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In-cloud processes of methacrolein under simulated conditions – Part 1: Aqueous phase photooxidation

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Abstract

The photooxidation of methacrolein was studied in the aqueous phase under simulated cloud droplet conditions. The obtained rate constant of OH-oxidation of methacrolein at 6°C in unbuffered solutions was 5.8 $(\pm 0.9) \times 10^9\ M^{-1}\ s^{-1}$. This kinetic study showed that the oxidation proceeds mainly by OH-addition on the C=C bond. This was confirmed by the mechanism established on the study of the reaction products (at 25°C in unbuffered solutions) where methylglyoxal, formaldehyde, hydroxyacetone and acetic acid/acetate were the main reaction products. An upper limit for the total carbon yield was estimated to range from 53 to 85%, indicating that some reaction products remain unidentified. A possible source of this mismatch is the formation of higher molecular weight compounds as primary reaction products which are presented in El Haddad et al. (2009) and Michaud et al. (2009).

1 Introduction

Clouds are present on a large part of the lower atmosphere (60% of the earth's surface, on the first 4–6 km in altitude). Lelieveld and Crutzen (1991) have shown that clouds exert a major influence, particularly by affecting gas phase concentrations of important tropospheric species such as O_3, NO_x and HO_x. Aqueous cloud droplets provide an efficient medium for liquid phase reactions of water soluble species formed by the photooxidation of reactive organics in the gas phase. These compounds readily partition into the droplets, and oxidize further in the aqueous phase to form less volatile organics. Several experimental and modelling studies have demonstrated that aldehydes such as glyoxal, methylglyoxal and glycolaldehyde can form low volatility products such as glyoxylic and oxalic acids as well as larger molecular weight compounds and oligomers by aqueous phase reactions (Warneck, 2003; Altieri et al., 2006, 2008; Carlton et al., 2007). Unlike gas-phase chemistry, the aqueous medium enables formation of new structures (e.g. gem diols) whose functional groups are susceptible to be oxidized during reactions with OH radical and other oxidants, while the initial C-C bond structures is preserved (Carlton et al., 2007). Differences between aqueous- and gas-phase chemistry suggest that oligomer formation from aldehydes is more favourable in the aqueous phase than in the gas phase.

Isoprene is the most abundant volatile organic compound with a global emission of 500–750 Tg/yr (Guenther et al., 2006). One of its principal first-generation gas phase oxidation carbonyl products is methacrolein, with a molar yield of 20–28% (Zimmermann and Poppe, 1995; Lee et al., 2005). Besides this natural source, methacrolein is also directly emitted by anthropogenic sources (Biesenthal and Shepson, 1997). These sources make methacrolein a high emitted compound in the atmosphere, with a global emission rate higher than 100 Tg y^{-1}. The atmospheric lifetime of methacrolein towards OH-oxidation is 6–10 h in the gas phase (Gierczak et al., 1997), thus enabling it to encounter a cloud. Iraci et al. (1999) have estimated that only 0.02% of methacrolein enters the aqueous phase under conditions of gas-aqueous equilibrium based on the Henry's law constant (5 M atm^{-1} at 298 K). However, ambient measurements have shown that methacrolein water concentrations exceed its Henry's law predicted concentrations by two orders of magnitude (van Pinxteren et al., 2005). Thus, in addition to its transfer from the gas phase, methacrolein may also appear into the aqueous phase by other sources.

Aqueous-phase kinetics of methacrolein towards ozone (Pedersen and Sehested, 2001; Zhu and Chen, 2005; Chen et al., 2008), NO_3 (Umschlag et al., 1997, 1999), and OH radicals at 293 K (Buxton et al., 2000) have been investigated. However, no mechanistic study of OH-oxidation of methacrolein in the aqueous phase has been made to date.

The aim of this study is to elucidate the atmospheric fate of methacrolein towards OH radicals within the aqueous phase. We present a laboratory study of the kinetic and reaction products formed during the OH-initiated oxidation of methacrolein under simulated atmospheric water droplet conditions.

2 Experimental section

OH-oxidation of methacrolein was studied in an aqueous phase photoreactor described in details in Monod et al. (2000, 2005). Briefly, it is a Pyrex thermostated reactor, equipped with an irradiation source (Xenon arc lamp (300 W; Oriel), or MSI (575 W, Phillips)), which irradiance spectrum is comparable to the one of the sun at the earth's ground level. OH radicals were produced by H_2O_2 photolysis. A Pyrex filter was employed to remove the UV irradiation below 300 nm, thus avoiding direct photolysis of methacrolein which was controlled through a specific experiment. Similarly, it was verified that reaction of methacrolein towards H_2O_2 can be neglected under our experimental conditions.

2.1 Kinetic experiments

The kinetic rate constant of OH-oxidation of methacrolein was determined at 6°C using the relative kinetic method. This method is based on the measure of the decay rate of OH-induced oxidation of the reactant (MACR) relatively to a reference compound (R) for which OH-oxidation rate constant is well known.

$$\mathrm{MACR} + \mathrm{OH} \longrightarrow \text{products } k_{\mathrm{MACR}}$$

$$\mathrm{R} + \mathrm{OH} \longrightarrow \text{products } k_R$$

where k_{MACR} and k_R are the rate constants of OH-oxidation of methacrolein and R, respectively. Therefore, the kinetic equation can be written as follows:

$$\ln\left(\frac{[\mathrm{MACR}]_0}{[\mathrm{MACR}]_t}\right) = \frac{k_{\mathrm{MACR}}}{k_R} \times \ln\left(\frac{[R]_0}{[R]_t}\right) \tag{1}$$

whith $[\mathrm{MACR}]_0$, $[\mathrm{MACR}]_t$, $[\mathrm{R}]_0$, $[\mathrm{R}]_t$, the concentrations of the reactant and the reference compound at times 0 and t, respectively. Plotting $\ln\left(\frac{[\mathrm{MACR}]_0}{[\mathrm{MACR}]_t}\right)$ versus

$\ln\left(\frac{[R]_0}{[R]_t}\right)$ yields a linear curve with slope equal to k_{MACR}/k_R and an intercept equal to zero. In this study, 1-propanol was chosen as the reference compound, with k_R=2.7(±0.7)×10^9 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at 6°C (Monod et al., 2005). Two kinetic experiments were performed (Table 1a).

