

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

Kinetic study of the gas-phase reaction of O₃ with three unsaturated alcohols

Weiran Li^{1,2}, Yi Chen^{2,3}, Shengrui Tong², Yucong Guo², Yunhong Zhang^{1,*}, Maofa Ge^{2,4,5,*}

1. The Institute of Chemical Physics, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

2. State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

3. State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Peking University, Beijing 100871, China

4. University of Chinese Academy of Sciences, Beijing 100049, China

5. CAS Research/Education Center for Excellence in Molecular Sciences, Beijing 100190, China

ARTICLE INFO

Article history:

Received 5 January 2018

Revised 10 April 2018

Accepted 11 April 2018

Available online 18 April 2018

Keywords:

Rate constant

Ozone

Unsaturated alcohols

Atmospheric lifetime

ABSTRACT

Rate constants for the reactions of ozone with 1-octen-3-ol, 1-nonen-3-ol and 1-nonen-4-ol have been determined at 298 ± 1 K and atmospheric pressure for the first time. The experiments were performed in a 100-L FEP Teflon film bag using absolute rate method; the rate constants were $(1.91 \pm 0.19) \times 10^{-17}$, $(1.89 \pm 0.20) \times 10^{-17}$, and $(0.83 \pm 0.08) \times 10^{-17}$ cm³/(molecule·sec) for 1-octen-3-ol, 1-nonen-3-ol, and 1-nonen-4-ol, respectively. The rate constants have been compared with those of unsaturated alcohols structural homologs, and used to estimate the reaction reactivity. The electronegativity of carbon–carbon double bond was calculated by atomic charges analysis. The calculated results show that the electronic effect of the lone pair electrons of hydroxyl oxygen is the main cause of the difference in rate coefficient. According to the obtained rate constants, the atmospheric lifetimes of studied unsaturated alcohols were also estimated, which indicates that the reaction with ozone is an important loss pathway in the atmosphere, especially in polluted areas.

© 2018 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

The oxidation of volatile organic compounds (VOCs) can lead to the formation of low volatility products that are responsible for secondary organic aerosol (SOA) production, SOA also was known to be a major contributor to the tropospheric particles (Kanakidou et al., 2005). SOA not only influences the climate and human health directly or indirectly, but also absorbs and scatters solar radiation. VOCs, a primary class of atmospheric pollutants, play a pivotal role in atmospheric chemistry and radiative forcing, which could be emitted from significant emission such as a full-scale food waste treatment plant (Ni et al., 2015), and reactivity toward atmospheric oxidants (Atkinson and Arey,

2003; Forster et al., 2007; Fry et al., 2014; Scott et al., 2014). They can be removed by reacting with OH radical (mainly during the day), NO₃ radical (at night), O₃ molecule, and Cl atom (in certain environments) (Atkinson, 2000), leading to the production of ozone and secondary organic aerosols (SOA) would be formed (Kanakidou et al., 2005; Lewis et al., 2000). Unsaturated oxygenated VOCs (OVOCs) such as unsaturated alcohols, ketones, esters, aldehydes and ethers (Grosjean, 1995) have been identified as a major component of VOCs.

The unsaturated alcohols are a capital class of OVOCs emitted into the atmosphere from both man-made and biogenic sources, and from solvent usage and industry directly. Unsaturated alcohols are very reactive towards the atmospheric oxidants,

* Corresponding authors. E-mails: yhz@bit.edu.cn (Yunhong Zhang), gemaofa@iccas.ac.cn (Maofa Ge).

and their degradation is controlled by chemical reactions with these oxidants (Mellouki et al., 2015). It is necessary to study the properties of the oxidation reaction of OVOCs with similar structure, so that we can estimate the kinetic parameters of the unknown substance. 1-Octen-3-ol, 1-nonen-3-ol, and 1-nonen-4-ol have similar structure, 1-nonen-3-ol has a $-\text{CH}_2$ group more than 1-octen-3-ol, and the position of 1-nonen-3-ol is different from 1-nonen-4-ol in the OH group. Furthermore, they also have various sources in the atmosphere. 1-octen-3-ol, “Mushroom alcohol,” is an 8-carbon alcohol formed from the enzymatic oxidation and cleavage of linoleic acid (Wurzenberger and Grosch, 1984). 1-Octen-3-ol is one of the richest VOCs produced by fungi, with the fungal aromas and flavors characteristics (Mau et al., 1992, 1997; Venkateshwarlu et al., 1999). In addition, 1-octen-3-ol can also be emitted from a widespread group of animals and plants (Bernier et al., 2000; Maggi et al., 2010; Ramoni et al., 2001). 1-Nonen-3-ol was used as a repellent for house flies (Wilson et al., 1987). It has been detected in the flower called *Rhododendron calophytum* Franch (Tian et al., 2010) and *Cynanchum stauntonii* (Tian et al., 2013). It also has been found during the storage of European seabass (Leduc et al., 2012). Emission of 1-nonen-4-ol has been reported to appear in the volatile oils from the Inflorescence of *Capillipedium parviflorum* (R. Br.) Stapf in Hainan Province of China, which has a very wide distribution (Yang et al., 2010).

