

Gas-phase oxidation of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$ initiated by OH radicals and Cl atoms: kinetics and fate of the alkoxy radical formed

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Relative kinetics of the reactions of OH radicals and Cl atoms with 3-chloro-2-methyl-1-propene has been studied for the first time at 298 K and 1 atm by GC-FID. Rate coefficients are found to be (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): k_1 ($\text{OH} + \text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$) = $(3.23 \pm 0.35) \times 10^{-11}$, k_2 ($\text{Cl} + \text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$) = $(2.10 \pm 0.78) \times 10^{-10}$ with uncertainties representing $\pm 2\sigma$. Product identification under atmospheric conditions was performed by solid phase microextraction/GC-MS for OH reaction. Chloropropanone was identified as the main degradation product in accordance with the decomposition of the 1,2-hydroxy alkoxy radical formed. Additionally, reactivity trends and atmospheric implications are discussed. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: atmosphere; gas-phase mechanisms; relative kinetics; VOCs degradation

INTRODUCTION

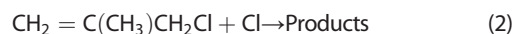
Volatile organic compounds (VOCs) are used as halogenated solvents, fuel additives, or alternative fuels. Therefore, substantial amounts of these compounds are emitted into the atmosphere and will be able to suffer chemical transformations. The main degradation pathway of these compounds in the troposphere is reaction with OH radicals or solar photolysis.^[1]

3-Chloro-2-methyl-1-propene is used as an intermediate for the synthesis of organic compounds and pesticides or as an additive in the textile industry and perfumery. In some countries, 3-chloro-2-methyl-1-propene is used as an insecticide for grain plagues, snuff plagues, and soil.^[2] Furthermore, 3-chloro-2-methyl-1-propene can be dissolved in droplets and aerosols, hydrolyze, and undergo further oxidation in the liquid phase.

It is known that the atmospheric degradation of halogenated unsaturated compounds is controlled mainly by chemical reaction with OH radicals, contributing to tropospheric ozone production and formation of other secondary photooxidants in polluted areas.^[3]

The reaction of chlorine atoms with VOCs is considered of potential relevance in the marine troposphere where significant chlorine atoms concentration could be present.^[4,5] In addition, the detection of these species in midcontinental areas has expanded the potential impact of Cl to tropospheric oxidation chemistry.^[6,7] Knowledge of the rate coefficients for the reactions with tropospheric oxidants like OH radicals and Cl atoms, as well as the degradation pathways are required to estimate the persistence, fate, and harmful effects of the chloroalkenes in the atmosphere.

In this work, we report the rate coefficient of the reaction of 3-chloro-2-methyl-1-propene ($\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$) with OH radicals and Cl atoms at 298 K and 760 Torr:



To the best of our knowledge, this is the first determination of the rate coefficients of the reactions (1) and (2) under atmospheric conditions. Kinetics results are rationalized in terms of reactivity trends by comparison with other halogenated alkenes. In addition, product studies using gas chromatography–mass spectrometry (GC-MS) technique under atmospheric conditions were carried out for the first time for the reaction of OH radicals with $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$. Consequently, degradation pathways in the atmosphere are discussed.

Atmospheric lifetimes of the VOC studied in this work were calculated taking into account the experimental rate coefficients obtained in this work and compared with other homogeneous sinks in the troposphere.

EXPERIMENTAL

All the experiments were performed in an 80-liter Teflon bag located in a wooden box with the internal walls covered with aluminum foil. Measured amounts of the organic reactants were flushed from calibrated bulbs into the bag through a stream of nitrogen or synthetic air. The bag was then filled to its full capacity at atmospheric pressure

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with nitrogen or air. Chlorine atoms were generated by photolysis at 254 nm of oxalyl chloride (ClC(O)C(O)Cl) :



OH radicals were generated by ultraviolet (UV) irradiation at 254 nm of H₂O₂:



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. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of zero grade N₂, and the bag was then filled with the zero grade N₂. 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 six germicidal lamps (Philips 30 W; Koninklijke Philips N.V., Amsterdam, Netherlands) with a UV emission at 254 nm, to produce O₃. After this procedure, the bag was cleaned again by repeated flushing with N₂ and checked before performing the experiments by GC that there were no observable impurities.

