

Laboratory Measurements of the $^{12}\text{C}/^{13}\text{C}$ Kinetic Isotope Effects in the Gas-Phase Reactions of Unsaturated Hydrocarbons with Cl Atoms at 298 ± 3 K

Rebecca S. Anderson^{1,*}, §, Lin Huang², Richard Iannone¹ and Jochen Rudolph¹

¹Centre for Atmospheric Chemistry and Chemistry Department, York University, Toronto, Canada

²Atmospheric Science and Technology Directorate, Science and Technology Branch, Environment Canada, Toronto, Canada

*Corresponding Author, National Center for Atmospheric Research, 3450 Mitchell Lane, Boulder, CO, 80301; phone: (303) 497-1493; facsimile: (303) 497-1477; E-mail: rsa@ucar.edu.

§now at the National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, CO.

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Abstract. The carbon kinetic isotope effects (KIEs) in the reactions of several unsaturated hydrocarbons with chlorine atoms were measured at room temperature and ambient pressure using gas chromatography combustion isotope ratio mass spectrometry (GCC-IRMS). All measured KIEs, defined as the ratio of the rate constants for the unlabeled and labeled hydrocarbon reaction k_{12}/k_{13} , are greater than unity or normal KIEs. The KIEs, reported in per mil according to $^{\text{Cl}}\epsilon = (k_{12}/k_{13} - 1) \times 1000\text{‰}$ with the number of experimental determinations in parenthesis, are as follows: ethene, 5.65 ± 0.34 (1); propene, 5.56 ± 0.18 (2); 1-butene, 5.93 ± 1.16 (1); 1-pentene, 4.86 ± 0.63 (1); cyclopentene, 3.75 ± 0.14 (1); toluene, 2.89 ± 0.31 (2); ethylbenzene, 2.17 ± 0.17 (2); *o*-xylene, 1.85 ± 0.54 (2). To our knowledge, these are the first reported KIE measurements for reactions of unsaturated NMHC with Cl atoms. Relative rate constants were determined concurrently to the KIE measurements. For the reactions of cyclopentene and ethylbenzene with Cl atoms, no rate constant has been reported in refereed literature. Our measured rate constants are: cyclopentene (7.32 ± 0.88) relative to propene (2.68 ± 0.32); ethylbenzene (1.15 ± 0.04) relative to *o*-xylene (1.35 ± 0.21), all $\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The KIEs in reactions of aromatic hydrocarbons with Cl atoms are similar to previously reported KIEs in Cl-reactions of alkanes with the same numbers of carbon atoms. Unlike the KIEs for previously studied gas-phase hydrocarbon reactions, the KIEs for alkene–Cl reactions do not exhibit a simple inverse dependence on carbon number. This can be explained by competing contributions of normal and inverse isotope effects of individual steps in the reaction mechanism. Implications for the symmetries of the transition state structures in these reactions and the potential relevance of Cl-atom reactions on stable carbon isotope ratios of atmospheric NMHC are discussed.

Keywords: alkene; aromatic; chlorine atom; KIE; stable carbon isotopes; symmetry; transition state structure.

1. Introduction

The impact of chlorine atom chemistry on the removal of unsaturated hydrocarbons from the atmosphere has been studied in a significant number of publications (Boudries and Bottenheim, 2000; Jobson *et al.*, 1994; Ramacher *et al.*, 1999; Rudolph *et al.*, 1999; Wingenter *et al.*, 1999). Although reactions with hydroxyl radicals and ozone are far more important on the global scale, particularly in continental mid-latitudes, it is agreed that at high latitudes during Polar Sunrise and in coastal environments in the marine boundary layer, where concentrations of Cl atoms can reach levels of up to 10^5 cm^{-3} (Chang *et al.*, 2004; Singh *et al.*, 1996), Cl-atom chemistry can significantly increase the removal rate of NMHC from the atmosphere.

