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loss of hexanal and
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Daytime tropospheric loss of hexanal and *trans*-2-hexenal: OH kinetics and UV photolysis

E. Jiménez, B. Lanza, E. Martínez, and J. Albaladejo

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, s/n, 13071 Ciudad Real, Spain

Correspondence to: J. Albaladejo (jose.albaladejo@uclm.es)

Abstract

The ultraviolet (λ=250–370 nm) photolysis and the OH-initiated oxidation of hexanal and *trans*-2-hexenal, which are relevant atmospheric processes, have been investigated at room temperature and as a function of temperature (T=263–353 K), respectively. This kinetic study as a function of temperature is reported here for the first time. Absolute absorption cross sections (σ_λ) were obtained using a recently built system operating in the UV region. This work represents the first reported σ_λ for *trans*-2-hexenal. The obtained σ_λ allowed the estimation of the photolysis rates (J) of hexanal and *trans*-2-hexenal across the troposphere. Kinetic measurements of the gas-phase reaction of hydroxyl radicals (OH) with hexanal and *trans*-2-hexenal were performed by using the laser pulsed photolysis/laser-induced fluorescence technique. Rate coefficients k_{OH} for both aldehydes were determined at temperatures between 263 and 353 K at 50 Torr in helium or argon bath gases. The temperature dependence of k_{OH} for both aldehydes was found to be slightly negative. The tropospheric lifetime of hexanal and *trans*-2-hexenal due to the chemical removal by OH radicals has been estimated across the troposphere. The loss rate due to the OH chemical removal was compared with the estimated photolysis rates. Our results show that OH-reaction and UV photolysis are the main loss processes for these aldehydes in the troposphere. For hexanal, both processes compete across the troposphere, however, UV photolysis can contribute up to 70% to the overall loss of *trans*-2-hexenal.

1 Introduction

Aldehydes are emitted into the atmosphere by different anthropogenic (they are the products of an incomplete combustion of petroleum fuels, vehicles, etc.) and natural sources (forest, pastures lawn mowing, etc.) (Grosjean et al., 2001; Kirstine et al., 1998; Owen et al., 1997; Wildt et al., 2003). These oxygenated compounds play a vital role in the formation of photochemical smog and in the determination of levels

of secondary pollutants, such as peroxyacetyl nitrate (PAN) and tropospheric ozone (Atkinson and Arey, 2003).

Photodissociation of aldehydes may also represent an important source of free radicals in the lower atmosphere, and thus may significantly influence the atmospheric oxidation capacity (Finlayson-Pitts and Pitts, 2000). The photochemistry of saturated and unsaturated C_6 aldehydes, such as hexanal and *trans*-2-hexenal, has not been widely studied and a few data are available concerning the photolysis quantum yields and the absorption cross sections (Plagens et al., 1998; Tadic et al., 2001; Tang and Zhu, 2004). Models of urban photochemistry generally assume that photolysis of aldehydes, RCHO, yields the alkyl radical (R) and the formyl radical (HCO), enhancing the radical flux present in the atmosphere. Tang and Zhu (2004) reported absolute quantum yields for HCO radical (ϕ_{HCO}) in the photolysis of hexanal between 305 and 320 nm in the presence of nitrogen. Tadic et al. (2001) reported total quantum yields between 275 and 380 nm in synthetic air (100–700 Torr). From the observed products in the photolysis of hexanal, these groups reported that other photodissociation channels, apart from the Norrish type I (R1a), were also possible.

For example, the molecular elimination process (R1b) and the Norrish type II (R1c):

$$CH_3(CH_2)_4CHO + h\nu \rightarrow n-C_5H_{11} + HCO \tag{R1a}$$

$$\rightarrow n-C_5H_{12} + CO \tag{R1b}$$

$$\rightarrow CH_2=C_3H_6 + CH_2=CHOH \tag{R1c}$$

Ultraviolet (UV) absorption cross sections (σ_λ) for hexanal have been reported at room temperature by Tang and Zhu (2004) and by Plagens et al. (1998). Nevertheless, other measurements of σ_λ for hexanal are reported in this paper in order to compare the photochemistry of the saturated aldehyde with that of *trans*-2-hexenal. Photochemistry of *trans*-2-hexenal has been less studied:

$$CH_3(CH_2)_2CH=CHCHO + h\nu \rightarrow \text{Products} \tag{R2}$$

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As far as we know, no UV absorption cross sections have been reported for this aldehyde. Thus, this work represents the first reported measurement for the absorption cross sections of *trans*-2-hexenal. However, a simultaneous study to ours on the UV absorption cross sections of *trans*-2-hexenal has been performed by O'Connor et al. (2006)[1].

Together with the photodissociation process, the main chemical degradation route of these aldehydes in the troposphere is thought to be the reaction with OH radicals:

$$OH + CH_3(CH_2)_4CHO \rightarrow Products \qquad (R3)$$

$$OH + CH_3(CH_2)_2CH=CHCHO \rightarrow Products \qquad (R4)$$

Up to now, only room temperature measurements of the rate coefficients of the OH reactions (k_{OH}) are reported for hexanal (Albaladejo et al., 2002; D'Anna et al., 2001; Papagni et al., 2000) and *trans*-2-hexenal (Albaladejo et al., 2002; Grosjean and Williams, 1992; Atkinson et al., 1995).