Periodically, gas samples were removed from the Teflon bag using calibrated gas syringes. The organics were monitored by GC (Shimadzu GC-14B; Shimadzu Corp., Kyoto, Japan) coupled with flame ionization detection, using a Porapak Q column held at a temperature of 160 °C for this compound.

In the presence of the oxidant X (Cl atom or OH radical), 3-chloro-2-methyl-1-propene (3-CIMP) and the references decay through the following reactions:



Provided that the reference compound and the reactant are lost only by reactions (5) and (6), then it can be shown that

$$\ln \left\{ \frac{[\text{3-CIMP}]_0}{[\text{3-CIMP}]_t} \right\} = \frac{k_5}{k_6} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (7)$$

where [3-CIMP]₀, [Reference]₀, [3-CIMP]_t, and [Reference]_t are the concentrations of the 3-CIMP and the reference compound at times *t* = 0 and *t*, respectively, and *k*₅ and *k*₆ are the rate coefficients of reactions (5) and (6), respectively.

The relative rate technique relies on the assumption that both 3-CIMP and the reference organics are removed solely by reaction with the oxidant species X (Cl or OH). To verify this assumption, mixtures of oxalyl chloride or hydrogen peroxide with N₂ or air 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 X (ClC(O)C(O)Cl or H₂O₂), in the absence of UV light, was of negligible importance over the typical time periods used in this work. Additionally, to test for possible photolysis of the reactants used, mixtures of 3-CIMP in nitrogen or air, in the absence of oxalyl chloride or hydrogen peroxide, were irradiated using the output of all germicidal lamps surrounding the chamber for 30 min. No photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of 224–262 ppm (1 ppm = 2.46 × 10¹³ molecule cm⁻³ at 298 K and 760 Torr of total pressure) for 3-CIMP. The concentration of Cl₂ ranged from 190 to 220 ppm in around 750 Torr of N₂ or air.

The analytical technique employed for qualitative identification of the products formed after irradiation was GC-MS on a Shimadzu GC-MS QP 5050 spectrometer equipped with a capillary column VF-5MS (5% phenyl, 95% dimethylpolysiloxane) of 30 m × 0.25 mm. Gas samples were removed from the Teflon bag using solid phase microextraction (SPME) as a preconcentration technique of the analytes. The SPME technique is based on the extraction of analytes from the sample matrix using a fused silica fiber generally cover with an absorbent polymer, followed by desorption of analytes by temperature on the injection port. In this work a [divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS)] fiber was used for all compounds. The exposure time was 15 and 3 min of desorption in the injection port.

MATERIALS

The following chemicals, with purities as stated by the supplier, were used without further purification: N₂ (AGA, 99.999%; American Gas Corporation, Washington, DC, USA), synthetic air (Air Liquide, 99.999%; Paris, France), 3-chloro-2-methyl-1-propene (Merck, 97%; Kenilworth, NJ, USA), methyl methacrylate (Aldrich, 99%; Sigma-Aldrich, St. Louis, MO, USA), allyl acetate (Aldrich, 99%), vinyl propionate (Aldrich, 98%), oxalyl chloride (Aldrich, 99%), and oxygen peroxide (Cicarelli, 60 wt.%; Farmaceutici Dottor Ciccarelli, Milano, Italy).

RESULTS AND DISCUSSION

Relative rate coefficients for the reactions of OH radicals and Cl atoms with 3-CIMP were determined by comparing the OH or Cl reaction with the chloroalkene studied with the reference compounds from Eqn (7). The data were fitted to a straight line by the linear least-squares procedure.

The losses of 3-CIMP by OH radicals or Cl atoms are shown with different reference compounds in Figures 1 and 2. For each reaction studied, four runs were performed for the rate coefficient determination; however, for the sake of clarity, only one example is displayed in Figures 1 and 2.