The usefulness of stable carbon isotope ratio measurements for investigating the OH chemistry of both saturated and unsaturated nonmethane hydrocarbons (NMHC) has been demonstrated recently (Rudolph *et al.*, 2000; Rudolph *et al.*, 2002; Rudolph *et al.*, 2003; Saito *et al.*, 2002; Thompson *et al.*, 2003; Tsunogai *et al.*, 1999). To accurately interpret the isotope ratio measurements of unsaturated hydrocarbons, knowledge of the kinetic isotope fractionations associated with their chemical removal is necessary. Measurements have been reported of the $^{12}\text{C}/^{13}\text{C}$ -KIEs in the reactions of alkenes and aromatic hydrocarbons with OH radicals (Anderson *et al.*, 2004a; Anderson *et al.*, 2004b; Rudolph *et al.*, 2000) and in the reactions of alkenes with ozone (Iannone *et al.*, 2003). To best interpret measurements of NMHC from environments with elevated Cl-atom

concentrations, however, the kinetic isotope effects (KIEs) in the reactions with Cl atoms must also be known. Although theoretical calculations and laboratory measurements of the methane-Cl $^{12}\text{C}/^{13}\text{C}$ -KIE have been reported, (Crowley *et al.*, 1999; Gupta *et al.*, 1997; Tanaka *et al.*, 1996; Tyler *et al.*, 2000) as have laboratory measurements of the H/D-KIEs of reactions of light alkenes with Cl atoms, (Stutz *et al.*, 1998) and more recently, measurements of H/D- and $^{12}\text{C}/^{13}\text{C}$ -KIEs in reactions of alkanes with Cl atoms (Anderson *et al.*, submitted 2006; Iannone *et al.*, 2005), to our knowledge there are no published $^{12}\text{C}/^{13}\text{C}$ -KIE values for the reactions of unsaturated hydrocarbons with Cl atoms. In this paper we present measurements of the carbon KIEs for reactions of light alkenes and alkylbenzenes with Cl atoms.

2. Experiment

The method for measuring carbon KIEs for the reactions of NMHC + Cl is similar to the method used for measuring OH-reaction KIEs which has been described in detail in a previous publication (Anderson *et al.*, 2003). The method required only a few minor changes to generate Cl atoms rather than OH radicals, described recently (Anderson *et al.*, submitted 2006). The Cl-reactions of unsaturated hydrocarbons with naturally occurring isotope abundances ($\geq 97\%$ purity grade from Sigma Aldrich, Air Products and Matheson Gas) were studied in 30 L PTFE reaction chambers housed inside a converted drying oven. Continuous flow isotope ratio mass spectrometry (CF-IRMS) was used to measure concentrations and stable carbon isotope ratios. Initial hydrocarbon concentrations ranged from 75 to 300 parts per million by volume (ppmV). Between each measurement at time intervals of approximately 1.5 hours, molecular chlorine ($\geq 99.5\%$,

Sigma-Aldrich) was injected into the reaction chamber. Then between 1 and 12 fluorescent lights emitting in the UV range, $\lambda_{\text{max}} = 350 \text{ nm}$, were turned on to generate chlorine atoms with average concentrations between 10^5 and $10^6 \text{ atoms cm}^{-3}$.

Using an automated system, the hydrocarbons in 5-mL samples from the reaction chamber were separated by gas chromatography (GC0 on an HP1 column (Agilent Technologies, 60 m 0.32 mm I.D., 5 μm film thickness), and for experiments including ethene, a second column was also used (Poraplot Q, 60 m, 0.32 mm I.D.) for two dimensional separation. For experiments not including ethene, the GC temperature was held at 243 K for 2.5 minutes, increased 4 K min^{-1} to 303 K, 1.5 K min^{-1} to 453 K, and held until the last peak eluted. For experiments including ethene, the initial temperature was held for 30 minutes. Approximately 0.3 mL min^{-1} of the 1.5 mL min^{-1} GC effluent was split to a Saturn 2000 ion trap mass spectrometer for peak identification and to verify peak purity. The remaining portion of the effluent passed through a combustion interface for conversion of all carbon containing species to CO_2 , followed by water removal by a Nafion® permeation dryer. Of the remaining dried gas flow, approximately 0.4 mL min^{-1} was then transferred through an open split interface to the ion source of a Finnigan MAT 252 IRMS for stable carbon isotope ratio measurement.