2.2 Reaction products experiments

In order to investigate the reactions products, nine experiments were performed: three type A, and six type B – Table 1a. During the reaction, 4 mL samples were taken at periodic intervals prior to chemical analysis.

2.3 Analytical determinations

Aqueous phase carbonyl compounds were derivatized with 2,4-DNPH at room temperature for at least 6 h, then analysed by HPLC-UV at 360 nm. The HPLC-UV (Kontron) device was equipped with a 20 μL injection loop, and reversed phase C_{18} pre-column and column (Uptisphere C_{18}, 10×4 mm, 5 μm ODB, and Alltima C_{18}, 250×4.6 mm, 5 μm, Alltech, Interchim, respectively) thermostated at 32°C. A binary eluent (H_2O:CH_3CN) was used at 1 mL min^{-1}, with H_2O:CH_3CN: 60%:40% from 0 to 25 min; 0%:100% at 45 min; 60%:40% at 50 min during 10 min.

GC-FID (HP serie II 5890) was used to analyze oxygenated organic compounds (such as 1-propanol, methacrolein and hydroxyacetone). It was equipped with a semi-polar capillary column (HP INNOWAX 15 m×0.25 mm×0.50 μm) which allowed us to inject aqueous phase samples. An internal standard (10 μL of 1-butanol at 0.1 M) was added to each sample of 1000 μL prior to injection. The GC injector and detector were heated at 250°C. Helium gas was used as carrier gas at 1.2 mL min^{-1}, with a 1/5 split. The oven temperature program was 40°C for 4 min, 10°C min^{-1} up to 120°C, 120°C for 5 min, 40°C min^{-1} up to 240°C, and 240°C for 5 min.

Aqueous phase carboxylic acids and polyfunctional species were analyzed by ESI-MS and ESI-MS/MS. The instrument is a triple quadrupole mass spectrometer (Varian

1200 L), equipped with an electrospray ionisation chamber (ESI). Samples and standard solutions were directly introduced into the ESI source at flow rate of 25 μl min^{-1}. The full-scan mass spectrum of the sample solutions were recorded every hour during the experiment. In order to avoid sample storage, two experiments (h and i) were performed by directly coupling the aqueous phase photoreactor with the ESI-MS-MS (Table 1b), according to Poulain et al. (2007). Additionally to prevent from contamination, this technique allowed us to obtain highly precise time profiles for reactants and oxidation products (see results).

For experiments a, b, c, d, e, g, h and i, ESI-MS and ESI-MS/MS analysis were performed in both positive and negative modes with capillary voltage of +40 V and −40 V, respectively, over the mass range of 30–1000 amu. Nitrogen served as the drying gas at a pressure of 15 PSI in both positive and negative modes. The nebulizing gases, air and nitrogen (at 60 PSI) in the negative and the positive mode respectively, were held at 350°C. During MS/MS experiments, argon was used as collision gas and was delivered at pressure of 2 mTorr. MS/MS collision energy was between 5 and 20 V depending on the compounds. This instrument was used to quantify the aqueous phase concentrations of polyfunctional molecules. Methacrylic, pyruvic, glyoxylic, and oxalic acids were analyzed in the ESI-MS negative mode, and methacrolein, hydroxyacetone and acetic acid were analyzed in the ESI-MS positive mode. Quantification of these compounds was conducted on the basis of mixed standard solutions, using the same instrumental conditions as the sample analysis described above. Statistical error limits and detection limits of the calibration for each compound (in the range covering the concentrations encountered in the experiments) are summarized in Table 1b. Additionally, some suspected polyfunctional oxidation products were quantified using standards whom chemical structures are similar: 2,3-dihydroxy-2-methylpropanal (DHMP) and 2-hydroxy-2-methylmalonaldehyde (HMM) were quantified using standards of methacrolein and hydroxyacetone whereas peroxymethacrylic acid (PMA) was quantified using standards of methacrylic acid.

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3 Results

3.1 Kinetics of OH-oxidation of methacrolein in the aqueous phase

A very good agreement between experiments 1 and 2 was obtained (Fig. 1). Taking into account the k_R value, we obtained: $k_{\mathrm{MACR,6°C}}$=5.8 (±0.9)×10^9 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The uncertainty was taken as twice the standard deviation on the linear regression, calculated taking into account errors on both abscissa and ordinate scales using the program developped by Brauers and Finlayson-Pitts (1997). The obtained rate constant value is slightly lower than the one obtained by Buxton et al. (2000) (8.0 (±0.7)×10^9 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at 20°C). However, the difference can be attributed to the difference of temperatures. This rate constant shows that the rate of OH-oxidation of methacrolein is high, near the diffusion limit. Compared to the rate constants of C_2-C_5 saturated aldehydes (which range from 2 to 4×10^9 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (Monod et al., 2005)), the obtained k_{MACR} is significantly higher, thus showing that OH-oxidation mainly proceeds by addition on the C=C bond. Moreover, the value of k_{MACR} is in good agreement with those reported for other unsaturated aldehydes, namely: crotonaldehyde and acrolein, with $k_{\mathrm{crotonaldehyde,20°C}}$=5.8×$10^9$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k_{\mathrm{acrolein,20°C}}$=7.0×$10^9$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (Lilie and Henglein, 1970). This confirms that, for unsaturated aldehydes, the mechanism of OH-oxidation should mainly proceed via a fast addition on the C=C bond. This is in good agreement with Buxton et al. (2000) who observed the formation of OH-adducts during the OH-oxidation of methacrolein in the aqueous phase.