One of the most significant meteorological impacts in modelling ozone concentrations is the temperature reduction with the altitude in the troposphere, which alters chemical reaction rates. Thus, the use of rate coefficient expressions rather than simple rate coefficients permits simulations over a wide range of temperatures for urban, suburban, rural and remote regions and seasons of the troposphere. Therefore, a kinetic study on the reactions R3 and R4 as a function of temperature is presented here in order to give a T-expression of k_{OH} which could be used in the evaluation of the impact of these aldehydes in PAN and ozone formation. Additionally, the aim of this work is to quantify the contribution of the photolysis process and the reaction with OH radicals to the tropospheric degradation of these C_6 aldehydes.

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[1]O'Connor, M. P., Temime-Roussel, B., Wenger, J. C., Doussin, J. F., and Mellouki, A.: Kinetics and mechanisms for the atmospheric oxidation of unsaturated C6 aldehydes, 19th International Symposium on Gas Kinetics, 2006.

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2 Experimental details

2.1 UV absorption cross section determination

The experimental setup employed in the determination of absolute absorption cross sections was the same as in our previous work (Jiménez et al., 2005a), therefore, only a brief description is given here. The system consisted of a Pyrex cell sealed with quartz windows, an irradiation source and a detection system. A wide emission (200–800 nm) deuterium lamp was employed as a photochemical source to irradiate the sample and the transmitted radiation was focused onto a 0.5-m spectrograph and detected by a CCD. The absorption cell was filled with pure vapours of 0.9–7.0 Torr for hexanal and 0.6–3.5 Torr for *trans*-2-hexenal, and were measured by using a pressure transducer.

The UV absorption spectra of hexanal and *trans*-2-hexenal were recorded at room temperature in the wavelength range from 210 to 370 nm with a spectral resolution of 0.2 nm. The absorption spectrum of hexanal exhibits a weak absorption between 240 and 350 nm as a result of the symmetry-forbidden $n{\rightarrow}\pi^*$ transition in the carbonyl group. This band appears shifted to longer wavelengths for *trans*-2-hexenal due to conjugation between the double bond and the C=O group. In addition to this weak band, *trans*-2-hexenal absorption spectrum shows a strong band corresponding to the $\pi{\rightarrow}\pi^*$ transition in the double bond. This transition has not been characterized in this work because of its little interest from the tropospheric point of view.

Examples of the $n{\rightarrow}\pi^*$ band for hexanal recorded at three different pressures are shown in Fig. 1a. A series of experiments was carried out (usually 5–6 independent determinations) at each pressure, p, under static conditions. The absorption cross section in base e at each wavelength (σ_λ) was obtained by applying the Beer-Lambert law in terms of pressure:

$$A_\lambda = \ln(I_0/I) = \sigma_\lambda \ell p \tag{1}$$

A_λ is the absorbance, I_0 and I are the transmitted light intensity measured in the ab-

sence and the presence of aldehyde, respectively, and $\ell\,(\pm 2\sigma)$ is the optical path length ((107.0±0.2) cm). Figure 1b shows several examples of the plots of Eq. (1). From the slope of these plots, σ_λ was determined. As it can be seen in this figure, no deviation of the Beer-Lambert law was observed over the studied range of pressures.

2.2 OH kinetic measurements

Absolute rate coefficients, k_{OH}, for hexanal and *trans*-2-hexenal were obtained by the pulsed laser photolysis/laser-induced fluorescence (PLP-LIF) technique as a function of temperature (263–353 K). The PLP-LIF setup, technique, and methodology have been already described in previous studies (Jiménez et al., 2005a, b). However, a brief description is given below.

Gas-phase reaction of OH radicals with hexanal or *trans*-2-hexenal takes place at the centre of a 200-cm^3 Pyrex reactor. OH(X$^2\Pi$) radicals were generated by the pulsed photolysis of H$_2$O$_2$(g) at 248 nm by using a KrF excimer laser. Gas-phase H$_2$O$_2$ was introduced in the reaction cell by bubbling the carrier gas (He or Ar) through a pre-concentrated liquid sample of hydrogen peroxide (Jiménez et al., 2005a). H$_2$O$_2$ concentrations in the reaction cell, measured optically as described in our previous paper (Jiménez et al., 2005a) were (1.1–2.4)×10^{14} molecule cm^{-3}. Therefore, OH concentration can be estimated from the known H$_2$O$_2$ concentration, taking into account the absorption cross section of H$_2$O$_2$ at 248 nm, the quantum yield for OH production (Sander et al., 2002), and the photolysis laser fluence ((1.3–20.0) mJ pulse^{-1} cm^{-2}). OH radical concentration was varied from 3.0×10^{11} molecule cm^{-3} to 1.1×10^{12} molecule cm^{-3}. At different reaction times, OH radicals were excited at 282 nm (OH(A$^2\Sigma^+$, v'=1)←OH(X$^2\Pi$, v''=0)) by using the frequency-doubled output of a dye laser pumped by a Nd-YAG laser. LIF signal from OH(A$^2\Sigma^+$) was detected at $\lambda\geq 282$ nm by a photomultiplier tube placed orthogonal to both light sources. LIF emissions were selected by a bandpass filter (90% transmittance at 350 nm and 150 nm of FWHM) and transferred to a personal computer for analysis.

