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## Kinetic and mechanism studies of the ozonolysis of three unsaturated ketones

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### ABSTRACT

Reaction rate constants and products of 1-octen-3-one, 3-octen-2-one and 4-hexen-3-one with ozone were studied in a 100-L fluorinated ethylene propylene (FEP) Teflon film bag using absolute rate method at  $298 \pm 1$  K and atmospheric pressure. The rate constants were  $(1.09 \pm 0.12) \times 10^{-17}$ ,  $(3.48 \pm 0.36) \times 10^{-17}$  and  $(5.70 \pm 0.60) \times 10^{-17}$   $\text{cm}^3/(\text{molecule} \cdot \text{sec})$ , respectively. According to the obtained rate constants, the effects of carbonyl were discussed. The carbonyl group in  $\beta$  position has a net withdrawing effect with respect to an olefinic bond, then causing the decline of rate constants. The quantum chemical calculation was used to explain the results of rate constants. The products of ozonolysis were mainly aldehydes, which have significant influence on the formation of SOA, and hence play an important role in the atmosphere. In this work, we detected the main products of reaction and proposed the reaction mechanism by combining the results of quantum chemical calculations. Atmospheric lifetime for three unsaturated ketones reacted with ozone was 36.4, 11.4 and 6.9 hr for 1-octen-3-one, 3-octen-2-one and 4-hexen-3-one, respectively.

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### Introduction

Air pollution has been regarded as a huge trouble to human health and life. The concentration of  $\text{PM}_{2.5}$ , the particulate matter smaller than  $2.5 \mu\text{m}$  in diameter, could reach up to  $> 300 \mu\text{g}/\text{m}^3$  in haze period. The  $\text{PM}_{2.5}$  can enter into the human respiratory system–lung, causing the respiratory

diseases and increasing the risk of cancer. The contribution of secondary organic aerosols (SOA) to particulate organic matter (POM) are 20%–80% of measured mass (Dechapanaya et al., 2004; Gouw et al., 2005; Yu et al., 2007). The SOA could be formed from the reaction of volatile organic compounds (VOCs) with atmospheric oxidants, such as, OH radicals (mainly during the day),  $\text{NO}_3$  radicals (at night),  $\text{O}_3$  molecule, and Cl atom (in certain environment) (Atkinson, 2013). Unsaturated oxygenated VOCs (OVOCs) have been identified as dominated components in the VOCs, for example, unsaturated alcohols, ketones, esters, aldehydes and ethers

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(Grosjean, 1995). The OVOCs are not only emitted into the atmosphere from both natural and anthropogenic sources, but also formed from the reaction of all hydrocarbons with oxidants in the atmosphere (Mellouki et al., 2015).

In recent years, field measurements have indicated high concentrations of ozone in Chinese megacities. The summer concentration of ozone increased by 1–3 ppbV/year during 2013–2017 (Li et al., 2019). And the models predicted that tropospheric ozone would increase 20%–25% between 2015 and 2050, if the current emission trends continuing (Wang et al., 2013). The gas-phase reactions of ozone with unsaturated compounds are important sources of free radical species (including OH radicals) and particulate material in the Earth's atmosphere (Johnson and Marston, 2008). The products of ozonolysis of unsaturated ketones are aldehydes, which have significant influence on the formation of O<sub>3</sub> and SOA, and hence play an important role in atmospheric chemistry (Mellouki et al., 2015; Shen et al., 2013). Therefore, studying the kinetic constants and the products of unsaturated ketones react with O<sub>3</sub> are important and useful for understanding the formation of SOA.

Among the unsaturated compounds, the unsaturated ketones are abundant in the atmosphere. They are very reactive towards the atmospheric oxidants and have a number of different sources. Ozonolysis of unsaturated hydrocarbons can form carbonyl oxides (known as Criegee intermediates, CIs). The atmospheric fate of these CIs has a pivotal influence on air quality and radiative forcing (Donahue et al., 2011; Johnson and Marston, 2008; Taatjes et al., 2014). Therefore, the ozonolysis of unsaturated ketones was very important, and a lot of researches were needed to determine its atmospheric chemistry implications. In this work, we selected three unsaturated ketones that has similar structure. 1-Octen-3-one has been observed from the pileus and stipe of pine-mushroom (Cho et al., 2008). After the rain, a lot of mushrooms appeared in the forest. Besides, mushrooms were planted by people (Marshall et al., 2009). 1-Octen-1-one was found to be produced during the storage of European seabass (Leduc et al., 2012). The emission of 3-octen-2-one has been observed in the volatile components of Canadian grown low-tannin faba bean (Oomah et al., 2014). 3-Octen-2-one has also been detected in the volatile aroma compounds from oxidized frozen whitefish (Josephson et al., 1984), and it has been identified as a kind of volatile compounds from the polished-graded wheat flour bread (Maeda et al., 2009). The species selected have a carbonyl group, but the carbon-carbon double bond of 1-octen-3-one was in the end, and that could lead to a difference in kinetic rate constants.

In this work, the ozonolysis of three unsaturated ketones with similar structure were studied in the smog chamber. The rate constants of them were obtained through absolute rate method at 298 K and a total pressure of  $1.01 \times 10^3$  mbar. Compared with the rate constants obtained in experiments, we discussed the effects of the structure and the substituent position of carbonyl group, and calculated the transition states of the reaction to understand the differences between the rate constants of them. The products of oxidation were detected by gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC). The atmospheric lifetimes of three unsaturated ketones were calculated, and then the potential impact was evaluated.

## 1. Materials and methods

### 1.1. Experimental process

All kinetic experiments of the reaction that O<sub>3</sub> react with unsaturated ketones were conducted in 100 L fluorinated ethylene propylene (FEP) Teflon film reactor and the condition