3.2 Reaction products of OH-oxidation of methacrolein in the aqueous phase

The formation of eight reaction products was observed, including methylglyoxal, formaldehyde, hydroxyacetone, acetic, methacrylic, oxalic, glyoxylic, and pyruvic acids (Fig. 2). These figures show that an excellent agreement was obtained between experiments performed in the same conditions. The pH of the unbuffered solution, which started at 5.6, decreased down to 4.5 due to the formation of the organic acids.

Therefore, due to their low pK_a (<4.2), the observed acids were in their ionic form, except for methacrylic/methacrylate and acetic/acetate (pK_a=4.7 for both) for which both neutral and ionic forms were present. Figure 2 shows that the major reaction products i.e. methylglyoxal, formaldehyde, hydroxyacetone and acetic acid/acetate are clearly primary reaction products (i.e. first generation reaction products). Methacrylic acid/methacrylate is both a primary and a secondary reaction product (Fig. 2a). The time profile of the latter shows that it also reacts rapidly during the course of the reaction, certainly due to the fast reaction of OH by addition on the C=C bond. Figure 2 shows that the minor reaction products, i.e. oxalate, glyoxylate and pyruvate are secondary products (i.e. second generation reaction products). The very small quantity of pyruvate observed can be due to its fast reactivity towards direct photolysis in addition to OH-oxidation (Guzmán et al., 2006; Altieri et al., 2006; Carlton et al., 2007). Finally, using the ESI-MS/MS identification technique, the formation of four polyfunctional compounds was observed, namely peroxymethacrylic acid (PMA), 2-hydroxy-2-methylmalonaldehyde (HMM), 2,3-dihydroxy-2-methylpropanal (DHMP), and 2,3-dihydroxymethacrylic acid (DHMA). Their identifications are explained hereafter.

- 2-hydroxy-2-methylmalonaldehyde (HMM: 102 g/mol) was detected in the positive mode at *m/z* 103^+ amu. As we have verified with commercial hydroxypropanedial which has the same chemical structure (except for a methyl group), after ionisation, the fragmentation of HMM can occur either on the carbonyl function, either on the alcohol one, thus explaining the major daughter ions observed in the MS/MS spectrum (Fig. 3a).

- Peroxymethacrylic acid (PMA: 102 g/mol) was detected in the negative mode at *m/z* 101^- amu. This peak was intense, and its intensity as a function of consumed MACR clearly showed a primary behaviour (Fig. 3c). The MS/MS fragmentation of this peak produced one neutral loss of 44, thus denoting the presence of an acid function. After ionisation, the fragmentation of this peak gave exactly the same spectrum as the one obtained with a standard of synthesized PMA (Fig. 3b).

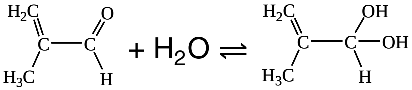
- 2,3-dihydroxy-2-methylpropanal (DHMP: 104 g/mol) was detected in the negative mode at *m/z* 103^- amu. As we have verified with commercial glyceraldehyde which has the same chemical structure (except for a methyl group), after ionisation, the fragmentation of DHMP can occur either on the carbonyl function, either on the alcohol one, thus explaining the major daughter ions observed on the MS/MS spectrum (Fig. 4a). The OH-oxidation of DHMP leads to the formation of 2,3-dihydroxymethacrylic acid (DHMA)
- 2,3-dihydroxymethacrylic acid (DHMA: 120 g/mol) was detected in the negative mode at *m/z* 119^- amu. After ionisation, the fragmentation of this peak gave exactly the same spectrum as the one obtained with a standard of synthesized DHMA (Fig. 4b), using the protocole of Claeys et al. (2004b). The intensities of peaks 103^- (DHMP) and 119^- (DHMA) as a function of consumed MACR clearly shows that they correspond respectively to a primary and a secondary reaction product (Fig. 4c), in good agreement with the proposed mechanism. It can be noted that DHMA was previously identified in ambient aerosols (Claeys et al., 2004a; Ion et al., 2005) and as a major reaction product of the oxidation by H_2O_2 of methacrylic acid in formic aqueous solutions (Claeys et al., 2004b).

We have verified that the peaks (at *m/z* 101^-, 103^+, 103^- and 119^-) corresponding to the four above mentioned molecules were not present in a standard mixture containing the quantified reaction products, even at high concentrations (i.e. methacrolein (3×10^{-3} M), hydroxyacetone, methylglyoxal, formaldehyde, acetic and formic acid (6×10^{-4} M), methacrylic acid, pyruvic acid, glyoxylic acid and oxalic acid 3×10^{-5} M). This shows that the observed formation of PMA, HMM, DHMP and DHMA was not an analytical artefact occurring during the electrospray ionisation, (i.e. adducts formed in the ionisation chamber by the combination of smaller molecules).