2.2.1 Aldehyde concentrations

Hexanal and *trans*-2-hexenal concentrations were measured by UV absorption spectroscopy at 185 nm. Firstly, the absorption cross section of both aldehydes was measured at that wavelength using a similar methodology than that described in the previous Sect. 2.1. The experimental system employed in these measurements has been recently setup. This setup consists in a Pyrex absorption cell (in this case, we used the 107-cm long cell described in Sect. 2.1), a low power light source (a Hg/Ar pen ray lamp from Oriel) and a detection system (a Hamamatsu phototube, model R5764). The absorption cell was irradiated by the Hg/Ar pen ray lamp. The transmitted 185-nm radiation was selected by an interference filter (Andover, centred at 182.8 nm with a transmittance of 19%, FWHM of 26 nm), and collected by the phototube. The transmitted intensity in the absence (I_0) or in the presence of aldehyde (I) was, then, monitored by a picoamperemeter (Keithley Instruments, model 6485).

Aldehydes were diluted in 760 Torr of the bath gas and stored in a 10-L blackened bulb. Usually, the dilution factor was set to 0.2–0.6%. A known pressure of this diluted aldehyde (p_T=47–70 Torr) was introduced into the absorption cell. Absorption cross sections (in base e) at 185 nm ($\sigma_{185\,nm}$) were obtained, under static conditions, by applying Beer-Lambert law (Eq. 1). The average of 4–5 measurements of the absorption cross sections ($\pm 2\sigma$) were found to be $(9.37\pm0.32)\times10^{-18}\,cm^2$ for hexanal and $(1.07\pm0.07)\times10^{-17}\,cm^2$ for *trans*-2-hexenal.

Secondly, knowing $\sigma_{185\,nm}$ for each aldehyde, their concentrations can be determined by using the following equation:

$$[RCHO]_{UV\ cell} = \frac{\ln(I_0/I)}{\ell \times \sigma_{185\,nm}} \tag{2}$$

During the kinetic measurements, a flow of diluted aldehyde ($f_{aldehyde}$), a flow of the carrier gas through H_2O_2(aq.) ($f_{peroxide}$), and the main flow of bath gas (f_{bath}) were introduced into the Pyrex reaction cell. The total flow rate was varied from 260 to 520 sccm (standard cubic centimetre per minute), corresponding to a linear velocity

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between 5 and 15 cm s^{-1}. Under flowing conditions, aldehyde concentrations were measured before and after entering the reaction cell. A difference of 7% for hexanal and 14% for *trans*-2-hexenal between both measurements was observed, which is within the experimental uncertainties. When aldehyde concentrations were measured before entering the reactor, the aldehyde is introduced into the absorption cell from the bulb, the rest of flows are introduced directly into the reaction cell. Thus, a correction has to be made in the measured $[RCHO]_{UV\ cell}$ in order to account for the further dilution in the reaction cell and the differences in temperature and pressure between the UV cell and the reactor. The expression for this correction was:

$$[RCHO]_{reactor} = [RCHO]_{UV\ cell} \frac{f_{aldehyde}}{f_{Total}} \frac{p_{reactor}}{p_{UV\ cell}} \frac{298\,K}{T_{reactor}} \tag{3}$$

where $f_{Total} = f_{aldehyde} + f_{peroxide} + f_{bath}$. Only the correction in temperature was needed when the RCHO concentrations were measured at the exit of the reactor. Aldehyde concentrations obtained were $(0.2–2.7) \times 10^{14}$ molecule cm^{-3} for hexanal and $(0.1–5.2) \times 10^{14}$ molecule cm^{-3} for *trans*-2-hexenal. Also, aldehyde concentrations were determined from gas flow rate measurements using calibrated mass flow meters and the total pressure inside the reaction cell. The difference found between both methods for hexanal was about 10% and between 8 and 24% for *trans*-2-hexenal. Optically measurements of aldehyde concentration were preferred in this work.

2.2.2 Reactants

He (Carburos Metálicos, 99.999%) and Ar (Praxair, 99.999%) were used as a bath gas without additional purification. Samples of hexanal (Aldrich, 98%) and *trans*-2-hexenal (Aldrich, 98%) were purified by freeze/pump/thaw cycles. Aqueous solution of H_2O_2 (Sharlau, 50% w/v) was treated as described earlier (Jiménez et al., 2005a).

3 Results and discussion

3.1 UV absorption cross sections (σ_λ)

The weighted average of σ_λ for hexanal (from 250 to 330 nm) and *trans*-2-hexenal (from 290 to 370 nm) determined in this work are listed at every nm in Table 1S of the supplementary information (http://www.atmos-chem-phys-discuss.net/6/13225/2006/acpd-6-13225-2006-supplement.pdf). The uncertainty in the absorption cross sections is estimated to be ∼4% at the absorption maximum and represents twice the standard deviation from the weighted average. These data are also shown in Fig. 2, where the measured σ_λ as a function of wavelength are plotted for both aldehydes. As it can be seen in this figure, σ_λ is on the order of 10^{-20} cm^2 in both cases.

The absorption maximum around 295 nm for hexanal and 329 nm for *trans*-2-hexenal corresponds to the $n \rightarrow \pi^*$ transition (C=O chromophore). Conjugation makes the maximum move to longer wavelengths ($\lambda \geq 290$ nm) in *trans*-2-hexenal, and the whole band lies in the actinic region. This fact indicates that photolysis can be an important removal pathway for this aldehyde in the troposphere.