For each experiment, before the Cl-atom reaction was initiated, two or three measurements of the reaction chamber contents were made to verify sufficient stability in both the concentration and stable isotope ratios of the hydrocarbons. From all of the hydrocarbons, the mean relative standard deviation of the individual hydrocarbon concentration measurements was 1.5%, with relative standard deviations ranging from 0.5–3.0%. The mean standard deviation of the stable carbon isotope compositions ($\delta^{13}\text{C}$)

was 0.15‰, with standard deviations ranging from 0.04–0.40‰. Measurements of the contents of the reaction chamber were taken approximately once every 1.5 hours, depending on the time required for the GC separation. After the reaction initiation, measurements were made until less than 50% of each original hydrocarbon concentration remained. Generally at least three measurements were made following the reaction initiation, but for the first of the two experiments containing aromatic hydrocarbons, due to the rapid reaction with Cl atoms, only two measurements of each hydrocarbon were made following the reaction initiation.

Using the mass 44, 45 and 46 traces generated by the IRMS software, the stable carbon isotope ratio and concentration for each hydrocarbon measurement were determined. The mass 44 trace, measuring $^{12}\text{C}^{16}\text{O}_2$, was used to directly monitor the changes in concentration with time, as the abundance of ^{12}C in the sample is proportional to hydrocarbon concentration. The relationship between the changes in stable carbon isotope ratio and the changes in concentration has been described previously (Anderson *et al.*, 2003) as

$$\ln\left(\frac{^{12}\text{C}_t}{^{12}\text{C}_0}\right) = \frac{k_{12}/k_{13}}{1 - k_{12}/k_{13}} \times \ln\left(\frac{^{13}\text{C}_t/^{12}\text{C}_t}{^{13}\text{C}_0/^{12}\text{C}_0}\right) \quad (1)$$

where C_t and C_0 are the abundances of carbon atoms at time t and $t = 0$, respectively. Cl-reaction KIEs, defined as $^{Cl}k_{12}/^{Cl}k_{13}$, the ratio of the rate constants for the reactions of Cl atoms with hydrocarbons containing only ^{12}C and compounds containing a ^{13}C atom, were determined from the slope of the linear least-squares fit of a plot according to Equation (1). The average of the pre-reaction measurements was used as the initial point

for the plot. The experimental uncertainty for each KIE measurement was determined using the standard error of the slope of the plot.

To confirm that the change in hydrocarbon concentration was due primarily to reaction with Cl atoms, a relative rate analysis was performed for each compound and, using one of the other hydrocarbons present in the experiment as a reference, experimental rate constants were calculated. Experimental rate constants were then compared to literature values.

3. Results

In four experiments with between two and four hydrocarbons each, the Cl-reaction KIEs of 5 alkenes and 3 aromatic hydrocarbons were measured in synthetic air at atmospheric pressure at 298 ± 3 K. A summary of the individual KIE measurements is given in Table I, with the KIE in epsilon notation: $^{Cl}\epsilon (\text{‰}) = (k_{12}/k_{13} - 1) \times 1000$. Included in Table I are the experimental rate constants. The results for each hydrocarbon reaction were averaged and are reported in Table II along with published OH- and O₃-reaction ¹²C/¹³C-KIEs, where available. Also included in Table II are published rate constants for each hydrocarbon studied.

4. Discussion

From the relative rate analyses, all experimentally determined rate constants are within $\pm 10\%$ of the average of the previously reported rate constants (Table II). From the relative rate analyses, we conclude that the changes in hydrocarbon concentration during the KIE experiments were primarily due to reaction with Cl atoms. Furthermore, the very

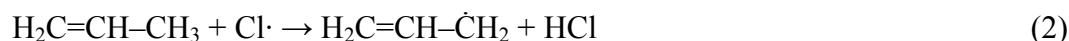
good agreement for the compounds where literature values are available gives credibility to the rate constant determined for the reaction of cyclopentene, for which no value has been published to our knowledge. Similarly, our results confirm the reliability of the ethylbenzene rate constant, for which the presently available information is limited to two measured values published in conference proceedings (Chadwick *et al.*, 2001).

For all the unsaturated hydrocarbons studied in this work, the KIE in the reaction with Cl atoms is significantly smaller than previously measured KIEs for reactions with OH radicals (Anderson *et al.*, 2004a; Anderson *et al.*, 2004b; Rudolph *et al.*, 2000) and ozone (Iannone *et al.*, 2003). Of particular interest is the $^{12}\text{C}/^{13}\text{C}$ -KIEs for the reaction of ethene + Cl, $(5.65 \pm 0.34)\text{‰}$. This is significantly lower than the $^{12}\text{C}/^{13}\text{C}$ -KIE for ethane + Cl $(10.7 \pm 0.2)\text{‰}$ (Anderson *et al.*, submitted 2006), which is in strong contrast to the OH-reaction KIEs: ethane + OH $(8.6 \pm 2.0)\text{‰}$ and ethene + OH $(19 \pm 3)\text{‰}$ (Anderson *et al.*, 2004a), in which the KIE for the unsaturated reaction is significantly higher.

