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# Kinetic study of the OH and Cl-initiated oxidation, lifetimes and atmospheric acceptability indices of three halogenated ethenes

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The gas-phase kinetics for the reactions of OH radicals and Cl atoms with (*E/Z*)-CHCl=CHF, (*E/Z*)-CFCl=CFCl, and CCl<sub>2</sub>=CF<sub>2</sub> were investigated at room-temperature and atmospheric pressure. A conventional relative-rate technique was used to determine the rate coefficients  $k(\text{OH} + (E/Z)\text{-CHCl=CHF}) = (6.3 \pm 1.2) \times 10^{-12}$ ,  $k(\text{OH} + (E/Z)\text{-CFCl=CFCl}) = (1.6 \pm 0.2) \times 10^{-12}$ ,  $k(\text{OH} + \text{CCl}_2=\text{CF}_2) = (5.0 \pm 0.7) \times 10^{-12}$ ,  $k(\text{Cl} + (E/Z)\text{-CHCl=CHF}) = (11 \pm 2) \times 10^{-11}$ ,  $k(\text{Cl} + (E/Z)\text{-CFCl=CFCl}) = (5.4 \pm 1.3) \times 10^{-11}$ , and  $k(\text{Cl} + \text{CCl}_2=\text{CF}_2) = (6.3 \pm 1.5) \times 10^{-11}$  cm<sup>3</sup> per molecule per s. These rate coefficients were compared with previous literature data to analyze the effect of halogen substitution in ethenes on the reactivity towards OH and Cl, and used to estimate the global atmospheric lifetimes for the studied haloethenes. The calculated lifetimes, using average global concentrations of OH radicals and Cl atoms, indicate that the atmospheric loss of these compounds is determined by the OH-initiated oxidation. Also, the atmospheric implications of the halogenated ethenes studied were evaluated by estimating acceptability indices such as the global warming potential (GWP) and the ozone depletion potential (ODP). From these potentials, the contribution of (*E/Z*)-CHCl=CHF, (*E/Z*)-CFCl=CFCl, and CCl<sub>2</sub>=CF<sub>2</sub> to radiative forcing of climate change and to ozone layer depletion is expected to be negligible.

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## 1. Introduction

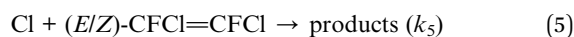
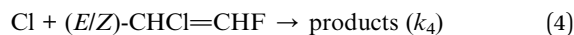
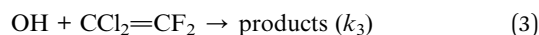
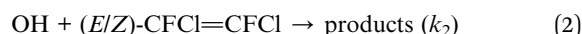
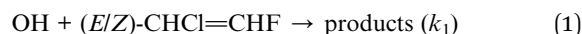
Recognition of the necessity to decrease the harmful effects of chlorofluorocarbons (CFCs) and their derivatives in the atmosphere has led to international efforts to replace them with alternative compounds which should have similar properties to CFCs except for environmental behavior such as depletion of stratospheric ozone layer and global warming.<sup>1,2</sup>

Anthropogenic volatile organic compounds like halogenated alkenes have been suggested as possible acceptable CFC replacement compounds in applications such as degreasing agents, industrial solvents, and refrigerant agents,<sup>3,4</sup> and thus released in increasing amounts to the atmosphere. These replacements, containing a >C=C< bond, can be oxidized by highly reactive species in the atmosphere, having the important environmental advantage of a short tropospheric lifetime and, thus, reducing their indices of atmospheric hazard, such as the

ozone depletion potential (ODP) and the global warming potential (GWP).

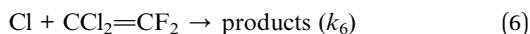
Removal of halogenated alkenes from the troposphere is expected to be controlled by chemical reaction with OH radicals (Atkinson and Arey, 2003),<sup>5</sup> although the Cl atom-initiated degradation reactions with Cl atoms may be an important homogeneous loss process in the boundary layer, particularly in marine and coastal environments,<sup>6,7</sup> and in continental regions.<sup>8,9</sup> Therefore, detailed kinetic and mechanistic information on the gas-phase reaction of OH and Cl with these anthropogenic species is required to assess their atmospheric fate and their possible impact on air quality.

In this work, we report a relative kinetic study of the oxidation reactions of (*E/Z*)-1-chloro-2-fluoroethene, (*E/Z*)-1,2-dichloro-1,2-difluoroethene, and 1,1-dichloro-2,2-difluoroethene initiated by OH radicals and Cl atoms at room-temperature and atmospheric pressure:



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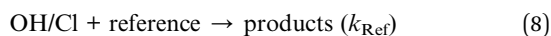
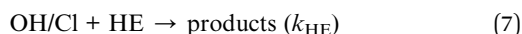
To the best of our knowledge, this work constitutes the first experimental determination of the rate coefficients for the reactions of OH radicals with (*E/Z*)-CHCl=CHF and (*E/Z*)-CFCl=CFCl, whereas for CCl<sub>2</sub>=CF<sub>2</sub> there is only one previous kinetic study, performed by Abbatt and Anderson using a high-pressure discharge flow apparatus at 297 K.<sup>10</sup> Moreover, there are no prior kinetic determinations for the gas-phase reactions of Cl atoms with these three halogenated ethenes.

Additionally, this study aims to extend the existing scant database on the reactivity of halogenated alkenes toward tropospheric oxidants as part of ongoing work in our laboratory regarding the fate and impact of these compounds in atmospheric chemistry.<sup>11,12</sup> Moreover, the investigation of the reactivity of these anthropogenic volatile organic compounds provides an opportunity to examine halogen substituent effects as a function of extent and position around the double bond. Finally, the environmental acceptability and atmospheric implications of the three haloolefins studied were evaluated calculating their lifetimes, radiative efficiencies (RE), and atmospheric hazard indices (ODP and GWP).

## 2. Experimental section

### 2.1. Relative-rate measurements

The second-order rate coefficients for the reactions (1)–(6) were determined using a relative-rate method which assumes that loss of the halogenated ethene (HE) and reference compound occurs only by the reactions (7) and (8):



The relative-rate coefficient,  $k_{\text{HE}}/k_{\text{Ref}}$ , is then given by

$$\ln([\text{HE}]_0/[\text{HE}]_t) = (k_{\text{HE}}/k_{\text{Ref}}) \times \ln([\text{Ref}]_0/[\text{Ref}]_t) \quad (9)$$

where  $[\text{HE}]_0$ ,  $[\text{Ref}]_0$ ,  $[\text{HE}]_t$  and  $[\text{Ref}]_t$  are the concentrations of the halogenated ethene and reference compound at times  $t = 0$  and  $t$ , respectively and  $k_{\text{HE}}$  and  $k_{\text{Ref}}$  are the rate coefficients of reactions (7) and (8), respectively. Thus, a plot of  $\ln([\text{HE}]_0/[\text{HE}]_t)$

versus  $\ln([\text{Ref}]_0/[\text{Ref}]_t)$  should be linear with a slope equal to  $k_{\text{HE}}/k_{\text{Ref}}$ .

Rate coefficients ( $k_1$ )–( $k_6$ ) were measured at  $(298 \pm 2)$  K and atmospheric pressure of synthetic air. The experimental set-up used to determine these rate coefficients was presented in a previous publication,<sup>13</sup> which consisted of a greaseless high vacuum system, a 200 L collapsible Teflon bag (reaction chamber), and a gas chromatograph (GC-FID, PerkinElmer Clarus 500) with flame-ionization detection.

