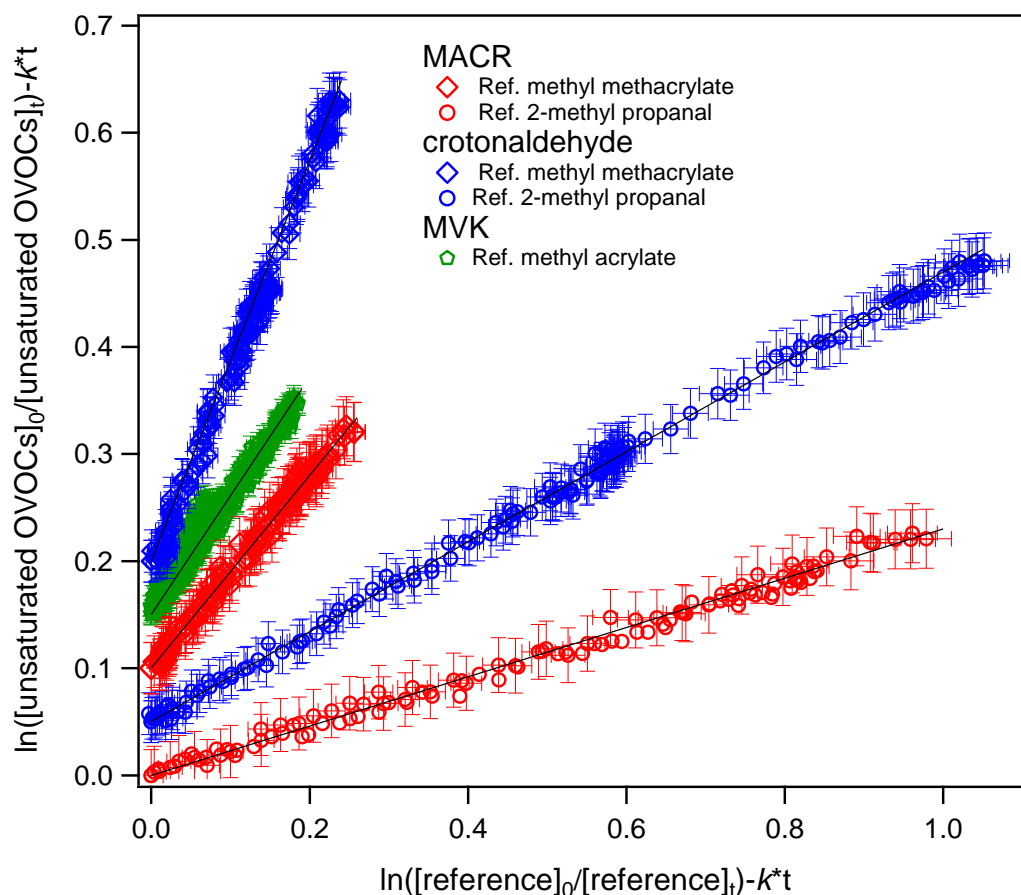
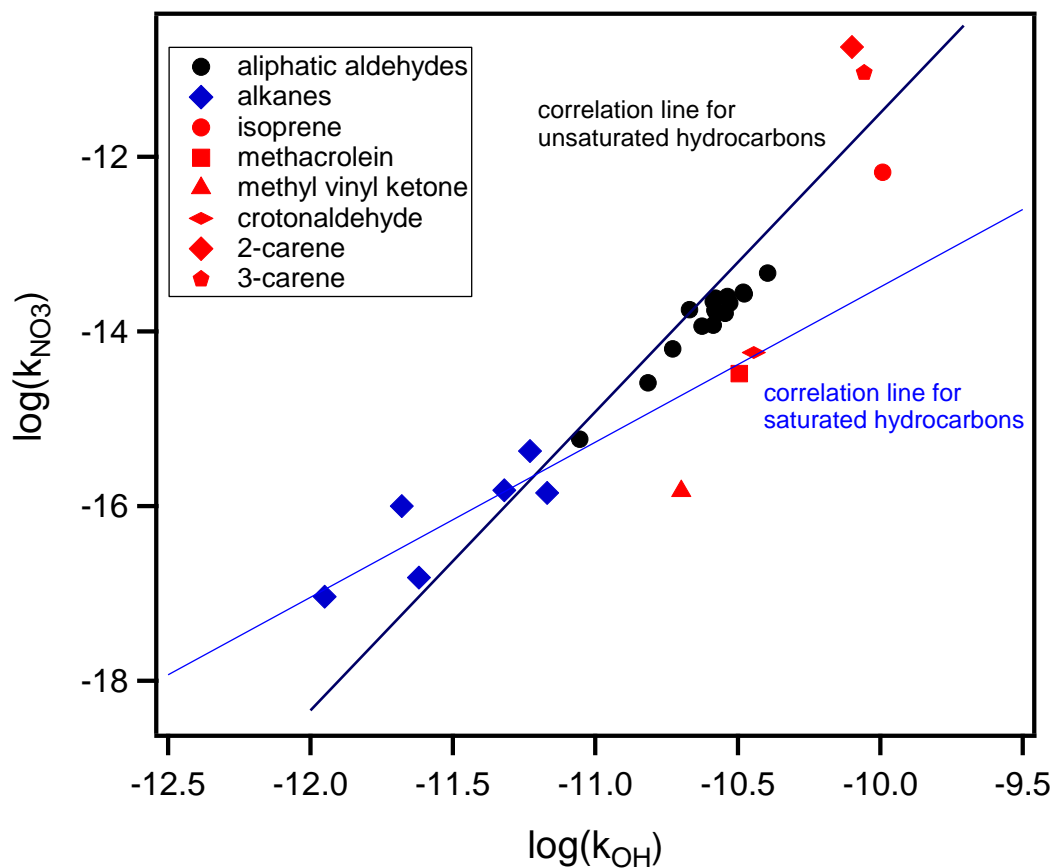