For every compound-reactant combination previously studied, a clear inverse dependence on the number of carbon atoms in the hydrocarbon N_{C} was found (Anderson *et al.*, 2004a; Anderson *et al.*, 2004b; Anderson *et al.*, submitted 2006; Iannone *et al.*, 2003; Iannone *et al.*, 2004; Iannone *et al.*, 2005; Rudolph *et al.*, 2000). In contrast to this, there is no straightforward N_{C}^{-1} dependence for the reactions of alkenes with Cl atoms. For the hydrocarbons measured, a plot of the Cl-reaction KIE against N_{C}^{-1} is shown in Figure 1. The linear best fit to the KIE data gives a relationship of $\varepsilon (\text{‰}) = (3.8 \pm 3.3) \times N_{\text{C}}^{-1} + (4.01 \pm 1.06)$ and an R^2 value of 0.303. Obviously, for the alkene–Cl KIEs, a dependence on N_{C}^{-1} does not provide a useful approximation. The exclusion of the ethene and propene data results in more reasonable N_{C}^{-1} dependence for the remaining alkenes,

with ε (‰) = $(22.5 \pm 1.6) \times N_C^{-1}$ and an R^2 value of 0.672. However, since this approximation includes only C_4 and C_5 KIE data, its applicability for a description of KIEs for reaction of C_6 and heavier alkenes with Cl atoms is very uncertain. Similarly, for the aromatic compounds KIE data is only available for C_7 and C_8 compounds. Consequently the general validity of the approximation of ε (‰) = $(17.7 \pm 1.6) \times N_C^{-1}$ with an R^2 value of 0.534 is also very uncertain. However, it is worth noting that the aromatic–Cl KIE approximation is closer to previously reported alkane–OH and alkane–Cl approximations, ε (‰) = $(16.6 \pm 1.0) \times N_C^{-1}$ (Anderson *et al.*, 2004a) and ε (‰) = $(18.3 \pm 1.2) \times N_C^{-1}$ (Anderson *et al.*, submitted 2006), respectively, than it is to the reported aromatic–OH approximation, ε (‰) = $(40.6 \pm 1.4) \times N_C^{-1}$ (Anderson *et al.*, 2004b).

The kinetics of the reactions of chlorine atoms with many simple alkenes have been well studied, including ethene, propene, 1-butene, and 1-pentene (Coquet and Ariya, 2000; Ezell *et al.*, 2002; Iyer *et al.*, 1983; Kaiser and Wallington, 1996; Pilgrim *et al.*, 1997; Stutz *et al.*, 1997; Stutz *et al.*, 1998; Wallington *et al.*, 1989; Wallington *et al.*, 1990). In general, these reactions occur via multiple reaction channels. For example, the reaction of propene with Cl atoms may occur via abstraction:



addition:



or addition-elimination:



Thus, the overall second order rate constant will be $k_2 + k_3[\text{M}] + k_4$, where the rate constant $k_4 = k_a k_b / (k_{-a} + k_b)$. Similar to reaction (4), reaction (3) proceeds in two steps:



Thus we obtain $k_3 = k_5 k_6 [\text{M}] / (k_{-5} + k_6 [\text{M}])$. At the high pressure limit where $[\text{M}]$ is sufficiently large, $k_{-5} \ll k_6 [\text{M}]$ such that $k_3 = k_5$ and the overall rate constant is determined by the first reaction step. This is the case for most alkene-OH reactions at ambient pressure, but for the reactions of small alkenes with Cl, the high-pressure limit is typically greater than one atmosphere (Stutz *et al.*, 1998).

At low temperatures and moderate pressures, the reactions of alkenes with Cl atoms proceed largely through the addition pathway. The additions are exothermic, with ΔH values typically in the range of -80 kJ mol^{-1} (Taatjes, 1999), as the formation of the C-Cl bond provides more energy than the difference between the C=C double bond and the C-C single bond of the chloroalkyl radical. Under tropospheric conditions, the reaction of ethene + Cl largely favours the addition pathway due to the large activation energy of the H-atom abstraction channel. However, for other alkenes, the abstraction

and addition-elimination channels (2) and (4) can have a significant impact on the overall reaction (Taatjes, 1999).

