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A new source of methyl glyoxal in the aqueous phase

M. Rodigast et al.

Correspondence to: H. Herrmann (herrmann@tropos.de)

S 1 Determination of photon flux of Xe/Hg lamp and the photolysis rate constants of H_2O_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 $K_3Fe(C_2O_4)_3$ in 0.05 mol L^{-1} of H_2SO_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_2SO_4 in water. To determine the photon flux, 300 mL of solution 1 was filled in the bulk reactor and illuminated (λ = 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 λ = 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_2O_2 was calculated according to Eq, (S1):

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

q	Photon flux [molecules s^{-1}]
θ	Quantum yield H_2O_2 (Kwon and Kwon, 2010)
V	Reaction volume [L]
N_A	Avogadro constant [molecules mol^{-1}]
ε	Extinction coefficient H_2O_2 [L mol^{-1} cm^{-1}]
c	Concentration H_2O_2 [mol L^{-1}]
d	Optical path length [cm]

Based on the decay of H_2O_2, a photolysis rate constant of $k_{pH2O2} = 7.6 \times 10^{-6}$ s^{-1} was calculated according to Eq. (S2):

$$k_{pH2O2} = \frac{\frac{d[H_2O_2]}{dt}}{c} \qquad \text{Eq. (2)}$$

S 2 Photolysis rate constants of MEK, 2,3-butanedione, hydroxyacetone and methyl glyoxal

Photolysis rate constants were determined using the decay of the respective precursor compound (MEK, 2,3-butanedione, hydroxyacetone, and methyl glyoxal). 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.

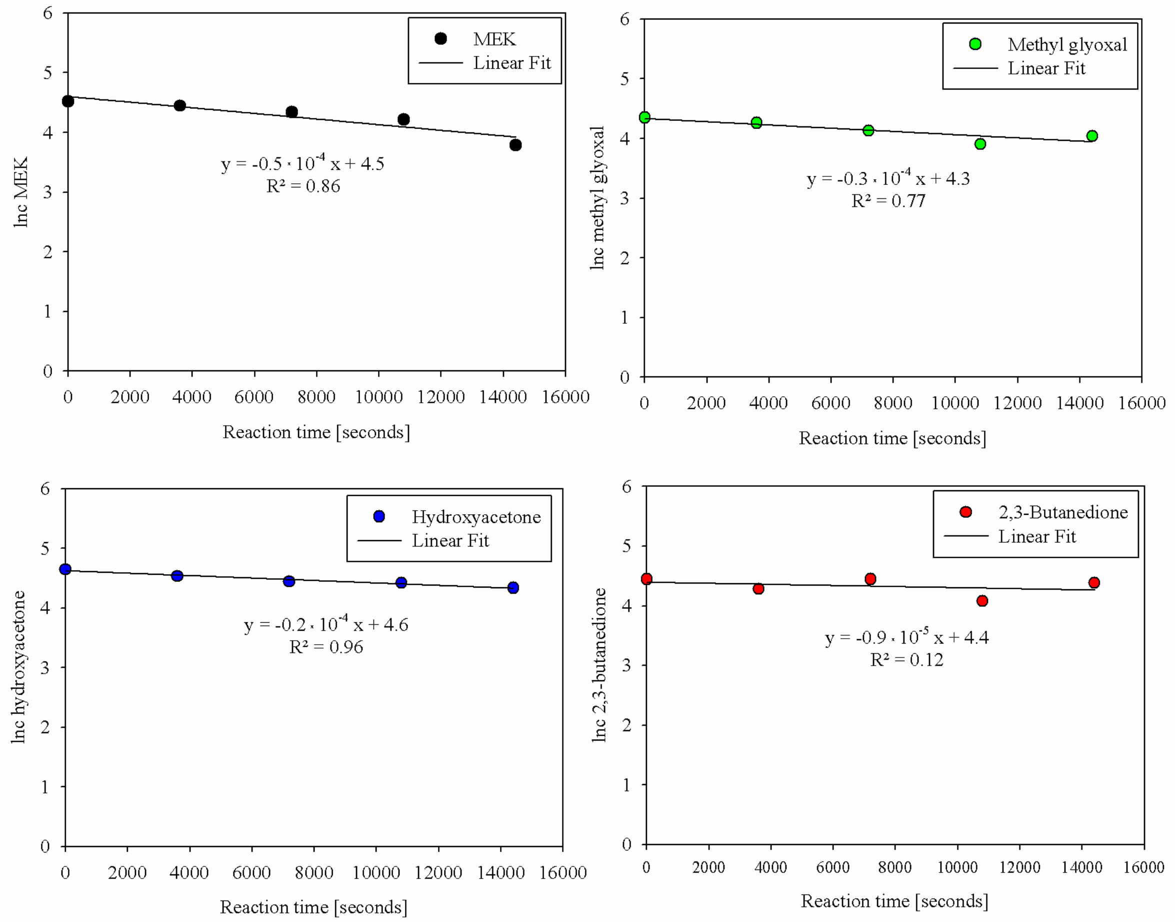

Figure S1: Photolysis rate constants of MEK, methyl glyoxal, hydroxyacetone, and 2,3-butanedione determined through the slope m of the linear fit.

