

Supplement of Atmos. Chem. Phys., 16, 2689–2702, 2016  
<http://www.atmos-chem-phys.net/16/2689/2016/>  
doi:10.5194/acp-16-2689-2016-supplement  
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Atmospheric  
Chemistry  
and Physics  
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*Supplement of*

## **A new source of methylglyoxal in the aqueous phase**

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## 1 S 1 Determination of photon flux of Xe/Hg lamp and the photolysis rate constants of H<sub>2</sub>O<sub>2</sub>

2 The photon flux of the 500-W Xe/Hg lamp used in the experimental setup was determined with ferrioxalate  
3 actinometry (Hatchard and Parker, 1956). For this method, two types of solutions were prepared. Solution 1  
4 contained 0.006 mol L<sup>-1</sup> of K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> in 0.05 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub> and was made under red light in the absence of  
5 oxygen to avoid Fe<sup>2+</sup> formation. Solution 2 contained 7.5 mL of phenanthroline (5 × 10<sup>-3</sup> mol L<sup>-1</sup>) and 1 mL of  
6 acetate solution. The acetate solution was made of 0.6 mol L<sup>-1</sup> of sodium acetate trihydrate and 0.17 mol L<sup>-1</sup> of  
7 H<sub>2</sub>SO<sub>4</sub> in water. To determine the photon flux, 300 mL of solution 1 was filled in the bulk reactor and illuminated  
8 (λ = 254 nm). In steps of 5 minutes, 2 mL of the solution were collected from the bulk reactor and mixed with  
9 solution 2. This mixture was allowed to react for 30 minutes. The absorption was measured with UV/Vis  
10 spectroscopy at λ = 510 nm. Based on the absorption, the photon flux was calculated with q = 4.94 × 10<sup>-9</sup> mol s<sup>-1</sup>  
11 (q = 2.96 molecules s<sup>-1</sup>). Using the photon flux, the decomposition rate of H<sub>2</sub>O<sub>2</sub> was calculated according to  
12 Eq. (S1):

$$13 \quad \frac{d[H_2O_2]}{dt} = \frac{q \times \theta}{V \times N_A} \times (1 - 10^{\varepsilon \times c \times d}) \quad \text{Eq. (1)}$$

14	q	Photon flux [molecules s <sup>-1</sup> ]
15	θ	Quantum yield H <sub>2</sub> O <sub>2</sub> (Kwon and Kwon, 2010)
16	V	Reaction volume [L]
17	N <sub>A</sub>	Avogadro constant [molecules mol <sup>-1</sup> ]
18	ε	Extinction coefficient H <sub>2</sub> O <sub>2</sub> [L mol <sup>-1</sup> cm <sup>-1</sup> ]
19	c	Concentration H <sub>2</sub> O <sub>2</sub> [mol L <sup>-1</sup> ]
20	d	Optical path length [cm]

21 Based on the decay of H<sub>2</sub>O<sub>2</sub>, a photolysis rate constant of k<sub>pH<sub>2</sub>O<sub>2</sub></sub> = 7.6 × 10<sup>-6</sup> s<sup>-1</sup> was calculated according to  
22 Eq. (S2):

$$23 \quad k_{pH_2O_2} = \frac{\frac{d[H_2O_2]}{dt}}{c} \quad \text{Eq. (2)}$$

## S 2 Photolysis rate constants of MEK, 2,3-butanedione, hydroxyacetone and methylglyoxal

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.