Reaction mixtures consisting of a haloethene, a reference organic compound, and the OH radical/Cl atom precursor, diluted in synthetic air, were prepared in the reaction chamber and left to mix, prior to photolysis, for at least 1 h. Measured amounts of the gaseous reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of synthetic air and the bag was then filled to its full capacity at atmospheric pressure. H<sub>2</sub>O<sub>2</sub> was introduced into the bag by a Hamilton syringe. Pressure measurements were performed with a capacitance manometer (MKS Baratron, range 10 Torr).

Auxiliary experiments were carried out using the same experimental set-up, in which ethane was added to the reaction mixtures in sufficient concentration to scavenge any Cl atoms potentially generated.

The initial concentration ranges, in ppm, of (*E/Z*)-CHCl=CHF, (*E/Z*)-CFCl=CFCl, CCl<sub>2</sub>=CF<sub>2</sub>, and reference compounds (methanol, cyclopentane, *n*-pentane, *n*-heptane, and 2-chloroethylmethylether) used in the experiments are shown in Tables 1 and 2, where 1 ppm =  $2.46 \times 10^{13}$  molecule per cm<sup>3</sup> at 298 K and 760 Torr of total pressure. The ethane concentration added was ~135 ppm. OH radicals and Cl atoms were generated *in situ* in the collapsible Teflon bag by the UV photolysis of H<sub>2</sub>O<sub>2</sub> (germicide lamps,  $\lambda_{\text{max}} \sim 254$  nm) and molecular chlorine (black lamps,  $\lambda_{\text{max}} \sim 360$  nm), respectively. In the present work, typically 4 of these lamps were used and the total time of photolysis varied from 2 to 8 min.

After each photolysis, reaction mixtures were removed from the Teflon bag using calibrated gas syringes (Hamilton gas tight). The organics were monitored by gas chromatography using an Elite-1 capillary column (PerkinElmer, 30 m, 0.32 mm i.d.) which was maintained at 33 °C ((*E/Z*)-CClF=CClF) or 45 °C ((*E/Z*)-CHCl=CHF and CCl<sub>2</sub>=CF<sub>2</sub>) during the chromatographic runs. Ultrapure He was used as the carrier gas.

**Table 1** Range of initial concentration of the reactants, rate coefficient ratios,  $k_{\text{HE}}/k_{\text{Ref}}$ , and the absolute rate coefficients,  $k_{\text{HE}}$ , for the reactions of OH radicals with the studied halogenated ethenes at 298 K and atmospheric pressure

Haloethene	$[\text{HE}]_0$ (ppm)	Reference compound	$[\text{Ref}]_0$ (ppm)	Number of runs	$k_{\text{HE}}/k_{\text{Ref}}$	$k_{\text{HE}}$ (cm <sup>3</sup> per molecule per s)
<i>(E/Z)</i> -CHCl=CHF	30–61	Cyclopentane	39–44	4	$1.34 \pm 0.03$	$(6.5 \pm 0.9) \times 10^{-12}$
	35–44	<i>n</i> -Heptane	35–44	3	$0.89 \pm 0.01$	$(6.0 \pm 1.2) \times 10^{-12}$
					Average	$(6.3 \pm 1.2) \times 10^{-12}$
<i>(E/Z)</i> -CClF=CClF	39–48	Methanol	39–61	3	$1.76 \pm 0.03$	$(1.6 \pm 0.2) \times 10^{-12}$
	39–48	<i>n</i> -Pentane	44–48	4	$0.42 \pm 0.01$	$(1.6 \pm 0.1) \times 10^{-12}$
					Average	$(1.6 \pm 0.2) \times 10^{-12}$
CCl <sub>2</sub> =CF <sub>2</sub>	44–48	Cyclopentane	39–61	2	$1.03 \pm 0.02$	$(5.0 \pm 0.7) \times 10^{-12}$
	42–48	<i>n</i> -Pentane	39–70	4	$1.28 \pm 0.02$	$(5.0 \pm 0.3) \times 10^{-12}$
					Average	$(5.0 \pm 0.7) \times 10^{-12}$

**Table 2** Range of initial concentration of the reactants, rate coefficient ratios,  $k_{\text{HE}}/k_{\text{Ref}}$ , and the absolute rate coefficients,  $k_{\text{HE}}$ , for the reactions of Cl atoms with the studied halogenated ethenes at 298 K and atmospheric pressure

Haloethene	[HE] <sub>0</sub> (ppm)	Reference compound	[Ref] <sub>0</sub> (ppm)	Number of runs	$k_{\text{HE}}/k_{\text{Ref}}$	$k_{\text{HE}}$ (cm <sup>3</sup> per molecule per s)
<i>(E/Z)</i> -CHCl=CHF	38–64	<i>n</i> -Pentane	41–44	2	0.42 ± 0.01	(11 ± 1) × 10 <sup>-11</sup>
	30–58	CLEME <sup>a</sup>	39–43	3	1.03 ± 0.01	(11 ± 2) × 10 <sup>-11</sup>
					<b>Average</b>	<b>(11 ± 2) × 10<sup>-11</sup></b>
<i>(E/Z)</i> -CClF=CClF	39–49	Methanol	40–61	3	1.04 ± 0.02	(5.7 ± 1.3) × 10 <sup>-11</sup>
	39–46	CLEME <sup>a</sup>	42–48	2	0.45 ± 0.01	(5.0 ± 1.0) × 10 <sup>-11</sup>
					<b>Average</b>	<b>(5.4 ± 1.3) × 10<sup>-11</sup></b>
CCl <sub>2</sub> =CF <sub>2</sub>	43–48	Methanol	42–76	3	1.15 ± 0.02	(6.3 ± 1.5) × 10 <sup>-11</sup>
	44–48	CLEME <sup>a</sup>	43–69	2	0.56 ± 0.01	(6.2 ± 1.2) × 10 <sup>-11</sup>
					<b>Average</b>	<b>(6.3 ± 1.5) × 10<sup>-11</sup></b>

<sup>a</sup> CLEME: 2-chloroethylmethylether.

Experiments such as ours are conventionally carried out in the presence of synthetic air in order to simulate the concentration of O<sub>2</sub> and N<sub>2</sub> in the atmosphere.

## 2.2. Infrared absorption spectra

Infrared spectra of the three haloethenes were recorded in the 500–1500 cm<sup>-1</sup> region at 298 K using a Nicolet FTIR spectrometer, with 1.0 cm<sup>-1</sup> resolution. An IR spectrum was obtained averaging 4 spectra of the pure compound varying its pressure between 0.2 and 2.0 Torr. The absorption cell used was a Pyrex cell sealed with NaCl windows and with an optical path-length equal to (23.0 ± 0.1) cm. Gas sample pressures were measured with a capacitance manometer (MKS Baratron, range 10 Torr). Background spectra were measured with the sample cell under vacuum.

