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## Kinetics of the Reactions of NO<sub>3</sub> Radical with Methacrylate Esters 2

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5 **1 Kinetics of the Reactions of NO<sub>3</sub> Radical with Methacrylate**  
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8 **2 Esters**  
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## 20 Abstract

21 Two different experimental methods (relative rate and absolute rate methods) were  
22 used to measure the rate coefficients for the reactions of NO<sub>3</sub> radical with six  
23 methacrylate esters: methyl methacrylate (MMA, k<sub>1</sub>), ethyl methacrylate (EMA, k<sub>2</sub>),  
24 propyl methacrylate (PMA, k<sub>3</sub>), isopropyl methacrylate (IPMA, k<sub>4</sub>), butyl methacrylate  
25 (BMA, k<sub>5</sub>), isobutyl methacrylate (IBMA, k<sub>6</sub>). In the relative rate method, the loss of the  
26 esters relative to that of a reference compound was followed in a 7300 L Teflon-walled  
27 chamber at (298±2) K and (1000±5) hpa. In the absolute method, the temporal profiles of  
28 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were followed using a dual channel cavity ring down spectrometer in the  
29 presence of an excess of ester in the 7300 L chamber. The rate coefficients from these two  
30 methods (weighted averages) in the units of 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K are: k<sub>1</sub> =  
31 (2.98±0.35); k<sub>2</sub> = (4.67±0.49); k<sub>3</sub> = (5.23±0.60); k<sub>4</sub> = (7.9<sub>1</sub>±1.0<sub>0</sub>); k<sub>5</sub> = (5.71±0.56); and k<sub>6</sub>  
32 = (6.24±0.66). The quoted uncertainties are at the 2σ level and include estimated  
33 systematic errors. Unweighted averages are also reported. In addition, the rate coefficient  
34 k<sub>7</sub> for the reaction of NO<sub>3</sub> radical with deuterated methyl methacrylate (MMA-D8) was  
35 measured using the relative rate method to be essentially the same as k<sub>1</sub>. The trends in the  
36 measured rate coefficient with the length and nature of the alkyl group, along with the  
37 equivalence of k<sub>1</sub> and k<sub>7</sub> strongly suggests that the reaction of NO<sub>3</sub> with the methacrylate  
38 esters proceeds via addition to the double bond on the methacrylate group. The present

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4 39 results are compared with those from previous studies. Using the measured values of the  
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7 40 rate coefficients, along with those for reactions of these esters with OH, O<sub>3</sub>, and chlorine  
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10 41 atoms, the atmospheric lifetimes of methacrylate esters are calculated. We suggest that  
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12 42 NO<sub>3</sub> radicals do contribute to the atmospheric loss of these unsaturated esters, but to a  
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15 43 lesser extent than their reactions with OH and O<sub>3</sub>.  
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## 1 Introduction

Methacrylate esters are important unsaturated oxygenated volatile organic compounds (OVOCs) used in the production of polymers. They are used extensively for manufacture of industrial products such as resins and plastics. Due to their high volatility, these unsaturated OVOCs may be released into the atmosphere, particularly in industrial areas. For example, more than 5,000 tonnes of methyl methacrylate is produced every year in the European Union. The maximum production capacity in each location methacrylates is estimated to be around 10,000 tonnes per year and release from these facilities are estimated to be between 0.005% to 1.1 % of the production values<sup>1</sup>. If emitted, their atmospheric degradation could lead to surface ozone and aerosols formation.

Once released, these unsaturated OVOCs are degraded in the atmosphere by reaction with various reactive species, which include OH and NO<sub>3</sub> radicals, chlorine atoms and O<sub>3</sub>.

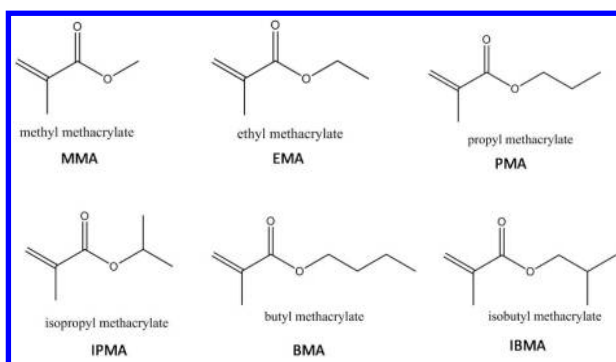
<sup>2</sup> The nitrate radical, NO<sub>3</sub>, is a photochemically unstable radical that is prevalent at night, especially in polluted areas that have large NO<sub>x</sub> emissions. NO<sub>3</sub> is known to be an important nighttime oxidant for OVOCs in the atmosphere.<sup>3</sup> Therefore, rate coefficients for the reactions of NO<sub>3</sub> radicals with methacrylate esters are needed to assess their atmospheric loss rates, especially at night.

Kinetics and products of reactions of OH radical reactions with acrylates and methacrylates has been the subject of several studies.<sup>4-5</sup> Reactions of several methacrylate

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4 77 esters with  $O_3$  have also been studied at room temperature.<sup>6-7</sup> Rate coefficients for the  
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7 78 reactions of chlorine atoms with methyl methacrylate (MMA) and ethyl methacrylate  
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10 79 (EMA) have been reported.<sup>8-9</sup> Several groups<sup>10-13</sup> have measured the rate constants for the  
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13 80 reaction of  $NO_3$  with several methacrylates near 298 K via the relative method, often  
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16 81 using the reaction of  $NO_3$  with propene as the reference.

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18 82 In this work, we report the room temperature ( $298 \pm 2K$ ) rate coefficients for the  
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21 83 reactions of  $NO_3$  radical with six of the methacrylate esters (shown below): methyl  
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24 84 methacrylate (MMA) -  $k_1$ ; ethyl methacrylate (EMA) -  $k_2$ ; propyl methacrylate (PMA) -  $k_3$ ;  
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27 85 isopropyl methacrylate (IPMA) -  $k_4$ ; butyl methacrylate (BMA) -  $k_5$ ; and isobutyl  
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30 86 methacrylate (IBMA) -  $k_6$ .

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49 90 We used two different experimental methods: (1) a relative rate method where the loss  
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52 91 of the ester was measured relative to that of a reference compound while competing for a  
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55 92 common pool of  $NO_3$  radicals; and (2) a direct method where the temporal profiles of  $NO_3$   
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58 93 and  $N_2O_5$  were measured using cavity ring down spectroscopy to detect  $NO_3$  and  $N_2O_5$  in

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4 94 an excess of known concentrations of esters. Both  $N_2O_5$  and  $NO_3$  (which are essentially in  
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7 95 equilibrium) decay together when  $NO_3$  is lost via its reaction with the hydrocarbon.  
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10 96 Therefore, we used a box model consisting of 5 reactions (see later) to simulate the  
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12 97 temporal profiles of  $NO_3$  and  $N_2O_5$  and quantitatively compare them (via least squares  
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15 98 method) with the observed profiles of these species. The use of these two complementary  
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18 99 methods enhances our confidence in the measured rate coefficients. In addition, the rate  
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21 100 coefficient of deuterated methyl methacrylate (MMA-D8) with  $NO_3$  radical was also  
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24 101 investigated to shed light on the mechanism of the reaction. Using the obtained kinetics  
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27 102 data, the atmospheric lifetimes of methacrylate esters towards  $NO_3$  radicals were  
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30 103 calculated and compared with those due to loss via reactions with OH radicals,  $O_3$  and  
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32 104 chlorine atoms (Cl). The kinetics results also enhance the available database on  $NO_3$   
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35 105 reactions.

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## 107 **2 Experiments and Results**

108 In this section, we will describe our results from the two methods that were used.

109 Because the experimental methods were somewhat different, we will first describe the  
110 chamber that was used for both methods followed by the analytical methods that were  
111 employed. Subsequently, the obtained data are presented.

### 112 **2.1 Experimental system: Indoor atmospheric simulation chamber**

113 The kinetic of  $\text{NO}_3$  with esters were studied at room temperature ( $298 \pm 2\text{K}$ ) in the  
114 ICARE-7300L Teflon chamber (Figure1), which has been described in detail.<sup>14-15</sup> We will  
115 describe here only the features necessary to understand this study. The chamber was  
116 equipped with three key analytical tools: (1) a proton transfer reaction mass spectrometer,  
117 which was fed from the center of the chamber, to measure the concentrations of  
118 hydrocarbon reactants (and some of the products); (2) a Nicolet 5700 Magna FT-IR  
119 spectrometer (which sampled approximately 2m near the center of the chamber) the  
120 coupled to a white-type mirror system with roughly 70 passes resulting in an optical path of  
121 about 140 m; and (3) a cavity ring down spectrometer fed from the center of the chamber  
122 (with its inlet next to that for the PTR-MS) to measure  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ . (We could also  
123 estimate the concentration of  $\text{NO}_2$  using this system.) All the three analytical tools sampled  
124 essentially the same part of the chamber. The contents of the chamber were mixed by two



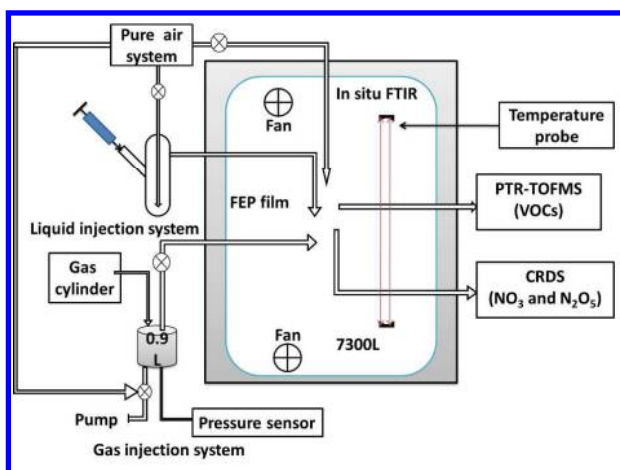
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4 125 fans internal to the chamber. In addition, the chamber was equipped with multiple  
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7 126 thermocouples to measure temperature and a set of capacitance manometers to measure  
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10 127 pressure within the chamber, and a gas handling system to input known amounts of gases  
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13 128 into the chamber.

