

A new source of methyl glyoxal in the aqueous phase

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Introduction

The oxidation of volatile organic compounds (VOCs) in the atmosphere leads to the formation of semivolatile products which can partition into the particle phase and contribute to the formation of secondary organic aerosol (SOA). Significant discrepancies exist in the literature regarding the global SOA burden predicted based on model and field studies (Goldstein and Galbally, 2007). Thus it can be expected that a so far unknown source can contribute to the SOA mass whereby the oxidation within the aqueous phase (aqSOA) might play an important role (Ervens et al., 2011, Herrmann et al., 1999). In this regard, methyl ethyl ketone (MEK) can be a potential aqSOA precursor compound as it is detected in significant amounts in cloud water, ice and rain (Grosjean and Wright, 1983; van Pinxteren et al., 2005). It is emitted primarily from biogenic sources including grass and clovers (Kirstine et al., 1998) and through anthropogenic processes like biomass burning and tobacco smoke (Yokelson et al., 2013). Therefore oxidation of MEK and formation of corresponding oxidation products especially methyl glyoxal, were investigated in the aqueous phase. Methyl glyoxal is often related to the formation of aqSOA, thus due to the detection of methyl glyoxal as oxidation product it can be pointed out that MEK has to be considered for aqSOA formation.

Bulk reactor experiments

The experiments were conducted in a 300 mL batch reactor using the photolysis of hydrogen peroxide (H_2O_2) as OH radical source (Figure 1). For the experiments, 0.1 mmol L^{-1} of the precursor compound was mixed with 2 mmol L^{-1} H_2O_2 . The solution was irradiated at $\lambda = 254$ nm with a xenon-mercury lamp for 4 hours.

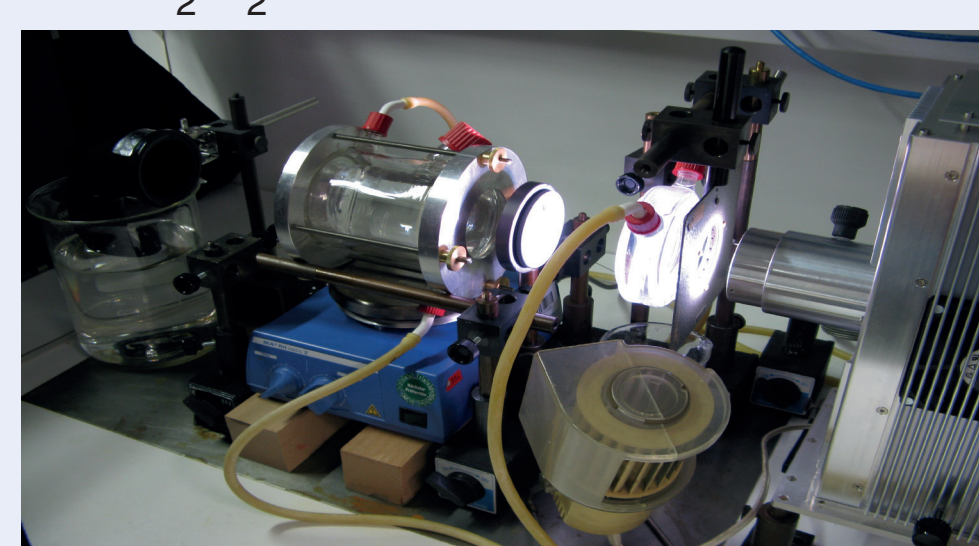


Figure 1: Experimental setup for aqueous phase experiments.