## 2.3. Materials

N<sub>2</sub> (Linde, 99.999%), O<sub>2</sub> (Linde, 99.999%), He (Linde, 99.999%), ultrapure air (synthetic air SS Linde), (*E/Z*)-CHCl=CHF (PCR, 99%), (*E/Z*)-CFCl=CFCl (PCR, 99%), and CCl<sub>2</sub>=CF<sub>2</sub> (PCR, 99%) were used as received. Methanol (Dorwill, 99.8%), cyclopentane (Merck, 99%), *n*-pentane (Dorwill, 99.1%), *n*-heptane (Merck, 99%), and 2-chloroethylmethylether (Aldrich, 98%) were degassed by repeated freeze–pump–thaw cycling and purified by vacuum distillation before use. A 70.5% H<sub>2</sub>O<sub>2</sub> solution was supplied by Atanor S.A. and it was concentrated by bubbling N<sub>2</sub> through this solution prior to use to remove water.

## 3. Results

The second-order rate coefficients ( $k_1$ )–( $k_6$ ) were determined at (298 ± 2) K and atmospheric pressure and obtained from the relative loss of the halogenated ethene *versus* that of the reference compounds in the presence of OH radicals or Cl atoms. For OH reactions, the rate coefficients were measured using as references cyclopentane and *n*-heptane for reaction (1), methanol and *n*-pentane for reaction (2), and cyclopentane and *n*-pentane for reaction (3). The rate coefficients in units of cm<sup>3</sup> per molecule per s of the reaction of OH with the reference compounds used in this work were taken as (4.85 ± 0.58) × 10<sup>-12</sup> for cyclopentane,<sup>14</sup> (6.76 ± 1.35) × 10<sup>-12</sup> for *n*-heptane,<sup>15</sup>

(9.1 ± 1.1) × 10<sup>-13</sup> for methanol,<sup>16</sup> and (3.92 ± 0.17) × 10<sup>-12</sup> for *n*-pentane.<sup>17</sup> *n*-Pentane and 2-chloroethylmethylether were used as references for the reaction of (*E/Z*)-CHCl=CHF with Cl atoms, and methanol and 2-chloroethylmethylether for (*E/Z*)-CFCl=CFCl and CCl<sub>2</sub>=CF<sub>2</sub>. The rate coefficients used were as follows:  $k_{n\text{-pentane}+\text{Cl}} = (2.5 \pm 0.1) \times 10^{-10}$ ,<sup>5</sup>  $k_{2\text{-chloroethylmethylether}+\text{Cl}} = (1.11 \pm 0.20) \times 10^{-10}$ ,<sup>13</sup>  $k_{\text{methanol}+\text{Cl}} = (5.5 \pm 1.2) \times 10^{-11}$ ,<sup>18</sup> in units of cm<sup>3</sup> per molecule per s.

The relative-rate technique relies on the assumption that both the haloethene and the reference compound are removed solely by reaction with OH radicals or Cl atoms. To verify the assumption, several experiments were performed to check unwanted loss of the halogenated ethenes or reference *via* photolysis, wall reactions or dark chemistry. To test for possible photolysis of the reactants used, mixtures of the reactants in the absence of oxidizing agents were irradiated for 15 min using the output of all the lamps surrounding the chamber. No photolysis or removal at the walls of the collapsible Teflon bag of any of the organic reactants was observed. Additionally, mixtures of H<sub>2</sub>O<sub>2</sub> or Cl<sub>2</sub> with both organics were prepared and allowed to stand in the dark. In all cases, the reaction of the organic species with oxidants, in the absence of UV light, was of negligible importance over the typical time periods used in this work.

Fig. 1 shows example plots of the relative rate data obtained for the reactions of OH radicals with (*E/Z*)-CHCl=CHF, (*E/Z*)-CFCl=CFCl, and CCl<sub>2</sub>=CF<sub>2</sub> using two different reference compounds. Similar plots for the reactions of Cl atoms with these three haloethenes are shown in Fig. 2. For each halogenated ethene studied, at least two runs were carried out to determine the rate coefficients and to test the internal consistency of the rate coefficient ratios. The results obtained using the different initial concentrations of the reactants were indistinguishable. Moreover, the linearity of the data points and the fact that plots show practically zero intercepts, suggest that the contribution of secondary reactions with the products of the reactions studied could be considered negligible. Additionally, rate coefficients ( $k_1$ )–( $k_3$ ) were indistinguishable in both the presence and absence of the Cl atom scavenger, indicating that the potential release of Cl atoms, following the reaction of OH radicals with these haloethenes, was of negligible importance and had no influence in the measurement of the relative rate

coefficients. Thus, the ratios of the rate coefficients,  $k_{\text{HE}}/k_{\text{Ref}}$ , obtained from the slopes of the plots shown in Fig. 1 and 2, were reliable for determining the rate coefficients in absolute terms for the reactions (1)–(6). The recommended second-order rate coefficient values obtained by averaging the values from different experiments were the following:

$$k_1 = (6.3 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ per molecule per s}$$

$$k_2 = (1.6 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ per molecule per s}$$

$$k_3 = (5.0 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ per molecule per s}$$

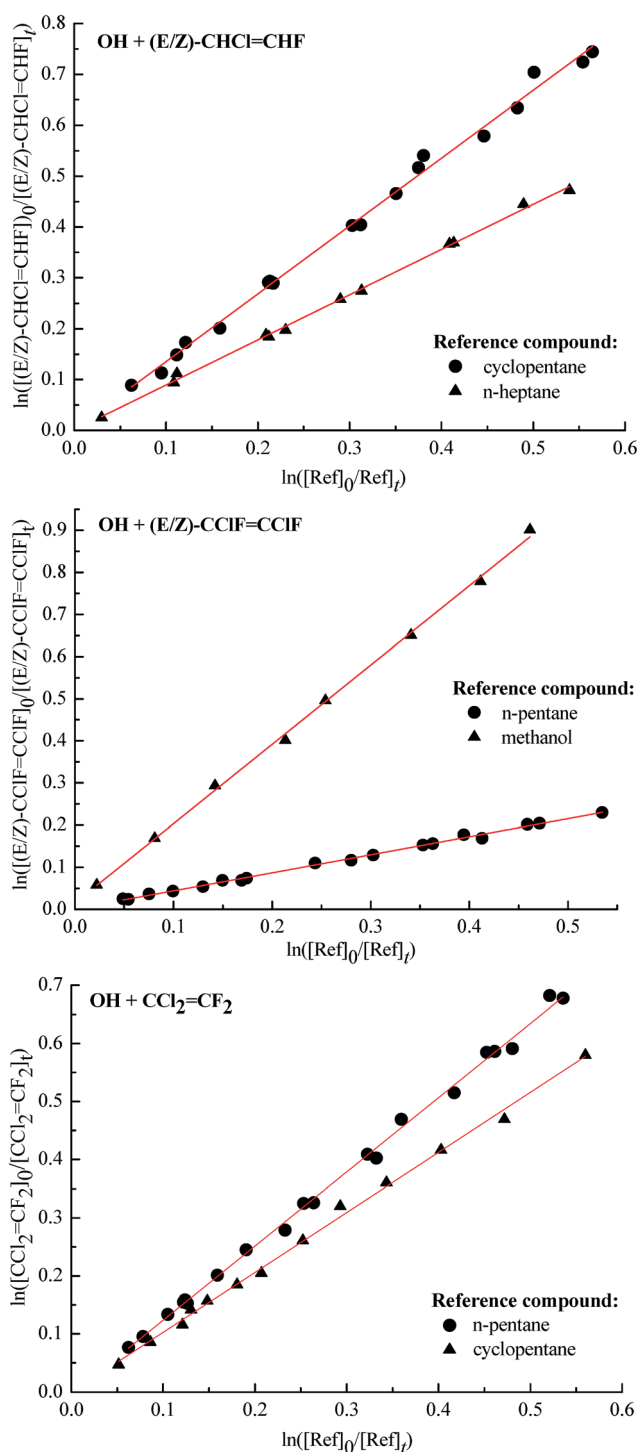


Fig. 1 Relative kinetic data for the OH reaction with (*E/Z*)-1-chloro-2-fluoroethene, (*E/Z*)-1,2-dichloro-1,2-difluoroethene, and 1,1-dichloro-2,2-difluoroethene at room-temperature and atmospheric pressure.