As far as we know, there are two previous studies on the absorption cross sections of hexanal (Plagens et al., 1998; Tang and Zhu, 2004). Plagens et al. (1998) determined σ_λ between 259 and 375 nm and the unpublished data are listed in the on-line database (Keller-Rudek and Moorgart, 2006). More recently, Tang and Zhu (2004) measured σ_λ in the 280–330 nm spectral range every 5 nm (11 discrete wavelengths). In Fig. 2 both measurements are compared with those from this work. The spectral range recorded in both studies is similar to that of this work. The wavelength of the absorption maximum (and the maximum absorption cross section) was found to be 294 nm ($\sigma_\lambda = 6.076 \times 10^{-20}$ cm^2) by Plagens et al. (1998) and 295 nm ($\sigma_\lambda = (6.45 \pm 0.18) \times 10^{-20}$ cm^2) by Tang and Zhu (2004). Their results are in reasonable agreement with our value ($(5.68 \pm 0.15) \times 10^{-20}$ cm^2) at 295 nm). The maximum σ_λ found in this work is less than 12% lower than that of previous studies (Plagens et al., 1998;

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Tang and Zhu, 2004). This small difference can be attributed to a systematic error in the measurement of the pressure inside the absorption cell. An underestimation or over-estimation of 10% especially at low pressures (0.9–7 Torr in this work and 0.5–8 Torr in Tang and Zhu's work) can lead to the observed difference. Another possible reason for the difference observed was pointed out by Tang and Zhu (2004). These authors at-tributed to a possible drop in the dye-laser fluence the slightly higher absorption cross sections measured respect to those of Plagens et al. (1998).

In contrast, only one measurement of the absorption cross sections for *trans*-2-hexenal has been recently performed by O'Connor et al. (2006). Their value of σ_λ at the absorption maximum of 6.2×10^{-20} cm^2 is in good agreement with our reported value ($\sigma_\lambda = (5.55 \pm 0.30) \times 10^{-20}$ cm^2).

3.2   OH kinetic measurements

In this kinetic study, the disappearance of OH radical in the reactor is mainly due to its reaction with hexanal (R3) or *trans*-2-hexenal (R4). However, its reaction with H$_2$O$_2$ (R5) and the diffusion loss (R6) have to be considered as well:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \quad k_{prec} \tag{R5}$$

$$OH \rightarrow \text{Diffusion loss} \quad k_{diff} \tag{R6}$$

Under pseudo-first order conditions, the temporal profiles of OH radical are described by Eq. (4):

$$[OH]_t = [OH]_0 \exp(-k't) \tag{4}$$

where k' (1138–8880 s^{-1}), extracted from the analysis of the exponential curves, is the pseudo-first order rate coefficient defined as:

$$k' = k_{OH}[RCHO] + k_0 \tag{5}$$

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k_0 (84–1260 s^{-1}) is the rate coefficient determined in the absence of aldehyde:

$$k_0 = k_{prec}[H_2O_2] + k_{diff} \qquad (6)$$

The bimolecular rate coefficient k_{OH} was then determined by plotting $k' - k_0$ versus the aldehyde concentration. An example of these plots at 263 and 353 K is shown in Fig. 3 for both aldehydes. As can be seen in this figure, the slopes (and, therefore, k_{OH}) are higher for *trans*-2-hexenal than for hexanal at all temperatures. OH rate coefficients for *trans*-2-hexenal are almost twice than that found for hexanal. That could indicate that the addition channel in Reaction (R4) is not negligible, similarly to other unsaturated aldehydes (Magneron et al., 2002).

In Table 1, the rate coefficients k_{OH} for both aldehydes at room temperature are listed and compared with those of previous studies on the same reactions. These values are the weighted average of several measurements performed at 50 Torr. As it can be seen, our reported k_{OH}(298 K) for hexanal is in excellent agreement, within the error limits given, with previous absolute measurements carried out in our laboratory (Albaladejo et al., 2002) and other relative measurements performed at atmospheric pressure (Papagni et al., 2000; D'Anna et al., 2001). Regarding k_{OH}(298 K) for *trans*-2-hexenal, there are several studies (Atkinson et al., 1995; Grosjean and Williams, 1992; Albaladejo et al., 2002) which are in reasonable agreement with the one reported here. The difference between our previously reported k_{OH}(298 K) for *trans*-2-hexenal (Albaladejo et al., 2002) and the one measured in this work is probably due to the different method used to measure the gas-phase concentration of *trans*-2-hexenal. In that case, the aldehyde concentration was estimated by using flow measurements.

The obtained rate coefficients k_{OH} as a function of temperature (T=263–353 K) are presented in Table 2 for hexanal and *trans*-2-hexenal. k_{OH}(T) are the weighted average of several measurements at each temperature and the error bars account for twice the standard deviation that include any systematic error. In Fig. 4, Arrhenius plots are presented for the rate coefficients listed in Table 2. Solid lines represent the fit to the experimental data. The resulting Arrhenius expressions (±2σ) are:

Hexanal: $k_{OH}(T)=(4.2\pm0.8)\times10^{-12}\exp((565\pm65)/T)\,cm^3\,molecule^{-1}\,s^{-1}$

trans-2-hexenal: $k_{OH}(T)=(9.8\pm2.4)\times10^{-12}\exp((455\pm80)/T)\,cm^3\,molecule^{-1}\,s^{-1}$

This study represents the first report of the temperature dependence of k_{OH} for hexanal and *trans*-2-hexenal. However, Dr. J. B. Burkholder's group[2] has performed a simultaneous study on the temperature dependence of the OH+*trans*-2-hexenal reaction (T=244–374 K), observing a negative activation energy, which is in agreement with our results.

