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# Kinetics of the gas-phase reaction between ozone and three unsaturated oxygenated compounds: Ethyl 3,3-dimethyl acrylate, 2-methyl-2-pentenal and 6-methyl-5-hepten-2-one at atmospheric pressure

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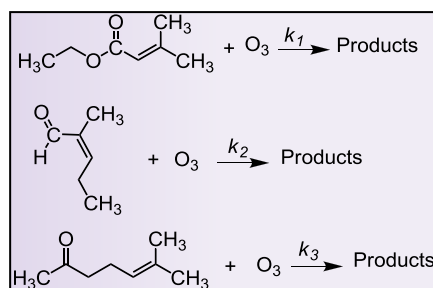
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## HIGHLIGHTS

- Kinetic study of O<sub>3</sub> with different unsaturated carbonyl VOCs by *in situ* FTIR.
- Rate coefficients increase with increasing methyl substituent at the double bond of the VOC.
- Reactivity towards O<sub>3</sub> correlates with HOMO energies of unsaturated compounds.
- Short lifetimes, in the order of minutes and hours, for O<sub>3</sub> reactions in urban regions.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Rate coefficients for the gas-phase reactions of O<sub>3</sub> molecules with three unsaturated oxygenated compounds have been determined using the relative kinetic technique in an environmental chamber with FTIR detection of the reactants at (298 ± 2) K in 760 Torr total pressure of synthetic air. The following rate coefficients (in units of 10<sup>-17</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were determined: ethyl 3,3-dimethyl acrylate (0.82 ± 0.19), 2-methyl-2-pentenal (0.71 ± 0.16) and 6-methyl-5-hepten-2-one (26 ± 7).

The different reactivity of the unsaturated oxygenated compounds toward O<sub>3</sub> is discussed in terms of their chemical structure. In addition, a correlation between the reactivity of structurally different unsaturated compounds (alkenes and unsaturated oxygenated VOCs, such as ethers, esters, aldehydes, ketones and alcohols) toward O<sub>3</sub> molecules and the HOMO (Highest Occupied Molecular Orbital) of the compounds is presented.

Using the kinetic parameters determined in this work, residence times of these unsaturated compounds in the atmosphere with respect to reaction with O<sub>3</sub> have been calculated. In urban and rural areas the main sink of 6-methyl-5-hepten-2-one is reaction with O<sub>3</sub> molecules with a residence time in the order of few minutes.

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## 1. Introduction

Oxygenated volatile organic compounds (OVOCs) are emitted into the atmosphere from anthropogenic and biogenic sources. Once in the atmosphere they will be subject to degradation by photolysis and/or reactions with oxidants such as OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub> molecules (Finlayson-Pitts and Pitts, 2000).

The compounds of interest in this study, ethyl 3,3-dimethylacrylate (CH<sub>3</sub>C(CH<sub>3</sub>)=CHC(O)OCH<sub>2</sub>CH<sub>3</sub>, EDMA) and 2-methyl-2-pentenal (CH<sub>3</sub>CH<sub>2</sub>CH=C(CH<sub>3</sub>)C(O)H, 2-MP) are widely used in the industry as flavouring agents (European Food Safety Authority Journal 2009, 2010) and 6-methyl-5-hepten-2-one (CH<sub>3</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>, 6-MHO) is released into the atmosphere mainly by vegetation (Grosjean et al., 1996), (biogenic sources: birch and oak) (König et al., 1995; Fruekilde et al., 1998).

The reaction of unsaturated compounds with O<sub>3</sub> molecule proceeds by electrophilic addition of O<sub>3</sub> to the double bond in the compounds leading to the formation of carbonyl products (Grosjean et al., 1993). The ozonolysis reaction can be an important homogeneous loss process for unsaturated oxygenated VOCs especially in highly polluted areas (Sato et al., 2004; Gai et al., 2009; Bernard et al., 2010; Wang et al., 2010). Recent studies on the ozonolysis of unsaturated and oxygenated organic compounds have pointed out that the reactivity of O<sub>3</sub> toward unsaturated compounds is affected by the presence of oxo groups such as esters, aldehydes, ketones and the presence of alkyl groups on the double bond (Bernard et al., 2010).

We report in this study the determination of rate coefficients for the reactions of ethyl 3,3-dimethylacrylate, 2-methyl-2-pentenal and 6-methyl-5-hepten-2-one with O<sub>3</sub> molecules at room temperature and atmospheric pressure using the relative kinetic method and employing different reference compounds:



There are no available kinetic data in literature for the reactions of O<sub>3</sub> with ethyl 3,3-dimethyl acrylate ( $k_1$ ) and 2-methyl-2-pentenal ( $k_2$ ). Therefore, this work provides the first kinetic study for reactions 1 and 2. The rate coefficient for the reaction of ozone with 6-methyl-5-hepten-2-one reaction ( $k_3$ ) has been reported previously by Grosjean et al. (1996) and Smith et al. (1996).

