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Yangang Ren, Min Cai, Véronique Daële, Abdelwahid S Mellouki. Rate coefficients for the reactions of OH radical and ozone with a series of unsaturated esters. *Atmospheric Environment*, 2019, 200, pp.243-253. 10.1016/j.atmosenv.2018.12.017. insu-01968878

**HAL Id: insu-01968878**

**<https://insu.hal.science/insu-01968878v1>**

Submitted on 4 Jan 2019

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# Rate coefficients for the reactions of OH radical and Ozone with a series of unsaturated esters

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**Abstract:** Unsaturated esters are emitted into the atmosphere from biogenic and anthropogenic sources. Their atmospheric degradation through reactions with the main atmospheric oxidants (OH, O<sub>3</sub>, NO<sub>3</sub>, Cl) contributes to the formation of important secondary pollutants. Kinetic and mechanistic parameters for these reactions are highly required in order to estimate the atmospheric lifetimes and hence the impacts of these important classes of VOCs. In this study, the gas-phase rate coefficients of the reaction of OH radical and O<sub>3</sub> with a series of unsaturated esters are reported. The esters investigated include methyl methacrylate (MMA), ethyl methacrylate (EMA), n-propyl methacrylate (nPMA), n-butyl methacrylate (nBMA), iso-propyl methacrylate (iPMA), iso-butyl methacrylate (iBMA) and fully deuterated methyl methacrylate (MMA-D<sub>8</sub>). The measurement combined the pulsed laser photolysis-laser induced fluorescence for the OH studies in the temperature range 257-376K and a 7300 L atmospheric simulation chamber for the O<sub>3</sub> reactions at 291 ± 2K. This work provides the first temperature-dependence studies of OH reaction with EMA, nPMA, iPMA and iBMA and of O<sub>3</sub> reaction with nPMA, iPMA and iBMA at room temperature. The obtained data are discussed in terms of the structure reactivity relationships and their atmospheric consequences by estimating the atmospheric lifetimes for the studied esters with respect to O<sub>3</sub>, OH radical and other oxidant in the troposphere.

**Keyword:** rate coefficient, ozone, OH radical, unsaturated esters, atmospheric lifetime

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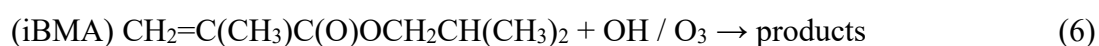
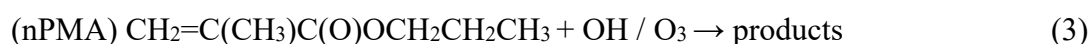
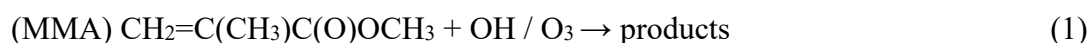
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## 1 Introduction

Unsaturated esters are among the most important oxygenated volatile organic compounds (OVOC) emitted into the atmosphere through a large number of commercial uses worldwide as well as from natural sources. They are largely used in the polymer industries. Indeed, the most important polymer types made by methyl methacrylate (MMA) are cast acrylic sheets and molding/extrusion compounds, besides emulsions and dispersion with total EU production of MMA to 470,000 t/yr (OECD). Polymers based upon ethyl methacrylate (EMA), iso-butyl methacrylate (iBMA), and n-butyl methacrylate (nBMA) are used to make automotive coatings, nail sculpturing, inks, lacquers, adhesives, oil additives, emulsions for textile, leather and paper refinishing and dental products etc (SIAM, 2004). The unsaturated esters such as the ones of interest in the present study may be released into the environment in fugitive and stack emissions or in wastewater during their production and use. For example, estimated releases into the environment in the EU are 23.5-5170 t/yr of MMA, < 0.3 t/yr of nBMA and < 0.15 t/yr of iBMA to air (OECD). Significant atmospheric releases of these unsaturated esters are also to be expected in various areas in the world such as the USA where these compounds are also produced in large quantities (EPA, 2016). Once released into the troposphere, the unsaturated esters will be subject to photo-degradation mainly through reaction with OH radicals during the day-time (Blanco et al., 2009a; Blanco et al., 2006) and to a lesser extent with NO<sub>3</sub> radicals during the night-time (Zhou et al., 2017) and ozone during both day and night-time (Bernard et al., 2010; Gai et al., 2009; Gaona Colmán et al., 2013) and Cl atoms in certain environments such as marine area (Blanco et al., 2009b; Martin Porrero et al., 2010). Knowledge of the rate coefficients for the unsaturated esters reactions with tropospheric reactive species, as well as the degradation mechanisms are required to estimate their persistence and fate in the atmosphere. Although, the available studies (Calvert et al., 2011) indicate that reaction with OH will probably be the dominant atmospheric loss pathway of the unsaturated esters in the troposphere, reaction with O<sub>3</sub> can also contribute significantly to their loss, especially in polluted areas where O<sub>3</sub> concentrations can be high enough.

In this work, the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique was used to determine the rate coefficients for the OH radical reactions with a series of seven unsaturated esters (MMA, MMA-D8, EMA, nPMA, iPMA, nBMA and iBMA) in the temperature range 257-376K at around 100 Torr. In addition, the absolute rate (AR) and relative rate (RR) methods were employed to measure the reactions rate coefficients of ozone with the same esters using an atmospheric simulation chamber at ambient temperature and atmospheric pressure:



To the best of our knowledge, the present work provides the first kinetic studies of nPMA, iPMA, and iBMA reactions with OH radical and O<sub>3</sub>, and the first temperature dependence rate coefficient determinations for OH reactions with EMA, nPMA, iPMA and iBMA. The results are discussed in terms of the reactivity of unsaturated esters toward OH radicals and O<sub>3</sub> and the atmospheric lifetime of the investigated unsaturated esters are estimated. In addition, the rate coefficients of OH and O<sub>3</sub> with the fully deuterated methyl methacrylate (MMA-D8) have been determined and compared to those with no deuterated MMA.

## 2 Experimental

### 2.1 PLP-LIF

The pulsed laser photolysis - laser induced fluorescence (PLP-LIF) technique was used to measure the rate coefficient of the reaction of OH with the investigated esters. This

technique has been described in detail in previous papers from this laboratory (Le Calvé et al., 1998; Mellouki et al., 1995), hence only a brief review is given here. Hydroxyl radicals were produced by photolysis of H<sub>2</sub>O<sub>2</sub> at  $\lambda = 248$  nm using a KrF excimer laser (2-15 mJ cm<sup>-2</sup> in the cell). The temporal concentration-time profiles of OH radicals were monitored at various reaction times ranging from 10  $\mu$ s to 10 ms by pulsed laser induced fluorescence. A Nd:YAG pumped, frequency-doubled dye laser was used to excite the OH radical at  $\lambda = 282$  nm and its fluorescence was detected by a photomultiplier, fitted with a 309 nm narrow bandpass filter. The output pulse from the photomultiplier was integrated for a preset period by a gated charge integrator. Typically, the fluorescence signal from 10 to 15 different delay times from 100 probe laser shots were averaged to generate OH concentration-time profiles over at least three lifetimes. Mixtures of esters/H<sub>2</sub>O<sub>2</sub> in helium diluent were flowed slowly through the cell so that each photolysis/probe sequence interrogated a fresh gas mixture and reaction products did not build up in the cell. The experiments were conducted in the temperature range 257-376 K at 100 Torr of total pressure.

All experiments were carried out under pseudo-first-order conditions with the concentration of unsaturated esters [esters] = (0.5-10)  $\times 10^{13}$  molecule cm<sup>-3</sup>, in large excess over OH concentration, typically [OH]  $\approx 6 \times 10^{11}$  radical cm<sup>-3</sup>. Under these conditions, the decay rate of OH was governed by its reactions with the unsaturated esters, H<sub>2</sub>O<sub>2</sub> and its removal from the detection zone due to diffusion:



$k_{\text{OH\_ester}}$ ,  $k_{\text{H}_2\text{O}_2}$ ,  $k_{\text{diff}}$  are the rate coefficients of the reactions of OH radical with title esters, H<sub>2</sub>O<sub>2</sub> and the diffusional loss, respectively. Under these conditions, the rate of disappearance of the OH radical should follow a simple exponential rate law:  $[\text{OH}]_t = [\text{OH}]_0 \times \exp(-k't)$ , where  $k'$  is the pseudo-first order rate coefficient that combines all OH loss processes:  $k' = k_{\text{OH\_ester}} \times [\text{esters}] + k_0'$  and  $k_0' = k_{\text{H}_2\text{O}_2} \times [\text{H}_2\text{O}_2] + k_{\text{diff}}$

The value of  $k'$  and  $k_0'$  were extracted from the linear least-square analysis of OH LIF

signal plotted vs. reaction time in the presence and absence of the esters. The linear least-squares fit of the data  $k' - k_0'$  vs. various esters concentration leads to the second-order rate coefficient  $k_{\text{OH\_ester}}$ .

