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## Kinetics and products study of the reaction of Cl atoms with methyl dichloroacetate: reactivity, mechanism, and environmental implications

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The relative rate coefficient of the gas-phase reaction of methyl dichloroacetate ( $\text{CHCl}_2\text{C}(\text{O})\text{OCH}_3$ ) with Cl atoms ( $k_{\text{Cl}}$ ) was obtained at 298 K and atmospheric pressure. All the experiments were performed in a 480 L Pyrex glass atmospheric simulation reactor coupled to an *in situ* Fourier transform infrared (FTIR) spectrometer. The rate coefficient obtained from the average of different experiments was:  $k_{\text{Cl}} = (3.31 \pm 0.88) \times 10^{-13} \text{ cm}^3$  per molecule per s. In addition, the product studies were performed in under similar conditions to those of the kinetic experiments in two different photoreactors by *in situ* FTIR spectroscopy and GC-MS/SPME. Dichloroacetic acid, phosgene, methyl trichloroacetate, and carbon monoxide were the main products identified and quantified. The obtained product yields for the reaction with Cl atoms were as follows:  $(24 \pm 2)$ ,  $(19 \pm 3)$ ,  $(16 \pm 1)$ , and  $(44 \pm 2)\%$  for  $\text{Cl}_2\text{CHCOOH}$ ,  $\text{COCl}_2$ ,  $\text{CO}$ , and  $\text{CCl}_3\text{C}(\text{O})\text{OCH}_3$ , respectively. The initial pathway for the degradation of methyl dichloroacetate in the reaction with Cl atoms occurs *via* H-atom abstraction at the alkyl groups. The atmospheric implications of the reactions were assessed by the estimation of the tropospheric lifetime of  $\tau_{\text{Cl}} = 3$  years. In addition, an acidification potential of 0.45 was estimated, suggesting a possible impact of the emission of methyl dichloroacetate on the rainfall acidification. On the other hand, significant global warming potentials of 8.2, 2.2, and 0.6 were calculated for the studied chloroester for the time horizons of 20, 100, and 500 years, respectively. Chlorinated persistent products, such as dichloroacetic acid, could have an impact on the atmosphere and other environmental matrixes as well as on human health and the biota.

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### Environmental significance

While kinetic data is essential for assessing the environmental impact of VOCs emissions and indicates the spatial extent of the spread of emissions, a thorough assessment also requires a complete understanding of the tropospheric degradation mechanism and the resulting products. In this work the rate coefficient of the Cl-initiated oxidation of methyl dichloroacetate, as an example of a polychlorinated ester, have been determined at atmospheric conditions. Complementary products studies were performed, where the molar yields of the reaction products were determined. The atmospheric lifetime of the dichloroester studied determines their contribution to the acid rain and global warming. Furthermore, dichloroacetic acid as other chlorinated products as emerging and persistent pollutants, could affect air quality and other environmental compartments.

## 1 Introduction

A large amount of volatile organic compounds (VOCs), which are emitted by different sources, are released to the troposphere and stratosphere.<sup>1</sup> This causes appreciable disturbances in the composition of the atmosphere, which can generate great changes in the future of the climate; some of these released gases increase the natural greenhouse effect, and as a consequence, an increase in the average temperature of the planet

can occur.<sup>2</sup> Once in the air, these compounds can react with the tropospheric oxidants (OH radicals, Cl atoms,  $\text{NO}_3$  radicals, or  $\text{O}_3$  molecules) to generate other oxygenated VOCs (OVOCs) as degradation products that possibly impact the environmental quality. In this sense, ethers, used as fuel additives and in chemical industries, are frequently released into the atmosphere. In addition, once in the air, methyl dichloroacetate (MDCA) could be generated by the atmospheric oxidation of some ethers<sup>3</sup> and, as well as, stand out as volatilization products that are released from the earth's surface due to its wide range of use, as chemical products for disinfection, painting, varnishing, and as the starting reagents for pharmaceutical and agrochemical products<sup>3</sup>. The presence of MDCA in the atmosphere makes it necessary to study the reaction kinetics with different atmospheric oxidants in order to know the impact it

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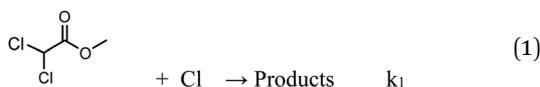


produces at different scales. Reactions with Cl atoms under atmospheric conditions have great importance in the oxidative processes that occur in areas where the concentration of this oxidant can be competitive with the concentration of OH radicals.<sup>4,5</sup>

This work carries out kinetics studies of the reaction of methyl dichloroacetate with Cl atoms under atmospheric conditions in a simulation chamber coupled with an *in situ* FTIR spectrometer. The relative overall rate coefficient of this reaction, using different reference compounds, was measured at 298 K and 1 atm.

Complementary, reaction products were identified and quantified by GC-MS/SPME and *in situ* FT-IR spectroscopy to postulate atmospheric chemical mechanisms at NO<sub>x</sub> free conditions.

Up to now, there are no kinetic and product studies reported for the reaction of methyl dichloroacetate with chlorine atoms. Consequently, this is the first reactivity and product distribution study of the title reaction. Furthermore, this work aims to clarify and contribute to the knowledge of the mechanisms through which polychlorinated esters are degraded by Cl atoms in the gas phase as indicated by the following reaction (eqn (1)):



The rate coefficient obtained is compared with experimental and theoretical values reported previously for other VOCs with similar structures.