was the air pressure at  $1.01 \times 10^3$  mbar and  $298 \pm 1$  K. An inlet and outlet made of the Teflon were used to introduce the reactants and sample the gas. The reactor and analytical instruments were linked through the tube that was made by Teflon. The carrier gas was zero air gas produced by a zero air gas generator (737 series, AADCO, USA) in all experiments. All the reactants were liquid. Certain amounts of the cyclohexane and unsaturated ketones were introduced into a 3-way glass tube and then flushed into the reactor using the carrier gas, warming the glass tube if necessary. In the kinetic experiments, ozone reacted with unsaturated ketones would produce the OH radicals, and OH radicals would react with unsaturated ketones. Thus, we added cyclohexane into the reactor to scavenge the OH radicals (Atkinson et al., 1992). The carrier gas flowed through a mass flow controller (D08-8C/ZM, Beijing Sevenstarnasha Electron Corporation, China) to record the total volume of the gas into the bag. After the reactants were introduced into the Teflon bag, plenty of time was needed to make the reactants in the bag to reach a steady state. After reaching a steady state, we added the O<sub>3</sub> into the bag. The O<sub>3</sub> was generated via electrical discharge by flowing oxygen pass an O<sub>3</sub> generator (BGF-YQ, Beijing Ozone, China). Then the bag was connected with ozone analyzer (Model 49i, Thermo Fisher, USA) by the Teflon tube, the sample flow of ozone analyzer is 700 mL/min. It is considered that the reaction was basically completed, when the ozone concentration reached 30% of the initial concentration. The concentrations of unsaturated ketones in the bag were calculated according to the amounts of unsaturated ketones introduced and the total volume of the reactor. The initial concentrations of 1-octen-3-one, 3-octen-2-one and 4-hexen-3-one were  $3.99 \times 10^{13}$ – $10.37 \times 10^{13}$ ,  $2.39 \times 10^{13}$ – $5.58 \times 10^{13}$  and  $3.09 \times 10^{13}$ – $7.22 \times 10^{13}$  molecule/cm<sup>3</sup>, respectively. The concentration of cyclohexane was  $5.58 \times 10^{15}$  molecule/cm<sup>3</sup>, and the original ozone in experiments was  $1.51 \times 10^{12}$ – $3.02 \times 10^{12}$  molecule/cm<sup>3</sup>.

### 1.2. Absolute rate method

The absolute rate method was used to measure the rate constants of the unsaturated ketones with ozone, and the detailed description was in our previous studies (Du et al., 2007; Li et al., 2018). In all of the experiments, the concentration of ozone was monitored by an ozone analyzer accurately and constantly. The ozone concentration changed over the time in two pathways: one was the loss of wall and another was reacting with unsaturated ketones. As shown in Eqs. (1) and (2).



where  $k_1$  was used on behalf of the rate of loss of O<sub>3</sub> without any unsaturated ketones and  $k_2$  represents the rate value for the reaction of O<sub>3</sub> with unsaturated ketones.

In all the experiments, the concentration of unsaturated ketones was in large excess over the ozone, so it could essentially be regarded as a constant throughout the reactions. Therefore, the unsaturated ketones reacted with ozone could be regarded as under pseudo-first order conditions. The  $k_1$  and concentration of unsaturated ketones were easy to obtain, while the  $k_2$  could be obtained through monitoring the change of O<sub>3</sub> with time. A plot of  $-\ln[\text{O}_3]/t$  against ketones should be a straight line, and the slope is the rate constant of reaction.

### 1.3. Theoretical calculation

In this work, all quantum chemical calculations were performed using Gaussian 09 program (Frisch et al., 2003). The

**Table 1 – Experimental conditions and results of the reactions of O<sub>3</sub> with unsaturated ketones.**

Ketones	[Ketones] ( $\times 10^{13}$ molecule/cm <sup>3</sup> )	[O <sub>3</sub> ] ( $\times 10^{12}$ molecule/cm <sup>3</sup> )	[Cyclohexane] <sup>a</sup> ( $\times 10^{15}$ molecule/cm <sup>3</sup> )	dln[O <sub>3</sub> ]/dt ( $\times 10^{-4}$ sec <sup>-1</sup> )
1-Octen-3-one	3.99	2.45	5.58	4.20 ± 0.004
	5.58	2.22	5.58	5.94 ± 0.03
	7.18	2.88	5.58	7.76 ± 0.03
	8.78	1.86	5.58	9.38 ± 0.01
	9.57	2.24	5.58	10.5 ± 0.04
	10.37	2.46	5.58	11.1 ± 0.05
3-Octen-2-one	$k_{1\text{-octen-3-one+O}_3} = (1.09 \pm 0.12) \times 10^{-17}$ cm <sup>3</sup> /(molecule·sec)			
	2.39	2.04	5.58	8.11 ± 0.03
	3.19	2.73	5.58	11.3 ± 0.03
	3.98	3.02	5.58	13.3 ± 0.07
	4.78	2.45	5.58	16.4 ± 0.13
	5.58	2.29	5.58	18.9 ± 0.14
4-Hexen-3-one	$k_{3\text{-octen-2-one+O}_3} = (3.48 \pm 0.36) \times 10^{-17}$ cm <sup>3</sup> /(molecule·sec)			
	3.09	1.51	5.58	18.2 ± 0.19
	4.13	2.03	5.58	22.8 ± 0.27
	5.16	2.39	5.58	31.0 ± 0.35
	6.19	1.91	5.58	35.6 ± 0.92
	7.22	1.93	5.58	41.6 ± 0.57
$k_{4\text{-hexen-3-one+O}_3} = (5.7 \pm 0.6) \times 10^{-17}$ cm <sup>3</sup> /(molecule·sec)				

<sup>a</sup> Cyclohexane was added into the reactor to scavenge the OH radicals.

density functional theory (B3LYP) combined with 6–31+G (d,f) basis set was carried out to optimize the relevant geometrical parameters and conclude frequencies of the reactions (R), transition states (TS), intermediates (POZ), products (P). The transition state has an imaginary frequency. In addition, calculating the single point energies at the M06-2X/6–311+G (3df, 2p) on the basis of the b3lyp/6–31+G (d, f) optimized geometries and meanwhile we used the zero-point vibrational energy to further strengthen the accuracy of the calculation.

#### 1.4. Detection of products

The main products of three unsaturated ketones react with O<sub>3</sub> were reactive carbonyl compounds, so we focused on detection of them, which were detected via a derivation method (Berndt et al., 2016; Kalberer et al., 2004). After reaction for 40 min, the gasses in smog chamber were collected through 2,4-dinitrophenyl hydrazine (DNPH) to derive carbonyl compounds for further detection (Kölliker et al., 1998; Van den Bergh et al., 2000). A DNPH-silica cartridge (350 mg, 1 mL) was connected after an ozone denuder, and pumped with flow velocity of 200 mL/min for 8.3 hr. Derivatives were extracted with 5 mL of acetonitrile and then hydrazines were analyzed by GC–MS (7890B-5977B, Agilent Technology, USA), the column used in study was 30 m  $\times$  250  $\mu$ m  $\times$  0.25  $\mu$ m (19091S-433UI, Agilent, USA). The GC oven temperature program was started at 50°C and kept for 2 min, then programmed at a rate of 20°C/min to 250°C and kept for 10 min. The temperature of injector port was 250°C. The mass detector (MSD) electron ionization (EI) energy was set at 70 eV, and the GC–MS interface temperature was set at 280°C. We used microinjectors to inject a specific volume of samples into the injector. In addition, we used the HPLC (LC-20A, Shimadzu, Japan) with the detector of ultraviolet-visible (SPD-20A, Shimadzu, Japan). And the wavelength used in this work is 360 nm. The column for separation of the hydrazones was Inter sustain C18 (5  $\mu$ m  $\times$  4.6 nm  $\times$  250 nm, Shimadzu), and the mobile phase consisted of two solvent mixtures: mixture A, water; mixture B, acetonitrile. The gradient program was 60% B and 40% A at 0–20 min, and 100% B at 30 min, then at 32 min 60% B and

40% A, and kept this for 8 min. The DNPH-carbonyl derivatives were analyzed by injecting 20  $\mu$ L through automatic sampler.

