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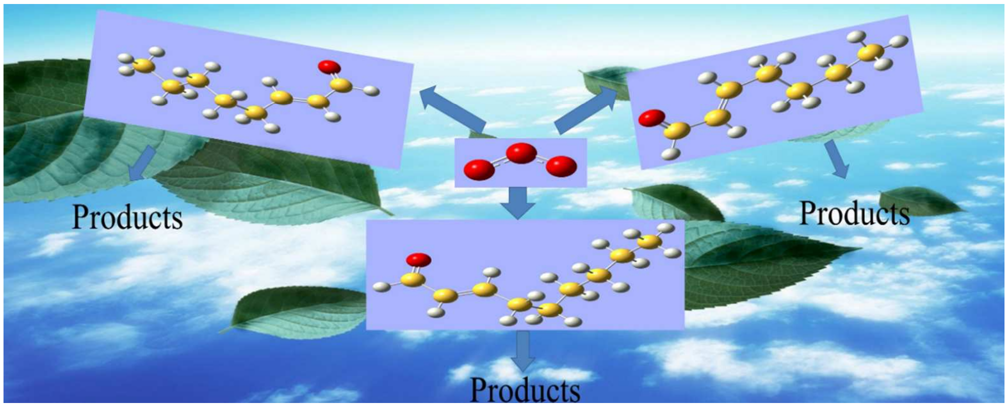

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Ozonolysis of a series of C7-C9 unsaturated biogenic aldehydes: reactivity study at atmospheric pressure

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Abstract

Rate coefficients for the reactions of ozone with the biogenic aldehydes *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal have been determined at 298 K and (990 ± 10) mbar of pressure in air in an environmental chamber using in situ FTIR spectroscopy to monitor the reactants. The following rate coefficients in units of $k_{O3} \times 10^{18}$ (cm^3/$molecule^{-1}$ s^{-1}) were obtained: (2.47 ± 0.73) for *trans*-2-heptenal, (2.37 ± 0.68) for *trans*-2-octenal and (2.05 ± 0.20) for *trans*-2-nonenal.

It is shown that rate coefficients for the addition of O_3 molecules and OH radicals to the double bond of alkenes and unsaturated and oxygenated volatile organic compounds (OVOCs) at 298 K are related to a good approximation by the expression: $\log k_{OH} = 0.16 \log k_{O3} - 7.55$. Furthermore, a correlation between the reactivity of unsaturated VOCs toward O_3 molecules and the energies of the Highest Occupied Molecular Orbit (HOMO) of the unsaturated VOCs is presented and potential atmospheric implications of the results are discussed.

Introduction

Volatile Organic Compounds (VOCs) emitted from vegetation, often referred to as biogenic volatile organic compounds (BVOCs), are considered to be the main source of reactive species in the troposphere[1,2,3]. Aldehydes play an important role in atmospheric chemistry since they are recognized as important key precursors in the formation of tropospheric ozone and OH radicals.[4-7] They are also potential prolific sources of secondary organic aerosols through their reactions with atmospheric oxidants and photolysis.[8]

Aldehydes are ubiquitous gaseous chemical constituents in the atmosphere and are emitted by a variety of sources. They arise, for example, from incomplete fossil fuel combustion, are emitted by vegetation and are produced during biomass burning. The photochemical oxidation of most VOCs in the atmosphere results in the formations of aldehydes to some degree.[4-7]

As mentioned above, in the troposphere aldehydes can be photolyzed[6,7,9] and will also be subject to reaction with the main atmospheric oxidants OH radicals, NO_3 radicals and O_3 molecules. In the marine boundary layer and coastal regions reactions with Cl atoms can also be important. The combination of the photodissociation of aldehydes and reaction with the atmospheric oxidants represents, in many cases, an important source of free radicals in the lower atmosphere which can significantly influence the atmospheric oxidation capacity.[7, 10]

A number of reviews on the gas-phase kinetics of the reactions of OH, NO_3, O_3 and Cl with different unsaturated aldehydes are available in the literature.[4-7] For long chain ($>C_4$) unsaturated aldehydes rate coefficients have been reported, by different groups using absolute and relative kinetic techniques, for the reaction of OH with *E*-2-pentenal, *E*-2-hexenal, *E*-2-heptenal, *E*-2-octenal and *E*-2-nonenal at room temperature and in some cases also as a function of temperature.[6,7] In the case of NO_3, rate coefficients have been reported at room temperature for the reaction of NO_3 with five C_5-C_8 aldehydes, *E*-2-pentenal, *E*-2-hexenal, *E*-2-heptenal, *Z*-4-heptenal and *E*-2-octenal using different techniques. Again in some cases the reactions were also studied as a function of temperature.[6,7] Rate coefficients for the reaction of Cl with C_5-C_7 2-enals (*E*-2-pentenal, *E*-2-hexenal, *E*-2-heptenal) have been reported in a single study by Rodriguez et al.[11] who performed the measurements at 298 K using a relative kinetic method.