Grosjean et al. (1996) studied the kinetics of reaction (3) in a 3.7 m<sup>3</sup> Teflon collapsible chamber at atmospheric pressure and ambient temperature (286–291) K. The investigations were performed under pseudo-first order conditions with the organic in excess and the concentration-time behaviour of O<sub>3</sub> was monitored by ultraviolet photometry. Smith et al. (1996) studied the kinetics of reaction (3) at (296 ± 2) K and 740 Torr total pressure of purified air using a relative method. They performed the measurements in a 6700 L Teflon chamber using GC-FID to monitor the organic reactants.

The kinetic results presented here are discussed in terms of the effect of the position of the methyl substituent and also the functional group to the double bond on the reactivity of the compounds toward O<sub>3</sub>. In addition, a correlation between the HOMO (Highest Occupied Molecular Orbital) energies of different unsaturated compounds and the natural logarithm of the corresponding O<sub>3</sub> rate coefficient is examined. Finally, the relevance of ozonolysis as an atmospheric sink of the carbonyl unsaturated compounds studied is considered.

## 2. Experimental section

The experiments were performed in 480 L and 1080 L chambers at (298 ± 2) K in 760 Torr of synthetic air. The 480 L chamber consists of a cylindrical borosilicate glass vessel (3 m in length and 45 cm inner diameter) closed at both ends by aluminium flanges. The 1080 L reactor consists of two cylindrical quartz glass vessels, each 3 m in length and 45 cm inner diameter, joined in the middle with both opened ends closed by aluminium flanges. The metal flanges in both reactors contain ports for the introduction of bath gases and reactants into the chambers. Magnetically coupled Teflon mixing fans are mounted inside the chambers to ensure homogeneous mixing of the reactants. The reactors can be evacuated by pumping systems, consisting of a turbomolecular pump backed by a double stage rotary fore pump, to 10<sup>−3</sup> Torr.

A White-type mirror system is mounted internally in both chambers and coupled to a FTIR spectrometer, a Thermo Nicolet 6700 in the case of the 480 L reactor and a Thermo Nicolet Nexus Erho in the case of the 1080 L reactor. Each spectrometer is equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector which enables “*in situ*” monitoring of the reactants in the infrared range 4000–700 cm<sup>−1</sup>. The “White” mirror system in the 480 L chamber was operated with the total optical absorption path length set to 48.11 m and the 1080 L reactor with the path length set to 484.7 m. Infrared spectra were recorded with a spectral resolution of 1 cm<sup>−1</sup>. Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 min and 15 such spectra were recorded per experiment. The chambers are described in greater detail elsewhere (Barnes et al., 1993, 1994).

An electrical discharge in a flow of pure oxygen was used to generate ozone and it was added stepwise to mixtures containing the unsaturated compound and reference compound.

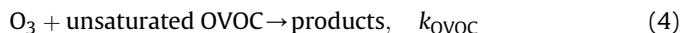
The initial concentrations of reactants in ppmV (1 ppmV = 2.46 × 10<sup>13</sup> molecule cm<sup>−3</sup> at 298 K) were: ethyl 3,3-dimethylacrylate, (1–3); 2-methyl-2-pentenal, (5–8); 6-methyl-5-hepten-2-one, (2–5); ozone, (1–2); isobutene, (7–9) and 1,3-butadiene (5–8), *trans*-2-butene (2–4) and  $\alpha$ -pinene (1–2). The reactants were monitored at the following infrared absorption frequencies (in cm<sup>−1</sup>): ethyl 3,3-dimethylacrylate at 1183; 2-methyl-2-pentenal at 2983; 6-methyl-5-hepten-2-one at 2928; isobutene at 890; 1,3-butadiene at 908; *trans*-2-butene at 900–1017 and  $\alpha$ -pinene at 2800–3070.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), ethyl 3,3-dimethylacrylate (Aldrich, 98%), 2-methyl-2-pentenal (Aldrich, 97%), 6-methyl-5-hepten-2-one (Aldrich, 99%), isobutene (Messer Griesheim, 99%), 1,3-butadiene (Aldrich, 99 + %), *trans*-2-butene (Messer Griesheim, 99%), and  $\alpha$ -pinene (Aldrich, 98%).