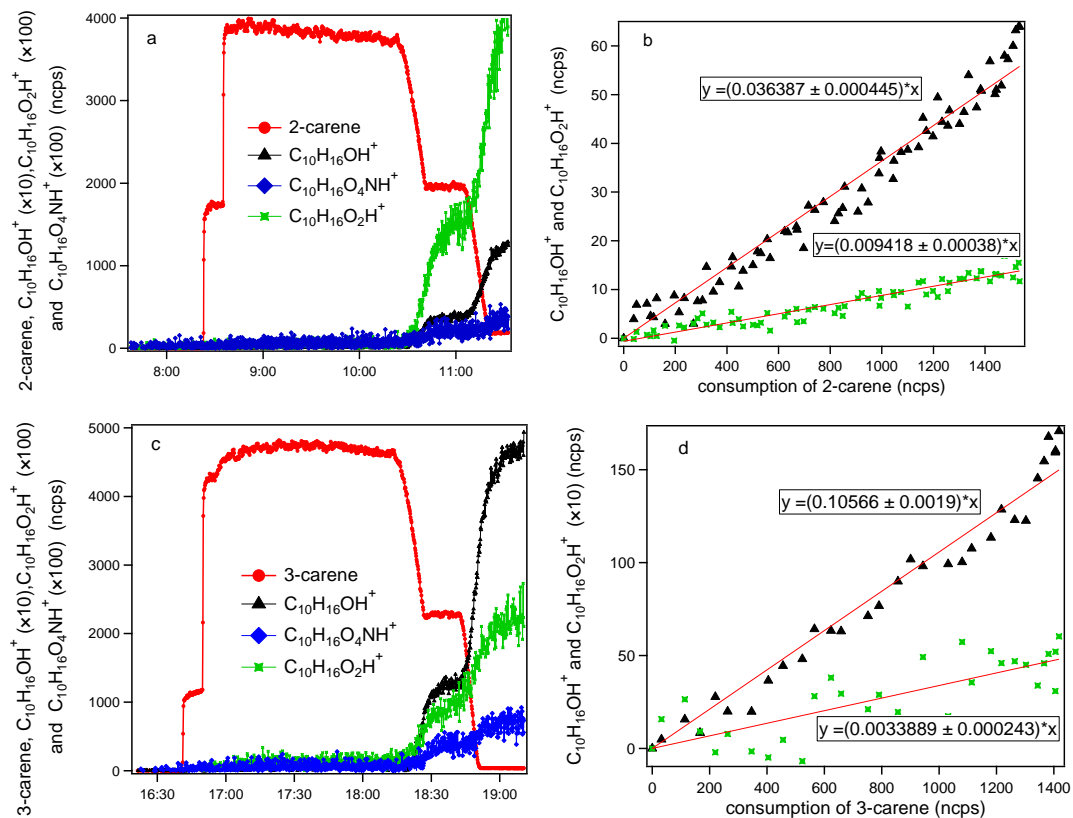
**Figure 1.** Plots of relative kinetic data obtained from the  $\text{NO}_3$  reaction with isoprene using cyclohexene as the reference, and  $\text{NO}_3$  radical reaction with 2-carene and 3-carene using  $\alpha$ -cedrene, 1,-cyclohexadiene as the reference.



