

Kinetic study of the reactions of Cl atoms with α,β -unsaturated carbonyl compounds at atmospheric pressure and structure activity relations (SARs)

Mariano A. Teruel*, Mariana Achad, María B. Blanco

Instituto de Investigaciones en Físicoquímica, I.N.F.I.Q.C., Departamento de Físicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

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ABSTRACT

The kinetics of the reactions of Cl atoms with three unsaturated carbonyl compounds at 298 K and atmospheric pressure were investigated for the first time using the GC–FID technique. Rate coefficients (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) of $k_1(\text{Cl} + \text{CH}_2=\text{CHC}(\text{O})\text{CH}_2\text{CH}_3) = (2.91 \pm 1.10) \times 10^{-10}$, $k_2(\text{Cl} + \text{CH}_2=\text{CHOC}(\text{O})\text{CH}_2\text{CH}_3) = (2.06 \pm 0.36) \times 10^{-10}$ and $k_3(\text{Cl} + \text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3) = (2.53 \pm 0.46) \times 10^{-10}$ were obtained using the relative rate method with different references. Structure activity relationships (SARs) were developed for the reactions of Cl with a wide range of unsaturated compounds. On the basis of our kinetic measurements, tropospheric lifetimes of the studied unsaturated compounds are estimated.

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1. Introduction

α,β -Unsaturated and oxygenated volatile organic compounds (VOCs) are olefins that can be formed by the photooxidation of isoprene, terpenes and other alkenes from vegetation [1,2] as well as from conjugated dienes emitted from the road traffic [3].

In particular, ethyl vinyl ketone (penten-1-3 one), which is a part of biogenic emissions, has been shown to be released to the troposphere by stressed-induced emissions from variety of plants [4].

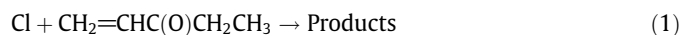
Other unsaturated carbonyl species constitute the vinyl ester compounds (acrylates, methacrylates, acetates and propionates with a structure of $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OR}$, $\text{CH}_2=\text{CHC}(\text{O})\text{OR}$ or $\text{CH}_2=\text{CHOC}(\text{O})\text{R}$), whose main releases to the troposphere are from anthropogenic sources as the result of their use in the production of polymers and resins. The sources of their emissions are manufacturers of plastics, aircraft and electronic components and they have wide applications as solvents and industrial feedstocks [5].

Once in the atmosphere, the atmospheric fate of these oxygenated and unsaturated compounds includes photolysis and gas-phase reactions initiated by oxidants like OH and NO_3 radicals, O_3 molecules or Cl atoms to produce ozone and other oxidants that can affect the oxidation capacity of the atmosphere [6].

Since large amounts of these compounds are continually released and produced in the atmosphere, it is necessary to understand the kinetic and mechanisms of their degradation reactions to assess their impact on the atmospheric oxidation capacity and air quality concerning ozone, secondary organic aerosol (SOA) and other photo oxidants formation.

While there are many studies of OH radical and Cl atom reactions with a variety of oxygenated volatile organic compounds (OVOCs), only limited information concerning α,β -unsaturated and oxygenated VOCs [7] is available. The database for Cl atoms with α,β -unsaturated esters and ketones is even scarcer [2,8].

The work reported in this Letter concerned a rate constant determination of the reactions of chlorine atoms with ethyl vinyl ketone ($\text{CH}_2=\text{CHC}(\text{O})\text{CH}_2\text{CH}_3$), vinyl propionate ($\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_2\text{CH}_3$) and ethyl acrylate ($\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$):



Experiments were conducted using a collapsible simulation chamber by the relative method at room temperature and atmospheric pressure.

To the best of our knowledge, this work provides the first kinetic study of the reactions (1)–(3). On the other hand, our work aims to better define the reactivity of the oxygenated and unsaturated VOCs towards Cl atoms as an extension of previous works involving the Cl-initiated degradation of acrylic acid, acrylonitrile and unsaturated acetates [8,9].

In addition, a structure activity relationship (SAR) method developed by Atkinson [10] was used for the first time for Cl addition reaction to substituted alkenes and oxygenated and unsaturated VOCs. It is shown that using this predictive technique is useful to obtain an estimation of unknown rate constants for the reactions of Cl atoms since the kinetic database for these reactions is scarce. Atmospheric lifetimes of the VOCs studied in this work were calculated taking into account the experimental rate constants obtained in this work and compared with other homogeneous sinks in the troposphere.