With regard to the ozonolysis of $>C_4$ unsaturated aldehydes, which is the subject of this study, Sato et al.[12] have determined rate coefficients at 298 K for the reaction of O_3 with three pentenals, *E*-2-pentenal, 3-methyl-2-butenal and *E*-2-methyl-2-butenal, using the relative kinetic method. Grosjean et al.[13] and Atkinson et al.[14] have both measured the rate coefficient for the reaction of O_3 with *E*-2-hexenal at room temperature using absolute and relative methods, respectively.

Since unsaturated aldehydes are released to the atmosphere in substantial amounts from combustion and vegetation and there are not many studies on the ozonolysis of these compounds, the motivation of this work was to investigate the ozonolysis of some longer carbon chain unsaturated aldehydes. The organic compounds studied in this work *trans*-2-heptenal, *trans*-2-octenal, *trans*-2-nonenal are biogenic aldehydes emitted from different types of vegetation[15-17]. As part of a systematic study on the kinetics of the atmospheric reactions of different unsaturated oxygenated VOCs, we report in this study rate coefficients for the reactions of O_3 molecules with the aforementioned aldehydes at 298 K and atmospheric pressure of synthetic air in a large volume photoreactor using the relative kinetic method:

$CH_3CH_2CH_2CH_2CH{=}CHC(O)H + O_3 \rightarrow$ Products, (1)

$CH_3CH_2CH_2CH_2CH_2CH{=}CHC(O)H + O_3 \rightarrow$ Products, (2)

$CH_3CH_2CH_2CH_2CH_2CH_2CH{=}CHC(O)H + O_3 \rightarrow$ Products. (3)

To the best of our knowledge rate coefficients of the above reactions have not been previously reported and this work, therefore, represents the first kinetic study of the reactions.

Additionally, the reactivity of the unsaturated aldehydes studied in this work together with other unsaturated VOCs toward O_3 molecules has been correlated i) with the reactivity of the same VOCs toward OH radicals and ii) with the energies of the Highest Occupied Molecular Orbit (HOMO) of the unsaturated compounds. Tropospheric lifetimes for the studied aldehydes have been calculated and potential atmospheric implications assessed.

The kinetic data and correlations presented here help to improve our understanding of the atmospheric oxidation mechanisms of aldehydes. They also help in assessments of the potential contributions of the compounds to the oxidizing capacity of the tropospheric and photochemical smog and SOA formation.

Experimental section

All the experiments were performed in a 1080 L chamber at (298 ± 2) K in 990 ± 10 mbar of synthetic air. The chamber is composed of a cylindrical quartz vessel (total length 6.2 m and an inner diameter of 0.47 m) closed at both ends by aluminum end flanges. The metal flanges contain ports for the introduction of bath gases and reactants into the chamber. A magnetically coupled Teflon mixing fan is mounted inside the chamber to ensure homogeneous mixing of the reactants. The reactor can be evacuated by a pumping system consisting of a turbomolecular pump backed by a double stage rotary fore pump to 10^{-3} Torr. A White-type mirror system mounted internally in the chamber and coupled to a FTIR spectrometer Nicolet Nexus equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector enables 'in situ' monitoring of the reactants in the infrared range 4000–700 cm. The White mirror system was operated with the total optical absorption path length set to 484.7 m and infrared spectra were recorded with a spectral resolution of $1cm^{-1}$, 100 interferograms were co-added per spectrum over a period of more than 1 min and 15 such spectra were recorded per experiment. The chamber is described in greater detail elsewhere.[18,19] Ozone was added stepwise to mixtures containing the unsaturated aldehydes and reference compound. An electrical discharge in a flow of pure oxygen was used to generate ozone. The initial concentrations of reactants in (ppmV) were approximately: 0.9 for *trans*-2-heptenal; 0.8 for *trans*-2-octenal; 0.7 for *trans*-2-nonenal; 3.0 for ethene; 4.0 for 1,3-butadiene; 0.5 for vinyl propionate and 6-9 for ozone. The reactants were monitored at the following infrared frequencies (cm^{-1}): *trans*-2-heptenal at

3077-2657; *trans*-2-octenal at 3000-2650; *trans*-2-nonenal at 3011-2649; ethene at 949; 1,3-butadiene at 908 and vinyl propionate at 1170. Typical IR spectra of the kinetics experiments performed for the reactions of O_3 with *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal are presented in the Supplementary Information (SI) as Figure S1, Figure S2 and Figure S3, respectively. In addition, the concentration-time profiles for the three unsaturated aldehydes (*trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal) are presented as Figures S4, S5 and S6, respectively in the SI.

