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Article

Rate Coefficient for the Reaction of Cl Atoms with *cis*-3-Hexene at 296 ± 2 K

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The rate coefficient of the *cis*-3-hexene + Cl atoms reaction at 296 ± 2 K and 750 ± 10 Torr was determined using the relative rate technique. The reaction was investigated using an 80 L Teflon reaction bag and a gas chromatograph coupled with flame-ionization detection. Chlorine atoms were produced by the photolysis of trichloroacetyl chloride. No previous experimental data was available in the literature, to the best of our knowledge. The mean second-order rate coefficient value found was $(4.13 \pm 0.51) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The experimental value agrees with the rate coefficient estimated by structure-reactivity analysis, 4.27×10^{-10} cm^3 molecule^{-1} s^{-1}. Moreover, both addition and hydrogen abstraction channels contribute to the global kinetics, with branching ratios 70:30. Effective lifetime with respect to Cl atoms is predicted as 67.2 hours; however, the *cis*-3-hexene + Cl channel is suggested to be non-negligible at atmospheric conditions. Other atmospheric implications are discussed.

Keywords: *cis*-3-hexene + Cl atoms, rate coefficient, experimental relative rate method

Introduction

Volatile organic compounds (VOCs) are emitted to the troposphere from different sources of biogenic and anthropogenic origin, playing a fundamental role in atmospheric chemistry. Among the anthropogenic origin compounds released, *cis*-3-hexene is of a particular interest, emitted in gasoline vapor.[1,2] In the troposphere, *cis*-3-hexene reacts with hydroxyl radicals, ozone and nitrate radicals. Barbosa *et al.*[3] have studied the kinetic for the reaction of *cis*-3-hexene with hydroxyl radicals using the relative rate method and the experimental mean second-order rate coefficient value was determined as $(6.27 \pm 0.66) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The kinetics of the reaction with ozone and nitrate radicals have been investigated at room temperature using the relative method and the rate coefficients values (in cm^3 molecule^{-1} s^{-1}) have been determined as $(1.44 \pm 0.17) \times 10^{-16}$ and $(4.37 \pm 0.49) \times 10^{-13}$, respectively.[4,5]

Chlorine atoms are also important atmospheric oxidants and have been observed in the marine boundary layer. In the early morning, the concentration of Cl atoms reaches the highest value and reactions of VOCs with Cl could be even more important than the reactions with OH radicals, the major daytime oxidant.[6] To the best of our knowledge, the reaction of Cl atoms with *cis*-3-hexene, despite the importance of such reaction to Atmospheric Chemistry, has not been studied yet.

The main goal of this work is the experimental study of the kinetics of the *cis*-3-hexene + Cl reaction. The rate coefficient at 298 K and atmospheric pressure is reported for the first time based on the use of the relative rate method. Aspects of the reaction mechanism and atmospheric implications are also discussed.

Experimental

The experimental study was performed at the Instituto de Investigaciones en Fisico Química de Córdoba, Argentina. An 80 L collapsible Teflon bag was used and

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the rate coefficients were determined by the relative rate method. This methodology has been carried out at this laboratory for the study of other reactions.[3,7-9]

Briefly, the reactant and the reference compound were introduced into the chamber using nitrogen or ultrapure air. Cl atoms were generated by the trichloroacetyl chloride photolysis using three germicide lamps (Philips 30 W), with a λ maximum around 254 nm, and the time of photolysis varied from 20 seconds to 1 minute. A gas syringe (Hamilton gas tight 5 mL) was periodically used to collect samples and the gas sample was analyzed using a gas chromatograph (Clarus 500, PerkinElmer) equipped with an Elite-1 column (PerkinElmer, length: 30 m, inner diameter 0.32 mm, film thickness: 0.25 μm) and a flame ionization detector (FID). The temperature of the column was 33 °C for 20 min. Helium was used as the carrier gas with flow rate of 0.8 mL min^{-1}.

cis-3-Hexene and reference compounds with trichloroacetyl chloride were introduced into the chamber and left in the dark for 2 hours. Under such conditions, no evidence for a reaction between *cis*-3-hexene and the reference compounds has been found. No reaction was observed for the organic specie and trichloroacetyl chloride in the absence of UV light.

The reactant and the reference compounds decay through the following reactions:

$$\text{Cl} + cis\text{-3-hexene} \rightarrow \text{products, } k_{hex} \quad (1)$$

$$\text{Cl} + \text{reference} \rightarrow \text{products, } k_{ref} \quad (2)$$

where, k_{hex} and k_{ref} are the rate coefficients for reactions of the *cis*-3-hexene and the reference compound with Cl atoms, respectively.

Assuming that the *cis*-3-hexene and the reference compounds are lost entirely due to the reactions 1 and 2, the following relation can be obtained:

$$\ln\left(\frac{[cis\text{-3-hexene}]_0}{[cis\text{-3-hexene}]_t}\right) = \frac{k_{hex}}{k_{ref}} \times \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \quad (3)$$

In equation 3, the subscripts 0 and t correspond to the time instants 0 and t, respectively.

Rate coefficients for the *cis*-3-hexene with Cl atoms were obtained, in each experiment, at 298 ± 2 K and atmospheric pressure 750 ± 10 Torr, relative to the rate coefficients of the Cl atoms reactions with *n*-heptane and cyclopentane used as reference compounds.