The data on relative rate coefficients *k*_{3-CIMP}/*k*_{Reference} and absolute rate coefficients *k*_{3-CIMP} at room temperature (298 K) are presented in Table 1. It is gratifying to note the agreement between the experiments conducted with different reference compounds. The rate coefficients obtained by averaging the values from different experiments were the following:

$$k_{\text{OH}} = (3.23 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{Cl}} = (2.10 \pm 0.78) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have considered also the corresponding error on the reference rate coefficients. The following compounds were used as reference

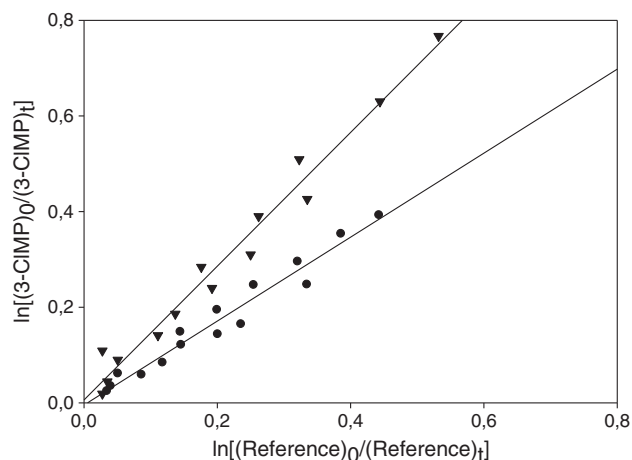


Figure 1. Relative kinetic plot of the reaction of OH radical with 3-chloro-2-methyl-1-propene using methyl methacrylate (●) and allyl acetate (▼) as references at atmospheric conditions and 298 K

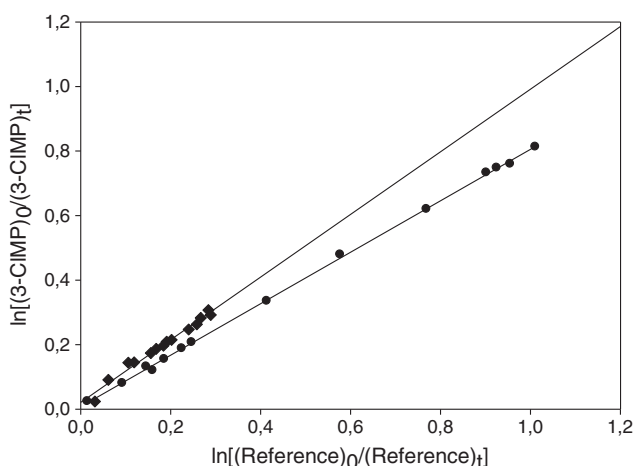
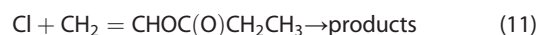
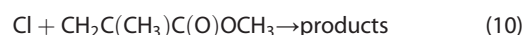


Figure 2. Relative kinetic plot of the reaction of Cl atoms with 3-chloro-2-methyl-1-propene using methyl methacrylate (●) and vinyl propionate (◆) as references at atmospheric conditions

reactions: methyl methacrylate, allyl acetate, and vinyl propionate to determine the rate coefficient of the reactions (1) and (2):



where $k_8 = (4.15 \pm 0.32) \times 10^{-11}$,^[8] $k_9 = (2.46 \pm 0.02) \times 10^{-11}$,^[9] $k_{10} = (2.82 \pm 0.93) \times 10^{-10}$,^[10] and $k_{11} = (2.06 \pm 0.36) \times 10^{-10}$.^[11] All the k values are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

To the best of our knowledge, there are no other prior reported values of the rate coefficients for the reactions (1) and (2) of OH radicals and Cl atoms with 3-chloro-2-methyl-1-propene. Thus, the present study is the first kinetic study of these reactions, and therefore, no direct comparison with the literature can be made. However, it is interesting to estimate and compare the rate coefficient for the reaction of OH with 3-CIMP using the US EPA AOPWIN program,^[12] which is based upon the structure–activity relationship (SAR) method described by Kwok and Atkinson.^[13] The estimated OH rate coefficient by this method was $3.95 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The SAR rate prediction for this reaction is in a reasonable agreement, within the experimental error, with the value of $(3.23 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined in this study.