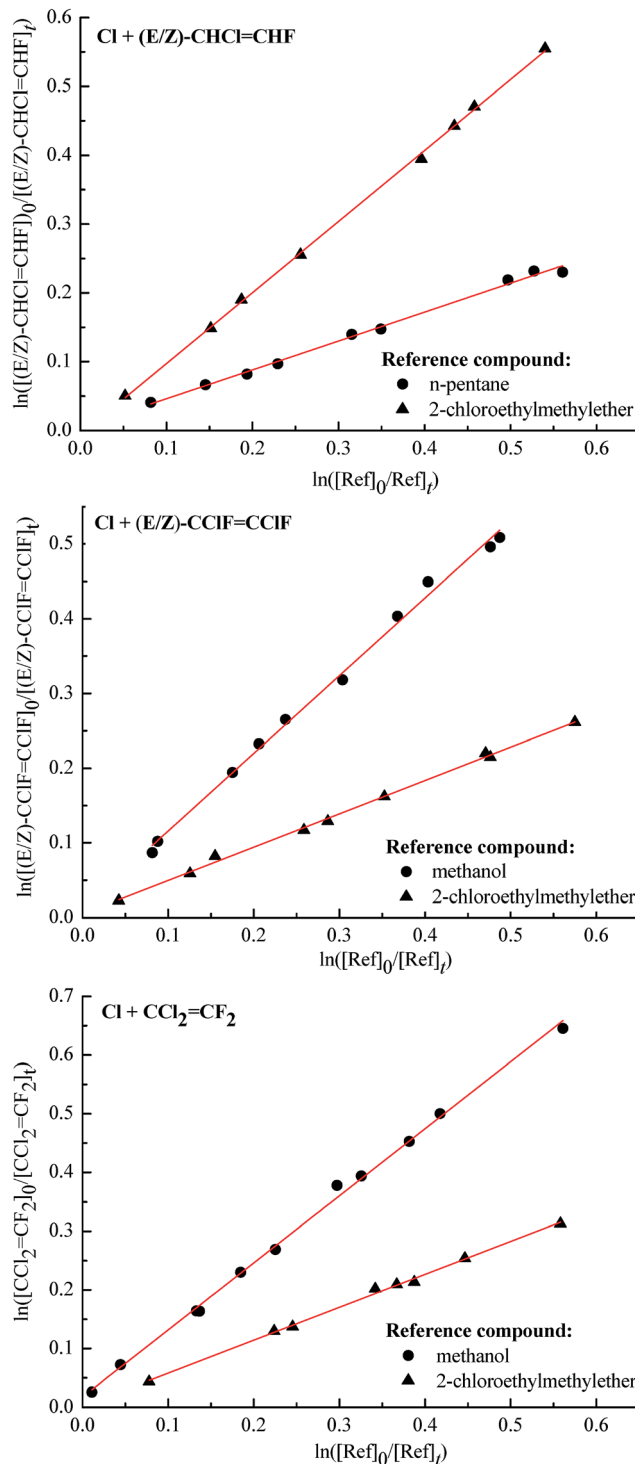


Fig. 2 Relative kinetic data for the Cl reaction with (*E/Z*)-1-chloro-2-fluoroethene, (*E/Z*)-1,2-dichloro-1,2-difluoroethene, and 1,1-dichloro-2,2-difluoroethene at room-temperature and atmospheric pressure.

$$k_4 = (11 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ per molecule per s}$$

$$k_5 = (5.4 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ per molecule per s}$$

$$k_6 = (6.3 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ per molecule per s}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines and include the corresponding statistical error in the reference rate constant. A summary of data on the relative-rate coefficients and the corresponding absolute rate coefficients for the reactions of OH radicals and Cl atoms with the halogenated ethenes here studied is given in Tables 1 and 2

## 4. Discussion

Kinetic data for the gas-phase reactions of OH radicals and Cl atoms with (*E/Z*)-CHCl=CHF, (*E/Z*)-CFCl=CFCl, and CCl<sub>2</sub>=CF<sub>2</sub> at (298 ± 2) K and atmospheric pressure were obtained in this work. To the best of our knowledge, this kinetic study represents the first experimental determination of the rate coefficients for the reactions of OH with (*E/Z*)-CHCl=CHF and (*E/Z*)-CFCl=CFCl, and for the reactions of Cl with these haloethenes, and therefore, no direct comparison with the literature can be made. However, for OH + CCl<sub>2</sub>=CF<sub>2</sub>, a previous value of the rate coefficient was reported by Abbatt and Anderson,<sup>10</sup> using a discharge flow tube apparatus at 297 K and 25 Torr of N<sub>2</sub>. This value ( $k = (7.44 \pm 0.40) \times 10^{-12} \text{ cm}^3 \text{ per molecule per s}$ ) is approximately a factor of 1.5 higher than our obtained value of  $(5.0 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ per molecule per s}$ . Presently, we have no satisfactory explanation for this apparent difference.

For the purpose of discussing reactivity trends, the rate coefficients for the OH and Cl reactions with the three halogenated ethenes studied in this work and several others, obtained from the literature, for a series of chlorine- and fluorine-substituted ethenes are listed in Table 3.

As the initial step for the OH reaction with halogenated alkenes is expected to be the electrophilic addition of the OH radical to the double bond to form a radical intermediate,<sup>5</sup> it is useful to examine the effects of halogenation on the reactivity of alkenes as a function of extent and positioning about the >C=C< bond. We must stress that the effect of halogenation on alkene reactivity is quite a complicated topic. However, one can reflect on the correlation between reactivity and structure of these halogenated alkenes.<sup>19</sup>

It is clear from the results in Table 3 that the inclusion of one or more halogen atoms in ethene changes its reactivity towards OH radicals. Substitution of H atoms by Cl or F atoms at any position in the molecule leads to a reduction in reactivity of the substituted ethene compared to that of the unsubstituted ethene, the only exceptions being CF<sub>2</sub>=CF<sub>2</sub> and CH<sub>2</sub>=CCl<sub>2</sub> which are more reactive than CH<sub>2</sub>=CH<sub>2</sub>.