## 2.2 Atmospheric Simulation chamber:

Kinetic measurements of ozone reaction with unsaturated esters were performed in the 7300 L ICARE-CNRS simulation chamber at  $291 \pm 2$  K and 760 Torr of pure air (<2% RH). The experimental set-up has been described in details previously (Bernard et al., 2010; Bernard et al., 2013), hence, only a brief description is given here. The chamber is surrounded by protection panels with two roll-up doors, which makes it easier to perform dark reaction. Two fans made of Teflon are installed in the chamber to ensure the rapid mixing of reactants. Known volumes of esters were introduced into a three-path glass tube and further driven into the chamber with a stream of zero air and the concentrations were calculated using the ideal gas law.  $\text{SF}_6$  was used to determine the dilution in the chamber, it was injected into the chamber by passing a stream of pure air through a known concentration of  $\text{SF}_6$  in a calibrated cylinder (0.9 L) equipped with two pressure gauges (0–10 Torr and 0–100 Torr, MKS Baratron). Temperature and relative humidity (RH) values were recorded continuously by a thermocouple (PT-100) and a combined probe (Vaisala HMT330 series transmitters). In order to compensate sampling flows and leaks, a flow of zero air (5 L/min) was added continuously during the experiments maintaining a slight inner overpressure, avoiding any contamination from outside air. After each experiment, the chamber was flushed with zero air in order to purge the remaining chemicals.

The unsaturated esters were monitored by in situ Fourier transform infrared spectrometry (FTIR, Nicolet 5700) coupled to a White-type multipass cell (143 m optical path length). Infrared spectra were recorded every 2 minutes by co-adding 32 interferograms with a resolution of  $1 \text{ cm}^{-1}$ . The MMA, EMA, nPMA, iPMA, nBMA and iBMA were monitored at the wavenumber region  $1162 \text{ cm}^{-1}$  and propene, cyclohexene, methyl vinyl ketone were monitored at the regions of 850-920, 2890-2970

and 1220-1270  $\text{cm}^{-1}$ , respectively. Quantitative analysis of IR spectra was performed using OMNIC software. Calibrations were made by introducing known volume of liquid chemical to the chamber for the studied esters to quantify their concentrations during the experiments and the uncertainty was estimated to be 2%. Ozone was generated through the photolysis of a controlled flow of high pure oxygen using a Hg Pen-ray lamp or a Trailigaz® ozone generator and its concentration was measured by two ozone monitors based on UV absorption (Horiba APOA-360 and APOA-370).

### 2.2.1 Absolute rate method (AR)

In the absolute rate method studies, the decay of ozone was measured in the presence of excess of esters ( $[\text{ester}]_0 = (3.3\text{-}21.1) \times 10^{12} \text{ molecules cm}^{-3}$ ). The initial ozone concentrations were  $[\text{O}_3]_0 = (1.7\text{-}15.2) \times 10^{11} \text{ molecules cm}^{-3}$ . Under pseudo-first-order conditions, the rate of disappearance of  $\text{O}_3$  followed a simple exponential rate law

$$[\text{O}_3]_t = [\text{O}_3]_0 \times e^{-k't} \quad (\text{eq.1})$$

where  $k' = k \times [\text{ester}] + k'_{\text{loss}}$  is the total ozone decay caused by its loss (wall loss and dilution, first-order rate coefficient for  $\text{O}_3$  removal in the absence of ester) and reaction with esters.



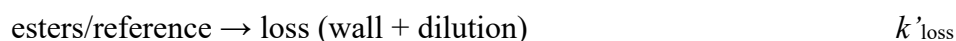
$k_{\text{AR\_ester}}$  was obtained from the linear fitting of the plots of  $(k' - k'_{\text{loss}})$  versus  $[\text{ester}]_0$ .

### 2.2.2 Relative rate method (RR)

Rate coefficients for the studied reactions are determined by comparing the  $\text{O}_3$  reaction rate with the esters to that with reference compounds:



The esters and reference could also be subject to lost due to the wall and dilution.



Considering these processes, it can be shown that:

$$\left\{ \ln\left(\frac{[\text{ester}]_0}{[\text{ester}]_t}\right) - k'_{\text{loss\_ester}} * t \right\} = \frac{k_{\text{RR\_ester}}}{k_{\text{ref}}} * \left\{ \ln\left(\frac{[\text{ref}]_0}{[\text{ref}]_t}\right) - k'_{\text{loss\_ref}} * t \right\} \quad (\text{eq.2})$$

where  $[\text{ester}]_0$ ,  $[\text{ester}]_t$  and  $[\text{reference}]_0$ ,  $[\text{reference}]_t$  are the initial concentrations of ester and reference and at reaction time  $t$ . Hence, plots of  $\{\ln(\frac{[\text{ester}]_0}{[\text{ester}]_t}) - k'_{\text{loss\_ester}} \times t\}$  against  $\{\ln(\frac{[\text{ref}]_0}{[\text{ref}]_t}) - k'_{\text{loss\_ref}} \times t\}$  should be straight lines with the slope =  $\frac{k_{\text{RR\_ester}}}{k_{\text{ref}}}$  and the intercept = 0. The experiments were conducted in the presence of an excess of CO used to scavenge OH radicals that could be formed during ozonolysis of unsaturated VOCs, hence avoiding secondary reactions.

### 2.3 Materials

Helium and oxygen, both UHP certified to > 99.9995% were provided by Air liquide. H<sub>2</sub>O<sub>2</sub> was obtained from Prolabo as 50 wt. % solution and was concentrated by bubbling helium through it for several days prior to use. Unsaturated esters MMA (99.8%), EMA (99%), iPMA (98%), nBMA (99%) and iBMA (98%) were supplied by TCI. nPMA (97%) was obtained from Sigma-Aldrich. The isotopic purity of methyl methacrylate-D8 (MMA-D8) from Apollo Scientific Limited was quoted to be 99.50% atom D. The vapor pressure of MMA, MMA-D8, EMA, iPMA, nPMA, nBMA and iBMA are as follow: 42, 39, 20, 16, 8.5, 2.1 and 4.8 hPa at 25 °C. The unsaturated esters were further purified by repeated freeze, pump, and thaw cycles before use. In PLP-LIF, the unsaturated esters were premixed in a 10 L glass light-tight bulb with helium to form (0.05 - 0.12)% mixtures.

## 3 Results

### 3.1 rate coefficients of OH + unsaturated esters using PLP-LIF

Experiments were carried out in the temperature range of 257-376K and a total pressure of 100 Torr. OH decays versus reaction time were found to be exponential in all conditions as shown in **Fig. 1** for OH + MMA. **Fig. 2** shows examples of the plots of  $(k' - k'_0)$  vs. the studied esters at room temperature. The experimental conditions and the measured rate coefficients are listed in **Table 1**. The quoted errors on the rate coefficients  $k_{\text{OH}}$  from each individual experiment were 2 times standard division (SD) of the  $(k' - k'_0)$  vs.  $[\text{ester}]$  plots using the method recommended by Brauers and



Finlayson-Pitts (Brauers and Finlayson-Pitts, 1997). This method weighted the error of x and y axis. The variation of flow rate and pressure in the cell did not show any measurable effect on the measured rate coefficients.

The rate coefficients, taken as the statistical average of all values obtained at (297±2) K are: unit in of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and quoted error is the 2 time SD from each individual values:

$$k_{\text{OH\_MMA}} = (4.24 \pm 0.12) \times 10^{-11}$$

$$k_{\text{OH\_EMA}} = (4.99 \pm 0.54) \times 10^{-11}$$

$$k_{\text{OH\_nPMA}} = (4.86 \pm 0.32) \times 10^{-11}$$

$$k_{\text{OH\_nBMA}} = (5.26 \pm 0.29) \times 10^{-11}$$

$$k_{\text{OH\_iPMA}} = (5.36 \pm 0.07) \times 10^{-11}$$

$$k_{\text{OH\_iBMA}} = (5.27 \pm 0.33) \times 10^{-11}$$

$$k_{\text{OH\_MMA-D8}} = (3.96 \pm 0.14) \times 10^{-11}$$

**Fig. 3** show the obtained rate coefficients for the title reactions plotted as a function of 1/T. Least-squares analysis of the ln(k) versus 1/T plots lead to the following expressions (in the conventional Arrhenius form  $k = Ae^{-E/RT}$ ). For the temperature dependence of  $k_2$ - $k_6$  in the temperature range 257–376K (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):

$$k_{\text{OH\_EMA}} = (4.25 \pm 0.54) \times 10^{-12} \exp[(726 \pm 39)/T]$$

$$k_{\text{OH\_nPMA}} = (4.49 \pm 0.74) \times 10^{-12} \exp[(708 \pm 50)/T]$$

$$k_{\text{OH\_nBMA}} = (5.07 \pm 0.79) \times 10^{-12} \exp[(696 \pm 48)/T]$$

$$k_{\text{OH\_iPMA}} = (4.62 \pm 0.48) \times 10^{-12} \exp[(735 \pm 32)/T]$$

$$k_{\text{OH\_iBMA}} = (5.53 \pm 0.76) \times 10^{-12} \exp[(680 \pm 42)/T]$$

Uncertainties are  $2A\sigma_{\ln A}$  and  $2\sigma_{E/R}$  for A and E/R, respectively.