Ozone (O_3) in the troposphere plays an important role in the oxidation of olefinic compounds. In recent years, field measurements have indicated very high concentrations of ozone in or near megacities of China. The contributions to both ozone from industry solvent use, industrial processes and domestic combustion are 24.7%, 23.0% and 17.8%, respectively (Wu et al., 2017). According to monitoring results from 74 Chinese cities, the mean daily 8-hour maximum concentrations raised from approximately 69.5 ppbv in 2013 to approximately 75.0 ppbv in 2015 (China Environment Report 2014 and 2015, available at <http://www.mep.gov.cn>, in Chinese). Recent observations found ozone concentrations exceeded the ambient air quality standard by 100%–200% in Chinese major urban centers such as Jing-Jin-Ji, the Pearl River delta, and the Yangtze River delta (Wang et al., 2017). Models predicted that tropospheric O_3 could increase 20%–25% between 2015 and 2050, and further will increase by 40%–60% by 2100 if current emission trends continuing. Previous projections suggested that ozone pollution was likely to worsen in future (Wang et al., 2013). Compared with the concentrations of OH radical in the range 2×10^6 molecule/ cm^3 (Atkinson, 2000) with O_3 of 7×10^{11} molecule/ cm^3 (Logan, 1985) indicated the concentration of ozone was higher than OH. Although the OH radical reaction is considered to be the dominant removal process for most of the organic compounds in the troposphere, the reactions with O_3 are also important degradation pathways under certain conditions (Finlayson-Pitts and Pitts, 1999). Under certain conditions, ozonolysis becomes important for the oxidation of olefinic compounds, especially where OH radical concentrations are suppressed, such as under high NO_x conditions or at night. The ozonolysis process will form free radical species including OH and SOA (Johnson and Marston, 2008). Therefore, exploring and studying the kinetic constant of the degradation of the unsaturated alcohols with O_3 is significant, which will be useful to evaluate the environmental impact.

In this work, the first kinetic studies for the homogeneous reactions of O_3 with 1-octen-3-ol, 1-nonen-3-ol and 1-nonen-4-ol

are obtained by using absolute rate method at 298 K and a total pressure of 1.01×10^3 mbar. By comparing the rate constants, the effects of the structure and the substituent position of OH group were discussed. In order to explain the differences of rate constant better, the structure of three substances will be analyzed by means of atomic charges analysis. These obtained rate constants of the unsaturated alcohols have been compared to those of unsaturated alcohols structural homologs and discussed in terms of the reactivity trends, and also can be used to calculate the atmospheric lifetimes and evaluate the potential impact, which is useful to understand the degradation pathways.

1. Experimental

1.1. Experimental methods

All experiments of O_3 reacting with unsaturated alcohols were carried out in a 100-L FEP Teflon film bag, which could maintain the air pressure at 1.01×10^3 mbar and 298 ± 1 K. An inlet and an outlet made of the Teflon were used for the introduction of reactants and gas sampling. Teflon tubes were used to link the chamber and analytical instruments. Cyclohexane was added into the reactor to scavenge the OH radicals which would be generated during the reactions (Atkinson et al., 1992). Certain amounts of the unsaturated alcohols and cyclohexane were injected into a 3-way glass tube and then flushed into the reactor using zero air produced by a zero air gas generator (AADCO 737 series, USA) as carrier gas through the Teflon tube, warming the glass tube if necessary. The carrier gas flowed through a flow accumulator (D08-8C/ZM, Beijing Sevenstar Electron Corporation, China) to record the total volume of the gas into the bag. The concentrations of unsaturated alcohols in the bag were calculated according to the amounts of organic compounds introduced and the total volume of the reactor. Plenty of time was allowed for the reactants in the bag to reach a steady state. After reaching a steady state, O_3 generated via electrical discharge by flowing oxygen pass an O_3 generator (BGF-YQ, Beijing Ozone, China) was injected into reactor. To mix the reactants with O_3 adequately, shaking and agitating the Teflon bag is necessary. Then the reactor was connected to the ozone analyzer with the flow of 700 mL/min (Model 49i, Thermo Fisher, USA), and the O_3 concentration was collected over 10-sec intervals. When the VOCs were introduced into the bag, it took about 10–15 min for mixing to occur, and the reacting time is determined by ozone concentration. When the ozone concentration reaches 30% of the initial concentration, it is considered that the reaction is basically completed. So the whole experiment process lasted about 40 mins. The initial concentrations of 1-octen-3-ol, 1-nonen-3-ol, and 1-nonen-4-ol were $(2.36\text{--}5.50) \times 10^{13}$, $(2.14\text{--}5.69) \times 10^{13}$, and $(4.95\text{--}10.61) \times 10^{13}$ molecule/ cm^3 , respectively. The concentration of cyclohexane was about 5.58×10^{15} molecule/ cm^3 . The concentration of O_3 was $(1.68\text{--}3.65) \times 10^{12}$ molecule/ cm^3 .

1.2. Absolute rate method

The absolute rate method described in previous works (Du et al., 2007; Gai et al., 2009) was used to study the rate constants of the

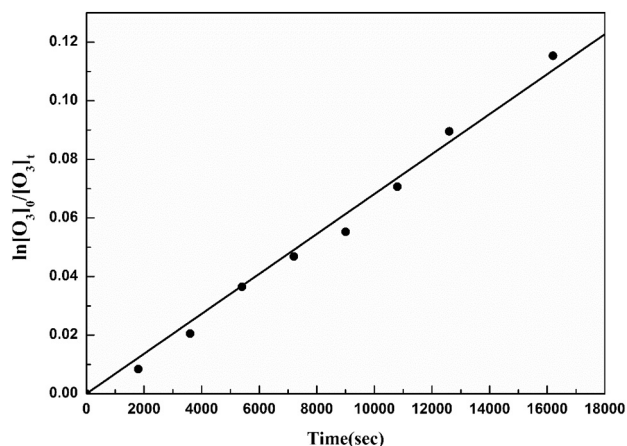


Fig. 1 – The wall loss of O₃.