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15 129 The atmospheric pressure ( $1000\pm 5$ hpa) chamber was made of Teflon film and kept  
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18 130 dark by shrouding it in a container equipped with black curtains. Purified dry air (relative  
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21 131 humidity  $<3\%$ ) was constantly flowed into the chamber. The chamber was flushed with a  
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24 132 large flow (about 120L/min) of dry air to clean out the chamber between experiments or to  
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27 133 clean it overnight. However, during kinetics studies, a small flow (about 5-10L/min,  
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30 134 depending on the sampling flow rate) of purified air was added just to compensate for the  
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33 135 continuous withdrawal of gas from the chamber for analysis; such a flow maintained a  
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36 136 constant pressure in the chamber that was slightly above ambient. This flow arrangement  
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39 137 resulted in a constant slow dilution of the reactants in the chamber. We measured the  
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42 138 dilution rate and mixing time in the chamber by injecting a sample of SF<sub>6</sub> (>99.99%, Alpha  
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45 139 Gaz) into the chamber and measuring the temporal profile of SF<sub>6</sub> using the in situ FTIR  
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48 140 spectrometer. The mixing time (for near complete mixing, >99%) was about 30 seconds,  
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51 141 much shorter than the times for reactions studied here, and the dilution rate could be  
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54 142 expressed as a first order rate coefficient of around  $2.5\times 10^{-5}\text{s}^{-1}$  (see below).

55 143 The gas handling system, external to the chamber, was designed to inject a known  
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58 144 volume of a gas into the chamber. We could also inject a known volume of liquid (that

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4 145 evaporated immediately within the chamber) through a septum into a gas flow that reached  
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7 146 the middle of the chamber. Pressures in the gas handling system were measured using  
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10 147 calibrated capacitance manometers (0-10 and 0-100 Torr, MKS Baratron).

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12 In the chamber, the organic reactants were detected in real time by using a  
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15 149 proton-transfer-reaction time of flight mass spectrometer (PTR-ToF-MS), and the  
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18 150 concentrations of  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  were monitored on line by a two-channel cavity ring down  
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21 151 spectrometer (CRDS). The details of these instruments are described in the following  
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24 152 sections.



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42 154 Figure1: Schematic diagram of the 7300 L chamber used to study the reaction of  $\text{NO}_3$  radicals  
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45 155 with methacrylate esters along with the analytical methods used to detect reactants. The gas  
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48 156 inlet system is shown on the left. The gas outlets and the curtains to keep the chamber dark are  
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51 157 not shown. The figure is not to scale.

### 158 2.1.2 PTR-TOFMS

159 The high-resolution proton-transfer-reaction time-of-flight mass spectrometer  
160 (PTR-ToF-MS)<sup>16</sup> (IoniconAnalytik, PTR-ToF-MS 8000) with hydronium ions (H<sub>3</sub>O<sup>+</sup>) ion  
161 source was used to measure methacrylates. The pressure and temperature in the  
162 PTR-ToF-MS drift tube was maintained at 2.1 mbar and 333 K. A drift voltage of 400 V  
163 was used such that the reduced electric field, E/N, was 98 Td (E is the field strength in V  
164 cm<sup>-1</sup> and N is the number density of gas in molecules cm<sup>-3</sup>). The flow rate of air from the  
165 chamber into the drift tube was approximately 150 mL min<sup>-1</sup>. The mass resolution of the  
166 mass spectrometer, m/Δm, typically ranged from 3500 to 4500. The mass spectral data  
167 were analyzed by a PTR-ToF Data Analyzer software<sup>17</sup> and the normalized peak  
168 intensities (in counts per second, ncps) were used for calibration and monitoring. The  
169 measured signals varied linearly with the concentrations of the hydrocarbon. The  
170 detection sensitivities for the hydrocarbons were derived from the slopes of the  
171 calibrations plots of the measured signal (ncps) versus the partial pressure of the  
172 hydrocarbon (ppbv) (See also Figure S1 in the supporting information). The detection  
173 sensitivities (in units of ncps/ppbv, 1ppbv = 2.46×10<sup>10</sup> molecule cm<sup>-3</sup> at 298K and  
174 101.3kpa) at their monitored mass are shown in Table 1.

175  
176 Table 1. A list of specific masses monitored to detect various VOCs using the proton

177 transfer mass spectrometry. The detection sensitivities are also listed.

	Mass charge ratio (m/z)	Detection sensitivities (ncps/ppbv)
propene	43.05	5.22±0.09
propanal	59.5	7.13±0.09
MMA	101.06	38.9±0.5
d8-MMA	109.09	40.0±0.6
EMA	115.07	5.95±0.47
	87.05	39.2±1.7
PMA	87.05	51.4±0.5
IPMA	87.05	46.8±1.4
BMA	87.05	53.8±2.1
IBMA	87.05	26.1±0.5

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### 179 2.1.3 CRDS

180 A two-channel cavity ring down spectrometer operating at 662 nm was used to  
181 simultaneously measure the concentrations of NO<sub>3</sub> (in one channel) and N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> (in  
182 another channel). The detection principle and operating characteristics of this instrument  
183 has been described in detail elsewhere.<sup>18-21</sup>

184 The first channel measured the concentration of NO<sub>3</sub>. The second, parallel, channel  
185 was heated to convert N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub>; total NO<sub>3</sub> (which upon quantitative conversion of  
186 N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub>) was measured and it represents the sum of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. The time  
187 resolution of the instrument was 1s with detection sensitivities of between 0.4 and 2 ppt  
188 for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> for 1 second integration, as described in detail by Fuchs et al.<sup>22</sup> The air  
189 sample entering the CRDS system was passed through a filter to remove aerosols, which

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4 190 scatter the 662 nm light and degrade the instrument sensitivity for gas phase measurement.  
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7 191 The combined loss of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  to the walls of the instrument and the filter located  
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10 192 upstream of this same device have been estimated<sup>22-25</sup> to be less than 20% and 4%,  
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13 193 respectively, for  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ ; these losses are accounted for in calculating the  
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16 194 concentrations. The uncertainties in the absorption cross section of  $\text{NO}_3$  radical at 662 nm  
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19 195 and the ratio of the cavity length to the length over which  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are present add to  
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22 196 the estimated uncertainties. Based on these factors, the overall (asymmetric) accuracy of  
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25 197 the  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  measurements, respectively, are estimated<sup>26</sup> to be -8% to +11% and  
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28 198 from -9% to +12%. Note that the precision of the measurements of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are  
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31 199 much better than the quoted absolute uncertainties under the concentration conditions used  
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34 200 in the present study (with initial mixing ratios of  $\text{NO}_3$  between 500 and 2,500 pptv and  
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37 201 initial mixing ratios of  $\text{N}_2\text{O}_5$  between 8,000 and 25,000 pptv).

#### 38 39 202 **2.1.4 Fourier Transform Spectrometer**

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43 203 A commercial Nicolet 5700 Magna FT-IR spectrometer was coupled to a white-type  
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46 204 mirror system located away from the walls and close to the center of the chamber. The  
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49 205 optical path length within the chamber was about 140 m. The instrument was operated at a  
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52 206 resolution of  $1\text{ cm}^{-1}$ . The spectra from the instrument were analyzed using the software  
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55 207 provided by the vendor. All the details of the instrument and data analyses are given  
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58 208 previously.<sup>14-15</sup> The FTS was used to measure  $\text{SF}_6$  ( $934\text{ cm}^{-1}$  -  $954\text{ cm}^{-1}$ ), hydrocarbons,

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4 209 and some other species during the course of this study; they are noted when appropriate.  
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## 7 8 210 **2.2 Chemicals** 9

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11 211 The purities of chemicals used in the experiments as given by the manufacturer were:  
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13 212 methyl methacrylate (MMA, > 99%, TCI), ethyl methacrylate (EMA, >99%, TCI), propyl  
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15 213 methacrylate (PMA, >97%, Aldrich), isopropyl methacrylate (IPMA, >98%, TCI), butyl  
16  
17 214 methacrylate (BMA, >99%, TCI), isobutyl methacrylate (IBMA, >98%, TCI), propene  
18  
19 215 (>99%, Air Liquid), and propanal (>98%, Aldrich). The isotopic purity of methyl  
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21 216 methacrylate-D8 (MMA-D8 from Apollo Scientific Limited) was quoted to be 99.50  
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23 217 Atom % D. The levels of stabilizers in the samples of esters are noted later. In this study,  
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25 218 the NO<sub>3</sub> radicals were produced by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> injected into the  
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27 219 chamber. Pure N<sub>2</sub>O<sub>5</sub> was synthesized by mixing NO with O<sub>3</sub> in a slow flow and collecting  
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29 220 N<sub>2</sub>O<sub>5</sub> at dry ice temperature, followed by purification, as described by Davidson et al.<sup>27</sup>  
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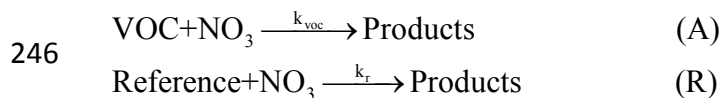
## 41 221 **2.3 Kinetic study methods and results** 42 43 44

45 222 As noted earlier, we measured the rate coefficients using two different methods: (a) a  
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47 223 relative rate method by following the depletion of a VOC and a reference compound, and  
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49 224 (b) an absolute method where the temporal profiles of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> in an excess of VOC.  
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53 225 For ease of presentation, these two experiments and the obtained results will be presented  
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56 226 separately below.  
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### 227 **2.3.1 Relative rate method**

228 The experiments were conducted in the chamber (7300L) at atmospheric pressure  
229 (1000±5hpa) and at temperature of 298±2K. The depletion of a reactant (each  
230 methacrylate esters; hereinafter VOC) and a reference (propene, propanal and MMA) in  
231 the presence and in the absence of NO<sub>3</sub> (and N<sub>2</sub>O<sub>5</sub> in equilibrium with NO<sub>3</sub> and NO<sub>2</sub>) were  
232 monitored by PTR-ToF-MS. To account for dilution, as noted earlier, the losses of VOCs  
233 in the absence of NO<sub>3</sub> were measured along with the depletion of SF<sub>6</sub> added  
234 simultaneously with the VOCs to the chamber. This small decay was essentially first order  
235 in the concentrations of VOC and SF<sub>6</sub>. The first order rate coefficient for the loss of each  
236 reactant in the absence of NO<sub>3</sub> was essentially the same as that for the loss of SF<sub>6</sub>; this  
237 decay is attributed to dilution caused by the continued injection of dry air into the  
238 chamber. The rate first order rate coefficient for the removal of SF<sub>6</sub> and the VOCs,  $k_d$ ,  
239 was  $(2.5 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$ . This rate coefficient is essentially what we calculate from the  
240 volume flow rates of pure air added to the known volume of the chamber to maintain a  
241 constant pressure. The related Figure S2 is given in the supporting information.

