The production of formaldehyde and hydroxyacetone in methacrolein photooxidation: New insights into mechanism and effects of water vapor

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ABSTRACT

Methacrolein (MACR) is an abundant multifunctional carbonyl compound with high reactivity in the atmosphere. In this study, we investigated the hydroxyl radical initiated oxidation of MACR at various NO/MACR ratios (0 to 4.04) and relative humidities (< 3% to 80%) using a flow tube. Meanwhile, a box model based on the Master Chemical Mechanism was performed to test our current understanding of the mechanism. In contrast to the reasonable predictions for hydroxyacetone production, the modeled yields of formaldehyde (HCHO) were twice higher than the experimental results. The discrepancy was ascribed to the existence of unconsidered non-HCHO forming channels in the chemistry of CH3C(==CH2)OO, which account for approx. 50%. In addition, the production of hydroxyacetone and HCHO were affected by water vapor as well as the initial NO/MACR ratio. The yields of HCHO were higher under humid conditions than that under dry condition. The yields of hydroxyacetone were higher under humid conditions at low-NOx level, while lower at high-NOx level. The reasonable explanation for the lower hydroxyacetone yield under humid conditions at high-NOx level is that water vapor promotes the production of methacrolein nitrate in the reaction of HOCH2C(==CH2)(OO')CHO with NO due to the peroxy radical-water complex formation, which was evidenced by calculational results. And the minimum equilibrium constant of this water complex formation was estimated to be 1.89 × 10^{-18} cm^3/molecule. These results provide new insights into the MACR oxidation mechanism and the effects of water vapor.

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Introduction

Methacrolein (MACR) is an important multifunctional carbonyl compound with substantial abundance (a global budget of 45–100 Tg/year) and high reactivity in the atmosphere (Crounse et al., 2012; Guenther et al., 2012; Zhao et al., 2014). It is a major primary oxidation product of isoprene (Liu et al., 2013) and can be emitted from anthropogenic sources (e.g., vehicles) (Kean et al., 2001; Dong et al., 2014). In the atmosphere, the dominant loss process for MACR is the reaction with hydroxyl radical (OH) (Gierczak et al., 1997).

Gas phase MACR-OH oxidation has been investigated for decades (Tuazon and Atkinson, 1990; Orlando et al., 1999; Galloway et al., 2011; Crounse et al., 2012; Kjærgaard et al.,...
investigated at different NO/MACR ratios and RH using a flow tube. A series of products, including carbonyl compounds, were identified and quantified. Furthermore, it should be noted that current laboratory studies about gaseous products of MACR photooxidation were mostly conducted at dry conditions. However, there are mounting evidences that the relative humidity (RH) can significantly affect kinetics and yields of products in the OH initiated oxidation (Vöhringer-Martinez et al., 2007; Nguyen et al., 2011; Berndt, 2012). The yields of hydroxyacetone and glycolaldehyde were observed higher under humid condition in an isoprene-air-NOx photooxidation chamber experiment (Nguyen et al., 2011). Berndt (2012) found that the total yield of MACR and methyl vinyl ketone (MVK) increased significantly at 50% RH compared to that under dry condition in isoprene-OH oxidation. Experimental and theoretical evidences showed that water vapor can act as a catalyst in the reaction of OH and acetaldehyde (Vöhringer-Martinez et al., 2007). Given that water vapor is ubiquitous in the atmosphere, it is necessary to explore the effects of water vapor in MACR photooxidation. In addition, NOx levels can perturb the chemical processes in MACR photooxidation. For example, different NO concentrations determine different predominant sources of hydroxyacetone in MACR oxidation (Crounse et al., 2012). Therefore, the effects of water vapor on MACR photooxidation under different NOx conditions need to be investigated.

In this work, the OH initiated MACR photooxidation was investigated at different NO/MACR ratios and RH using a flow tube. A series of products, including carbonyl compounds, organic acids and peroxides, were identified and quantified. We examined the mechanism of MACR oxidation by employing a box model, and explored the effects of water vapor under different NOx conditions.