4 Discussion

4.1 Mechanism of OH-oxidation of methacrolein in the aqueous phase

As most of short chain aldehydes, methacrolein is able to hydrate in the aqueous phase (Melichercik and Treindl, 1981) (Reaction R1).



(R1)

However, its hydration equilibrium constant has not been experimentally determined to date (to our knowledge). In the aqueous phase, carbonyl groups absorb UV light in the region 200–350 nm. Carbonyl compounds that are known to be totally hydrated in the aqueous phase, such as formaldehyde and glyoxal, do not absorb in this region (Fig. 5). Methacrolein shows a strong absorption with a maximum at 311 nm, comparable to that of acetone, which hydration constant is as low as 0.0014 (Guthrie et al., 2000). Compared to isobutyraldehyde (K_{hyd}=0.5–0.6 (Bell et al., 1966; Guthrie et al., 2000), the absorbance of methacrolein is more intense. This may be due to a mesomeric effect between the C=C and C=O bonds in methacrolein, which prevents from hydration. Finally, based on the method developed by Hilal et al. (2005) the SPARC online calculator (SPARC on-line v4.2) evaluates the hydration constant of methacrolein to 0.046. For all these reasons, we assumed that methacrolein is mainly in its carbonyl form in the aqueous phase.

As mentioned earlier, OH-oxidation of methacrolein can proceed via addition on the C=C bond (pathway A) (Fig. 6). We also consider here the H-abstraction of the carbonyl function (pathway B). The external addition of OH (A2) is more likely than the internal addition (A1), because i) it leads to a tertiary radical, which is more stable than the primary radical formed in pathway A1, and ii) the internal addition of OH (A1) generates more steric hindrance than the external one (A2) (Buxton et al., 2000). The H-abstraction on the methyl group is not presented here because no reaction product associated to it was detected: this pathway is certainly of minor importance compared to the three others (Buxton et al., 2000; Herrmann, 2003; Monod and Doussin, 2008). Hereafter are presented and discussed the three possible pathways presented in Fig. 6.

4.1.1 Pathway A: OH-addition on the C=C bond

Pathway A1: internal addition

The internal addition of OH leads to the formation of an alkyl radical, which rapidly adds to dissolved oxygen to form a peroxy radical (P_{A1}) which can react following two different pathways:

- *Pathway A1.1:* Radical P_{A1} reacts with itself to form an unstable tetroxide which rapidly decomposes to form different reaction products through pathways A1.11, 12, 13, and 14 (von Sonntag and Schuchmann, 1997). DHMP and HMM were observed as primary reaction products in good agreement with pathways A1.11 and 12. The peroxide formed in pathway A1.14 contains a weak O-O bond which is sensitive to UV-Visible radiations. This compound was not detected: it is thus likely that, under our experimental conditions, its photolysis undergoes a homolytic break of the O-O bond leading to the alkoxy radical formed via pathway A1.13. This alkoxy radical can further decompose to form formaldehyde and methyglyoxal as primary reaction products in good agreement with our observations (Fig. 2). The obtained molar yields for DHMP+HMM were 10.1±5.2% with standards of methacrolein, and 4.1±2.0% with standards of hydroxyacetone. We can thus deduce a branching ratio for pathways A1.11 + A1.12 ranging from 3 to 11%.

- *Pathway A1.2:* Radical P_{A1} can also react with O_2^- to form the corresponding hydroperoxide (Docherty et al., 2005). However, the latter was not detected in our experiments.

Pathway A2: external addition

The external addition of OH leads to the formation of an alkyl radical, which rapidly adds to dissolved oxygen to form another peroxy radical (P_{A2}).

- *Pathway A2.1:* Radical P_{A2} reacts with itself to form an unstable tetroxide. Due to the absence of H in α position, this tetroxide can decompose through only two different pathways (A2.13 and 14). The peroxide formed through pathway A2.14 was not detected in our experiments, it is thus likely that it was photolyzed under our experimental conditions, leading to the alkoxy radical formed through pathway A2.13. This alkoxy radical undergoes β-decomposition via pathways A2.13a, b, and d (von Sonntag and Schuchmann, 1997) to form formaldehyde, hydroxymethylhydroperoxide (HMHP), formate (Monod et al., 2000, 2007) and methylglyoxal as primary reaction products (channel A2.13a); hydroxyacetone and formate (Mc Elroy and Waygood, 1991) as primary reaction products (channel A2.13b) and acetic acid/acetate, formaldehyde, formate and HMHP (channel A2.13d). Although this last pathway requires a number of simultaneous bond breaks, a special attention was paid to it, because it was the only one that could explain the formation of acetic acid/acetate observed in our experiments. Radical $CH_3C{=}O$ hydrates in the aqueous phase (K_{hyd}=2.10^4 s^{-1}) faster than O_2 addition (Schuchmann and von Sonntag, 1988), leading to a diol radical, which undergoes O_2 addition, and eliminates HO_2 to form acetic acid/acetate. Pathway A2.13c was considered to be a minor process because 3-hydroxy-2-oxopropanal has not been detected in our experiments.

  All the reaction products obtained through pathways A2.13a, b, and d are in good agreement with our experiments, except from formate and HMHP which were not measured.

- *Pathway A2.2:* Radical P_{A2} can also react with O_2^- to form the corresponding hydroperoxide. However, the latter was not detected in our experiments.