The initial concentrations used during the experiments were in the range of $4.67\text{-}9.59 \times 10^{14}$ molecule cm^{-3} for the cyclopentane, 7.38×10^{14} molecule cm^{-3} for the *cis*-3-hexene, 6.15×10^{14} molecule cm^{-3} for *n*-heptane and $1.0\text{-}3.4 \times 10^{15}$ molecule cm^{-3} for the trichloroacetyl chloride.

The chemicals used were trichloroacetyl chloride (99%, CAS: 76-02-8) supplied by Sigma-Aldrich, *n*-heptane (99.9%, CAS: 142-82-5) and cyclopentane (99.9%, CAS: 287-92-3) supplied by Mallinckrodt and *cis*-3-hexene (97%, CAS: 7642-09-3) supplied by Alfa Aesar. Synthetic air (purity 99.999%) and chromatographic gases (N_2, H_2 and chromatographic air) were obtained from Linde. The organic reagents were degassed by repeated freeze-pump-thaw cycling and purified by vacuum distillation before use.

The infrared (IR) spectrum of *cis*-3-hexene was recorded with a Nicolet FTIR (Fourier transform infrared) spectrometer, with 1.0 cm^{-1} resolution. 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. The infrared spectrum, recorded in the 500-1500 cm^{-1} region at 298 K, was used to calculate radiative efficiencies (RE)[10] and the global warming potential.

The model adopted for calculating the radiative efficiencies considers a uniform distribution of the compound over the troposphere. The RE values for short-lived compounds calculated from this model can be significantly lower, since the concentration should strongly decrease with altitude. Taking this assumption into account, the calculated RE values, as estimated in this work, should be better considered as an upper limit.

The global warming potential (GWP) is calculated relative to CO_2 over a specified time horizon from a model which also takes into account the RE values and tropospheric lifetimes. In some cases, $CFCl_3$ (CFC-11) is used as the standard, and this GWP is called the halocarbon global warming potential (HGWP). The HGWP was calculated relative to CFC-11 using the following expression:[11]

$$\text{HGWP} = \frac{\tau_{cis\text{-3-hexene}}}{\tau_{CFCl_3}} \frac{M_{CFCl_3}}{M_{cis\text{-3-hexene}}} \frac{RE_{cis\text{-3-hexene}}}{RE_{CFCl_3}} \left(\frac{1-e^{-t/\tau_{cis\text{-3-hexene}}}}{1-e^{-t/\tau_{CFCl_3}}}\right) \quad (4)$$

where $\tau_{cis\text{-3-hexene}}$ and $\tau_{CFC\text{-}11}$ (τ_{CFCl_3}) are the corresponding tropospheric lifetimes; $M_{cis\text{-3-hexene}}$ and $M_{CFC\text{-}11}$ (M_{CFCl_3}) are the corresponding molar masses; $RE_{cis\text{-3-hexene}}$ and $RE_{CFC\text{-}11}$ (RE_{CFCl_3}) are the radiative efficiencies of the hexene and $CFCl_3$, respectively, and t is the time horizon over which the RE is integrated.

The GWPs of the *cis*-3-hexene, relative to CO_2, were calculated by multiplying the HGWP values by the scaling factors of 6730 and 4750 on a time horizon of 20 and 100 years, respectively.[12] These scaling factors are the GWP values of the CFC-11.

Results and Discussion

Rate coefficient for *cis*-3-hexene + Cl → products

The rate coefficient for the *cis*-3-hexene + Cl atoms reaction is the sum of the coefficients for the addition and abstraction channels and was measured at 296 ± 2 K and atmospheric pressure. The reference reactions are:

$$\text{Cl} + n\text{-heptane} \rightarrow \text{products},\ k_1 \quad (5)$$

$$\text{Cl} + \text{cyclopentane} \rightarrow \text{products},\ k_2 \quad (6)$$

where k_1 and k_2 are the rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}): $k_1 = (3.97 \pm 0.27) \times 10^{-10}$ and $k_2 = (3.26 \pm 1.0) \times 10^{-10}$, as reported by Ezell *et al.*[6] and Wallington *et al.*,[13] respectively. Four experiments with each reference compound were performed.

Different initial concentrations of the reference compounds were used in each experiment.

Figures 1 and 2 show the plot of ln([*cis*-3-hexene]$_0$/[*cis*-3-hexene]$_t$) *vs.* ln([reference]$_0$/[reference]$_t$), using *n*-heptane and cyclopentane as reference compounds, respectively.