unsaturated alcohols with O₃. The concentration of unsaturated alcohols was in large excess over that of O₃, and could essentially be regarded as a constant throughout the reactions. Therefore, all the experiments could be regarded as under pseudo-first-order conditions. The concentration of O₃ was monitored by an ozone analyzer accurately and constantly. The O₃ concentration-time profiles were governed by the following processes:



and hence

$$-d[\text{O}_3]/dt = (k_1 + k_2[\text{alcohols}])[\text{O}_3] \quad (3)$$

where k_1 is on behalf of the rate of loss of O₃ without any unsaturated alcohols; k_2 represents the rate value for the reaction of O₃ with unsaturated alcohols. Eq. (4) was given from Eq. (3)

$$-d \ln [\text{O}_3]/dt = k_1 + k_2[\text{alcohols}] \quad (4)$$

In Eq. (4), k_1 and the concentration of alcohols are easy to obtain, so k_2 can be obtained by monitoring the decay of ozone

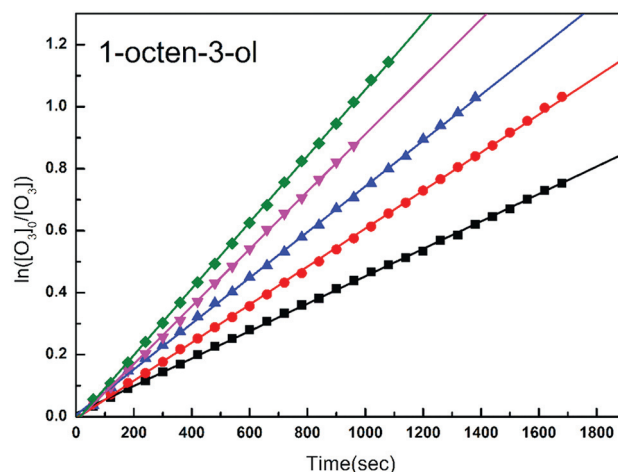


Fig. 2 – The pseudo-first-order plots for O₃ with different concentrations of 1-octen-3-ol at room temperature. 2.36×10^{13} molecule/cm³ (■), 3.14×10^{13} molecule/cm³ (●), 3.93×10^{13} molecule/cm³ (▲), 4.72×10^{13} molecule/cm³ (▼), 5.50×10^{13} molecule/cm³ (◆).

with time. A plot of $-d \ln [\text{O}_3]/dt$ against alcohols should be a straight line, and the slope is the rate constant of reaction.

1.3. Calculation

Electronic structure calculations were carried out by using the Gaussian series of programs (Frisch et al., 2003). The structure of the compounds was fully optimized at B3LYP/aug-cc-pVTZ. Atomic charges for the C and O, calculated with the B3LYP/aug-cc-pVTZ approximation.

1.4. Materials

The chemicals used were all commercially available. 1-Octen-3-ol (99.9%) was obtained from Acros; 1-nonen-3-ol (99.4%) and 1-nonen-4-ol (98.8%) were obtained from Alfa Aesar.

Table 1 – Experimental conditions and results from the reactions of O₃ with unsaturated alcohols.

Alcohols	[alcohol] ($\times 10^{13}$ molecule/cm)	[O ₃] ₀ ($\times 10^{12}$ molecule/cm ³)	[Cyclohexane] ($\times 10^{15}$ molecule/cm ³)	dln[O ₃]/dt ($\times 10^{-4}$ /sec)
1-octen-3-ol	2.36	2.53	5.58	4.52 ± 0.01
	3.14	2.93	5.58	6.12 ± 0.01
	3.93	2.33	5.58	7.44 ± 0.02
	4.72	2.30	5.58	9.04 ± 0.04
	5.50	2.19	5.58	10.50 ± 0.04
$k_{1\text{-octen-3-ol} + \text{O}_3} = (1.91 \pm 0.19) \times 10^{-17}$ cm ³ /(molecule·sec)				
1-nonen-3-ol	2.14	3.18	5.58	4.03 ± 0.01
	2.85	2.63	5.58	5.44 ± 0.02
	3.56	2.47	5.58	6.72 ± 0.02
	4.98	1.68	5.58	9.49 ± 0.04
	5.69	1.80	5.58	10.80 ± 0.05
$k_{1\text{-nonen-3-ol} + \text{O}_3} = (1.89 \pm 0.20) \times 10^{-17}$ cm ³ /(molecule·sec)				
1-nonen-4-ol	4.95	3.33	5.58	4.02 ± 0.01
	6.37	3.65	5.58	5.24 ± 0.007
	7.78	2.02	5.58	6.51 ± 0.02
	9.20	2.80	5.58	7.54 ± 0.04
	10.61	2.91	5.58	8.76 ± 0.04
$k_{1\text{-nonen-4-ol} + \text{O}_3} = (0.83 \pm 0.08) \times 10^{-17}$ cm ³ /(molecule·sec)				