Type of Experiment	[Precursor] in mmol L^{-1}	[H_2O_2] in mmol L^{-1}	UV light ($\lambda = 254$ nm)	Reaction time [hours]	Number of repetitions
Oxidation of precursors	0.1	2	✓	4	3
Reaction of H_2O_2 with MEK	0.1	2	-	4	1
Photolysis of MEK	0.1	-	✓	4	1
Photolysis of H_2O_2	-	2	✓	4	1

Sample preparation

To obtain time resolved data, samples were taken once per hour (0, 1 hour, 2 hours, 3 hours, 4 hours; $n = 3$) or in steps of 15 minutes ($n = 1$). To avoid further reactions of the organics present in the sample with remaining H_2O_2 , 100 μL catalase (4 mg mL^{-1} in water) was added to each sample to destroy remaining H_2O_2 . Samples of all sets were derivatised with 300 μL *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 internal standard (150 μL , 100 $\mu mol L^{-1}$) 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 dichloromethane using an orbital shaker (1500 rpm, revolutions per minutes). Finally, 1 μL of the organic phase was used for GC/MS analysis.

Results

Experiments with MEK

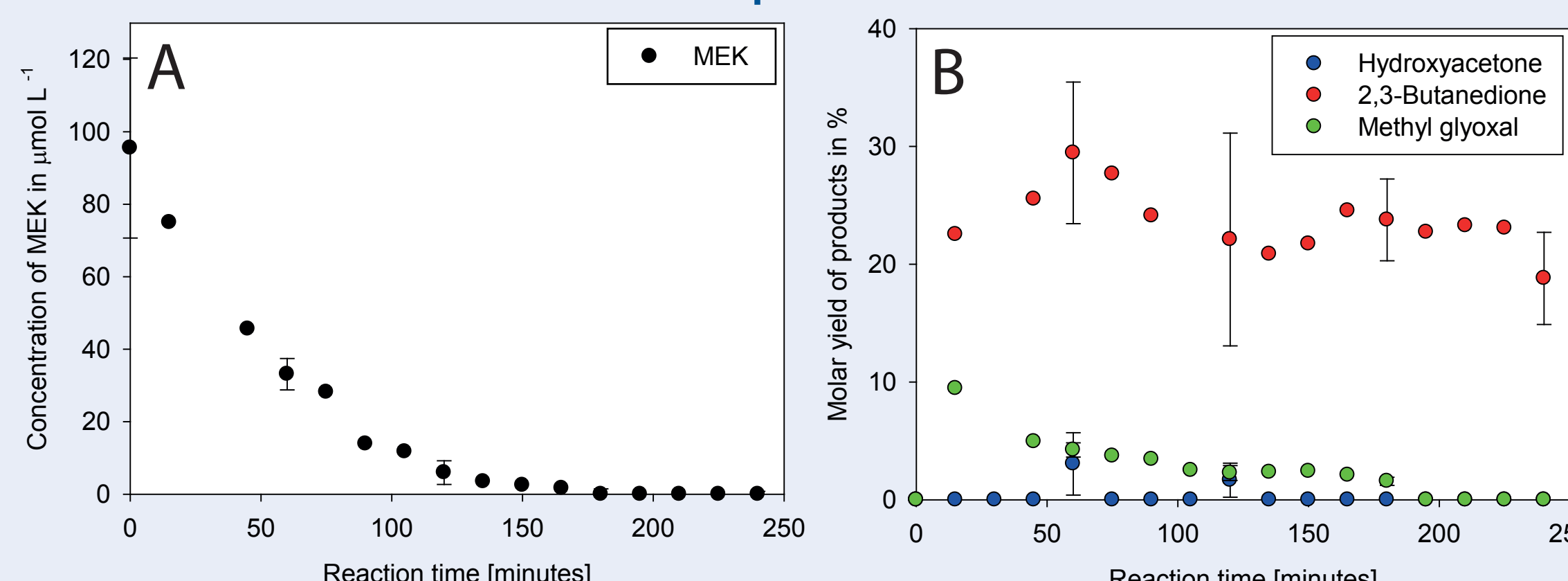


Figure 2: Oxidation of MEK (A) and the formation of corresponding oxidation products (B).