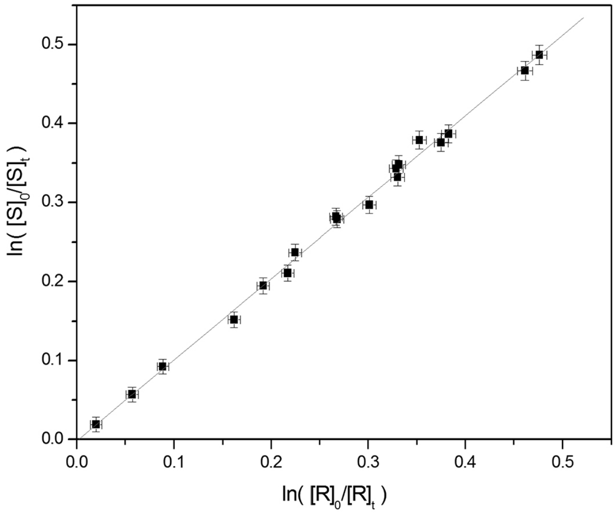

Figure 1. Plot of the kinetic data for the reaction of *cis*-3-hexene with Cl atom using *n*-heptane as reference compound. [S]$_0$ and [S]$_t$ are the concentrations of the *cis*-3-hexene at times 0 and t, respectively; [R]$_0$ and [R]$_t$ are the concentrations of the reference compound at times 0 and t, respectively.

The linearity of the data points is observed in all experiments, with correlation coefficients greater than 0.99. Moreover, the intercepts are close to zero, suggesting that the contribution of secondary reactions with the products of the reactions studied can be neglected.

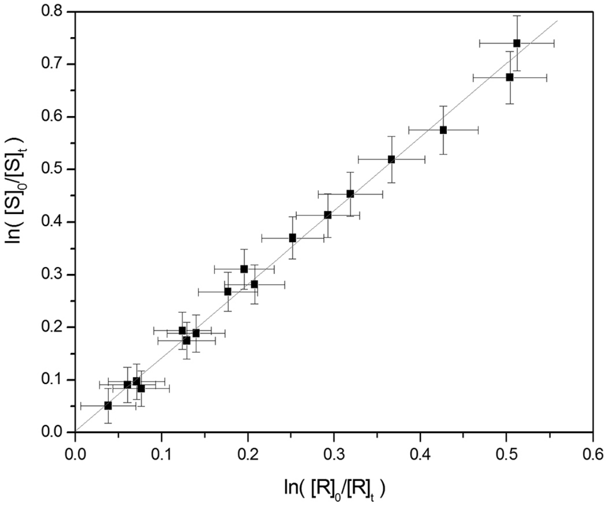

Figure 2. Plot of the kinetic data for the reaction of *cis*-3-hexene with Cl atom using cyclopentane as reference compound. [S]$_0$ and [S]$_t$ are the concentrations of the *cis*-3-hexene at times 0 and t, respectively; [R]$_0$ and [R]$_t$ are the concentrations of the reference compound at times 0 and t, respectively.

The initial concentrations of *cis*-3-hexene and of the reference compounds are presented in Table 1, as well as the number of experiments, the k_{hex}/k_{ref} ratio and the k_{hex} rate coefficient.

Error propagation was considered to estimate the uncertainty on rate coefficients. As previously discussed,[3] these uncertainties have been calculated by assuming both the standard error of the slopes of the logarithm concentration curves and the reported errors on the reference rate coefficients.[6,13] Errors due to sample handling and chromatographic method were introduced in the standard error of the slope.

At least four experiments using two reference compounds were performed and the k_{hex} rate coefficient was determined. Consequently, the final rate coefficient is a mean value achieved from all experiments and the uncertainty is equal to twice the standard deviation.

Reactivity and reaction mechanism

A comparison of the room temperature rate coefficients determined for the reactions of *cis*-3-hexene with Cl atoms and OH radicals[3] shows that the former is 6.6 times higher. In order to (*i*) evaluate the rate coefficient for the reaction of Cl atoms with *cis*-3-hexene determined in this work, (*ii*) explain the higher reactivity towards Cl atoms and (*iii*) to infer about the reaction mechanism, the reactivity of a series of alkenes was compared and the contributions of hydrogen abstraction and electrophilic addition channels

Table 1. Initial concentration of the reactants (hex: *cis*-3-hexene and ref: reference compound), rate constant ratios (k_{hex}/k_{ref}) and the relative rate constant (k_{hex}) for the reaction of OH radicals with *cis*-3-hexene at 298 K and atmospheric pressure

Reference compound	Run	Bath gas	$[hex]_0 \times 10^{14}$ / (molecule cm^{-3})	$[ref]_0 \times 10^{14}$ / (molecule cm^{-3})	k_{hex}/k_{ref}	$k_{hex} \times 10^{-10}$ / (cm^3 molecule^{-1} s^{-1})
n-Heptane	1	N_2	7.31	6.16	1.044 ± 0.018	4.15 ± 0.29
	2	N_2	7.31	6.16	1.087 ± 0.032	4.31 ± 0.32
	3	air	7.31	6.16	1.023 ± 0.022	4.06 ± 0.29
	4	air	7.31	6.16	1.071 ± 0.013	4.25 ± 0.29
Cyclopentane	1	N_2	7.31	9.67	1.116 ± 0.44	3.64 ± 0.182
	2	air	7.31	4.83	1.255 ± 0.059	4.09 ± 0.231
	3	air	7.31	9.67	1.235 ± 0.032	4.03 ± 0.162
	4	air	7.31	9.67	1.388 ± 0.030	4.53 ± 0.171
Average						4.13 ± 0.51

were evaluated. These issues can be assessed by comparing the rate coefficients of the reactions of a series of alkenes with Cl and OH radicals.