* Corresponding author. Fax: +54 351 4334188.

E-mail address: mteruel@fcq.unc.edu.ar (M.A. Teruel).

2. Experimental

All experiments were performed in an 80-l Teflon bag located in a wooden box with the internal walls covered with aluminum foil. Measured amounts of the organic reactants were flushed into the bag through a stream of nitrogen. The bag was then filled to its full capacity at atmospheric pressure with ultra pure nitrogen. Chlorine atoms were generated by photolysis at 254 nm of oxalyl chloride (ClC(O)C(O)Cl).

Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in N₂, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. Before each set of experiments, the bag was cleaned by filling it with a mixture of O₂ and N₂ which was photolyzed for 15–25 min using four germicidal lamps (Philips 30 W) with a UV emission at 254 nm, to produce O₃. After this procedure, the bag was cleaned up again by repeated flushing with N₂ and checked the absence of impurities by gas chromatography before performing the experiments.

Gas samples were periodically removed from the Teflon bag using Hamilton gas-tight calibrated syringes. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held from 140 to 180 °C for the three carbonyl compounds.

In the presence of the oxidant Cl atom the VOCs studied and the references decay through the following reactions:



Provided that the reference compound and the reactant are lost only by reactions (4) and (5), then it can be shown that:

$$\ln \left\{ \frac{[\text{VOC}]_0}{[\text{VOC}]_t} \right\} = \frac{k_4}{k_5} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (6)$$

where [VOC]₀, [Reference]₀, [VOC]_t and [Reference]_t are the concentrations of the VOC and the reference compound at times *t* = 0 and *t*, respectively, and *k*₄ and *k*₅ are the rate constants of reactions (4) and (5), respectively.

The relative rate technique relies on the assumption that both the VOC and the reference compounds are removed solely by reaction with Cl atoms. To verify this assumption, mixtures of the chlorine atoms precursor and N₂ with both organics were prepared and allowed to stand in the dark for 2 h. In all cases, the reaction of the organic species with the precursor of Cl (oxalyl chloride), in the absence of UV light, was of negligible importance over the typical time periods used in this work.

Furthermore, to test for possible photolysis of the reactants used, mixtures of the VOCs in N₂, in the absence of oxalyl chloride, were irradiated using the output of all the black or germicidal lamps surrounding the chamber for 30 min. No significant photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of 176–228 ppm (1 ppm = 2.46 × 10¹³ molecule cm⁻³ at 298 K and 760 Torr of total pressure) for the VOCs, and 191–261 ppm for 1,1-dichloroethene, (*E*)-1,2-dichloroethene and acrylonitrile used as reference compounds. The concentration of oxalyl chloride ranged from 140 to 220 ppm in around 750 Torr of N₂.

3. Materials

The chemicals N₂ (AGA, 99.999%), ethyl vinyl ketone (Aldrich, 97%), vinyl propionate (Aldrich, 98%), ethyl acrylate (Aldrich 99%), 1,1-dichloroethene (Aldrich, 99.99%), (*E*)-1,2-dichloroethene (Aldrich, 99%), acrylonitrile (Aldrich, 99%), oxalyl chloride (Aldrich,

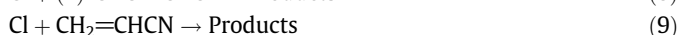
98%) were used as supplied and no significant impurities were observed by CG.

4. Results and discussion

By using this technique, the rate constants for the three reactions studied were obtained from Eq. (6). The data were fitted to a straight line by the unweighted linear least-squares procedure.

The losses of ethyl vinyl ketone, vinyl propionate and ethyl acrylate by Cl atoms are shown with different references in Figs. 1–3. For each organic reactant studied, several runs were performed for the rate constant determination; however, for the sake of clarity, only one example using two different references is presented in Figs. 1–3.

The following compounds were used as reference reactions to determine the rate coefficient of reactions (1)–(3):



where *k*₇ = (1.40 ± 0.02) × 10⁻¹⁰ [11], *k*₈ = (0.96 ± 0.02) × 10⁻¹⁰ [11] and *k*₉ = (1.11 ± 0.23) × 10⁻¹⁰ [9]. The *k* values are in units of cm³ molecule⁻¹ s⁻¹.