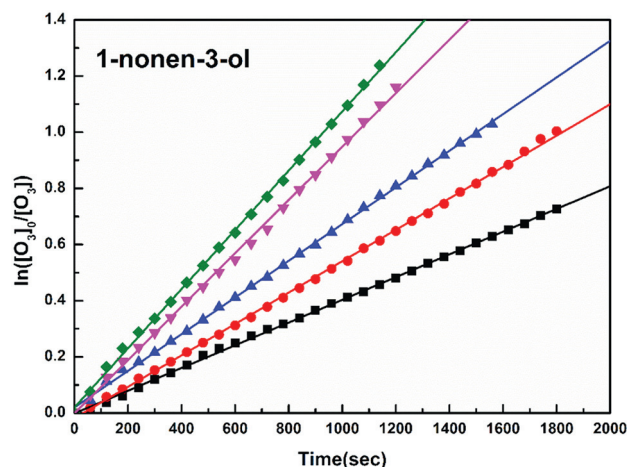


Fig. 3 – The pseudo-first-order plots for O_3 with different concentrations of 1-nonen-3-ol at room temperature: 2.14×10^{13} molecule/cm³ (■), 2.85×10^{13} molecule/cm³ (●), 3.56×10^{13} molecule/cm³ (▲), 4.98×10^{13} molecule/cm³ (▼), 5.69×10^{13} molecule/cm³ (◆).

C_6H_{12} (cyclohexane) in a purity of 99.98% was from Acros. O_2 ($\geq 99.999\%$) was supplied by Beijing Tailong Electronics Company. A Zero air generator (AADCO 737 series, USA) and ozone analyzer (Model 49i, Thermo Fisher, USA) were used as well.

2. Results and discussion

2.1. The wall loss of O_3

In the reactor, the loss of O_3 can be contributed by two parts, one is to oxidize reactants and the other is wall loss. Therefore, it is essential to obtain the wall loss rate constant of O_3 . As shown in Eq. (1), the inner wall of the reactor wall loss of O_3 could be regarded as a first-order reaction. The slope

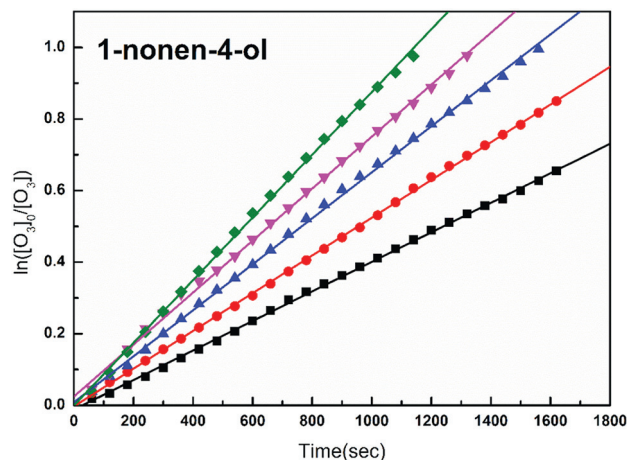


Fig. 4 – The pseudo-first-order plots for O_3 with different concentrations of 1-nonen-4-ol at room temperature: 4.95×10^{13} molecule/cm³ (■), 6.37×10^{13} molecule/cm³ (●), 7.78×10^{13} molecule/cm³ (▲), 9.20×10^{13} molecule/cm³ (▼), 10.61×10^{13} molecule/cm³ (◆).

of $\ln([O_3]_0/[O_3]_t)$ plotted against time is the O_3 wall loss rate, where the $[O_3]_0$ and $[O_3]_t$ represent for the concentration of O_3 initially, and at time t respectively. O_3 wall loss curve is shown in Fig. 1, and $k_{\text{wall}} = 6.816 \times 10^{-6}/\text{sec}$.

2.2. Determination of rate constants

For each reaction, five runs were conducted in the case of different initial unsaturated alcohols concentrations. The detail information is shown in Table 1. In all experiments, the decays

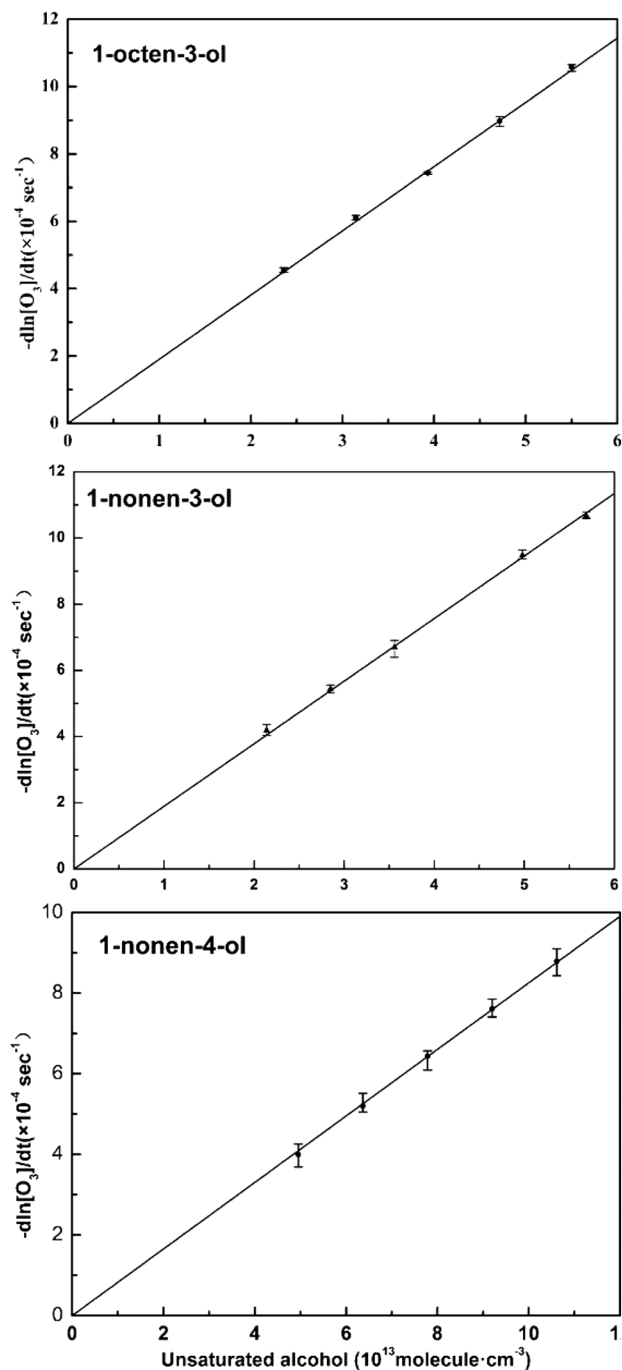
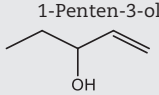
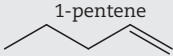
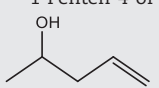
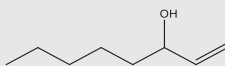
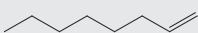
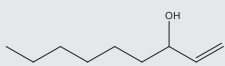