Concerning the differences between the rate coefficients for the reaction of the alkene with OH radicals and Cl atoms, let us first note that the electrophilic character of chlorine atom and OH radicals are different and can be investigated from the experimental electron affinity values, which are 3.61 and 1.827 eV for Cl and OH, respectively. Since both reactions are initiated by the electrophilic attack of the oxidation agent, the higher electrophilic character of the Cl atoms explains the higher rate coefficient for the reaction of hydrocarbons with this specie.

Moreover, the rate coefficients for the reactions of OH radicals with alkenes are always lower than the rate coefficients for the corresponding reactions with Cl. Rate coefficients, in cm^3 molecule^{-1} s^{-1}, at 296 ± 2 K and 1 atm, for the reactions of OH radicals with alkenes are: $k_{OH,propene} = 3.0 \times 10^{-11}$,[14] $k_{OH,ethylene} = 8.5 \times 10^{-12}$, $k_{OH,1\text{-butene}} = 3.1 \times 10^{-11}$, $k_{OH,\mathit{cis}\text{-2-butene}} = 5.6 \times 10^{-11}$, $k_{OH,1\text{-pentene}} = 3.1 \times 10^{-11}$, $k_{OH,2\text{-methyl-2-butene}} = 8.7 \times 10^{-11}$, $k_{OH,2,3\text{-dimethyl-2-butene}} = 1.1 \times 10^{-10}$,[15] $k_{OH,1\text{-hexene}} = 3.7 \times 10^{-11}$,[16] $k_{OH,1\text{-heptene}} = 3.9 \times 10^{-11}$, $k_{OH,1\text{-octene}} = 4.1 \times 10^{-11}$ and $k_{OH,1\text{-nonene}} = 4.3 \times 10^{-11}$.[17] Room temperature rate coefficients (cm^3 molecule^{-1} s^{-1}), at 1 atm, for the reactions of chlorine atoms with the same alkenes are: $k_{Cl,ethylene} = 3.0 \times 10^{-10}$,[18] $k_{Cl,propene} = 2.6 \times 10^{-10}$,[6] $k_{Cl,1\text{-butene}} = 3.0 \times 10^{-10}$,[19] $k_{Cl,1\text{-pentene}} = 3.9 \times 10^{-10}$, $k_{Cl,2\text{-methyl-2-butene}} = 4.0 \times 10^{-10}$,[6] $k_{Cl,\mathit{cis}\text{-2-butene}} = 3.1 \times 10^{-10}$,[20] $k_{Cl,1\text{-hexene}} = 4.0 \times 10^{-10}$, $k_{Cl,1\text{-heptene}} = 4.4 \times 10^{-10}$, $k_{Cl,1\text{-octene}} = 5.5 \times 10^{-10}$ and $k_{Cl,1\text{-nonene}} = 5.9 \times 10^{-10}$.[21]

The Cl and OH reactions with alkenes and the corresponding rate coefficients are collected in two different groups. In the first group, hydrogen atoms connected to carbon atoms at the double bound are replaced by methyl groups (ethylene, propene, *cis*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene) and an increase on the rate coefficients, from $k_{OH,ethylene}$ to $k_{OH,2,3\text{-dimethyl-2-butene}}$ (or from $k_{Cl,propene}$ to $k_{Cl,2\text{-methyl-2-butene}}$), is observed, as evidenced in Figure 3.

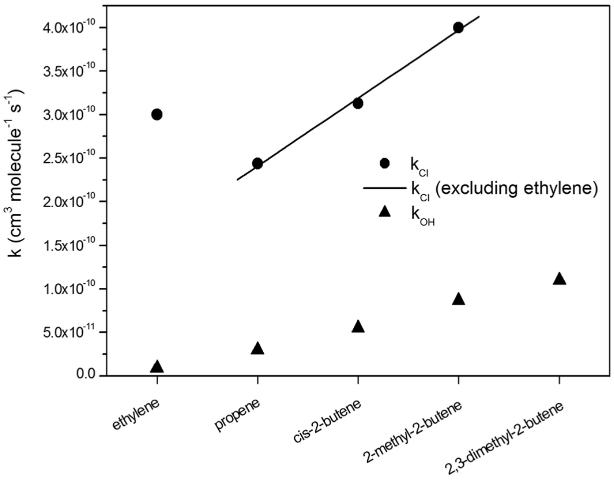

Figure 3. Replacement of hydrogen atoms by methyl groups in alkenes and comparison of the reactivity of their reactions with chlorine atoms and with OH radicals.

In Figure 3, rate coefficients for the OH reactions with alkenes are highly correlated with the number of hydrogen atoms replaced by methyl groups in the molecule (triangles), whereas similar correlation is not observed for the rate coefficients for Cl reactions (circles). However, neglecting the ethylene from this group, a much better correlation is found between the rate coefficients for the Cl reactions with alkenes and the number of replaced hydrogen atoms (black line), showing that the contribution of the replacement of a hydrogen atom by a methyl group to the reactivity towards chlorine atoms is greater than for the kinetics of OH reactions with alkenes. In fact, the rate coefficients were expected to increase, since the replacement of the hydrogen atom by an alkyl group causes the electronic density on the π orbitals to increase, favoring the electrophilic attack. Therefore, the higher slope observed for the k_{Cl} rate coefficients can also be attributed to the higher electrophilic character of the Cl atoms.