Reactivity trends

Table 2 shows a comparison between the rate coefficients of the reactions of OH radicals and Cl atoms with a series of halogenated alkenes and the kinetic data obtained in this study for 3-CIMP. It is possible to observe that the presence of different substituents produces significant variations on the rate coefficient values. For example, comparing the rate k_{OH} of 3-CIMP ($3.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and 3-chloropropene ($1.69 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),^[16] it is possible to observe a significant increase in the rate coefficient of 3-CIMP respect to 3-chloropropene. This difference can be attributed to the presence of the $-\text{CH}_3$ group as a H substituent attached to the olefinic carbon. Both molecules are influenced by a negative inductive effect on to the double bond induced by the chlorine substituent, but in the case of 3-CIMP, this effect appears to be overridden by the methyl group attached at C2, generating a positive inductive effect over the $>\text{C}=\text{C}<$.

Table 1. Reference compound, measured rate coefficient ratios, $k_{3\text{-CIMP}}/k_{\text{Reference}}$ and the obtained rate coefficients for the reactions of OH radicals and Cl atoms with 3-chloro-2-methyl-1-propene at 298 K in 760 Torr of nitrogen

Reaction	Reference	$k_{3\text{-CIMP}}/k_{\text{Reference}}$	$k_{3\text{-CIMP}}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl} + \text{OH}$	Methyl methacrylate	0.72 ± 0.03	$(3.00 \pm 0.35) \times 10^{-11}$
	Methyl methacrylate	0.85 ± 0.02	$(3.52 \pm 0.34) \times 10^{-11}$
	Allyl acetate	1.25 ± 0.05	$(3.08 \pm 0.14) \times 10^{-11}$
	Allyl acetate	1.34 ± 0.06	$(3.30 \pm 0.18) \times 10^{-11}$
	Average		$(3.23 \pm 0.35) \times 10^{-11}$
$\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl} + \text{Cl}$	Methyl methacrylate	0.81 ± 0.01	$(2.26 \pm 0.77) \times 10^{-10}$
	Methyl methacrylate	0.79 ± 0.02	$(2.20 \pm 0.78) \times 10^{-10}$
	Vinyl propionate	1.01 ± 0.08	$(2.08 \pm 0.52) \times 10^{-10}$
	Vinyl propionate	0.91 ± 0.02	$(1.85 \pm 0.37) \times 10^{-10}$
	Average		$(2.10 \pm 0.78) \times 10^{-10}$

Table 2. Rate coefficients of the reactions of OH radicals and Cl atoms with a series of halogenated alkenes compared with the kinetic data obtained in this study

Volatile organic compound	$k_{\text{OH}} \times 10^{11}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$k_{\text{Cl}} \times 10^{10}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{CH}_2 = \text{CHCH}_3$	3.01 ^a	2.64 ^b
$\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$	3.23 ^c	2.10 ^c
$\text{CH}_2 = \text{CHCH}_2\text{Cl}$	1.69 ^d	2.40 ^e
$\text{CH}_2 = \text{CHCH}_2\text{Br}$	1.66 ^f	1.23 ^g
$\text{CH}_2 = \text{CHCH}_2\text{F}$	1.64 ^f	0.49 ^g

a[14]
b[15]
c^cThis work.
d[16]
e[17]
f[18]
g[19]

Moreover, Table 2 shows the influence of the nature of the halogen attached to the double bond of the alkenes. It is possible to observe that the rate coefficient diminishes with the electronegativity of the halogen atom attached to the haloalkene. This trend could be observed in reactions initiated with both oxidants, OH radical and Cl atoms. However, the trend observed on the OH rate coefficients are too small to affirm a real tendency influenced by the electronegativity character of the substituents in the molecule as it is in the case of the significant variation observed in the rate coefficients of the Cl atoms initiated reactions (in $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$k_{\text{CH}_2 = \text{CHCH}_2\text{Cl}} = 2.40 > k_{\text{CH}_2 = \text{CHCH}_2\text{Br}} = 1.23 > k_{\text{CH}_2 = \text{CHCH}_2\text{F}} = 0.49. \quad [17-19]$$

Product identification

In addition to the kinetic studies, the products of the reaction of 3-CIMP with OH radicals were identified, as it is shown in Fig. 3. A first approach reveals that the main path of reaction is the electrophilic addition of the OH radical to the double bond in either carbon (C1 or C2) of the double bond, preferably to the terminal carbon of the double bond to generate a more stable radical.^[20]

The main reaction pathway of 3-CIMP toward OH radicals is shown in Scheme 1: The reaction proceeds via an addition mechanism of the OH radical to the double bond. The 1-2-hydroxyalcoxy radical formed in the OH addition step decomposes in the presence of O_2 and in the absence of NO, leading mainly to the corresponding carbonyl compound.