In the work by Stutz *et al.* (1998), it was shown that the H/D-KIE (k_H/k_D) for the reaction of Cl atoms with an alkene may be either normal (>1) or inverse (<1). In general, they suggest that the abstraction of a hydrogen atom from an alkene by a chlorine atom has a normal H/D-KIE (>1), while the addition of Cl atoms to a double bond contributes an inverse H/D-KIE (<1). This is explained by the excited adduct in Reaction (5) having an increased lifetime due to deuteration and thereby an increased density of vibrational states, which results in lower excess energy and a slower decomposition rate back to reactants. This increase in lifetime increases the likelihood that the adduct will be stabilized by the third-body Reaction (6) rather than decompose back to the reactants, via Reaction (-5). This inverse effect is more significant for the KIEs of smaller alkenes. At 100 kPa, the H/D-KIE for propene + Cl is close to unity, while the H/D-KIEs in the Cl-reactions of ethene and 1-butene are 0.74 and 1.1, respectively (Stutz *et al.*, 1998).

There is likely a similar increase in the lifetime of the excited adduct formed in Reaction (5) due to the presence of a ^{13}C atom, which would contribute an inverse effect to the overall KIE. This inverse effect would be smaller than the impact of deuteration because the differences in zero-point energy would be smaller with ^{13}C -labeling. The difference between the ethene-Cl and ethane-Cl KIEs in comparison to the OH-reaction KIEs corresponds with a lowered ethene-Cl KIE due to the inverse isotope effect contribution of Reaction (-5). Unlike the inverse H/D-KIE measured by Stutz *et al.* (1998), however, the measured $^{12}\text{C}/^{13}\text{C}$ -KIEs for alkene-Cl reactions are greater than

unity. This indicates that there are other contributing isotope effects that result in overall normal KIEs, such as the collision frequencies for Reactions (5) and (6).

For the simplest case, the reaction of ethene with Cl atoms, there is little impact at tropospheric conditions from the abstraction and addition-elimination channels (Taatjes, 1999). Thus, the overall rate constant k is primarily dictated by the addition channel. By writing the overall rate constant k as k_{12} and k_{13} , the KIE can be written as:

$$\frac{k_{12}}{k_{13}} = \frac{{}^{12}k_5}{{}^{13}k_5} \frac{{}^{12}k_6}{{}^{13}k_6} \frac{({}^{13}k_{-5} + {}^{13}k_6[M])}{({}^{12}k_{-5} + {}^{12}k_6[M])}. \quad (7)$$

In principle, there are three regimes. For situations where $k_{-5} \gg k_6[M]$, the overall KIE is the product of the equilibrium isotope effect for Reaction (5) and the KIE for Reaction (6). Where $k_{-5} \ll k_6[M]$, the overall KIE is the KIE of Reaction (5). Finally, there is the transition range, where $k_{-5} \sim k_6[M]$. In these situations, the isotope effects for each reaction step can influence the overall KIE. At ambient pressure, the ethene + Cl reaction is below the high-pressure limit (Stutz et al., 1998) and is therefore in the first regime where the overall KIE is strongly influenced by Reactions (-5) and (6). The reactions of 1-butene and 1-pentene with Cl atoms fall into the second regime, where the KIE is primarily determined by Reaction (5). The reaction of propene + Cl falls into the transitional third regime where the contribution of the equilibrium KIE for Reaction (5) to the overall KIE is not as pronounced as it is for ethene.

As demonstrated previously, these small $^{12}\text{C}/^{13}\text{C}$ -KIEs are not only dependent on differences in the zero-point energies of the isotopologues, but also in differences in the reaction entropies, for which individual partition functions can be analyzed separately