For the sake of clarity and order of this discussion, we will first analyze the fluoroethenes, then the chloroethenes, and finally the chloro-fluoro-ethenes. The rate coefficient values for the fluoroethene + OH reactions show that as the number of fluorine atoms attached to the carbon atoms of the double bond

Table 3 Rate coefficients for the reactions of OH radicals and Cl atoms with ethene and haloethenes at room-temperature

Alkenes	$k_{\text{OH}}$ (cm <sup>3</sup> per molecule per s)	$k_{\text{Cl}}$ (cm <sup>3</sup> per molecule per s)
CH <sub>2</sub> =CH <sub>2</sub>	$8.52 \times 10^{-12a}$	$30 \times 10^{-11i}$
	$7.5 \times 10^{-12b}$	$31 \times 10^{-11b}$
CH <sub>2</sub> =CHF	$4.82 \times 10^{-12c}$	$0.18 \times 10^{-11k}$
	$5.0 \times 10^{-12b}$	
CH <sub>2</sub> =CF <sub>2</sub>	$2.82 \times 10^{-12c}$	—
	$2.8 \times 10^{-12b}$	
CHF=CF <sub>2</sub>	$7.90 \times 10^{-12c}$	—
CF <sub>2</sub> =CF <sub>2</sub>	$10 \times 10^{-12b}$	—
CH <sub>2</sub> =CHCl	$6.9 \times 10^{-12b}$	$12.7 \times 10^{-11l}$
<i>(E)</i> -CHCl=CHCl	$2.50 \times 10^{-12d}$	$9.58 \times 10^{-11l}$
	$2.34 \times 10^{-12e}$	
	$2.5 \times 10^{-12f}$	
	$2.13 \times 10^{-12g}$	
	$2.40 \times 10^{-12h}$	
<i>(Z)</i> -CHCl=CHCl	$2.71 \times 10^{-12d}$	$9.65 \times 10^{-11l}$
	$11 \times 10^{-12b}$	
CH <sub>2</sub> =CCl <sub>2</sub>	$2.0 \times 10^{-12i}$	$14.0 \times 10^{-11l}$
CHCl=Cl <sub>2</sub>	$2.2 \times 10^{-12b}$	$8.08 \times 10^{-11l}$
	$0.16 \times 10^{-12i}$	
CCl <sub>2</sub> =CCl <sub>2</sub>	$0.17 \times 10^{-12b}$	$4.0 \times 10^{-11b}$
	$6.3 \times 10^{-12j}$	$4.13 \times 10^{-11l}$
<i>(E/Z)</i> -CHCl=CHF	$1.6 \times 10^{-12j}$	$11 \times 10^{-11j}$
<i>(E/Z)</i> -CClF=CClF	$1.6 \times 10^{-12j}$	$5.4 \times 10^{-11j}$
CClF=CF <sub>2</sub>	$7.57 \times 10^{-12h}$	—
CCl <sub>2</sub> =CF <sub>2</sub>	$7.44 \times 10^{-12h}$	$6.3 \times 10^{-11j}$
	$5.0 \times 10^{-12j}$	

<sup>a</sup> Ref. 5. <sup>b</sup> Ref. 16. <sup>c</sup> Ref. 20. <sup>d</sup> Ref. 21. <sup>e</sup> Ref. 22. <sup>f</sup> Ref. 23. <sup>g</sup> Ref. 24. <sup>h</sup> Ref. 10. <sup>i</sup> Ref. 18. <sup>j</sup> This work. <sup>k</sup> Ref. 25. <sup>l</sup> Ref. 26.

increases, the reactivity of the ethene does not continue to decrease but appears to pass through a minimum:  $k_{\text{CH}_2=\text{CF}_2} < k_{\text{CH}_2=\text{CHF}} < k_{\text{CHF}=\text{CF}_2} < k_{\text{CF}_2=\text{CF}_2}$ . Thus, asymmetric fluorination of the olefinic carbon atom seems to lessen reactivity, whereas further fluorination (more symmetric substitution) compensates for the original deactivation, so much so that CF<sub>2</sub>=CF<sub>2</sub> has a rate coefficient greater than that of CH<sub>2</sub>=CH<sub>2</sub>. This trend, which has been previously described by Orkin *et al.*,<sup>19</sup> suggests that the localization of π-electron density in the center of the >C=C< bond promotes OH addition, whereas the shift of electron density towards the carbon atom due to the electron-withdrawing capacity of the F atom obstructs it. Therefore, both a geometrical factor and the electron affinity of the substituent on the delocalization of the π electrons could influence the substituted ethene reactivity towards OH radicals.

An analysis of the experimental data presented in Table 3 for the reactions of OH with chlorine-substituted ethenes indicates that the addition of a single chlorine atom to ethene leads to a decrease in the rate coefficient, while the addition of the second chlorine on the same carbon leads to:  $k_{\text{CH}_2=\text{CCl}_2} > k_{\text{CH}_2=\text{CH}_2}$ . However, if the two Cl atoms are located on different carbon atoms of ethene, a considerable reduction in the olefin reactivity is observed. Moreover, progressive substitutions of H by Cl result in further decreases in the rate coefficients of chloroethenes:  $k_{\text{CH}_2=\text{CH}_2} > k_{\text{CH}_2=\text{CHCl}} > k_{\text{(E/Z)-CHCl=CHCl}} > k_{\text{CHCl=CCl}_2} > k_{\text{CCl}_2=\text{CCl}_2}$ . Thus, the general trend in the reactivity of

chloroethenes could be accounted for considering mainly two factors: (a) the reduction of the electron density of the double bond through an inductive effect due to the addition of Cl atoms in a fully hydrogenated ethene causing deactivation toward electrophilic attack; and (b) an increase in steric hindrance due to substitution of H atoms with a bulky atom preventing the OH addition on the  $\pi$  orbital of the chloroalkene.

It can be observed in Table 3 that the rate coefficients for OH radical addition to chloro-fluoro-ethenes are affected because of electronic effects introduced by halogen substitution, but here again steric hindrance by increased Cl substitution seems to play a major role in the reactivity changes. It can be inferred that the steric effect rather than electronic effect dominates when F atoms are successively replaced by Cl atoms. Thus,  $k_{\text{CF}_2=\text{CF}_2} > k_{\text{CClF}=\text{CF}_2} > k_{\text{CCl}_2=\text{CF}_2} > k_{(E/Z)\text{-CClF}=\text{CClF}} > k_{\text{CCl}_2=\text{CCl}_2}$ , and  $k_{(E/Z)\text{-CHCl}=\text{CHF}} > k_{(E/Z)\text{-CHCl}=\text{CHCl}}$ .

Fig. 3 displays the values for the rate coefficients determined in the present study alongside those indicated for the reactions of OH radicals and Cl atoms in Table 3. This plot shows that the variation of the reactivity of halogenated ethenes with Cl atoms is similar as that observed for the reactivity with OH radicals.<sup>29</sup> Therefore, it is reasonable to assume that the reactivity towards Cl atoms also depends on various factors such as the geometrical localization of the  $\pi$ -electron density, the electron affinity of the substituents and their steric hindrance, as it is the case for the reactivity with OH radicals.

## 5. Atmospheric implications

When assessing the atmospheric impact of the halogenated ethenes studied, a suitable approach is to estimate their global lifetimes,  $\tau_{\text{global}}$ , with respect to individual sink processes such as oxidation reactions initiated by OH,  $\text{NO}_3$  and  $\text{O}_3$ , photolysis, and dry and wet deposition, which can be obtained from the following expression:

$$\tau_{\text{global}} = \left[ \frac{1}{\tau_{\text{Cl}}} + \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} + \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{other processes}}} \right]^{-1} \quad (10)$$

Unfortunately, no kinetic data for the reactions of  $(E/Z)$ - $\text{CHCl}=\text{CHF}$ ,  $(E/Z)$ - $\text{CFCl}=\text{CFCl}$  and  $\text{CCl}_2=\text{CF}_2$  with  $\text{NO}_3$  radicals or  $\text{O}_3$  molecules are available. Since the tropospheric removal rate of chloro or fluoroethenes with both oxidants are very slow,<sup>20,27</sup> we can assume that the contribution due to reactions of the three halogenated ethenes studied with  $\text{NO}_3$  and  $\text{O}_3$  will also be negligible. Atmospheric photolysis is another potential loss process, but it can be considered of minor importance since the absorption cross-sections of halogenated ethenes reported by Lacher *et al.* for tropospheric UV radiation are insignificant.<sup>28</sup> The same happens with “other processes” such as wet and dry deposition, since the three haloalkenes are expected to be sparingly soluble in water and highly volatile. Therefore, the persistence of these halogenated compounds in the atmosphere appears to be determined by photo-oxidation with OH radicals and Cl atoms, and kinetic data determined in this work allow an estimation of their global lifetimes.