Results and discussion

Rate coefficients for the reactions of the aldehydes with O_3 were determined using the relative rate method in which the rates of decay of the aldehydes were monitored relative to the decay of reference compounds.

$$O_3 + \text{aldehyde} \rightarrow \text{products}, \qquad k_1 \qquad (4)$$

$$O_3 + \text{reference} \rightarrow \text{products}, \qquad k_2 \qquad (5)$$

If the unsaturated aldehydes and reference organics are removed solely by reaction with O_3 molecules according to equation (4) and (5) then equation (I) is valid:

$$\ln\left\{\frac{[\text{aldehyde}]_0}{[\text{aldehyde}]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[\text{reference}]_0}{[\text{reference}]_t}\right\} \qquad \text{(I)}$$

where $[\text{aldehyde}]_0$, $[\text{reference}]_0$, $[\text{aldehyde}]_t$ and $[\text{reference}]_t$ are the concentrations of the unsaturated aldehyde compound under study and the reference compound at times $t = 0$ and t, respectively, and k_1 and k_2 are the rate coefficients of reactions (4) and (5) respectively.

Experiments were carried out to assess the loss of the unsaturated aldehyde and reference compound through deposition to the reactor wall. The wall losses of the unsaturated aldehyde and reference compound before the addition of O_3 were found to be negligible. Three experiments were performed per reference compound and two reference compounds were employed for each of the investigated aldehydes. Data plotted in the form of Eq. (I) are presented in Figures 1-3 and the values of the rate coefficient k_1/k_2 are summarized in Table 1 together with the absolute values of the rate coefficients for the reactions of O_3 with the aldehydes calculated from the k_1/k_2 ratios. The error bars in Figures 1-3 are the 2σ statistical errors from the scatter in the plots. The rate coefficients for the reactions of O_3 molecules with the unsaturated aldehydes were placed on an absolute basis using the following values for the reference reactions at 298 K: O_3 + ethene $(1.37 \pm 0.08) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} [20]; O_3 + 1,3-butadiene $(6.3 \pm 0.4) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} [20] and O_3 + vinyl propionate $(5.3 \pm 1.3) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.[21]

The errors quoted for the rate coefficients for the reactions of O_3 with the aldehydes in Table 1 are a combination of the 2σ statistical errors from the linear regression analyses of the plots plus the corresponding error of the reference reaction rate coefficient. As can be seen from Table 1 there is good agreement between the rate coefficients obtained for the reaction of O_3 with the aldehydes using two different reference compounds. Because of this good agreement, we prefer to give final rate coefficients for the reactions which are an average of all the determinations, i.e.

$$k_{(O3\ +\ \text{trans-2-heptenal})} = (2.47 \pm 0.73) \times 10^{-18}\ cm^3\ molecule^{-1}\ s^{-1}$$

$k_{(O3 + \text{trans-2-octenal})} = (2.37\pm0.68) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

$k_{(O3 + \text{trans-2-nonenal})} = (2.05\pm0.20) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}

It is well established that the ozonolysis of alkenes produces OH radicals which can interfere with relative kinetic studies of the type presented here. To minimize this inference an organic compound or CO is often added to the system to scavenge the OH radicals. The rate coefficients for the reactions of the unsaturated aldehydes under investigation in this study are very high, thus in order to effectively scavenge any OH radicals produced during the ozonolysis reaction high concentrations of a scavenger would be necessary. Since such high concentrations of the scavenger in the reaction system would render monitoring of the reactants in the infrared impossible, the experiments have been performed in the absence of a scavenger. We have obtained values of the rate coefficients for the reactions of O_3 with the aldehydes using two reference compounds which are in excellent agreement with one another. Since the rate coefficients for the reactions of O_3 with the reference compounds differ by a factor of approximately 4 and their rate coefficients with OH are all quite different we argue that any influence by OH in the reaction systems can not be very significant.

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. However, it is still important to keep in mind when making rate coefficient comparisons that the present values were determined in the absence of an OH radical scavenger.

The rate coefficients values obtained for the three reactions studied are very similar and within the error limits can be considered the same. The rate coefficients for the reactions of ozone with the three aldehydes have been estimated using the US EPA AOPWIN program[22] which is based upon the structure-activity relationship (SAR) method described in Kwok and Atkinson.[23] This estimation method predicts a rate coefficient value of 1.82×10^{-18} cm^3 $molecule^{-1}$ s^{-1} for all three of the unsaturated aldehydes which is lower than experimental values reported here by approximately 35% for *trans*-2-heptenal, 30% for *trans*-2-octenal and 13% for *trans*-2-nonenal. This agreement is quite acceptable considering the uncertainties in the rate coefficient determinations.

The rate coefficient of $(2.0 \pm 1.0) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} reported by Atkinson et al.[14] for the reaction of O_3 with *trans*-2-hexenal is very similar, within the error limits, to the rate coefficients determined in this work for the reactions of O_3 with *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal. This similarity in the reactivity for ≥C6 unsaturated-2-enals toward O_3 supports that above C6 further increases in the alkyl chain length of the aldehyde has a negligible effect on the magnitude of the electron donation to the double bond.