## 3. Results and discussion

The relative rate method was used to determine the rate coefficients for the reactions of O<sub>3</sub> molecules with ethyl 3,3-

dimethylacrylate, 2-methyl-2-pentenal and 6-methyl-5-hepten-2-one using 1,3-butadiene, isobutene, *trans*-2-butene and  $\alpha$ -pinene as reference hydrocarbons.



Assuming that the reference compounds and the studied OVOCs are lost only by reactions (4) and (5), it can be shown that:

$$\ln \left\{ \frac{[\text{OVOC}]_0}{[\text{OVOC}]_t} \right\} = \frac{k_4}{k_5} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (1)$$

where  $[\text{OVOC}]_0$ ,  $[\text{reference}]_0$ ,  $[\text{OVOC}]_t$  and  $[\text{reference}]_t$  are the concentrations of the unsaturated and oxygenated volatile organic compound of interest and the reference compound at times  $t = 0$  and  $t$ , respectively, and  $k_4$  and  $k_5$  are the rate coefficients of reactions (4) and (5), respectively. Loss of both the unsaturated oxygenated organics and reference compounds through deposition on the reactor surface were found to be negligible under the experimental conditions.

Figs. 1–3 show the kinetic data obtained from experiments on the reactions of  $\text{O}_3$  molecules with the unsaturated OVOCs plotted according to the equation (1). Each plot represents 3 experiments for each reference compound. Reasonable linear relationships (with  $r^2 > 0.99$ ) with zero or near-zero intercepts were obtained in all cases implying that interferences due to secondary reactions in the experimental systems were negligible.

The  $k_{\text{OVOC}}/k_{\text{reference}}$  ratios determined from the slopes of the straight-line plots in Figs. 1–3 are listed in Table 1 together with the number of experiments performed, and the absolute values of the rate coefficients,  $k_{\text{OVOC}}$ , calculated from the  $k_{\text{OVOC}}/k_{\text{reference}}$  ratios. The following room temperature rate coefficients were used for the reactions of  $\text{O}_3$  with the reference compounds: isobutene =  $(1.13 \pm 0.12) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Calvert et al., 2000), 1,3-butadiene =  $(6.3 \pm 1.3) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Calvert et al., 2000), *trans*-2-butene =  $(2.38 \pm 0.15) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Wegener et al., 2007) and  $\alpha$ -pinene =  $(8.4 \pm 1.9) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson et al.,

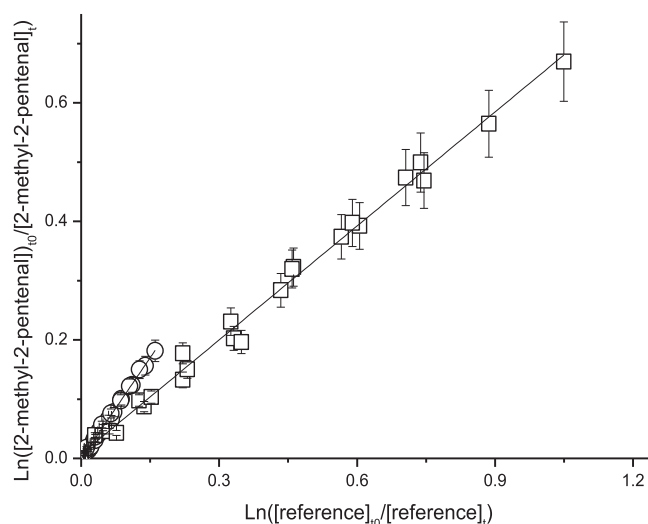


Fig. 2. Plot of the kinetic data for the reaction of  $\text{O}_3$  molecules with 2-methyl-2-pentenal measured relative to isobutene ( $\square$ ) and 1,3-butadiene ( $\circ$ ) at  $298 \pm 2 \text{ K}$  and atmospheric pressure of air.

1982). The errors for the  $k_{\text{OVOC}}/k_{\text{reference}}$  ratios given in Table 1 are the  $2\sigma$  statistical errors from the scatter in the plots shown in Figs. 1 to 3. The errors quoted for  $k_{\text{OVOC}}$  are a combination of the  $2\sigma$  statistical errors from the linear regression analysis plus an additional error from the uncertainties in the recommended reference values of the rate coefficients for the reference reactions.