In complementary studies, the products were determined and quantified using two different environmental chambers coupled with FTIR spectroscopy and GC-MS, which gave information to postulate the atmospheric chemical mechanism for the reaction studied under NO<sub>x</sub>-free conditions.

With the kinetic and product data, the atmospheric implications of the interest reaction were assessed in terms of possible transport, acidification, and global warming potentials as well as the impact of the chlorinated products on the environment and the biosphere.

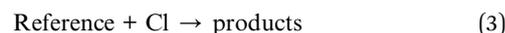
## 2 Methods and materials

### 2.1 Kinetics studies

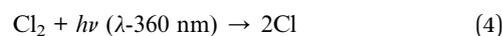
The experiments were performed in a 480 L Pyrex glass atmospheric simulation reactor coupled to a Fourier Transform Infrared Spectrometer, Nicolet Magna 520 and the spectral range was 4000–700 cm<sup>-1</sup>. The chamber surrounded by 32 fluorescence lamps, emitting at a maximum of 360 nm, was used to photochemically initiate the experiments at 750 torr and 298 K. A full description of the reactor can be found in the literature.<sup>6</sup> The system was evacuated by a pumping system consisting of a turbo-molecular pump backed by a double-stage rotary fore pump to 10<sup>-3</sup> torr. The reactor has a support system for multiple reflection mirrors of type “White” with a base length of (48.11 ± 0.01) m. The mirrors allow reactions to be

carried out at low concentrations simulating quasi-real atmospheres.

Kinetic determinations were obtained by a relative method indirectly from their relationship with the rate coefficient of reference compounds. Methyl dichloroacetate and different reference compounds reacted competitively with the oxidants as the following:



Cl atoms were produced by photolysis at 360 nm of molecular Cl<sub>2</sub> as (eqn (4)):



Considering that reactions (2) and (3) are the only reactions that deplete both compounds, it is possible to determine the relative rate coefficient of the reactions of interest as:

$$\text{Ln} \left[ \frac{[\text{MDCA}]_0}{[\text{MDCA}]_t} \right] = \frac{k_{\text{MDCA}}}{k_{\text{Reference}}} \text{Ln} \left[ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right] \quad (5)$$

where [MDCA]<sub>0</sub>, [MDCA]<sub>t</sub>, [Reference]<sub>0</sub>, and [Reference]<sub>t</sub>, are the concentrations of the methyl dichloroacetate and reference compound at times *t* = 0 and *t*, respectively.

Representing  $\text{Ln}[\text{MDCA}]_0/[\text{MDCA}]_t$  versus  $\text{Ln}[\text{Reference}]_0/[\text{Reference}]_t$  a straight line is observed whose slope is the ratios,  $k_{\text{MDCA}}/k_{\text{reference}}$  where the rate coefficient of reference with Cl atoms is known in the literature.<sup>7</sup>

Before kinetics experiments, some tests were performed to check that reactions (2) and (3) were the only reactions occurring inside the reactor. First, we made sure that the MDCA and the reference compound did not react with each other in the dark, and then with the lamps on to avoid some photolysis. On the other hand, the possible reaction of the organic compounds with the radical precursor in the dark and wall loss was checked.

### 2.2 FTIR product study

The reaction products between methyl dichloroacetate with Cl atoms were studied using the same experimental setup of the kinetic study. Mixtures of MDCA/Cl/air were irradiated with fluorescent lamps. With the residual spectrum, when possible, product identification and quantification were performed from a relationship with calibrated reference spectra stored in the IR spectral database of the laboratories at the University of Wuppertal, Germany.

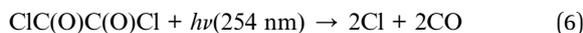
### 2.3 GC-MS product study

In addition, the reaction products under NO<sub>x</sub>-free conditions were monitored by gas-chromatography-mass spectrometry in LUQCA at Córdoba University. The experiments were carried out in an 80 L collapsible Teflon chamber at 296 ± 2 K and ~750 torr of pressure situated in a wooden box with the internal walls protected by aluminium foil and four germicidal lamps (Philips 30W) with a UV emission at a maximum of 254 nm. Before and after each experiment, the collapsible Teflon chambers were



cleaned by filling them with a mixture of O<sub>2</sub> and N<sub>2</sub> and photolyzed for 30 min using germicidal lamps to produce O<sub>3</sub>. The compounds and oxidant were flushed from the calibrated Pyrex bulbs into the Teflon chamber by a stream of zero grade N<sub>2</sub> and then the chamber was filled with pure synthetic air.

Cl atoms were generated by UV photolysis of oxalyl chloride (ClCOCOCl) (eqn (6))



The gas sample was taken from the Teflon bag using The Solid Phase Micro Extraction Technique (SPME), with the method of pre-concentration of the sample during 10 minutes of absorption for each measurement of the products. The organic compounds were monitored by gas chromatography coupled with a mass detector in a GC-MS VARIAN Saturn 2200 with column HP-5MS, Agilent (Part 19091S-433) of 30 meters in length, 0.25 mm internal diameter and film thickness 0.25 μm.

## 2.4 Materials

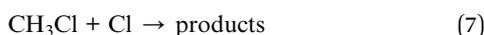
The initial concentrations used in the experiments were 4.92 ppm for methyl dichloroacetate and in a range of 6–32 ppm for the reference compounds (chloromethane and cyclopropane). (1 ppm =  $2.46 \times 10^{13}$  molecule per cm<sup>3</sup> at 298 K and 760 torr of total pressure).