Chloropropanone was identified as the major product formed from reaction (1). Fragments with m/e 43, 49, 77, 92, and 94 (Fig. 3, panel C), characteristic of this compound were found in the mass spectrum of the 4.2 min retention time peak obtained after irradiation of OH/3-CIMP/air mixture (Fig. 3, panel B). In addition, an experiment was performed by GC-MS with a pure standard of chloropropanone to confirm the identity of the peak obtained at 4.2 min of retention time.

The reaction product found, together with the observed reactivity trends, suggests that the reaction proceeds via an addition mechanism of the OH radical to the double bond similar to that proposed by Atkinson for the OH radical addition to alkenes.^[5,6]

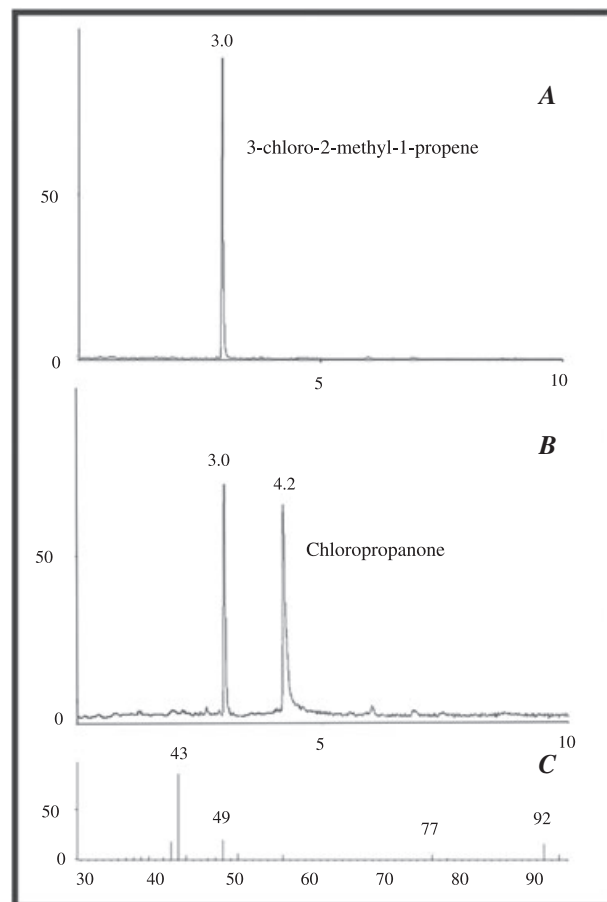


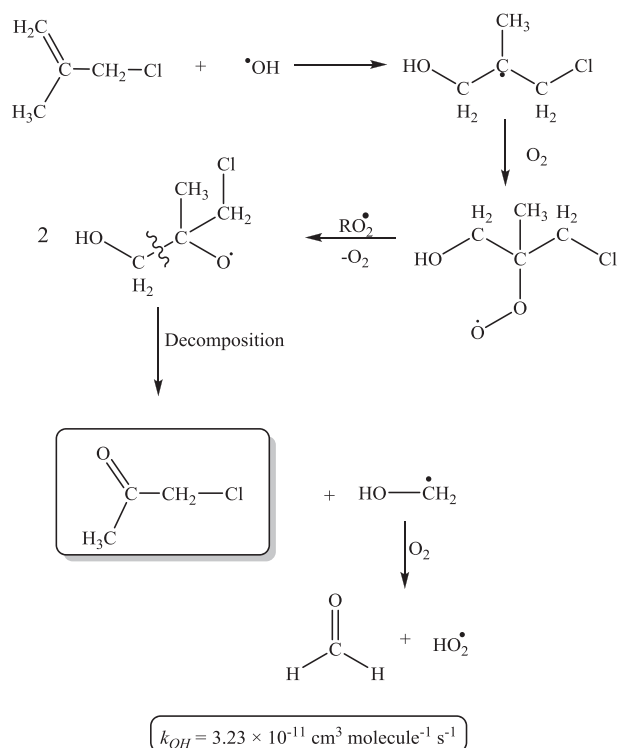
Figure 3. Gas chromatography–mass spectrometry chromatogram before (A) and after photolysis (B) of a mixture of 3-CIMP with H_2O_2 in air at 298 K and atmospheric pressure. Chloropropanone was identified as the unique product reaction by comparing the m/z mass fragmentation (panel C) of the product peak centered at 4.2 min of retention time