For MEK, 2,3-butandione, methylglyoxal, and hydroxyacetone, the photolysis rate constants were determined with $k_{pMEK} = 5 \times 10^{-5}\ s^{-1}$, $k_{pMethyl\ glyoxal} = 3 \times 10^{-5}\ s^{-1}$, $k_{pHydroxyacetone} = 2 \times 10^{-5}\ s^{-1}$, and $k_{p2,3\text{-}Butanedione} = 9 \times 10^{-6}\ s^{-1}$. During the photolysis of 2,3-butanedione and hydroxyacetone, methyl glyoxal was formed with molar yields of ≈ 17.0% and 19.5% (Fig. S2).

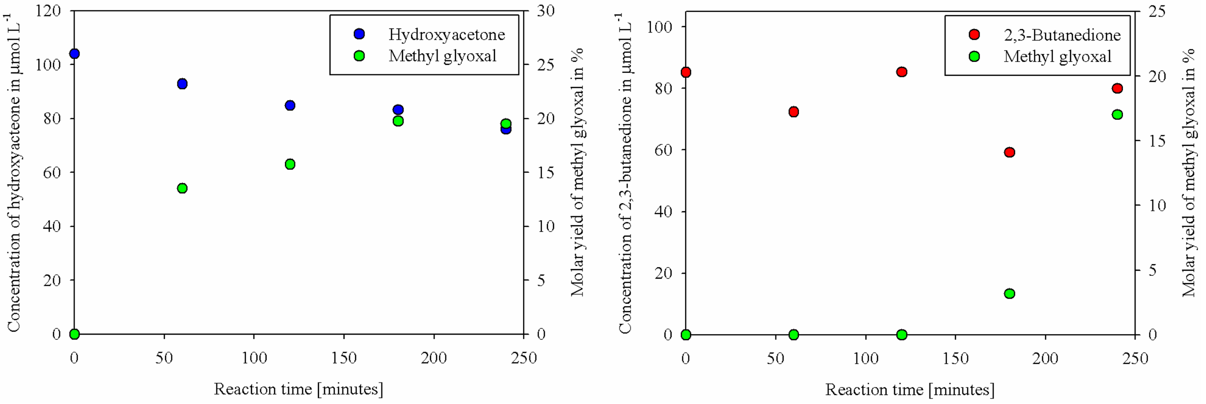

Figure S2: Formation of methyl glyoxal (green) due to the photolysis of hydroxyacetone (blue) and 2,3-butanedione (red).

These two additional methyl glyoxal 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 methyl glyoxal during the oxidation of MEK (Fig. S3). The contribution of the oxidation of 2,3-butanedione to the methyl glyoxal formation is discussed in the manuscript.

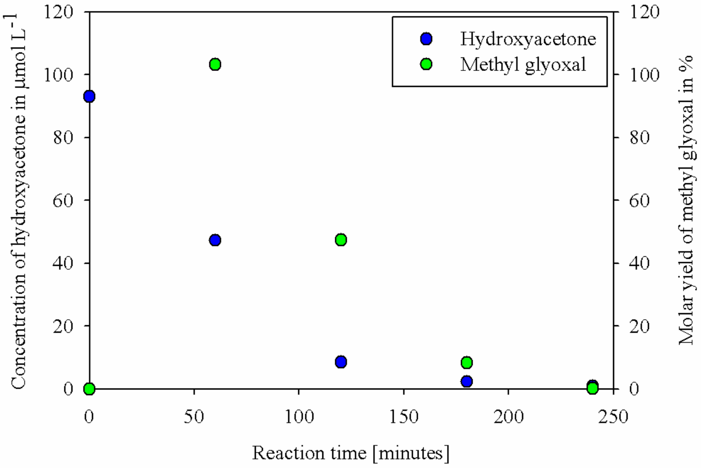

Figure S3: Oxidation of hydroxyacetone (blue) and formation of methyl glyoxal (green).

During the oxidation, hydroxyacetone was completely consumed after a reaction time of 240 minutes. After 60 minutes, methyl glyoxal was formed with a molar yield of ≈ 100%. Afterwards, the concentration of methyl glyoxal 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 methyl glyoxal. 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 methyl glyoxal 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 methyl glyoxal formation.

References

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