242 Subsequent to these measurements, a sample of N<sub>2</sub>O<sub>5</sub> was introduced into the  
243 chamber where it dissociated to give NO<sub>3</sub>. The rates of depletion of VOCs and reference  
244 compound were monitored using the PTR-MS. The VOCs and reference compound are  
245 competing for the same pool of NO<sub>3</sub> radicals and are represented by the reactions:



247 Under these conditions, their relative losses of the VOC and reference compound are given  
248 by:

$$\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d t = \frac{k_{\text{VOC}}}{k_r} \left( \ln \frac{[\text{Reference}]_0}{[\text{Reference}]_t} - k_d t \right) \quad \text{(I)}$$

250 where  $[\text{VOC}]_0$  and  $[\text{VOC}]_t$  are the concentration of reactant at initial time  $t_0$  and at time  $t$ ,  
251  $[\text{Reference}]_0$  and  $[\text{Reference}]_t$  are the concentration of reactant at  $t_0$  and  $t$ ,  $k_{\text{VOC}}$  and  $k_r$  were  
252 the rate coefficients for reaction (A) and (R),  $k_d$  is the first order rate constant for dilution in  
253 the chamber. A plot of  $\ln([\text{VOC}]_0/[\text{VOC}]_t) - k_d t$  versus  $\ln([\text{Reference}]_0/[\text{Reference}]_t) - k_d t$   
254 would be a straight line with a zero intercept and a slope of  $k_{\text{VOC}}/k_r$ . In our experiments, the  
255 rate constants of the reactions of the reference compounds with  $\text{NO}_3$  radicals were taken  
256 to be  $k_r(\text{propene}) = (9.5 \pm 5.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>28</sup>,  $k_r(\text{propanal}) = (6.3 \pm 2.6) \times 10^{-15}$   
257  $\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>28</sup>,  $k_r(\text{MMA}) = (2.98 \pm 0.35) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (weighted average  
258 of the absolute and relative methods from this work; see below). Note that the weighted  
259 average for MMA is essentially that measured via the absolute method. The initial  
260 concentration of each reactant used in this work is shown in Table 2. A complete  
261 summary of the initial concentrations and experimental conditions are given in the  
262 supporting information as Table S1.

263 Figures 2-1 and 2-2 show the loss of the esters relative to propene and MMA,  
264 respectively, according to Equation I. For measurement of each rate constant, several

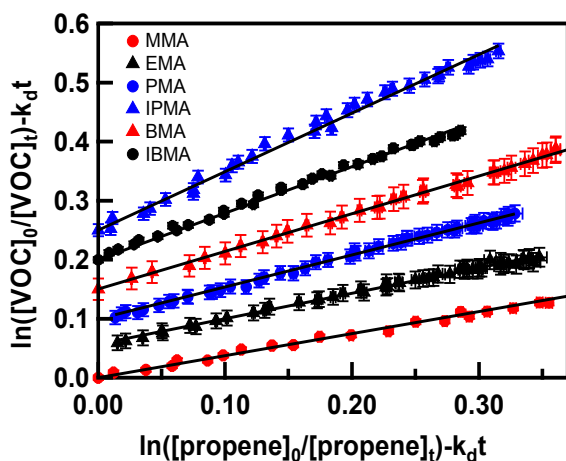


265 mixtures of the reactant and standard were used and they are all included in the same plots.

266 Clearly, the plots show good linearity for all reactions. These plots were analyzed via

267 linear least squares analyses to obtain the slope of  $k_{\text{voc}}/k_r$ . The obtained values (average of

268 multiple measurements) of the rate constants are summarized in Table 2.



269

270 Figure 2-1 Plots of the losses of esters relative to those of propene, which was used as the reference.

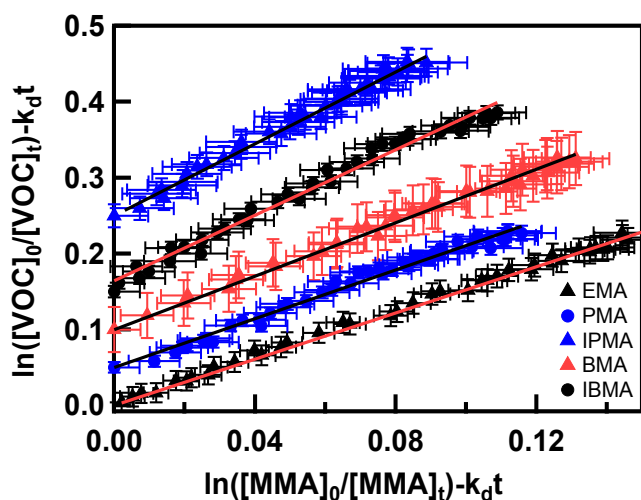
271 The losses shown are for: MMA, red filled circles; EMA, black triangles, Y axis offset by 0.05;

272 PMA, blue filled circles, Y axis offset by 0.1; IPMA, blue triangles, Y axis offset by 0.25; BMA,

273 red triangles, Y axis offset by 0.15; IBMA, black filled circles, Y axis offset by 0.20. The linear

274 least squares fits are shown as lines.

275



276

277 Figure 2-2 Plots of the losses of esters relative to those of MMA used as reference.

278 The specific esters are noted in the legend within the figure (EMA, filled black circles;

279 PMA, blue filled circles, Y axis offset by 0.05; IPMA, blue triangles, Y axis offset by

280 0.25; BMA, red triangles, Y axis offset by 0.1; IBMA, blue filled circles, Y axis

281 offset by 0.15). The linear least squares fits are shown as lines.

282

283 The quoted errors in the rate constant ratios ( $k_{\text{voc}}/k_r$ ) are twice the standard deviation284 ( $2\sigma_{k_{\text{voc}}/k_r}$ ) in the linear least-squares fit of the measured losses to Equation I. In addition to

285 the precision of this ratio, we have included the estimated uncertainty (as given by the

286 IUPAC evaluations) in the rate coefficient ( $k_r \pm \sigma_{k_r}$ ) for the reaction of  $\text{NO}_3$  with the

287 reference compound.

288

289 Table 2. Summary of the results from the relative rate study for reaction of  $\text{NO}_3$  with

290 methacrylate esters at 298±2K.

VOCs	[VOC] <sub>0</sub> 10 <sup>12</sup> (molecule cm <sup>-3</sup> )	Ref. Compound	No. of experiments	$\frac{k_{voc}}{k_r} \pm 2\sigma_{\left(\frac{k_{voc}}{k_r}\right)}$	$k_{voc} \pm 2\sigma_{voc}$ 10 <sup>-15</sup> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
Methyl methacrylate (MMA)	1.13 to 3.40	propene	6	0.37±0.04	(3.52±2.07)
		propanal	2	0.58±0.06	(3.77±1.56)
				Average	(3.6 <sub>5</sub> ±1.3 <sub>0</sub> )
				Weighted average	(3.6 <sub>8</sub> ±1.2 <sub>4</sub> )
Ethyl methacrylate (EMA)	1.28 to 2.56	propene	3	0.53±0.05	(5.04±2.95)
		MMA	2	1.55±0.07	(4.62±0.58)
				Average	(4.8 <sub>3</sub> ±1.5 <sub>0</sub> )
				Weighted average	(4.6 <sub>3</sub> ±0.5 <sub>7</sub> )
Propyl methacrylate (PMA)	1.10 to 1.66	propene	3	0.56±0.04	(5.32±3.10)
		MMA	3	1.70±0.16	(5.07±0.76)
				Average	(5.2 <sub>0</sub> ±1.6 <sub>0</sub> )
				Weighted average	(5.0 <sub>8</sub> ±0.7 <sub>4</sub> )
Isopropyl methacrylate (IPMA)	1.10 to 1.65	propene	3	0.91±0.30	(8.65±5.76)
		MMA	3	2.71±0.61	(8.08±2.05)
				Average	(8.3 <sub>7</sub> ±3.0 <sub>6</sub> )

				Weighted average	(8.1 <sub>4</sub> ±1.9 <sub>3</sub> )	
Butyl methacrylate (BMA)	1.01 to 2.53	propene	3	0.70±0.08	(6.65±3.87)	
		MMA	3	1.84±0.12	(5.48±0.74)	
					Average	(6.0 <sub>7</sub> ±1.9 <sub>7</sub> )
					Weighted average	(5.52±0.72)
Isobutyl methacrylate (IBMA)	0.99 to 2.48	propene	3	0.75±0.02	(7.13±4.13)	
		MMA	3	1.95±0.23	(5.81±0.96)	
					Average	(6.4 <sub>7</sub> ±2.1 <sub>2</sub> )
					Weighted average	(5.88±0.94)

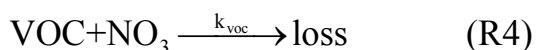
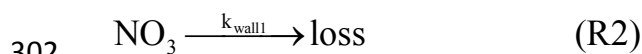
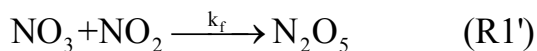
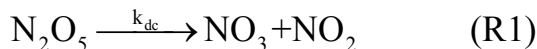
291 The number of appropriate significant figures are shown for the averages. The number of significant  
 292 figures in the reported values are more than what is warranted by the errors, but are shown for  
 293 completeness. To maintain consistent number of significant figures, some numbers with larger errors are  
 294 shown with the last digit as a subscript.

### 295 **2.3.2 Rate coefficients via monitoring temporal profiles of NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> loss using**

#### 296 **CRDS**

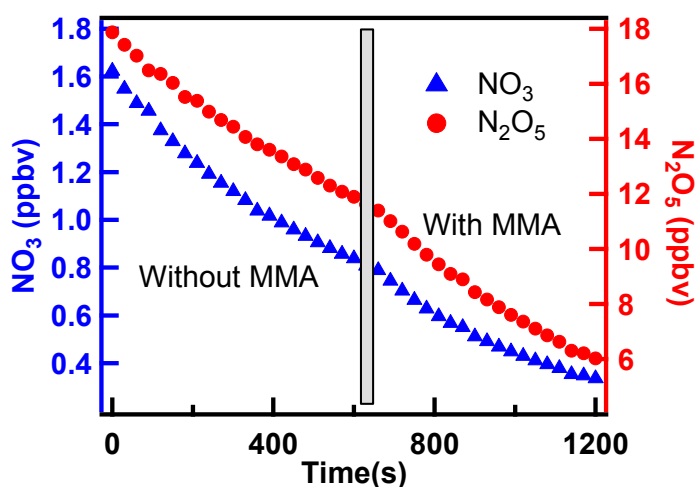
297 The rate coefficients for the reactions of NO<sub>3</sub> radicals with methacrylate esters were  
 298 also measured by following the temporal profiles of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> in an excess of esters.  
 299 During this process, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are nearly in equilibrium such that one could simply

300 attempt to fit the temporal profiles to obtain the rate coefficients. However, we fitted the  
 301 observed profiles to the following set of reactions that occur in the chamber:



303 First,  $\text{N}_2\text{O}_5$  was injected into the middle of the chamber.  $\text{N}_2\text{O}_5$  decomposed  
 304 immediately in the chamber to give  $\text{NO}_3$  and  $\text{NO}_2$  and set up an equilibrium with remaining  
 305  $\text{N}_2\text{O}_5$ . The temporal variation of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  in the chamber were continuously  
 306 measured using CRDS. The concentrations of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  decreased with time as  $\text{N}_2\text{O}_5$   
 307 and  $\text{NO}_3$  were lost in the chamber due to wall loss and reaction with impurities.

