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Kinetic study of the gas-phase reaction of atomic chlorine with a series of aldehydes

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Abstract. The reactions of Cl atoms with a series of unsaturated aldehydes have been investigated for the first time using a relative method. In order to obtain additional information for a qualitative structure versus reactivity discussion, we have also determined the rate coefficients for the reactions of atomic chlorine with their respective saturated aldehydes. These relative measurements were performed at room temperature and atmospheric pressure of air and N_2, by using ethane, propene and 1-butene as reference compounds. The weighted average relative rate constants obtained, $k_{Cl}\pm 2\sigma$ (in units of cm^3 $molecule^{-1}$ s^{-1}) were: trans-2-pentenal $(1.31\pm0.19)\times10^{-10}$; trans-2-hexenal $(1.92\pm0.22)\times10^{-10}$; trans-2-heptenal $(2.40\pm0.29)\times10^{-10}$; n-pentanal $(2.56\pm0.27)\times10^{-10}$; n-hexanal $(2.88\pm0.37)\times10^{-10}$; n-heptanal $(3.00\pm0.34)\times10^{-10}$.

Finally, results and atmospheric implications are discussed and compared with the reactivity with OH and NO_3 radicals.

1 Introduction

Large quantities of aldehydes are directly emitted into the atmosphere from biogenic and anthropogenic sources and are also produced in the atmosphere as intermediates in the photooxidation of volatile organic compounds (Papagni et al., 2000). Recently, several saturated aliphatic aldehydes have been identified and quantified in on-road vehicle emissions (Grosjean et al., 2001). Moreover, higher aldehydes have been observed in ambient air in urban and rural areas due to the emissions from vegetation (Prates et al., 1998). In relation to the tropospheric sinks, carbonyl compounds generally show a weak absorption spectrum in the region 220–370 nm resulting from a dipole forbidden n-π^* transition which may lead to photo-dissociation, generating organic free radicals in the lower troposphere.The primary reaction of these organic compounds can occur with many atmospheric oxidants such as OH (in the day-time), NO_3 (in the night-time), O_3 (mainly with unsaturated compounds) and Cl (in the marine environment and coastal areas). In this sense, the reactions with Cl atoms have been postulated to be an additional and significant removal process of VOCs in marine troposphere, where the concentration of Cl precursor species from the reactions of NaCl in sea salt particles has been reported to be high (Spicer et al., 1998), and it may significantly contribute to the formation of ozone and other components of the photochemical smog in these areas. Assuming a peak Cl concentration from $5–15\times10^3$ atoms cm^{-3} (Pszenny et al., 1993) to 10^4–10^5 atoms cm^{-3} (Wingenter et al., 1996; Singh et al., 1996) the effect on the removal of aldehydes can be relevant. Therefore, more information about Cl-initiated oxidation processes is needed to assess the impact of VOCs on air quality.

In this work, we report a kinetic study at room temperature and high pressure conditions of the reactions between Cl and a series of aldehydes which have not been studied previously, excepting n-pentanal, n-hexanal and n-heptanal. The obtained results are compared with those corresponding to the reactions with OH and NO_3 radical. In this sense, the study of the reactions of trans-2-pentenal trans-2-hexenal, trans-2-heptenal, n-pentanal, n-hexanal, n-heptanal with OH radical has been carried out recently by Albaladejo et al. (2002) by means of PLP/LIF technique at room temperature and as a function of the total pressure. Cabañas et al. (2001a, b) also studied the temperature dependence of the reaction of these saturated and unsaturated aldehydes with NO_3 using a fast-flow discharge system with LIF detection. The relative rate of these three reactions may define the global distribution of products from the atmospheric oxidation of aldehydes under local conditions.

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Table 1. Summary of relative rate measurements for aldehydes at room temperature and 1 atm pressure of N_2 or air, and the corresponding absolute value.