The atmospheric lifetimes and global lifetimes of the studied haloethenes are presented in Table 4. The lifetimes were calculated using the relationship  $\tau_x = 1/k_x[X]$ , where X = OH radical or Cl atom, and assuming a global weighted-average atmospheric concentration of OH radicals of  $1 \times 10^6$  molecule per  $\text{cm}^3$ ,<sup>29</sup> and an average global concentrations of  $1 \times 10^3$  atoms per  $\text{cm}^3$  of Cl atoms.<sup>30</sup> The estimated lifetimes are based on the assumption of a uniform distribution of the compounds emitted into the troposphere; however, the calculated global lifetimes of the three halogenated ethenes in the range of 1.8–7.0 days do not ensure such condition. For this short-lived compounds is not possible to indicate a correct atmospheric residence time, which may vary depending on the emission location and season, as well as local atmospheric conditions.<sup>4</sup>

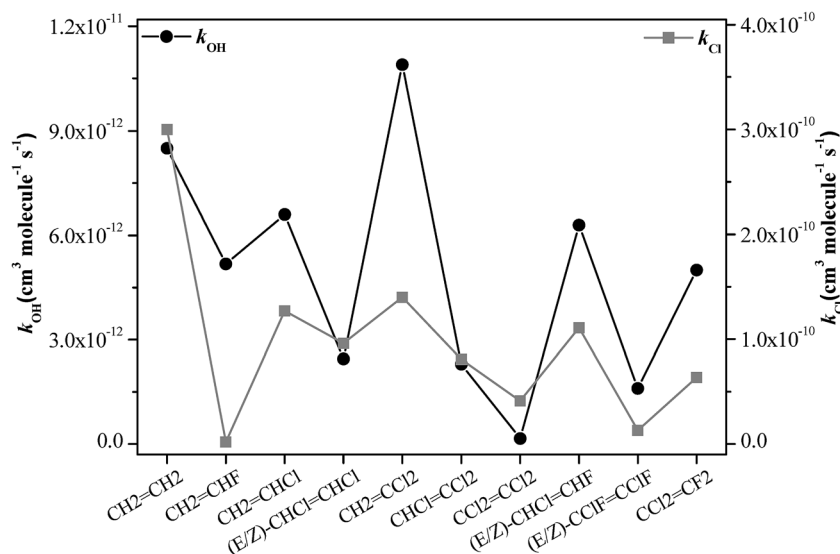


Fig. 3 Halogen substituent effects on the reactivity of ethenes with OH radicals and Cl atoms.

Nevertheless, these approximated lifetimes are still a useful atmospheric parameter to assign for short-lived species. Thus, the estimated global lifetimes in Table 4 indicate that the studied haloethenes are likely to be rapidly removed when emitted to the atmosphere, that the main degradation process is reaction with OH radicals, and that these compounds will be involved in tropospheric chemistry on local to regional scales.

The atmospheric impact of the emission of the halogenated ethenes studied here can be evaluated through the estimation of acceptability indices such as HGWP (halocarbon global warming potential), GWP (global warming potential), and ODP (ozone depletion potential).

Calculation of GWP for short lived species has not been considered appropriate by the World Meteorological Organization, since a detailed global modeling and emission scenarios would be needed.<sup>31</sup> However, GWPs have been calculated for some halogenated compounds with lifetimes shorter than 0.5 year from their radiative efficiencies (RE).<sup>11,12,32–35</sup> As RE is an intermediate parameter in GWP calculation and is not affected by  $\tau$  values, it would be worthwhile to make a comparison of the RE for the three haloethenes with  $\text{CFCl}_3$  (CFC-11) or  $\text{CO}_2$ , together with GWP. Radiative efficiencies of the studied compounds were calculated using the method of Pinnock *et al.*<sup>36</sup> and their IR spectra recorded in the 500–1500  $\text{cm}^{-1}$  region at 298 K. Plots of the cross-sections ( $\text{cm}^2$  per molecule) as a function of wavenumber ( $\text{cm}^{-1}$ ) of the haloolefins studied are shown in Fig. 4. The integrated IR absorption cross-section (500–1500  $\text{cm}^{-1}$ ) values for (*E/Z*)- $\text{CHCl}=\text{CHF}$ , (*E/Z*)- $\text{CClF}=\text{CClF}$ , and  $\text{CCl}_2=\text{CF}_2$  are  $2.78 \times 10^{-17}$ ,  $5.63 \times 10^{-17}$ , and  $5.45 \times 10^{-17}$  (in units of  $\text{cm}^2$  per molecule per cm), respectively. Unfortunately, there are no literature data for the absorption cross-sections of these compounds to compare with. Since that method is based on the assumption of the uniform distribution of the compound over the troposphere, the calculated REs for the short-lived compounds studied here can be significantly lower because their abundances will decrease strongly with altitude. Table 5 shows the calculated values of the RE for (*E/Z*)- $\text{CHCl}=\text{CHF}$ , (*E/Z*)- $\text{CFCl}=\text{CFCl}$ , and  $\text{CCl}_2=\text{CF}_2$ , together with the RE of CFC-11<sup>37</sup> (in units of  $\text{W m}^{-2}$ ) and the estimated values of HGWP and GWP on a time horizon of 20 and 100 years. The HGWP for the studied haloethenes (HE) was calculated relative to CFC-11 using the following expression:<sup>38</sup>

$$\text{HGWP}_{\text{HE}} = \frac{\tau_{\text{HE}}}{\tau_{\text{CFC-11}}} \frac{M_{\text{CFC-11}}}{M_{\text{HE}}} \frac{\text{RE}_{\text{HE}}}{\text{RE}_{\text{CFC-11}}} \frac{(1 - \exp^{-t/\tau_{\text{HE}}})}{(1 - \exp^{-t/\tau_{\text{CFC-11}}})} \quad (11)$$