308



309

310 Figure 3 Measured temporal profiles of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  mixing ratios in the chamber in the

311 absence (up to the vertical gray bar) and presence of MMA (after the gray bar). The gray bar

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4 312 indicates the time at which VOCs were injected into the chamber and the time it took for  
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7 313 complete mixing.  $k_{\text{wall1}}=0.0065 \text{ s}^{-1}$ ,  $k_{\text{wall2}}=0.00032 \text{ s}^{-1}$ .  
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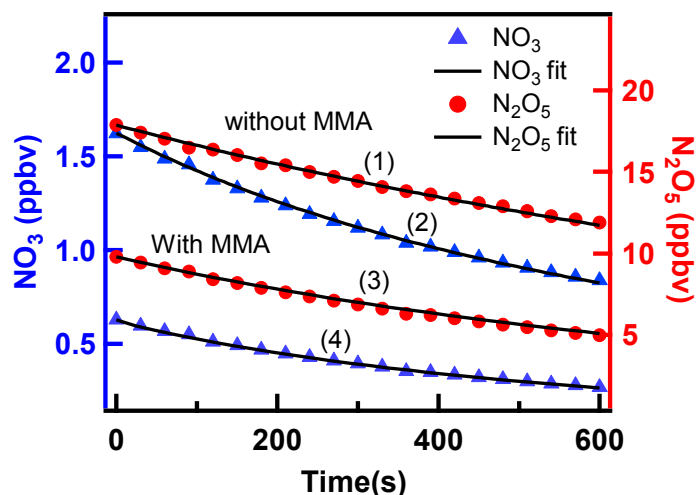
11  
12 315 Typical observed temporal profiles of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  in such experiments after  
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15 316 injection of  $\text{N}_2\text{O}_5$  into the chamber are shown in Figure 3. The measured temporal profiles  
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18 317 were fit using a box model that integrated the set of reactions shown above to derive the  
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21 318 time dependence of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ . The fitting was done by minimizing the sum of least  
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24 319 squares for both  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  profiles, by changing the input parameters that included  
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27 320 wall loss rates, the equilibrium constant, the rate coefficient for the reaction of  $\text{NO}_3$  with  
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29  
30 321 VOC as well as the initial  $\text{NO}_2$  concentration. First, the data in the absence of VOC was  
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32  
33 322 fit to the reaction scheme with VOC concentration set to zero. Using the known values of  
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36 323 the rate coefficients for Reactions R1 and R1', the values of  $k_{\text{wall1}}$ ,  $k_{\text{wall2}}$ , and the initial  
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39 324 concentration of  $\text{NO}_2$  were derived from the fit. The equilibrium constant was slightly  
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41  
42 325 varied to improve the fit, if necessary. The first-order wall loss rate constants of  $\text{NO}_3$  and  
43  
44  
45 326  $\text{N}_2\text{O}_5$ , respectively,  $k_{\text{wall1}} (\text{s}^{-1})$  and  $k_{\text{wall2}} (\text{s}^{-1})$ . Note that we did not have an accurate  
46  
47  
48 327 independent measure of  $\text{NO}_2$  in the chamber since our  $\text{NO}_2$  detector (which converted  $\text{NO}_2$   
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51 328 to  $\text{NO}$  by passing it over a hot molybdenum catalyst) also detected  $\text{N}_2\text{O}_5$ . Occasionally, we  
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54 329 needed to change the  $\text{N}_2\text{O}_5$  dissociation rate constant by at most 10% to improve the fit,  
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56  
57 330 which reflected the uncertainty in the temperature in the chamber of about 1 K. The  
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60 331 equilibrium constant,  $k_{\text{eq}} = [\text{N}_2\text{O}_5]/[\text{NO}_3][\text{NO}_2] = k_f/k_{\text{dc}}$ , and value of  $k_{\text{dc}}$ ,  $k_{\text{eq}}$  and  $k_f$  at

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4 332 different temperature were taken from NASA/JPL recommendation.<sup>29</sup>  
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7 333 After about 10 minutes, a sufficient length of time for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> observations that  
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9 334 enabled an accurate calculation of the equilibrium constant, a known concentration of the  
10  
11 335 VOC was introduced into the chamber and its concentration was measured using PTR-MS  
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13 336 and/or FTIR instruments. The concentration of the ester was always much greater than  
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15 337 those of N<sub>2</sub>O<sub>5</sub> or NO<sub>3</sub> in the chamber. The temporal profile of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> measured  
16  
17 338 after 60 s of VOC injection were again fit to minimize the sum of least squares for NO<sub>3</sub> and  
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19 339 N<sub>2</sub>O<sub>5</sub> decays in the above reaction scheme with only the rate coefficient for the reaction of  
20  
21 340 VOC with NO<sub>3</sub> being the variable As noted earlier, the time for complete mixing was 30 s.  
22  
23 341 The initial concentration of NO<sub>2</sub> was taken to be equal to that calculated just prior to adding  
24  
25 342 the VOC assuming equilibrium between NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, i.e.,  
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$$[\text{NO}_2]_0 = \frac{[\text{N}_2\text{O}_5]_0}{[\text{NO}_3]_0 k_{\text{eq}}} \quad (\text{II})$$
  
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39 344 Figure 4 shows a fit of the observed temporal profiles of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> and the fit of the  
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41 345 profiles to the above reaction scheme.  
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347 Figure 4: Observed  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  mixing ratios (circles and triangles) and their simulated348 temporal profiles (lines) after the injection of VOC into the chamber where  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  were349 present at equilibrium. Profile (1) - loss of  $\text{N}_2\text{O}_5$  without MMA; Profile (2) - loss of  $\text{NO}_3$ 350 without MMA; Profile (3) - loss of  $\text{N}_2\text{O}_5$  with MMA; Profile (4) - loss of  $\text{NO}_3$  with MMA.351 The concentration of MMA was  $3.06 \times 10^{12}$  molecule  $\text{cm}^{-3}$ . The fits yield a value of  $k_{\text{voc}} =$ 352  $2.98 \times 10^{-15}$  molecule $^{-1}$   $\text{cm}^3$   $\text{s}^{-1}$ .353 Multiple experiments were carried out by varying VOC and initial  $\text{N}_2\text{O}_5$ 354 concentrations. In some cases, we included additional  $\text{NO}_2$  in the chamber before the355 addition of  $\text{N}_2\text{O}_5$  (to shift the equilibrium). The uncertainty in obtained value of  $k(\text{VOC})$ 

356 due to fitting was very small, often much less than 3 %. However, the fits alone do not

357 determine the uncertainty in the precision of our measured rate coefficient. They were

358 obtained the standard deviation of the mean of multiple measurements and including the

359 Student t value for the limited number of measurements. The results of our measurements

360 are given in Table 3.



361

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Table 3. Summary of the experimental conditions for and results from the absolute

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method to measure the rate constants for reaction of NO<sub>3</sub> with VOCs at 298±2K. The

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k<sub>VOC</sub> values shown are those derived from fitting the observed profiles of NO<sub>3</sub> and

365

N<sub>2</sub>O<sub>5</sub> to a least squares algorithm.

Compound	T (K)	Initial mixing ratio (ppbv)			k <sub>VOC</sub> measured <sup>a</sup>	k <sub>VOC</sub> incl. systematic errors <sup>b</sup>
		VOC	NO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	10 <sup>-15</sup> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	
Propene	296	156.6	0.54	10.16	9.15	
	296	70.0	0.45	9.77	9.97	
					(9.56±1.36)	(9.56±1.80)
MMA	295	121.9	0.68	11.05	2.90	
	296	124.3	0.63	9.79	2.98	
	298	363.7	0.78	11.46	2.89	
					(2.92±0.12)	(2.92±0.37)
EMA	298	126.1	0.81	10.85	4.56	
	300	130.1	0.59	6.79	5.09	
	298	333.3	1.13	16.58	4.69	
					(4.78±0.65)	(4.78±0.93)

PMA	297	113.5	0.79	11.15	5.14	
	300	279.7	1.11	10.13	5.77	
	296	113.6	0.83	8.33	5.59	
					(5.50±0.76)	(5.50±1.00)
IPMA	297	101.6	0.81	10.28	7.94	
	296	86.2	0.91	13.01	7.56	
	300	209.3	0.84	13.69	8.00	
					(7.83±0.56)	(7.83±1.15)
BMA	299	264.2	1.00	8.80	6.16	
	299	199.2	1.25	11.42	5.86	
	300	251.8	1.10	12.92	6.00	
					(6.00±0.35)	(6.00±0.89)
IBMA	296	142.3	0.77	10.90	6.52	
	297	154.5	1.09	13.00	6.46	
	297	162.6	0.99	9.44	6.82	
					(6.60±0.45)	(6.60±0.94)

366 <sup>a</sup> Quoted error is at the 95% confidence level and is a measure of the precision of our measurements. It  
 367 includes Student t-distribution contribution due to the limited number of measurements. To maintain  
 368 consistent number of significant figures, some numbers with larger errors are shown with the last digit as

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4 369 a subscript.  
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7 370 <sup>b</sup> The quoted errors include estimated systematic errors as described in the text.  
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## 12 13 372 **2.4 Error estimation** 14 15