The chemicals used in the experiments had the following purities as provided by the manufacturer and were used as supplied: synthetic air (air liquid, 99.999%), nitrogen (air liquid 99.999%), molecular chlorine (Messer Griesheim, 2.8), methyl dichloroacetate (Sigma-Aldrich, 99%), chloromethane (Sigma-Aldrich, 99%), cyclopropane (Sigma-Aldrich 99%) and oxalyl chloride (Aldrich, 99%).

## 3 Results and discussion

### 3.1 Kinetics

Eqn (5) was used to determine the relative rate coefficient for reactions of methyl dichloroacetate with Cl atoms employing the relative method with different reference compounds as follows (eqn (7) and (8)):



where  $k_7 = (5.20 \pm 0.40) \times 10^{-13}$  (ref. 8) and  $k_8 = (1.15 \pm 0.17) \times 10^{-13}$ .<sup>9</sup> All the  $k$  values are in units of cm<sup>3</sup> per molecule per s.

For the reaction studied, at least two experiments were performed for the rate coefficient determination for both oxidant reactions. Fig. 1 shows the plots  $\ln[\text{MDCA}]_0/[\text{MDCA}]_t$  versus  $\ln[\text{Reference}]_0/[\text{Reference}]_t$  of two examples for each reference. All the experiments were developed using N<sub>2</sub>. All plots showed linearity for the obtained straight lines, with correlation coefficients close to 1 and nearly zero intercepts indicating that secondary reactions are negligible.

Table 1 shows the rate coefficient ratios ( $k_{\text{MDCA}}/k_{\text{reference}}$ ) obtained for each reference and the corresponding rate

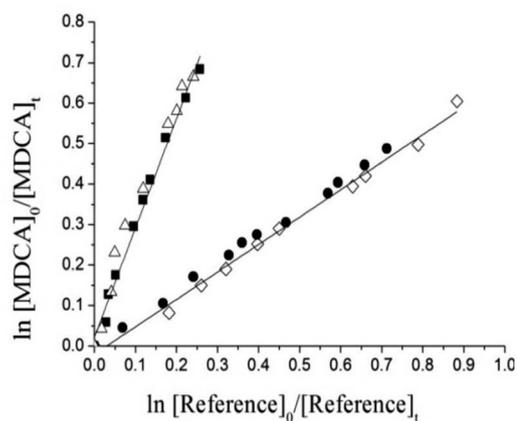


Fig. 1 Plots of the kinetics data for the reaction of methyl dichloroacetate with Cl atoms using chloromethane (□ and ●) and cyclopropane (Δ and ■) as a reference at 298 K.

coefficient in absolute terms. These rate coefficient ratios are each from the average of three measurements and in some cases with a variation of the initial concentration. A good agreement between the results obtained with different reference compounds was observed. The recommended value for the rate coefficient after averaging, a minimum of 3 experiments is as follows:

$$k_{\text{MDCA}+\text{Cl}} = (3.31 \pm 0.88) \times 10^{-13} \text{ cm}^3 \text{ per molecule per s}$$

The errors shown are twice the standard deviation that results from the least squares fit of the straight lines and the corresponding error of the reference rate coefficient.

In the present study, the rate coefficient of the reaction of methyl dichloroacetate with Cl atoms was determined (in units of cm<sup>3</sup> per molecule per s) to be  $(3.31 \pm 0.88) \times 10^{-13}$ . This is the first kinetic determination of the reactions cited above and no comparison with previous work was possible.

The rate coefficient obtained for the reaction of Cl atoms with methyl dichloroacetate can be compared with the corresponding reaction of Cl with methyl chloroacetate, a similar structure compound reported previously of  $8.5 \times 10^{-13}$  cm<sup>3</sup> per molecule per s. The addition of a second chlorine substituent in the ester molecule could generate a steric hindrance for H-atom abstraction that reduces the rate coefficient by a factor of three. A similar trend was previously observed in our laboratory for the reactivity of halogenated esters.<sup>11</sup>

A comparison between rate coefficients of the reactions of some chloro compounds towards OH radicals and with Cl atoms is shown in Table 2. It is possible to note that rate coefficients decrease with the number of chlorine substituents in the ester molecule.<sup>11,12</sup> From Table 2, it is possible to observe that the rate coefficients for reactions of CH<sub>3</sub>C(O)OCH<sub>3</sub>, ClCH<sub>2</sub>C(O)OCH<sub>3</sub>, and Cl<sub>2</sub>CHC(O)OCH<sub>3</sub> with Cl atoms are (22.00; 8.50 and  $3.31) \times 10^{-13}$  cm<sup>3</sup> per molecule per s, respectively. In the same way, for some chloro alkanes the rate coefficient of CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub> with Cl atoms are 4.90, 3.60, and  $0.76 \times 10^{-13}$  cm<sup>3</sup> per molecule per s, respectively.