Since for all of the compounds investigated there is good agreement between the values of the ozonolysis rate coefficient determined using two different reference compounds, we choose to quote final values for the rate coefficients at 298 K which are an average of the all the individual values with errors which encompass the extremes of all the determinations:

$$k_1 = (8.3 \pm 1.9) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

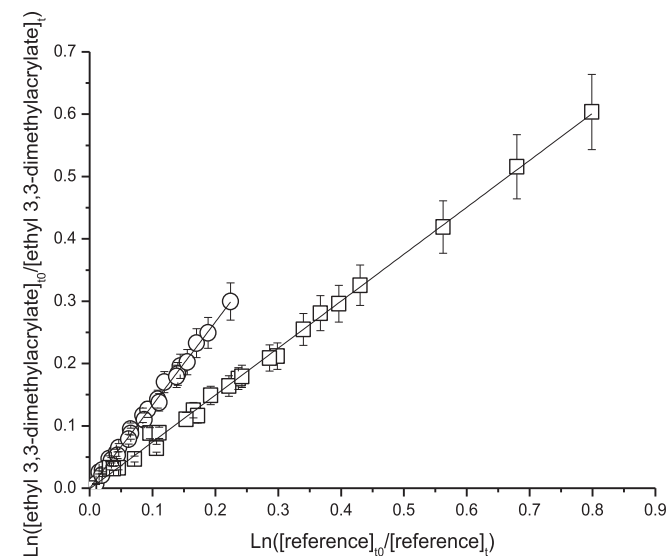


Fig. 1. Plot of the kinetic data for the reaction of  $\text{O}_3$  molecules with ethyl 3,3-dimethylacrylate measured relative to isobutene ( $\square$ ) and 1,3-butadiene ( $\circ$ ) at  $298 \pm 2 \text{ K}$  and atmospheric pressure of air.

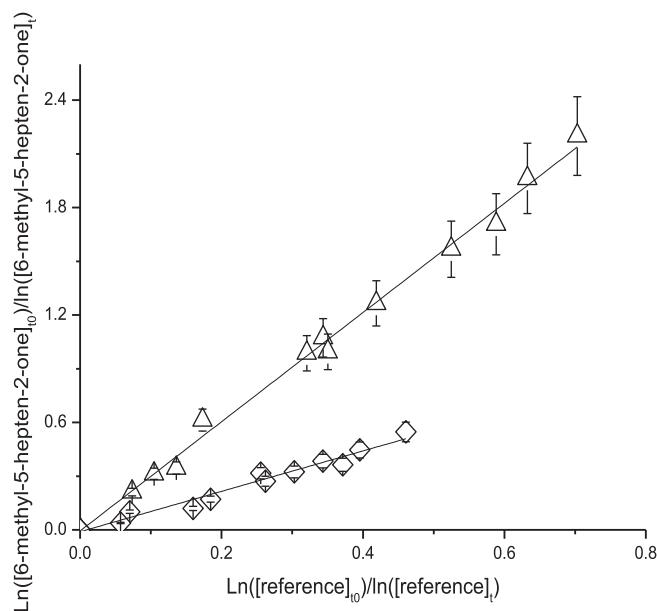


Fig. 3. Plot of the kinetic data for the reaction of  $\text{O}_3$  molecules with 6-methyl-5-hepten-2-one measured relative to  $\alpha$ -pinene ( $\Delta$ ) and *trans*-2-butene ( $\diamond$ ) at  $298 \pm 2 \text{ K}$  and atmospheric pressure of air.

**Table 1**

Rate coefficient ratios  $k_{\text{OVOC}}/k_{\text{reference}}$  and rate coefficients for the reactions of ozone with ethyl 3,3-dimethylacrylate, 2-methyl-2-pentenal and 6-methyl-5-hepten-2-one at  $(298 \pm 2)$  K in  $760 \pm 10$  Torr of air.