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17 373 *Relative rate measurements:* One of the advantages of relative rate measurements is that  
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20 374 uncertainties in absolute concentrations of either reactant do not lead to an error in the  
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23 375 measured values since we depend on the relative concentrations changes as the reaction  
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26 376 proceeds to derive the rate constant. The concentrations of the reactant, in our case esters,  
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29 377 and the reference compound (propene, propanal, or MMA) were measured using the same  
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31 378 PTR-ToF-MS system. The calibration plots of the concentration of VOC versus their  
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34 379 signals were linear. The precision of the measured signal contributes to the precision of  
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36  
37 380 the measured rate constants. The slopes of the plots shown in Figures 2-1 and 2-2 yielded  
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39  
40 381 the precision of the measurement. The errors in the values of rate constant ratios ( $k_{\text{voc}}/k_r$ )  
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42  
43 382 are twice the standard deviation ( $2\sigma_{k_{\text{voc}}/k_r}$ ) in the least-squares fit of the measured losses to  
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46 383 Equation I. In addition to the precision, the main contributor to the accuracy of the  
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49 384 measured rate constant is the accuracy of the rate coefficients for the reference reactions.  
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51 385 The rate coefficient for the reactions of  $\text{NO}_3$  with propene and propanal have been  
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54 386 evaluated and we assume the accuracy to be those assessed by the evaluation panels,  
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56 387  $k_r(\text{propene})^{28} = (9.5 \pm 5.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_r(\text{propanal})^{28} = (6.3 \pm 2.6) \times 10^{-15} \text{ cm}^3$   
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388 molecule<sup>-1</sup>s<sup>-1</sup>. (As noted later, we believe that the uncertainty for the reaction of NO<sub>3</sub> with  
389 propene is less than that noted by the evaluation.) We combined the precision of our  
390 measured values with the quoted uncertainties in the rate coefficient for the reference  
391 reaction to estimate the overall accuracy of the measured rate coefficients.

$$\sigma_{\text{voc}} = k_{\text{voc}} \sqrt{\left[ \frac{2\sigma_{\left(\frac{k_{\text{voc}}}{k_r}\right)}}{\frac{k_{\text{voc}}}{k_r}} \right]^2 + \left[ \frac{\sigma_{k_r}}{k_r} \right]^2} \quad (\text{III})$$

393 *Absolute rate constant measurements*- The errors in determining the rate coefficients by  
394 monitoring the temporal profiles of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> arise from the precision in the  
395 measurements of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, the absolute values of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> and the uncertainty  
396 in the concentration of the excess reagent, the esters in our study. Ordinarily, the absolute  
397 values of the NO<sub>3</sub> reactant would not be needed in an absolute method where NO<sub>3</sub> temporal  
398 profile is monitored in an excess of esters. However, in the present study, NO<sub>3</sub> is in  
399 equilibrium (or almost in equilibrium) with N<sub>2</sub>O<sub>5</sub> and this situation requires absolute  
400 concentrations of the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. The systematic errors in measurements of NO<sub>3</sub> and  
401 N<sub>2</sub>O<sub>5</sub> using the CRDS system employed here have been assessed to be -8/+11% for NO<sub>3</sub>  
402 and -9/+12% for N<sub>2</sub>O<sub>5</sub>, as noted earlier. The uncertainty in the fitting, as noted above, is  
403 better than 3%. Systematic errors in the measured concentration of the esters are estimated  
404 for each compound using the uncertainty of the slope in the calibration plots (<4%) and the  
405 uncertainty in measuring ester concentration for the calibration (5%); all at 95%

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4 406 confidence level. We just added these two errors to get the estimated uncertainty in the  
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7 407 concentration of esters in the chamber since they could be correlated. Then, the overall  
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10 408 estimated error was calculated by adding in quadrature the fitting error, estimated  
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13 409 contribution of absolute concentrations of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , the precision of the  
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16 410 measurements of  $k_{\text{VOC}}$ , and the estimated uncertainty in the concentration of the esters.  
17  
18 411 Table 3 lists the uncertainties in the measured values of the rate constants along with the  
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21 412 estimated systematic errors.  
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23  
24 413 We measured the rate coefficient for the reaction of  $\text{NO}_3$  with propene using the  
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27 414 absolute method. Our obtained results are in very good agreement with most of the  
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30 415 literature values. This adds further confidence in our measured values of the rate  
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33 416 coefficients using the absolute method. We note that most of the reported values for the  
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36 417 rate coefficient for the  $\text{NO}_3$  reaction with propene in the IUPAC assessment appears to  
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39 418 agree reasonably well, though there are a few outliers. We suggest that the error bars given  
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42 419 for the reaction of  $\text{NO}_3$  with propene in the IUPAC is excessively conservative.  
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44 420 Another potential source of error in the rate coefficient measured using the absolute  
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47 421 method is presence of reactive impurities in the sample of the esters. The methacrylates  
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50 422 used in the study were the purest we could obtain from commercial vendors (see materials  
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53 423 section for purity levels). However, they contained some stabilizers, which could  
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56 424 potentially react more rapidly with  $\text{NO}_3$  than the esters. The stabilizers used in the  
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59 425 methacrylates were normally around 10-20 ppmv, the maximum was about 200 ppmv of  
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4 426 4-Methoxyphenol (MEHQ) in isopropyl methacrylate (IPMA). Stabilizers used with these  
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7 427 esters are aromatic compounds with a large side chain containing a saturated group. If  
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10 428 MEHQ reacted very rapidly with  $\text{NO}_3$ , we could indeed overestimate this rate coefficient.  
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12 429 Indeed, if the rate coefficient for the reaction of MEHQ with  $\text{NO}_3$  were  $1 \times 10^{-10} \text{ cm}^3$   
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15 430  $\text{molecule}^{-1} \text{ s}^{-1}$  as quoted for other methoxyphenols by Lauraguais et al.<sup>30</sup> we should have  
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18 431 measured a value of roughly  $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for IPMA. However, our measured  
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21 432 values using the direct and relative methods agree well (see Table 4). Therefore, we do not  
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24 433 believe that our reported values were greatly affected by the presence of MEHQ. In case of  
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27 434 the other esters, the presence of stabilizers at the quoted levels would contribute at most 20%  
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30 435 to the measured value using the direct method. Again, the agreement between the relative  
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33 436 and direct method suggests that the contributions of the stabilizer to the measured rate  
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36 437 coefficients were not large. We note that the PTR-ToF-MS spectra of each of the esters did  
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39 438 not show any measurable hydrocarbons other than the ester. Based on these observations,  
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42 439 we conclude that our measured absolute rate coefficients were not significantly influenced  
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45 440 by the presence of impurities.

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47 441 Lastly, we note that the rate coefficients measured here reflect that for the reaction of  
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49 442  $\text{NO}_3$  with esters and there is no significant contribution from any possible reaction of  $\text{N}_2\text{O}_5$   
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52 443 with esters. First, we varied the ratio of  $\text{NO}_3$  to  $\text{N}_2\text{O}_5$  by changing  $\text{NO}_2$  and the measured  
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55 444 rate coefficients were insensitive to this ratio. Second, the rate coefficients measured using  
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58 445 the absolute method agrees with that from the relative method, where some of the reference

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4 446 molecules are known to be non-reactive towards  $\text{N}_2\text{O}_5$ . Again, in these experiments, the  
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7 447 ratios of  $\text{NO}_3$  to  $\text{N}_2\text{O}_5$  were very different and it also varied with the extent of reaction, with  
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10 448 no effect on the derived rate coefficients.

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### 14 15 16 450 **3 Discussion**

#### 17 18 19 20 451 **3.1 Comparison of rate coefficients obtained from two methods**

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24 452 We used two different methods to measure the rate coefficients for the reactions of  
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27 453  $\text{NO}_3$  with methacrylate esters; they are summarized in Table 4. The rate constants values  
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30 454 we measured using the two methods are in good agreement with each other, given the  
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33 455 estimated uncertainties in the rate constants. The largest difference is for the reaction of  
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36 456  $\text{NO}_3$  with MMA, where the rate coefficients from the two methods differ by about 25%.

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38 457 We have used weighted average of the two methods, i.e., the absolute and the relative  
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41 458 rate methods, to derive the best possible values for the rate coefficients for the reactions  
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44 459 of  $\text{NO}_3$  with methacrylate esters studies here. They are shown in Table 4.

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49 461 Table 4 Rate constants values obtained in two methods for the reactions of  $\text{NO}_3$  with  
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52 462 methacrylate esters.

	Rate constants $k_{\text{voc}}(10^{-15})$	Ratio	$k_{\text{voc}}$
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	molecule <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>		(k <sub>rm</sub> /k <sub>ab</sub> )	(10 <sup>-15</sup> molecule <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup> )	
	Relative method (k <sub>rm</sub> )	Absolute method (k <sub>ab</sub> )		Unweighted average	Weighted average
MMA(k <sub>1</sub> )	(3.68±1.24)	(2.92±0.37)	1.26	(3.30±0.65)	(2.98±0.35)
EMA(k <sub>2</sub> )	(4.63±0.57)	(4.78±0.93)	0.97	(4.70±0.55)	(4.67±0.49)
PMA(k <sub>3</sub> )	(5.08±0.74)	(5.50±1.00)	0.92	(5.29±0.62)	(5.23±0.60)
IPMA(k <sub>4</sub> )	(8.14±1.93)	(7.83±1.15)	1.04	(7.9 <sub>9</sub> ±1.1 <sub>2</sub> ) <sup>a</sup>	(7.9 <sub>1</sub> ±1.0 <sub>0</sub> ) <sup>a</sup>
BMA(k <sub>5</sub> )	(5.52±0.72)	(6.00±0.89)	0.92	(5.76±0.57)	(5.71±0.56)
IBMA(k <sub>6</sub> )	(5.88±0.94)	(6.60±0.94)	0.89	(6.24±0.66)	(6.24±0.66)

463 a. To maintain consistent number of significant figures, some numbers with larger errors are shown with the

464 last digit as a subscript.

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466 Indeed, one could opt to use an unweighted average. Therefore, we have also listed them

467 in the table. We prefer the weighted average mostly to put more weight on the direct

468 method, especially since the quoted uncertainty in the rate coefficient for the reaction of

469 NO<sub>3</sub> with propene, a common reference for relative rate studies, is unusually large. This

470 is discussed later.



### 471 **3.2 Comparison with the kinetic results in literature**

472 Several groups have measured the rate constants of  $\text{NO}_3$  radical reactions with MMA,  
473 EMA and BMA using relative methods in small chambers (<150L) at room temperature  
474 and atmospheric pressure. In their experiments, the initial mixing ratios of the  
475 methacrylate esters were in a range of 5-20ppmv. A comparison of rate coefficients  
476 determined in this study with the literature data is shown in Table 5. As can be seen in the  
477 table, our values are in good agreement with previously reported values, given the reported  
478 uncertainties, whenever such comparisons are possible.