Aldehyde	[Ald.]10^{15} (molecule cm^{-3})	Reference	[Ref.]10^{15} (molecule cm^{-3})	Diluent gas (No. of runs)	[Cl_2]10^{15} (molecule cm^{-3})	k_{ald}/k_{ref}	k_{ald} (cm^3 molecule^{-1} s^{-1})
Pentanal	1.9–3.0	Ethane	1.4 –2.7	N_2(2) Air (2)	3.0–4.5	4.46	2.61×10^{-10}
	1.9–2.9	Propene	1.9–2.9	N_2(3) Air (3)	3.0–4.5	1.03	2.37×10^{-10}
	1.9–3.5	1-Butene	1.9–3.5	N_2(2) Air (3)	3.0–4.5	0.90	2.69×10^{-10}
							$\mathbf{(2.56\pm0.27)\times10^{-10}}$
Hexanal	1.6–3.2	Ethane	1.4–3.0	N_2(2) Air (2)	3.0–5.0	4.65	2.72×10^{-10}
	1.6–3.5	Propene	1.6–3.5	N_2(3) Air (2)	3.4–5.0	1.21	2.79×10^{-10}
	1.8–3.5	1-Butene	1.6–3.5	N_2(2) Air (2)	3.0–4.5	1.05	3.14×10^{-10}
							$\mathbf{(2.88\pm0.37)\times10^{-10}}$
Heptanal	1.5–3.0	Ethane	1.2–2.7	N_2(2) Air (3)	2.8–4.5	5.00	2.92×10^{-10}
	1.6–3.0	Propene	2.3–3.0	N_2(2) Air (2)	3.0–4.5	1.31	3.03×10^{-10}
	1.6–3.0	1-Butene	2.3–3.0	N_2(3) Air (2)	3.0–4.2	1.02	3.06×10^{-10}
							$\mathbf{(3.00\pm0.34)\times10^{-10}}$
trans-2-pentenal	1.6–2.9	Ethane	1.2–2.2	N_2(3) Air (2)	2.5–4.0	2.08	1.22×10^{-10}
	1.9–3.0	Propene	1.9–3.0	N_2(3) Air (3)	2.5–4.0	0.60	1.38×10^{-10}
	1.9–3.0	1-Butene	1.9–3.0	N_2(2) Air (2)	2.3–3.8	0.44	1.32×10^{-10}
							$\mathbf{(1.31\pm0.19)\times10^{-10}}$
trans-2-hexenal	1.6–2.9	Ethane	1.2–2.2	N_2(2) Air (2)	2.5–4.0	3.24	1.89×10^{-10}
	1.9–3.0	Propene	1.9–3.0	N_2(2) Air (2)	2.5–4.0	0.84	1.94×10^{-10}
	1.9–3.0	1-Butene	1.9–3.0	N_2(2) Air (2)	2.4–3.7	0.65	1.94×10^{-10}
							$\mathbf{(1.92\pm0.22)\times10^{-10}}$
trans-2-heptenal	1.2–2.5	Ethane	1.0–2.0	N_2(3) Air (3)	2.5–4.0	4.48	2.62×10^{-10}
	1.4–2.5	Propene	1.4–2.5	N_2(2) Air (2)	2.5–3.9	1.06	2.46×10^{-10}
	1.4–2.5	1-Butene	1.4–2.5	N_2(3) Air (3)	2.2–3.8	0.71	2.13×10^{-10}
							$\mathbf{(2.40\pm0.29)\times10^{-10}}$

2 Experimental

The rate constants were measured by following the simultaneous losses of the aldehyde and the different reference compounds (ethane, propene and 1-butene) during their reactions with chlorine atoms, using a 200 L Teflon reaction chamber with GC-FID detection. The arrangement of the apparatus and experimental procedures were described in detail previously, (Martínez et al., 2004), so only a brief description is given here. Relative rate experiments were carried out in air or N_2 to check the potential interference from OH chemistry.