	Reference	$k_{\text{OVOC}}/k_{\text{Reference}}$	$k_{\text{OVOC}}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3 + \text{O}_3$ Ethyl 3,3-dimethylacrylate	isobutene	$0.75 \pm 0.01$	$(8.3 \pm 1.0) \times 10^{-18}$
	isobutene	$0.74 \pm 0.02$	$(8.2 \pm 1.1) \times 10^{-18}$
	isobutene	$0.75 \pm 0.04$	$(8.3 \pm 1.4) \times 10^{-18}$
	1,3-butadiene	$1.33 \pm 0.02$	$(8.3 \pm 1.8) \times 10^{-18}$
	1,3-butadiene	$1.33 \pm 0.03$	$(8.3 \pm 1.9) \times 10^{-18}$
	1,3-butadiene	$1.31 \pm 0.02$	$(8.2 \pm 1.8) \times 10^{-18}$
	Average		$(8.3 \pm 1.9) \times 10^{-18}$
$\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{COH} + \text{O}_3$ 2-methyl-2-pentenal	isobutene	$0.64 \pm 0.02$	$(7.1 \pm 1.0) \times 10^{-18}$
	isobutene	$0.65 \pm 0.02$	$(7.2 \pm 1.0) \times 10^{-18}$
	isobutene	$0.65 \pm 0.02$	$(7.2 \pm 1.0) \times 10^{-18}$
	1,3-butadiene	$1.14 \pm 0.03$	$(7.1 \pm 1.6) \times 10^{-18}$
	1,3-butadiene	$1.12 \pm 0.03$	$(7.0 \pm 1.6) \times 10^{-18}$
	1,3-butadiene	$1.13 \pm 0.02$	$(7.1 \pm 1.5) \times 10^{-18}$
	Average		$(7.1 \pm 1.6) \times 10^{-18}$
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3 + \text{O}_3$ 6-methyl-5-hepten-2-one	<i>trans</i> -2-butene	$1.11 \pm 0.05$	$(2.6 \pm 0.3) \times 10^{-16}$
	<i>trans</i> -2-butene	$1.02 \pm 0.07$	$(2.4 \pm 0.3) \times 10^{-16}$
	<i>trans</i> -2-butene	$1.19 \pm 0.09$	$(2.8 \pm 0.4) \times 10^{-16}$
	$\alpha$ -pinene	$3.07 \pm 0.08$	$(2.6 \pm 0.7) \times 10^{-16}$
	$\alpha$ -pinene	$2.92 \pm 0.06$	$(2.5 \pm 0.6) \times 10^{-16}$
	$\alpha$ -pinene	$3.09 \pm 0.03$	$(2.6 \pm 0.6) \times 10^{-16}$
	Average		$(2.6 \pm 0.7) \times 10^{-16}$

$$k_2 = (7.1 \pm 1.6) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (2.6 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

It is known that the ozonolysis of alkenes produces OH radicals. In relative kinetic studies of the type presented here an OH radical scavenger such as an organic compound or CO is added to the system to minimize any interference by OH. The rate coefficients for the reactions of the compounds under investigation in this study are very high thus in order to effectively scavenge any OH radicals formed very high concentrations of a scavenger would need to be added. Such high concentrations of the scavenger in the reaction system would unfortunately render monitoring of the reactants in the infrared impossible and thus the experiments were performed without a scavenger. We argue here, however, that the effect of any OH produced in the system cannot be very large. We obtain excellent agreement for the rate coefficients for the reactions of  $\text{O}_3$  with the compounds using reference compound combinations where the  $\text{O}_3$  rate coefficients differ by factors of approximately 2 and 3. Since the reference compounds and also the compounds under investigation generally have quite similar OH rate coefficients any significant interference by OH should have resulted in significant differences in the  $\text{O}_3$  rate coefficients for the compound under investigation. Even for 6-methyl-5-hepten-2-one, which has a much higher OH rate coefficient than any of the other hydrocarbons used in the study, reasonable agreement is obtained with previous studies in the literature (see below). Therefore, since all of the hydrocarbons in the system will react with OH it would appear that in the systems investigated any interference by OH that might possibly be occurring is largely self-compensating.

### 3.1. Comparison with literature

To the best of our knowledge, there are no previously reported values of the rate coefficients for the ozonolysis reactions of ethyl 3,3-dimethylacrylate and 2-methyl-2-pentenal. The rate coefficient  $k_3 = (2.6 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained in this study for the reaction of  $\text{O}_3$  molecules with 6-methyl-5-hepten-2-one is 1.5 times lower than the value determined experimentally by Smith et al. (1996) of  $(3.9 \pm 1.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  relative to 2-methyl-2-butene in a 6700 L Teflon chamber at  $(296 \pm 2)$  K and 740

Torr of synthetic air using CG-FID for the analysis. The value is, however, in agreement with the value of Smith et al. (1996) within the combined experimental errors. Grosjean et al. (1996) have been reported a value of  $k_3 = (3.94 \pm 0.40) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained in a collapsible Teflon chamber under pseudo-first order conditions. The value of Grosjean et al. (1996) agrees well with the value reported by Smith et al. (1996) and is marginally outside the error limits of this study. Since rate coefficients for ozonolysis reactions are difficult to measure with a high degree of accuracy because of the slow rates of the reactions we consider the agreement between this study and the other determinations satisfactory. In addition, our relative kinetic study is the only study where the decay of the reactants was measured directly *in situ* which eliminates potential errors in sampling and absolute concentration determinations.