479 Given the reasonably good agreement between various reported studies and a lack of  
480 obvious reasons to prefer one study over the other, we suggest that an un-weighted average  
481 of all the results be used as recommended values for the rate coefficient. Such average  
482 values are also reported in the Table 5. Clearly, there are no previous reports for the rate  
483 coefficients for the reactions of  $\text{NO}_3$  with PMA, IPMA, and IBMA. However, given the  
484 similarities of those compounds with the other methacrylates studied here, it appears that  
485 our rate coefficients are also accurate to about 20% and could be used with confidence.

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487

488 Table 5 Summary of the rate coefficients of  $\text{NO}_3$  with MMA, EMA and BMA obtained  
489 from literatures and this work.

Reactant	Reference Chemical	$k_{\text{VOC}}$ reported $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference
MMA	propene	$(3.7_1 \pm 2.2_2)^a$	10
	propene	$(3.5_1 \pm 2.0_4)^a$	12
	propene	$(3.6_1 \pm 2.1_0)^a$	13
	propene	$(3.5_2 \pm 2.0_7)$	This work
	methacrolein	$(3.5_1 \pm 1.0_8)$	13
	1-butene	$(3.7_2 \pm 1.1_5)$	12
	propanal	$(3.7_7 \pm 1.5_6)$	This work
	AM <sup>b</sup>	$(2.92 \pm 0.37)$	This work
		$(3.12 \pm 0.31)$	Weighted average of all work
		$(3.53 \pm 0.60)$	Unweighted average of all work
EMA	propene	$(4.8_1 \pm 2.8_0)^a$	12
	propene	$(5.7_0 \pm 3.3_1)^a$	13
	propene	$(5.04 \pm 2.95)$	This work
	1-butene	$(5.0_9 \pm 1.6_1)$	12
	methacrolein	$(5.1_6 \pm 1.5_9)$	13
	MMA	$(4.62 \pm 0.58)$	This work
	AM <sup>b</sup>	$(4.78 \pm 0.93)$	This work

		(4.76±0.44)	Weighted average of all work
		(5.03±0.83)	Unweighted average of all work
BMA	propene	(8.2 <sub>7</sub> ±4.8 <sub>3</sub> ) <sup>a</sup>	13
	propene	(6.6 <sub>5</sub> ±3.8 <sub>7</sub> )	This work
	1-butene	(7.5 <sub>8</sub> ±4.3 <sub>6</sub> )	13
	MMA	(5.48±0.74)	This work
	AM <sup>b</sup>	(6.00±0.89)	This work
		(5.78±0.55)	Weighted average of all work
		(6.8 <sub>0</sub> ±1.5 <sub>3</sub> )	Unweighted average of all work
PMA		(5.23 ± 0.60)	This work
IPMA		(7.9 <sub>1</sub> ±1.0 <sub>0</sub> )	This work
IBMA		(6.24±0.66)	This work

490 <sup>a</sup> The values from the literatures were recalculated by using the rate constant of propene with NO<sub>3</sub> (9.5  
 491 ± 5.5) × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>, which was used in our study. Note that these uncertainties are likely to  
 492 be overestimated because of the large uncertainty quoted by IUPAC. To maintain consistent number of  
 493 significant figures, some numbers with larger errors are shown with the last digit as a subscript.

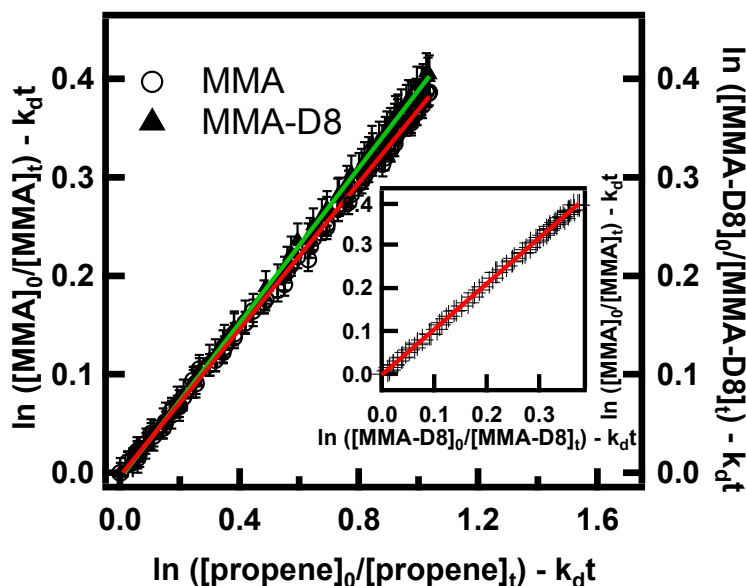
494 <sup>b</sup> Measured from the temporal profiles of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, referred to as the absolute method.

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4 495 **3.3 Mechanism and Relationship between structure and reactivity of the**  
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7 496 **methacrylate esters**

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11 497 The rate coefficients for all the methacrylate measured here are roughly in the same  
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13 498 range, with the rate coefficient slightly increasing with extent of substitution going from  
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16 499 methyl to ethyl to propyl to butyl methacrylate. We observe an increase in the reactivity  
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19 500 with the chain length of the alkyl group.  $k_{\text{voc}}(\text{MMA}) < k_{\text{voc}}(\text{EMA}) < k_{\text{voc}}(\text{PMA}) < k_{\text{voc}}(\text{BMA})$ .  
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22 501 Further, the isoalkyl methacrylates react a little faster than their normal analogs. This is  
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25 502 consistent with the electron donating inductive effect of the substituents ( $-\text{C}(\text{O})\text{OR}$ ),  
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27 503 consistent with an electrophilic addition mechanism.<sup>31</sup> Such variations are consistent with  
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30 504  $\text{NO}_3$  reaction proceeding via electrophilic addition to the double bond in the methacrylate  
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33 505 group. These rate constants that have been measured for unsaturated esters, help  
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36 506 understand the structure activity relationship (SAR) and complete the parameterization of  
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39 507 this family of compounds. We have refrained from calculating SAR relations till data is  
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42 508 available for esters. Curiously, however, the isopropyl methacrylate reacts faster than the  
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45 509 normal analog while the isobutyl methacrylate reacts with almost the same rate  
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48 510 coefficient as the butyl methacrylate. It would be interesting to see if there is enhanced H  
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51 511 abstraction in IPMA reaction and leads to  $\text{HNO}_3$  as a product.

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53 512 To further examine this mechanism for the reaction, we studied the reaction of  $\text{NO}_3$   
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56 513 with deuterated MMA. The rate coefficients for the reactions of MMA and MMA-D8 with  
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514  $\text{NO}_3$  radicals are essentially identical, with  $k_H/k_D = 0.98$ , as shown in Figure 5. The  
 515 isotopic purity of the MMA-D8 was high (>99%); therefore, this equality is not due to  
 516 the deuteration being insufficient. The observed equality of the rate coefficients for the  
 517 deuterated and non-deuterated MMA further strengthens the expectation that H atom  
 518 abstraction is insignificant in the reaction of  $\text{NO}_3$  with methacrylates.

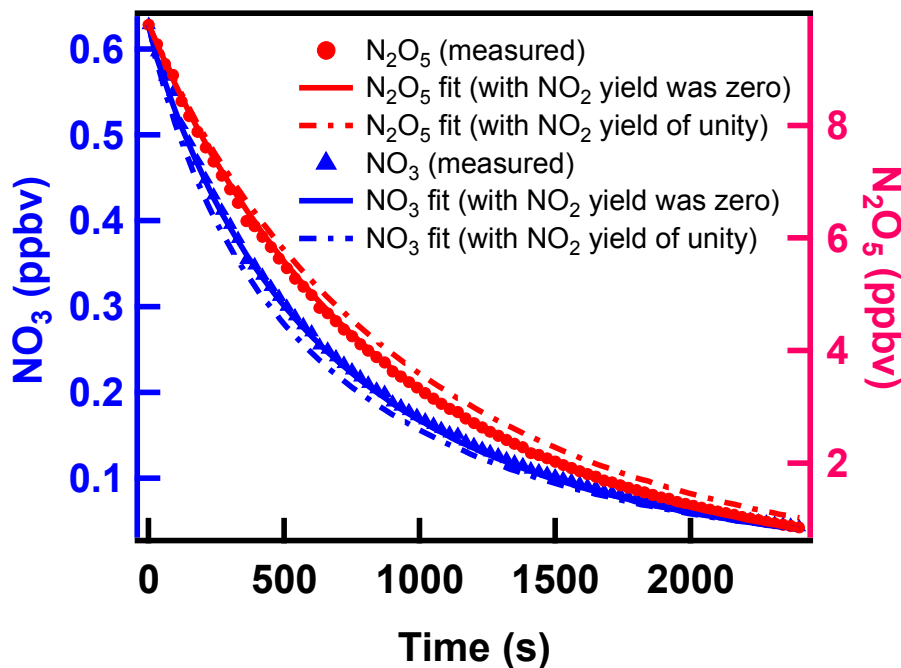


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 520 Figure 5: The rates of losses of MMA-D8 relative to those for propene while competing for the same  
 521 pool of  $\text{NO}_3$  radicals. The green line is a fit to the MMA-D8 and the red line is a fit to the MMA data. The  
 522 inset shows a similar plot for the loss of MMA relative that for MMA-D8, with a slope of essentially  
 523 unity showing the both deuterated and non-deuterated MMA react with  $\text{NO}_3$  with the same rate  
 524 coefficient, i.e.,  $k_1 \approx k_7$ .

525 Furthermore, in our experiments, we deduced  $\text{NO}_2$  was not produced after  $\text{NO}_3$  was  
 526 removed. Figure 6 shows the observed  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  profiles in the presence of MMA.  
 527 Simulation of these profiles where we include a yield of  $\text{NO}_2$  of unity is shown as the

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4 528 dashed line. Clearly, we cannot fit the data to a scheme where  $\text{NO}_2$  is produced from the  
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7 529 reaction with a large yield. If  $\text{NO}_2$  were the product of the reaction, we would expect a  
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10 530 production of one  $\text{NO}_2$  for each  $\text{NO}_3$  lost, unless there is stoichiometric removal of  $\text{NO}_2$   
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13 531 by a peroxy radical formed by the  $\text{NO}_3$  reaction with the methacrylate ester that reacts  
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15 532 very rapidly with  $\text{NO}_2$  to form a stable nitrate. Since, we cannot rule out the formation of  
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18 533 such a nitrate, we cannot unequivocally rule out the formation of  $\text{NO}_2$  as a product of the  
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21 534 reaction. Future studies in a chamber that were constrained by an accurate measurements  
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24 535 of  $\text{NO}_2$  and total  $\text{NO}_y$  would be useful in constraining the branching ratio toward  $\text{NO}_2$  or  
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27 536 organic nitrate production, even if the former were small. Similarly, a simulation of the  
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30 537 all the subsequent reactions would be useful when the majority of the stable products are  
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32 538 identified and quantified.