Consequently, the main fate of the 1-2-hydroxyalcoxy radicals formed seems to be the decomposition channel, where the OH preferably attacks the terminal carbon of the double bond. In our experimental conditions, at NO_x-free air, there are negligible contributions of other molecular reaction channels such as isomerization or H abstraction by O_2 molecules.

ATMOSPHERIC IMPLICATIONS

Atmospheric lifetimes, τ_x , of the 3-CIMP studied in this work were calculated through the expression: $\tau_x = 1/k_x[X]$ with $X = \text{OH}$, Cl, NO_3 , and O_3 . Table 3 lists the atmospheric lifetimes with respect to the reaction with OH radicals, Cl atoms, NO_3 radicals, and O_3 molecules for the chloroalkene studied in this work.^[21,22]

Tropospheric lifetimes are calculated assuming a 12 h average concentration of OH of $2 \times 10^6 \text{ molecule cm}^{-3}$.^[23] The lifetime of the reaction with OH radicals is 9 h, and the corresponding lifetimes of the reaction with chlorine is around 5 days, considering a global average chlorine concentration of $1 \times 10^4 \text{ atoms cm}^{-3}$,^[24] while the concentration of O_3 molecules and NO_3 radicals are $7 \times 10^{11} \text{ molecule cm}^{-3}$ ^[25] and $5 \times 10^8 \text{ radical cm}^{-3}$,^[26] respectively.



Scheme 1. Reaction mechanism proposed for the main pathway of reaction of 3-CIMP with OH radicals

Table 3. Estimated tropospheric lifetimes of the 3-chloro-2-methyl-1-propene with different tropospheric oxidants

Volatile organic compound	τ_{OH}^a	τ_{Cl}^a	$\tau_{NO_3}^b$	$\tau_{O_3}^c$
3-Chloro-2-methyl-1-propene	9 h	5 days	1 day	4 days

^aThis work.
^b[21]
^c[22]

In light of these results, the atmospheric lifetime of 3-CIMP is determined by the OH-initiated degradation during day time and at night time; when the concentration of OH decay and the NO₃ radical will not be affected by photolysis, the nitrate radical is the main sink of this halogenated compound. Moreover, in marine areas where the chlorine concentration can reach a peak as high as $1 \times 10^5 \text{ atoms cm}^{-3}$,^[27,28] Cl chemistry could compete or dominate the OH radical chemistry.

The short lifetimes estimated, in order of hours, indicate that the compound is likely to be rapidly removed in the gas phase, being the reaction with OH radicals, the major loss process. Losses of 3-chloro-2-methyl-1-propene by photolysis can be considered negligible because it is expected, by the UV-Vis spectrum of halogenated alkenes, to be photolytically stable in the actinic region of the electromagnetic spectrum.

Because kinetics and product distribution data are considerably scarce, further experiments should be performed to obtain product yields of the different channels of the alkoxy radical formed. This information could contribute to elucidate and to give confidence on the atmospheric degradation mechanism of this chloroalkene and their derivatives in different scenarios of

NO_x, pressure and temperature ranges to be included in more realistic atmospheric models.