Rate coefficients for the addition of OH and NO_3 radicals, Cl atoms and O_3 molecules to alkenes and unsaturated VOCs has been shown previously to correlate with the energy of the HOMO of the different VOCs.[24,25,26] The electron density in the π-bond that is attacked by the O_3 molecule should be reflected in the energy of the highest occupied molecular orbital (E_{HOMO}) with the lowest negative value being expected for the compound with the largest rate coefficient. To contribute to and extend the correlations reported previously for the rate coefficients of OH and Cl reactions with E_{HOMO} energies,[27] a new correlation for the ozonolysis of different unsaturated VOCs has been determined using the Gaussian 03 package[28]. The geometry optimizations and initial values of the energies were obtained at the B3LYP level with a 6-311G(d,p) bases set. The E_{HOMO} calculated for the unsaturated aldehydes and the other unsaturated VOCs are listed in Table 2. Figure 4 shows a plot of the natural logarithms of the O_3 rate coefficients plotted as a function of the calculated E_{HOMO} in eV. A linear relationship is obtained. The linear relationship in Figure 4 is well described by:

$$-\ln k_{O3}\ (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (9.52 \pm 1.12)\ (-E_{HOMO}) + (26.50 \pm 2.35),\ \ r^2=0.97 \qquad \text{(II)}$$

The quality of the correlation is such that it can be used for reasonable estimations of rate coefficients for the reactions of O_3 molecules with other unsaturated VOCs where data does not yet exist.

In addition, we present for the first time, a correlation between k_{OH} and k_{O3} for a wide range of different unsaturated VOCs. The rate coefficients for the reactions of different unsaturated VOCs with O_3 molecules and OH radicals at 298 K are listed in Table 1. The correlation obtained between the rate coefficients for the reactions of O_3 molecules with a given alkene or unsaturated VOC and those for the corresponding reactions with OH radicals is shown in Figure 5. A reasonable correlation is obtained and a least-squares treatment of the data points in Figure 5 yields the following expression (with the rate coefficients in units of $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$):

$$\log k_{OH} = 0.16 \log k_{O3} - 7.55,\ \ r^2=0.95 \qquad \text{(III)}$$

The quality of this correlation is also such that it can be used to make reasonable estimations of rate coefficients for reactions of O_3 molecules with other unsaturated VOCs where data does not yet exist.

The atmospheric lifetime of the studied aldehydes with respect to reaction with the main tropospheric oxidants can be estimated using the expression:

$$\tau_x = \frac{1}{k_x \times [X]} \qquad \text{(IV)}$$

where X= O_3, OH, NO_3 or Cl and k_x is the rate coefficient of the aldehyde with the oxidant X, The following typical tropospheric oxidant concentrations have been used in calculating the lifetimes: $[O_3] = 7\times10^{11}$ molecule cm^{-3} [29]; $[OH] = 2\times10^{6}$ radical cm^{-3} [30]; $[Cl] = 1\times10^{4}$ atom cm^{-3} [31] and $[NO_3] = 5\times10^{8}$ radical cm^{-3} [32]. The atmospheric lifetimes for the reaction of the aldehydes with ozone and the other oxidants, where data are available, are presented in Table 3. The lifetimes show that the unsaturated aldehydes will be degraded by reaction with NO_3 radical during the night and with OH radicals during the day. At the levels of O_3 typically present in the troposphere, decay of the unsaturated aldehyde with O_3 will be insignificant but could potentially be of some importance during episodes of elevated O_3 levels. Wet and dry deposition will be a minor loss process for the aldehydes since they are highly volatile and sparingly soluble in water.

Degradation of longer chain aldehydes constitutes a significant source of aldehydes containing less carbon atoms than the precursor. In the presence of OH, NO_3, O_3 longer chain unsaturated aldehyde will probably be degraded to much shorter chain aldehydes, which have longer lifetimes and can contribute effectively to tropospheric ozone and SOA formation. In addition, longer chain aldehydes in the course of their degradation can undergo isomerization reactions forming carbonyl compounds which in further oxidation reactions can form thermally stable PAN type compounds.

For the reactions studied in this work we expect, based on existing ozonolysis studies, that pentanal, hexanal and heptanal will be major reaction products from the reactions of O_3 with *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal, respectively. Glyoxal will also be a major reaction product for all three aldehydes. However, the exact nature and yields of the products formed in the ozonolysis of the unsaturated aldehydes studied here still remains to be elucidated.

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Figure captions

Figure 1. Plot of the kinetic data for the reaction of O_3 molecules with *trans*-2-heptenal measured relative to ethene (□) and vinyl propionate (○) at (298 ± 2) K and atmospheric pressure of air.

Figure 2. Plot of the kinetic data for the reaction of O_3 molecules with *trans*-2-octenal measured relative to ethene (□) and vinyl propionate (○) at (298 ± 2) K and atmospheric pressure of air.

Figure 3. Plot of the kinetic data for the reaction of O_3 molecules with *trans*-2-nonenal measured relative to ethene (□) and 1,3-butadiene (Δ) at (298 ± 2) K and atmospheric pressure of air.

Figure 4. Correlation of ln k_{O3} (cm^3 $molecule^{-1} \cdot s^{-1}$) against E_{HOMO} calculated using the Gaussian 3.0 package B3LYP/6-311G(d,p) for the reactions of volatile organic compounds with ozone. The numbers correspond to the compounds listed in Table 2 and the filled circles highlight the aldehydes, *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal, studied in this work.