The second group comprises the OH and Cl reactions (and the corresponding rate coefficients) with 1-alkenes (Figure 4). The values of rate coefficients for OH radicals with 1-alkenes suggest that the increase of the side chain along a homolog series has a small effect in the rate coefficient when the double bond is at the terminal carbon atom.

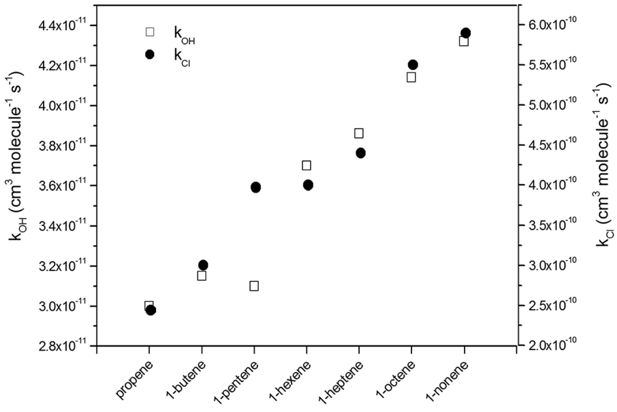

Figure 4. Homologous series of alkenes and comparison of the reactivity between their reactions with chlorine atoms and with OH radicals.

Different from the trend observed for the k_{OH} values, a significant increase is observed for the k_{Cl} rate coefficients, as evidenced in Figure 4. Note that the k_{OH} rate coefficients (squares) are found in the range from 3.0×10^{-11} to 4.3×10^{-11} cm^3 molecule^{-1} s^{-1}, whereas the k_{Cl} rate coefficients (circles) are found in the range from 2.5×10^{-10} to 6.0×10^{-10} cm^3 molecule^{-1} s^{-1}. Since the increase of the side chain along a homolog series produces a minor effect over the electronic density on the π orbitals, thus representing a minor contribution to the electrophilic addition, the different slopes observed for k_{OH} and k_{Cl} in this group can only be attributed to the hydrogen abstraction channel. As the side chain increases in the homolog series, the number of hydrogen atoms also increases and therefore the contribution of the hydrogen abstraction channel to the global kinetics can be increased.

The question now is how to predict how much the contribution of each possible channel to the global kinetics is.

The rate coefficients for alkane reactions with OH radicals and chlorine atoms, where only the hydrogen abstraction channel is predominant, were also compared. The contribution of the carbon chain length increase in the alkanes reactivity towards OH radicals and Cl atoms is shown in Figure 5.

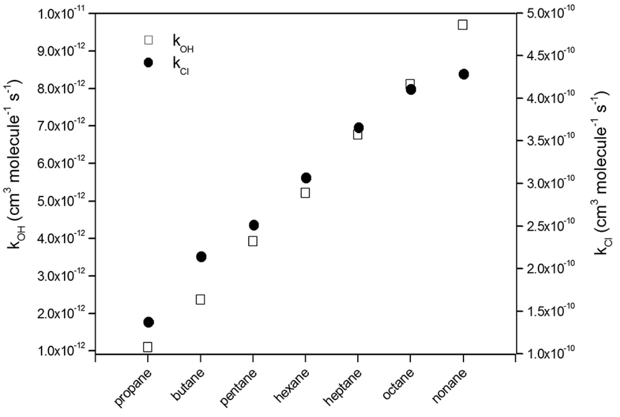

Figure 5. Homologous series of alkanes and comparison of the reactivity between their reactions with chlorine atoms and with OH radicals.

In Figure 5, the rate coefficients for the reaction of the OH radicals with propane (1.1×10^{-12} cm^3 molecule^{-1} s^{-1}), butane (2.4×10^{-12} cm^3 molecule^{-1} s^{-1}), hexane (5.2×10^{-12} cm^3 molecule^{-1} s^{-1}), heptane (6.8×10^{-12} cm^3 molecule^{-1} s^{-1}), octane (8.1×10^{-12} cm^3 molecule^{-1} s^{-1}) and nonane (9.7×10^{-12} cm^3 molecule^{-1} s^{-1}) were determined by Atkinson,[22] whereas the rate coefficient for the pentane + OH reaction (3.9×10^{-12} cm^3 molecule^{-1} s^{-1}) was determined by Sivaramakrishnan and Michael.[23] The following rate coefficients (cm^3 molecule^{-1} s^{-1}) for the reaction of the Cl atoms with alkanes have been used: 1.4×10^{-10} (propane),[19] 2.1×10^{-10} (butane),[24] 2.5×10^{-10} (pentane), 3.1×10^{-10} (hexane), 3.6×10^{-10} (heptane), 4.1×10^{-10} (octane),[25] and 4.3×10^{-10} (nonane).[26]

The comparison of the slopes for k_{Cl} rate coefficients (Figures 4 and 5) suggests that the contribution of the increase in carbon length to the reactivity is similar for alkanes and alkenes, suggesting that the contribution from the hydrogen abstraction channel to the kinetics of the alkenes + Cl reaction is similar to that for the corresponding alkane + Cl reactions. Same comparison for k_{OH} shows that the rate coefficients for the reactions of alkenes increase with the carbon length faster: the slope for the k_{OH} rate coefficients of the reactions of alkenes is almost twice the slope for the reactions of alkanes, suggesting that the hydrogen abstraction channel is of minor contribution to the alkene + OH reactions. Therefore, the hydrogen abstraction channel contributes more to the overall kinetics of the reactions of Cl with alkenes, than for the reactions of OH with alkenes.