In the presence of atomic chlorine (molecular chlorine was photolyzed using a set of UV fluorescent lamps with a maximum intensity at 370 nm), the corresponding aldehyde and reference compound decay via the following reactions:

$$\mathrm{Cl} + \mathrm{Aldehyde} \rightarrow \mathrm{Products}\ k_{ald} \quad (1)$$

$$\mathrm{Cl} + \mathrm{Reference} \rightarrow \mathrm{Products}\ k_{ref} \quad (2)$$

If the reaction with Cl radicals is the only sink for the aldehyde and reference compounds, and no reactant is reformed in the process, it can be shown that

$$\ln\left(\frac{[\mathrm{aldehyde}]_0}{[\mathrm{aldehyde}]_t}\right) = \frac{k_{ald}}{k_{ref}} \ln\left(\frac{[\mathrm{reference}]_0}{[\mathrm{reference}]_t}\right)$$

where $[\mathrm{aldehyde}]_0$ and $[\mathrm{reference}]_0$ and $[\mathrm{aldehyde}]_t$ and $[\mathrm{reference}]_t$ are the concentrations of reactant and reference compound at time t=0 and t, respectively; and k_{ald} and k_{ref}

are the rate constants of Reactions (1) and (2), respectively. Given an accurate value for the rate constant of the reference compound (k_{ref}), the rate constant for the aldehyde (k_{ald}) can be calculated immediately, i.e. k_{ald}=(slope) k_{ref}. The corresponding ranges of concentrations for the aldehydes, reference compounds, Cl-atom source, etc. are given in Table 1.

The reaction chamber was manually agitated prior to the irradiation to ensure good mixing. The reagents were allowed to mix for 2 h before the first chromatogram was taken. The mixture was then photolysed. Total irradiation times ranged from 60 to 120 min.

Aldehydes were expected to be lost by direct photolysis or adsorption in the smog chamber. For such reason, the carbonylic compounds were introduced alone in the reactor. Then the bag was irradiated using all fluorescent tubes for twice the duration of kinetic experiments to evaluate both photolysis and wall losses. No measurable changes were observed.

In additional experiment, reaction mixtures were sampled in the dark to test for potential losses of the aldehydes or reference compound by a dark reaction with Cl_2, but no secondary reactions was observed under the experimental conditions.

The chemicals used were as follows: Synthetic Air (99.999%, Air Liquide), N_2 (99.998%, Air Liquide), Cl_2 (99.8%, Praxair); ethane (99+%, Aldrich), propene (99+%, Aldrich), 1-butene (99+%, Aldrich), trans-2-pentenal (95%, Aldrich), trans-2-hexenal (98%, Aldrich), trans-2-heptenal (98%, Acros Organic), n-pentanal (97%, Aldrich), n-hexanal (98%, Aldrich) and n-heptanal (95%, Aldrich) were further purified before use by repeated trap-to-trap distillation.

3 Results and discussion

Figure 1 shows the obtained relative loss of the aldehydes versus the reference compounds in the presence of Cl atoms at room temperature and atmospheric total pressure. Typically, a set of experiments was repeated on different days with a total of approximately 8–10 runs. The plot of $\ln([\text{aldehyde}]_0/[\text{aldehyde}]_t)$ vs. $\ln([\text{reference}]_0/[\text{reference}]_t)$ yields a straight line with the slope of k_{ald}/k_{ref}, showing in all cases a good linearity which suggests that the extent of secondary reactions was negligible. The rate constants of the reactions of Cl with the compounds used as reference in this work were taken as, from reference Hitsuda et al. (2001) $(5.85\pm0.55)\times10^{-11}$, Stutz et al. (1998) $(2.31\pm0.29)\times10^{-10}$ and Orlando et al. (2003) $(3.00\pm0.40)\times10^{-10}$ ($cm^3\,molecule^{-1}\,s^{-1}$) for ethane, propene and 1-butene, respectively. The slopes of such sets were calculated using a weighted linear least-squares fit and the quoted errors in the final results are 2σ. The obtained results were independent to the bath gas used, air or N_2 and so the reported kinetic rate constants are the average values, Table 1.

No previous experimental rate constant values have been found for the reactions of the studied aldehydes with Cl atoms, except for n-pentanal (Thèvenet et al., 2000), n-hexanal and n-heptanal (Plagens, 2001). Our experimental result for n-pentanal is in excellent agreement with the value reported by Thèvenet et al., $(2.6\pm0.3)\times10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$. These authors reported the average rate constant derived from the experiments with different reference compounds (ethane, propane, n-butane) and also using a relative technique. Plagens determined the coefficients for some alkyl aldehydes in a chamber, using the relative technique and FTIR for the analysis and 1,3-butadiene as the reference compound. The values obtained by Plagens for hexanal and heptanal $(3.23\pm0.15)\times10^{-10}$ and $(3.53\pm0.10)\times10^{-10}$ (in $cm^3\,molecule^{-1}\,s^{-1}$), respectively are around 12 and 18% higher than those reported for the same compounds in the present work but agree within the combined error limits of both determinations. Recent unpublished work in another laboratory (Cuevas et al., personal communication) using the absolute method of Laser Photolysis-Resonance Fluorescence (PLP-RF), has also demonstrated a Cl+n-pentanal rate constant that is 27% lower than that reported by Thevenet et al. (2000) at room temperature, but that is consistent with the findings of this present study.

