Responses to Referee #2:

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.

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 alkylperoxy 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 $[RO_2]/[HO_2]$ the formation of organic peroxides might become of minor importance. In

addition, if RO_2 radical concentration is not sufficient side reactions like recombination of HO_2 radicals (R5) or the reaction of HO_2 radicals with OH radicals (R4) and H_2O_2 (R6) get more importance. This will lead to additional sinks for OH and HO_2 radicals.
Furthermore, if the concentrations of MEK or H_2O_2 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 $k = 0.490 \pm 0.005 \times 10^{-9}$ M^{-1} s^{-1} at 1.5 °C to $k = 1.35 \pm 0.07 \times 10^{-9}$ M^{-1} s^{-1} at 66.5 °C (Table 2).

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

Henry constant [M atm^{-1}]^{a}	**Temperature [°C]**	**Rate constant × 10^{-9} [M^{-1} s^{-1}]**	**Temperature [°C]**
49.0 ± 0.8	10	0.490 ± 0.005	1.5
19.8 ± 1.4	25	0.590 ± 0.001	13.5
14.1 ± 0.2	30	0.734 ± 0.008	24.4
10.9 ± 0.5	35	0.936 ± 0.009	41.5
		1.35 ± 0.07	66.5

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 $K_H = 49 \pm 0.8$ M atm^{-1} at 0°C to $K_H = 7.1 \pm 0.7$ 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.

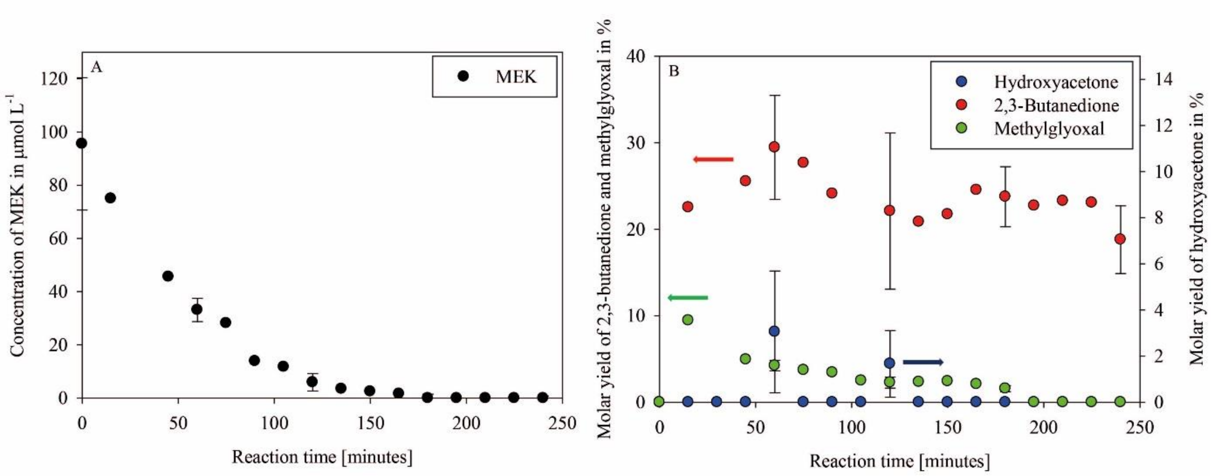
In summary, the influence of the temperature cannot be finally estimated because of the contrary dependency of the Henry constant and the rate constant for the OH radical oxidation.

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 butanedione (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:

Docherty, K. S., and Ziemann, P. J.: Effects of Stabilized Criegee Intermediate and OH Radical Scavengers on Aerosol Formation from Reactions of β-Pinene with O_3, Aero. Sci. Technol, 37, 877-891, 2003.

Keywood, M. D., Kroll, J. H., Varutbangkul, V., Bahreini R., Flagan, R. C., and Seinfeld, J. H.: Secondary Organic Aerosol Formation from Cyclohexene Ozonolysis: Effect of OH Scavenger and the Role of Radical Chemistry, Environ. Sci. Technol, 38, 3343-3350, 2004.

Mezyk, S. P.: Rate constant and activation energy determination for reaction of e^-(aq) and OH with 2-butanone and propanal, Can. J. Chem., 72, 116 – 1119, 1994.

Zhou, X. L., and Mopper, K.: Apparent partition-coefficients of 15 carbonyl-compounds between air and seawater and between air and fresh-water – implications for air sea exchange, Environ. Sci. Technol., 24, 1864–1869, 1990.

The following changes were made to the manuscript

Page 31895 Line 8: The sentence *"The experiments were conducted at a temperature of 298 K."* 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 31930: 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

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."*