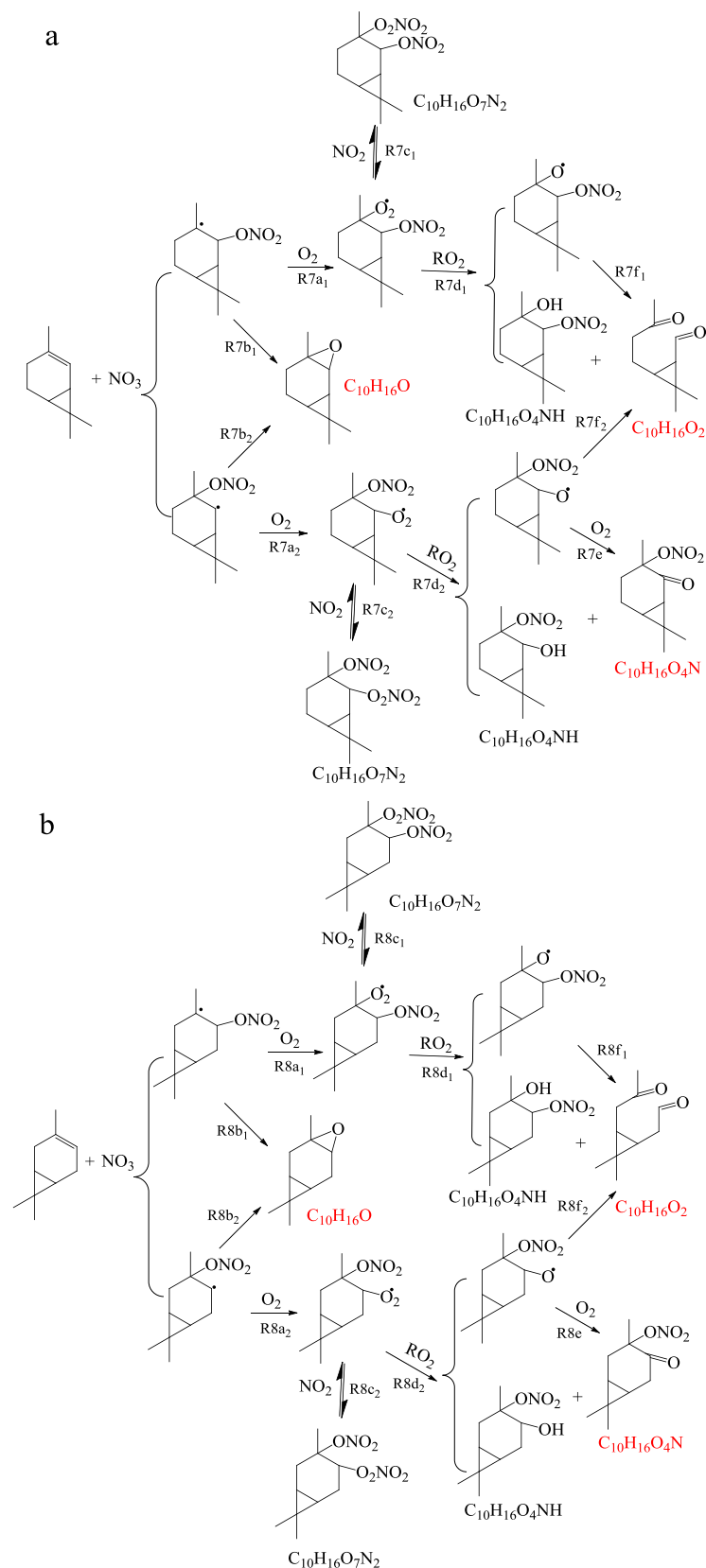
**Figure 2.** Plots of relative kinetic data obtained from the  $\text{NO}_3$  reaction with methyl vinyl ketone using methyl acrylate as the reference, and  $\text{NO}_3$  radical reaction with methacrolein and crotonaldehyde using methyl methacrylate, 2-methyl propanal as the reference. Note: crotonaldehyde with reference 2-methyl propanal, methacrolein with reference methyl methacrylate, methyl vinyl ketone with reference methyl acrylate and crotonaldehyde with reference methyl methacrylate were shifted on the y-axis 0.05, 0.1, 0.15 and 0.2 respectively for clarity.