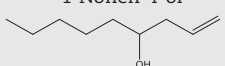


Fig. 5 – Plots of the decay rate coefficient of O_3 , $-\text{dln}[O_3]/\text{dt}$, vs. the concentration of three unsaturated alcohols at room temperature.

Table 2 – Ozonolysis rate coefficients of some unsaturated alcohols and analogous alkenes. *

Unsaturated alcohols	Rate coefficients (10^{-17} cm ³ /(molecule·sec))	Reference	Analogous alkene	Rate coefficients (10^{-17} cm ³ /(molecule·sec))	Reference
 1-Penten-3-ol	1.64 ± 0.15	O'Dwyer et al. (2010)	 1-pentene	0.998 ± 0.02	Avzianova and Ariya (2002)
 1-Penten-4-ol	0.488 ± 0.08	Gai et al. (2011)			
 1-Octen-3-ol	1.91 ± 0.19	This work	 1-octene	1.25 ± 0.04	Grosjean and Grosjean (1995)
 1-Nonen-3-ol	1.89 ± 0.20	This work	 1-nonene	1.15 ± 0.39	Protczak and Trzeszczynski (2002)
 1-Nonen-4-ol	0.83 ± 0.08	This work			

* Replacing OH group in unsaturated alcohols by H.

of O_3 concentration were obtained as a function of time, and decay rate of O_3 ($-d\ln[O_3]/dt$) was calculated by the slope of the straight-line plot of $\ln[O_3]_0/[O_3]_t$ against time(t), as shown in Table 1 and Figs. 2–4 for 1-octen-3-ol, 1-nonen-3-ol, and 1-nonen-4-ol, respectively. Ozone decay profiles were found to be linear in all cases. Five decay rates of O_3 with different concentrations of unsaturated alcohols were obtained, and k_2 was obtained through linear least-squares analysis of the plot of decay rates of O_3 ($-d\ln[O_3]/dt$) versus unsaturated alcohols concentrations in Fig. 5. The straight lines with excellent correlation coefficients have intercepts close to zero, indicating that secondary reactions could be neglected. The obtained rate constants for the studied unsaturated alcohols with O_3 were as follow:

$$\begin{aligned}
 k_{1\text{-octen-3-ol}+O_3} &= (1.91 \pm 0.19) \times 10^{-17} \text{ cm}^3/(\text{molecule} \cdot \text{sec}) \\
 k_{1\text{-nonen-3-ol}+O_3} &= (1.89 \pm 0.20) \times 10^{-17} \text{ cm}^3/(\text{molecule} \cdot \text{sec}) \\
 k_{1\text{-nonen-4-ol}+O_3} &= (0.83 \pm 0.08) \times 10^{-17} \text{ cm}^3/(\text{molecule} \cdot \text{sec}).
 \end{aligned}$$

The errors given contained twice the standard deviation from the least-squares analysis and about 10% errors estimated systematic error. Compared with the pseudo-first-order decay rates (see Table 1), the rate constant of wall loss was about two orders of magnitude lower than the pseudo-first-order reaction rate constants in the range $(4.52\text{--}10.8) \times 10^{-4}/\text{sec}$ in this work. Therefore, the ozone loss caused by background decay can be negligible.

2.3. Discussion

To the best of our knowledge, the rate constants of the reactions of 1-octen-3-ol, 1-nonen-3-ol and 1-nonen-4-ol presented here were obtained for the first time. O'Dwyer et al. (2010) investigated the 1-penten-3-ol reacting with O_3 using absolute rate method in two atmospheric simulation chambers at 293 ± 2 K and atmospheric pressure (O'Dwyer et al., 2010). The rate constant of 1-penten-3-ol is $(1.64 \pm 0.15) \times 10^{-17}$ cm³/(molecule·sec). The

rate constants of the reaction of O_3 with unsaturated alcohols and their analogous alkenes are listed in Table 2.