Pathway B: OH-attack by hydrogen abstraction on the carbonyl function

This pathway leads to the formation of a α-carbonyl radical which may hydrate through pathway B1, leading to methacrylic acid as primary reaction product. However, the time profile of methacrylic acid/methacrylate (Fig. 2) shows a singular behaviour which can represent both a primary *and* a secondary reaction product. It is probable that the hydration of the α-carbonyl radical is slow because of the mesomeric effect between the C=C and the C=O bonds which stabilises the radical, thus enabling the addition of O_2, through pathway B2. This reaction leads to the formation of a peroxycarbonyl radical. Schuchmann and von Sonntag (1988) found that an analogous radical formed from non hydrated acetaldehyde was found to react towards O_2^-, to form peroxyacetic acid. Extrapolating these findings to our compound, it is probable that pathway B2 leads to the formation of peroxymethacrylic acid (PMA) as a primary reaction product (Fig. 8), in good agreement with our observations. Furthermore, Schuchmann and von Sonntag (1988) have shown that peroxyacetic acid slowly reacts on non hydrated acetaldehyde to yield acetic acid, under experimental conditions similar to ours. It is thus probable that PMA slowly reacts with methacrolein to form methacrylic acid. This explains the observed formation of methacrylic acid as a secondary reaction product.

PMA represents only pathway B2. This compound was quantified using standards of methacrylic acid which structure is very similar. The resulting branching ratio for pathway B2 is 4.1±2.6%. Therefore, taking into account the yield of methacrylic acid, we deduced a branching ratio for pathway B (=B1+B2) of 4.8±3.0%. This low branching ratio confirms that H-abstraction by OH on the carbonyl function of methacrolein is of minor importance compared to the OH addition on the C=C bond.

The mechanism shown in Fig. 6 gives explanation for the formation of methylglyoxal, formaldehyde, hydroxyacetone, acetic acid/acetate, DHMP, HMM and PMA as primary reaction products, and methacrylic acid/methacrylate as a primary and a secondary reaction product, observed in our experiments (Table 2). Most of these reaction products are highly reactive towards OH radicals, and can be oxidized under our experimental conditions to form secondary products. For example, the aqueous phase OH-oxidation of one of the major products, i.e. methylglyoxal, is relatively fast ($k_{OH25°C}$=5.3 (±0.4)×10^8 M^{-1} s^{-1} Monod et al., 2005), and leads to the formation of pyruvate, glyoxylate and oxalate (Altieri et al., 2008). This can explain the formation of these three reaction products observed as secondary products in our experiments (Fig. 2 and Table 2).

4.2 Carbon balance

The molar yield of the primary reaction products was determined by plotting their concentration versus the concentration of consumed methacrolein at the same reaction time (Fig. 2). The slope of the linear regression gives the molar yield of each product. The molar yields obtained for all the experiments are summarized in Table 2, together with the total carbon yields. The comparison between experiment type A and B shows a good agreement, thus indicating that initial concentrations do not significantly influence the yields. However, taking into account the estimated formation yields of HMM+DHMP and DMA, the total carbon yield ranges between 25 and 57%, thus indicating that a large part of the reaction products is missing.

Formate and HMHP were not measured in our experiments, and their detection limits (with ESI/MS) are too high to establish an experimental upper limit. Therefore using the mechanism (Fig. 6), we have evaluated an upper limit for their yields:

- Formate is formed through pathways A2.13a, b, c and d. Assuming that pathways A2.2 and A1 are of minor importance compared to A2.1, one can estimate an upper limit for the molar yield of formate of 95% (taking into account a yield for pathway B of 4.8%).

- HMHP is formed through pathways A2.13a and c and d, after the evolution of CH_2OH radicals, which were shown to form HMHP and formate with a ratio of $\frac{[\mathrm{HMHP}]}{[\mathrm{Formic/Formate}]}=\frac{1.5}{9}$ (Monod et al., 2007). Thus, one can estimate an upper limit for the molar yield of HMHP of 95%×1.5/9=16%.

The estimated upper limit for the molar yields of formate and HMHP added to the experimental carbon yields reported in Table 2 result in an upper limit for the total carbon yield ranging from 53 to 85%. This shows that a part of the reaction products remain still unidentified. The formations of higher molecular weight compounds as primary reaction products have been observed, and are presented in El Haddad et al. (2009). These non quantified molecules and oligomers may explain the lack of carbon. These molecules can also explain the formation of Secondary Organic Aerosol (SOA) which was experimentally observed (El Haddad et al., 2009). These findings indicate that multiphase photooxidation of methacrolein may be an important precursor of SOA in the atmosphere.

5 Conclusion

The photooxidation of methacrolein was studied in the aqueous phase under simulated cloud droplet conditions. The obtained rate constant of OH-oxidation of methacrolein at 6°C in unbuffered solutions was $5.8\ (\pm 0.9) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. This kinetic study showed that the oxidation proceeds mainly by OH-addition on the C=C bond. The reaction products obtained at 25°C in unbuffered solutions were methylglyoxal, formaldehyde, hydroxyacetone, acetic acid/acetate, 2,3-dihydroxy-2-methylpropanal, 2-hydroxy-2-methylmalonaldehyde and peroxymethacrylic acid as primary reaction products. Methacrylic acid/methacrylate was observed as both primary and secondary reaction product. Pyruvate, oxalate, glyoxylate and 2,3-dihydroxymethacrylic acid were detected as secondary reaction products. A chemical mechanism was proposed for the OH-oxidation of methacrolein and the calculation of the branching ratios confirmed that the OH-addition on the C=C bond is of major importance (higher than 95%) compared to the other pathways. An upper limit for the total carbon yield was estimated to range from 53 to 85%, indicating that some reaction products remain unidentified. A possible source of this mismatch is the formation of higher molecular weight compounds as primary reaction products which are presented in El Haddad et al. (2009).