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541 Figure 6 Experimental and simulated results for  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  profiles from chamber experiment542 (MMA+ $\text{NO}_3$ ) when  $\text{NO}_2$  was set as a product of unit yield in the modeled reaction scheme.

543 Based on these observation we suggest that, the atmospheric oxidation mechanism

544 of  $\text{NO}_3$  reactions with unsaturated carbonyl group compounds proceeds mostly via

545 electrophilic addition to the C=C double bond.

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### 3.4 Atmospheric implication

547 Once emitted into the atmosphere, the studied methacrylate esters are removed

548 mainly through their reactions with reactive species such as OH,  $\text{NO}_3$ ,  $\text{O}_3$  and chlorine

549 atoms. The lifetimes for the removal of the esters were calculated using nominal

550 concentrations of the reactive radicals and ozone in the lower troposphere. Note that these

551 lifetimes are nominal values and are expected to be location and time dependent. The

lifetimes were calculated using the equation:

$$\tau = \frac{1}{k_{\text{voc+x}} [\text{X}]} \quad (\text{IV})$$

where  $k_{\text{voc+x}}$  is the rate coefficient for the reaction of the oxidant with the methacrylate ester and  $[\text{X}]$  is the nominal representative atmospheric concentration of the oxidants.

Tropospheric concentrations of OH, NO<sub>3</sub>, O<sub>3</sub> and chlorine atoms that could be expected were used in the calculations to approximate the loss of esters in the troposphere. Here we take their concentrations to be:  $[\text{Cl}] = 1 \times 10^4 \text{ molecule cm}^{-3}$ <sup>32</sup>,  $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$ <sup>33</sup>,  $[\text{NO}_3] = 5 \times 10^8 \text{ molecule cm}^{-3}$ <sup>34</sup>,  $[\text{O}_3] = 1 \times 10^{12} \text{ molecule cm}^{-3}$  (~40 ppbv). Note that NO<sub>3</sub> concentration in locations where esters are emitted (such as urban plumes) can be much larger<sup>35</sup>. However, the lifetimes would still be many days such that the esters would be dispersed. Therefore, the calculated atmospheric lifetimes of the methacrylate esters summarized in Table 6 would be reasonably representative of the removal processes for these esters.

The atmospheric lifetimes for methacrylate esters due to reaction with OH radicals are roughly a few hours, followed by that due to loss via reaction with ozone of ~40 hours. Clearly, the reaction of NO<sub>3</sub> would contribute only about 5% to the overall lifetime. However, in dark areas with large NO<sub>x</sub> emissions, the loss via reaction with NO<sub>3</sub> could be significant compared to that via reaction with OH. However, the abundances of NO<sub>3</sub> are closely related to those of O<sub>3</sub> since it is formed by the reaction of NO<sub>2</sub> with O<sub>3</sub>.



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4 571 Therefore, clearly, both the reaction of  $O_3$  and  $NO_3$  will contribute significantly at night  
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7 572 when the  $NO_x$  emissions are high.  
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573 Table 6. Summary of rate constants and estimated atmospheric lifetimes of methacrylate esters with respect to their reactions with  
 574 OH, NO<sub>3</sub>, O<sub>3</sub> and Cl at (298±2)K and atmospheric pressure.

	Rate constants (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )				Lifetime (hours)			
	k <sub>OH</sub>	k <sub>NO<sub>3</sub></sub>	k <sub>O<sub>3</sub></sub>	k <sub>Cl</sub>	τ <sub>OH</sub>	τ <sub>NO<sub>3</sub></sub>	τ <sub>O<sub>3</sub></sub> <sup>i</sup>	τ <sub>Cl</sub>
MMA	(4.2)×10 <sup>-11</sup> [b,c,d]	(2.98)×10 <sup>-15</sup> [a]	(7.51)×10 <sup>-18</sup> [d]	(2.17)×10 <sup>-10</sup> [f]	6.6	186	37	128
EMA	(4.58)×10 <sup>-11</sup> [c]	(4.67)×10 <sup>-15</sup> [a]	(7.68)×10 <sup>-18</sup> [e]	(2.71)×10 <sup>-10</sup> [f]	6.1	119	36	103
PMA		(5.23)×10 <sup>-15</sup> [a]				106	~40	
IPMA		(7.91)×10 <sup>-15</sup> [a]				70	~40	
BMA	(7.08)×10 <sup>-11</sup> [c]	(5.71)×10 <sup>-15</sup> [a]		(3.72)×10 <sup>-10</sup> [f,g]	3.3	97	~40	75
IBMA		(6.24)×10 <sup>-15</sup> [a]				89	~40	

575 Assuming [OH] = 1×10<sup>6</sup> molecule cm<sup>-3</sup>,<sup>33</sup> [NO<sub>3</sub>] = 5×10<sup>8</sup> molecule cm<sup>-3</sup>,<sup>34</sup> [O<sub>3</sub>] = 1×10<sup>12</sup> molecule cm<sup>-3</sup> (~40 ppbv), and [Cl] = 1×10<sup>4</sup> molecule cm<sup>-3</sup>.<sup>32</sup>

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9 577 b,c,d are from references 3, 4, and 5: Value reported by ref. d is roughly a factor of 2 lower than that reported by ref. b and c. We used the average value from ref. b  
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11 578 and c.  
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14 579 e from reference 7, f from reference 36, and g from reference 9.  
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17 580 i. When the rate coefficients for the reactions of esters with ozone were not available, we have assumed it to be roughly the same as that for MMA.  
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5 581 **Supporting Information.**  
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9 582 Table S1-S2, a complete summary of the initial concentrations and experimental  
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11 583 conditions for the relative rate method and absolute rate methods; Figure S1, Calibration  
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13 584 of each reactants and references in PTR-ToF-MS; Figure S2, the first order decay rate of  
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15 585 SF<sub>6</sub> and MMA in the absence of NO<sub>3</sub>; Figure S3, experimental and simulated results for  
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20 586 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> profiles from absolute rate method experiments.  
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28 588 **Acknowledgments**  
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38  
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43 593 decades. It is our pleasure to be a part of her Festschrift.  
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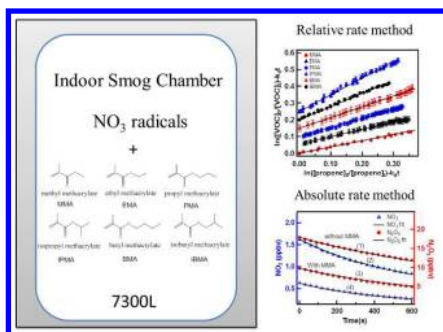
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## 715 TOC Graphic



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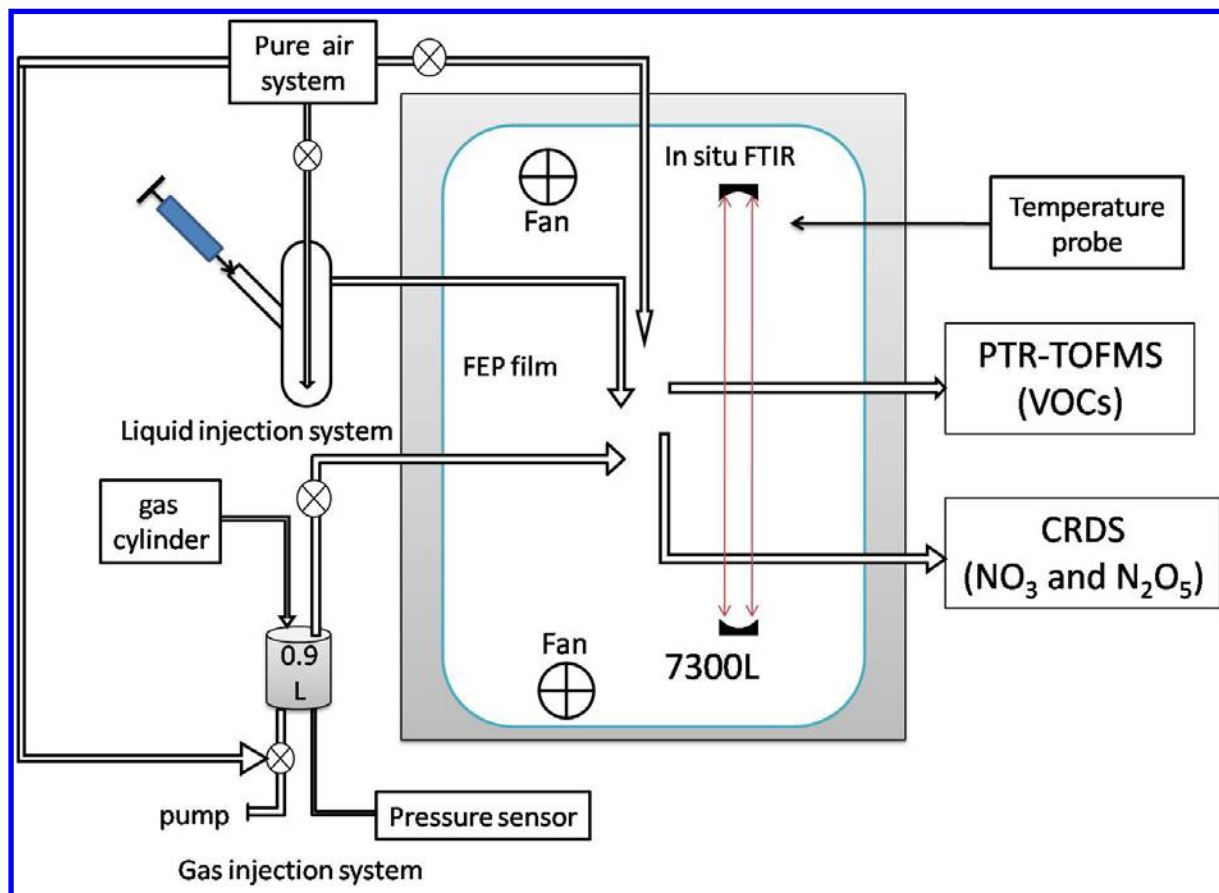
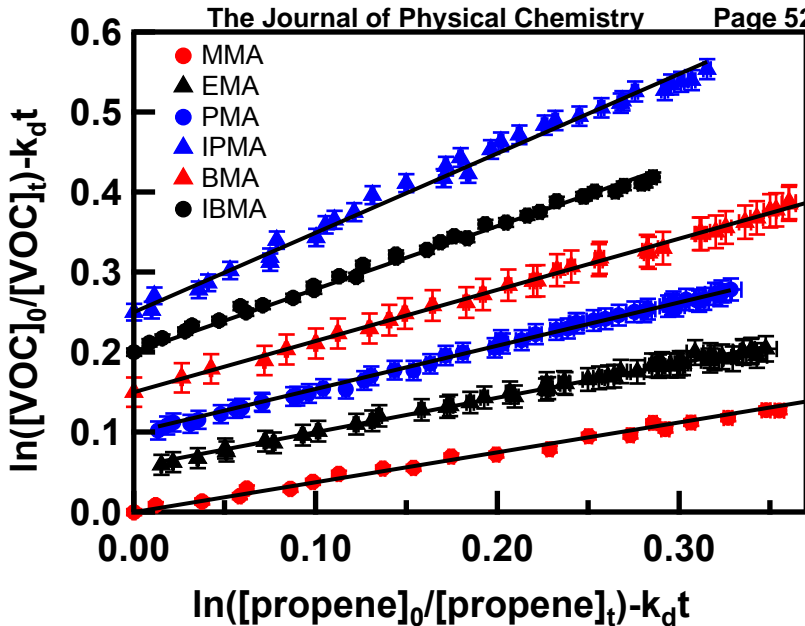
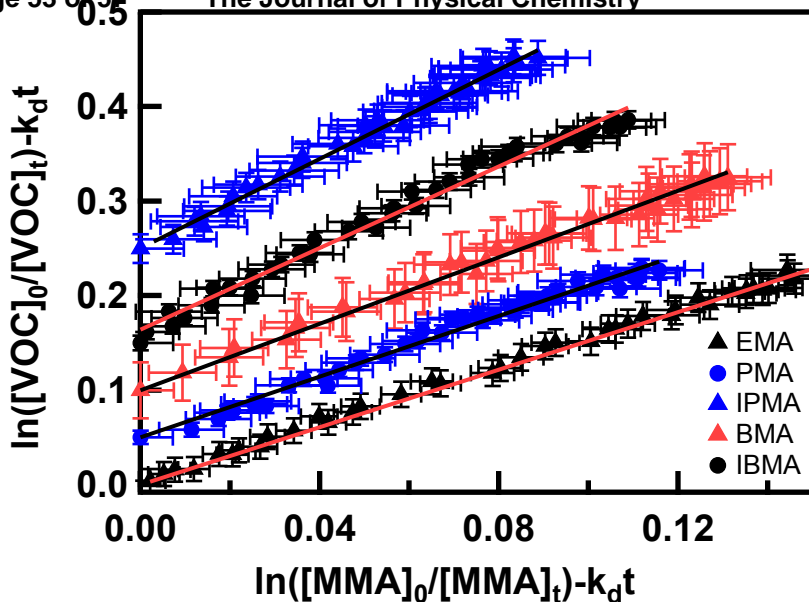