- MEK was completely consumed after 240 minutes (Figure 2)
- Maximum molar yields of oxidation products: 29.5 % of 2,3-butanedione, 3.0 % of hydroxyacetone and 9.5 % of methyl glyoxal

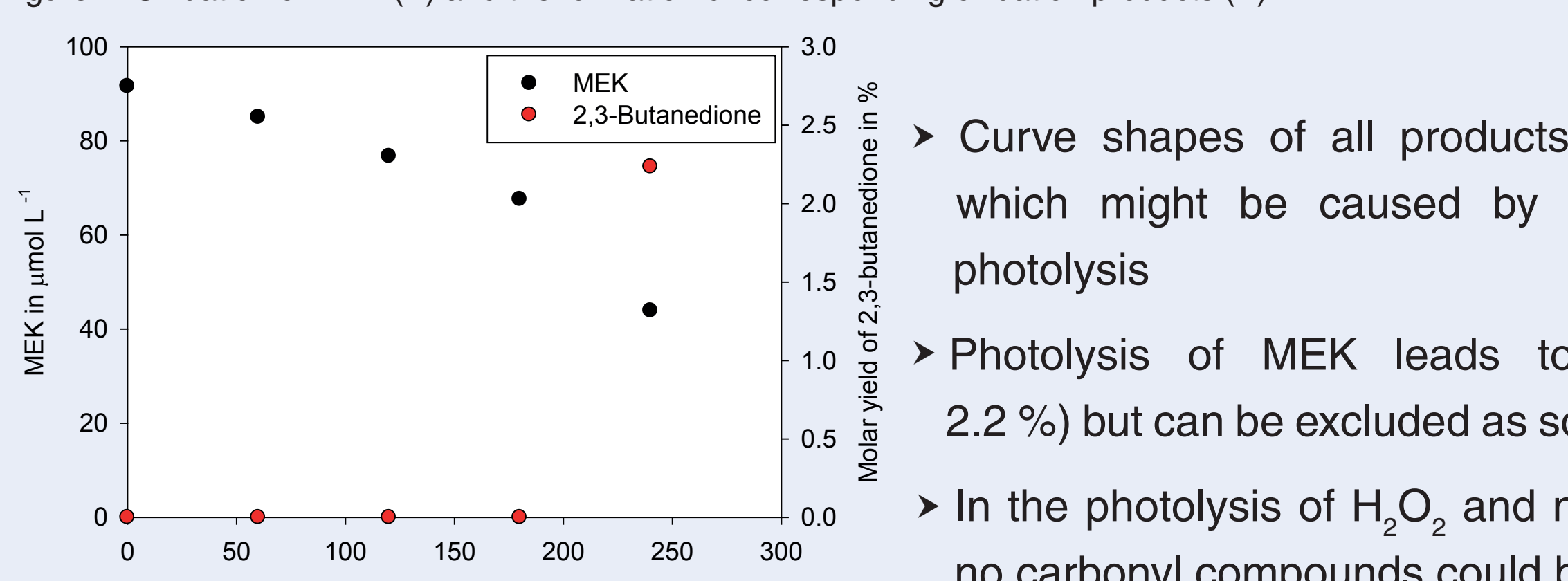


Figure 3: Photolysis of MEK and formation of 2,3-butanedione.

- Curve shapes of all products indicate consecutive reactions which might be caused by oxidation with OH radicals or photolysis
- Photolysis of MEK leads to 2,3-butanedione (molar yield 2.2 %) but can be excluded as source for methyl glyoxal (Figure 3)
- In the photolysis of H_2O_2 and non-radical reactions with MEK no carbonyl compounds could be detected