1. Materials and methods

1.1. Chemicals

Methacrolein (Aldrich, 95%), hydrogen peroxide (Alfa Aesar, 35 wt. %), formaldehyde (Sigma-Aldrich, 37 wt. %), acetaldehyde (Amethyst Chemicals, 49 wt. %), acetone (Fluka, ≥ 99.7%), hydroxyacetone (Aldrich, 90%), methylglyoxal (Aldrich, 40 wt. %), acetonitrile (Alfa Aesar, ≥97%), formic acid (Alfa Aesar, 97%), acetic acid (Alfa Aesar, 99.998%), ortho-phosphoric acid (Fluka, 85–90%), 2,4-dinitrobenzene hydrazine (DNPH) (30 wt. %, TCI), hemin (Sigma, ≥98.0%), 4-hydroxyphenylacetic acid (Alfa Aesar, 99%), ammonia solution (NH3·H2O, Beijing Tongguang Fine Chemicals Company, 25.0–28.0%), ammonium chloride (NH4Cl, Beijing Chemicals Works, ≥99.5%), N2 (≥99.999%, Beijing Haikyuanchang Practical Gas Company Limited, Beijing, China), O2 (≥99.999%, Beijing Haikyuanchang Practical Gas Company Limited, Beijing, China), NO (100 ppmv, National Institute of Metrology, China) and Sep-Pak DNPH-Silica Cartridges (Waters Corp.) were used in this work.

1.2. Apparatus

All experiments were conducted in an 8 L quartz flow tube (2 m length, 70 mm inner diameter), which was equipped with a water jacket to keep reactions proceeding at a constant temperature. There were forty-four 30 W UV lamps (λmax = 312 nm) surrounding the flow tube. Fig. 1 shows the schematic diagram of the experimental setup. H2O2 gas was generated by passing N2 through H2O2 solution. MACR was put in a diffusion tube and a flow of N2 blew its vapor to the reactor. Water vapor was generated by passing N2 or O2 to water bubblers. All the gases, including MACR, H2O2, NO and dry or wet synthetic air (N2: O2 = 80%: 20%), were mixed in a glass tube and then continuously introduced into the reactor at a flow rate of 2 L/min. The gas mixture formed a lamina flow in the flow tube (Reynolds number = 38.83) and the residence time was 4 min. The initial concentrations of MACR and H2O2 were 600–700 ppbv and 7 ppmv respectively. The initial NO concentration was set at five levels: 0, 50, 200, 1000 and 2500 ppbv. The RH was set at four levels: <3% (dry condition), 30%, 60% and 80% RH. All the experiments were performed at 298 K under the same illumination intensity condition. The concentration of OH was 1.64–4.39 pptv, depending on the initial NO concentration, which was calculated from the MACR decay. OH was evenly distributed in the flow tube based on the simulation results that the OH concentration increased rapidly in several seconds and then tended to be stable during the MACR photooxidation. The gas mixture was pumped into a coil collector immediately out of the reactor and was extracted by H3PO4 solution (pH 3.5) for peroxides analysis or by ultrapure water for organic acids analysis. DNPH cartridges were used to collect gas samples and then were eluted by 5 mL acetonitrile for carbonyls analysis.

1.3. Reactants and products analysis

Peroxides were detected on-line by high performance liquid chromatography (HPLC) (Agilent 1100, USA) coupled with post-column derivatization and fluorescence detection (with
the detection limit of 35 pptv under the sampling conditions). The methods have been described in our previous study (Hua et al., 2008). Briefly, peroxides were separated by column chromatography and then reacted with p-hydroxyphenylacetic acid (POPHA) by the catalysis of hemin, forming POPHA dimers, which were finally quantified by a fluorescence detector. The calibrations were performed with standard solutions, and the synthetic methods for peroxides were reported in our previous study (Huang et al., 2013). Carbonyl-contained eluent samples were injected into HPLC (Agilent 1100, USA) for separation and ultraviolet detection after derivatization for 12–24 hr in darkness at room temperature (with the detection limit of 224 pptv under the sampling conditions). This method was also described in our previous work (Wang et al., 2009). The calibrations were performed with standard solutions. Organic acids were analyzed immediately using ion chromatography (IC) (DIONEX 2650, USA) with an ED50 conductivity detector (with the detection limit of 26 pptv under the sampling conditions). The calibrations were performed with standard solutions.