**Table 1** Slopes  $k_{\text{MDCA}}/k_{\text{reference}}$  and rate coefficients with their respective errors for the reaction of Cl atoms with methyl dichloroacetate with two reference compounds at 298 K in 750 torr

	Reference	$k_{\text{reference}} \times 10^{13} \text{ cm}^3 \text{ per molecule per s}$	$k_{\text{MDCA}}/k_{\text{reference}}$	$k_{\text{MDCA}} \times 10^{13} \text{ cm}^3 \text{ per molecule per s}$
CHCl <sub>2</sub> C(O)OCH <sub>3</sub> + Cl	CH <sub>3</sub> Cl	5.20 ± 0.40	0.67 ± 0.02	3.48 ± 0.13
			0.68 ± 0.02	3.54 ± 0.13
	C <sub>3</sub> H <sub>6</sub>	1.15 ± 0.17	2.75 ± 0.16	3.16 ± 0.65
			2.65 ± 0.10	3.05 ± 0.56
			Average	3.31 ± 0.88

Furthermore, the OH oxidation of ketones show the same trend, *e.g.*, CH<sub>3</sub>COCH<sub>2</sub>Cl, CH<sub>3</sub>COCHCl<sub>2</sub>, and CH<sub>3</sub>COCCL<sub>3</sub> with rate coefficients of (4.20; 3.80 and 0.15) × 10<sup>-13</sup> cm<sup>3</sup> per molecule per s, respectively.<sup>7,10,12-14</sup>

It is important to mention that the trends observed in the reactivity of methyl dichloroacetate cannot be explained only by the halogens substitution in the ester, other contributions that should be considered are the strength of the bonds and the steric effects.

Currently, there is not much information on the reactivity of chlorinated esters with different atmospheric oxidants. Therefore, it is not possible to make an extended evaluation of the dependence of the different contributions to the reactivity of chloroesters. Consequently, it is necessary to carry out more experiments and theoretical studies to increase the kinetic

database of the atmospheric degradation reactions of chloroacetates and understand the reactivity changes associated with halogen substitution under different atmospheric conditions.

### 3.2 Free energy relationships

Many studies have reported a linear correlation between the rate coefficients of different compounds in reaction with tropospheric oxidants such as OH radicals, Cl atoms, O<sub>3</sub> molecules, and NO<sub>3</sub> radicals.<sup>14,27,28</sup>

In this work, we present a correlation between  $k_{\text{OH}}$  and  $k_{\text{Cl}}$  of a series of chlorine-containing compounds from the literature and included the kinetic data obtained for the methyl dichloroacetate through a free energy graph from Table 2.<sup>13-17</sup>

The correlations obtained between the rate coefficients for the reactions of OH radicals and Cl atoms obtained in this work

**Table 2** Comparison between  $k_{\text{OH}}$  and  $k_{\text{Cl}}$  of alkanes, esters, and ketones with different degrees of Cl substitution at 296 ± 2 K. Each value shows the reported experimental error

VOC	$k_{\text{Cl}} \times 10^{-13} \text{ (cm}^3 \text{ per molecule per s)}$	$k_{\text{OH}} \times 10^{-13} \text{ (cm}^3 \text{ per molecule per s)}$
CH <sub>3</sub> C(O)OCH <sub>3</sub>	22.00 ± 0.30 <sup>c</sup>	3.26 ± 0.08 <sup>f</sup>
ClCH <sub>2</sub> C(O)OCH <sub>3</sub>	8.50 ± 1.90 <sup>c</sup>	—
Cl <sub>2</sub> CHC(O)OCH <sub>3</sub>	3.31 ± 0.88 <sup>b</sup>	1.956 <sup>a</sup>
Cl <sub>3</sub> CC(O)OCH <sub>3</sub>	—	—
<b>Alkanes</b>		
CH <sub>3</sub> Cl	4.90 ± 0.15 <sup>d</sup>	0.42 ± 0.10 <sup>d</sup>
CH <sub>2</sub> Cl <sub>2</sub>	3.60 ± 0.15 <sup>d</sup>	1.20 ± 0.20 <sup>d</sup>
CHCl <sub>3</sub>	0.76 ± 0.30 <sup>d</sup>	1.00 ± 0.01 <sup>e</sup>
C <sub>2</sub> H <sub>5</sub> Cl	57.60 ± 5.00 <sup>h</sup>	4.35 ± 0.35 <sup>j</sup>
CH <sub>3</sub> CCl <sub>3</sub>	0.095 ± 0.001 <sup>m</sup>	0.40 ± 0.01 <sup>m</sup>
CH <sub>3</sub> CHCl <sub>2</sub>	16.40 ± 0.80 <sup>s</sup>	2.59 ± 0.20 <sup>r</sup>
CH <sub>2</sub> ClCH <sub>2</sub> CH <sub>3</sub>	490.0 ± 150 <sup>i</sup>	11.20 ± 2.80 <sup>i</sup>
CH <sub>3</sub> CHClCH <sub>3</sub>	200.0 ± 60.0 <sup>i</sup>	9.20 ± 2.30 <sup>i</sup>
C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	110.0 ± 30.0 <sup>i</sup>	7.80 ± 1.90 <sup>i</sup>
CH <sub>2</sub> ClCH <sub>2</sub> Cl	12.70 ± 3.80 <sup>q</sup>	2.55 ± 0.51 <sup>p</sup>
C(CH <sub>3</sub> ) <sub>3</sub> Cl	130.0 ± 40.0 <sup>i</sup>	4.10 ± 1.00 <sup>i</sup>
CH <sub>2</sub> ClCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	110.0 ± 20.0 <sup>k</sup>	20.0 ± 1.50 <sup>l</sup>
CH <sub>3</sub> CHClCH <sub>2</sub> CH <sub>3</sub>	700.0 ± 90.0 <sup>k</sup>	24.5 ± 3.00 <sup>l</sup>
CH <sub>3</sub> CHClCH <sub>2</sub> Cl	39.0 ± 6.00 <sup>o</sup>	4.59 ± 0.60 <sup>n</sup>
<b>Ketones</b>		
CH <sub>3</sub> COCH <sub>3</sub>	22.0 ± 0.40 <sup>g</sup>	2.20 ± 0.50 <sup>e</sup>
CH <sub>3</sub> COCH <sub>2</sub> Cl	20.0 ± 0.20 <sup>g</sup>	4.20 ± 0.80 <sup>g</sup>
CH <sub>3</sub> COCHCl <sub>2</sub>	1.70 ± 0.30 <sup>g</sup>	3.80 ± 0.80 <sup>g</sup>
CH <sub>3</sub> COCCL <sub>3</sub>	0.17 ± 0.30 <sup>g</sup>	0.15 ± 0.30 <sup>g</sup>

