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Q1 **The production of formaldehyde and hydroxyacetone in**
 2 **methacrolein photooxidation: New insights into mechanism**
 3 **and effects of water vapor**

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A B S T R A C T

Methacrolein (MACR) is an abundant multifunctional carbonyl compound with high 16 reactivity in the atmosphere. In this study, we investigated the hydroxyl radical initiated 17 oxidation of MACR at various NO/MACR ratios (0 to 4.04) and relative humidities (RH) 18 (<3% to 80%) using a flow tube. Meanwhile, a box model based on the Master Chemical 19 Mechanism was performed to test our current understanding of the mechanism. In 20 contrast to the reasonable predictions for hydroxyacetone production, the modeled 21 yields of formaldehyde (HCHO) were twice higher than the experimental results. This 22 discrepancy was ascribed to the existence of unconsidered non-HCHO forming channels 23 in the chemistry of CH₃C(=CH₂)OO', which account for approx. 50%. In addition, the 24 production of hydroxyacetone and HCHO were affected by water vapor as well as the initial 25 NO/MACR ratio. The yields of HCHO were higher under humid conditions than that under 26 dry condition. The yields of hydroxyacetone were higher under humid conditions at 27 low-NO_x level, while lower at high-NO_x level. The reasonable explanation for the lower 28 hydroxyacetone yield under humid conditions at high-NO_x level is that water vapor 29 promotes the production of methacrolein nitrate in the reaction of HOCH₂C(CH₃)(OO')CHO 30 with NO due to the peroxy radical-water complex formation, which was evidenced by 31 calculational results. And the minimum equilibrium constant of this water complex formation 32 was estimated to be 1.89 × 10⁻¹⁸ cm³/molecule. These results provide new insights into the 33 MACR oxidation mechanism and effects of water vapor. 34

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48 **Introduction**

51 Methacrolein (MACR) is an important multifunctional carbonyl 52 compound with substantial abundance (a global budget 53 of 45–100 Tg/year) and high reactivity in the atmosphere 54 (Crouse et al., 2012; Guenther et al., 2012; Zhao et al., 2014). 55 It is a major primary oxidation product of isoprene (Liu

et al., 2013) and can be emitted from anthropogenic sources 56 (e.g., vehicles) (Kean et al., 2001; Dong et al., 2014). In the 57 atmosphere, the dominant loss process for MACR is the 58 reaction with hydroxyl radical (OH) (Gierczak et al., 1997). 59

Gas phase MACR-OH oxidation has been investigated for 60 decades (Tuazon and Atkinson, 1990; Orlando et al., 1999; 61 Galloway et al., 2011; Crouse et al., 2012; Kjaergaard et al., 62

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2012; Fuchs et al., 2014; Brégonzio-Rozier et al., 2015). Previous studies mainly focused on the MACR-OH oxidation under high-NO_x conditions and inferred the oxidation mechanism by identifying the major products as formaldehyde (HCHO), hydroxyacetone, methylglyoxal and peroxyacetyl nitrate (MPAN) (Tuazon and Atkinson, 1990; Orlando et al., 1999). Furthermore, recent theoretic and laboratory works have provided new insights into the MACR oxidation mechanism under low-NO_x conditions (Crounse et al., 2012; Kjaergaard et al., 2012; da Silva, 2012; Fuchs et al., 2014). An isomerization reaction of HOCH₂C(CH₃)(OO[•])CHO (MACRO₂) was proposed to generate hydroxyacetone and OH (Crounse et al., 2012), which was supported by a chamber study (Fuchs et al., 2014). Kjaergaard et al. (2012) theoretically investigated further OH oxidation of methacrylicperoxy acid (an intermediate in MACR-OH oxidation), which can also contribute to hydroxyacetone production in MACR photooxidation. Theoretic work by da Silva (2012) identified a double activation process, yielding hydroxyacetone, methylglyoxal and HCHO. Overall, these studies suggested that some important trace gases (e.g., hydroxyacetone and HCHO) can be generated from MACR photooxidation, while to the best of our knowledge, the yields of these products under low-NO_x conditions are still unclear. Completing the MACR photooxidation mechanism is essential for the assessment of its atmospheric impact. It is also necessary to evaluate the extent and accuracy of our mechanistic understanding about MACR oxidation via comparing model predictions with experimental data.

Furthermore, it should be noted that current laboratory studies about gaseous products of MACR photooxidation were mostly conducted at low relative humidity (RH). However, there are mounting evidences that RH can significantly affect kinetics and yields of products in 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-NO_x 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 evidence showed that water vapor can act as 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, NO_x levels can affect the products of MACR photooxidation by perturbing the chemistry of organic peroxy radicals (RO₂). 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 NO_x 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 NO_x 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, 99.7 + %), formic acid (Alfa Aesar, 97%), acetic acid (Alfa Aesar, 99.9985%), 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 Haikeyuanchang Practical Gas Company Limited, Beijing, China), O₂ (≥99.999%, Beijing Haikeyuanchang 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 (λ_{max} = 312 nm) surrounding the flow tube. Fig. 1 shows the schematic diagram of experimental system 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 standard 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. 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 conditions. 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 OH concentration increased rapidly in several seconds and then tended to be stable during the MACR photooxidation. 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

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