Figure 5. Linear free energy plot of logk_{OH} against logk_{O3} at room temperature for a series of unsaturated volatile organic compounds. The numbers correspond to the compounds listed in Table 2 and the filled circles highlight the aldehydes, *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal, studied in this work.

Table 1

Rate coefficient ratios k_1/k_2 and rate coefficients for the reactions of ozone with *trans*-2-heptenal, *trans*-2-octenal and *trans*-2-nonenal at (298 ± 2) K in (990 ± 10) mbar of air.

Unsaturated aldehyde	Reference	k_1/k_2	$k_{(O3+aldehyde)} \times 10^{18}$ (cm^3 $molecule^{-1} s^{-1}$)
trans-2-heptenal + O_3	Ethene	1.738 ± 0.048	2.38 ± 0.21
	Ethene	1.745 ± 0.069	2.39 ± 0.23
	Ethene	1.878 ± 0.086	2.57 ± 0.27
	Vinyl propionate	0.484 ± 0.010	2.57 ± 0.68
	Vinyl propionate	0.456 ± 0.010	2.42 ± 0.65
	Vinyl propionate	0.479 ± 0.019	2.54 ± 0.73
	Average		**2.47 ± 0.73**
trans-2-octenal + O_3	Ethene	1.626 ± 0.039	2.23 ± 0.19
	Ethene	1.774 ± 0.064	2.43 ± 0.22
	Ethene	1.595 ± 0.023	2.19 ± 0.16
	Vinyl propionate	0.434 ± 0.010	2.30 ± 0.62
	Vinyl propionate	0.484 ± 0.010	2.57 ± 0.68
	Vinyl propionate	0.472 ± 0.010	2.50 ± 0.67
	Average		**2.37 ± 0.68**
	1,3-butadiene	0.322 ± 0.010	2.01 ± 0.19
	1,3-butadiene	0.346 ± 0.010	2.16 ± 0.20
	1,3-butadiene	0.335 ± 0,010	2.09 ± 0.20

trans-2-nonenal + O_3	Ethene	1.468 ± 0.041	2.01 ± 0.17
	Ethene	1.479 ± 0.037	2.03 ± 0.17
	Ethene	1.471 ± 0.016	2.02 ± 0.15
	Average		**2.05 ± 0.20**

Table 2. Rate coefficients of O_3 and OH with different VOCs and E_{HOMO} for the corresponding VOCs.

	Volatile organic compounds	k_{OH} (cm^3 molecule^{-1}s^{-1})	k_{O3} (cm^3 molecule^{-1}s^{-1})	E_{homo} (eV)
1	$CH_3CH{=}CHCHO$ Crotonaldehyde	3.51×10^{-11}[a]	1.74×10^{-18}[a]	-6.99986
2	$CH_3CH_2CH{=}CHCHO$ *trans*-2-pentenal	2.35×10^{-11}[a]	1.59×10^{-18}[a]	-6.97047
3	$CH_3CH_2CH_2CH{=}CHCHO$ *trans*-2-hexenal	2.95×10^{-11}[a]	2.0×10^{-18}[a]	-6.96204
4	$H_2C{=}C(CH_3)CHO$ Methacrolein	2.90×10^{-11}[a]	1.3×10^{-18}[a]	-7.16639
5	$CH_3CH{=}C(CH_3)CHO$ *trans*-2-methyl-2-butenal	4.08×10^{-11}[a]	5.34×10^{-18}[a]	-6.96884
6	$CH_2{=}CHCHO$ Acrolein	1.99×10^{-11}[a]	2.61×10^{-18}[a]	-7.22027
7	$CH_3(CH_2)_3CH{=}CHCHO$ *trans*-2-heptenal	2.45×10^{-11}[a]	2.47×10^{-18}[c]	-6.95088
8	$CH_3(CH_2)_4CH{=}CHCHO$ *trans*-2-octenal	4.05×10^{-11}[b]	2.37×10^{-18}[c]	-6.97129
9	$CH_3(CH_2)_5CH{=}CHCHO$ *trans*-2-nonenal	4.35×10^{-11}[b]	2.05×10^{-18}[c]	-6.96993
10	$CH_3CH{=}CH_2$ Propene	2.52×10^{-11}[a]	1.06×10^{-17}[a]	-7.07197
11	$CH_3CH{=}CHCH_3$ *trans*-2-butene	7.07×10^{-11}[a]	2.38×10^{-16}[a]	-6.64448
12	$CH_3CH{=}CHCH_3$ *cis*-2-butene	5.48×10^{-11}[a]	1.29×10^{-16}[a]	-6.63849
13	$CH_3CH_2CH_2CH{=}CH_2$ 1-pentene	2.74×10^{-11}[a]	9.97×10^{-18}[a]	-7.05347
14	$C_2H_5CH{=}CHCH_3$ *cis*-2-pentene	6.38×10^{-11}[a]	1.28×10^{-16}[a]	-6.65101
15	$CH_3CH_2CH_2CH{=}CHCH_3$ *cis*-2-hexene	6.19×10^{-11}[a]	1.06×10^{-16}[a]	-6.64285
16	$CH_3(CH_2)_5CH{=}CH_2$ 1-octene	3.62×10^{-11}[a]	1.01×10^{-17}[a]	-7.02979
17	$C_2H_5CH{=}CHCH_3$ *trans*-2-pentene	6.86×10^{-11}[a]	1.59×10^{-16}[a]	---