From the analysis of the data given in Table 1, reaction rate constants are of the order of $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ and they increase when the length of the organic chain increases in both saturated and unsaturated aldehydes,

$$k_{\text{n-pentanal}} < k_{\text{n-hexanal}} < k_{\text{n-heptanal}}$$

$$k_{\text{trans-2-pentenal}} < k_{\text{trans-2-hexenal}} < k_{\text{trans-2-heptenal}}$$

A similar behavior, the increase of the rate constant value with the number of methylene groups, was also found in the reactions of Cl atoms with alkanes (Wallington et al., 1988; Hooshiyar and Niki, 1995; Qian et al., 2001).

On the other hand, in Table 2, the rate constants for the reactions of Cl radicals with the studied aldehydes and with similar structured alkanes and alkenes are given for comparison. The constants for the reaction of Cl with saturated aldehydes, are similar to the values for the reaction of Cl with saturated alkanes (Hooshiyar and Niki, 1995; Qian et al., 2001). However, the obtained coefficients for α,β-unsaturated aldehydes with Cl are smaller than the rate constants for the reaction of Cl with the saturated aldehydes and the reference alkenes (see Table 2). In this sense, reactivity ratios of 0.43 and 0.40 may be calculated for Cl trans-2-pentenal/1-butene and trans-2-hexenal/1-pentene, respectively. In the case of the trans-2-heptenal/1-hexene reactivity ratio, no data about the rate constant has been found for the reaction of 1-hexene with Cl atoms. Nevertheless, on the basis of the increase of the reactivity of the series Cl+propene, Cl+1-butene and Cl+1-pentene, $(2.31\pm0.29)\times10^{-10}$, $(3.00\pm0.40)\times10^{-10}$ and 4.83×10^{-10}