#### 1.5. Reagents

The chemicals used in all the experiments were all commercially available. 1-Octen-3-one (99.22%) was obtained from Adamas. 3-Octen-2-one (98.3%) was bought from J&K Scientific company. 4-Hexen-3-one (98%) was obtained from 3A. Cyclohexane (C<sub>6</sub>H<sub>12</sub>) in a purity of 99.98% was from Acros. Acetonitrile ( $\geq 99.9\%$ ) for HPLC was bought from Innochem. O<sub>2</sub> ( $\geq 99.999\%$ ) was supplied by Beijing Tailong Electronics Company. 2,4-Dinitrophenylhydrazine (DNPH, 98%) was obtained from J&K Scientific company. Formaldehyde-2,4-dinitrophenyl-hydrazone ( $\geq 98\%$ ) and acetaldehyde-2,4-dinitrophenyl-hydrazone ( $\geq 98\%$ ) were brought from TCI (Shanghai). Methylglyoxal was got from Sigma-Aldrich.

## 2. Results and discussion

### 2.1. Wall loss of O<sub>3</sub>

In the reaction of unsaturated ketones with O<sub>3</sub>, the loss of O<sub>3</sub> can be contributed by two parts, one was the wall loss of O<sub>3</sub> and another was the reaction of O<sub>3</sub> with unsaturated ketones. The wall loss of O<sub>3</sub> is a first-order reaction, it is easy and essential to obtain the wall loss rate constant of O<sub>3</sub>. The slope of ln ([O<sub>3</sub>]<sub>0</sub>/[O<sub>3</sub>]<sub>t</sub>) plotted against time is the O<sub>3</sub> wall loss rate, where the [O<sub>3</sub>]<sub>0</sub> and [O<sub>3</sub>]<sub>t</sub> represent for the initial concentration of O<sub>3</sub>, and at time t, respectively. In Fig. 1, the rate constant of wall loss was  $6.816 \times 10^{-6}$  sec<sup>-1</sup>.

### 2.2. Rate constants and discussions

In the experiments of O<sub>3</sub> react with unsaturated ketones, several runs were conducted in the case of different initial concentration of unsaturated ketones reacted with O<sub>3</sub>, the detail information of experiments were listed in Table 1. In all experiments, the decays of O<sub>3</sub> concentration were obtained

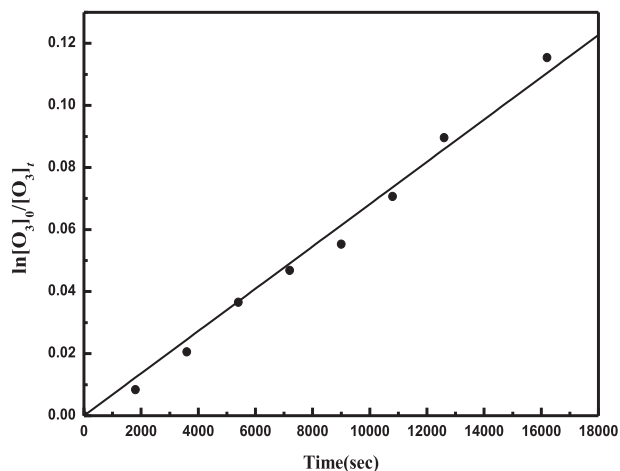


Fig. 1 – Wall loss of  $O_3$ .  $[O_3]_0$ : the initial concentrations of  $O_3$ ;  $[O_3]_t$ : the concentration of  $O_3$  at time  $t$ .

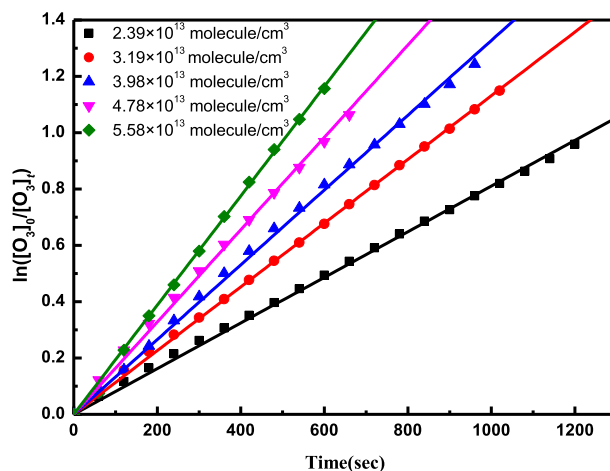


Fig. 3 – Five different initial concentrations of 3-octen-2-one react with  $O_3$  at room temperature.

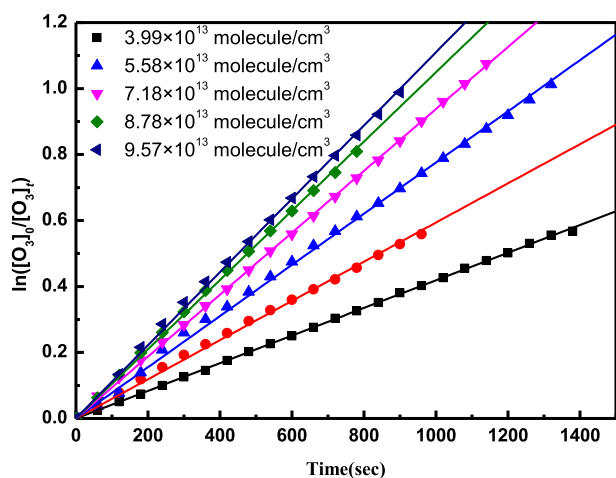


Fig. 2 – Six different initial concentrations of 1-octen-3-one react with  $O_3$  at room temperature.