Figure 1

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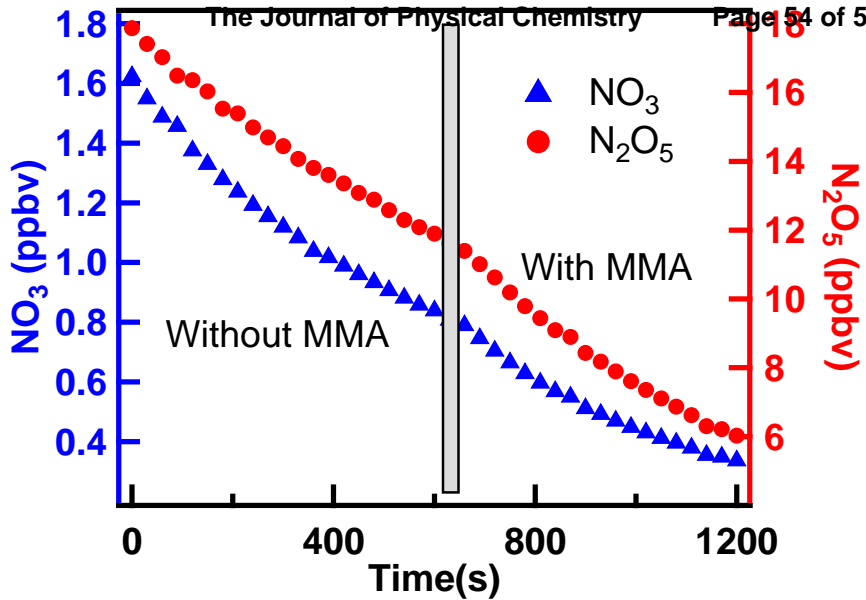
ACS Paragon Plus Environment

Figure 2-1

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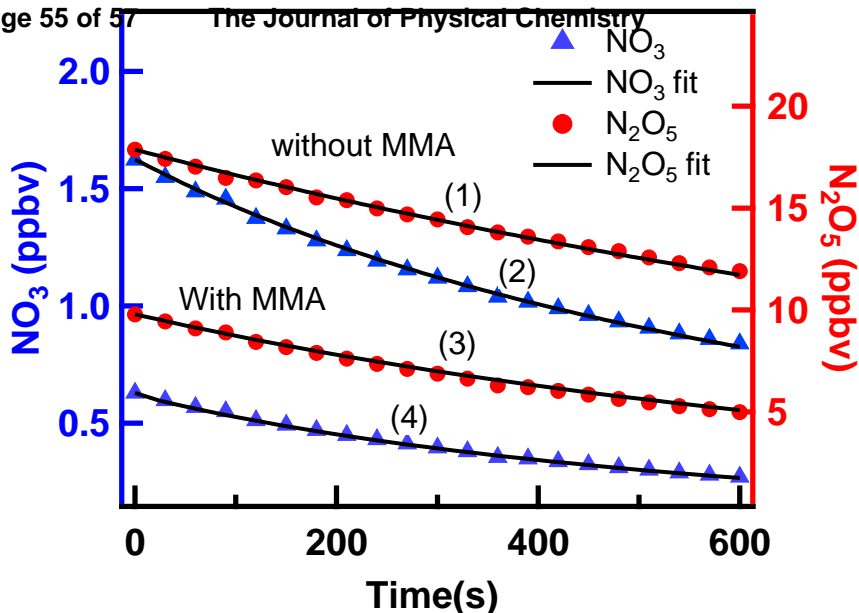
Figure 2-2



ACS Paragon Plus Environment

Figure 3

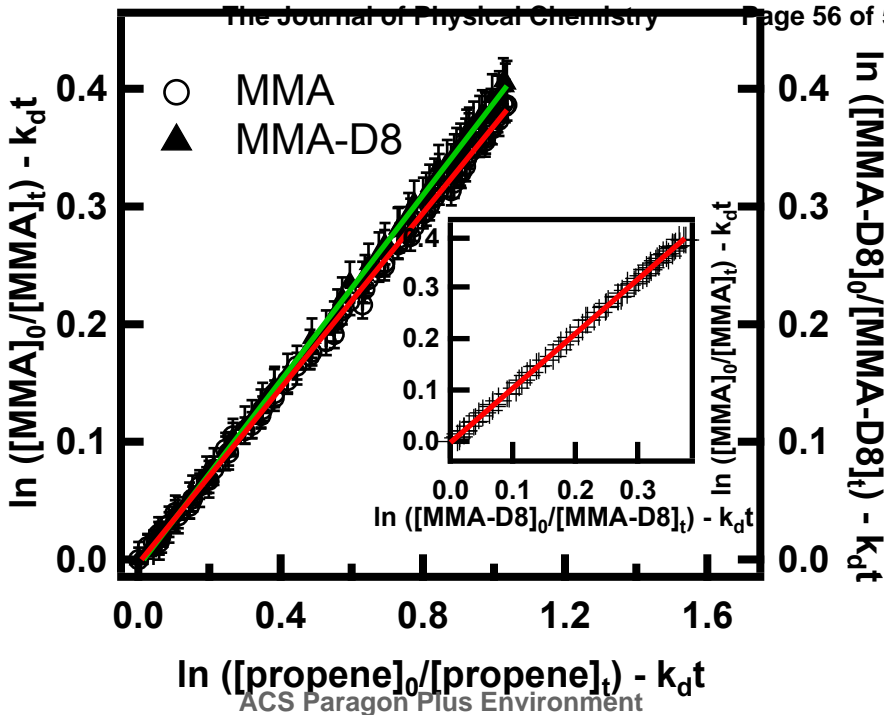
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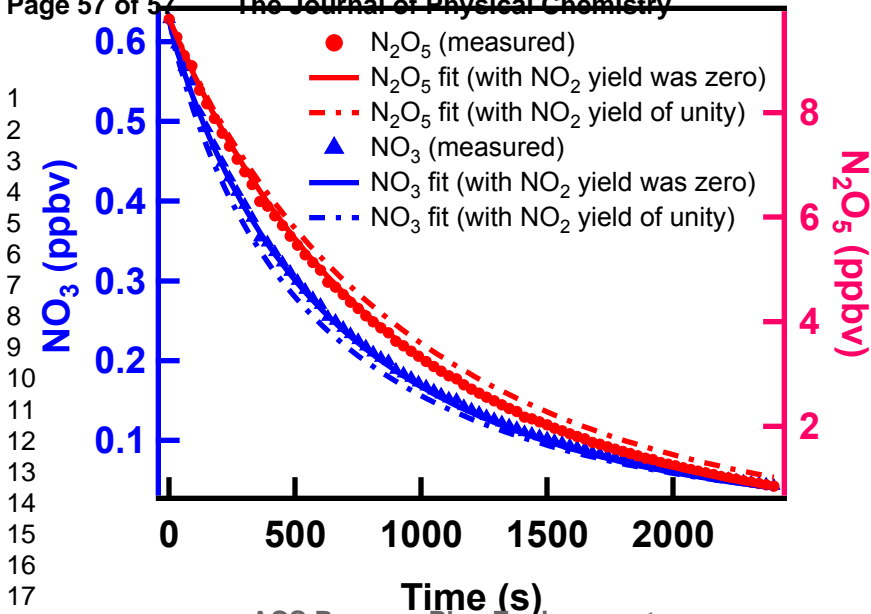
Figure 4



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ACS Paragon Plus Environment

Figure 5



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Figure 6