## 3.2 Rate coefficients of O<sub>3</sub> + unsaturated esters

### 3.2.1 Absolute Rate (AR) method measurement

O<sub>3</sub> was firstly introduced to the chamber and kept for 2 hours to estimate its loss rate ( $k'_{\text{loss}}$ ) in the absence of unsaturated esters, which was found to be in the range (2.5 -

$3.0) \times 10^{-5} \text{ s}^{-1}$ . This value was at least 2 times lower than the pseudo-first-order  $\text{O}_3$  decay rate in the presence of unsaturated esters. In this work, the kinetic studies were carried out using large excess of ester concentrations over that of  $\text{O}_3$ , hence, the esters consumptions by OH radical were made negligible under our experimental conditions. Indeed, there is evidence that gas-phase reactions of  $\text{O}_3$  with unsaturated VOC produce OH radicals, which may further react with the VOCs during the kinetic measurements (Mellouki et al., 2015; Stone et al., 2012). For this reason, high concentrations of CO ( $3 - 9 \times 10^{16} \text{ molecule cm}^{-3}$ ) were added to chemical system to scavenge OH radicals in some experiments. **Fig. 4** displays an example of the typical  $\text{O}_3$  decays versus reaction time in the presence of different concentrations of MMA (examples of  $\text{O}_3$  decays for the other reactions are provided in the supporting information, **Fig. S1-S6**). **Fig. 5** shows the plots of  $(k' - k'_{\text{loss}})$  versus the concentrations for different esters in absence and presence of large excess of CO (used as OH scavenger) to obtain the  $k_{\text{AR\_ester}}$  using the method recommended by Brauers and Finlayson-Pitts (Brauers and Finlayson-Pitts, 1997), this method weighted the error of x and y axis. The measured rate coefficients  $k_{\text{AR\_ester}}$  along with the experimental conditions are summarized in **Table S1**. The final values unit in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  are taken as the weighted average data obtained at  $291 \pm 2 \text{ K}$  with the quoted errors of 2 times SD

$$\begin{aligned}
 k_{\text{AR\_MMA}} &= (6.79 \pm 0.28) \times 10^{-18} \\
 k_{\text{AR\_EMA}} &= (7.80 \pm 0.35) \times 10^{-18} \\
 k_{\text{AR\_nPMA}} &= (8.46 \pm 0.20) \times 10^{-18} \\
 k_{\text{AR\_nBMA}} &= (9.55 \pm 0.60) \times 10^{-18} \\
 k_{\text{AR\_iPMA}} &= (10.92 \pm 0.12) \times 10^{-18} \\
 k_{\text{AR\_iBMA}} &= (9.76 \pm 0.43) \times 10^{-18} \\
 k_{\text{AR\_MMA-D8}} &= (6.44 \pm 1.04) \times 10^{-18}
 \end{aligned}$$

### 3.2.2 RR method measurement

Propene, isoprene, and cyclohexene were used as the reference compounds. The loss rates of esters and references were measured in the presence of excess of CO ((3 – 9)

$\times 10^{16}$  molecule  $\text{cm}^{-3}$ )  $k_{\text{loss}} = (1.2 - 1.5) \times 10^{-5} \text{ s}^{-1}$ . The concentrations of the esters and references were in the range  $(0.4 - 4) \times 10^{13}$  molecule  $\text{cm}^{-3}$ . **Fig. 6** displays the decay losses of the unsaturated esters vs. those of the reference compounds. The ratios  $\frac{k_{\text{RR\_ester}}}{k_{\text{ref}}}$  were derived from the linear-least square analysis which enables to obtain  $k_{\text{RR\_ester}}$ . **Table 2** summarizes the experimental conditions and the data obtained. The rate coefficients of  $\text{O}_3$  reaction with the reference compounds were:  $k_{\text{propene}} = 5.51 \times 10^{-15} \exp[-1878/T]$  (Calvert et al., 2000),  $k_{\text{cyclohexene}} = 2.6 \times 10^{-15} \exp[-1063/T]$  (Sidebottom and Tracy, 1997) and  $k_{\text{isoprene}} = 7.86 \times 10^{-15} \exp[-1913/T]$  (Calvert et al., 2000). The quoted uncertainties of  $\frac{k_{\text{RR\_ester}}}{k_{\text{ref}}}$  were obtained using the method recommended by Brauers and Finlayson-Pitts (Brauers and Finlayson-Pitts, 1997).

The derived rate coefficients are weighted average of the obtained data with various references taking into account of the uncertainties on the references rate coefficients values as:  $k_{\text{av}} = (w_{\text{ref1}}k_{\text{ref1}} + w_{\text{ref2}}k_{\text{ref2}} + \dots) / (w_{\text{ref1}} + w_{\text{ref2}} + \dots)$ , where  $w_{\text{ref1}} = 1/\sigma_{\text{ref1}}^2$ , etc.  $\sigma_{\text{av}} = (1/\sigma_{\text{ref1}} + 1/\sigma_{\text{ref2}})^{-0.5}$  (Farrugia et al., 2015): unit of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

$$k_{\text{RR\_MMA}} = (6.45 \pm 0.29) \times 10^{-18}$$

$$k_{\text{RR\_EMA}} = (7.69 \pm 0.32) \times 10^{-18}$$

$$k_{\text{RR\_nPMA}} = (8.46 \pm 0.33) \times 10^{-18}$$

$$k_{\text{RR\_nBMA}} = (10.19 \pm 0.79) \times 10^{-18}$$

$$k_{\text{RR\_iPMA}} = (11.21 \pm 0.38) \times 10^{-18}$$

$$k_{\text{RR\_iBMA}} = (10.77 \pm 0.88) \times 10^{-18}$$

$$k_{\text{RR\_MMA-D8}} = (6.29 \pm 0.32) \times 10^{-18} \text{ cm}^3$$

## 4 Discussions

### 4.1 Comparison with the literature

#### 4.1.1 OH radical reaction with unsaturated esters

**Table 3** shows the rate coefficients values obtained in this work along with those from literature. To the best of our knowledge, this work provides the first room temperature rate coefficient measurement for MMA-D8, nPMA, iPMA, iBMA reaction with OH radical and the first temperature dependence studies for EMA, nPMA, iPMA, iBMA,

hence no direct comparison with the literature can be made. Comparison with the existing data can be made only for the reactions of OH with MMA, EMA and nBMA. Moreover, the previous studies of OH with EMA and nBMA have been conducted only at room temperature or in a limited temperature range.

The rate coefficient value  $k_{\text{OH\_MMA}}$  reported here is in excellent agreement with the ones from Blanco et al. (2006) and Teruel et al. (2006) which are higher than that from Saunders et al. (1994). Note that the measurement of Saunders et al. was performed at low pressure (1 Torr) and that the rate coefficient measurements were not in the high-pressure-limiting regime. The study of Teruel et al. (2006) has been conducted using the same experimental set up as the one used in the present work. This is basically the reason for why we have limited our present investigation to the room temperature.

The only previous study on the reaction of OH with EMA was the one from Blanco et al. (2006) in which the relative method was used. Their work was limited to room temperature.  $k_{\text{OH\_EMA}}$  measured here and that reported by Blanco et al. (2006) are in excellent agreement.

$k_{\text{OH\_nBMA}}$  values reported by Blanco et al. (2006) and Blanco et al. (2009a) are 30-40% higher than the one we measured in the present work. The value obtained in their second study,  $k_{\text{OH\_nBMA}} = (6.63 \pm 1.42) \times 10^{-11}$  (Blanco et al., 2009a) was slightly lower but with a larger uncertainty than that they reported earlier  $k_{\text{OH\_nBMA}} = (7.08 \pm 0.75) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Blanco et al., 2006).

This work provides the first temperature dependence for  $k_{\text{EMA\_OH}}$ ,  $k_{\text{nBMA\_OH}}$ ,  $k_{\text{iPMA\_OH}}$  and  $k_{\text{iBMA\_OH}}$  and second one for  $k_{\text{EMA\_OH}}$ . The temperature dependence of  $k_{\text{MMA\_OH}}$  has been investigated in our laboratory using the same PLP-LIF experimental system (Teruel et al., 2006). Blanco et al. (2009a) have studied the reaction of OH with nBMA in the temperature range 287-313 using a 1080 L glass reactor equipped with FTIR. The values they obtained are systematically higher than the ones we report in the present work. Note that the same observation could be made for the reaction of OH with MMA as shown in **Fig. 3**.

The reaction rate coefficients determined here have been found to decrease with

increasing temperature in the range 257-376 K. The results show a negative temperature dependence which is consistent with an addition mechanism as expected for the reactions of the OH radicals with unsaturated compounds (Atkinson and Arey, 2003).