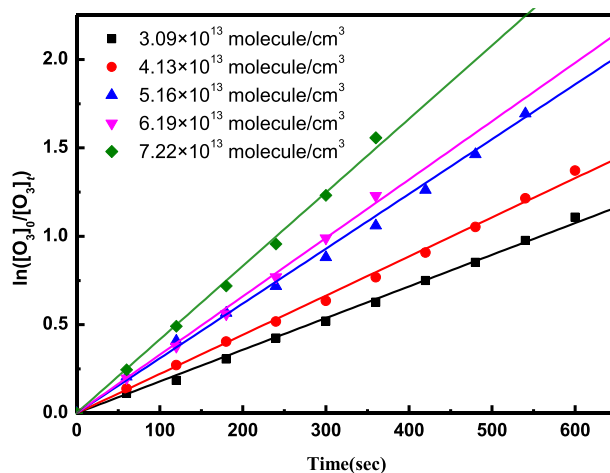


Fig. 4 – Five different initial concentrations of 4-hexen-3-one react with  $O_3$  at room temperature.

as a function of time. As shown in Table 1 and Figs. 2–4, the decay rate of  $O_3$  ( $-\ln[O_3]/dt$ ) was gained through the slope of the straight-line plot of  $\ln[O_3]_0/[O_3]_t$  against time ( $t$ ) for 1-octen-3-one, 3-octen-2-one and 4-hexen-3-one, respectively. As several decay rate of  $O_3$  under different initial concentrations of unsaturated ketones, the  $k_2$  could be easy to obtain by linear least-squares analysis of the plot of decay rates of  $O_3$  ( $-\ln[O_3]/dt$ ) versus unsaturated ketones concentrations in Figs. 5 and 6.

The straight lines with excellent correlation coefficients have intercepts close to zero, indicating that secondary reactions in the experiments can be neglected. As shown below, the rate constants of 1-octen-3-one with  $O_3$  ( $k_{1\text{-octen-3-one}+O_3}$ ), 3-octen-2-one with  $O_3$  ( $k_{3\text{-octen-2-one}+O_3}$ ) and 4-hexen-3-one ( $k_{4\text{-hexen-3-one}+O_3}$ ) with  $O_3$  were  $(1.09 \pm 0.12) \times 10^{-17}$ ,  $(3.48 \pm 0.36) \times 10^{-17}$  and  $(5.70 \pm 0.60) \times 10^{-17} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$ , respectively.

The wall loss of  $O_3$  in experiments was  $6.816 \times 10^{-6} \text{ sec}^{-1}$ , compared with the decay rate of  $O_3$  with unsaturated ketones ( $4.2 \times 10^{-4}$ – $41.6 \times 10^{-4} \text{ sec}^{-1}$ ) which was about two orders of magnitude lower. Therefore, the loss of  $O_3$  caused by the wall could be neglected in all experiments.

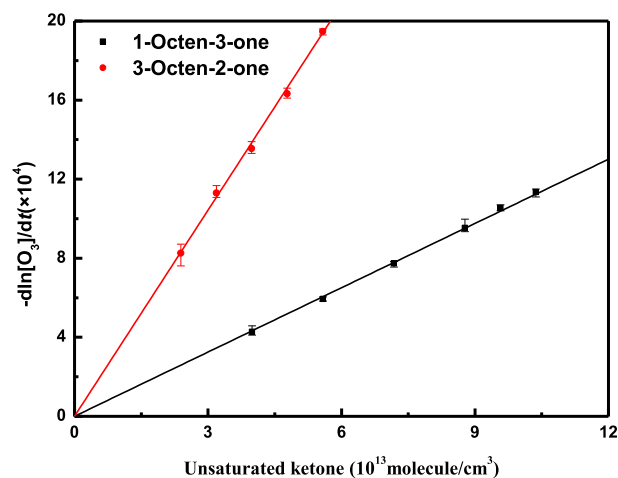


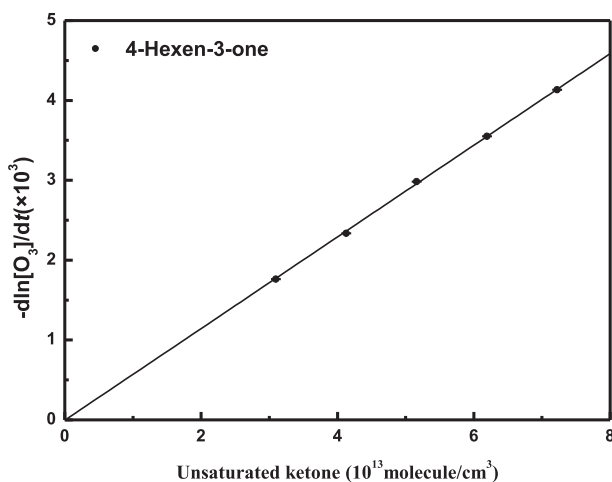
Fig. 5 – Plots of the decay rate coefficient of  $O_3$  ( $-\ln[O_3]/dt$ ) vs. different concentration of 1-octen-3-one and 3-octen-2-one at room temperature.



**Table 2 – Ozonolysis rate coefficients of some unsaturated ketones and parent olefins.**

Unsaturated ketones	Rate constants (cm <sup>3</sup> /(molecule·sec))	References	Parent olefins <sup>a</sup>	Rate constants (cm <sup>3</sup> /(molecule·sec))	References
1-Octen-3-one	1.09 ± 0.12	This work	1-Octen	1.25 ± 0.04	Grosjean and Grosjean, 1995
3-Octen-2-one	3.48 ± 0.36	This work	3-Octen	–	–
4-Hexen-3-one	5.70 ± 0.6	This work	2-Hexen	15.5 ± 0.6	Avzianova and Ariya, 2002
1-Penten-3-one	0.61 ± 0.04	Grosjean et al., 1993	1-Penten	0.998 ± 0.02	Avzianova and Ariya, 2002
3-Penten-2-one	2.13 ± 0.38	Atkinson et al., 1981	2-Penten	16.2 ± 0.06	Avzianova and Ariya, 2002

<sup>a</sup> Replacing carbonyl group in unsaturated ketones by H.



**Fig. 6 – Plots of the decay rate coefficient of O<sub>3</sub> (-dln[O<sub>3</sub>]/dt) vs. different concentration of 4-hexen-3-one at room temperature.**

In this work, the rate constants of 1-octen-3-one and 3-octen-2-one were obtained for the first time, and the rate constant of 4-hexen-3-one was  $(6.37 \pm 0.99) \times 10^{-17}$  cm<sup>3</sup>/(molecule·sec) in other work (Grosjean and Grosjean, 1999). The rate constant in this work was  $(5.70 \pm 0.6) \times 10^{-17}$  cm<sup>3</sup>/(molecule·sec), they were in good agreement within the error range. Furthermore, some of the rate constants for the similar structure of unsaturated ketones and its parent olefins reaction with O<sub>3</sub> were listed in Table 2.