**Figure 3** Linear free energy plot for the reactions of OH and NO<sub>3</sub> radicals with a series of 15 aliphatic aldehydes and studied unsaturated VO. The correlation line for addition is given by:  $\log(k_{\text{NO}_3}) = (3.43 \pm 0.24) \times \log(k_{\text{OH}}) + (22.7 \pm 2.5)$  from D'Anna et al. (2001) and the correlation line for H-atom abstraction is given by:  $\log(k_{\text{NO}_3}) = (1.78 \pm 0.57) \times \log(k_{\text{OH}}) + (4.26 \pm 6.59)$  from the updated alkane data of Zhou et al., 2019.

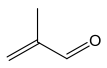
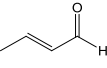
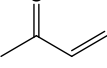

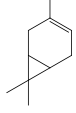
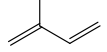


**Figure 4.** The time profile (a / c) of 2-carene/3-carene (m/z 137.133), epoxide ( $C_{10}H_{16}OH^+$ , m/z 153.127), nitrooxy-ketone ( $C_{10}H_{16}O_4NH^+$ , m/z 215.115) and caronaldehyde ( $C_{10}H_{16}O_2H^+$ , m/z 169.122) measured by PTR-TOF-MS. Plots (b, d) show product formation as function of 2-carene/3-carene consumption.



**Figure 5.** The proposed reaction mechanism of 2-carene (a) and 3-carene (b) reaction with  $\text{NO}_3$  radical under the condition of this work: in the absence of  $\text{NO}$  and in excess of 2-carene/3-carene. The products identified in PTR-TOF-MS of this work were highlighted in red.

**Table 1.** List of specific masses monitored to detect various studied VOCs using the PTR-TOF-MS along with detection sensitivities.

| VOCs                | structure  | Mass charge ratio.H <sup>+</sup><br>(m/z) | detection sensitivity<br>(ncps/ppbv) |
|---------------------|--|---|--------------------------------------|
| Methacrolein        |   | 71.049                                    | 31.73                                |
| Crotonaldehyde      |   | 71.049                                    | 41.71                                |
| Methyl vinyl ketone |   | 71.049                                    | 34.83                                |
| 2-carene            |   | 137.133                                   | 19.58                                |
| 3-carene            |   | 137.133                                   | 15.93                                |
| Isoprene            |  | 69.07                                     | 7.61                                 |

**Table 2.** The experimental conditions and rate constants for the reaction of isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene and 3-carene with NO<sub>3</sub> radical by relative method.

| VOC                 | [VOC] (10 <sup>12</sup> molecule cm <sup>-3</sup> ) | ref <sup>a</sup>            | No. runs | $\frac{k}{k_{ref}} \pm error$ <sup>b</sup> | $k \pm 2\sigma$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>c</sup> |
|---------------------|---|-----------------------------|----------|--|--|
| methacrolein        | 1.7-4.1   | 2-methyl propanal           | 2        | 0.23±0.07                                  | (2.7±0.6) × 10 <sup>-15</sup>  |
|                     |   | methyl methacrylate         | 2        | 0.90±0.27                                  | (2.7±0.5) × 10 <sup>-15</sup>  |
|                     |   | <b>Average</b> <sup>d</sup> |          |  | (2.7±0.8) × 10 <sup>-15</sup>  |
| crotonaldehyde      | 2.0-4.0   | 2-methyl propanal           | 2        | 0.42±0.06                                  | (4.9±0.7) × 10 <sup>-15</sup>  |
|                     |   | methyl methacrylate         | 2        | 1.87±0.29                                  | (5.6±0.6) × 10 <sup>-15</sup>  |
|                     |   | <b>Average</b> <sup>d</sup> |          |  | (5.3±1.0) × 10 <sup>-15</sup>  |
| methyl vinyl ketone | 1.0-4.0   | methyl acrylate             | 2        | 1.11±0.15                                  | (1.3±0.6) × 10 <sup>-16</sup>  |
| 2-carene            | 0.8-1.7   | 1,3-cyclohexadiene          | 2        | 0.36±0.04                                  | (2.2±0.6) × 10 <sup>-11</sup>  |
|                     |   | α-cedrene                   | 2        | 1.66±0.23                                  | (2.5±0.3) × 10 <sup>-11</sup>  |
|                     |   | <b>Average</b> <sup>d</sup> |          |  | (2.5±0.6) × 10 <sup>-11</sup>  |
| 3-carene            | 0.8-2.8   | 1,3-cyclohexadiene          | 2        | 0.39±0.03                                  | (1.1±0.4) × 10 <sup>-11</sup>  |
|                     |   | α-cedrene                   | 2        | 1.71±0.20                                  | (1.4±0.2) × 10 <sup>-11</sup>  |
|                     |   | <b>Average</b> <sup>d</sup> |          |  | (1.3±0.4) × 10 <sup>-11</sup>  |
| isoprene            | 0.8-3.3   | cyclohexene                 | 2        | 1.19±0.18                                  | (6.8±1.0) × 10 <sup>-13</sup>  |