#### 4.1.2 O<sub>3</sub> reaction with unsaturated esters

The rate coefficient values obtained using both absolute and relative methods are in excellent agreement. Hence, the rate coefficients recommended in this work are the weighted average values obtained using method:  $(w_1k_1 + w_2k_2)/(w_1+w_2)$ , where  $w_1=1/\sigma_1^2$ , with error =  $(1/\sigma_1+1/\sigma_2)^{-0.5}$ , unit in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

$$k_{O_3\_MMA} = (6.63 \pm 0.38) \times 10^{-18}$$

$$k_{O_3\_EMA} = (7.74 \pm 0.41) \times 10^{-18}$$

$$k_{O_3\_nPMA} = (8.46 \pm 0.36) \times 10^{-18}$$

$$k_{O_3\_nBMA} = (9.78 \pm 0.58) \times 10^{-18}$$

$$k_{O_3\_iPMA} = (10.94 \pm 0.30) \times 10^{-18}$$

$$k_{O_3\_iBMA} = (9.96 \pm 0.54) \times 10^{-18}$$

$$k_{O_3\_MMA-D8} = (6.30 \pm 0.49) \times 10^{-18}$$

The other measurements reported in the literature so far on the title reactions are from Grosjean et al. (1993), Bernard et al. (2010), Gai et al. (2009) and Gaona Colmán et al. (2013). As shown in **Table 4**, Grosjean et al. (1993) and Bernard et al. (2010) reported  $k_{O_3\_MMA} = (7.5 \pm 0.9) \times 10^{-18}$  and  $(6.7 \pm 0.9) \times 10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The value obtained by Grosjean et al. is 13% higher than the ones from Bernard et al. and this work, these later two measurements being in excellent agreement. For the reaction of O<sub>3</sub> with EMA, our measured value is in excellent agreement with that from Gai et al. (2009) who reported a rate coefficient of  $(7.68 \pm 0.88) \times 10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Similarly, the  $k_{O_3\_nBMA}$  obtained in this study is in a very good agreement with the one reported by Gaona Colmán et al. (2013) ( $k_{O_3\_nBMA} = (10 \pm 3) \times 10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). To the best of our knowledge, there are no previously reported values for the rate coefficients of O<sub>3</sub> reactions with nPMA, iPMA iBMA, and MMA-D8. Hence, the present work represents the first kinetic determination of these reactions and therefore

no direct comparison with other literature values can be made.

## 4.2 Reactivity of title unsaturated esters toward OH radical and O<sub>3</sub>

### 4.2.1 OH radical reaction with unsaturated esters

**Table 5** lists the reactivity of OH radicals towards unsaturated esters and the corresponding alkenes in 1 atmospheric pressure and 298K. As seen in this table, all the studied unsaturated methacrylates are less reactive than their corresponding alkenes. This observation can be explained at least partly by the deactivation of C=C bond toward OH addition by the negative inductive effect of C=O group adjacent to the C=C bond. **Table 5** also lists the rate coefficients for the reactions of OH with the titled esters estimated using the US EPA AOPWIN program (Meylan and Howard, 1993), which is based upon the structure-activity relationship (SAR) method described in Kwok and Atkinson (Kwok and Atkinson, 1995). As seen in this table, the SAR rate coefficients for OH reaction with titled unsaturated esters are 2~3 factors lower than experimental values reported the present study and showing that this SAR method inadequately predicts the reactivity of a C=C bond adjacent to the C=O of the ester group. The rate coefficients for OH reactions with the studied esters were also estimated using the very recent approach reported by Jenkin et al. (2018). As shown in Table 5, the results indicate that this new approach improves the SAR calculation but still presents some differences with the measurements and needs continuous adjustment as accurate experimental data become available.

The obtained results indicate that the rate coefficients for all methacrylates measured here are roughly in the same range, with the rate coefficient slightly increasing with the extent of substitution going from methyl to ethyl and propyl to butyl. This is consistent with the positive inductive effect of the alkoxy groups  $-\text{O}(\text{CH}_2)_x\text{CH}_3$ , which increase the charge density on the C=C bond and hence increase the reactivity of the C=C bond toward OH electrophilic attack as already discussed by Blanco et al. (2009a). In addition, it is interesting to point out that the iPMA reacts faster than nPMA with OH radical whereas the iBMA presents almost the same rate coefficient as does the nBMA,

which leads to a doubt about the enhanced H-abstraction in methacrylates reaction. To further understand the reaction mechanism of OH radical with methacrylates, the rate coefficient of deuterated MMA (MMA-D8:  $\text{CD}_2=\text{C}(\text{CD}_3)\text{C}(\text{O})\text{OCD}_3$ ) reaction with OH radical was also measured by PLP-LIF. As shown in Table 3, its room temperature rate coefficient was found to be essentially equal to that of MMA ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$ ), as  $k_{\text{MMA\_OH}}/k_{\text{MMA-D8\_OH}} = 1.07$ . This further strengthens the expectation that H-atom abstraction is insignificant in the reaction of OH with methacrylates.

#### 4.2.2 O<sub>3</sub> reaction with unsaturated esters

The gas-phase reaction of O<sub>3</sub> with unsaturated VOCs involves electrophilic addition of O<sub>3</sub> on  $>\text{C}=\text{C}<$  followed by unimolecular decomposition of the 1,2,3-trioxolane adduct (Alam et al., 2013). Therefore, the reactivity of unsaturated esters toward O<sub>3</sub> should reflect the electronic density at the C=C double bond. **Table 5** summarizes the available rate coefficients for unsaturated esters and their corresponding alkenes (removing -C(O)O- group between the C=C and R group). As seen from this table, methacrylates,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OR}$ , are less reactive than their corresponding alkenes. This lower reactivity presumably reflects the delocalization of the electron density associated with C=C double bond by the neighboring electron withdrawing C=O group and then reduces its reactivity towards the electrophilic ozone. The SAR for the prediction of gas-phase ozonolysis rate coefficients reported by McGillen et al. (2011) based on the inductive and steric effects of heteroatomic substitution acting upon olefinic bonds was also applied in this work. This SAR method does not distinguish the difference between the different alkyl groups attached to the ether group -O- and result to lower rate coefficients,  $2.93 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , for all the studied esters reactions with O<sub>3</sub>. As shown in **Table 5**, the rate coefficients of the reactions of unsaturated esters with O<sub>3</sub> are increasing with the extent of substitution going from methyl to ethyl to propyl to butyl as:  $k_{\text{O}_3\_MMA} < k_{\text{O}_3\_EMA} < k_{\text{O}_3\_nPMA} < k_{\text{O}_3\_nBMA}$ , which could indicate that the longer length of the R group in R'C(O)OR may enhance the reactivity of C=C bond toward O<sub>3</sub> electrophilic addition. This trend has also been found for the reaction of O<sub>3</sub> with acrylate

by Bernard et al. (2010). To further estimate the reaction mechanism of O<sub>3</sub> reaction with unsaturated esters, the reaction of MMA-D8 with O<sub>3</sub> has also been investigated in this work. As shown in **Table 5**, rate coefficients for the deuterated and no-deuterated MMA are essentially identical, with  $k_{O_3\_MMA}/k_{O_3\_MMA-D8} = 1.05$ , further strengthens the reaction mechanism of O<sub>3</sub> with unsaturated VOCs following electrophilic addition of O<sub>3</sub> on C=C bond.

## 5 Conclusion and atmospheric implication:

In the troposphere, unsaturated esters are mainly removed by their reaction with the major atmospheric oxidants O<sub>3</sub>, OH, and NO<sub>3</sub> radicals and Cl atoms. Their tropospheric lifetimes can be calculated using the expression:  $\tau_x = \frac{1}{k_x[X]}$  where [X] is the average concentration of OH, Cl, NO<sub>3</sub>, and O<sub>3</sub>, and  $k_x$  the reactions rate coefficients with the oxidant X. The room-temperature rate coefficients obtained in this work and from the literatures (unit in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were used to conduct the calculations:  $k_{OH\_MMA} = 4.24 \times 10^{-11}$ ,  $k_{OH\_EMA} = 4.99 \times 10^{-11}$ ,  $k_{OH\_nPMA} = 4.86 \times 10^{-11}$ ,  $k_{OH\_nBMA} = 5.26 \times 10^{-11}$ ,  $k_{OH\_iPMA} = 5.36 \times 10^{-11}$ ,  $k_{OH\_iBMA} = 5.27 \times 10^{-11}$ ,  $k_{O_3\_MMA} = 6.63 \times 10^{-18}$ ,  $k_{O_3\_EMA} = 7.74 \times 10^{-18}$ ,  $k_{O_3\_nPMA} = 8.46 \times 10^{-18}$ ,  $k_{O_3\_nBMA} = 9.78 \times 10^{-18}$ ,  $k_{O_3\_iPMA} = 10.94 \times 10^{-18}$ ,  $k_{O_3\_iBMA} = 9.96 \times 10^{-18}$ ,  $k_{Cl\_MMA} = 2.82 \times 10^{-10}$  (Blanco et al., 2009b),  $k_{Cl\_EMA} = 2.71 \times 10^{-10}$  (Martin Porrero et al., 2010),  $k_{Cl\_nBMA} = 3.72 \times 10^{-10}$  (Blanco et al., 2009b; Martin Porrero et al., 2010).  $k_{NO_3\_MMA} = 2.98 \times 10^{-15}$ ,  $k_{NO_3\_EMA} = 4.67 \times 10^{-15}$ ,  $k_{NO_3\_nPMA} = 5.23 \times 10^{-15}$ ,  $k_{NO_3\_nBMA} = 7.91 \times 10^{-15}$ ,  $k_{NO_3\_iPMA} = 5.91 \times 10^{-15}$ ,  $k_{NO_3\_iBMA} = 6.24 \times 10^{-15}$  extracted from study of Zhou et al. (2017).