As shown in Table 2, from the comparison of rate constants for 1-penten and 1-penten-3-one, we can clearly find that the 1-penten-3-one was lower than 1-penten. 1-Penten-3-one has a carbonyl group in  $\beta$  position. Thus, the difference of rate constant between 1-penten and 1-penten-3-one was caused by the carbonyl group in  $\beta$  position. From Table 2, the same conclusion was obtained between 3-penten-2-one and 2-penten, and the rate constant of 3-penten-2-one was much lower than 2-penten. Compared with the rate constants of 1-octen-3-one and 4-hexen-3-one in this work and their parent olefins, the same conclusion mentioned above could be gained. The carbonyl group in  $\beta$  position has a net withdrawing effect with respect to an olefinic bond, which makes the rate constants of unsaturated ketones lower than their parent olefins. The similar conclusion appeared in previous work by McGillen et al. (2011). The rate constants of three unsaturated ketones were lower than that of their parent olefins, because of the carbonyl group in  $\beta$  position. Among three compounds, the rate constant of 1-octen-3-one was the lowest. Comparing the 1-octen-3-one with 3-octen-2-one and 4-hexen-3-one, the

carbon-carbon double bond of 1-octen-3-one located in the end, the electron donating inductive effect caused by alkyl substitution was receded. The rate constant of 4-hexen-3-one was highest in three ketones. The differences of rate constant between 3-octen-2-one and 4-hexen-3-one were caused by the alkyl at both ends of carbon-carbon double bond.

To further verify the experimental results and clarify the reaction mechanism, we calculated the reactions for the O<sub>3</sub>-cycloaddition to the 1-octen-3-one, 3-octen-2-one, 4-hexen-3-one. The detail reaction mechanism for the initial reaction of the three unsaturated ketones, the decomposition of the primary ozonides (POZs), and the potential barriers were given in Figs. 7 and 8. The energy barriers of the three unsaturated ketones in the initial reactions were 0.98, -2.10 and -3.33 kcal/mol, respectively. The decomposition reactions of the POZs have two channels, both of them can produce CIs and ketones. Among the three reactants, the energy barriers of the 4-hexen-3-one was the lowest in the decomposition reactions. The initial reactions were the decisive step of the reaction. Altogether, the reactions of the O<sub>3</sub>-cycloaddition to 4-hexen-3-one was the most favorable thermodynamically.

### 2.3. Results of GC-MS and HPLC

The products of unsaturated ketones reacted with O<sub>3</sub> were measured by HPLC and GC-MS. We got the HPLC spectrum of standard species, and then the retention time of characteristic peaks in the spectrum was obtained. The corresponding retention time peaks were also seen in the HPLC spectra of the products, so the corresponding products were determined. What's more, we measured the products by GC-MS, and then determined the product according to the NIST database and retention time of characteristic peak. The standard species including formaldehyde-2,4-dinitrophenyl-hydrazone and methylglyoxal-2,4-dinitrophenyl-hydrazone were detected by HPLC solely, the retention time was 7.037 and 7.058 min, respectively. The standard compound of acetaldehyde-2,4-dinitrophenyl-hydrazone was detected by GC-MS and the retention time was at 12.61 min. The standard pentanal-2,4-dinitrophenyl-hydrazone was confirmed by its MS peaks comparing the NIST library. For 1-octen-3-one, the main products that had been detected was formaldehyde, which was detected as the DNPH derivative (formaldehyde-2,4-dinitrophenyl-hydrazone) by HPLC at 7.031 min. By the analyzing of 2,4-dinitrophenyl-hydrazone derivatisation in GC-MS, the identification of pentanal and acetaldehyde was confirmed as major products of the reaction of O<sub>3</sub> with 3-octen-2-one and 4-hexen-3-one, respectively. Besides, the methylglyoxal-2,4-dinitrophenyl-hydrazone with the retention time at 7.038 min was detected in the products of 3-octen-2-one by using HPLC. As shown in the results of theoretical calculation, the compounds reacted with O<sub>3</sub> by initial O<sub>3</sub> addition to the C=C bond, then formed a POZ, which rapidly decomposed through two pathways to carbonyl and CIs shown in Fig. 7.

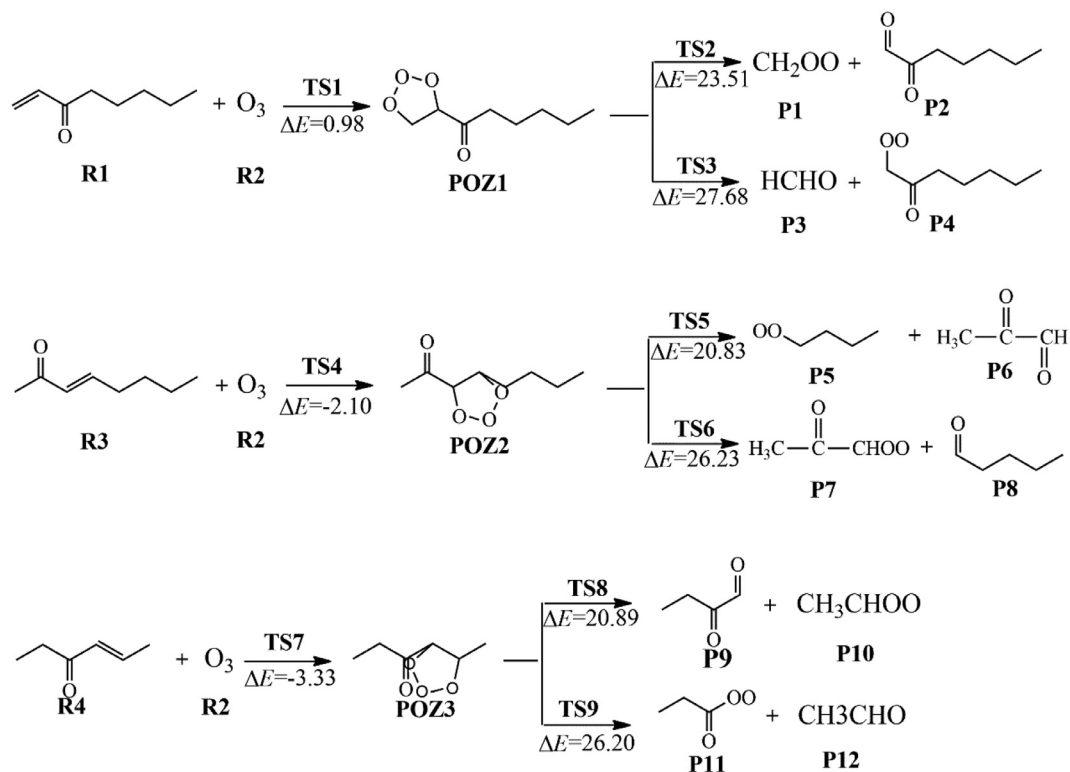


Fig. 7 – Three different unsaturated ketones initial reactions and the decomposition reaction of primary ozonides (POZs) embedded with the potential barrier  $\Delta E$  (kcal/mol). R: the reactant; TS: transition state; P: the product.