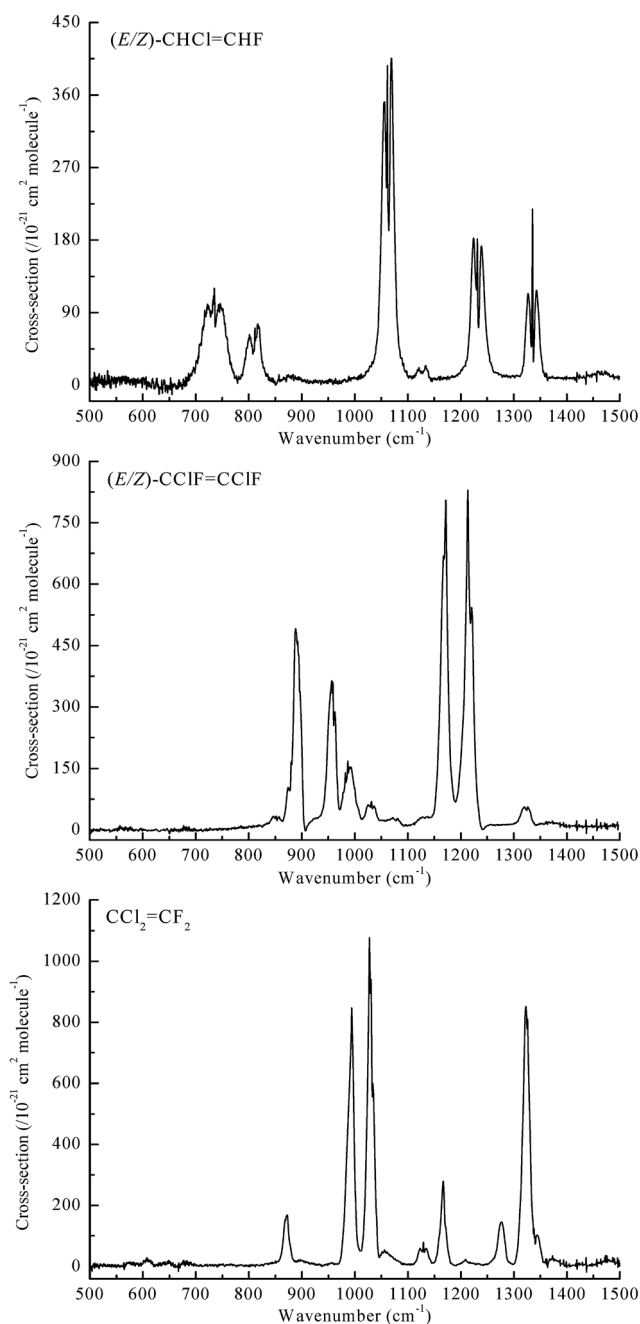
where  $\tau_{\text{HE}}$  and  $\tau_{\text{CFC-11}}$  are the corresponding tropospheric lifetimes,  $M_{\text{HE}}$  and  $M_{\text{CFC-11}}$  are the corresponding molar masses,

**Table 4** Estimated atmospheric lifetimes of the studied halogenated ethenes with OH radicals and Cl atoms, and their global lifetimes

Haloethenes	$\tau_{\text{OH}}$ (days)	$\tau_{\text{Cl}}$ (days)	$\tau_{\text{global}}$ (days)
( <i>E/Z</i> )- $\text{CHCl}=\text{CHF}$	1.8	104.3	1.8
( <i>E/Z</i> )- $\text{CClF}=\text{CClF}$	7.2	213.2	7.0
$\text{CCl}_2=\text{CF}_2$	2.3	183.1	2.3

$\text{RE}_{\text{HE}}$  and  $\text{RE}_{\text{CFC-11}}$  are the radiative efficiencies of the haloethene and  $\text{CFCl}_3$ , and  $t$  is the time horizon over which the RE is integrated. The GWPs of the halogenated ethenes, relative to  $\text{CO}_2$ , were calculated multiplying the HGWP values by the scaling factors, 6730 and 4750 on a time horizon of 20 and 100 years, respectively.<sup>37</sup> These scaling factors are the GWP values of the CFC-11.

Since the three haloolefins studied have chlorine in the molecule, they could enter the stratosphere and contribute to the halogen burden, thus promoting stratospheric ozone depletion. A semi-empirical approach has been developed by



**Fig. 4** Infrared spectra of (*E/Z*)- $\text{CHCl}=\text{CHF}$ , (*E/Z*)- $\text{CFCl}=\text{CFCl}$ , and  $\text{CCl}_2=\text{CF}_2$  at 298 K.

**Table 5** Global lifetimes ( $\tau_{\text{global}}$ ), estimated radiative efficiency (RE), halocarbon global warming potential (HGWP), and global warming potential (GWP) for the three haloethenes and the reference compound

Compounds	$\tau_{\text{global}}$ (years)	RE ( $\text{W m}^{-2}$ )	HGWP20	HGWP100	GWP20	GWP100
(E/Z)-CHCl=CHF	$4.9 \times 10^{-3}$	0.040	$8.26 \times 10^{-5}$	$3.32 \times 10^{-4}$	0.556	0.158
(E/Z)-CClF=CClF	$1.9 \times 10^{-2}$	0.107	$5.20 \times 10^{-4}$	$2.09 \times 10^{-4}$	3.503	0.995
$\text{CCl}_2=\text{CF}_2$	$6.3 \times 10^{-3}$	0.08	$1.29 \times 10^{-4}$	$5.19 \times 10^{-5}$	0.869	0.247
$\text{CFCl}_3$	45 <sup>a</sup>	0.25 <sup>a</sup>	1	1	6730 <sup>a</sup>	4750 <sup>a</sup>

<sup>a</sup> Ref. 37.

Solomon and Albritton<sup>39</sup> and applied to the estimation of ODPs on short and long time scales according to the following expression, adapted to the present work:

$$\text{ODP}_{\text{HE}} = \frac{(\tau_{\text{HE}} n_{\text{HE}} / M_{\text{HE}})}{(\tau_{\text{CFCl}_3} n_{\text{CFCl}_3} / M_{\text{CFCl}_3})} \quad (12)$$

where  $M$  denotes the molar mass of each species,  $n$  is the number of chlorine atoms in the compound considered, and  $\tau_{\text{HE}}$  and  $\tau_{\text{CFCl}_3}$  are the corresponding global atmospheric lifetimes. The value of  $\tau_{\text{CFCl}_3}$  is taken as 45 years.<sup>37</sup> The obtained ODP values for (E/Z)-CHCl=CHF, (E/Z)-CClF=CClF, and  $\text{CCl}_2=\text{CF}_2$  are  $6.2 \times 10^{-5}$ ,  $2.9 \times 10^{-4}$ , and  $9.6 \times 10^{-5}$ , respectively.

Summarizing, the estimated global lifetime of the studied halogenated ethenes indicates that they will be removed from the troposphere in a few days time and mainly by reaction with OH radicals. In addition, their short lifetimes will hinder the transport of these organic compounds into the stratosphere and their contribution to the ozone depletion through  $\text{ClO}_x$  catalytic cycles is expected to be negligible, which is clear from the ODP values obtained for the three haloethenes. Moreover, their small GWPs allow predicting a low impact of these compounds to the radiative forcing of climate change. The expected major products of haloethene oxidation in the troposphere are mainly small halogenated carbonyl compounds *via* the formation of peroxy and alkoxy radicals.<sup>4,23,40–42</sup> Although these products could contribute to the greenhouse effect, it can be considered of minor importance due to the removal of them from the atmosphere into raindrops/aerosol on a time scale of days to weeks. Furthermore, the additional burden of acid products and  $\text{CO}_2$  from carbonyl compound hydrolysis can be considered environmentally negligible.<sup>4,43</sup> Therefore, (E/Z)-CHCl=CHF, (E/Z)-CClF=CClF, and  $\text{CCl}_2=\text{CF}_2$  can be considered to be environmentally acceptable and a good alternative to CFCs and their derivatives. Finally, it is important to remark that we have assumed in the present work, for the calculation of the atmospheric lifetimes and acceptability indices of the three compounds studied, a uniform distribution in the troposphere which might not be the actual condition for such short-lived compounds as these. Hence, the estimated values may vary depending on the atmospheric conditions at the emission points such as chemical composition, location and season.