(Anderson *et al.*, submitted 2006). For the addition step in Reaction (5), the ratio of the differences in collision frequencies for the unlabeled and labeled ethene isotopologues contributes a normal isotope effect of 1.0098 for the ethene-Cl reaction. Using transition state theory, factors such as the vibrational and rotational partition functions can be estimated. The contribution to the KIE from the vibrational entropy partition function S_{vib}^\ddagger can be determined for each vibrational degree of freedom using the following equation (Benson, 1976):

$$S_{vib}^\ddagger = R \ln[(1 - e^{-hc\nu/\kappa T})^{-1}] + R \quad (8)$$

where κ and h are Boltzmann's and Planck's constants, respectively, R is the gas constant, c is the speed of light in vacuum and T is the temperature. Generally, all bonds with carbon atoms can contribute to the vibration partition function. For most bonds, however, the contribution from Equation (8) from the two isotopologues to the overall KIE will be near unity due to the magnitude of the vibration frequencies. It is only from ν values of weak bonds that the differences in Equation (8) will contribute a significant factor to the overall KIE. Thus, the vibrational partition function likely has only a very small contribution to the KIE of Reaction (5), as the vibration frequencies of the newly formed C–Cl bonds would be too large to have a significant impact. There is likely a significant difference, however, between the changes in zero-point energies of the two isotopologues due to the formation of the new C–Cl bond.

As previously discussed, the intermediate formed by Reaction (5) is more stable if the double bond contains a ^{13}C atom than the ^{12}C isotopologue intermediate. Therefore

Reaction (-5) contributes an inverse KIE with $^{12}k_{-5} > ^{13}k_{-5}$, contributing ^{13}C -enrichment to the addition adduct. For Reaction (6), collision frequency suggests that the ratio of collisional stabilization $^{12}k_6/^{13}k_6 = 1.0025$, using the molecular mass $M = 28.8 \text{ g mol}^{-1}$ for ethene. From the latter term in Equation (7), $(^{13}k_{-5} + ^{13}k_6[M])/(^{12}k_{-5} + ^{12}k_6[M])$, the overall KIE is dependent on the rate constant of decomposition back to the reactants in Reaction (-5), provided $k_6[M]$ is not large compared to k_{-5} , and on the product of the overall pressure and the rate constant for the stabilization of the intermediate in Reaction (6).

As alkene size increases, the fractionation between isotopologues due to the adduct stabilization becomes less important, and the overall KIE is affected to a lesser extent by the inverse KIE of the reversible addition step in the mechanism. Thus, initially the overall KIEs increase with increasing alkene size. Once the dependence on reaction (-5) subsides, the resultant KIEs will likely return to the same N_C^{-1} dependence seen in published alkene-OH $^{12}\text{C}/^{13}\text{C}$ -KIEs since then the reaction rate will primarily depend on k_5 .

For hydrocarbons with allylic hydrogen atoms, abstraction may occur as a competing reaction to a small degree, although the overall impact on the KIE from this pathway is likely small, as in general the $^{12}\text{C}/^{13}\text{C}$ -KIEs for H-atom abstractions are small in comparison to addition reactions (Anderson *et al.*, 2004a; Anderson *et al.*, 2004b; Rudolph *et al.*, 2000). The impact from the addition-elimination pathway in Reaction (4) on alkenes with three or more carbon atoms will also likely contribute a normal KIE, as the secondary step involving the decomposition of the chloroalkyl radical and the elimination of the HCl group would most likely have $k_{12} > k_{13}$ due to the increased

stability of the ^{13}C transition state isotopologue, also lessening the contribution of the inverse KIE of the addition mechanism with increasing N_C .

For the ethene reaction, depending on the symmetry of the transition state, there could theoretically be a significant change in the external rotation partition function due to ^{13}C -labeling. According to basic quantum mechanics (Benson, 1976), the external rotational entropy of a nonlinear molecule can be described as:

$$S_{\text{rot-ext}}^{\ddagger} = 11.5 + \frac{R}{2} \ln \left(\frac{I_M^3}{\sigma_e} \right) + \frac{3}{2} R \ln \left(\frac{T}{298} \right) \quad (9)$$

where I_M^3 is the product of the three principle moments of inertia around the center of mass, and σ_e is the external symmetry number of the molecule. The differences between the changes in the external rotational entropy partition functions for stable carbon isotopologues are thus dependent on the ratios of the moments of inertia of the isotopologues and their transition states and on the external symmetries of the isotopologues and their transition states, such that:

$$\exp(\Delta\Delta S_{\text{rot-ext}}^{\ddagger} / R) = \left(\frac{{}^{13}I_M^3 \times {}^{12}I_{M,TS}^3 \times {}^{12}\sigma_e \times {}^{13}\sigma_{e,TS}}{{}^{12}I_M^3 \times {}^{13}I_{M,TS}^3 \times {}^{13}\sigma_e \times {}^{12}\sigma_{e,TS}} \right)^{1/2}. \quad (10)$$