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Table 1. Experimental and analytical conditions. **(a)** Experimental conditions and initial concentrations of reactants (1-pOH=1-propanol); **(b)** Calibration of each compound with each analytical technique. The detection limits represent 3 times the background signal.

Exp. type	Exp. number	$[H_2O_2]_0$ (M)	$[MACR]_0$ (M)	$[1\text{-pOH}]_0$ (M)	T (°C)	Duration	pH
kinetics	1, 2	8.0×10^{-3}	5.0×10^{-5}	1.0×10^{-4}	6	11–19 h	free
Reaction products A	a, b, c	6.0×10^{-2}	4.0×10^{-4}	–	25		
Reaction products B	d, e, f, g h, i	0.40	5.0×10^{-3} 2.0×10^{-3}				

Table 1. Continued.

Compound	Analytical technique	Statistical error (±2 σ) %	Experiment	Detection limit (M)
1-propanol	GC-FID	10	1,2	1×10^{-6}
Methacrolein	HPLC-UV	8.6	1,2,a,b,c,d,f	1.4×10^{-7}
	GC-FID	10	1,2,g	1.0×10^{-5}
	ESI-MS	34.0	a,b,c,d,e,g	7.1×10^{-6}
	On-line ESI-MS	22	h,i	2.5×10^{-5}
Formaldehyde	HPLC-UV	4.7	a,b,c,d,f	5.0×10^{-8}
Methylglyoxal	HPLC-UV	9.0	a,b,c,d,f	5.0×10^{-8}
Hydroxyacetone	GC-FID	15	g	6.0×10^{-6}
	ESI-MS	22.7	a,b,c,d,e,g	2.7×10^{-6}
	On-line ESI-MS	19	h,i	2.0×10^{-5}
Acetate/Acetic acid	ESI-MS	28.6	a,b,c,d,e,g	3.3×10^{-6}
	On-line ESI-MS	13	h,i	2.0×10^{-5}
Pyruvate	ESI-MS	25.6	a,b,c,d,e,g	1.1×10^{-6}
	On-line ESI-MS	18	h,i	3.0×10^{-7}
Oxalate	ESI-MS	23.5	a,b,c,d,e,g	2.2×10^{-6}
	On-line ESI-MS	32	h,i	1.0×10^{-6}
Glyoxylate	ESI-MS	25.0	a,b,c,d,e,g	1.4×10^{-6}
	On-line ESI-MS	16	h,i	1.0×10^{-6}
Methacrylate/Methacrylic acid	ESI-MS	26.1	a,b,c,d,e,g	5.8×10^{-7}
	On-line ESI-MS	20	h,i	1.0×10^{-6}

Table 2. Molar yields and total carbon yield during the OH-oxidation of methacrolein in the aqueous phase for all the experiments (described in Table 1). [a] Uncertainties take into account the analytical uncertainties of both the reaction products and the consumed methacrolein. [b] total carbon yield taking into account the estimated formation yields for HMM, DHMP and PMA. [c] estimated formation yields based on standards of other compounds, with similar chemical structure (see text).

Reaction products	Molar yields (%)[a]		Total carbon yield (%)		
	Exp. A a, b, c	Exp. B d, e, f, g, h, i	Exp. A a, b, c	Exp. B d, e, f, g, h, i	Exp. B[b] d, e, f, g, h, i
Methylglyoxal	6.0±1.2	9.1±1.7	21.4±9.5	30.3±9.8	25–57
Formaldehyde	10.2±1.0	12.2±1.7			
Hydroxyacetone	9.8±5.5	15.0±6.2			
Acetic acid/acetate	8.7±5.4	17.0±6.0			
Methacrylic acid/methacrylate	2.6±1.6 (and secondary)	0.7±0.4 (and secondary)			
HMM+DHMP	not measured	3–11%[c]			
PMA	not measured	4.1±2.6%[c]			
Pyruvate Oxalate Glyoxylate DHMA	Secondary products				

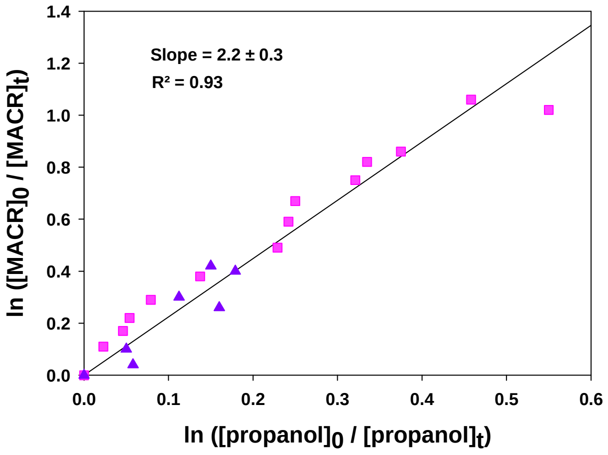

Fig. 1. Kinetics of OH-oxidation of methacrolein in the aqueous phase relative to 1-propanol at 6°C in unbuffured solutions. Experiments 1 and 2 (squares and triangles) are reported here. The uncertainty of the slope was calculated using the method developed by Brauers and Finlayson-Pitts (1997), taking into account both the standard deviation on the linear fit and the analytical uncertainties of methacrolein and 1-propanol. Indicated errors are $2\times\sigma$.