Oxidation of 2,3-butanedione

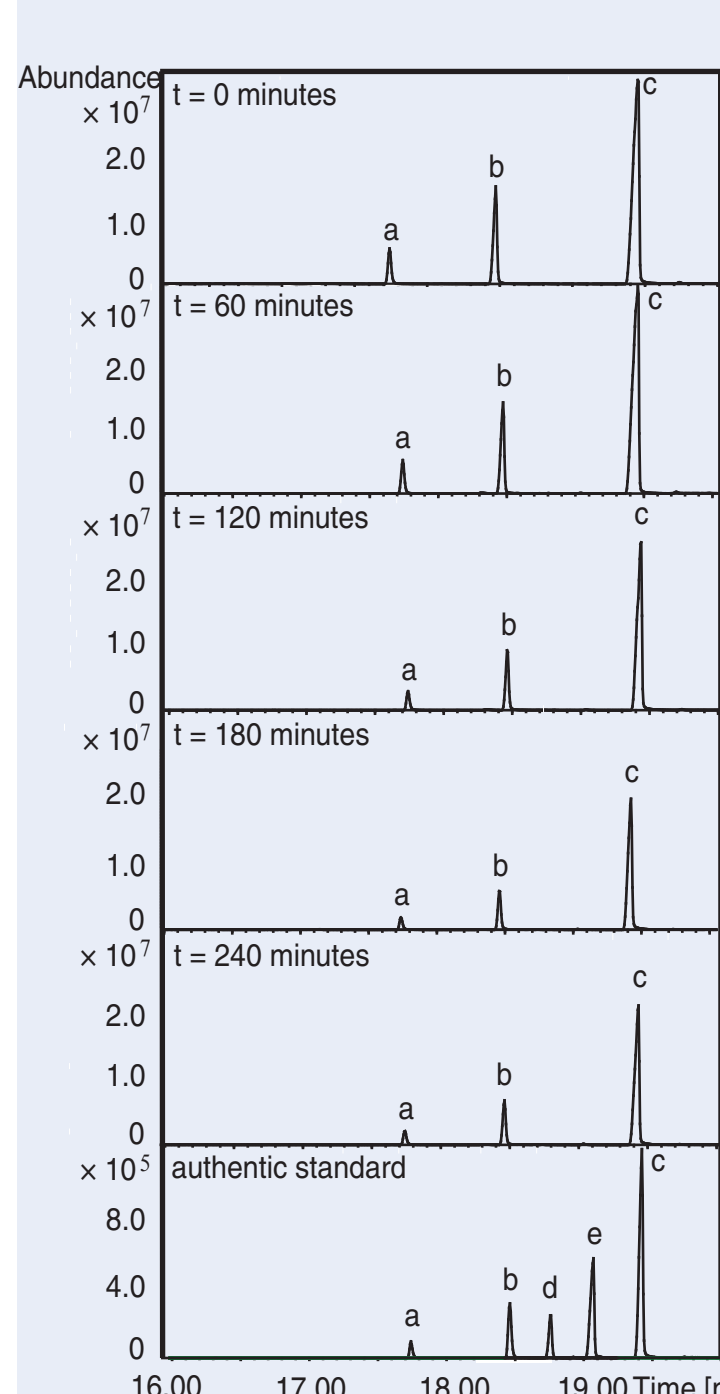


Figure 4: GC/MS chromatogram for the oxidation of 2,3-butanedione and the authentic standard compounds 2,3-butanedione (a,b,c) and methyl glyoxal (d,e).

- Investigation of the contribution of 2,3-butanedione to methyl glyoxal formation
- During the reaction time of 240 minutes no methyl glyoxal was formed
- The oxidation of 2,3-butanedione can be excluded as source for methyl glyoxal