A possible estimate for the addition and hydrogen abstraction branching ratios can be done on the basis of the structure-reactivity scheme suggested by Ezell *et al.*,[6] which considers the rate coefficient (k) as a sum of terms corresponding to the direct abstraction of non-allylic hydrogen atoms, addition to the double bond and abstraction of the allylic hydrogen atoms:

$$k = k^{alkyl} + k^{add} + k^{allyl} \quad (7)$$

The first term in this sum is obtained from the following expression:

$$k^{alkyl} = \sum\left[\left(k^{1o}F(X)\right) + \left(k^{2o}F(X)F(Y)\right) + \left(k^{3o}F(X)F(Y)F(Z)\right)\right] \quad (8)$$

where k^{1o}, k^{2o} and k^{3o} are the contributions of hydrogen abstractions from primary, secondary and tertiary groups, respectively, to the overall rate coefficient and F(X), F(Y) and F(Z) are factors necessary to take into account the neighboring group effects. Values for individual parameters were given by Atkinson.[27]

The second term in equation 7, k^{add}, represents the contribution of the addition rate coefficient for the overall rate coefficient and takes into account the possible formation of primary and secondary radicals, two equivalent secondary radicals, tertiary and primary radicals or tertiary and secondary radicals.

The k^{allyl} term in equation 7 is the contribution of the allylic hydrogen abstraction to the overall rate coefficient and assumes three possible values for the hydrogen bounded to primary, secondary or tertiary carbon atoms.

Taking this scheme into account, the overall rate coefficient for *cis*-3-hexene + Cl reaction can be predicted as 4.27×10^{-10} cm^3 molecule^{-1} s^{-1}, in agreement with our experimental result (($(4.13 \pm 0.51) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Moreover, the branching ratios for addition and hydrogen abstraction channels are 70 and 30%, supporting the conclusion that the contribution of the hydrogen abstraction channel is not negligible.

Atmospheric implications

In the atmosphere, *cis*-3-hexene can also be removed by reactions with O_3, NO_3 and OH radicals. The effective lifetimes of *cis*-3-hexene with respect to reaction with each of the oxidants were calculated using the relationship expressed as:

$$\tau_X = \frac{1}{k_X[X]} \quad (9)$$

with X = Cl atoms, OH and NO_3 radicals and O_3 molecules, using the estimated 12 h average day-time global concentration of OH radicals (1×10^6 radicals cm^{-3}),[28] the 12 h average night-time concentration of NO_3 radicals (5×10^8 molecule cm^{-3})[29] and 24 h average O_3 concentration (7×10^{11} molecule cm^{-3})[30] and considering average global concentrations of 1×10^4 atoms cm^{-3} of chlorine.[31] From the rate coefficients available in the literature[3-5] and the experimental rate coefficient obtained in this work, the lifetimes were calculated and ranged from 1.27 h to 2.8 days. These calculations do not take into account local atmospheric conditions and seasonal variations which are capable of changing these oxidant concentrations.

Table 2. Calculated atmospheric lifetimes, τ_X (hours), of *cis*-3-hexene with OH and NO_3 radicals, O_3 molecules and Cl atoms

X	[X]^a / (molecule cm^{-3})	$k_X{}^b$ / (cm^3 molecule^{-1} s^{-1})	τ_X / hours
OH	1×10^6	$6.27 \pm 0.66 \times 10^{-11}$	4.43
NO_3	5×10^8	$4.37 \pm 0.49 \times 10^{-13}$	1.27
O_3	7×10^{11}	$1.44 \pm 0.17 \times 10^{-16}$	2.75
Cl	1×10^4	$4.13 \pm 0.51 \times 10^{-10}$	67.2

^{a}Concentration values were taken from references: 28 (OH), 29 (NO_3), 30 (O_3) and 31 (Cl); ^{b}rate coefficients values at 298 K and were taken from references: 3 (OH), 4 (O_3), 5 (NO_3) and this work (Cl).

The tropospheric lifetimes shown in Table 2 indicate that *cis*-3-hexene is rapidly removed by OH radicals and O_3 during day-time and by NO_3 radicals at night. The contribution of Cl atoms is small, but maybe significant in those areas with higher Cl concentrations. For instance, with an OH concentration of 5×10^5 cm^{-3}, observed in the early morning hours,[32] atomic chlorine concentrations of only 1% of that OH could contribute significantly to the chemical removal of volatile organic compounds in the marine boundary layer.[33] Moreover, maximum Cl concentrations as high as 1×10^5 atom cm^{-3} have been reported in the marine boundary layer at mid-latitudes at dawn emphasizing the locally significant effect of Cl atoms on the concentration and lifetimes of some atmospheric organic compounds in both remote marine boundary layer and coastal urban regions.[34] Significant Cl concentrations may also be found in mid-continental polluted areas from photolysis of $ClNO_2$, a particular pollutant formed at night by reactions of soluble chloride specie (emitted by anthropogenic sources) with nitrogen oxides, as reported by Thornton *et al.*[35] Therefore, the importance of chlorine reactions, with respect to the OH reactions, with hydrocarbons may also be inferred beyond the marine boundary layer.