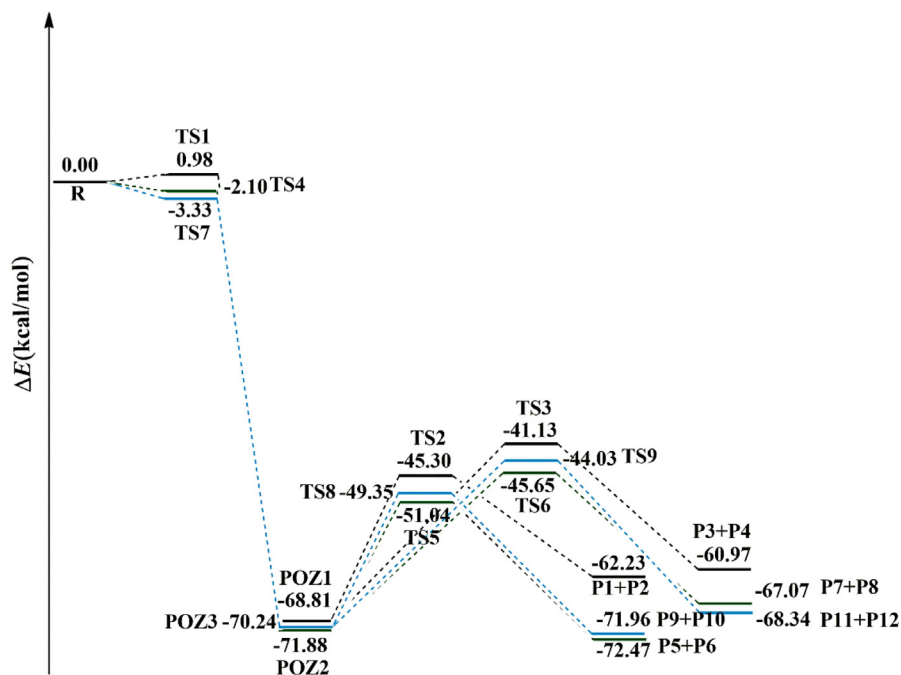


Fig. 8 – Potential energy for the reaction of 1-octen-3-one, 3-octen-2-one, 4-hexen-3-one on the M06-2X/6–311 + G(3df,2p)//B3LYP/6–31 + G(d,f) level.

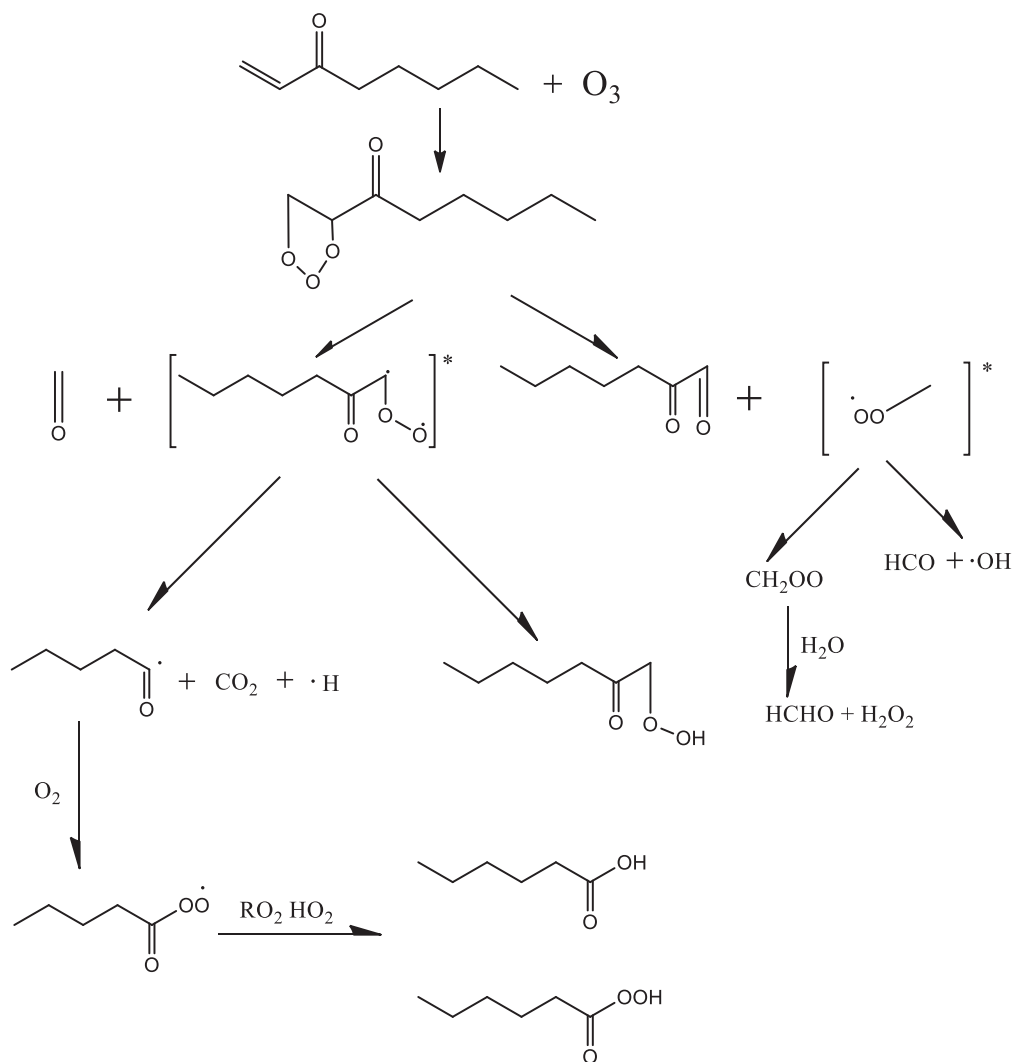


Fig. 9 – Simple mechanism of 1-octen-3-one with O<sub>3</sub>. RO<sub>2</sub>: peroxyalkyl radical.

The simplest CI, (CH<sub>2</sub>OO)\*, was a product of ozonolysis of 1-octen-3-one, the main products from decomposition of (CH<sub>2</sub>OO)\* were CO<sub>2</sub>, H<sub>2</sub>O, OH, CO, H<sub>2</sub> and the stabilized CIs (Johnson and Marston, 2008). The stabilized CI, CH<sub>2</sub>OO, could undergo the reactions with water to yield HCHO and H<sub>2</sub>O<sub>2</sub>. The (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>C(O)CHOO)\*, (CH<sub>3</sub>C(O)CHOO)\* and (CH<sub>3</sub>CH<sub>2</sub>C(O)CHOO)\* were the major CIs for 1-octen-3-one, 3-octen-2-one and 4-hexen-3-one, respectively. If there was no hydrogen atom on the β-carbon, the hydroperoxide channel was not possible (O'Dwyer et al., 2010). The CIs can rearrangement to a "hot" ester followed by decomposition, and formed CO<sub>2</sub> + RH + acyl radical. Then acyl radical reacted with RO<sub>2</sub> or HO<sub>2</sub> to form alcohols. The (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHOO)\* and (CH<sub>3</sub>CH<sub>2</sub>C(O)CHOO) were the main CIs for the ozonolysis of 3-octen-2-one and 4-hexen-3-one, the OH was formed by 1,5-H- migration for them (Kidwell et al., 2016). In combination with theoretical calculation and the results of products detected, the POZ, CIs and carbonyls including the species with dicarbonyl group were confirmed, then the reaction mechanisms of three unsaturated ketones with O<sub>3</sub> were proposed as shown in Figs. 9–11.