1.4. Model simulations

A box model coupled with MACR oxidation mechanism, which was extracted from the Master Chemical Mechanism version 3.3.1 (MCM v3.3.1) (website: http://mcm.leeds.ac.uk/MCMv3.3.1; Jenkin et al., 1997, 2015; Saunders et al., 2003), was performed to simulate MACR photooxidation processes occurring in the flow tube under various conditions. The primary concentrations of MACR, NO and H2O2 were set according to the experimental conditions. There were 91 species and 697 reactions involved in the model. Assuming that the rate of OH formation equals to its destruction, which is known as pseudo-steady-state approximation (PSSA), H2O2 photolysis rate is approximately half the sum rate of OH reacting with H2O2 and MACR (major sinks of OH in this system). The photolysis rate of H2O2 was calculated to be 8.6 x 10^{-5} sec^{-1}, from which the photolysis rates for other species were determined. Photolysis rates given in the MCM are as a function of solar zenith angle (SZA) (Eq. (1)). Modeled photolysis rates were calculated for SZA = 0, and then all J values were scaled by a common factor (with the value of 11) to ensure the modeled and known H2O2 photolysis rate were equivalent.

\[
J = l (\cos \chi)^m \exp(-n \cdot \sec \chi)
\]

where, l, m and n are three optimized parameters from Jenkin et al. (1997); \( \chi \) is SZA.

1.5. Theoretical calculation methods

All the calculations were performed using Gaussian 09 program. The initial geometries of MACRO2·H2O and their monomers were obtained by B3LYP-D3 with 6-311++G(d,p) basic set. The most stable structures were further optimized at the B3LYP-D3/aug-cc-pVTZ level. The empirical dispersion correction is shown to give an important contribution for general thermochemistry, kinetics and noncovalent interaction (Goerigk and Grimme, 2011). Containing the empirical dispersion correction, B3LYP-D3 functional was found to be an excellent choice for the geometry and energy prediction (DiLabio et al., 2013). In addition, the binding energies (BEs) corrected with zero point vibrational energies (ZPVE), enthalpies (\( \Delta H_{298.15} \)) and Gibbs free energies (\( \Delta G_{298.15} \)) for the complex formation were calculated from these higher-level
results. BE was determined as the difference between the complex energy and the sum energy of its monomers (BE = E(MACRO$_2$·H$_2$O) – E(MACRO$_2$) – E(H$_2$O)), without correction for basis set superposition error (BSSE). 

\[ \Delta H_{298 \, K} \] and \[ \Delta G_{298 \, K} \] were calculated in the same way.

2. Results and discussion

2.1. Yields of products at different initial NO/MACR ratios under dry condition

Carbonyl compounds, organic acids and peroxides were detected and well characterized in MACR photooxidation at different initial NO/MACR ratios under dry condition (Table 1). It was found that the molar yields of all the products showed high sensitivity to the initial NO/MACR ratio. The molar yields of measured carbonyl compounds, i.e., hydroxyacetone, HCHO, acetaldehyde and methylglyoxal, were significantly higher in the presence of NOx compared to that under NOx-free condition. Meanwhile, the yields of organic acids, i.e., formic acid and acetic acid, and peroxides, i.e., peroxyformic acid, methyl hydroperoxide and peroxyacetic acid, decreased in the presence of NOx. These changes are due to the influence of NO on organic peroxy radicals (RO$_2$) chemistry. Under NO$_x$-free condition, RO$_2$ primarily reacts with hydroperoxy radical (HO$_2$) or RO$_2$, and the main products are hydroperoxides and organic acids. With the increasing of the initial NO/MACR ratio, RO$_2$ + NO becomes increasingly competitive, inducing more carbonyls production. The yields of carbonyl products under high NOx conditions obtained in our work were in well agreement with literature results (Table 2), and the yields of formic acid and acetic acid were also in consistence with the values obtained in Brégonzio-Rozier et al. (2015) (8% and 6% respectively). To the best of our knowledge, the yields of these products under NOx-free condition are reported for the first time.

2.2. Model simulations and mechanism exploration

2.2.1. Overestimation of HCHO in the model

Two major products, HCHO and hydroxyacetone, were employed as indicators to test our current understanding of MACR photooxidation. We performed a box model coupled with a near-explicit MACR oxidation mechanism (extracted from the MCM v3.3.1) to simulate the oxidation processes, predicting the yields of HCHO and hydroxyacetone, and then the modeled yields were compared with experimental data under dry condition. As shown in Fig. 2, the modeled yields of hydroxyacetone agreed well with the observed values at different initial NO/MACR ratios. Although the modeled yields of HCHO showed a similar trend with the increasing initial

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Table 1 – Yields (%) of products in methacrolein (MACR) photooxidation at various initial NO/MACR ratios under dry condition.