Another atmospheric concern of VOCs is their contribution to the greenhouse warming, as expected by the global warming potential (GWP) which is calculated

Table 3. Global lifetime (years), estimated RE (W m^{-2}), HGWP and GWP for the *cis*-3-hexene, over a specified time horizon of 20 and 100 years

	τ_{global} / years	RE / (W m^{-2})	HGWP20	HGWP100	GWP20	GWP100
cis-3-Hexene	8.20×10^{-5}	0.017	5.64×10^{-7}	2.27×10^{-7}	3.79×10^{-3}	1.08×10^{-4}
$CFCl_3$	45.0[a]	0.25[a]	1	1	6730[a]	4750[a]

[a] Reference 12.

relative to CO_2 over a specified time horizon. In fact, GWPs for short-lived compounds have been reported recently.[36-39]

The plot of the cross-sections (cm^2 molecule^{-1} cm^{-1}) as a function of wavenumber (cm^{-1}) of the *cis*-3-hexene is shown in Figure 6.

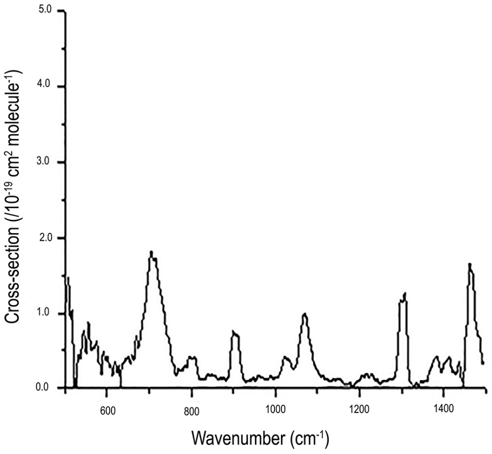

Figure 6. Infrared spectra of *cis*-3-hexene at 298 K.

The integrated IR absorption cross-section (500 and 1500 cm^{-1}) value for the *cis*-3-hexene is 1.35×10^{-17} cm^2 mol^{-1} cm^{-1}. Uncertainties in the cross-section measurement arise from the following sources: the sample concentration (1%), sample purity (3%), path length (1%), spectrum noise and residual baseline offset after subtraction of background (1.5%). Considering these individual uncertainties, we quote a conservative uncertainty of ± 6%. Unfortunately, there are no literature data for the absorption cross-section of the studied hexene to compare with.

Table 3 shows the calculated value of the RE for the *cis*-3-hexene with the RE of CFC-11[12] (in units of W m^{-2}) and the calculated values of HGWP and GWP on a time horizon of 20 and 100 years.

Summarizing, the lifetime of the studied compound indicates that they will be removed from the troposphere in few hours. In addition, it is clear from the GWP values that these compounds will not have a significant contribution to the radiative efficiencies of climate change.

Conclusions

In this work the rate coefficient for the reactions of Cl atoms with *cis*-3-hexene has been determined using the relative rate method. The rate coefficients, obtained from the experiments with the two reference compounds (*n*-heptane and cyclopentane), showed negligible dispersion among the determinations. Our final recommended value is $(4.13 \pm 0.51) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

This value is in agreement with the estimate from structure-reactivity relations, 4.27×10^{-10} cm^3 molecule^{-1} s^{-1}. Such analysis also suggests that 30% of the rate coefficient for the reaction of *cis*-3-hexene with chlorine atoms is due to abstraction of hydrogen atoms.

The tropospheric lifetimes indicate that *cis*-3-hexene is rapidly removed by the typical oxidants in troposphere and that the contribution of Cl atoms to the global chemical removal can be significant in areas with high concentrations of this species.

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References

1. Heath, J. S.; Koblis, K.; Sager, S. L.; *J. Soil Contam.* **1993**, *2*, 1.
2. Ramnäs, O.; Östermark, U.; Petersson, G.; *J. Chromatogr.* **1993**, *638*, 65.
3. Barbosa, T. S.; Peirone, S.; Barrera, J. A.; Abrate, J. P. A.; Lane, S. I.; Arbillla, G.; Bauerfeldt, G. F.; *Phys. Chem. Chem. Phys.* **2015**, *17*, 8714.
4. Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G.; *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press, Inc.: New York, 2000.
5. Pfrang, C.; Martin, R. S.; Nalty, A.; Waring, R.; Canosa-Mas, C. E.; Wayne, R. P.; *Phys. Chem. Chem. Phys.* **2005**, *7*, 2506.
6. Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J.; *Phys. Chem. Chem. Phys.* **2002**, *4*, 5813.
7. Dalmasso, P. R.; Taccone, R. A.; Nieto, J. D.; Teruel, M. A.; Lane, S. I.; *Atmos. Environ.* **2006**, *40*, 7298.