#### 2.4. Atmospheric implications

The main elimination of three unsaturated ketones in atmosphere is through oxidation reaction with major troposphere

oxidants (OH, NO<sub>3</sub>, O<sub>3</sub> and Cl atom). The atmospheric lifetimes of the studied ketones with O<sub>3</sub> can be estimated by using the obtained rate constants in this work, which are shown in Table 3, together with the values from OH radicals. The atmospheric lifetimes were calculated according to the following equation:

$$\tau = 1/(k[X]) \quad (3)$$

where the  $k$  is the rate constant of ketones react with oxidants X, and the  $[X]$  represents the typical concentration of the oxidant X in atmosphere. The rate constants of 1-octen-3-one and 3-octen-2-one react with OH were not found in previous works. Then we used the AOPWIN software to estimate the value. AOPWIN software uses a similar methodology to the well-established structure-activity relationship (SAR) of Kwok and Atkinson (1995). Compared with the rate constants from experimental, the results of estimating were consistent in order of magnitude. The rate constant of 4-hexen-3-one react with OH radical was  $(9.04 \pm 2.12) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$  reported by Blanco et al. (2012).

The atmospheric lifetimes of three unsaturated ketones react with O<sub>3</sub> were about 0.5–1 day, and the atmospheric lifetimes of reacting with OH radicals were about 1–5 hr, that indicated they will be degraded close to their emission sources through reacting with OH radicals. However, in high photochemical pollution area where the concentration of O<sub>3</sub> is mea-

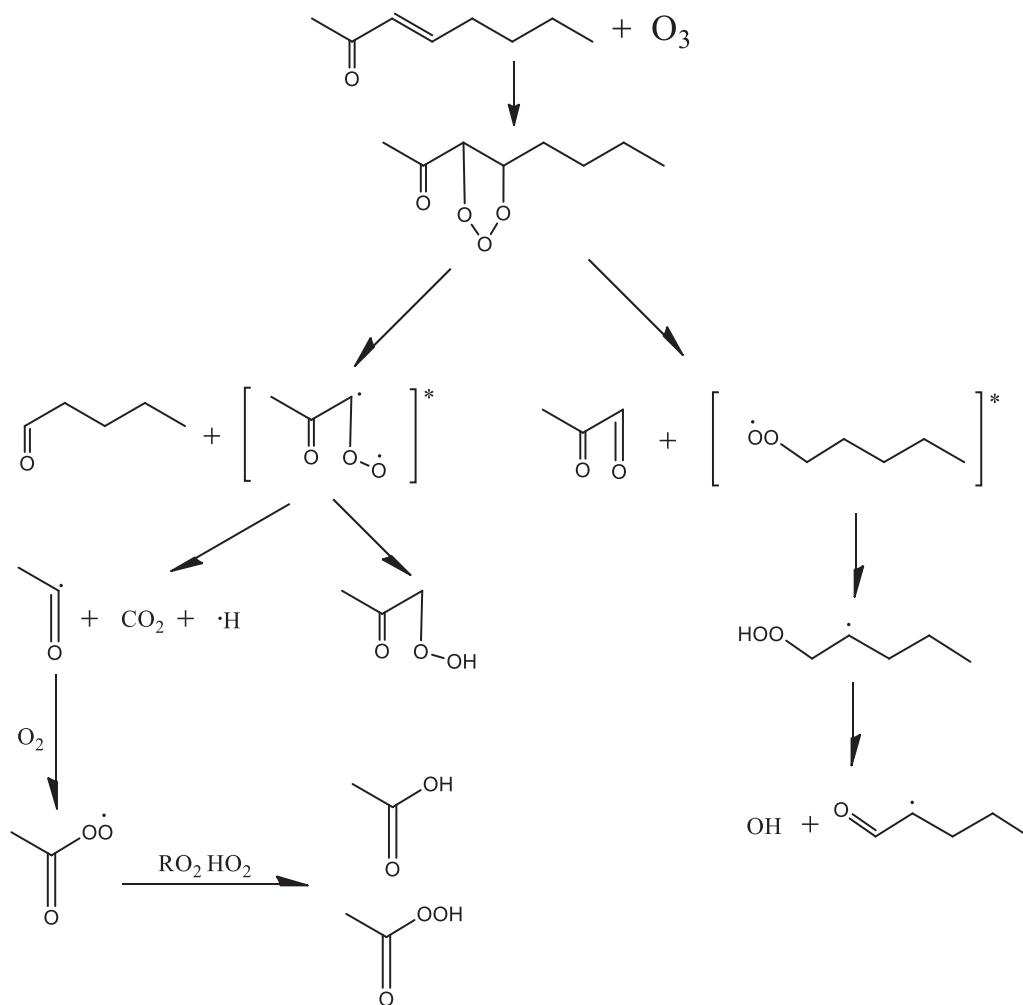


Fig. 10 – Simple mechanism of 3-octen-2-one with O<sub>3</sub>.

Table 3 – Atmospheric lifetimes for the unsaturated ketones in this work.

Unsaturated ketones	$k_{O_3}$ ( $\times 10^{17}$ cm <sup>3</sup> /molecule·sec)	$k_{OH}$ ( $\times 10^{11}$ cm <sup>3</sup> /molecule·sec)	$\tau_{OH}$ (hr)	$\tau_{O_3}$ (hr)
1-Octen-3-one	1.09	3.1	4.5	36.4
3-Octen-2-one	3.47	5.4	2.57	11.4
4-Hexen-3-one	5.71	9.04	1.54	6.9

Conditions: [O<sub>3</sub>] =  $7 \times 10^{11}$  molecule/cm<sup>3</sup> (Logan, 1985); [OH] =  $2 \times 10^6$  molecule/cm<sup>3</sup> (Hein et al., 1997).