<sup>a</sup>  $k_{ref+NO_3}$  was shown in the text

<sup>b</sup> the error for  $\frac{k}{k_{ref}}$  are 2 times of standard deviation in the least-squares fit of  $\ln \frac{[VOC]_0}{[VOC]_t} - k_d * t$  vs  $\ln \frac{[reference]_0}{[reference]_t} - k_d * t$ , and then multiply 2.9 as the Student *t*-distribution contribution due to the limited number of measurements.

<sup>c</sup> the uncertainties for *k* were combined the precision of our measured values with the quoted uncertainties in the rate constant of references by using the propagation of uncertainty in Eq.2

<sup>d</sup> Weighted average as shown in Eq.3 and Eq.4

**Table 3.** Kinetic results of this study and comparison with the literature for the reactions of NO<sub>3</sub> radical with isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), crotonaldehyde (CA), 2-carene and 3-carene.

|                                  | Technique <sup>i</sup>            | k (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>k</sup> | T (K) | Reference                    |
|----------------------------------|-----------------------------------|--|-------|------------------------------|
| Isoprene                         | relative, trans-2-butene          | (5.97±1.20)×10 <sup>-13 a</sup>  | 295±1 | Atkinson et al., 1984        |
|                                  | absolute, DF-MS                   | (1.3±0.2)×10 <sup>-12</sup>  | 298   | Benter and Schindler, 1988   |
|                                  | absolute, LIF                     | (6.52±0.07)×10 <sup>-13</sup>  | 297   | Dlugokencky and Howard, 1989 |
|                                  | relative, trans-2-butene          | (1.21±0.31)×10 <sup>-12 a</sup>  | 298±2 | Barnes et al., 1990          |
|                                  | absolute, DF-MS                   | (7.8±0.6)×10 <sup>-13</sup>  | 298   | Wille et al., 1991           |
|                                  | absolute, PR-A                    | (1.07±0.20)×10 <sup>-12</sup>  | 295±2 | Ellermann et al., 1992       |
|                                  | relative, trans-2-butene          | (6.86±2.60)×10 <sup>-13</sup>  | 298   | Berndt and Böge, 1997        |
|                                  | absolute, F-CIMS                  | (7.3± 0.2)×10 <sup>-13</sup>   | 298±2 | Suh et al., 2001             |
|                                  | relative, trans-2-butene          | (5.3± 1.1)×10 <sup>-13 a</sup>   | 296±2 | Stabel et al., 2004          |
|                                  | relative, 2-buten-1-ol            | (5.75± 0.47)×10 <sup>-13 b</sup>   |       |                              |
| MACR                             | relative, trans-2-butene          | (6.16 ± 1.24)×10 <sup>-13 a</sup>  | 295±2 | Zhao et al., 2011            |
|                                  | relative                          | (6.8±1.0)×10 <sup>-13</sup>  | 297±2 | This work                    |
|                                  | <b>recommended<sup>e,f</sup></b>  | <b>(6.6±0.8)×10<sup>-13</sup></b>  |       |                              |
|                                  | absolute, F-A                     | <8×10 <sup>-15</sup>   | 298   | Rudich et al., 1996          |
|                                  | relative, propene                 | (4.4±1.7)×10 <sup>-15</sup>  | 296±2 | Kwok et al., 1996            |
|                                  | relative, propene                 | (3.07±1.09)×10 <sup>-15</sup>  | 298±2 | Chew et al., 1998            |
|                                  | relative, but-1-ene               | (3.50±1.06)×10 <sup>-15</sup>  | 298±2 |                              |
|                                  | relative, propene                 | (3.7±1.0)×10 <sup>-15</sup>  | 296±2 | Canosa-Mas et al. 1999       |