We can compare the experimental value of  $k_1 = (0.83 \pm 0.19) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained in this work for the reaction of  $\text{O}_3$  with ethyl-3,3-dimethylacrylate with the value estimated using the Structure Activity Relationship (SAR) method developed by Pfrang et al. (2007). The SAR predicts a value of  $1.18 \times 10^{-17} \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{O}_3$  with ethyl-3,3-dimethyl acrylate which is 42% higher than the value determined in this work. In the case of 6-methyl-5-hepten-2-one, the group-reactivity factor  $-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$  with  $\text{O}_3$  molecules could not be estimated through the SAR method. Therefore, direct comparison cannot be made for the reaction 3. In the same way, it was not possible to estimate the rate coefficient for the reaction 2 ( $\text{O}_3 + 2$ -methyl-2-pentenal).

### 3.2. Reactivity trends

In the reactions of  $\text{O}_3$  with ethyl 3,3-dimethylacrylate and 2-methyl-2-pentenal, the replacement of a  $-\text{CH}_3$  group on the double bond by an  $-\text{H}$  atom leads to a decrease in the ozonolysis rate coefficient, i.e.  $k_{(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3} = 8.3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this work)  $> k_{\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3} = 1.3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Bernard et al., 2010) and  $(k_{\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{H}} = 7.1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this work)  $> k_{\text{CH}_3\text{CH}_2\text{CH}=\text{CHC}(\text{O})\text{H}} = 1.59 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (Sato et al., 2004). This effect is attributed to the positive inductive effect of the  $\text{CH}_3$  group donating electron density to the  $\pi$  electrons

of the double bond and thus enhancing the electrophilic addition of  $O_3$  molecule to the double bond. The same effect is observed for the reactions OH radicals with unsaturated compounds (Blanco et al., 2009; Jiménez et al., 2009; Teruel et al., 2012). However, when one compares the ozonolysis rate coefficients for ethyl-3,3-dimethyl acrylate and ethyl crotonate,  $k_{\text{ethyl 3,3-dimethyl acrylate}} = 8.3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this work) and  $k_{\text{ethyl crotonate}} = 8.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Gaona Colmán et al., 2013), no significant difference between the rate coefficients is observed. The presence of  $-CH_3$  on the  $\beta$ -carbon group in ethyl 3,3-dimethylacrylate suggests that steric hindrance may be important in the reaction. This is possibly also the reason for the small difference observed between the ozonolysis rate coefficients for 3-methyl-2-butenal ( $CH_3(CH_3)C=CHC(O)H$  and crotonaldehyde ( $CH_3CH=CHC(O)H$ ), i.e.  $k_{\text{3-methyl-2-butenal}} = 1.82 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sato et al., 2004) and  $k_{\text{crotonaldehyde}} = 1.58 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sato et al., 2004).

### 3.3. Free energy relationship

The reactivity of different kinds of electrophiles such as O atoms, OH and  $NO_3$  radicals and  $O_3$  molecules toward alkenes, methyl-substituted alkenes and unsaturated oxygenated VOCs has been found to correlate with the ionization potential (IP) or the energy of the highest occupied molecular orbital (HOMO) of the unsaturated VOC from the Frontier Molecular Orbital Theory (FMOT) (Fleming, 1976; Wayne et al., 1991; Atkinson, 1997; Baumgartner et al., 2002; Blanco et al., 2012). The correlation between the rate coefficients and  $E_{\text{HOMO}}$  for the reactions of the saturated and unsaturated VOCs with the electrophiles is presented in the literature (Marston et al., 1999) in the form:

$$\ln k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = aE_{\text{HOMO}} + b \quad (\text{II})$$

Thus, the use of the rate coefficients determined in this work together with those for other different kinds of alkenes and unsaturated oxygenated VOCs reported in the literature enables a

**Table 2**

Rate coefficients of the reactions of  $O_3$  molecules with different unsaturated VOCs and HOMO energies for the corresponding VOCs.