<table>
<thead>
<tr>
<th>Products</th>
<th>Initial NO/MACR ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>18.77 ± 1.61</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>11.05 ± 1.20</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>1.89 ± 1.29</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>1.70 ± 0.55</td>
</tr>
<tr>
<td>Formic acid</td>
<td>22.29 ± 1.31</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>20.38 ± 1.67</td>
</tr>
<tr>
<td>Peroxyformic acid</td>
<td>1.00 ± 0.22</td>
</tr>
<tr>
<td>Methyl hydroperoxide</td>
<td>2.49 ± 0.46</td>
</tr>
<tr>
<td>Peroxyacetic acid</td>
<td>1.15 ± 0.18</td>
</tr>
</tbody>
</table>

n.d.: not detected.

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Table 2 – Comparing yields of carbonyl products under dry condition with previous studies.

<table>
<thead>
<tr>
<th>Initial MACR (ppbv)</th>
<th>OH precursor</th>
<th>Initial NO (ppbv)</th>
<th>Initial NO$_2$ (ppbv)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyacetone</td>
<td>HCHO</td>
<td>9800</td>
<td>1750/320</td>
<td>41.00 ± 3.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13,000–39,000</td>
<td>0</td>
<td>47.00 ± 5.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42</td>
<td>321</td>
<td>39.50 ± 1.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>396–927</td>
<td>&lt;123</td>
<td>1.00–0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>627</td>
<td>1000</td>
<td>38.22 ± 2.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>618</td>
<td>2500</td>
<td>38.23 ± 2.93</td>
</tr>
</tbody>
</table>

MACR: Methacrolein.

a Tuazon and Atkinson, 1990.
b Orlando et al., 1999.
c Galloway et al., 2011.
d Brégonzio-Rozier et al., 2015.
e This work.
The initial NO/MACR ratio as experimental data, the simulated values were about twice higher than the experimental results under various NOx conditions.

To find out the cause of the discrepancy between the modeled and experimental HCHO yields, we analyzed the sources of HCHO in MACR photooxidation. Three major pathways for HCHO production are shown in Fig. 3. Path a: the isomerization and subsequent decomposition of CH3C(=CH2)OO. Path b: the reaction of CH3O with O2. Path c: the decomposition of CH2(O)C(CH3)(OH)CHO formed in internal OH addition channel. The relative contributions of these three pathways to HCHO production at different initial NO/MACR ratios were determined on the basis of model simulations (Fig. 4). As shown in Fig. 4, path a and path b contributed to most of the HCHO production under various NOx conditions. As path a and path b are both subsequent processes of CH3C(=CH2)OO, we speculate that the overestimation of HCHO in the model is related to CH3C(=CH2)OO.

In MCM v3.3.1, CH3C(=CH2)OO yields 0.65 (CH3OO + HCHO + CO) and 0.35 (CH3C(O)OO' + HCHO) via an isomerization process, which was proposed by Orlando et al. (1999). They plotted the amount of HCHO generated in MACR photooxidation via H-atom abstraction channel (Excess [HCHO]) as a function of calculated CH3C(=CH2)OO'. The yield of HCHO from CH3C(=CH2)OO' was 1.9 (joint contributions from path a and path b). In their study, Excess [HCHO] was derived from subtracting the observed methylglyoxal concentration from the observed HCHO concentration, as methylglyoxal is the co-product of HCHO in internal OH addition channel (Fig. 3). The calculated CH3C(=CH2)OO' was equal to the consumed MACR minus the sum of observed hydroxyacetone, MPAN and methylglyoxal. We extracted the experimental data in Tuazon and Atkinson (1990) to re-estimate the yield of HCHO from CH3C(=CH2)OO' using the same method from Orlando et al. (1999). It is noted that the initial NO/MACR ratio in Tuazon and Atkinson (1990) is comparable to that in Orlando et al. (1999) (Table 2). The yield of HCHO from CH3C(=CH2)OO' was recalculated to be 1.08 ± 0.18, half of the value used in the model. Since path a and path b contribute equally to the HCHO production, the yield of HCHO directly contributed by CH3C(=CH2)OO' (path a) should be approx. 0.5, indicating that there may exist other non-HCHO forming channels in the chemistry of CH3C(=CH2)OO'. Under NOx-free condition when HCHO was predominantly from CH3C(=CH2)OO' via path a, the yield of HCHO was also overestimated, which suggests that the missing non-HCHO forming channels of CH3C(=CH2)OO' are not related to NOx.