$k_{O_3}$ : rate constant of ketones with O<sub>3</sub>;  $k_{OH}$ : rate constant of ketones with OH;  $\tau_{OH}$ : atmospheric lifetime of ketones with OH;  $\tau_{O_3}$ : atmospheric lifetime of ketones with O<sub>3</sub>

sured up to about  $4.57 \times 10^{12}$  molecule/cm<sup>3</sup> (Wang et al., 2010), and the lifetimes for reactions of three unsaturated ketones with O<sub>3</sub> could turn from 36.4 to 5.57, 11.4 to 1.57 and 6.9 to 1.06 hr for 1-octen-3-one, 3-octen-2-one and 4-hexen-3-one, respectively. The lifetime of 1-octen-3-one decreases under this environment was lower, and the lifetimes of 3-octen-2-one and 4-hexen-3-one were lower than that they react with OH radicals. That indicated the reactions of unsaturated ketones investigated in this work with O<sub>3</sub> may serve as a competitive degradation pathway in some certain circumstances.

As shown above, the products of three unsaturated ketones react with O<sub>3</sub> were carbonyls. It is well known that carbonyls are important members of OVOCs and have a significant in-

fluence on the formation of ozone and SOA. The formaldehyde and acetaldehyde have been classified as toxic air pollutants and even human carcinogens by World Health Organization (WHO). Besides, the photolysis of formaldehyde dominated HO<sub>2</sub> formation and that HO<sub>2</sub> then further oxidizes NO to NO<sub>2</sub>, which facilitating the formation of O<sub>3</sub> (Wang et al., 2018). A common conclusion was that of the carbonyl species, especially formaldehyde and acetaldehyde, had the highest O<sub>3</sub> formation potential (OFP) because of their relatively high concentrations and reactivity (Zhang et al., 2019). The methylglyoxal was extremely water-soluble, which can hydrate and polymerize at low humidity, and hence having a contribution to the formation of SOA (Shen et al., 2013). Furthermore, dicar-



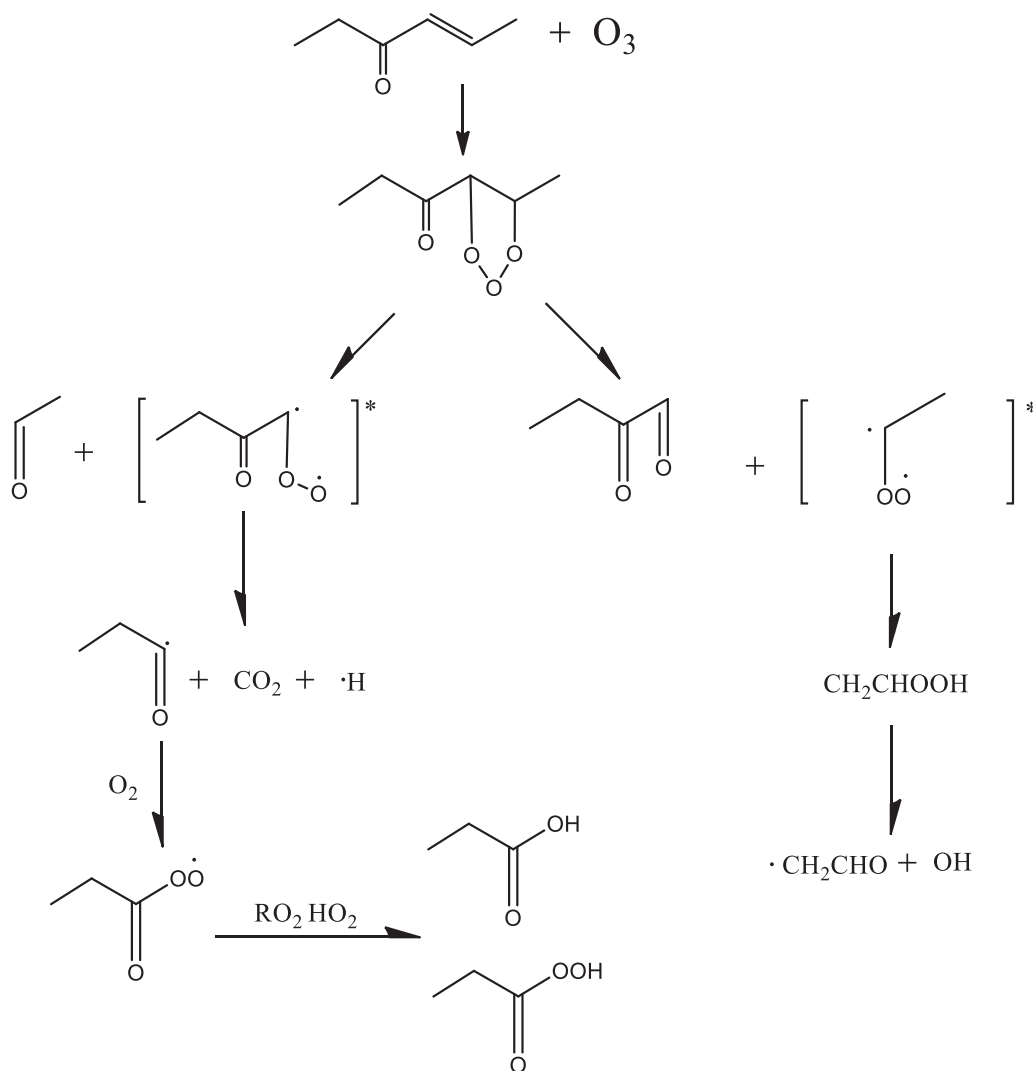


Fig. 11 – Simple mechanism of 4-hexen-3-one with  $O_3$ .

bonyls (e.g. methylglyoxal and glyoxal) were found to make a great contribution to the formation of simulated surface SOA through irreversible uptake by aqueous particle (Li et al., 2013).

### 3. Conclusions

The ozonolysis experiment on three unsaturated ketones, important OVOCs emitted from plants and solvents, was performed in a 100-L FEP Teflon film bag by using absolute methods. The rate constants were obtained and then the effects of carbonyl were discussed. Carbonyl in  $\beta$  position has an electron withdrawing and hence the rate constants were lower than their parent olefins. The reasons of differences in rate constants of three unsaturated ketones were further analyzed by using the quantum chemical calculation. The energy barrier of 4-hexen-3-one was the lowest among three compounds, which was agreed with the experimental results.

The products of three unsaturated ketones reacted with ozone were detected by using GC-MS and HPLC via a derivation method, and the main products were aldehydes. Formaldehyde, acetaldehyde, and pentanal were detected. All of products have significant influence on the formation of  $O_3$  and SOA. Besides, the atmospheric lifetimes of three com-

pounds were calculated through rate constants obtained in this work. Although the atmospheric lifetimes of three unsaturated ketone in this work with respect to ozone vary between 6.9 and 36.4 hr, the contribution of ozonolysis reactions to atmospheric lifetime of that ketones may be important in polluted areas where the concentration of ozone is higher. The rate constants and products obtained in this work enrich the kinetic databases for models that involving the unsaturated oxygenated compounds particularly.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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