Oxidation of hydroxyacetone

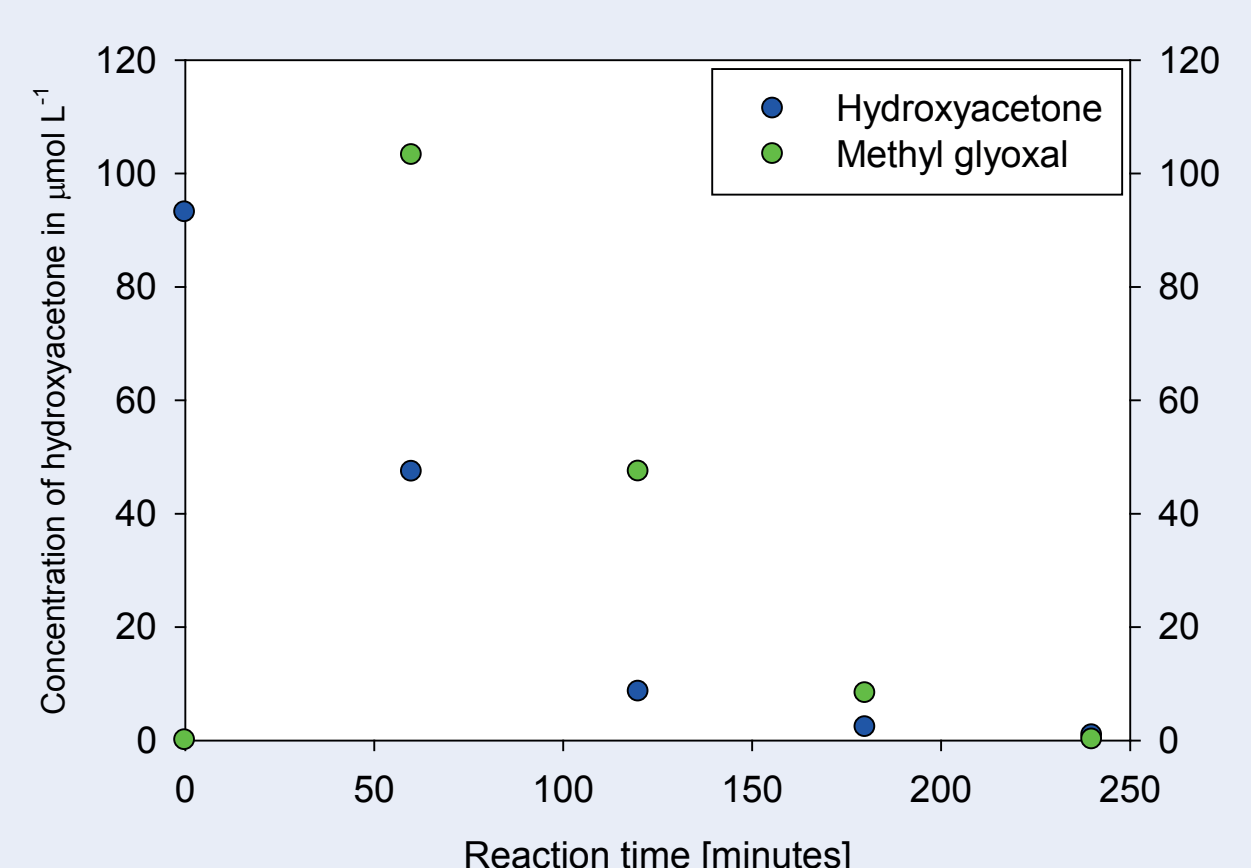


Figure 5: Oxidation of hydroxyacetone.

- Hydroxyacetone was completely consumed after 240 minutes reaction time
- Methyl glyoxal was formed with a molar yield of 100 % after 60 minutes
- Minor importance for methyl glyoxal formation due to the low molar yield of hydroxyacetone

Description of the oxidation mechanism

- The OH radical attack can occur at three different positions (Figure 6, H-atoms at carbon 1, 3, and 4)