The data on relative rate constants *k*_{VOC}/*k*_{Reference} and absolute rate constants *k*_{VOC} at room temperature (298 K) are presented in Table 1. The ratios were obtained from the average of several experiments using different initial concentrations of the reactants. It is gratifying to notice the agreement between the experiments conducted with different reference compounds. The rate constants obtained by averaging the values from different experiments were the following:

$$k_1 = (2.91 \pm 1.10) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (2.06 \pm 0.36) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (2.53 \pm 0.46) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation arising from the unweighted least-squares fit of the straight lines, to which we have also considered the corresponding error on the reference rate constants [9,11].

To the best of our knowledge, there are no other prior reported values of the rate constants for the reactions (1)–(3) of Cl atoms

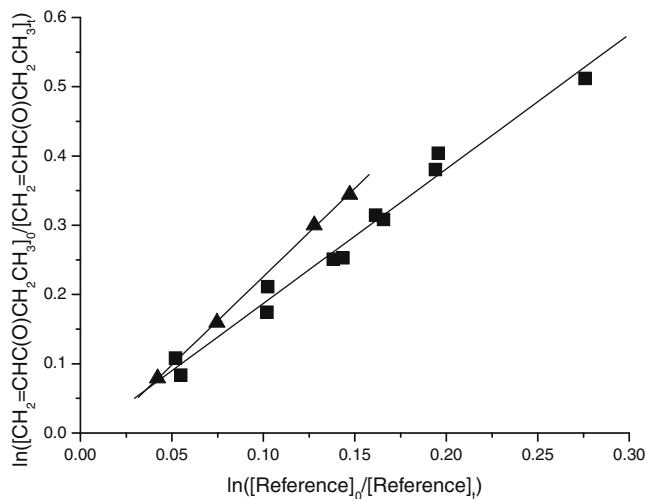


Fig. 1. Relative-rate plot for the Cl reaction with ethyl vinyl ketone at 298 K and atmospheric pressure. (▲) Acrylonitrile and (■) 1,1-dichloroethene used as references.

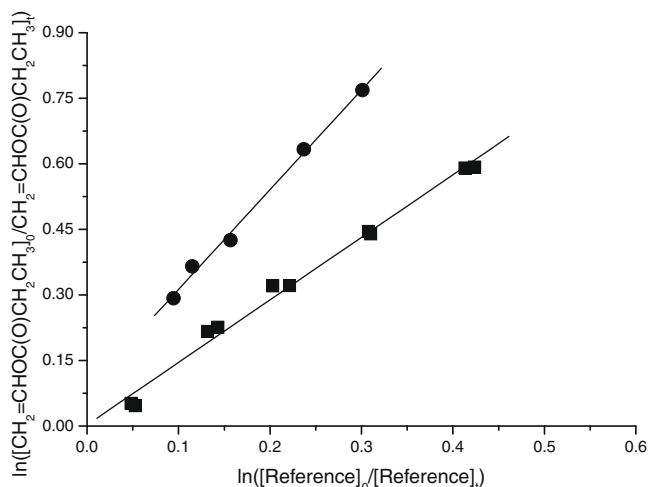


Fig. 2. Relative-rate plot for the Cl reaction with vinyl propionate at 298 K and atmospheric pressure. (●) (*E*)-1,2-dichloroethene and (■) 1,1-dichloroethene used as references.

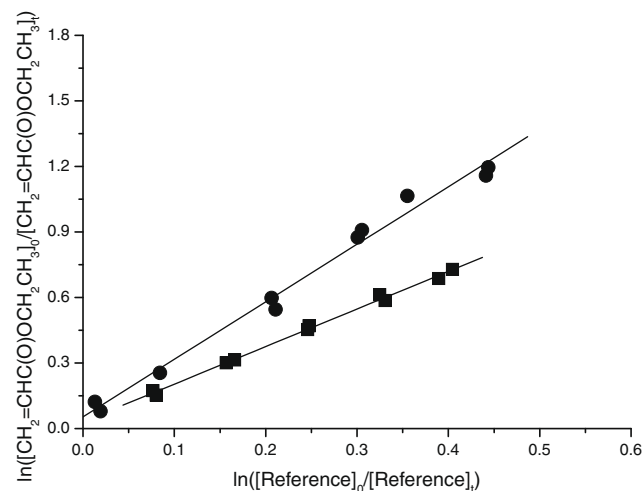


Fig. 3. Relative-rate plot for the Cl reaction with ethyl acrylate at 298 K and atmospheric pressure. (●) (*E*)-1,2-dichloroethene and (■) 1,1-dichloroethene used as references.