We re-simulated the oxidation processes under different NOx conditions after revising the relevant mechanism used in the box model according to the recalculated yield of HCHO from CH3C(=CH2)OO'. The modeled results, as shown in Fig. 5, demonstrated that the modified model predicted the yields of HCHO more accurately. The detailed non-HCHO forming channels of CH3C(=CH2)OO' need further research.

2.2.2. Effects of initial NO/MACR ratios on the sources of hydroxyacetone and HCHO
To further explore the roles of NOx in MACR photooxidation, we analyzed the sources of hydroxyacetone and HCHO at different initial NO/MACR ratios using the modified model. Sources of hydroxyacetone and HCHO showed high dependence on the initial NO/MACR ratio (Fig. 6). The renewed relative contributions of three pathways to HCHO production at different initial NO/MACR ratios are shown in Fig. 6a. Under NOx-free condition, almost all of HCHO was produced from path a. With the increase of the initial NO/MACR ratio, path b and path c, which are both closely associated with RO2 + NO, contributed increasingly to the production of HCHO. However, as path c is the subsequent process of internal OH addition, which is a minor channel in the MACR-OH oxidation (8% in MCM v3.3.1), the contribution of path c was less than 18% under various NOx conditions. Under NOx-dominated conditions, path b occurs following path a, in other words, once one molecular HCHO forms via path a, one more molecular HCHO formation via path b ensues. Therefore, when the initial NO/MACR ratio was greater than 0.33, path a and path b contributed equivalently to HCHO production, both accounting for about a half.

Via analysis, we identified three main pathways contributing to more than 90% of the total hydroxyacetone production at various NO/MACR ratios (Fig. 3). Path d: 1.4 H-atom shift isomerization and subsequent decomposition of MACRO2. Path e: the decomposition of HOCH2C(CH3)(O)CHO (MACRO) followed by MACRO2 reacting with NO. Path f: the reaction of OH with HOCH2C(CH3)(OOH)CHO (MACROOH) that is formed by MACRO2 + HO2. The initial NO/MACR ratio altered the relative contributions of these three pathways to the hydroxyacetone production, as shown in Fig. 6b. It is apparent that hydroxyacetone was dominantly produced from path d under NOx-free condition. When the initial NO/MACR ratio was 0.08, the contribution of path d decreased, while the contributions of path e and path f both increased. The increased contribution from path f reflected the improved
competitiveness of MACRO$_2$ + HO$_2$ under this low-NO$_x$ condition, according with the modeled results that the concentration of HO$_2$ raised from 1.42 ppbv under NO$_x$-free condition to 2.65 ppbv. With the increase of the initial NO/MACR ratio, NO gradually dominated the chemistry of MACRO$_2$, inducing more hydroxyacetone production from path $e$, and suppressing the production of hydroxyacetone from path $d$ and path $f$. When the initial NO/MACR ratio was greater than 1.59, almost all of hydroxyacetone was produced from path $e$.

2.3. Effects of water vapor

2.3.1. Effects of water vapor on the yields of hydroxyacetone and HCHO

In this study, we further investigated the RH dependence of the yields of hydroxyacetone and HCHO at low-NO$_x$ (NO/MACR = 0) and high-NO$_x$ (NO/MACR = 1.59) levels. As shown in Fig. 7, the yields of HCHO were higher under humid conditions than that under dry condition. The yields of hydroxyacetone were higher under humid conditions at low-NO$_x$ level, while lower at high-NO$_x$ level. Nguyen et al. (2011) found that the production of hydroxyacetone generated from isoprene photooxidation at high-NO$_x$ level (NO$_x$: MACR was about 3:1) was obviously higher under humid condition. We speculate that this discrepancy may be originated from the different reaction conditions in our study and their study. Hydroxyacetone is a second-generation product in isoprene photooxidation. When most of hydroxyacetone was formed from MACR in their experiments, NO may have been largely converted to other nitrogenous substances. Therefore, it explains why the relation between RH and hydroxyacetone yield at high-NO$_x$ level in Nguyen et al. (2011) is the same as that at low-NO$_x$ level in this study. However, the inference is not certain, as the instantaneous NO$_x$ level was not given in the literature, and in addition to further oxidation of MACR, hydroxyacetone has other sources like the decomposition of alkoxy radicals or the degradation of hydroxyl alkenyl nitrates in isoprene photooxidation (Nguyen et al., 2011).