VOC	$E_{\text{HOMO}}$ (eV)	$k_{O_3}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
1 $CH_2=CHO(CH_2)_3CH_3$	9.5985	$2.59 \times 10^{-16a}$
2 $CH_2=CHOCH_2CH_3$	9.5707	$2 \times 10^{-16a}$
3 $CH_3C(CH_3)=CHCH_2CH_2C(O)CH_3$	9.0665	$2.6 \times 10^{-16b}$
4 $CH_3C(CH_3)=CHC(O)OCH_2CH_3$	9.9324	$8.3 \times 10^{-18b}$
5 $CH_3CH_2CH=C(CH_3)C(O)H$	9.8812	$7.1 \times 10^{-18b}$
6 $CH_3CH_2C(O)OCH=CH_2$	9.9324	$5.3 \times 10^{-18c}$
7 $CH_2=CHCH_3$	10.105	$1.06 \times 10^{-17a}$
8 $CH_2=CHCH_2OH$	10.3632	$1.80 \times 10^{-17a}$
9 $CH_3CH=CHC(O)OCH_2CH_3$	10.2762	$8 \times 10^{-18c}$
10 $CH_3CH=CHC(O)OCH_3$	10.2862	$4.38 \times 10^{-18a}$
11 $CH_2=C(CH_3)C(O)O(CH_2)_3CH_3$	10.5328	$1 \times 10^{-17c}$
12 $CH_2=C(CH_3)C(O)OCH_2CH_3$	10.5258	$7.68 \times 10^{-18d}$
13 $CH_2=C(CH_3)C(O)OCH_3$	10.561	$6.7 \times 10^{-18e}$
14 $CH_2=CHC(O)CH_3$	10.7266	$5.4 \times 10^{-18a}$
15 $CH_2=CHOC(O)CH_3$	10.64	$3 \times 10^{-18f}$
16 $CH_2=CHC(O)O(CH_2)_3CH_3$	11.0441	$2.40 \times 10^{-18d}$
17 $CH_2=CHC(O)OCH_2CH_3$	11.0401	$1.30 \times 10^{-18e}$
18 $CH_2=CHC(O)OCH_3$	11.0667	$9.5 \times 10^{-19e}$
19 $CH_2=CHC(O)OH$	11.1457	$6.51 \times 10^{-19a}$
20 $CH_2=CHC(O)H$	10.6936	$3.01 \times 10^{-19a}$

<sup>a</sup> NIST-Chemical Kinetics Data Base on the Web.

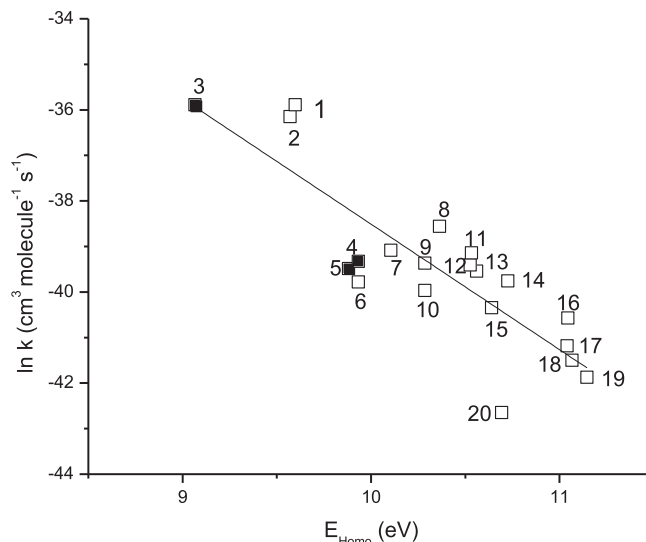
<sup>b</sup> This work.

<sup>c</sup> Gaona Colmán et al., 2013.

<sup>d</sup> Gai et al., 2009.

<sup>e</sup> Bernard et al., 2010 and.

<sup>f</sup> Picquet-Varrault et al., 2010.



**Fig. 4.** Correlation plot of  $\ln(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  versus calculated  $E_{\text{HOMO}}$  for the reactions of  $O_3$  molecules with unsaturated VOCs. Filled squares are the VOCs reported in this work and the open squares are the different VOCs (alkenes, esters, aldehydes, ketones, alcohols, and acids) reported in literature (<http://kinetics.nist.gov/kinetics/index.jsp>).

relationship with  $E_{\text{HOMO}}$  to be proposed for the reactions of  $O_3$  with unsaturated VOCs (alkenes and oxygenated VOCs).

The HOMO energies for the alkenes and unsaturated oxygenated VOCs (ethers, esters, aldehydes, ketones and alcohols) listed in Table 2 were calculated using the Gaussian 03 package. The geometry optimizations and initial values of energies were obtained at the Hartree-Fock (HF) level, and an ab initio Hamiltonian with a 6-31++ G (d, p) bases set was used. The correlation between  $\ln k$  and  $E_{\text{HOMO}}$  is shown graphically in Fig. 4. The best linear fit to the points in Fig. 4 is given by:

$$\ln k_{O_3} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -(10.96 \pm 2.16) E_{\text{HOMO}} - (2.76 \pm 0.28) \quad (\text{III})$$

With a correlation coefficient of ( $r$ ) = 0.97.