Table 1

Reactant concentrations, slopes $k_{\text{VOC}}/k_{\text{Reference}}$ and rate constants obtained for the reaction of ethyl vinyl ketone, vinyl propionate and ethyl acrylate with Cl atoms at 298 ± 2 K.

VOC	Reference	$k_{\text{VOC}}/k_{\text{Reference}}$	$k_{\text{VOC}} (\times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
CH ₂ =CHC(O)CH ₂ CH ₃	CH ₂ =CCl ₂	(1.94 ± 0.09)	(2.71 ± 0.16)
	CH ₂ =CCl ₂	(2.10 ± 0.14)	(2.94 ± 0.24)
	CH ₂ =CH(CN)	(2.55 ± 0.04)	(2.83 ± 0.63)
	CH ₂ =CH(CN)	(2.83 ± 0.18)	(3.14 ± 0.85)
	Average		(2.91 ± 1.10)
CH ₂ =CHOC(O)CH ₂ CH ₃	CH ₂ =CCl ₂	(1.43 ± 0.05)	(2.00 ± 0.10)
	CH ₂ =CCl ₂	(1.38 ± 0.03)	(1.93 ± 0.07)
	(<i>E</i>)-ClCH=CHCl	(2.22 ± 0.11)	(2.13 ± 0.15)
	(<i>E</i>)-ClCH=CHCl	(2.28 ± 0.09)	(2.18 ± 0.13)
	Average		(2.06 ± 0.36)
CH ₂ =CHC(O)OCH ₂ CH ₃	CH ₂ =CCl ₂	(1.72 ± 0.04)	(2.41 ± 0.09)
	CH ₂ =CCl ₂	(1.75 ± 0.19)	(2.45 ± 0.30)
	(<i>E</i>)-ClCH=CHCl	(2.63 ± 0.10)	(2.52 ± 0.15)
	(<i>E</i>)-ClCH=CHCl	(2.86 ± 0.08)	(2.74 ± 0.13)
	Average		(2.53 ± 0.46)

The errors in the average rate constant were quoted as $(\sum \sigma_i^2)^{1/2}$.

Table 2

Group rate constants (k_{basic}) at 298 K for Cl addition reactions to alkenes structural basic units.

Basic structure	Alkene	$k_{\text{exp}} (\times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^a$	$k_{\text{basic}} (\times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^b$
CH ₂ =CHR	Propene	2.64	2.89
		3.16	
		2.87	
CH ₂ =CR ₂	2-Methylpropene	3.40	3.40
(Z)-RHC=CHR	(Z)-2-Butene	3.76	3.63
		3.50	
(E)-RHC=CHR	(E)-2-Butene	4.00	3.63
		3.27	
RHC=CR ₂	2-Methyl-2-butene	3.95	3.95

^a The rate constant values (k_{exp}) are taken from Ref. [7].

^b Derived from the average reaction rate constants of the alkenes shown in the table.

with ethyl vinyl ketone, vinyl propionate and ethyl acrylate. Thus, this study is the first kinetic study of these reactions and therefore, no direct comparison with the literature can be made.

It is also interesting to compare the reactivity of the unsaturated carbonyls towards Cl atoms with the corresponding alkenes since it has been postulated that unsaturated oxygenated VOCs react via similar addition mechanisms [2,6]. It can be observed that the rate coefficients of the unsaturated carbonyls are in the same order of magnitude that the rate coefficient of the corresponding alkenes, in general about 7–55% lower. This could be explained by the negative inductive effect of the –C(O)–, –CO–

Table 3

Substituent factors C_x at 298 K.

Substituent X	C_x	Substituent X	C_x
–F	0.64 ^a	–C(O)OCH ₂ CH ₃	0.84 ^h
–Cl	0.57 ^b	–C(O)O(CH ₂) ₂ CH ₃	0.87 ⁱ
–CF ₃	0.31 ^c	–OC(O)CH ₃	0.93 ^j
–CH ₂ CH ₃	1.10 ^d	–OC(O)CH ₂ CH ₃	0.73 ^k
–COCH ₃	0.73 ^e	–CH ₂ OC(O)CH ₃	0.45 ^l
–COCH ₂ CH ₃	0.87 ^f	–C(O)H	0.87 ^m
–C(O)OCH ₃	0.74 ^g	–CH ₂ OH	0.60 ⁿ

^a Derived from the experimental reaction rate constants of Cl atom with CH₂=CHF.