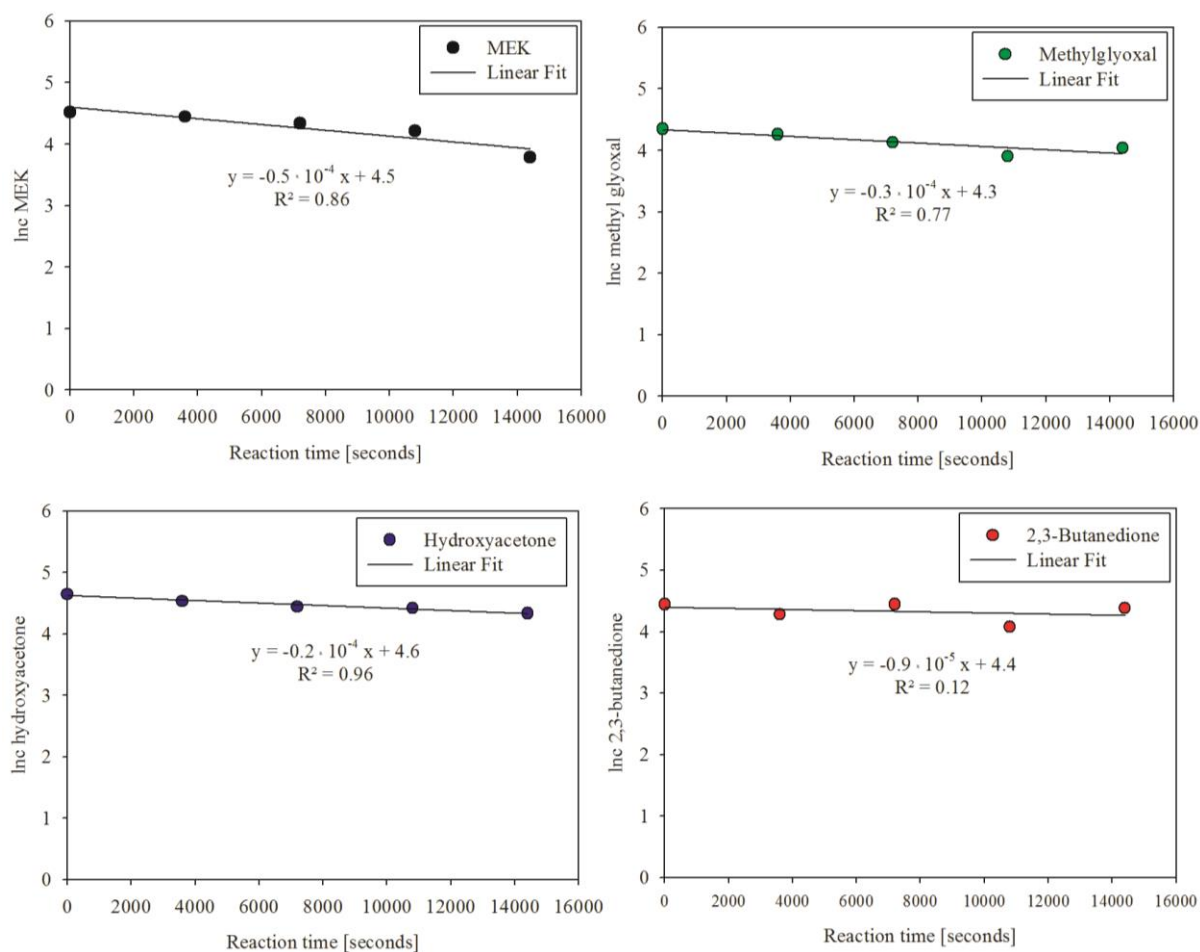


Figure S1: Photolysis rate constants of MEK, methylglyoxal, hydroxyacetone, and 2,3-butanedione determined through the slope  $m$  of the linear fit.

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  $k_{p2,3\text{-Butanedione}} = 9 \times 10^{-6} \text{ s}^{-1}$ .

During the photolysis of 2,3-butanedione and hydroxyacetone, methylglyoxal was formed with molar yields of  $\approx 17.0\%$  and  $19.5\%$  (Fig. S2).

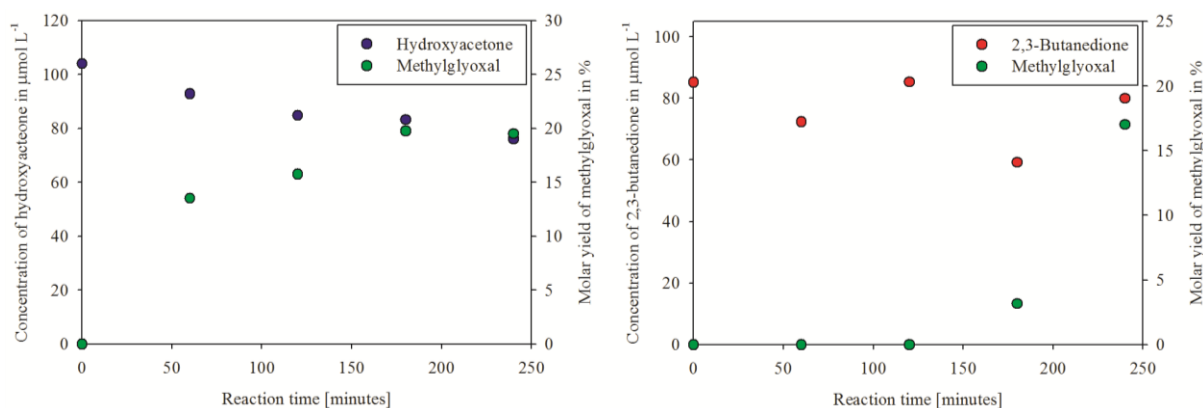


Figure S2: Formation of methylglyoxal due to the photolysis of hydroxyacetone and 2,3-butanedione.

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.

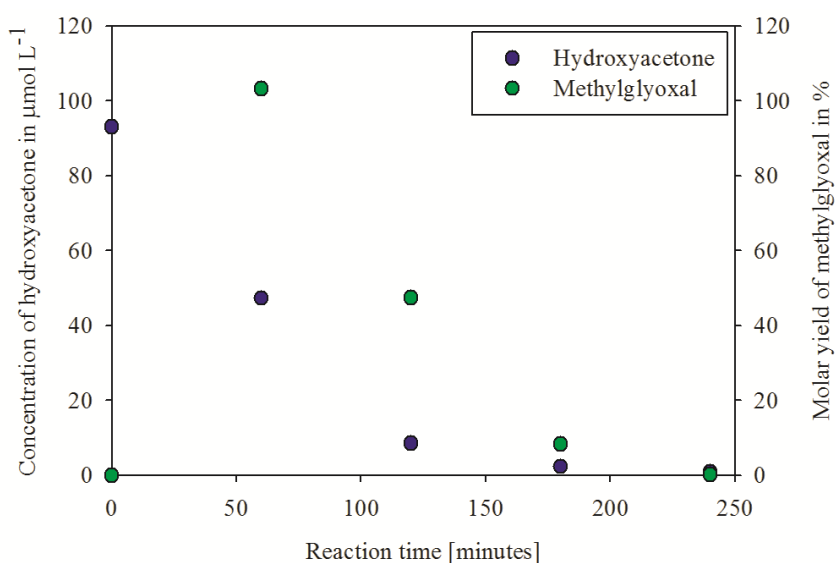


Figure S3: Oxidation of hydroxyacetone and formation of methylglyoxal.

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  $\approx 100\%$ . 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  $\approx 3.0\%$  ( $1.9 \mu\text{mol L}^{-1}$ ). 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

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