As shown in Table 6, the tropospheric lifetimes of the studied unsaturated esters due to the OH-reaction were calculated using the reported OH concentration (12-h averaged daytime) of  $2 \times 10^6$  molecule cm<sup>-3</sup> (Spivakovsky et al., 2000) to be  $\approx 3$  hrs. Assuming a typical 24 h average ozone concentration of  $7 \times 10^{11}$  molecule cm<sup>3</sup> (Logan, 1985) results in atmospheric lifetimes of title unsaturated esters with respect to ozone are calculated to be the range of 36-59 hours. However, in areas where ozone concentrations have been reported as high as  $7 \times 10^{12}$  molecule cm<sup>-3</sup> (Guo et al., 2017), the atmospheric



lifetimes of title unsaturated esters could be  $\approx$  4-6 hours. It is important to point out that  $O_3$  could have also an important contribution to the loss of the unsaturated ester during the nighttime. Zhou et al. (2017) have reported the tropospheric lifetimes of the studied species with respect to  $NO_3$  reactions (occurring mainly at nighttime) using the rate coefficients they have measured and  $[NO_3] = 5 \times 10^8$  molecule  $cm^{-3}$  (Shu and Atkinson, 1995). The calculated lifetimes ranges from 70 to 186 hrs. For the reactions with Cl atom, only the rate coefficients of MMA, EMA and nBMA have been measured (Blanco et al., 2009b; Martin Porrero et al., 2010). Using the available data, lifetimes of these unsaturated esters have been estimated to be in the range 75-99 hrs based on a global Cl atom concentration of  $1 \times 10^4$  atoms  $cm^{-3}$  (Wingenter et al., 1996). However, the reaction of Cl with the unsaturated esters can be a significant loss process in coastal areas and in the marine boundary layer, where peak concentrations of Cl atoms as high as  $1 \times 10^5$  atoms  $cm^{-3}$  (Spicer et al., 1998). It is expected that the photolysis of the studied esters is a negligible process in their removal from the atmosphere (Teruel et al., 2006). The use of the existing Henry's law constants (for MMA, PMA and BMA in the range of  $(1.8-4.4) \times 10^{-2}$  mol/( $m^3 \cdot Pa$ ), Sander (2015)) indicates that the unsaturated esters are expected to be slightly soluble in water, hence their washout is not an important atmospheric process.

The above calculations indicate that unsaturated esters are removed from the atmosphere through their gas phase reactions with the main atmospheric oxidants OH,  $O_3$ ,  $NO_3$  and Cl. These four pathways are all important but may have different contributions depending in the conditions and the location where these unsaturated esters are emitted or formed.

### **Acknowledgements:**

This work is supported by Labex Voltaire (ANR-10-LABX-100-01), ARD PIVOTS program (supported by the Centre-Val de Loire regional council), and the European Union's Horizon 2020 research and innovation programme through the

EUROCHAMP-2020 Infrastructure Activity under grant agreement No. 730997.

Yangang REN is grateful to the China Scholarship Council for the financial support.

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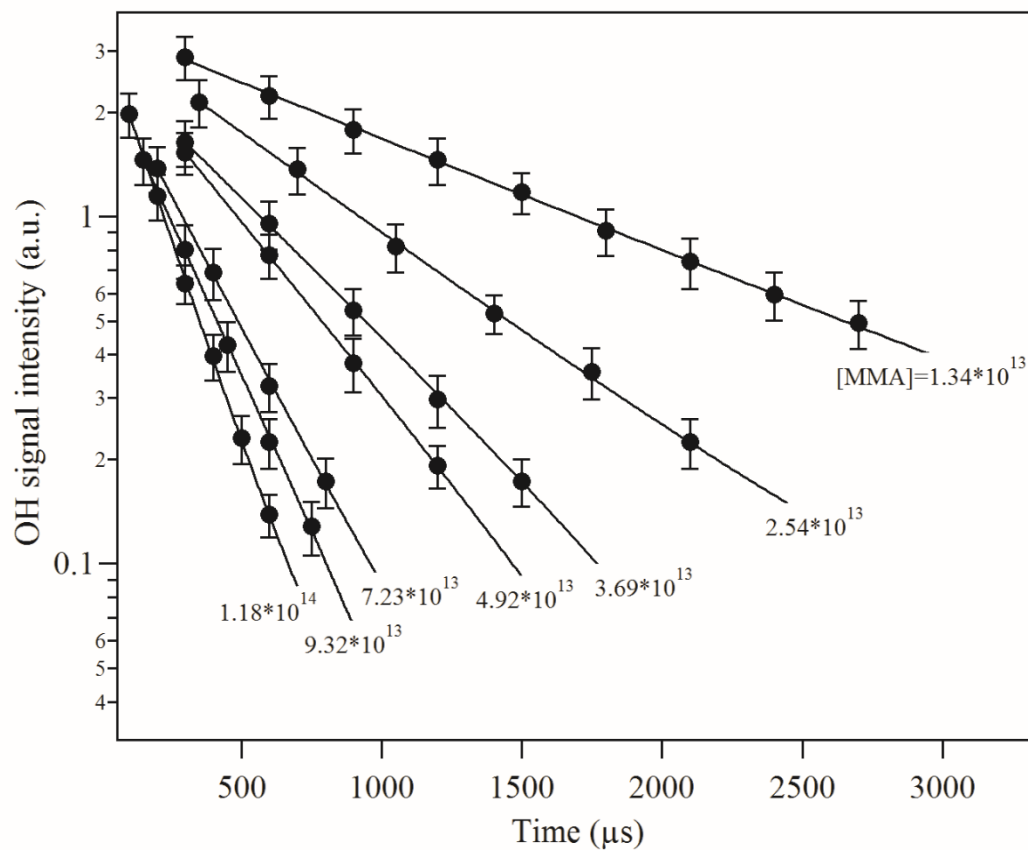
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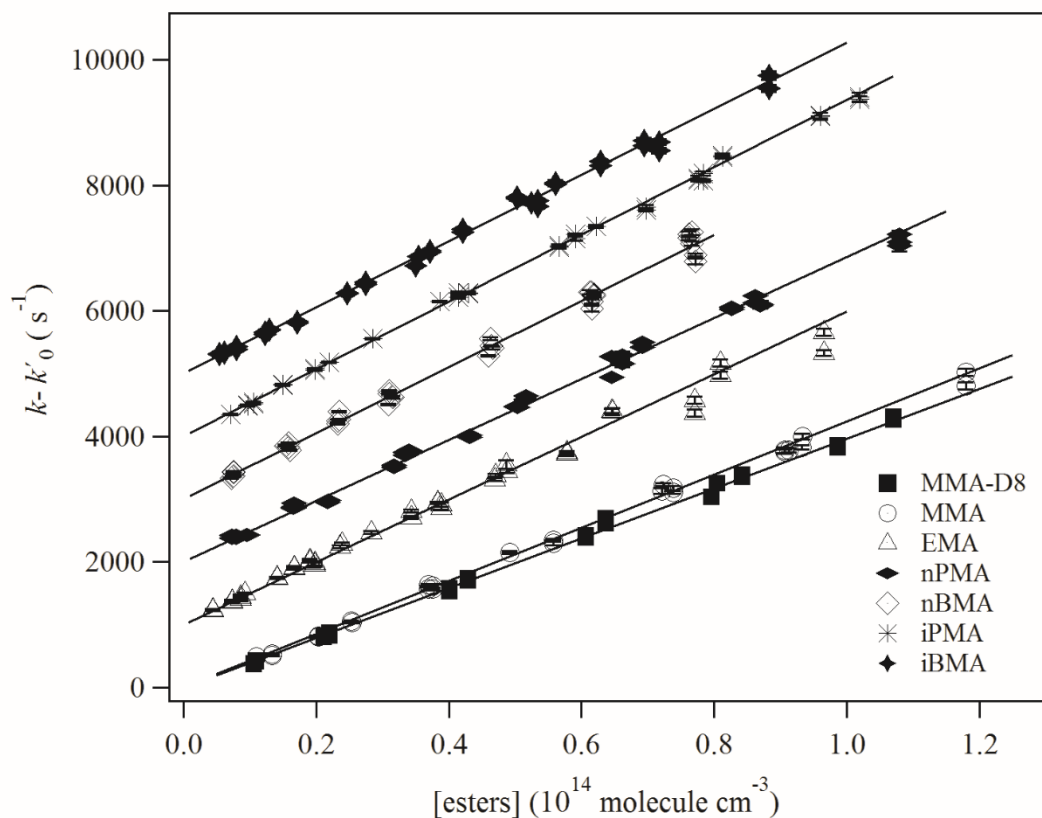
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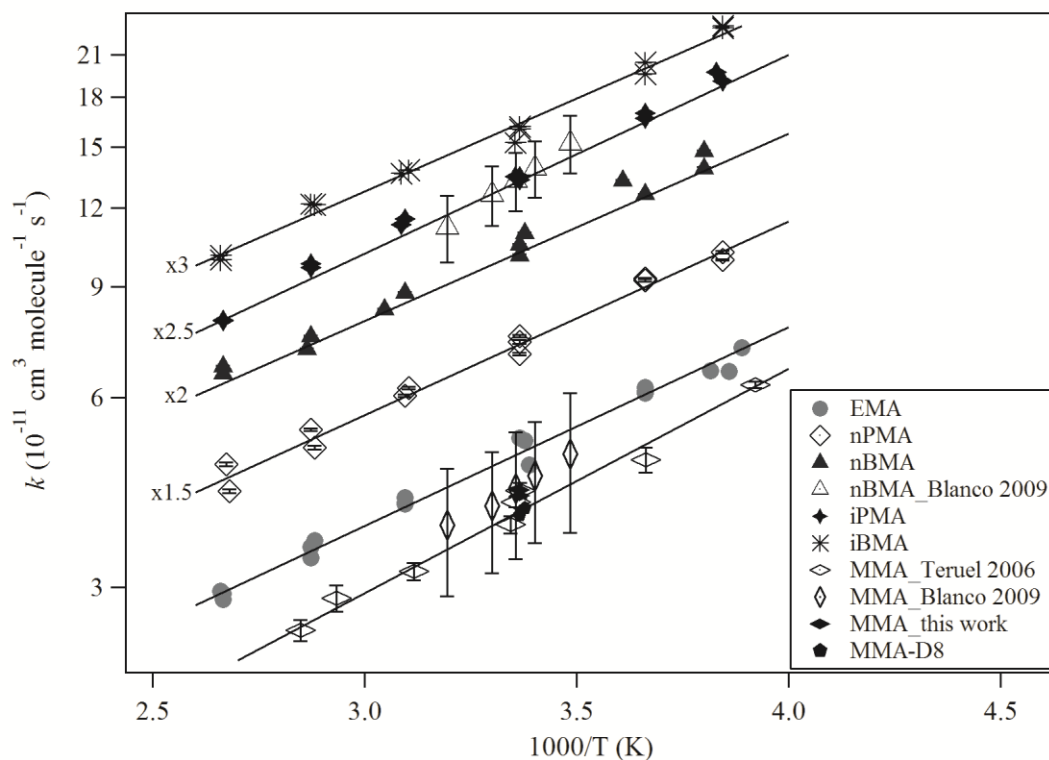
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**Fig. 1.** Typical profiles of OH vs. reaction time at different concentration of Methyl methacrylate (unit in molecule  $\text{cm}^{-3}$ ) at  $T = (297 \pm 1)$  K.