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## References

- 1 B. J. Finlayson-Pitts and J. N. Pitts Jr, *Chemistry of the Upper and Lower Atmosphere*, Academic Press, N.Y., 2000.
- 2 World Meteorological Organization, *Global Ozone Research and Monitoring Project, Report No 56, Assessment for Decision-Makers: Scientific Assessment of Ozone Depletion*, 2014.
- 3 T. J. Bruno, *Strategy for Chemical Analysis of Alternative Refrigerants*, NIST Technical Note 1340, U.S.A., 1990.
- 4 T. J. Wallington, M. P. Sulbaek Andersen and O. J. Nielsen, *Chemosphere*, 2015, **129**, 135.
- 5 R. Atkinson and J. Arey, *Chem. Rev.*, 2003, **103**, 4605.
- 6 B. J. Finlayson-Pitts and J. C. Hemminger, *J. Phys. Chem. A*, 2000, **104**, 11463.
- 7 C. W. Spicer, E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastidge, J. M. Hubbe, J. D. Fast and C. M. Berkowitz, *Nature*, 1998, **394**, 353.
- 8 J. A. Thornton, J. P. Kercher, T. P. Riedel, N. L. Wagner, J. Cozic, J. S. Holloway, W. P. Dubé, G. M. Wolfe, P. K. Quinn, A. M. Middlebrook, B. Alexander and S. S. Brown, *Nature*, 2010, **464**, 271.
- 9 R. von Glasow, *Nature*, 2010, **464**, 168.
- 10 J. P. D. Abbatt and J. G. Anderson, *J. Phys. Chem.*, 1991, **95**, 2382.
- 11 J. P. Aranguren Abrate, I. Pisso, S. A. Peirone, P. M. Cometto and S. I. Lane, *Atmos. Environ.*, 2013, **67**, 85.
- 12 P. M. Cometto, R. A. Taccone, J. D. Nieto, P. R. Dalmasso and S. I. Lane, *ChemPhysChem*, 2010, **11**, 4053.
- 13 P. R. Dalmasso, R. A. Taccone, J. D. Nieto, M. A. Teruel and S. I. Lane, *Int. J. Chem. Kinet.*, 2005, **37**, 420.
- 14 M. A. Gennaco, Y.-W. Huang, R. A. Hannun and T. J. Dransfield, *J. Phys. Chem. A*, 2012, **116**, 12438.
- 15 R. Atkinson, *Atmos. Chem. Phys.*, 2003, **3**, 2233.
- 16 S. P. Sander, J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17*, <http://jpldataeval.jpl.nasa.gov>, 2011.



- 17 J. G. Calvert, R. G. Derwent, J. J. Orlando, G. S. Tyndall and T. J. Wallington, *Mechanisms of Atmospheric Oxidation of the Alkanes*, Oxford University Press, U.S.A., 2008.
- 18 R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson Jr, R. G. Hynes, M. E. Jenkin, J. A. Kerr, M. J. Rossi and J. Troe, *Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry*, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, 2006.
- 19 V. L. Orkin, F. Louis, R. E. Huie and M. J. Kurylo, *J. Phys. Chem. A*, 2002, **106**, 10195.
- 20 L. Chen, T. Uchimaru, S. Kutsuna, K. Tokuhashi and A. Sekiya, *Int. J. Chem. Kinet.*, 2010, **42**, 619.
- 21 Z. Zhang, R. Liu, R. E. Huie and M. J. Kurylo, *J. Phys. Chem.*, 1991, **95**, 194.
- 22 R. Atkinson, *J. Phys. Chem. Ref. Data*, 1992, 116, monograph no. 2.
- 23 C. E. Canosa-Mas, T. J. Dillon, H. Sidebottom, K. C. Thompson and R. P. Wayne, *Phys. Chem. Chem. Phys.*, 2001, **3**, 542.
- 24 T. Yamada, A. El-Sinawi, M. Siraj and P. H. Taylor, *J. Phys. Chem. A*, 2001, **105**, 7588.
- 25 R. Subramonia Iyer, C.-Y. Chen and F. S. Rowland, *J. Phys. Chem.*, 1985, **89**, 2042.
- 26 R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.*, 1987, **19**, 1097.
- 27 C. Pfrang, M. D. King, C. E. Canosa-Mas and R. P. Wayne, *Atmos. Environ.*, 2006, **40**, 1170.
- 28 J. R. Lacher, L. E. Hummel, E. F. Bohmfalk and J. D. Park, *J. Am. Chem. Soc.*, 1950, **72**, 5486.
- 29 R. G. Prinn, J. Huang, R. F. Weiss, D. M. Cunnold, P. J. Fraser, P. G. Simmonds, A. McCulloch, C. Harth, P. Salameh, S. O'Doherty, R. H. J. Wang, L. Porter and B. R. Miller, *Science*, 2001, **292**, 1882.
- 30 U. Platt and C. Janssen, *Faraday Discuss.*, 1995, **100**, 175.
- 31 K. S. Law and W. T. Sturges, in *Scientific Assessment of Ozone Depletion: 2006*, World Meteorological Organization, Switzerland, 2007.
- 32 B. Rajakumar, J. B. Burkholder, R. W. Portmann and A. R. Ravishankara, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2498.
- 33 E. J. K. Nilsson, O. J. Nielsen, M. S. Johnson, M. D. Hurley and T. J. Wallington, *Chem. Phys. Lett.*, 2009, **473**, 233.
- 34 M. Baasandorj, G. Knight, V. C. Papadimitriou, R. K. Talukdar, A. R. Ravishankara and J. B. Burkholder, *J. Phys. Chem. A*, 2010, **114**, 4619.
- 35 E. Jiménez, M. Antiñolo, B. Ballesteros, E. Martínez and J. Albaladejo, *ChemPhysChem*, 2010, **11**, 4079.
- 36 S. Pinnock, M. D. Hurley, K. P. Shine, T. J. Wallington and T. J. Smyth, *J. Geophys. Res.*, 1995, **100**, 23227.
- 37 P. Forster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. W. Fahey, J. Haywood, J. Lean, D. C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. van Dorland, *Climate Change 2007: The Physical Science Basis*, Cambridge University Press, U.K., 2007.
- 38 D. A. Fisher, C. H. Hales, W. C. Wang, M. K. W. Ko and N. D. Sze, *Nature*, 1990, **344**, 513.
- 39 S. Solomon and D. L. Albritton, *Nature*, 1992, **357**, 33.
- 40 G. Acerboni, N. R. Jensen, B. Rindone and J. Hjorth, *Chem. Phys. Lett.*, 1999, **309**, 364.
- 41 M. D. Hurley, J. C. Ball and T. J. Wallington, *J. Phys. Chem. A*, 2007, **111**, 9789.
- 42 C. J. Christiansen and J. S. Francisco, *J. Phys. Chem. A*, 2010, **114**, 9163.
- 43 T. J. Wallington, W. F. Scheinder, D. R. Worsnop, O. J. Nielsen, J. Sehested, W. J. Debruyne and J. A. Shorter, *Environ. Sci. Technol.*, 1994, **28**, 320A.