18	$CH_3CH_2CH=CHCH_2CH_3$ *cis*-3-hexene	6.29×10^{-11}[a]	1.44×10^{-16}[a]	---
19	$CH_2=C(CH_3)_2$ Isobutene	5.48×10^{-11}[a]	1.11×10^{-17}[a]	---
20	$CH_2=C(CH_3)COOC_2H_5$ ethyl methacrylate	4.58×10^{-11}[a]	7.68×10^{-18}[a]	---
21	$CH_2=C(CH_3)COOCH_3$ methyl methacrylate	4.15×10^{-11}[a]	4.67×10^{-17}[a]	---
22	$CH_3COOCH=CH_2$ vinyl acetate	2.49×10^{-11}[a]	3.2×10^{-18}[a]	---
23	$CH_2=CHCOO(CH_2)_3CH_3$ n-butyl acrylate	2.28×10^{-11}[a]	2.4×10^{-18}[a]	---
24	$CH_3CH=CHCOOC_2H_5$ ethyl crotonate	4.96×10^{-11}	8.0×10^{-18}[a]	---
25	$CH_3CH=CHCOOCH_3$ methyl crotonate	4.65×10^{-11}[a]	4.4×10^{-18}[a]	---

[a](33), [b](34), [c](This work).

Table 3. Estimated tropospheric lifetimes for the unsaturated aldehydes studied with respect to their reactions with O_3, OH, NO_3 and Cl.

Aldehyde	k_{O3} $cm^3 molecule^{-1} s^{-1}$	τ_{O3} (days)	k_{OH} $cm^3 molecule^{-1} s^{-1}$	τ_{OH} (hours)	k_{NO3} $cm^3 molecule^{-1} s^{-1}$	τ_{NO3} (hours)	k_{Cl} $cm^3 molecule^{-1} s^{-1}$	τ_{Cl} (days)
trans-2-heptenal	2.47×10^{-18a}	7	2.45×10^{-11b}	6	0.23×10^{-13d} 5.3×10^{-15e}	0,4 2	2.40×10^{-10f}	5
trans-2-octenal	2.37×10^{-18a}	7	40.5×10^{-12c}	3	5.6×10^{-15e}	2	--	--
trans-2- nonenal	2.05×10^{-18a}	8	43.5×10^{-12c}	3	--	--	--	--

[a](This work), [b] (35), [c] (34), [d] (36), [e] (37) and [f](11).

Figure 1

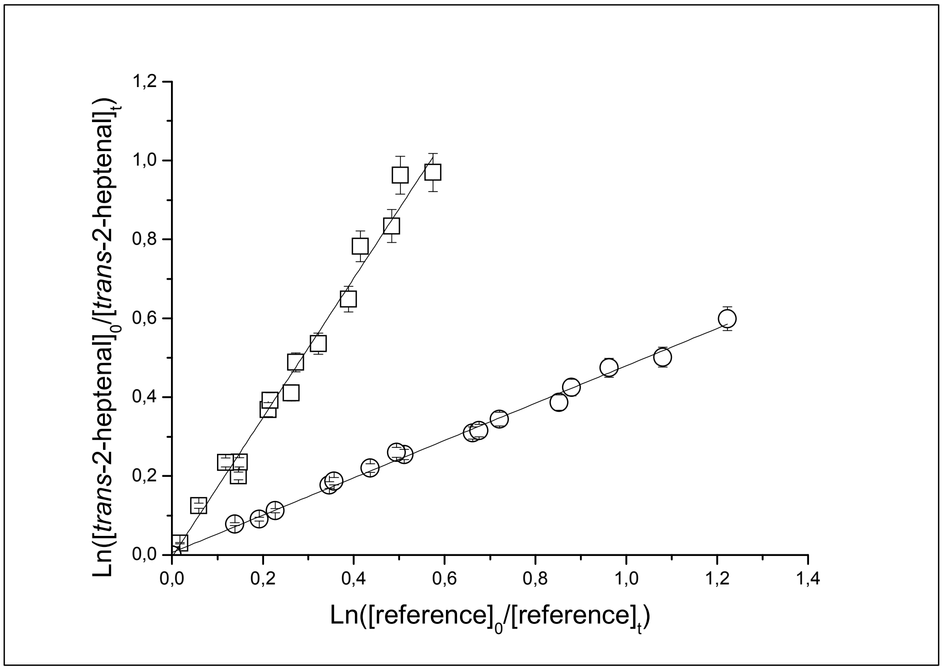

Ln([*trans*-2-heptenal]$_0$/[*trans*-2-heptenal]$_t$)
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
Ln([reference]$_0$/[reference]$_t$)