Negative activation energies for both reactions were found to be in concordance with the temperature dependence observed for other aldehydes (Atkinson and Arey, 2003). The E_a/R values for the reactions of *trans*-2-hexenal and hexanal with OH are similar, within the uncertainties given. Despite the negative temperature dependence observed for k_{OH} in the reaction with hexanal, the main reaction pathway for the reaction of saturated aldehydes with OH radicals seems to be H-atom abstraction from the CHO group (Albaladejo et al., 2002; Atkinson and Arey, 2003). This behaviour could be explained by the formation of an OH-addition complex, as pointed out by Smith and Ravishankara (2002), even though a pressure dependence of the rate coefficient was not observed (see Table 1). On the other hand, the negative temperature dependence observed in k_{OH} for *trans*-2-hexenal could indicate that the addition channel for the unsaturated aldehydes is not negligible, similarly to other aldehydes (Magneron et al., 2002).

4 Atmospheric implications

The contribution of the photolysis process in the actinic region ($\lambda \geq 290$ nm) and the chemical removal by the reaction with OH radicals to the total loss rate for these aldehydes has been calculated in order to estimate the atmospheric fate of hexanal and

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[2]Private communication.

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trans-2-hexenal. For ease of presentation, the estimation of the rate loss for each process and the total rate loss for both aldehydes has been described separately.

4.1 Photolysis rate estimation

The photolysis rate coefficient, $J_i(\theta,z)$, for a given compound in the actinic region at a certain zenith angle (θ) and altitude (z) can be estimated by solving the integral (Finlayson-Pitts and Pitts, 2000):

$$J_i(\theta, z) = \int_{\lambda_1 \geq 290\,nm}^{\lambda_2} \sigma_\lambda \phi_\lambda F(\lambda, \theta, z) d\lambda \tag{7}$$

Here $F(\lambda, \theta, z)$ is the solar actinic flux (in photons cm^{-2} s^{-1}) which are usually reported for a given wavelength range. For that reason, the photolysis rate can be expressed as follows:

$$J_i(\theta, z) \cong \sum_{\lambda_1 \geq 290\,nm}^{\lambda_2} \sigma_\lambda \phi_\lambda F(\lambda, \theta, z) \tag{8}$$

This summatory was extended over the wavelength range 290–330 nm and 290–370 nm for hexanal and *trans*-2-hexenal, respectively. Photolysis rates for hexanal (J_1) and *trans*-2-hexenal (J_2) have been calculated as a function of altitude (z) for Ciudad Real, Spain (38°56′16″ N, 3°55′ W) at noon (June, 2000) by using σ_λ from Table 1S. This situation corresponds to a zenith angle of 16°. The actinic solar flux was calculated by using the Tropospheric Ultraviolet Visible (TUV) model (Madronich and Flocke, 1999). An overhead ozone column and surface albedo were assumed to be 300 DU and 0.1, respectively. We also assumed that absorption cross sections were no temperature dependent and quantum yields, ϕ_λ, are taken as the unity (ϕ_λ=1) in both cases. Thus, J values obtained here are upper limits for the photolysis rate loss for both hexanal and *trans*-2-hexenal.

$J_1(z)$ and $J_2(z)$ are listed in Table 3 and plotted in Fig. 5. As it can be seen, the photolysis loss rate ranges from $2.31\times10^{-5}\,s^{-1}$ to $4.26\times10^{-5}\,s^{-1}$ for hexanal, whilst the corresponding values for *trans*-2-hexenal vary between 1.07×10^{-4} and $1.52\times10^{-4}\,s^{-1}$. That means that the tropospheric lifetimes due to UV photolysis ($\tau_{h\nu}(i)=1/J_i$) for hexanal and *trans*-2-hexenal are less than 12 h and less than 3 h, respectively. Tang and Zhu (2004) also estimated $\tau_{h\nu}$(hexanal), assuming a quantum yield of unity, for a zenith angle between 0 and 60° to be on the order of 4.5–12.6 h. These values are in good agreement with our results obtained at θ=16°. Plagens et al. (1998) also estimated maximum J_2 from the measurements carried out in EUPHORE under natural light conditions. They observed a fast photoisomerisation of *trans*-2-hexenal and reported that J_2=1.45×10^{-4} s^{-1}, in excellent agreement with the values obtained in this work.

4.2 Estimation of the aldehyde loss rate by OH reaction

The temperature dependences of k_{OH} derived from this work were used to estimate the loss rate of hexanal and *trans*-2-hexenal by chemical removal by OH radicals in the troposphere. At a certain temperature T (corresponding to a certain altitude in the troposphere), this loss rate is defined as the product of the rate coefficient $k_{OH}(T)$ and the OH concentration at that altitude. A 24-h averaged OH concentration of 1×10^6 molecule cm^{-3} was assumed in these estimations (Krol et al., 1998). In addition, an average environmental lapse rate of 6.5 K/km was used to calculate the temperature profile between 0 and 10 km (considering a temperature of 298.15 K at 0 km). In Table 3 the temperature variation as a function of altitude is shown together with aldehyde loss rates. Hexanal loss rate due to the reaction with OH radicals ranges from 2.79×10^{-5} s^{-1} at sea level to $4.74\times10^{-5}\,s^{-1}$ near the tropopause. In the case of *trans*-2-hexenal, the loss rate is larger than that of hexanal at all altitudes, as expected taking into account the larger rate coefficients $k_{OH}(T)$. In Fig. 5, these loss rates are also plotted as a function of the altitude (z=0–10 km).