|                                  | relative                          | (2.7±0.8)×10 <sup>-15</sup>  | 298±2 | This work                    |
|                                  | <b>recommended<sup>e</sup></b>    | <b>(3.3±0.9)×10<sup>-15</sup></b>  |       |                              |
| CA                               | relative, propene                 | (5.15±2.58)×10 <sup>-15 c</sup>  | 298   | Atkinson et al. 1987         |
|                                  | relative, propene                 | (6.0±0.8)×10 <sup>-15</sup>  | 297   | Ullerstam et al. 2001        |
|                                  | absolute, DF-LIF                  | (16.0±1.9)×10 <sup>-15</sup>   | 298   | Cabanas et al. 2001          |
|                                  | absolute, LIF                     | (13.5±0.4)×10 <sup>-15</sup>   | 298   | Salgado et al. 2008          |
|                                  | relative                          | (5.3±1.0)×10 <sup>-15</sup>  | 298±2 | This work                    |
|                                  | <b>recommended<sup>e,g</sup></b>  | <b>(5.7±1.2)×10<sup>-15</sup></b>  |       |                              |
| MVK                              | absolute, F-A                     | ≤1.2×10 <sup>-16</sup>   | 298   | Rudich et al., 1996          |
|                                  | relative, propene                 | <6×10 <sup>-16</sup>   | 296±2 | Kwok et al., 1996            |
|                                  | relative, ethene                  | (4.7±1.7)×10 <sup>-16</sup>  | 296±2 | Canosa-Mas et al., 1999      |
|                                  | relative                          | (1.3±0.6)×10 <sup>-16</sup>  | 298±2 | This work                    |
|                                  | <b>Recommended<sup>h</sup></b>    | <b>(1.3±0.6)×10<sup>-16</sup></b>  |       |                              |
| 2-carene                         | absolute, DF-LIF                  | (1.66±0.18)×10 <sup>-11</sup>  | 298   | Martínez et al., 1999        |
|                                  | relative, 2,3-dimethyl-2-butene   | (2.15±0.46)×10 <sup>-11</sup>  | 295   | Corchnoy and Atkinson, 1990  |
|                                  | relative, 2-methyl-2-butene       | (1.87±0.27)×10 <sup>-11</sup>  |       |                              |
|                                  | relative                          | (2.5±0.6)×10 <sup>-11</sup>  | 296±2 | This study                   |
| <b>recommended<sup>e,i</sup></b> | <b>(1.8±0.6)×10<sup>-11</sup></b> |  |       |                              |
| 3-carene                         | relative, 2-methyl-2-butene       | (1.01±0.35)×10 <sup>-11 d</sup>  | 295±1 | Atkinson et al., 1984        |
|                                  | relative, 2-methyl-2-butene       | (8.1±1.2)×10 <sup>-12</sup>  | 298   | Barnes et al., 1990          |
|                                  | relative                          | (1.3±0.4)×10 <sup>-11</sup>  | 297±2 | This study                   |
|                                  | <b>recommended<sup>e,i</sup></b>  | <b>(8.7±0.5)×10<sup>-12</sup></b>  |       |                              |



<sup>a, b, c, d</sup> The values from the literatures were recalculated by using the rate constants as follow: <sup>a</sup>  $k_{\text{trans-2-butene}}=(3.90\pm 0.78)\times 10^{-13}$  (IUPAC), <sup>b</sup>  $k_{\text{2-buten-1-ol}}=(3.23\pm 0.12)\times 10^{-13}$  (Zhao et al., 2011), <sup>c</sup>  $k_{\text{propene}}=(9.50\pm 5.50)\times 10^{-15}$  (IUPAC), <sup>d</sup>  $k_{\text{2-methyl-2-butene}}=(9.37\pm 0.33)\times 10^{-12}$  (Calvert et al., 2000), unit in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

<sup>e</sup> the recommended value was weighted average in Eq.3 and Eq.4

<sup>f</sup> recommended value included all the literatures excluded Benter and Schindler, 1988, Barnes et al., 1990 and Ellermann et al., 1992.