Figure 2

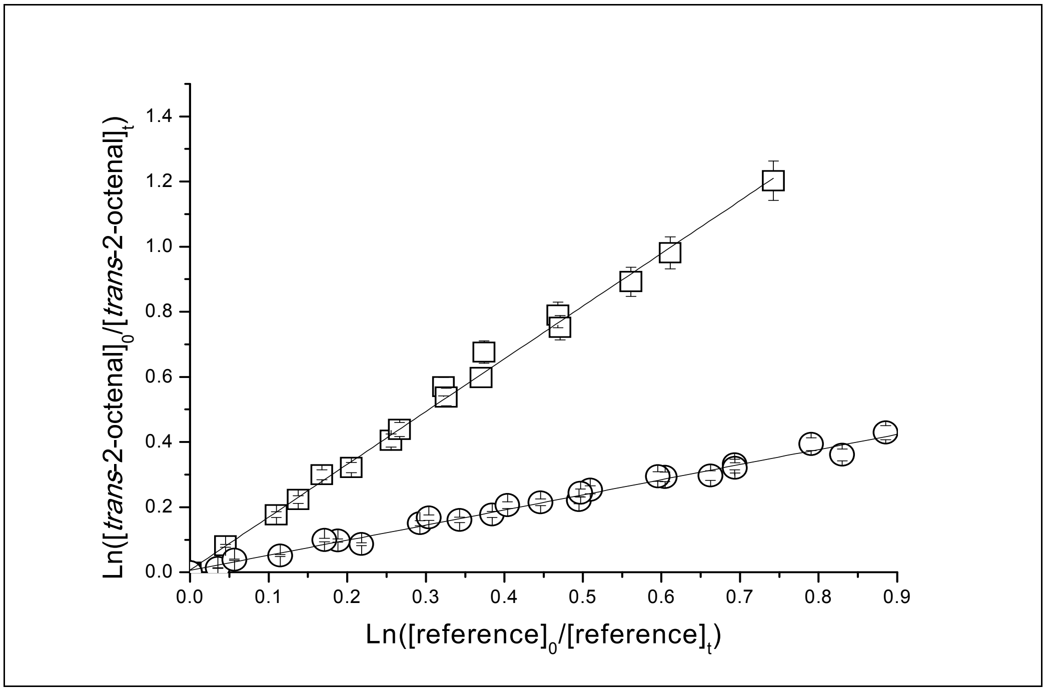

Ln([*trans*-2-octenal]$_0$/[*trans*-2-octenal]$_t$)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Ln([reference]$_0$/[reference]$_t$)

Figure 3

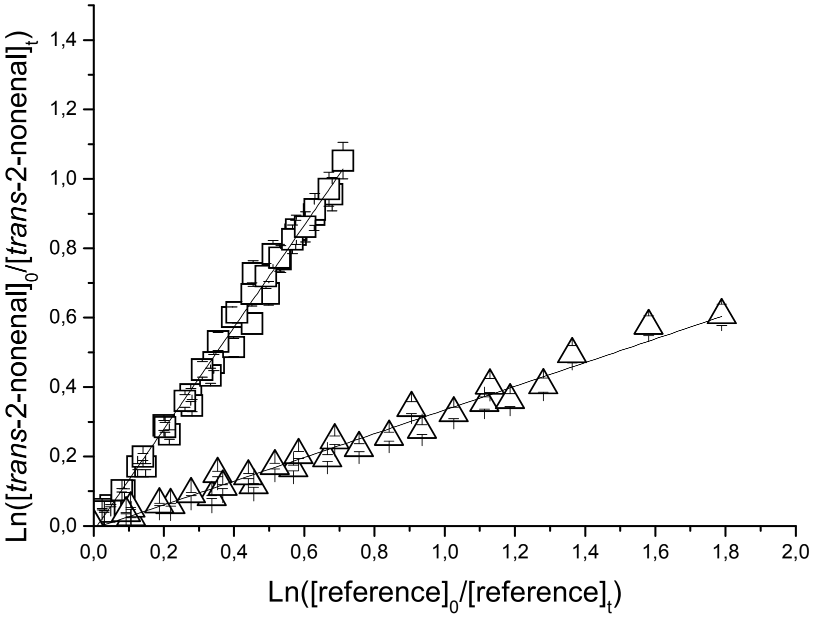

Ln([trans-2-nonenal]0/[trans-2-nonenal]t)
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8
2,0
Ln([reference]0/[reference]t)