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4.3 Tropospheric loss rate for hexanal and *trans*-2-hexenal

The tropospheric lifetime of these aldehydes can be defined as:

$$\tau_i = \frac{1}{J_i + \sum k_{\text{oxid}} \, [\text{Oxidant}]} \tag{9}$$

In this definition only UV photolysis (J_i) and homogeneous reactions with different oxidants (ozone (O_3), nitrate radical (NO_3), OH, and Cl atoms) have been considered.

In general, the reactivity of O_3 with saturated and unsaturated aldehydes is very slow (less than 10^{-18} cm^3 molecule^{-1} s^{-1}) (Atkinson and Arey, 2003; Grosjean et al., 1996). Only the rate coefficient for the reaction of O_3 with *trans*-2-hexenal has been measured at room temperature by Grosjean et al. (1996) ((1.28 ± 0.28)$\times10^{-18}$ cm^3 molecule^{-1} s^{-1}). Assuming an average ozone concentration of 7.4×10^{11} molecule cm^{-3} (30 ppb) (Logan, 1985), the tropospheric lifetimes at room temperature for hexanal and *trans*-2-hexenal are expected to be more than 10 days. The reaction of hexanal with NO_3 has been studied at 298 K by D′ Anna et al. (2001) by a relative method. The rate coefficient obtained was (1.54 ± 0.19)$\times10^{-14}$ cm^3 molecule^{-1} s^{-1}. For the corresponding reaction with *trans*-2-hexenal, the reported value for the room temperature rate coefficient by Cabañas et al. (2001) was (5.49 ± 0.95)$\times10^{-14}$ cm^3 molecule^{-1} s^{-1}. Considering an average NO_3 concentration of 2.0×10^7 molecule cm^{-3} (8 ppt) (Finlayson-Pitts and Pitts, 2000), the tropospheric lifetimes of hexanal and *trans*-2-hexenal would be more than one month and 10 days, respectively. Regarding Cl atoms, their reaction with hexanal and *trans*-2-hexenal has been recently studied by Rodríguez et al. (2005) reporting atmospheric lifetimes at 298 K of 8 and 12 days, respectively. As can be extracted from the results in Table 3, the tropospheric lifetimes for these aldehydes due to the reaction with OH are about 6 h for *trans*-2-hexenal and 10 h for hexanal. Thus, the chemical removal by other tropospheric oxidants, such as O_3, NO_3 radicals, and Cl atoms is negligible compared to the reaction with OH radicals. Therefore, the total loss rate of hexanal and *trans*-2-hexenal can be defined as the sum of the photolysis rate loss (J_1 and

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J_2) and the loss rate due to Reactions (R3) and (R4). Taking into account all these values, the tropospheric lifetimes τ_{OH} are expected to be smaller than 5 and 2 h for hexanal and *trans*-2-hexenal, respectively. As can also be seen in Table 3 and Fig. 5, the major contribution to the total loss rate for *trans*-2-hexenal is the photolysis process (around 70%). However, the reaction with OH is not negligible at all, since it accounts for ca. 30% of the total loss rate. For hexanal, both processes contribute almost equally to the total loss rate.

5   Conclusions

As shown in Table 3, the major tropospheric transformation processes for the aliphatic aldehydes, hexanal and *trans*-2-hexenal are photolysis and reaction with the OH radical.

Photolysis is calculated to be competitive with the OH radical reaction as a tropospheric loss process for hexanal, while the photochemistry of the unsaturated aldehyde is more important than removal by homogeneous reaction with OH radicals. This is not surprising, since the whole $n \rightarrow \pi^*$ band is lying in the actinic region for *trans*-2-hexenal. We must remark that the photolysis loss rates estimated in this work are upper limits, since some approximations have been made.

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Table 1. Comparison of the OH rate coefficient at 298 K obtained in this work with previous studies.

Aldehyde	p_T (Torr)	$k_{OH} \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	Technique[a]	Reference
hexanal	50	2.78±0.50	PLP-LIF	This work
	100–400	2.60±0.21	PLP-LIF	Albaladejo et al. (2002)
	760	2.86±0.13	RR-FTIR	D'Anna et al. (2001)
	740	3.17±0.15	RR-GC	Papagni et al. (2000)
trans-2-hexenal	50	4.68±0.50	PLP-LIF	This work
	100–400	2.95±0.45	PLP-LIF	Albaladejo et al. (2002)
	760	3.10	Estimated	Grosjean and Williams (1992)
	740	4.41±0.94	RR-GC	Atkinson et al. (1995)

[a] PLP-LIF, pulsed laser photolysis-laser induced fluorescence; RR, relative rate

Table 2. Averaged rate coefficients (k_{OH}) as a function of temperature for the gas-phase reaction of OH radicals with hexanal and *trans*-2-hexenal.