As demonstrated in Section 2.2.2, the sources of hydroxyacetone and HCHO are different, which are also affected by NO$_x$ levels. Hence, it is discussed below how water vapor affects these different processes. Previous studies...
have concurred that peroxy radicals (including HO$_2$) can complex with water, among which, the water complex formation of $\beta$-hydroxy peroxy radicals ($\beta$-position is relative to the carbon where O$_2$ adds to) have been supported by calculational and experimental evidences (Hamilton, 1975; Suma et al., 2006; Clark et al., 2008, 2010; Burrell et al., 2012; Kumbhani et al., 2015). The formation of water complex can affect the kinetics and mechanism of subsequent reactions (Kanno et al., 2005; Stone and Rowley, 2005; Butkovskaya et al., 2005, 2009; Tang et al., 2010; Kumbhani et al., 2015). Butkovskaya et al. (2009) found that the production of HNO$_3$ from the HO$_2$ + NO reaction was significantly enhanced in the presence of water vapor and they explained that the reaction of HO$_2$·H$_2$O with NO yields more HNO$_3$ as the rate of HO$_2$·H$_2$O + NO $\rightarrow$ HNO$_3$ is higher than HO$_2$ + NO $\rightarrow$ HNO$_3$. MACRO$_2$, as a kind of $\beta$-hydroxy peroxy radical, has potential to complex with water, which is evidenced by calculational results in Section 2.3.2. At high-NO$_x$ level, MACRO$_2$ predominantly reacts with NO yielding MACRO or methacrolein nitrate (MACRNO$_3$). We infer that water vapor may also influence the branching ratio of reaction MACRO$_2$ + NO via the similar mechanism as in HO$_2$ system, enhancing the production of MACRNO$_3$, and alternatively inhibiting the production of MACRO, further decreasing the yield of hydroxyacetone.

It is coincidence that the production of hydroxyacetone at low-NO$_x$ level and the production of HCHO at both low-NO$_x$ and high-NO$_x$ levels are all closely related to isomerization processes. The isomerization and subsequent decomposition of MACRO$_2$ (path d) is the main source of hydroxyacetone at low-NO$_x$ level. The isomerization and subsequent decomposition of CH$_3$C$(\text{=CH}_2)$OO$^-$ (path a) is a key pathway for HCHO production at both low-NO$_x$ and high-NO$_x$ levels. However, our additional calculational results indicate that the water complex of CH$_3$C$(\text{=CH}_2)$OO$^-$ is not stable (with binding energies of 2.5 kcal/mol). Hence, we speculate that water vapor may accelerate isomerization processes, which is not concerned with the formation of stable water complex, while it needs further research.

### 2.3.2. Formation of water complex

We employed theoretical calculations to verify the formation of the water complex. Fig. 8 shows two optimized structures of MACRO$_2$ that have approximate energies and their associated water complexes stabilized by two intermolecular hydrogen bonds. The binding energies along with other thermodynamic properties were calculated as shown in Table 3. The binding energies of the water complexes were
calculated to be 6.1 kcal/mol, comparable to the binding energies of four \( \beta \)-hydroxy isoprene peroxy radical-water complexes (5.3–5.8 kcal/mol at the MP2(full)/6-311++G(2d,2p) and CCSD(T)/6-311++G(d,p) level) (Clark et al., 2010), two \( \beta \)-hydroxy hexenal peroxy radical-water complexes (6.0 and 6.1 kcal/mol at the B3LYP/6-311++G(2d,2p) level) (Burrell et al., 2012) and the \( \beta \)-hydroxy ethyl peroxy radical-water complex (6.5 kcal/mol at the B3LYP/aug-cc-pVDZ level) (Kumbhani et al., 2015). Clark et al. (2008) predicted that water complex with the largest binding energy larger than 5 kcal/mol are of vital importance in the atmosphere. Therefore, we infer that MACRO\(_2\)·H\(_2\)O exists in MACR photooxidation under humid conditions and affects the kinetics of the subsequent reactions.