<sup>g</sup> recommended value included all the literatures excluded Cabanas et al. 2001 and Salgado et al. 2008

<sup>h</sup> recommended value was the one obtained in this work

<sup>i</sup> recommended value included all the literature data

<sup>j</sup> DF-MS: discharge flow system and mass spectrometer; LIF: Laser Induced Fluorescence; DF-LIF: discharge flow system and Laser Induced Fluorescence; PR-A: pulse radiolysis combined with kinetic spectroscopy in the visible; F-CIMS: flow tube and chemical ionization mass spectrometer; F-A: flow tube coupled to a diode laser absorption system; CRDS: cavity ring-down spectroscopy

<sup>k</sup> the uncertainties of the literature data were revised by including the quoted uncertainties in the rate constant of references by using the propagation of uncertainty in Eq.2

**Table 4.** Summary of rate constants and estimated atmospheric lifetimes of studied VOCs with respect to their reactions with OH, NO<sub>3</sub>, O<sub>3</sub>, and Cl at 298 ± 2 K and atmospheric pressure.

| VOCs                | Rate constant (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) |                             |   |                             | Lifetime (hours) |                 |                 |                 |
|---------------------|---|-----------------------------|---|-----------------------------|------------------|-----------------|-----------------|-----------------|
|                     | NO <sub>3</sub> <sup>b</sup>  | OH<br>(×10 <sup>-11</sup> ) | O <sub>3</sub><br>(×10 <sup>-18</sup> ) | Cl<br>(×10 <sup>-10</sup> ) | τ <sub>NO3</sub> | τ <sub>OH</sub> | τ <sub>O3</sub> | τ <sub>Cl</sub> |
| Isoprene            | 6.6×10 <sup>-13</sup>   | 10.2 <sup>c</sup>           | 11.3 <sup>e</sup>                       | 4.00 <sup>h</sup>           | 0.84             | 2.7             | 35              | 69              |
| methacrolein        | 3.3×10 <sup>-15</sup>   | 3.20 <sup>d</sup>           | 0.71 <sup>e</sup>                       | 3.30 <sup>i</sup>           | 170              | 8.7             | 559             | 84              |
| methyl vinyl ketone | 1.5×10 <sup>-16</sup>   | 2.00 <sup>d</sup>           | 4.50 <sup>e</sup>                       | 0.99 <sup>i</sup>           | 3736             | 13.9            | 88              | 281             |
| crotonaldehyde      | 5.7×10 <sup>-15</sup>   | 3.60 <sup>d</sup>           | 1.58 <sup>f</sup>                       | 2.20 <sup>j</sup>           | 98               | 7.7             | 251             | 126             |
| 2-carene            | 1.8×10 <sup>-11</sup>   | 7.95 <sup>c</sup>           | 239 <sup>g</sup>                        | 5.80 <sup>k</sup>           | 0.03             | 3.5             | 1.7             | 48              |
| 3-carene            | 9.1×10 <sup>-12</sup>   | 8.78 <sup>c</sup>           | 38.0 <sup>g</sup>                       | 5.20 <sup>k</sup>           | 0.06             | 3.2             | 10              | 53              |

<sup>a</sup> Assuming [OH] = 1 × 10<sup>6</sup> molecules cm<sup>-3</sup> (Spivakovsky et al., 2000) , [NO<sub>3</sub>]=5 × 10<sup>8</sup> molecules cm<sup>-3</sup> (Atkinson et al., 1991), [O<sub>3</sub>]= 7 × 10<sup>11</sup> molecules cm<sup>-3</sup> (Monks et al., 2009) and [Cl] = 1 × 10<sup>4</sup> molecules cm<sup>-3</sup> (Wingenter et al. 1996).

<sup>b</sup> rate constants from this work; <sup>c</sup> rate constants from Calvert et al., 2002; <sup>d</sup> rate constants from Calvert et al., 2011; <sup>e</sup> rate constants from Ren et al., 2017; <sup>f</sup> rate constant from Sato et al., 2004; <sup>g</sup> rate constants from Chen et al., 2015; <sup>h</sup> rate constant from Suh et al., 2000; <sup>i</sup> rate constants from Canosa-Mas et al., 2001; <sup>j</sup> rate constant from Ullerstam et al., 2001; <sup>k</sup> rate constants from Timerghazin et al., 2001.