} \text{ s}^{-1}\), \(k_{p,\text{Hydroxyacetone}} = 2 \times 10^{-5} \text{ s}^{-1}\), and \(k_{p,2,3-\text{Butanedione}} = 9 \times 10^{-6} \text{ s}^{-1}\). During the photolysis of 2,3-butanedione and hydroxyacetone, methylglyoxal was formed with molar yields of \(\approx 17.0\%\) and \(19.5\%\) (Fig. S2).
Figure S2: Formation of methylglyoxal due to the photolysis of hydroxyacetone and 2,3-butanedione. These two additional methylglyoxal sources were included in the model as well.

S 3 Oxidation of hydroxyacetone

The oxidation of hydroxyacetone was investigated to determine its contribution to the formation of methylglyoxal during the oxidation of MEK (Fig. S3). The contribution of the oxidation of 2,3-butanedione to the methylglyoxal formation is discussed in the manuscript.

Figure S3: Oxidation of hydroxyacetone and formation of methylglyoxal.

During the oxidation, hydroxyacetone was completely consumed after a reaction time of 240 minutes. After 60 minutes, methylglyoxal was formed with a molar yield of ≈ 100%. Afterwards, the concentration of methylglyoxal starts to decrease and resulted in complete consumption at the end of the experiment. It can be concluded that hydroxyacetone is an important source of methylglyoxal. Notably, hydroxyacetone was formed in the present study with a molar yield of ≈ 3.0% (1.9 µmol L⁻¹). Such a low concentration cannot explain the huge amount of methylglyoxal formed from the oxidation of MEK. Based on this, it can be stated that the oxidation of hydroxyacetone has only a small contribution to the methylglyoxal formation.
References