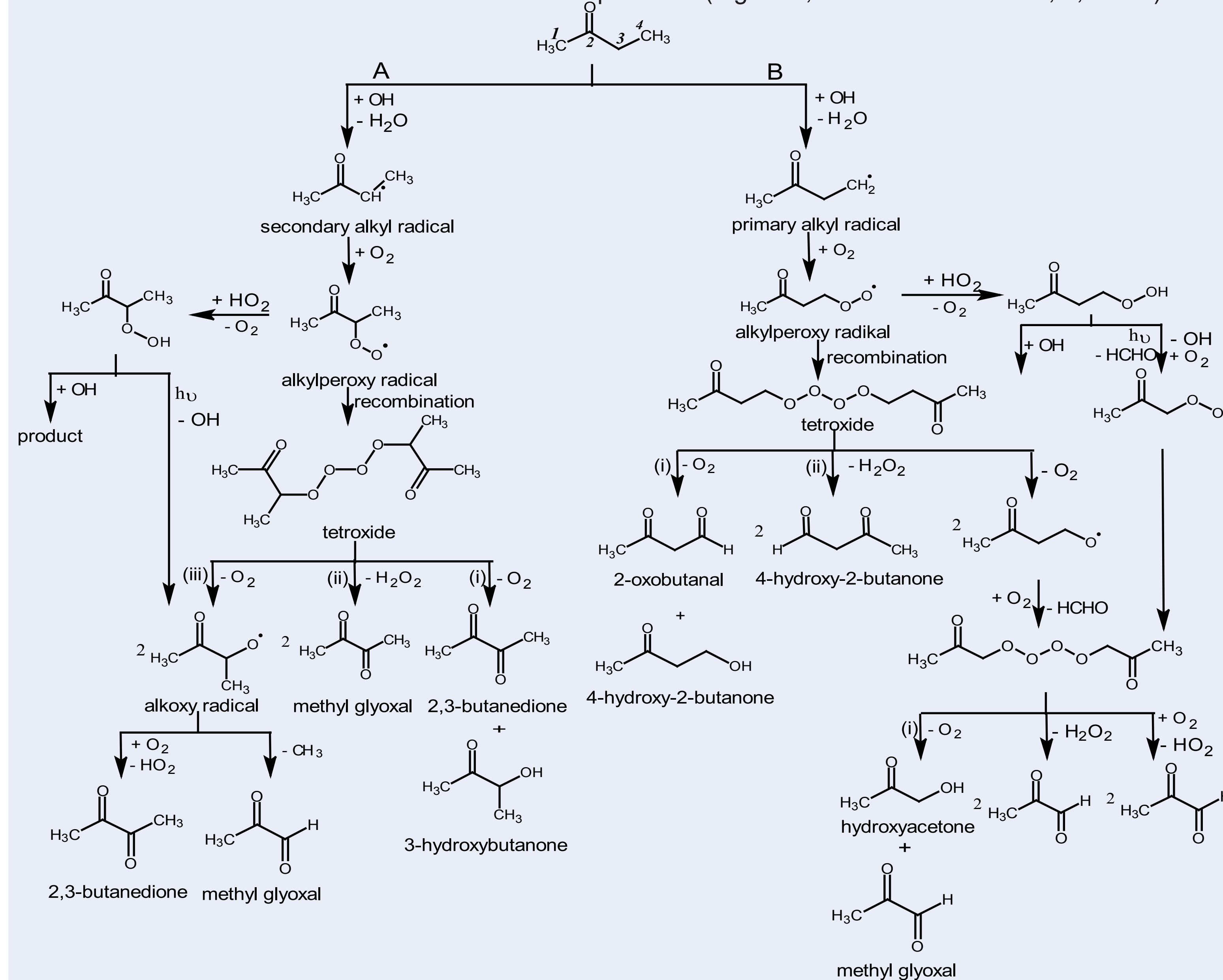


Figure 6: Oxidation mechanism of MEK for the formation of 2,3-butanedione, hydroxyacetone and methyl glyoxal.

- A secondary (A) and primary alkyl radical (B) are formed through H-atom abstraction
- Primary and secondary alkyl radicals react rapidly with oxygen to an alkylperoxy radical
- Alkylperoxy radical recombines to a tetroxide and react further (von Sonntag and Schuchmann, 1991) by:
 - (i) formation of a carbonyl compound and an alcohol
 - (ii) formation of two carbonyl compounds and H_2O_2
 - (iii) decomposition to alkoxy radicals
- H-atom abstraction at carbon 3 leads to the formation of 2,3-butanedione and methyl glyoxal
- H-atom abstraction at carbon 4 leads to the formation of hydroxyacetone and methyl glyoxal

Conclusion

- Oxidation of MEK leads to carbonyl compounds like 2,3-butanedione, hydroxyacetone and methyl glyoxal
 - 2,3-Butanedione is the main oxidation product
 - Methyl glyoxal was formed with 9.5 % molar yield
 - Products are prone for photolysis and further oxidation through OH radicals
- MEK acts as precursor compound for methyl glyoxal
- MEK should be considered as aqSOA precursor compound

Acknowledgement

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