<sup>a</sup> SAR-calculation. <sup>b</sup> This work. <sup>c</sup> (Ref. 10). <sup>d</sup> (Ref. 14). <sup>e</sup> (Ref. 13). <sup>f</sup> (Ref. 15). <sup>g</sup> (Ref. 12). <sup>h</sup> (Ref. 16). <sup>i</sup> (Ref. 17). <sup>j</sup> (Ref. 18). <sup>k</sup> (Ref. 19). <sup>l</sup> (Ref. 20). <sup>m</sup> (Ref. 21). <sup>n</sup> (Ref. 22). <sup>o</sup> (Ref. 23). <sup>p</sup> (Ref. 24). <sup>q</sup> (Ref. 16). <sup>r</sup> (Ref. 25). <sup>s</sup> (Ref. 26).





**Table 3** Oxidation products from the reaction of Cl atoms with methyl dichloroacetate, and their formation yields and their respective errors

Reaction	Products	Yields (%)
$\text{Cl}_2\text{CHC}(\text{O})\text{OCH}_3 + \text{Cl}$	$\text{Cl}_2\text{CHCOOH}$	$24 \pm 2$
	$\text{COCl}_2$	$19 \pm 3$
	$\text{Cl}_3\text{CCOOCH}_3$	$44 \pm 2$
	$\text{CO}$	$16 \pm 1$

### 3.3 Products

To investigate the mechanism of Cl atoms initiating degradation of methyl dichloroacetate, mixtures of oxidant/methyl dichloroacetate/air/were photolyzed with fluorescent lamps under similar conditions of the kinetic experiments for approximately 20 minutes. Each measurement was performed at approximately 50% of the consumption of methyl dichloroacetate.

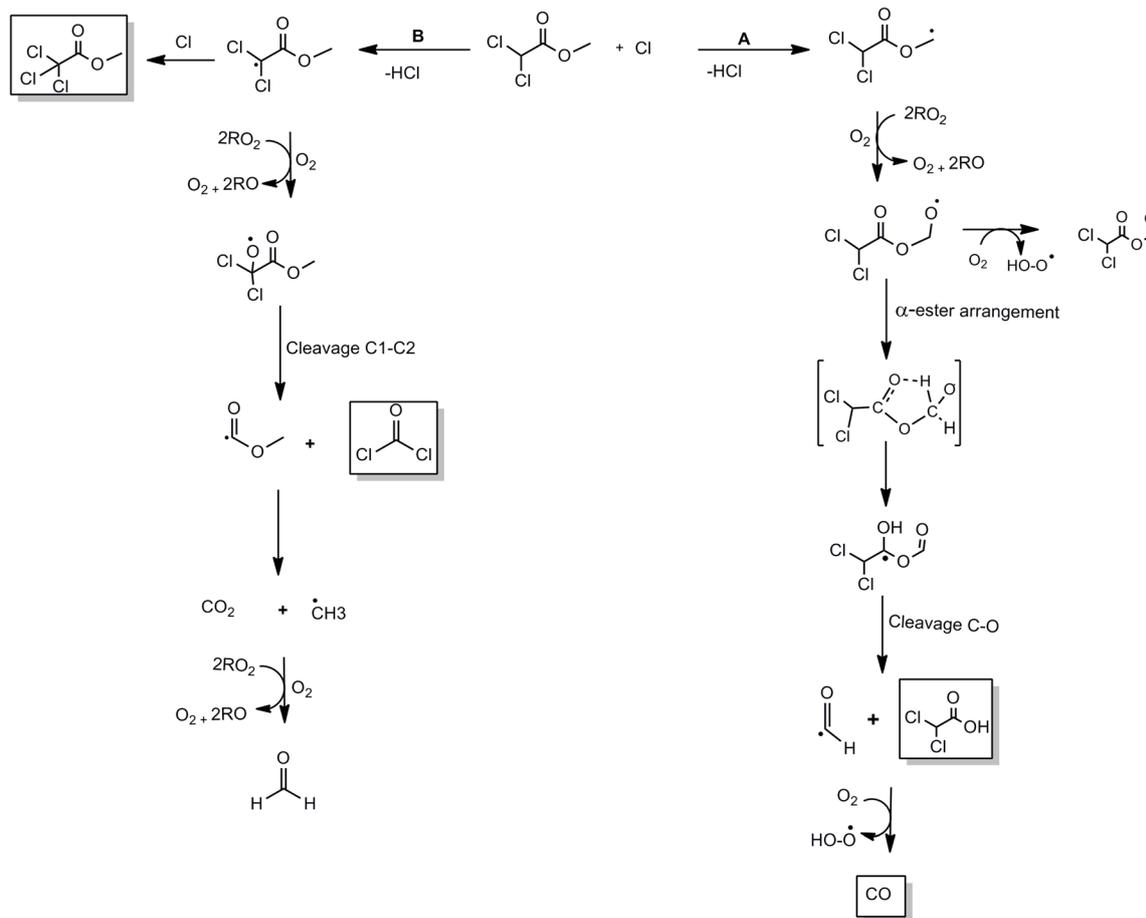
The possible reaction pathway that can develop in the reaction of Cl atoms with methyl dichloroacetate will occur *via* H-atoms abstraction at the  $\text{CH}_3$  or  $\text{CHCl}_2$ , followed by the addition of  $\text{O}_2$  to form peroxy radicals with further alkoxy radicals formation. The atmospheric sink of the alkoxy radicals formed can have several pathways of the reaction: decompose with