The relatively good quality of this correlation should allow reasonable estimations to be made of rate coefficients for reactions which have not yet been investigated.

### 3.4. Atmospheric implications

The rate coefficients summarized in Table 1 can be used to calculate atmospheric lifetimes for the unsaturated compounds due to reaction with  $O_3$ . Lifetimes have been calculated using the expression:  $\tau_x = 1/k_x[X]$  with  $X = O_3$  where  $k_x$  is the rate coefficient for the reaction of the oxidant X with the unsaturated compounds studied and  $[X]$  is the atmospheric concentration of the oxidant. For the calculations, the following  $O_3$  concentrations have been used: typical concentration for remote areas  $[O_3] = 7 \times 10^{11} \text{ molecule cm}^{-3}$  (Logan, 1985); concentration for rural areas  $[O_3] = 2.09 \times 10^{12} \text{ molecule cm}^{-3}$  (Seinfeld and Pandis, 1998); concentration for urban areas  $[O_3] = 6.15 \times 10^{12} \text{ molecule cm}^{-3}$  (Seinfeld and Pandis, 1998). The estimated tropospheric lifetimes at room temperature of the unsaturated compounds with respect to reaction with different tropospheric concentration levels of  $O_3$  are presented in Table 3.

The short lifetimes for the unsaturated compounds in rural and urban areas in the range of just over a day to a few hours, implies



**Table 3**

Estimated tropospheric lifetimes for the unsaturated compounds studied in this work with respect to their reactions with O<sub>3</sub> at 298 K.

Unsaturated compound	Remote O <sub>3</sub> <sup>a</sup>	Rural O <sub>3</sub> <sup>a</sup>	Urban O <sub>3</sub> <sup>a</sup>
CH <sub>3</sub> C(CH <sub>3</sub> )=CHC(O)OCH <sub>2</sub> CH <sub>3</sub> Ethyl 3,3-dimethylacrylate	48 h	16 h	5 h
CH <sub>3</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )COH 2-methyl-2-pentenal	56 h	19 h	6 h
CH <sub>3</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> CH <sub>2</sub> C(O)CH <sub>3</sub> 6-methyl-5-hepten-2-one	1.5 h	31 min	10 min

<sup>a</sup> In the calculations the following ozone concentrations have been used (in units of molecule cm<sup>-3</sup>): remote  $7.00 \times 10^{11}$  (Logan, 1985), rural  $2.09 \times 10^{12}$  (Seinfeld and Pandis, 1998) and urban  $6.15 \times 10^{12}$  (Seinfeld and Pandis, 1998).

that any of the unsaturated VOCs emitted in these areas are likely to be removed rapidly in the gas phase close to their source of emission. In polluted areas, where high peak concentrations of O<sub>3</sub> molecules can occur, loss of the compounds through ozonolysis could be more important or comparable to their loss through reaction with OH radicals. The lifetime for 6-methyl-5-hepten-2-one with OH radicals at 296 K, where  $k_{OH} = (1.57 \pm 0.39) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Smith et al., 1996), is 53 min using a OH atmospheric concentration of  $2.00 \times 10^6$  radical cm<sup>-3</sup> (Hein et al., 1997) implying that the unsaturated ketone: 6-methyl-5-hepten-2-one will be mainly degraded by O<sub>3</sub> molecules in rural and urban areas rather than by OH-radical initiated degradation. Unfortunately, rate coefficients data for the reaction of OH with ethyl 3,3-dimethylacrylate and 2-methyl-2-pentenal are not available in literature and direct comparison between both sinks (O<sub>3</sub> and OH) can not be made.

The O<sub>3</sub> initiated atmospheric degradation of the studied oxygenated compounds in polluted areas is expected to result in the formation of carbonyl compounds which will be subject to further reaction with oxidants like OH radicals and also photolysis.

In separate experiments, 4-oxopentanal, acetone and formaldehyde were identified as reaction products of 6-methyl-5-hepten-2-one + O<sub>3</sub> system. On the other hand, methyl glyoxal, formaldehyde and propanal were observed in the reaction of 2-methyl-2-pentenal + O<sub>3</sub> molecules. For the reaction of O<sub>3</sub> + ethyl 3,3-dimethylacrylate acetone and ethyl glyoxyal were observed together with formaldehyde. Products yields are still in analysis.

The high reactivity of these studied compounds and also their primary products imply they will be important contributors to the photochemical smog formation and secondary organic aerosol formation (SOA) in urban areas.

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