T (K)	$(k_{OH} \pm 2\sigma) \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	
	hexanal	*trans*-2-hexenal
263	3.30±0.40	5.44±0.20
268	3.19±0.44	5.40±0.32
273	3.46±0.22	5.50±0.40
278	3.22±0.44	5.17±0.20
286	3.18±0.40	4.83±0.20
298	2.78±0.50	4.68±1.00
307	2.78±0.22	4.07±1.10
321	2.55±0.22	3.91±0.41
336	2.09±0.14	3.83±0.34
353	2.10±0.07	3.50±0.44

Table 3. Total loss rate estimated for hexanal and for *trans*-2-hexenal as a function of altitude (z) in the troposphere.

z (km)	T (K)	J_1 (10^{-5} s^{-1})	$k_{OH}(T)[OH]_{avg}$ (10^{-5} s^{-1})	J_2 (10^{-4} s^{-1})	$k_{OH}(T)[OH]_{avg}$ (10^{-4} s^{-1})
		hexanal		trans-2-hexenal	
0	298.15	2.31	2.79	1.07	0.45
1	291.65	2.98	2.91	1.19	0.47
2	285.15	3.38	3.05	1.27	0.49
3	278.65	3.68	3.19	1.34	0.50
4	272.15	3.88	3.35	1.38	0.52
5	265.65	3.99	3.52	1.42	0.55
6	259.15	4.14	3.72	1.45	0.57
7	252.65	4.21	3.93	1.48	0.60
8	246.15	4.26	4.17	1.50	0.63
9	239.65	4.29	4.44	1.51	0.66
10	233.15	4.26	4.74	1.52	0.70

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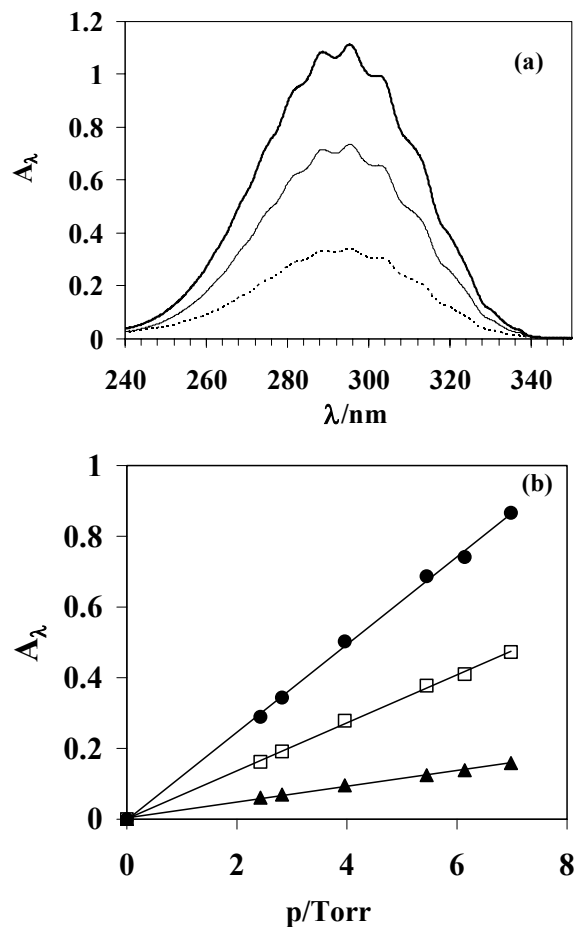
Fig. 1. **(a)** Absorption spectra for hexanal recorded at 1.07 (dashed line), 3.09 (thin line), and 5.01 Torr (thick line). **(b)** Beer-Lambert law plots at 310 nm (•); 320 nm (□), and 330 nm (▲).

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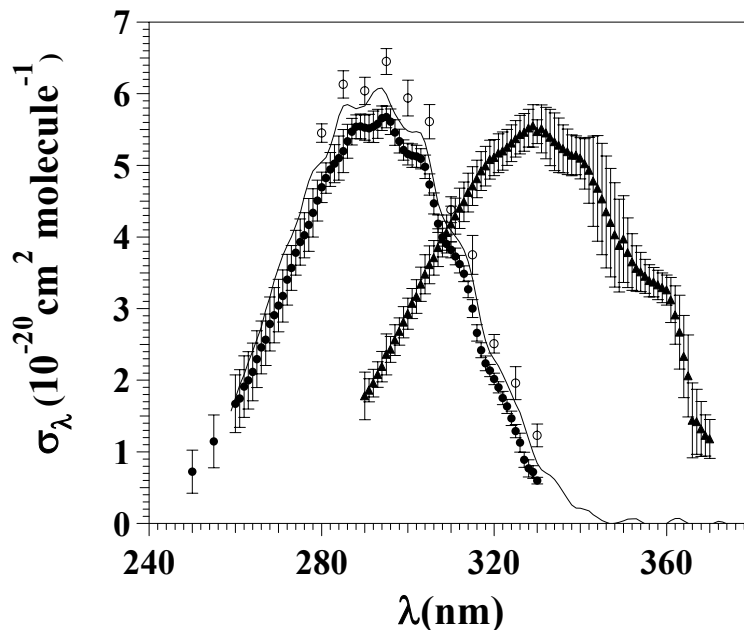
Fig. 2. Absorption spectra for hexanal (•) and *trans*-2-hexenal (▲) reported in this work. Comparison of the σ_λ determined in this work for hexanal with those found in the bibliography (solid line from Plagens et al., 1998, and open circles from Tang and Zhu, 2004).
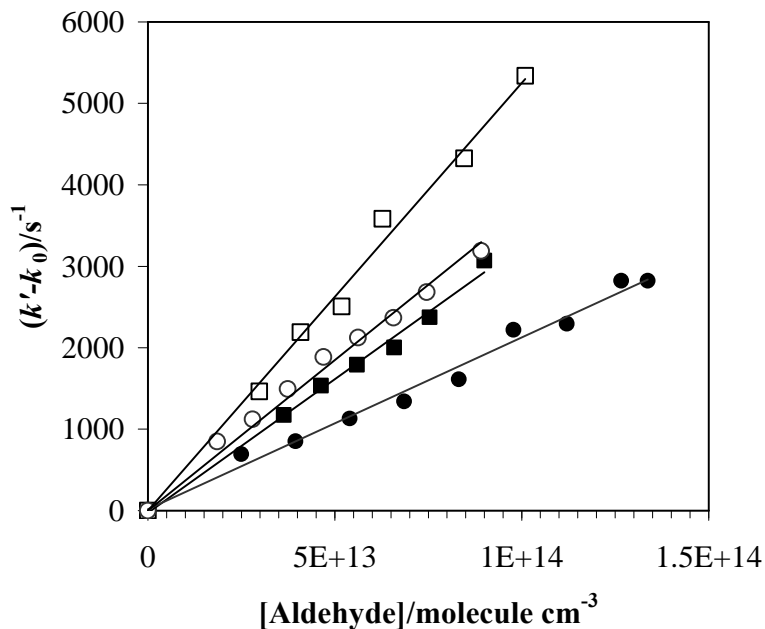
Fig. 3. Pseudo-first order plots of $k' - k_0$ versus aldehyde concentration hexanal (filled symbols) and *trans*-2-hexenal (open symbols) at 263 K (squares) and 353 K (circles).