a C–C or C–O bond cleavage,  $\alpha$ -ester rearrangement with a further decomposition, or, react with  $\text{O}_2$ .

Fig. 3a shows IR spectra for the reaction of MDCA with Cl atoms before trace (i) and after trace (ii) UV irradiation with the lamps, dichloroacetic acid ( $\text{Cl}_2\text{CHCOOH}$ ) trace (iii), phosgene ( $\text{COCl}_2$ ) trace (iv), methyl trichloroacetate ( $\text{Cl}_3\text{CCOOCH}_3$ ) trace (v), and carbon monoxide (CO) trace (ii). These compounds have been successfully identified as reaction products. Trace (vi) shows the residual spectrum after the subtraction of the features of the above products.

Fig. 3b shows plots of the concentration–time performance of MDCA with Cl atoms and the products were identified. Fig. 3c shows that the plots of the formation of the product *versus* the loss of MDCA are linear with near zero intercepts and least squares analyses of the slopes of these plots show yields of ( $24 \pm 2$ ;  $19 \pm 3$ ;  $16 \pm 1$  and  $44 \pm 2$ ) % for  $\text{Cl}_2\text{CHCOOH}$ ,  $\text{COCl}_2$ ,  $\text{CO}$ , and  $\text{CCl}_3\text{C}(\text{O})\text{OCH}_3$ , respectively. The first five points were considered to fit the line and to calculate the product's yield of dichloroacetic acid and trichloroacetate (Table 3). The errors are a combination of  $2\sigma$  statistical errors from the regression.

A condensed reaction mechanism for the reaction of MDCA with Cl atoms in the absence of  $\text{NO}_x$  is shown in Scheme 1. Degradation of MDCA was initiated by Cl atoms occurring *via* H-atoms abstraction from the alkyl groups. Therefore, there are

**Scheme 1** The mechanism of the Cl-atoms initiated oxidation of methyl dichloroacetate at  $\text{NO}_x$ -free conditions *via* H-abstraction.

two possible routes for the reaction. According to SAR (US Environmental Protection Agency), H-atoms abstraction is estimated to account for 55% and 45% at  $-\text{CH}_3$  and  $-\text{Cl}_2\text{HC}$ -groups, respectively, in the overall reaction.<sup>29</sup> The probability of H-atom abstraction for both groups is similar, and this fact was observed in the yields calculated for phosgene and dichloroacetic acid formation.

Route A shows H-atoms abstraction from the ester  $\text{CH}_3$  group followed by the addition of  $\text{O}_2$  and further formation of an alkoxy radical. These  $\text{Cl}_2\text{CHC}(\text{O})\text{OCH}_2(\text{O}^\cdot)$  radicals can: (a) react with  $\text{O}_2$  to produce the polyfunctional compound  $\text{Cl}_2\text{CHC}(\text{O})\text{OC}(\text{O})\text{H}$  (b) undergo an  $\alpha$ -ester rearrangement followed by C–C bond cleavage to give the carboxylic acid  $\text{Cl}_2\text{CHC}(\text{O})\text{OH}$  and  $^\cdot\text{C}(\text{O})\text{H}$  radicals. These radicals can further react with  $\text{O}_2$  to give carbon monoxide. Both compounds ( $\text{Cl}_2\text{CHC}(\text{O})\text{OC}(\text{O})\text{H}$  and  $\text{Cl}_2\text{CHC}(\text{O})\text{OH}$ ) were identified and positively quantified. No evidence was observed for the formation of formaldehyde (HCHO) in the product spectra, supporting that the reaction route involving the C–O bond cleavage in the alkoxy  $\text{Cl}_2\text{CHC}(\text{O})\text{OCH}_2(\text{O}^\cdot)$ , is negligible in our experimental conditions.

Route B will occur if the H-atoms abstraction is from the  $\text{CCl}_2\text{H}$  group to form  $^\cdot\text{CCl}_2\text{C}(\text{O})\text{OCH}_3$  radicals. These radicals could add Cl atoms to produce methyl trichloroacetate  $\text{Cl}_3\text{CC}(\text{O})\text{OCH}_3$ . This compound was effectively identified and quantified by FTIR. On the other hand, the alkyl radicals will add  $\text{O}_2$  followed by the decomposition with C–C bond cleavage with phosgene,  $\text{COCl}_2$ , and  $^\cdot\text{C}(\text{O})\text{OCH}_3$  radical formation. These  $^\cdot\text{C}(\text{O})\text{OCH}_3$  radicals can be decarboxylated to form  $\text{CO}_2$  and  $^\cdot\text{CH}_3$  radicals. HCHO could not be detected in the experiments; however, formaldehyde could be an important source of the CO observed. Methyl radicals produce formaldehyde by the reaction with  $\text{O}_2$  with further CO and  $\text{CO}_2$  production by its degradation.