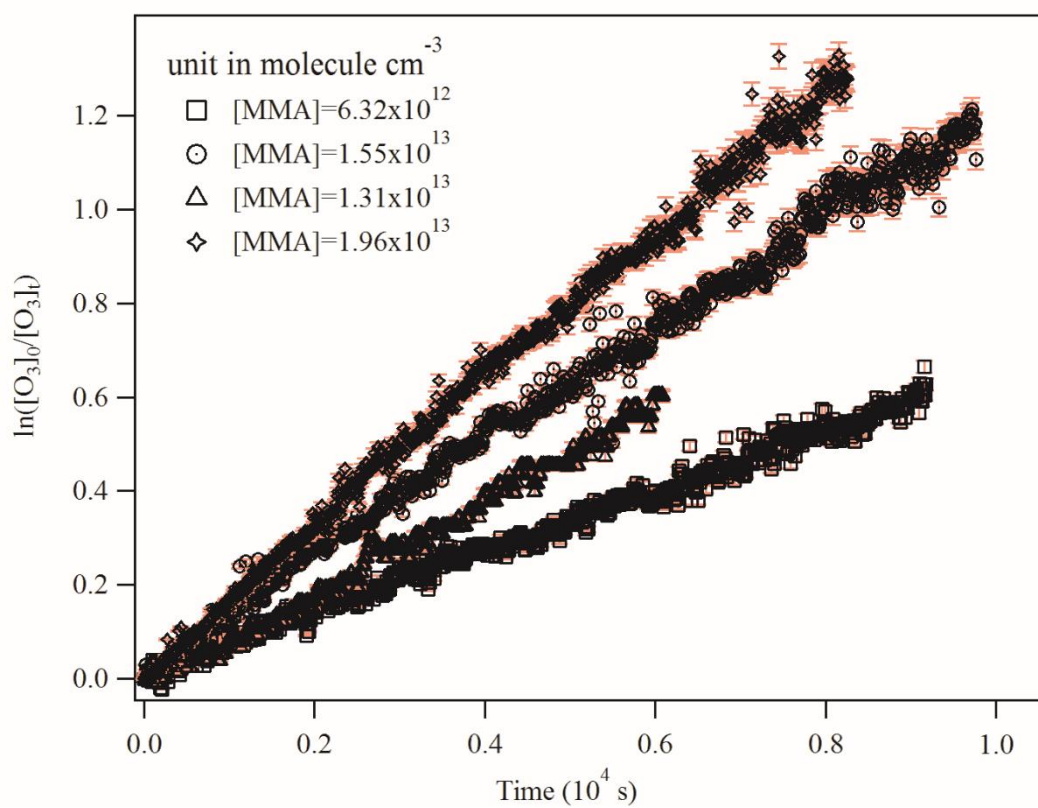


**Fig. 2.** Plots of  $(k'_1 - k'_0)$  through  $(k'_7 - k'_0)$  vs. ester concentration at  $(297 \pm 1) \text{ K}$ . The lines represent the linear least-squares fitting. For clarity Plots obtained for EMA, nPMA, nBMA, iPMA and iBMA shifted vertically by 1000, 2000, 3000, 4000 and 5000  $\text{s}^{-1}$ , respectively.

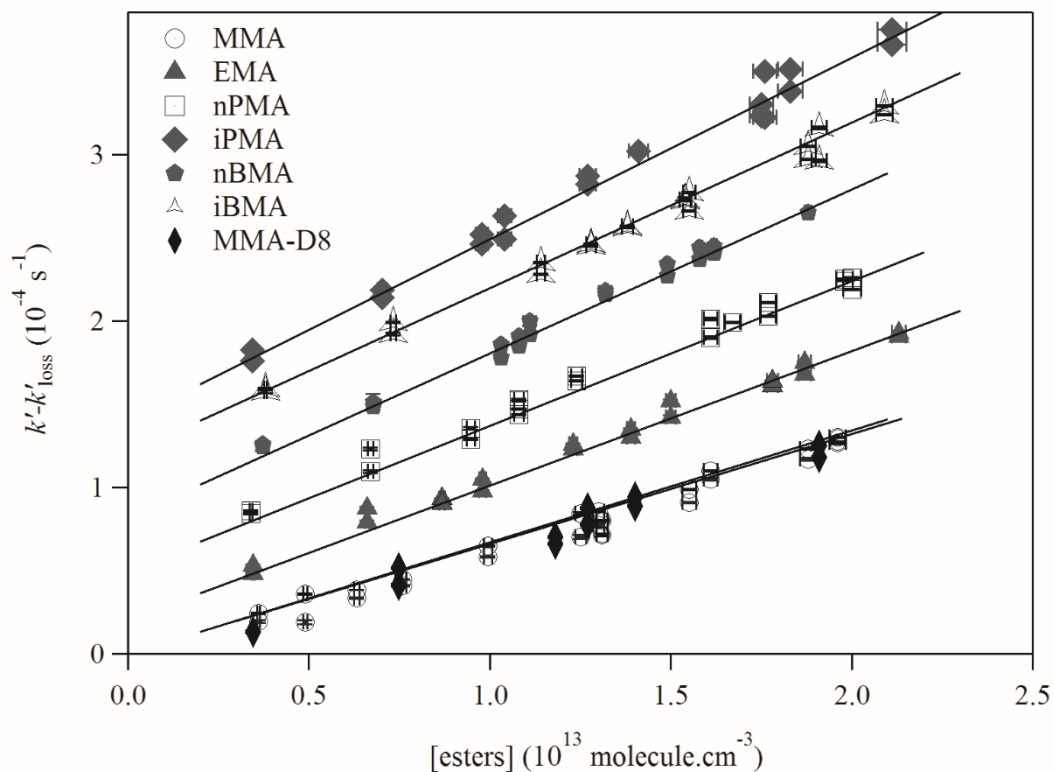


**Fig. 3.** Plots of  $k_{1\_OH}$  and  $k_{6\_OH}$  vs.  $1/T$ . The solid lines represent the Arrhenius parameter least-squares fits to the individual data points for each ester. The error bars of the individual points are  $2\sigma$ . The error bars of value from Treruel et al. 2006 and Blanco et al. 2009 were published by the authors. For clarity,  $k(T)$  obtained for nPMA, nBMA, iPMA and iBMA were multiplied 1.5, 2, 2.5 and 3, respectively.