Ozonolysis rate coefficients of some unsaturated alcohols are compared with analogous alkenes (see Table 2). The kinetic rate constant of 4-methyl-1-pentene with ozone is $k_{298} = 9.37 \times 10^{-18}$ cm³/(molecule·sec) investigated by Leather et al. (2010). Comparing the rate coefficients of 1-pentene ($k_{298} = 9.98 \times 10^{-18}$ cm³/(molecule·sec)) and 4-methyl-1-pentene, it is observed that there is only a small difference between them. Therefore, we can establish that the presence of an additional CH_3 group in this configuration does not increase the electron density in the double bond significantly, and any minor decrease in rate coefficient is likely to be the result of increased steric hindrance as suggested by McGillen et al. (2008). In Table 2, the distinction of rate constants among 1-octen-3-ol, 1-nonen-3-ol and 1-penten-3-ol is insignificant; the delicate difference is likely to be the result of increased steric hindrance. However, when we compared 4-methyl-1-pentene with 1-penten-4-ol (a CH_3 group is replaced with an OH group), we noticed a significant decrease in the rate coefficient. This suggested that the presence of an OH group has an electron withdrawing effect.

Table 3 – Results of atomic charges for the C and O, calculated with the B3LYP/aug-cc-pVTZ approximation.

	C1 Charge (au)	C2 Charge (au)	O Charge (au)
1-Octen-3-ol	−0.959	−0.194	−0.634
1-Nonen-3-ol	−0.961	−0.196	−0.633
1-Nonen-4-ol	−0.949	−0.085	−0.676
1-Octene	−0.883	−0.113	–
1-Nonene	−0.885	−0.120	–

The C2 refers to the second carbon atoms from the right side of molecule structure in Table 3.

Table 4 – Atmospheric lifetimes for the unsaturated alcohols studied.

Unsaturated alcohols	$k_{O_3} \times 10^{17}$ (cm ³ /(molecule·sec))	$k_{OH} \times 10^{12}$ (cm ³ /(molecule·sec))	τ_{OH} (hr)	τ_{O_3} (hr)
1-Octen-3-ol	1.91	40.35	3.44	20.7
1-Nonen-3-ol	1.89	41.76	3.33	20.9
1-Nonen-4-ol	0.83	43.42	3.20	47.8

[O₃] = 7×10^{11} molecule/cm³ (Logan, 1985); [OH] = 2×10^6 molecule/cm³ (Hein et al., 1997).

As listed in Table 2, comparing the rate coefficients of 1-pentene, 1-penten-3-ol and 1-penten-4-ol, we deduced that the OH group in β -position has an electron donating inductive effect, while the OH group in γ -position has a net withdrawing effect with respect to an olefinic bond. The similar phenomenon was also observed between 1-octene and 1-octen-3-ol. However, interesting things came out by comparing the 1-nonen-3-ol with 1-nonen-4-ol and the 1-penten-3-ol with 1-penten-4-ol in Table 2; the rate constant of 1-penten-3-ol is almost three times as much as 1-penten-4-ol. The same phenomenon is also observed between 1-nonen-3-ol and 1-nonen-4-ol. 1-nonen-3-ol is more than twice the rate of 1-nonen-4-ol. These also indicate the OH group is electron withdrawing when it is in the gamma position. That has been observed previously in the Structure–activity relationship (SAR) of McGillen et al. (2011). The substituent factors for beta OH and gamma OH are 1.95 and 0.78 respectively, which indicates that an alkyl substitution with a beta OH is more electron supplying than an ordinary alkyl group whereas an alkyl substitution with a gamma OH is more electron withdrawing than an ordinary alkyl group.

In order to further verify the results of the above discussion, the electronegativities of the olefinic bonds of these compounds were calculated theoretically. The results obtained from atomic charges analysis are summarized in Table 3. The electronegativity of C atom in position NO.2 of 1-nonen-3-ol is obviously stronger than 1-nonen-4-ol, which indicates the OH group in γ -position has a net withdrawing effect, and the OH group has an electron donating inductive effect in the beta position with respect to an olefinic bond. The atomic charges analysis can prove what we explained above is correct. Considering the effect of substituent group on unsaturated alcohol and O₃ reaction rate constant, it is able to explain that the reaction of unsaturated alcohols with O₃ was initiated by the electrophilic addition to the double bond (Atkinson and Carter, 1984).

2.4. Atmospheric implications

The unsaturated alcohols in the atmosphere will be subject to removal by the major troposphere oxidants (OH, NO₃, O₃ and Cl atom). On the basis of rate constants obtained in this work, the atmospheric lifetimes of the unsaturated alcohols with O₃ are calculated by using the expression $\tau = 1/(k[X])$, in which the k represents the rate constants of reaction of unsaturated alcohols with the oxidant X, and [X] is the typical concentration of the oxidant X in atmosphere. We estimated the rate coefficients of three unsaturated alcohols with OH radicals using a free computer program called AOPWIN, which is part of the EPISUITE program. AOPWIN uses a similar methodology

to the well-established SAR of Kwok and Atkinson (1995). The atmospheric lifetimes of unsaturated alcohols in this work with O₃ and OH radical are listed in Table 4.

Intuitively, the lifetimes for the reactions of the unsaturated alcohols with O₃ are about 1 day to 2 days, comparing with the lifetimes of reacting with OH radical indicating that these compounds will be degraded close to their emission sources. But in high photochemical pollution area where O₃ concentration is measured up to about 4.57×10^{12} molecule/cm³ (Wang et al., 2010), the lifetime based on the O₃ reactions could turn 20.7 to 3.1 hr, 20.9 to 3.2 hr and 47.8 to 7.3 hr for 1-octen-3-ol, 1-nonen-3-ol and 1-nonen-4-ol, respectively. As shown in the Table 4, we can see that the reaction with OH may be the remove process of three unsaturated alcohols, but, in some certain circumstances, the unsaturated alcohols investigated in this work react with O₃ may serve as a competitive degradation pathway.