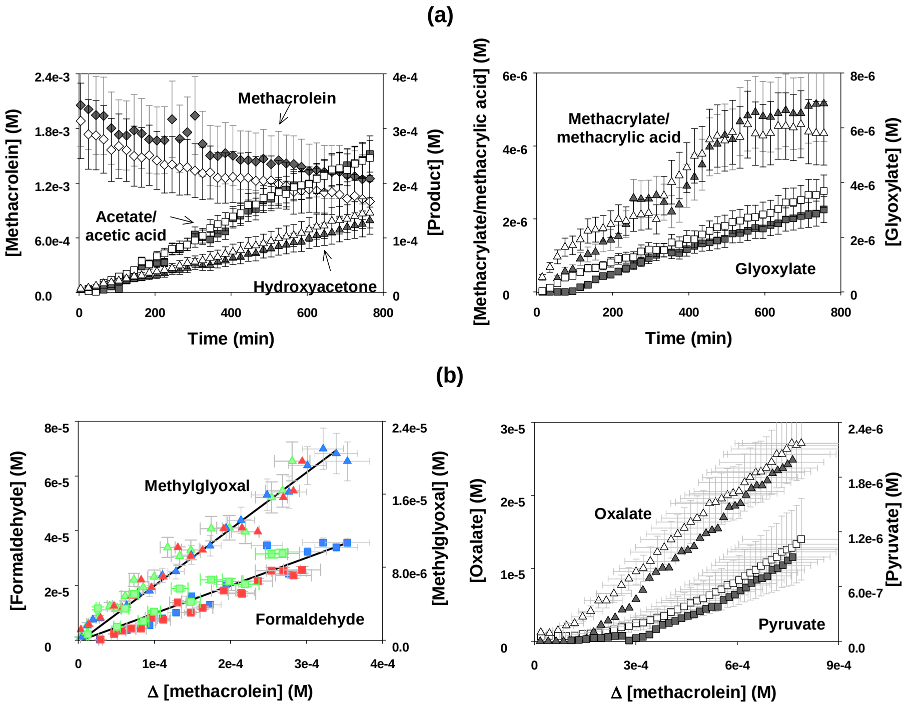

Fig. 2. Concentrations of methacrolein and its reaction products during OH-oxidation of methacrolein at 25°C in unbuffured solution (experiments a (blue), b (red) and c (green), h (grey) and i (white)). **(a)** Time profiles; **(b)** Reaction products' yields: Δ[methacrolein] is the consumed concentration of methacrolein.

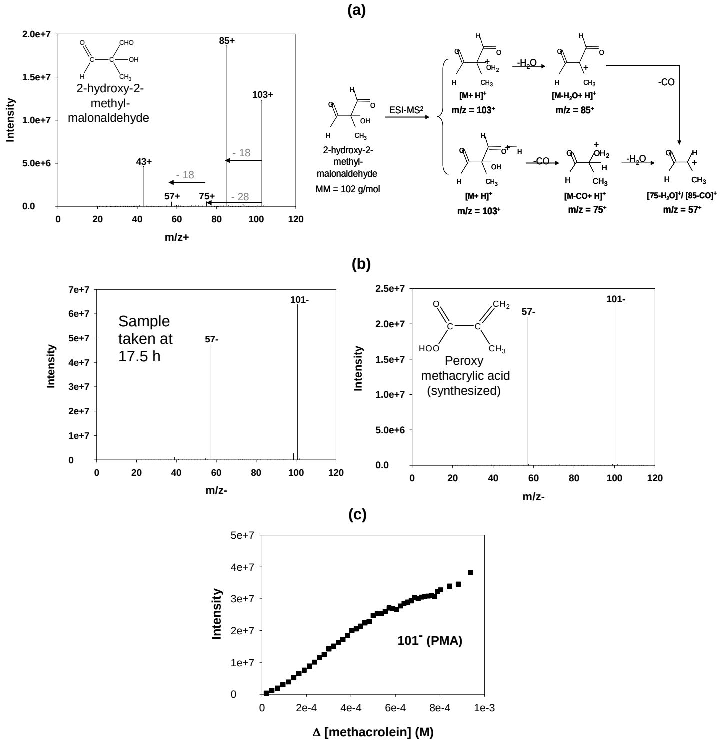

Fig. 3. Identification of 2-hydroxy-methylmalonaldehyde (HMM) and peroxymethacrylic acid (PMA) during the course of the reaction. **(a)** HMM was identified by ESI-MS/MS fragmentation mechanism (collision energy = 8 eV on a sample taken after 16 h of reaction). **(b)** PMA was identified by comparison of the ESI-MS/MS fragments of a sample (taken after 17.5 h of reaction) to those of the synthesized molecule (with a 8 eV collision Energy for both); **(c)** intensity of peak 101$^-$ (PMA) (obtained by on-line ESI-MS) as a function of consumed methacrolein during 14 h of reaction. The synthesis of PMA consisted in mixing 250 μl of pure methacrylic acid with 250 μl of H_2O_2 (50%) and 125 μl of pure acetic acid during 10 days.