Complementary studies were performed concerning the products of the reactions of methyl dichloroacetate with Cl atoms monitoring the nascent products by GC-MS at LUQCA in the Córdoba, University.

Fig. 4 shows the chromatograms before (i) and after (ii) photolysis, where MDCA was observed at the retention time of 4.9 min, together with the characteristic fragments ( $m/z$ ) for the 3 main products found: dichloroacetic acid (iii) at 10 min, phosgene (iv) at 2.5 min and methyl trichloroacetate (v) at 3 min.

Dichloroacetic acid and phosgene were observed with ions with  $m/z = 45, 48, 76, 84, 35, 63,$  and  $65$ , respectively. Methyl trichloroacetate showed the fragments  $m/z = 15, 59, 82,$  and  $117$ . All of these fragments  $m/z$  are characteristic of these cited compounds.

Products identified by Fourier transform infrared spectroscopy and gas chromatography coupled to a mass detector were matched.

## 4 Atmospheric chemistry implications

Some species can last a long time in the atmosphere. The residence time can be calculated from the kinetic data of the oxidation reactions with tropospheric oxidants such as OH radicals, Cl atoms,  $\text{O}_3$  molecules, or  $\text{NO}_3$  radicals. The tropospheric lifetime ( $\tau$ ) was calculated using the determined rate coefficients and the average tropospheric oxidant concentrations.

From Table 4, the atmospheric lifetimes obtained was  $\tau_{\text{Cl}} = 2.96$  years for methyl dichloroacetate. This value was calculated with the expression  $\tau = 1/k_{\text{MDCA}} \times [\text{oxidants}]$ , where the concentrations of Cl atoms are reported as follows  $[\text{Cl}] = (3.3 \pm 1.1) \times 10^4$  atoms  $\text{cm}^{-3}$  for 24 hours<sup>30</sup> This chlorine atoms concentration value is an average obtained in marine areas of the North Atlantic as determined by Oliver W. Wingenter *et al.*, 1996.

Using eqn (9), of the free energy relationship, the rate coefficient for the reaction with OH radicals was estimated to be  $k_{\text{OH}} = 7.24 \times 10^{-13}$   $\text{cm}^3$  per molecule per s. With this kinetic value, and the concentration of  $[\text{OH}]^{\text{31}} = 2.0 \times 10^6$  radicals  $\text{cm}^{-3}$  for about 12 hours, the tropospheric lifetimes for the reaction with OH radicals could be estimated.

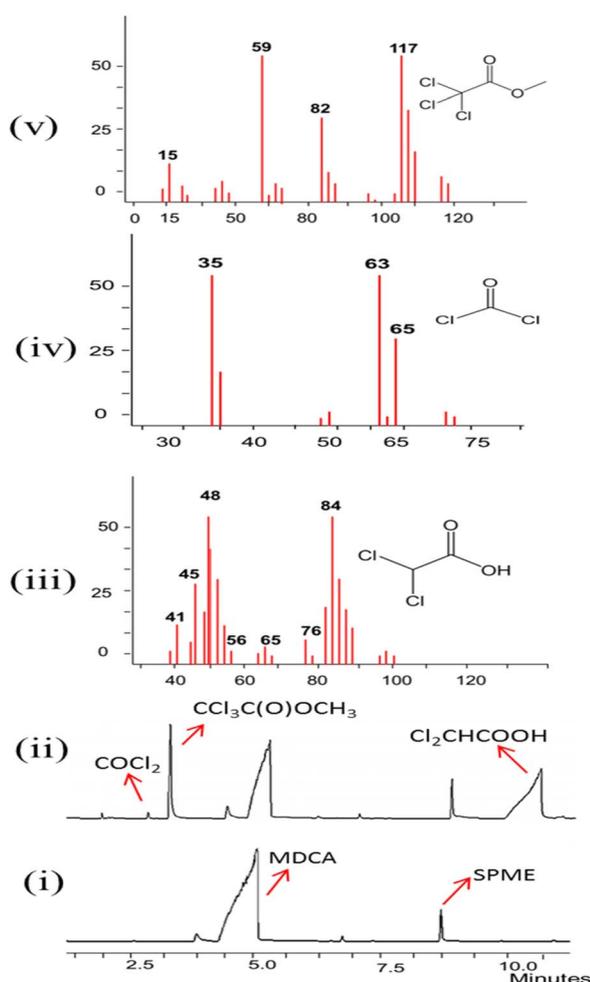


Fig. 4 GC-MS chromatogram of a mixture of MDCA/Cl/air in the absence of  $\text{NO}_x$ . (i) Chromatogram obtained before photolysis. (ii) Chromatogram obtained after the photolysis where products were observed. (iii), (iv), and (v) Mass spectra obtained for dichloroacetic acid, phosgene, and methyl trichloroacetate, respectively.



Table 4 Atmospheric implications of methyl dichloroacetate

Reaction	$k_{\text{Cl}}$ (cm <sup>3</sup> per molecule per s)	$\tau_{\text{Cl}}$ years	$\tau_{\text{OH}}^a$ days	AP <sup>b</sup>	GWP (CO <sub>2</sub> ) <sup>c</sup>		
					20	100	500
MDCA + Cl	$3.31 \times 10^{-13}$	2.96	80	0.45	8.2	2.2	0.6

<sup>a</sup> Reference compounds: calculated from eqn (9). <sup>b</sup> SO<sub>2</sub> = 1. <sup>c</sup> CO<sub>2</sub> = 1.