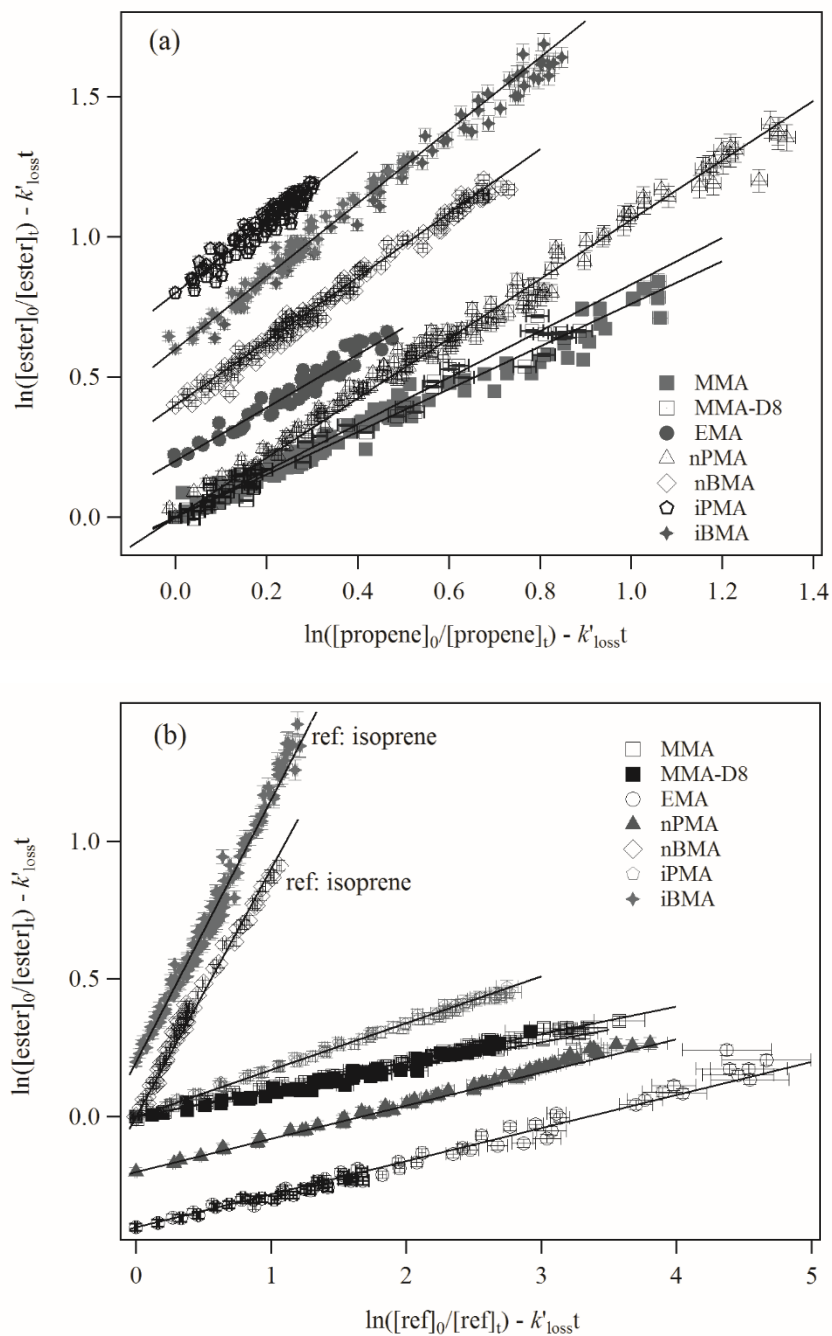




**Fig. 4.** Example of plots of  $\text{O}_3$  consumption versus reaction time in the presence of different concentration of Methyl Methacrylate, the error bar was estimated from the uncertainty of Ozone monitor as 5%.



**Fig. 5.** Plots of absolute rate data for the  $O_3$  reaction with Methyl Methacrylate (MMA), Ethyl Methacrylate (EMA), n-Propyl Methacrylate (nPMA), iso-Propyl Methacrylate (iPMA), n-Butyl Methacrylate (nBMA), iso-Butyl Methacrylate (iBMA) and MMA-D8 in the presence & absence of CO as OH scavenger. Note: EMA, nPMA, nBMA, iBMA and iPMA shift  $0.2, 0.5, 0.8, 1.2, 1.4 \times 10^{-4} \text{ s}^{-1}$  for clarity.



**Fig. 6.** Plots of relative kinetic data from the ozonolysis of the esters using propene, isoprene, cyclohexene as references in the presence of CO as the OH scavenger. Note: EMA, nBMA, iBMA and iPMA were shifted by 0.2, 0.4, 0.6 and 0.8 for clarity in (a), nPMA and iBMA were shift by -0.2 and 0.2, respectively, in (b). Isoprene was used as the reference compounds for nBMA and iBMA studies and cyclohexene for the other esters.

**Table 1.** Reactions OH + unsaturated esters ( $k_1$ -  $k_7$ ): PLP-LIF measurements, summary of experimental conditions and results.

$T$ (K)	[MMA] <sup>a</sup>	$k_{1\_OH\pm 2\sigma^b}$	[EMA] <sup>a</sup>	$k_{2\_OH\pm 2\sigma^b}$	[nPMA] <sup>a</sup>	$k_{3\_OH\pm 2\sigma^b}$	[nBMA] <sup>a</sup>	$k_{4\_OH\pm 2\sigma^b}$	[iPMA] <sup>a</sup>	$k_{5\_OH\pm 2\sigma^b}$	[iBMA] <sup>a</sup>	$k_{6\_OH\pm 2\sigma^b}$	[MMA-D8] <sup>a</sup>	$k_{7\_OH\pm 2\sigma^b}$
257			0.59-6.44	7.19±0.04										
259			1.82-9.20	6.60±0.04										
260					0.87-10.1	6.80±0.04					0.71-8.16	7.78±0.04		
260					1.14-12.3	6.62±0.03			1.19-11.9	7.64±0.04	0.92-10.2	7.73±0.08		
261									0.77-7.62	7.89±0.04				
262			0.97-10.8	6.61±0.02										
263							0.87-8.86	7.39±0.04						
263							0.88-8.83	6.94±0.05						
273			0.84-9.30	6.10±0.02	1.06-12.4	6.18±0.02			0.79-7.63	6.79±0.04	0.67-7.74	6.81±0.03		
273			0.56-5.96	6.23±0.04	0.78-9.06	6.14±0.02			1.36-11.1	6.67±0.03	0.83-9.71	6.52±0.04		
273			1.0-10.9	6.13±0.03			0.81-8.43	6.32±0.01						
277							1.70-8.45	6.64±0.04						
295			0.86-9.66	4.69±0.04										
296			0.44-4.70	5.13±0.03			1.54-7.62	5.45±0.02					1.09-10.7	4.01±0.02
297	1.37-11.8	4.28±0.01	0.74-8.10	5.17±0.04	0.80-8.27	5.00±0.04	1.58-7.67	5.25±0.03					1.05-9.86	3.91±0.03
297	1.10-9.13	4.19±0.03			0.96-10.8	4.69±0.03	1.60-7.72	5.04±0.05	0.71-6.98	5.32±0.02	0.62-6.94	5.34±0.04		
297					0.73-8.62	4.90±0.04			1.06-10.2	5.39±0.03	0.54-6.29	5.39±0.04		
298									0.97-9.60	5.38±0.02	0.80-8.83	5.08±0.04		
322					0.69-7.70	4.14±0.03								
323			0.75-7.80	4.08±0.02	0.89-10.1	4.02±0.04								
323			0.39-4.22	4.07±0.02										
323			0.91-9.71	4.16±0.04			0.70-7.32	4.41±0.02	0.98-9.47	4.61±0.04	0.57-6.71	4.59±0.03		
324									0.69-6.56	4.52±0.04	0.72-8.64	4.54±0.03		

328					0.69-6.96	4.14±0.02				
347	0.35-3.92	3.56±0.02	0.84-9.47	3.33±0.04				0.69-8.09	4.05±0.04	
348	0.72-7.91	3.47±0.02	0.61-6.86	3.56±0.03			0.63-6.26	3.86±0.04	0.54-6.21	4.06±0.03
348	0.83-9.10	3.33±0.03			0.65-6.85	3.75±0.02	0.97-8.80	3.92±0.05		
349					0.63-6.54	3.58±0.02				
373			0.77-8.70	2.84±0.03						
374			0.58-6.62	3.14±0.04						
375	0.58-6.28	2.93±0.02			0.59-6.11	3.36±0.02	0.61-5.82	3.19±0.05		
375	0.80-8.51	2.87±0.04			0.62-6.43	3.28±0.04	0.87-8.20	3.18±0.05		
376	0.33-3.67	2.96±0.03							0.48-5.75	3.37±0.04
376									0.64-7.45	3.31±0.04

<sup>a</sup> Units in  $\times 10^{13}$  molecule  $\text{cm}^{-3}$ , <sup>b</sup> Units in  $\times 10^{-11}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>

**Table 2:** Reaction of O<sub>3</sub> with Methyl Methacrylate (MMA), Ethyl Methacrylate (EMA), n-Propyl Methacrylate (nPMA), iso-Propyl Methacrylate (iPMA), n-Butyl Methacrylate (nBMA), iso-Butyl Methacrylate (iBMA) and MMA-D8: Summary of the Experimental Conditions and Results from the Relative Study at 291±2 K and 760 Torr of Air.