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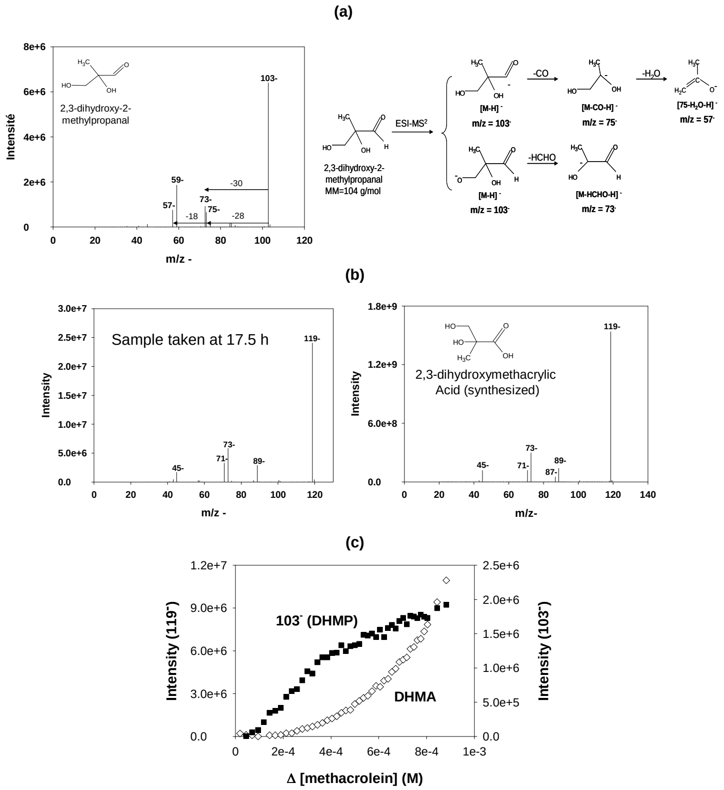

Fig. 4. Identifications of 2,3-dihydroxy-2-methylpropanal (DHMP) and 2,3-dihydroxymethacrylic acid (DHMA). **(a)** DHMP was most probably identified (in the absence of standards) by ESI-MS/MS (with a 8 eV collision Energy on a sample taken after 17.5 h of reaction); **(b)** DHMA was identified by comparison of the ESI-MS/MS fragments of a sample (taken after 17.5 h of reaction) to those of the synthesized molecule (with a 10 eV collision Energy for both); **(c)** DHMP (103^-) and DHMA (119^-) intensities' yields during 14 h of reaction (obtained by on-line ESI-MS).

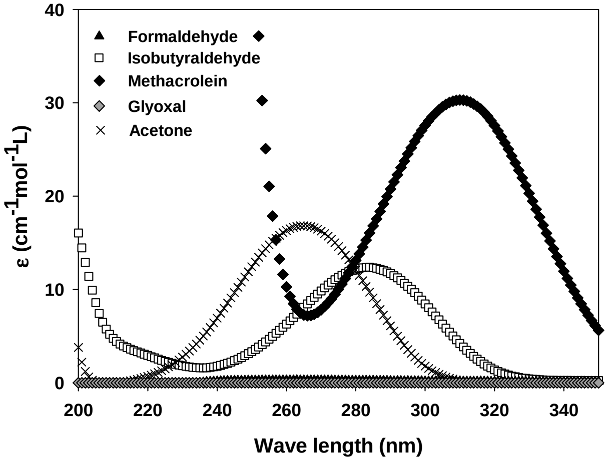

Fig. 5. Molar extinction coefficients in the UV-visible for carbonyl compounds compared to that of methacrolein in the aqueous phase.

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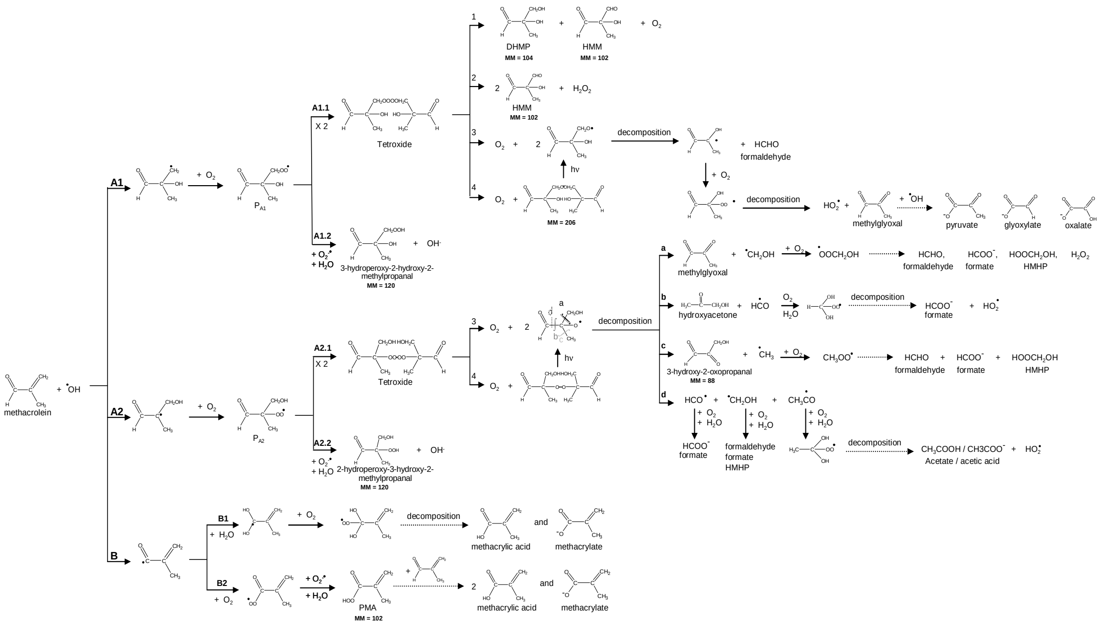

Fig. 6. Chemical mechanism of the three main pathways for the OH-initiated oxidation of methacrolein in the aqueous phase. DHMP = 2,3-dihydroxy-2-methylpropanal; HMM = 2-hydroxy-2-methylmalonaldehyde; PMA = peroxymethacrylic acid; MM = Molecular mass.