3. Conclusions

The rate constants of the reactions of unsaturated alcohols with O₃ were obtained using absolute methods in a 100-L FEP Teflon film bag at 298 K and atmospheric pressure. The rate constants determined in this work could be useful for increasing the kinetic database and supplying parameters in the atmospheric chemical models with the data of $(1.91 \pm 0.19) \times 10^{-17}$ cm³/(molecule·sec) for 1-octen-3-ol, $(1.89 \pm 0.20) \times 10^{-17}$ cm³/(molecule·sec) for 1-nonen-3-ol, and $(0.83 \pm 0.08) \times 10^{-17}$ cm³/(molecule·sec) for 1-nonen-4-ol, respectively. The results of experiments and calculation show that the electronic effect of the lone pair electrons of hydroxyl oxygen is the main cause of the rate difference, and the position of the substituent plays a fundamental role in the reactivity of studied unsaturated alcohols reacting with O₃.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 41571130022, 91544223, 21473009).

REFERENCES

- Atkinson, R., 2000. Atmospheric chemistry of VOCs and NOx. *Atmos. Environ.* 34, 2063–2101.
- Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* 103, 4605–4638.

- Atkinson, R., Carter, W.P., 1984. Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.* 84, 437–470.
- Atkinson, R., Aschmann, S.M., Arey, J., Shorees, B., 1992. Formation of OH radicals in the gas phase reactions of O₃ with a series of terpenes. *J. Geophys. Res.-Atmos.* 97, 6065–6073.
- Avzianova, E.V., Ariya, P.A., 2002. Temperature-dependent kinetic study for ozonolysis of selected tropospheric alkenes. *J. Chem. Kinet.* 34, 678–684.
- Bernier, U.R., Kline, D.L., Barnard, D.R., Schreck, C.E., Yost, R.A., 2000. Analysis of human skin emanations by gas chromatography/mass spectrometry. 2. Identification of volatile compounds that are candidate attractants for the yellow fever mosquito (*Aedes aegypti*). *Anal. Chem.* 72, 747–756.
- Du, L., Xu, Y.F., Ge, M.F., Jia, L., Yao, L., Wang, W.G., 2007. Rate constant of the gas phase reaction of dimethyl sulfide (CH₃SCH₃) with ozone. *Chem. Phys. Lett.* 436, 36–40.
- Finlayson-Pitts, B.J., Pitts Jr., J.N., 1999. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*. Elsevier.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D.W., et al., 2007. Changes in Atmospheric Constituents and in Radiative Forcing. *Climate Change 2007. The Physical Science Basis* (Chapter 2).
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., et al., 2003. Gaussian 03, revision B. 04; Gaussian. Gaussian, Inc., Pittsburgh.
- Fry, M., Schwarzkopf, M., Adelman, Z., West, J., 2014. Air quality and radiative forcing impacts of anthropogenic volatile organic compound emissions from ten world regions. *Atmos. Chem. Phys.* 14, 523–535.
- Gai, Y.B., Ge, M.F., Wang, W.G., 2009. Kinetic studies of O₃ reactions with 3-bromopropene and 3-iodopropene in the temperature range 288–328 K. *Atmos. Environ.* 43, 3467–3471.
- Gai, Y.B., Ge, M.F., Wang, W.G., 2011. Kinetics of the gas-phase reactions of some unsaturated alcohols with Cl atoms and O₃. *Atmos. Environ.* 45, 53–59.
- Grosjean, D., 1995. Atmospheric chemistry of biogenic hydrocarbons-relevance to the Amazon. *Quim Nova* 18, 184–201.
- Grosjean, E., Grosjean, D., 1995. Rate constants for the gas-phase reaction of C₅–C₁₀ alkenes with ozone. In: *J. Chem. Kinet.* 27, 1045–1054.
- Hein, R., Crutzen, P.J., Heimann, M., 1997. An inverse modeling approach to investigate the global atmospheric methane cycle. *Glob. Biogeochem. Cycles* 11, 43–76.
- Johnson, D., Marston, G., 2008. The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere. *Chem. Soc. Rev.* 37, 699–716.
- Kanakidou, M., Seinfeld, J., Pandis, S., Barnes, I., Dentener, F., Facchini, M., et al., 2005. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* 5, 1053–1123.
- Kwok, E.S., Atkinson, R., 1995. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update. *Atmos. Environ.* 29, 1685–1695.
- Leather, K.E., McGillen, M.R., Percival, C.J., 2010. Temperature-dependent ozonolysis kinetics of selected alkenes in the gas phase: an experimental and structure-activity relationship (SAR) study. *Phys. Chem. Chem. Phys.* 12, 2935–2943.
- Leduc, F., Tournayre, P., Kondjoyan, N., Mercier, F., Malle, P., Kol, O., Berdagué, J.L., Duflos, G., 2012. Evolution of volatile odorous compounds during the storage of European seabass (*Dicentrarchus labrax*). *Food Chem.* 131, 1304–1311.
- Lewis, A.C., Carslaw, N., Marriott, P.J., Kinghorn, R.M., Morrison, P., Lee, A.L., et al., 2000. A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature* 405, 778.