Ester	reference	[reference] × 10 <sup>13</sup> molecule cm <sup>-3</sup>	N <sup>o</sup> of runs	( <i>k</i> / <i>k</i> <sub>ref</sub> ±1σ)	<i>k</i> × 10 <sup>-18</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> <sup>b</sup>
<b>MMA</b>	propene	1.2 - 3.4	4	0.76±0.04	6.54±0.82
	cyclohexene	2.1 - 2.9	3	0.10±0.01	6.45±0.09
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>6.45±0.29</b>
<b>EMA</b>	propene	2.7 - 2.8	2	0.95±0.02	8.46±1.50
	cyclohexene	1.8 - 2.9	3	0.12±0.01	7.68±0.11
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>7.69±0.32</b>
<b>nPMA</b>	propene	2.6 - 3.1	3	1.03±0.01	8.71±1.26
	cyclohexene	1.6 - 2.5	3	0.12±0.01	8.46±0.12
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>8.46±0.33</b>
<b>nBMA</b>	propene	1.9 - 2.2	3	1.14±0.04	9.92±1.43
	isoprene	1.9 - 2.2	2	0.95±0.10	10.36±1.10
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>10.19±0.79</b>
<b>iPMA</b>	propene	1.9 - 3.5	3	1.26±0.04	11.43±1.65
	cyclohexene	0.4 - 1.6	3	0.17±0.01	11.21±0.16
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>11.21±0.38</b>
<b>iBMA</b>	propene	2.4 - 3.1	3	1.30±0.02	11.05±1.60
	isoprene	1.2 - 1.6	3	0.95±0.07	10.52±1.52
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>10.77±0.88</b>
MMA-D8	propene	1.5 - 2.3	2	0.83±0.05	7.21±1.28
	cyclohexene	2.2 - 2.3	2	0.09±0.01	6.28±0.11
				<b><i>k</i><sub>av</sub><sup>a</sup></b>	<b>6.29±0.32</b>

<sup>a</sup> Weighted average  $k_{av} = (w_{ref1}k_{ref1} + w_{ref2}k_{ref2} + \dots) / (w_{ref1} + w_{ref2} + \dots)$ , where  $w_{ref1} = 1/\sigma_{ref1}^2$ , etc. The error,  $\sigma_{av}$ , was given by:  $\sigma_{av} = (1/\sigma_{ref1} + 1/\sigma_{ref2} + \dots)^{-0.5}$

<sup>b</sup> The uncertainty was calculated using  $\frac{1}{n} \sqrt{\sigma_1^2 + \sigma_2^2 + \dots + \sigma_n^2}$  from each individual run within same reference

**Table 3.** Comparison of OH Reaction Rate Coefficients with Previous Work

	$T$ (K)	$k \times 10^{-11}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$A \times 10^{-12}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	E/R (K)	$T$ range (K)	technique	ref
MMA	298	2.6±0.5				DF-LIF	Saunders, et al. (1994).
	298	4.15±0.32				RR_GC-FID	Blanco, et al. (2006)
	298±2	4.2±1.1				RR_GC-FID	Teruel, et al. (2006)
	298	4.09±0.08	2.5±0.8	-(821±55)	255- 351	PLP-LIF	Teruel, et al. (2006)
	298	4.30±0.98	1.97±0.95	-(921±52)	287- 313	RR_FTIR	Blanco, et al. (2009)
	297±1	4.24±0.12				PLP-LIF	This work
MMA-D8	297±1	3.96±0.14				PLP-LIF	This work
EMA	298	4.58±0.59				RR_GC-FID	Blanco, et al. (2006)
	297±1	4.99±0.54	4.25±0.54	-(726±39)	257- 376	PLP-LIF	This work
nPMA	297±1	4.86±0.32	4.49±0.74	-(708±50)	260- 374	PLP-LIF	This work
nBMA	298	7.08±0.75				RR_GC-FID	Blanco, et al. (2006)
	298	6.63±1.42	16.5±10.5	-(413±34)	287- 313	RR_FTIR	Blanco, et al. (2009)
	297±1	5.26±0.29	5.07±0.79	-(696±48)	263- 375	PLP-LIF	This work
iPMA	297±1	5.36±0.07	4.62±0.48	-(735±32)	260- 375	PLP-LIF	This work
iBMA	297±1	5.27±0.33	5.53±0.76	-(680±42)	260- 376	PLP-LIF	This work

**Table 4.** Comparison of room temperature rate coefficients obtained in this work with literature values for the reaction of O<sub>3</sub> with unsaturated esters (Methyl Methacrylate (MMA), Ethyl Methacrylate (EMA), n-Propyl Methacrylate (nPMA), iso-Popyl Methacrylate (iPMA), n-Butyl Methacrylate (nBMA) and iso-Butyl Methacrylate (iBMA)).

Ester	$k \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T$ (K)	technique	ref
MMA	7.5±0.9	291±1	AR, cHx scavenger	Grosjean, D., et al. (1993)
	6.8±0.4	294±2	AR, cHx scavenger	Bernard, F., et al. (2010)
	6.5±0.7	294±2	RR-FTIR, cHx scavenger,	Bernard, F., et al. (2010)
	6.63±0.38	291±2	AR and RR, CO scavenger	This work
EMA	7.68±0.88	293 ± 1	AR, CO scavenger	Gai, Y., et al. (2009)
	7.74±0.41	291±2	AR and RR, CO scavenger	This work
nPMA	8.46±0.36	291±2	AR and RR, CO scavenger	This work
nBMA	10±3	298 ± 1	RR-FTIR, CO scavenger	Gaona Colmán, E., et al. (2013)
	9.78±0.58	291±2	AR and RR, CO scavenger	This work
iPMA	10.94±0.30	291±2	AR and RR, CO scavenger	This work
iBMA	9.96±0.54	291±2	AR and RR, CO scavenger	This work
MMA-D8	6.30±0.49	291±2	AR and RR, CO scavenger	This work

<sup>a</sup> Weighted average of values from AR method and RR method in this work:  
 $k = (w_1 k_1 + w_2 k_2 + \dots) / (w_1 + w_2 + \dots)$ , where  $w_i = 1/\sigma_i^2$ , etc.



**Table 5.** Rate constants for the gas-phase reaction of ozone with unsaturated esters (Methyl Methacrylate (MMA), Ethyl Methacrylate (EMA), n-Propyl Methacrylate (nPMA), iso-Propyl Methacrylate (iPMA), n-Butyl Methacrylate (nBMA) and iso-Butyl Methacrylate (iBMA)) and their alkene structural homologues (unit in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).

Ester		$k_{\text{O}_3}^{\text{a,c}}$	$k_{\text{OH}}^{\text{b,c}}$	$k_{\text{OH}}^{\text{i}}$ SAR	$k_{\text{OH}}^{\text{j}}$ SAR	Alkene		$k_{\text{O}_3}^{\text{a,d}}$	$k_{\text{OH}}^{\text{b}}$
Name	Formula					Name	Formula		
MMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$	6.71±0.42	4.24±0.06	1.83	2.90	2-methyl-1-propene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_3$	11.3	5.14 <sup>d</sup>
EMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3$	7.77±0.46	4.99±0.27	1.98	3.06	2-methyl-1-butene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$	13.3 <sup>e</sup>	6.10 <sup>d</sup>
nPMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$	8.46±0.38	4.86±0.16	2.13	3.24	2-methyl-1-pentene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$	16.0	6.30 <sup>d</sup>
iPMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	10.93±0.31	5.36±0.04	2.16	3.36	2,3-dimethyl-1-butene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$	10.0 <sup>f</sup>	5.50 <sup>h</sup>
nBMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	9.78±0.58	5.26±0.14	2.27	3.04	2-methyl-1-hexene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	12.0 <sup>g</sup>	5.70 <sup>h</sup>
iBMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)_2$	9.97±0.54	5.27±0.17	2.27	3.40	2,4-dimethyl-1-pentene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$	12.0 <sup>g</sup>	5.80 <sup>h</sup>

<sup>a</sup> rate constant of their reaction with  $\text{O}_3$ , unit in  $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

<sup>b</sup> rate constant of their reaction with OH radical, in  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

<sup>c</sup> obtained in this work

<sup>d</sup> cited from Calvert et al. (2000)

<sup>e, f</sup> are the rate constants at 288 K and 285 K, respectively, otherwise at 298 K.

<sup>g</sup> data for 1-heptene because the data for 2-methyl-1-hexene and 2,4-dimethyl-1-pentene are unavailable

<sup>h</sup> calculation data using Structure-activity Relationship (SAR) and cited from Grosjean, D. and E. L. Williams (1992)

<sup>i</sup> Calculated using the AOPWIN program

<sup>j</sup> Calculated using the very recent approach reported by Jenkin et al. (2018)

**Table 6.** Estimated tropospheric lifetimes for the unsaturated esters studied in this work with respect to their reactions with O<sub>3</sub>, OH radical, Cl atom and NO<sub>3</sub> radical.

Ester	$\tau_{\text{O}_3}$ (hrs)		$\tau_{\text{OH}}$ (hrs) <sup>c</sup>		$\tau_{\text{NO}_3}$ (hrs) <sup>e</sup>	$\tau_{\text{Cl}}$ (hrs) <sup>e</sup>	
	low <sup>a</sup>	high <sup>b</sup>	low <sup>c</sup>	high <sup>d</sup>		low <sup>f</sup>	high <sup>g</sup>
MMA	59	6	7	3	186	99	10
EMA	51	5	6	3	119	103	10
nPMA	47	5	6	3	106		
nBMA	41	4	5	3	94	75	7
iPMA	36	4	5	3	70		
iBMA	40	4	5	3	89		

<sup>a</sup> lifetime was calculated using the averaged O<sub>3</sub> concentrations as:  $7 \times 10^{11}$  molecule cm<sup>-3</sup> (Logan, 1985.)

<sup>b</sup> lifetime was calculated using the relative high O<sub>3</sub> concentrations as:  $7 \times 10^{12}$  molecule cm<sup>-3</sup> (Guo, et al. 2017)

<sup>c</sup> [OH] =  $1 \times 10^6$  molecules cm<sup>-3</sup> (Spivakovsky, et al. 2000)

<sup>d</sup> [OH] =  $2 \times 10^6$  molecules cm<sup>-3</sup> (Hein,, et al. 1997)

<sup>e</sup> value from Zhou, et al. 2017.

<sup>f</sup> [Cl] =  $1 \times 10^4$  molecules cm<sup>-3</sup> (Wingenter, et al. 1996)

<sup>g</sup> [Cl] =  $1 \times 10^5$  molecules cm<sup>-3</sup> (Spicer, et al. 1998)