^b Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCl, CH₂=CCl₂, CHCl=CCl₂, (*E*)-CHCl=CHCl, (*Z*)-CHCl=CHCl, CHCl=CCl₂ and CCl₂=CCl₂.

^c Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCF₃.

^d Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCH₂CH₃ and CH₂=C(CH₂CH₃)₂.

^e Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCOCH₃.

^f Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCOCH₂CH₃.

^g Derived from the experimental reaction rate constants of Cl atom with CH₂=CHC(O)OCH₃.

^h Derived from the experimental reaction rate constants of Cl atom with CH₂=CHC(O)OCH₂CH₃.

ⁱ Derived from the experimental reaction rate constants of Cl atom with CH₂=CHC(O)O(CH₂)₂CH₃.

^j Derived from the experimental reaction rate constants of Cl atom with CH₂=CHOC(O)CH₃.

^k Derived from the experimental reaction rate constants of Cl atom with CH₂=CHOC(O)CH₂CH₃.

^l Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCH₂OC(O)CH₃.

^m Derived from the experimental reaction rate constants of Cl atom with CH₂=CHC(O)H.

ⁿ Derived from the experimental reaction rate constants of Cl atom with CH₂=CHCH₂OH.

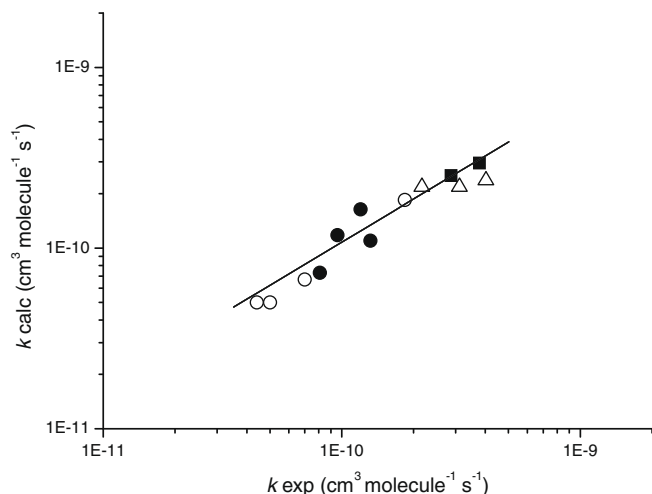


Fig. 4. Comparison of the SAR calculated and experimental room-temperature Cl atom. Addition rate constants for fluoroalkenes (○), chloroalkenes (●), unsaturated esters (■) and unsaturated alcohols (△) at atmospheric pressure.

and –OC(O)– groups on the double bond, indicating that the reactions of Cl with unsaturated carbonyls proceeds essentially by Cl addition to the C=C double bond.

In addition, the kinetic data obtained in this work together with previous literature data, were used for the first time to extend the structure activity relationship (SAR) approach developed by Atkinson to Cl atoms addition reactions for alkenes and different unsaturated and oxygenated VOCs [10]. The method is based on the structure of the alkene, the number of unconjugated double bonds and the degree, identity, position and configuration of the substitution around of the double bonds. The rate constants for the ‘basic structures’ are calculated from the average of the experimental rate constants for the parent alkenes given in Table 2, taking the reactivity factor for CH₃, as unity. The group factors (C_x) given in Table 3 are defined by the equation:

$$k = k_{\text{basic}} \cdot \prod_{i=1}^{i=1-4} (C_x)$$

The group factors given in Table 3 are the energies of the contributions selected on the basis of the reliability of the data as expressed in recent reviews. A good correlation between the calculated and experimental room-temperature rate constants for alkenes and unsaturated and oxygenated VOCs with C=C bonds is given in Fig. 4 and the corresponding values are shown in Table 4.