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REFERENCES

- [1] G. Moortgat, *Chemical, Physical and Biogenic Processes in the Atmosphere* Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Obernai, France, **2001**.
- [2] U.S. Department of Health and Human Services Secretary Kathleen Sebelius released the 12th Report on Carcinogens, <http://ntp.niehs.nih.gov/ntp/roc/twelfth/roc12>, 2011.
- [3] A. Mellouki, G. Le Bras, H. Sidebottom, *Chem. Rev.* **2003**, *103*, 5077–5096.
- [4] B. Finlayson-Pitts, *J. Res. Chem. Intermed.* **1993**, *19*, 235–249.
- [5] W. C. Keene, D. J. Jacob, S. M. Fan, *Atmos. Environ.* **1996**, *30*, 1–3.
- [6] J. A. Thornton, J. P. Kercher, T. P. Riedel, N. L. Wagner, J. Cozic, S. Holloway, W. P. Dube, G. M. Wolfe, P. K. Quinn, A. M. Middlebrook, B. Alexander, S. Brown, *Nature*. **2010**, *464*, 271–274.
- [7] L. H. Mielke, A. Furgeson, H. D. Osthoff, *Environ. Sci. Technol.* **2011**, *45*, 8889–8896.
- [8] M. B. Blanco, R. A. Taccone, S. I. Lane, M. A. Teruel, *Chem. Phys. Lett.* **2006**, *429*, 389–394.
- [9] C. Ferrari, A. Roche, V. Jacob, P. Foster, P. Baussand, *Int. J. Chem. Kin.* **1996**, *28*, 609–614.
- [10] M. B. Blanco, I. Bejan, I. Barnes, P. Wiesen, M. A. Teruel, *Atmos. Environ.* **2009**, *43*, 5996–6002.
- [11] M. A. Teruel, M. Achad, M. B. Blanco, *Phys. Chem. Lett.* **2009**, *479*, 25–29.
- [12] W. M. Meylan, P. H. Howard, *Chemosphere*. **1993**, *26*, 2293–2299.
- [13] E. C. Kwok, R. Atkinson, *Atmos. Environ.* **1995**, *29*, 1685–1695.
- [14] R. Atkinson, D. L. Baulch, R. A. Cox, Hampson Jr., R. F. Kerr, J. A. Troe, *Phys. Chem.* **1989**, *18*, 881–1097.
- [15] M. J. Ezell, W. Wang, A. A. Ezell, G. Soskin, B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **2002b**, *4*, 5813–5820.
- [16] E. C. Tuazon, R. Atkinson, S. M. Aschmann, *Int. J. Chem. Kinet.* **1990**, *22*, 591–602.
- [17] D. Grosjean, E. L. Williams, *Atmos. Environ. Part A* **1992**, *26*, 1395–1405.
- [18] J. Albaladejo, B. Ballesteros, E. Jimenez, D. de Mera, E. Martínez, *Atmos. Environ.* **2003**, *37*, 2919–2926.
- [19] J. Albaladejo, A. Notario, C. A. Cuevas, B. Ballesteros, E. J. Martinez, *Atmos. Chem.* **2003**, *45*, 35–50.
- [20] M. B. Smith, J. March, *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* John Wiley & Sons, Hoboken, New Jersey, **2007**.
- [21] R. W. S. Aird, C. E. Canosa-Mas, D. J. Cook, G. Marston, P. S. Monks, R. P. Wayne, E. J. Ljungstrom, *Chem. Soc. Faraday Trans.* **1992**, *88*, 1093–1099.
- [22] D. Johnson, A. R. Rickard, C. D. McGill, G. Marston, *Phys. Chem. Chem. Phys.* **2000**, *2*, 323–328.
- [23] R. Hein, P. J. Crutzen, M. Heimann, *Global Biogeochem. Cycles*. **1997**, *11*, 43–76.
- [24] O. W. Wingenter, M. K. Kubo, N. J. Blake, T. W. Smith, D. R. Blake, F. S. Rowland, *J. Geophys. Res.* **1996**, *101*, 4331–4340.
- [25] J. A. Logan, *J. Geophys. Res.* **1985**, *90*, 463.
- [26] Y. Shu, R. Atkinson, *J. Geophys. Res.* **1995**, *100*, 7275.
- [27] T. P. Riedel, N. L. Wagner, W. P. Dube, A. M. Middlebrook, C. J. Young, F. Öztürk, R. Bahreini, T. C. VandenBoer, D. E. Wolfe, E. J. Williams, J. M. Roberts, S. S. Brown, J. A. Thornton, *J. Geophys. Res. Atmos.* **2013**, *118*, 8702–8715.
- [28] H. B. Singh, G. L. Gregory, B. Anderson, E. Browell, G. W. Sachse, D. D. Davis, J. Crawford, J. D. Bradshaw, R. Talbot, D. R. Blake, D. Thornton, R. Newell, J. Merrill, *J. Geophys. Res.* **1996**, *101*, 1907–1917.