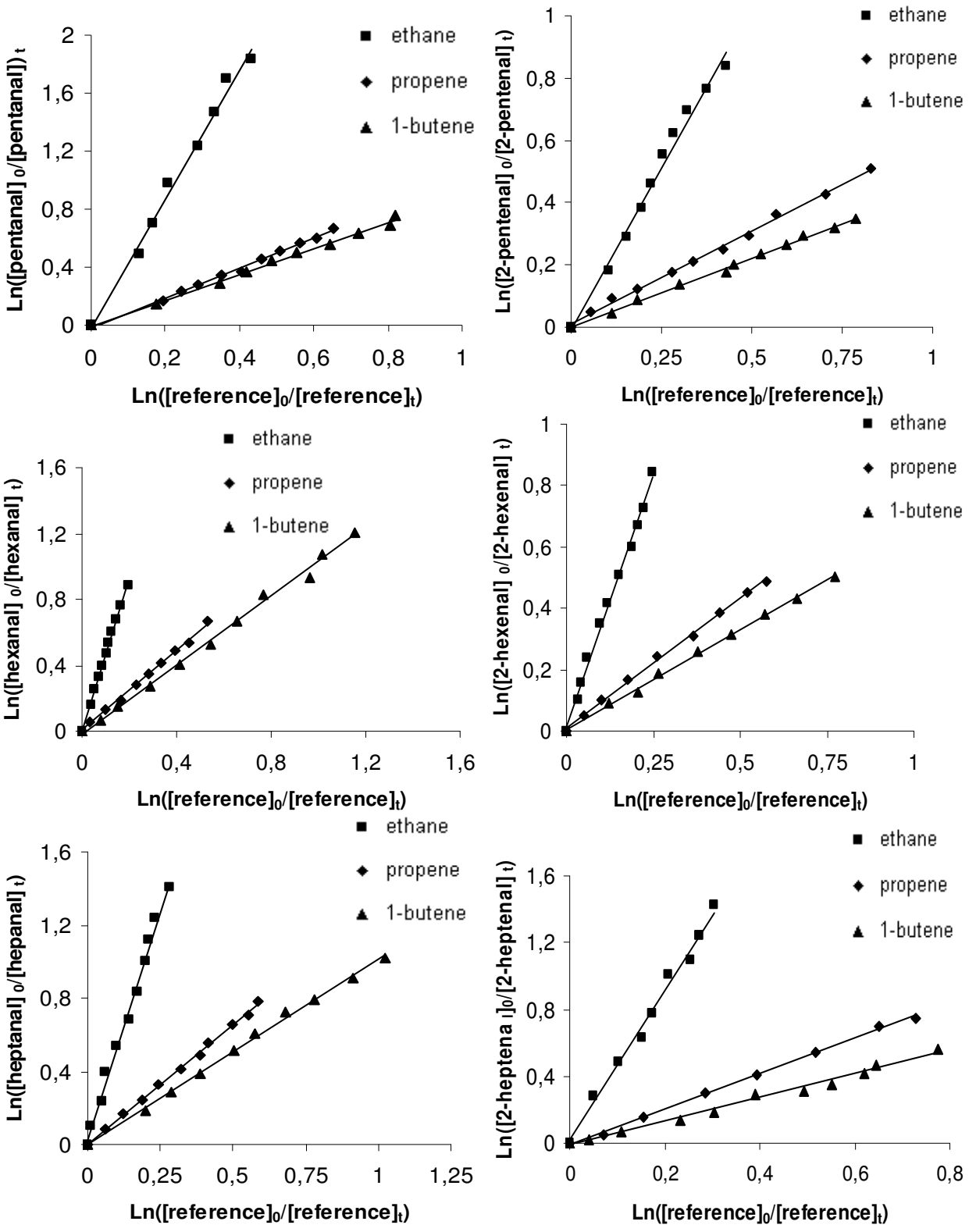

Fig. 1. Decays of aldehydes vs. reference compounds in the presence of Cl atoms at room temperature and atmospheric total pressure of N_2 or Air.

Table 2. Room temperature rate constants of Cl with aldehydes and with the corresponding alkanes or alkenes at room temperature. k_{alkane} or k_{alkene} and $k_{aldehyde}$ are in units of cm^3 $molecule^{-1}$ s^{-1}.

Alkane, k_{alkane} Alkene, k_{alkene}	Aldehyde, $k_{aldehyde}$	$k_{aldehyde}/k_{alkane}$ $k_{aldehyde}/k_{alkene}$
butane, 2.15×10^{-10} [a]	n-pentanal, 2.56×10^{-10} [b]	1.19
Pentane, 2.5×10^{-10} [c]	n-hexanal, 2.88×10^{-10} [b]	1.15
hexane, 3.06×10^{-10} [c]	n-heptanal, 3.00×10^{-10} [b]	0.98
1-butene, 3.00×10^{-10} [d]	trans-2-pentenal, 1.31×10^{-10} [b]	0.43
1-pentene, 4.83×10^{-10} [e]	trans-2-hexenal, 1.92×10^{-10} [b]	0.40
1-hexene, $>4.83\times10^{-10}$ [f]	trans-2-heptenal, 2.40×10^{-10} [b]	<0.49[f]

[a] Tyndall et al. (1997); [b] This work; [c] Hooshiyar et al. (1995); [d] Orlando et al. (2003); [e] Coquet et al. (2000); [f] See Text.

(cm^3 $molecule^{-1}$ s^{-1}), respectively, one can assume a reactivity ratio trans-2-heptenal/1-hexene <0.5 which is similar to the other two unsaturated aldehydes, in light of the probable value for the Cl+1-hexene constant, $>4.83\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

The deactivation effects observed in this work for aldehydes is smaller than those found for reactions of ketones (both saturated and unsaturated) and the corresponding alkanes with Cl atoms (Albaladejo et al., 2003). The reason may reside in the fact that the CHO group is a reactive site itself (and so it contributes to the global rate constant) while reactions on the CO group are not expected.