The ratio of MACRO\(_2\)·H\(_2\)O to MACRO\(_2\) monomer in our flow tube is equal to \( K_p \) [H\(_2\)O] (\( K_p \) is the equilibrium constant for the equilibrium of MACRO\(_2\) + H\(_2\)O \( \leftrightarrow \) MACRO\(_2\)·H\(_2\)O), and can be expressed via Eq. (2):

\[
0.47 \times \left( \frac{0.987 \times \frac{1}{1 + K_p[H_2O]} + Y' \times \frac{K_p[H_2O]}{1 + K_p[H_2O]}}{Y_{HA}} \right) = Y_{HA}
\]

where [H\(_2\)O] (molecule/cm\(^3\)) is the concentration of water vapor, \( Y' \) is the yield of MACRO from the reaction of MACRO\(_2\)·H\(_2\)O + NO, \( Y_{HA} \) is our experimental hydroxyacetone yield at different RH, 0.47 is the branching ratio of external OH addition channel and 0.987 is the yield of MACRO from MACRO\(_2\) + NO (MCM v3.3.1). Solving Eq. (2), \( K_p \) is finally expressed as:

\[
K_p = \frac{0.46389 - Y_{HA}}{[H_2O] \times \left( Y_{HA} - 0.47Y' \right)}
\]

Fig. 6 – Sources of (a) HCHO and (b) hydroxyacetone in MACR photooxidation at various initial NO/MACR ratios, which were determined using the modified model.

Fig. 7 – Dependence of the yields of (a) hydroxyacetone and (b) HCHO on the relative humidity (RH) at low-NO\(_x\) (NO/MACR = 0) and high-NO\(_x\) (NO/MACR = 1.59) levels.
Assuming that MACRO$_2$·H$_2$O complex could be converted to MACRNO$_3$ completely reacting with NO ($\gamma' = 0$), the calculated minimum $K_p$ is $(1.89 \pm 1.01) \times 10^{-18}$ cm$^3$/molecule. The derived minimum $K_p$ value is of the same magnitude as other experiment determined values for the formation of HO$_2$·H$_2$O and $\beta$-hydroxy ethyl peroxy radical-water complex (Aloisio et al., 2000; Kanno et al., 2005; Kumbhani et al., 2015). From the value, we can estimate that the ratio of MACRO$_2$·H$_2$O to MACRO$_2$ is about 0.44 at 298 K and 30% RH, when the number concentration of water vapor is $2.31 \times 10^{17}$ molecule/cm$^3$.

### 3. Conclusions and atmospheric implications

In this study, we combined laboratory experiments with box model simulations to investigate the OH initiated oxidation of MACR and focused on the production of hydroxyacetone and HCHO. It was found that the box model performed well in simulating the yields of hydroxyacetone, while the modeled yields of HCHO were twice higher than our experimental results. We speculate that the discrepancy is caused by the overestimation of HCHO formed from CH$_3$C(—CH$_3$)OO'. Via revaluation, the yield of HCHO from CH$_3$C(—CH$_3$)OO' should be 0.5. There may exist other non-HCHO forming channels in the chemistry of CH$_3$C(—CH$_3$)OO', which account for approx. 50%, while the detailed mechanism needs to be investigated in the future. In some isoprene-dominated areas, discrepancies were reported between model simulations and observations for HCHO (Butler et al., 2008; Galloway et al., 2012; Luecken et al., 2012; Li et al., 2014; Zeng et al., 2015). Our finding helps to better simulate atmospheric HCHO concentration and to better constrain isoprene emission via the top-down inventory in turn as HCHO has been used widely as an efficient proxy to constrain the emission of isoprene (Palmer et al., 2003; Barkley et al., 2013; Dufour et al., 2009; Marais et al., 2012; Fu et al., 2007; Shim et al., 2005).

Our laboratory study also reveals that both NO/MACR ratios and water vapor affect the yields of hydroxyacetone and HCHO via affecting RO$_2$ chemistry. The yields of HCHO were higher under humid conditions than that under dry condition. The yields of hydroxyacetone were higher under humid conditions at low-NOx level, while lower at high-NOx level. The results present here suggest that water vapor may accelerate isomerization processes, which deserves further investigations. In addition, we ascribed the lower hydroxyacetone yield under humid conditions at high-NOx level to the formation of MACRO$_2$·H$_2$O, whose binding energy was calculated to be 6.1 kcal/mol. The branching ratio of MACRO$_2$·H$_2$O + NO may be different from MACRO$_2$ + NO, with higher yield of MACRNO$_3$. However, current experimental techniques are limited for...
isoprene and terpenes, can all generate radical-water complexes \((C_{n}H_{2n}O_{2n+1}-H_{2}O)\). J. Phys. Chem. A 114 (23), 6534–6541.


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References