8. Dalmasso, P. R.; Taccone, R. A.; Nieto, J. D.; Cometto, P. M.; Lane, S. I.; *Atmos. Environ.* **2010**, *44*, 1749.
9. Abrate, J. P. A.; Pisso, I.; Peirone, S. A.; Cometto, P. M.; Lane, S. I.; *Atmos. Environ.* **2013**, *67*, 85.
10. Pinnock, S.; Hurley, M. D.; Shine, K. P.; Wallington, T. J.; Smyth, T. J.; *J. Geophys. Res.* **1995**, *100*, 23227.
11. Fisher, D. A.; Hales, C. H.; Wang, W. C.; Ko, M. K. W.; Sze, N. D.; *Nature* **1990**, *344*, 513.
12. Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; van Dorland, R. In *Climate Change 2007: The Physical Science Basis*; Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K. B.; Tignor, M.; Miller, H. L., eds.; Cambridge University Press: Cambridge, United Kingdom, 2007, ch. 2.
13. Wallington, T. S.; Skewes, L. M.; Siegl, W. O.; *J. Phys. Chem.* **1989**, *93*, 3649.
14. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson Jr., R. F.; Kerr, J. A.; Troe, J.; *J. Phys. Chem. Ref. Data* **1989**, *18*, 881.
15. Atkinson, R.; *Chem. Rev.* **1986**, *86*, 69.
16. Atkinson, R.; Aschmann, S. M.; *Int. J. Chem. Kinet.* **1985**, *17*, 33.
17. Aschmann, S. M.; Atkinson, R.; *Phys. Chem. Chem. Phys.* **2008**, *10*, 4159.
18. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson Jr., R. F.; Kerr, J. A.; Rossi, M. J.; Troe, J.; *J. Phys. Chem. Ref. Data* **1997**, *26*, 521.
19. Orlando, J. J.; Tyndall, G. S.; Apel, E. C.; Riemer, D. D.; Paulson, S. E.; *Int. J. Chem. Kinet.* **2003**, *35*, 334.
20. Kaiser, E. W.; Donahue, C. J.; Pala, I. R.; Wallington, T. J.; Hurley, M. D.; *J. Phys. Chem. A* **2007**, *111*, 1286.
21. Walavalkar, M.; Sharma, A.; Alwe, H. D.; Pushpa, K. K.; Dhanya, S.; Naik, P. D.; Bajaj, P. N.; *Atmos. Environ.* **2013**, *67*, 93.
22. Atkinson, R.; *Atmos. Chem. Phys.* **2003**, *3*, 2233.
23. Sivaramakrishnan, R.; Michael, J. V.; *J. Phys. Chem. A* **2009**, *113*, 5047.
24. Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W.; *Int. J. Chem. Kinet.* **1997**, *29*, 43.
25. Hooshiyar, P. A.; Niki, H.; *Int. J. Chem. Kinet.* **1995**, *27*, 1197.
26. Aschmann, S. M.; Atkinson, R.; *Int. J. Chem. Kinet.* **1995**, *27*, 613.
27. Atkinson, R.; *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.
28. Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Harth, C.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller, B. R.; *Science* **2001**, *292*, 1882.
29. Shu, Y.; Atkinson, R.; *J. Geophys. Res.* **1995**, *100*, 7275.
30. Logan, J. A.; *J. Geophys. Res.* **1985**, *90*, 10463.
31. Wingenter, O. W.; Kubo, M. K.; Blake, N. J.; Smith, T. W.; Blake, D. R.; Rowland, F. S.; *J. Geophys. Res.* **1996**, *101*, 4331.
32. Brauers, T.; Aschmutat, U.; Brandenburger, U.; Dorn, H.-P.; Hausmann, M.; Heβling, M.; Hofzumahaus, A.; Holland, F.; Plass-Dülmer, C.; Ehhalt, D. H.; *Geophys. Res. Lett.* **1996**, *23*, 2545.
33. Finlayson-Pitts, B. J.; Keoshian, C. J.; Buehler, B.; Ezell, A. A.; *Int. J. Chem. Kinet.* **1999**, *31*, 491.
34. Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastridge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M.; *Nature* **1998**, *394*, 353.
35. Thornton, J. A.; Kercher, J. P.; Riedel, T. P.; Wagner, N. L.; Cozic, J.; Holloway, J. S.; Dube, W. P.; Wolfe, G. M.; Quinn, P. K.; Middlebrook, A. M.; Alexander, B.; Brown, S. S.; *Nature* **2010**, *464*, 271.
36. Nilsson, E. J. K.; Nielsen, O. J.; Johnson, M. S.; Hurley, M. D.; Wallington, T. J.; *Chem. Phys. Lett.* **2009**, *473*, 233.
37. Baasandorj, M.; Knight, G.; Papadimitriou, V. C.; Talukdar, R. K.; Ravishankara, A. R.; Burkholder, J. B.; *J. Phys. Chem. A* **2010**, *114*, 4619.
38. Jiménez, E.; Antiñolo, M.; Ballesteros, B.; Martínez, E.; Albaladejo, J.; *ChemPhysChem* **2011**, *11*, 4079.
39. Peirone, S. A.; Barrera, J. A.; Taccone, R. A.; Cometto, P. M.; Lane, S. I.; *Atmos. Environ*. **2014**, *85*, 92.

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