The previous observations may be explained if we take into account the reaction mechanism. The observed mechanism for the reactions of NO_3 radical with aldehydes proceeds by H-atom abstraction from the CHO group (Atkinson and Arey, 2003). OH reactions with formaldehyde, acetaldehyde and propanal are considered to proceed also exclusively by H-atom abstraction from the CHO group although contributions to the rate constants are expected from other CH bonds for higher aldehydes (Atkinson and Arey, 2003).

The results obtained in this work may by justified by the higher reactivity of Cl atoms compared to NO_3 and OH radicals, (approximately four and one order of magnitude, respectively, Table 3). Cl atoms are much more reactive and thus less selective than NO_3 and even OH radicals. In this sense, H-atom transfer from the alkyl groups is much faster with Cl than with NO_3 or OH. So, the CHO group is no longer the exclusive site of reaction. The rate constants of the related alkanes are similar to those of the aldehydes, Table 2, indicating that the contribution of CH bonds (other than CHO) to the global rate constant must be important. This was also observed even for shorter aliphatic aldehydes like acetaldehyde and propanal (Thevenet et al., 2000). In the case of propanal, Structure-Activity Relationships based calculations predicted the aliphatic chain as the dominant reaction site (Thevenet et al., 2000). Nevertheless, for the relatively large saturated aldehydes studied in this work, the increase of the rate constant with the number of CH_2 groups is slight and it may not be exclusively due to the increase of the number of reactive sites. The kinetic rate constants are so high that reactions are becoming limited by the collision frequency (which also increases with the size of the molecule) rather than by the reaction itself.

With respect to the series of unsaturated aldehydes, these compounds have an additional reactive site, the double bond. The addition mechanism may even be predominant for Cl – alkenes reactions at atmospheric pressure and room temperature (Lee and Rowland, 1977). So an increase of reactivity from the alkene or the saturated aldehyde was expected but was not observed.

The conjugation of the double bond with the carbonylic group could be responsible for the decrease of reactivity when both groups are found together. First, the presence of the double bond involves the substitution of two CH_2 groups by CH=CH. These hydrogen atoms are linked to "sp^2" hybridized carbon atoms with bonds of higher energy dissociation and so less susceptible to abstraction. Second, the conjugation with the carbonylic group significantly reduces the partial negative charge on the β carbon atom and thus the electrophylic addition is inhibited in that position compared to the reference alkene. In this sense the addition mechanism is expected to occur only (mainly) on the α carbon atom. Semi-empirical PM3 calculations were performed within the MOPAC package to obtain the partial charge on the β carbon atoms, giving similar results for the three studied unsaturated aldehydes, -0.125 ± 0.001 while the partial charge on the same carbon atom of the equivalent alkene was clearly higher, 0.204 ± 0.001.

Concerning the atmospheric implications of the studied Cl atoms reactions, the results are compared with the reactivity with O_3, OH and NO_3 radicals in Table 3. The rate constants summarised in the table can be used to calculate the atmospheric lifetimes expressed in hours ($\tau=1/k[X]$, where X=Cl, OH, NO_3 or O_3) using the average global concentrations: $[Cl]=10^3$–10^4 (Pszenny et al., 1993; Wingenter et al., 1996), $[OH]=5.0\times10^5$ (Brauers et al., 1996), $[NO_3]=7.4\times10^6$ (Noxon, 1983) and $[O_3]=7.4\times10^{11}$ (Logan, 1985) (in units of molecule cm^{-3}).

Table 3. Summary of the rate coefficients for OH, NO_3, O_3 and Cl reaction with the aldehydes studied in this work (in cm^3 $molecule^{-1}$ s^{-1}) and atmospheric lifetimes, τ (in hours).
a: This work;
b: Albaladejo et al. (2002).
c: Cabañas et al. (2001b).
d: Cabañas et al. (2001a).
e: Grosjean et al. (1996).
[Cl]=5×10^3 molecule cm^{-3} (Pszenny et al., 1993; Wingenter et al., 1996), [OH]=5.0×10^5 molecule cm^{-3} (Brauers et al., 1996) and [NO_3]=7.4×10^6 molecule cm^{-3} (Noxon, 1983), [O_3]=7.4×10^{11} molecule cm^{-3} (Logan, 1985).