Figure 4

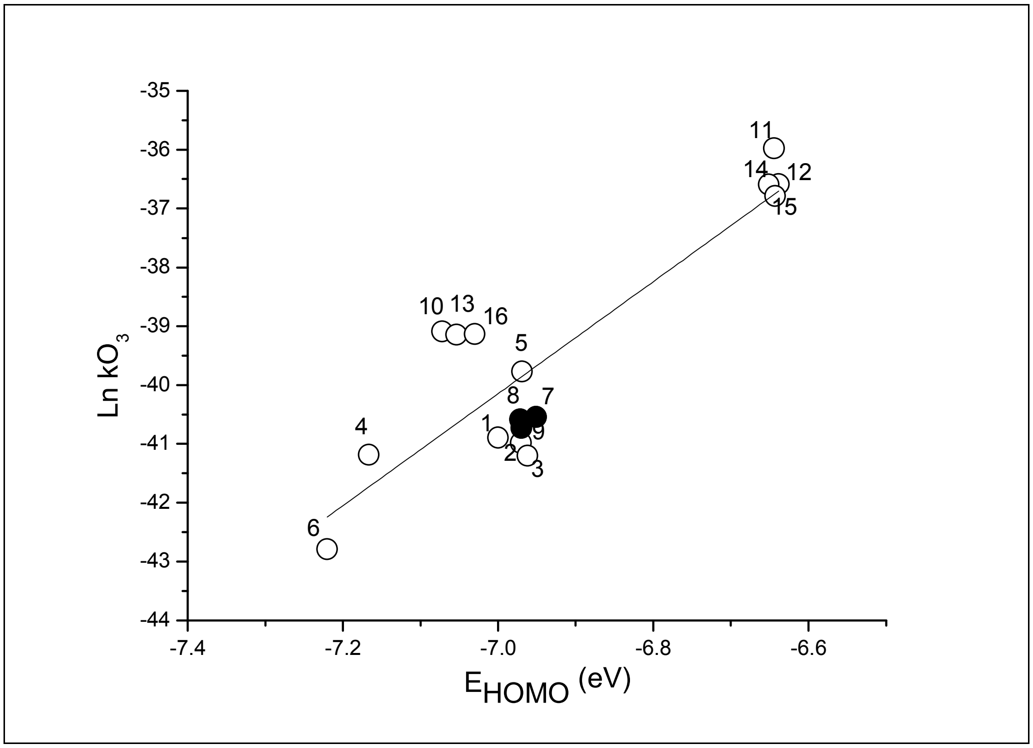
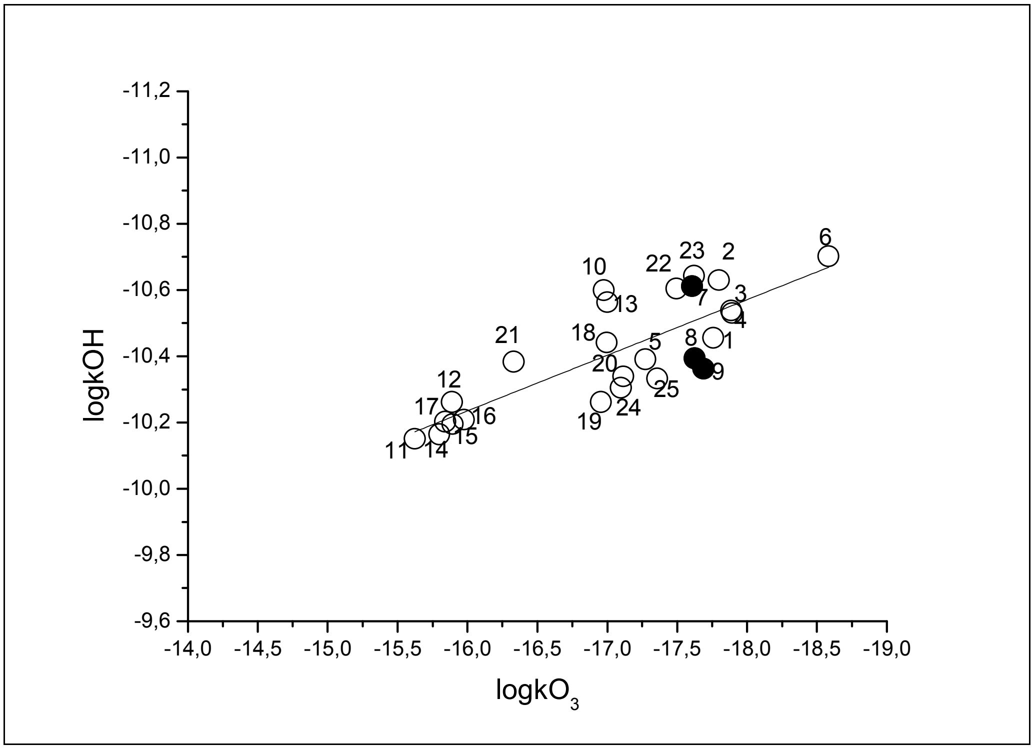

-35
-36
-37
-38
-39
-40
-41
-42
-43
-44
Ln kO_3
-7.4
-7.2
-7.0
-6.8
-6.6
E_{HOMO} (eV)
11
14
12
15
10
13
16
5
8
7
1
9
2
3
4
6

Figure 5


-11,2
-11,0
-10,8
-10,6
-10,4
-10,2
-10,0
-9,8
-9,6
logkOH
-14,0
-14,5
-15,0
-15,5
-16,0
-16,5
-17,0
-17,5
-18,0
-18,5
-19,0
logkO$_3$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
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