- Logan, J.A., 1985. Tropospheric ozone: seasonal behavior, trends, and anthropogenic influence. *J. Geophys. Res.-Atmos.* 90, 10463–10482.
- Maggi, F., Papa, F., Cristalli, G., Sagratini, G., Vittori, S., 2010. Characterisation of the mushroom-like flavour of *Melittis melissophyllum* L. subsp. *melissophyllum* by headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography (GC-FID) and gas chromatography-mass spectrometry (GC-MS). *Food Chem.* 123, 983–992.
- Mau, J.-L., Beelman, R.O.B., Ziegler, G.R.R., 1992. 1-Octen-3-ol in the cultivated mushroom, *Agaricus bisporus*. *J. Food Sci.* 57, 704–706.
- Mau, J.-L., Chyau, C.-C., Li, J.-Y., Tseng, Y.-H., 1997. Flavor compounds in straw mushrooms *Volvariella volvacea* harvested at different stages of maturity. *J. Agric. Food Chem.* 45, 4726–4729.
- McGillen, M.R., Carey, T.J., Archibald, A.T., Wenger, J.C., Shallcross, D.E., Percival, C.J., 2008. Structure-activity relationship (SAR) for the gas-phase ozonolysis of aliphatic alkenes and dialkenes. *Phys. Chem. Chem. Phys.* 10, 1757–1768.
- McGillen, M.R., Archibald, A.T., Carey, T., Leather, K.E., Shallcross, D.E., Wenger, J.C., et al., 2011. Structure-activity relationship (SAR) for the prediction of gas-phase ozonolysis rate coefficients: an extension towards heteroatomic unsaturated species. *Phys. Chem. Chem. Phys.* 13, 2842–2849.
- Mellouki, A., Wallington, T., Chen, J., 2015. Atmospheric chemistry of oxygenated volatile organic compounds: impacts on air quality and climate. *Chem. Rev.* 115, 3984–4014.
- Ni, Z., Liu, J., Song, M., Wang, X., Ren, L., Kong, X., 2015. Characterization of odorous charge and photochemical reactivity of VOC emissions from a full-scale food waste treatment plant in China. *J. Environ. Sci.* 29, 34–44.
- O'Dwyer, M.A., Carey, T., Healy, R., Wenger, J., Picquet-Varrault, B., Doussin, J., 2010. The gas-phase ozonolysis of 1-penten-3-ol, (Z)-2-penten-1-ol and 1-penten-3-one: kinetics, products and secondary organic aerosol formation. *Z. Phys. Chem.* 224, 1059–1080.
- Protczak, A., Trzeczczynski, J., 2002. Studies on reactions of ozone with alkenes. *Environ. Sci. Pollut. Res. Int.* 9, 377–380.
- Ramoni, R., Vincent, F., Grolli, S., Conti, V., Malosse, C., Boyer, F.-D., et al., 2001. The insect attractant 1-octen-3-ol is the natural ligand of bovine odorant-binding protein. *J. Biol. Chem.* 276, 7150–7155.
- Scott, C., Rap, A., Spracklen, D., Forster, P., Carslaw, K., Mann, G., et al., 2014. The direct and indirect radiative effects of biogenic secondary organic aerosol. *Atmos. Chem. Phys.* 14, 447–470.
- Tian, P., Fu, X., Zhuang, P., Bai, J., Chen, F., 2010. Analysis on volatile oil from *Rhododendron calophyllum* Franch by GC-MS. *Chin. J. Appl. Environ. Biol.* 16, 734–737.
- Tian, X.M., Feng, L.I., Huang, S.J., Liu, J.H., Huo, X., 2013. GC-MS analysis of volatile constituents of *Cynanchum stauntonii*. *Chin. J. Exp. Tradit. Med. Form.* 19, 111–113.
- Venkateshwarlu, G., Chandravadana, M., Tewari, R., 1999. Volatile flavour components of some edible mushrooms (*Basidiomycetes*). *Flavour Fragr. J.* 14, 191–194.
- Wang, T., Nie, W., Gao, J., Xue, L., Gao, X., Wang, X., et al., 2010. Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact. *Atmos. Chem. Phys.* 10, 7603–7615.
- Wang, Y., Shen, L., Wu, S., Mickley, L., He, J., Hao, J., 2013. Sensitivity of surface ozone over China to 2000–2050 global changes of climate and emissions. *Atmos. Environ.* 75, 374–382.
- Wang, T., Xue, L., Brimblecombe, P., Lam, Y.F., Li, L., Zhang, L., 2017. Ozone pollution in China: a review of concentrations,

- meteorological influences, chemical precursors, and effects. *Sci. Total Environ.* 575, 1582–1596.
- Wilson, R.A., Butler, J.F., Withycombe, D., Mookherjee, B.D., Katz, I., Schrankel, K.R., 1987. Use of 1-nonen-3-ol for repelling insects. US, US 4693890 A.
- Wu, W.J., Zhao, B., Wang, S.X., Hao, J.M., 2017. Ozone and secondary organic aerosol formation potential from anthropogenic volatile organic compounds emissions in China. *J. Environ. Sci.* 53, 224–237.
- Wurzenberger, M., Grosch, W., 1984. The formation of 1-octen-3-ol from the 10-hydroperoxide isomer of linoleic acid by a hydroperoxide lyase in mushrooms (*Psalliota bispora*). *Biochim. Biophys. Acta, Lipids Lipid Metab.* 794, 25–30.
- Yang, H.B., Li, X.X., Yu, D.G., Luo, L.j., 2010. Chemical constituents of volatile oils from the inflorescence of *Capillipedium parviflorum*(R.Br.) Stapf in Hainan determined with GC-MS. *Chin. J. Trop. Crop.* 31, 1845–1848.