A least-squares treatment of the data points in Fig. 4 yields the following expression:

$$k_{\text{calc}} = 0.8k_{\text{exp}} - 2.0$$

Atmospheric homogeneous lifetimes, τ_x , of the unsaturated carbonyl VOCs studied in this work were calculated through the expression: $\tau_x = 1/k_x[X]$ with X = Cl, OH, NO₃ or O₃.

VOC	Cl	OH	NO ₃	O ₃
CH ₂ =CHC(O)CH ₂ CH ₃	4.0 days	5.9 h	8.2 months	2.8 days
CH ₂ =CHOC(O)CH ₂ CH ₃	5.6 days	–	–	–
CH ₂ =CHC(O)OCH ₂ CH ₃	4.6 days	8.2 h	–	2.9 days

In these calculations the following rate constant values were used: $k_{\text{Cl}} = 2.91 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work), $k_{\text{OH}} = 2.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14], $k_{\text{NO}_3} = 9.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [15] and $k_{\text{O}_3} = 6.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [16] for ethyl

Table 4

Comparison of the experimental (k_{exp}) and calculated (k_{calc}) room-temperature rate constants for unsaturated volatile organic compounds.

VOC	$k_{\text{calc}} (\times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$k_{\text{exp}} (\times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^a$
CH ₂ =CHF	1.85	1.84
CClH=CH ₂	1.64	1.20
CH ₂ =CCl ₂	1.10	1.32
(E/Z)-CHCl=CHCl	1.18	0.96
CHCl=CCl ₂	0.73	0.81
(E)-CF ₃ CF=CHF	0.50	0.50
(Z)-CF ₃ CF=CHF	0.50	0.44
CF ₃ CF=CH ₂	0.67	0.70
CH ₂ =C(CH ₃)C(O)O(CH ₂) ₃ CH ₃	2.96	3.78 ^b
CH ₂ =C(CH ₃)C(O)OCH ₃	2.52	2.87 ^c
CH ₃ CH ₂ CH=CHC(O)H	3.47	1.31
CH ₃ CH=CHCH ₂ OH	2.18	3.12
(CH ₃) ₂ C=CHCH ₂ OH	2.37	4.02
CH ₂ =C(CH ₃)CH ₂ OH	2.18	2.17

^a The experimental rate constant values at room temperature (k_{exp}) are taken from Ref. [7].

^b From Ref. [12].

^c From Ref. [13].

vinyl ketone; $k_{\text{Cl}} = 2.06 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work) for vinyl propionate; $k_{\text{Cl}} = 2.53 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work), $k_{\text{OH}} = 1.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [17] and $k_{\text{O}_3} = 5.71 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18] for ethyl acrylate. Typical atmospheric concentrations were used, $[\text{OH}] = 2 \times 10^6 \text{ radical cm}^{-3}$ [19]; $[\text{O}_3] = 7 \times 10^{11} \text{ radical cm}^{-3}$ [20], $[\text{NO}_3] = 5 \times 10^8 \text{ radical cm}^{-3}$ [21] and $[\text{Cl}] = 1 \times 10^4 \text{ atoms cm}^{-3}$ [22]. Unfortunately, no kinetic data are available for the reactions of vinyl propionate with OH, NO₃ radicals or O₃ molecules and for the reaction with ethyl acrylate with NO₃ radicals.

Moreover, there was no indication of significant photolysis losses of these compounds in the kinetic experiments performed in this study.

Tropospheric lifetimes from 5.9 to 8.2 h are calculated, assuming a 12 h average concentration of OH of $2 \times 10^6 \text{ molecule cm}^{-3}$ [19]. The corresponding lifetimes of the reaction with chlorine ranged of 4.0–5.6 days, considering a global average chlorine concentration of $1 \times 10^4 \text{ atoms cm}^{-3}$ [22].

In conclusion, the atmospheric lifetime is determined by the OH-initiated oxidation for the three unsaturated carbonyl compounds studied. These lifetimes, in the range of few hours, indicate that the VOCs are likely to be removed rapidly in the gas phase, being the reaction with OH the major loss process for unsaturated carbonyls. Nevertheless, in coastal areas and in the marine boundary layer, with peak concentrations of Cl atoms as high as $1 \times 10^5 \text{ atom cm}^{-3}$ [23,24], the Cl-initiated degradation of ethyl vinyl ketone, vinyl propionate and ethyl acrylate can be a significant if not the dominant homogeneous loss process.

The short estimated lifetimes indicate that these compounds will be degraded closely to their emission sources.

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