Unfortunately, there are no kinetic data available in the literature for the reactions of this compound with O<sub>3</sub> molecules and NO<sub>3</sub> radicals. Photolysis studies performed before the kinetics experiments for MDCA did not show an important decrease in the signals of the FTIR that is, the MDCA was stable to actinic radiation. This leaves the solar photolysis of the compound. MDCA has a low solubility in water, so the wet deposition is negligible.

The stability of methyl dichloroacetate in the atmosphere is considerably high. This compound survives a long time before it is transferred from its source of emission to other areas and can contribute to tropospheric ozone formation or it can ascend to the stratosphere and contribute to destroying the ozone layer depletion.

Rainfall acidification is a well-known environmental problem caused by the presence of acids in the atmosphere, the most important of which are HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and HCl. However, compounds with Cl, F, N, and S substituents may contribute to acidification. AP is defined as the number of acid equivalent potentials (H<sup>+</sup>) per unit mass of a compound relative to the number of H<sup>+</sup> per unit mass of a reference compound, (SO<sub>2</sub> = 1).

$$AP = \frac{M_{\text{SO}_2}}{M_{\text{NS}}} \times \frac{n_{\text{Cl}} + n_{\text{F}} + n_{\text{N}} + 2n_{\text{S}}}{2} \quad (10)$$

AP was estimated using the empirical eqn (10) given by Frank A. A. M. de Leeuw.<sup>32</sup> The number of equivalent potentials (H<sup>+</sup>) per molecule is obtained by adding the number of substituents of nitrogen (N), chlorine (Cl), fluorine (F), and double sulfur (2 × S).

Table 4 shows that the potential of acidifying MDCA is 0.45, it is almost half that of the reference compound. This value indicates that methyl dichloroacetate degradation could be involved in acidifying rainwater and increasing environmental problems. However, since the time scale between emission and washout, as acidic species is not known, these values should be regarded as upper limits for the acidification potential of the studied compound.

To evaluate the contribution to greenhouse warming, the Global Warming Potential (GWP) using the method by Ø. Hodnebrog *et al.* with the eqn (11).<sup>33</sup>

$$\text{GWP}_i(H) = \frac{\int_0^H \text{RF}_i(t) dt}{\int_0^H \text{RF}_{\text{CO}_2}(t) dt} = \frac{\text{AGWP}_i(H)}{\text{AGWP}_{\text{CO}_2}(H)} \quad (11)$$

The GWP of a specific gas is calculated as the ratio of the time-integrated radiative forcing from a pulse emission of a unit

mass of gas (1 kg) of that gas relative to that of 1 kg of a reference gas, normally CO<sub>2</sub> where H is the time horizon, this is for 20, 100, and 500 years.

GWPs for MDCA were calculated to be 8.2; 2.2, and 0.6 for a time horizon of 20, 100, and 500 years, respectively. These potentials were estimated using the  $k_{\text{OH}}$  value calculated by SAR. Its impact on global warming could be significant compared with carbon dioxide CO<sub>2</sub> = 1 due to its long lifetime. However, as we mentioned before since the exact emissions of MDCA to the troposphere are not possible to be determined yet in comparison with CO<sub>2</sub> emissions, these values must be considered higher limits for the GWP of the MDCA.

Atmospheric degradation of methyl dichloroacetate can produce phosgene gas (COCl<sub>2</sub>). Phosgene is an extremely toxic gas, which can be gradually degraded through UV radiation to produce ClO<sub>x</sub>, which has an important impact on the depletion of the ozone layer.<sup>34</sup> This gas can react with the humidity of the rains and form hydrochloric acid that can cause acid rains.<sup>31–33</sup>

Dichloroacetic acid as a product of methyl dichloroacetate degradation is a stable tropospheric product and it can dissolve in the water droplets of the clouds.<sup>35</sup> This persistent acid is a potentially hazardous compound since it is still more toxic than the other chlorinated compounds such as trichloroethylene<sup>36</sup>.

## 5 Conclusions

There are no previous kinetic and product distribution data for the reactions of Cl atoms with methyl dichloroacetate under atmospheric conditions. Consequently, this work reports the first kinetic and product distribution data for the photo-degradation reaction of the mentioned chloroester initiated by atmospheric oxidants.

The correlation between  $k_{\text{OH}}$  and  $k_{\text{Cl}}$  gives evidence that the degradation mechanisms of both reactions occur in the same way, the abstraction of hydrogen atoms. On the other hand, these results can be useful for predictive reaction modelers and further laboratory studies, in case of atmospheric reactions not yet studied.

The residence time of methyl dichloroacetate around 3 three years, will have a regional and global impact. Loss by photolysis can be considered negligible since MDCA is photolytically stable in the actinic region of the electromagnetic spectrum.

The acidification potential suggests that the degradation of MDCA could contribute to the acidification of rainwater and since the GWPs, calculated as 8.2, 2.2, and 0.6 (with times horizon of 20, 100, and 500 years, respectively), are higher than



the reference of CO<sub>2</sub>, this compound could contribute to the positive radiative forcing as a greenhouse gas.

Furthermore, the reaction products formed on the oxidation of the chloroester in the air, such as phosgene and dichloroacetic acid could have a negative impact on the atmosphere-biosphere in different environmental matrixes and on the ozone layer.

## Conflicts of interest

There are no conflicts to declare.

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