Aldehyde	$k_{Cl}\times10^{10}$ a	τ_{Cl}	$k_{OH}\times10^{11}$ b	τ_{OH}	$k_{NO3}\times10^{14}$	τ_{NO3}	$k_{O3}\times10^{18}$ e	τ_{O3}
$CH_3(CH_2)_3CHO$	2.56±0.27	217	2.48±0.24	22.4	1.75±0.16[c]	2145	–	–
$CH_3(CH_2)_4CHO$	2.88±0.37	192.9	2.60±0.21	21.4	1.83±0.36[c]	2051	–	–
$CH_3(CH_2)_5CHO$	3.00±0.34	185.2	2.96±0.23	18.8	2.37±0.42[c]	1584	–	–
$CH_3CH_2CH{=}CHCHO$	1.31±0.19	424.1	2.35±0.32	23.6	2.88±0.29[d]	1303	–	–
$CH_3(CH_2)_2CH{=}CHCHO$	1.92±0.22	289.3	2.95±0.45	18.8	5.49±0.95[d]	684	1.28±0.28	293
$CH_3(CH_2)_3CH{=}CHCHO$	2.40±0.29	231.5	2.45±0.30	22.7	9.59±0.19[d]	391	–	–

Furthermore, Martínez et al. (1992) and Plagens have reported the absorption spectra of several aliphatic and unsaturated aldehydes and ketones. These compounds absorb actinic radiation in the range 270–340 nm and so the estimates about the degradation under atmospheric conditions must include the photolysis contribution. In this sense, Plagens reports photolytic lifetimes of 15 and 10 hour for hexanal and trans-2-hexenal, respectively. These data suggest that photodissociation and gas-phase reactions with OH radicals will dominate over reactions with Cl atoms and NO_3.

Although the reactions of chlorine atoms with this series of aldehydes are very fast, the average measured Cl concentration is lower than the concentrations of other oxidants. For this reason, the aldehydes lifetime is in the order of 200–400 h, which is comparable to the lifetimes due to O_3 with trans-2-hexenal (only the trans-2-hexenal has been studied (Grosjean et al., 1996). Nevertheless, the contribution of Cl atoms may be significant in those areas with higher concentrations. If we assume that the Cl local peak concentrations may be as high as 10^5 atom cm^{-3} (Wingenter et al., 1996; Singh et al., 1996), then these lifetimes are around between twice and one hundred times lower than those with respect to reaction with OH and NO_3, respectively. So chlorine atoms reactions are expected to play a significant role in the degradation of the studied aldehydes at dawn in the marine boundary layer and in coastal areas. That may be also the case of some urban contaminated areas, where high levels of chlorine may originate from industrial emissions (Galan et al., 2002). In this sense, regional-scale photochemical modeling and ambient observations in southeastern Texas suggest that chlorine radical chemistry enhances ozone formation (Chang et al., 2002). The ozone enhancement demonstrated strong spatial and temporal variations. Maximum enhancement occurred in the mornings in the industrialized areas and was primarily associated with estimated emissions of chlorine from cooling towers. A secondary maximum in the late afternoon was observed in the urban area and was associated with estimated emissions from swimming pools (Chang et al., 2002).

In the case of heterogeneous processes, it is well known that alcohols, aldehydes and ketones undergo efficient uptake into cloud droplets (Jayne et al., 1992) where chemical transformation can occur. For example, aldehydes can react with aqueous SO_2 to form the complex hydroxymethanesulfonate. In this sense, field studies have measured organic species in cloud droplets and carbonyl species have been detected in the snowpack (Sumner and Shepson, 1999). Also recently, several authors have investigated the involvement of aldehydic compounds in the formation of oligomeric components in secondary organic aerosols (Gao et al., 2004; Kalberer et al., 2004; Jang et al., 2002). The distinct effects of carbon numbers, substituent groups, and isomeric structures of the precursor hydrocarbons on the composition and yield of secondary organic aerosols formed are also discussed, for example, by Gao et al. (2004). Thus, further studies are required to evaluate the contribution of heterogeneous processes to the atmospheric degradation of aldehydes.

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