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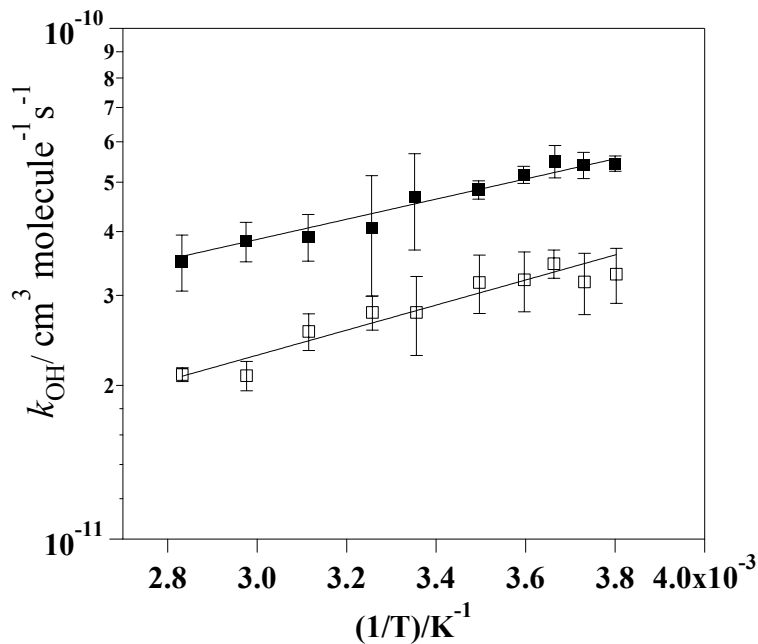
**Fig. 4.** Arrhenius plots for the reactions of OH radicals with hexanal (□) and *trans*-2-hexenal (■).

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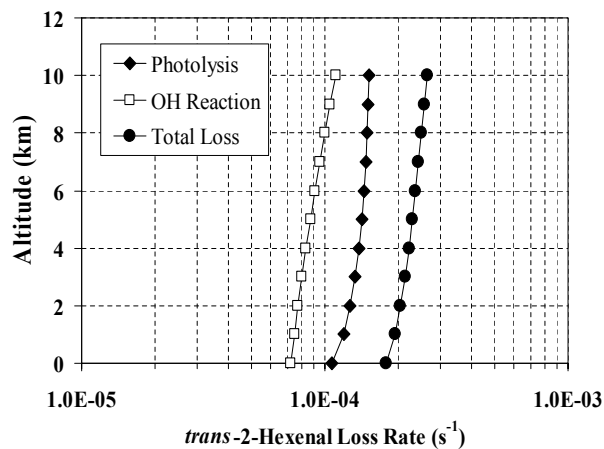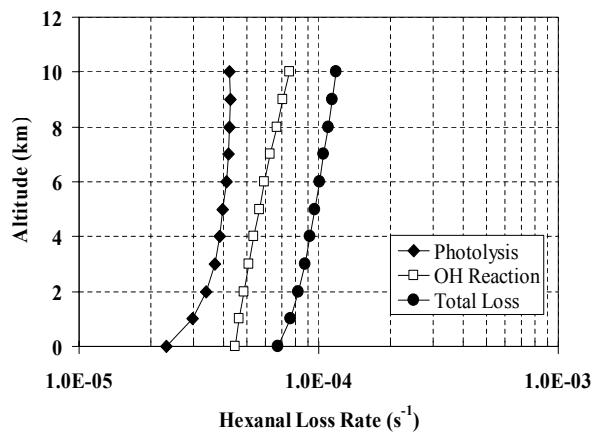
Fig. 5. Tropospheric loss rate for hexanal and *trans*-2-hexenal due to UV photolysis and reaction with OH radicals.