In general for hydrocarbons, the ratio ${}^{13}I_M^3 / {}^{12}I_M^3$ is greater than unity and is in magnitude in the range of per mil effects. For example, the ratio is 1.02 for ethene. The ratio of the moments of inertia of the transition states will generally be slightly larger

than those of the reactants due to increased mass and increased distances to the centres of mass such that $^{13}I_M^{3/12}I_M^3 < ^{13}I_{M,TS}^{3/12}I_{M,TS}^3$. This results in overall small inverse effects for compounds that experience no change in symmetry due to ^{13}C -labeling, both as the reactant NMHC and in the transition state.

However, for molecules where there is a change in external symmetry between the reactants and the transition state, such as ethene, symmetry effects could be large, depending on the symmetry of the transition state. $^{12}\text{CH}_2^{12}\text{CH}_2$ has a symmetry number of 4 while $^{13}\text{CH}_2^{12}\text{CH}_2$ has a symmetry number of 2. If all symmetry is lost during the formation of the transition state, the ratio of the changes in symmetry for the two isotopologues would be 2 and the corresponding contribution to the KIE would be a factor of approximately 1.4 ($2^{1/2}$). Because the overall KIE for the Cl-reaction of ethene is very close to 1 and not near 1.4, we conclude that there must not be significant change in the symmetry of the ethene molecule in the formation of the transition state. Thus, the difference in symmetry between labeled and unlabeled transition state also must be a factor of two. The most likely explanation is that the Cl atom is located symmetrically to the two carbon atoms, and not yet predisposed to addition to a specific carbon atom.

Reactions between aromatic compounds and Cl atoms occur almost exclusively as hydrogen atom abstractions from an alkyl group (Fantechi *et al.*, 1998; Markert and Pagsberg, 1993). For this reason, we expect the KIEs for reactions of aromatics with Cl atoms to be similar in magnitude to the reactions of Cl atoms with saturated hydrocarbons of the same size, in contrast to the large difference between the KIEs for OH-reactions of alkanes and aromatic hydrocarbons.(Anderson *et al.*, 2004a; Anderson *et al.*, 2004b) Indeed, as shown in Table III, the KIEs in Cl-atom reactions with aromatic compounds

are close to the corresponding KIEs for reactions of *n*-alkanes having equal numbers of carbon atoms. Nevertheless, there are indications that they are somewhat higher. Although the difference is statistically significant only in the case of ethylbenzene, the fact that all three Cl-reaction KIEs are higher for the aromatic compounds suggests that this difference is systematic. This may be due to the aromatic ring system, such that ^{13}C atoms present in the phenyl group may contribute enhanced secondary isotope effects to the overall KIE. This would suggest that not only is a ^{13}C atom present at the reaction site on an alkyl group significant, but that a ^{13}C atom at any location in the aromatic structure may contribute to a small extent to the isotope effect. The higher KIEs for aromatic-Cl reactions may also be due to differences in rotational partition functions. However, from the only slight difference in KIEs between alkanes and aromatic compounds, it can be concluded that these contributions are likely small.

5. Atmospheric Relevance

There are two major considerations for the impact of Cl-atom reactions on stable carbon isotope ratios of ambient light hydrocarbons. By what magnitude will Cl-atom reactions contribute to changes in stable carbon isotope ratios, and is it possible to use isotope ratios to differentiate between the impacts of Cl-atom chemistry and OH-radical chemistry? For the former to be significant, Cl-atom chemistry has to contribute significantly to changes in concentration. For the latter to be possible, the KIEs for OH and Cl chemistry have to be different.

For example, if the propane mixing ratio in an air mass was observed to decrease from 2 ppbV to 200 pptV, because the KIEs for the reactions of propane with Cl atoms and OH radicals are very similar, $(5.46 \pm 0.35)\%$ (Anderson *et al.*, submitted 2006) and

$(6.44 \pm 0.14)\text{‰}$ (Anderson *et al.*, 2004a) respectively, it would be difficult to use the change in stable carbon isotope ratio distinguish between the Cl- and OH-reactions without outside information regarding the radical concentrations. However, for a similar tenfold change in the mixing ratio of toluene, the change in stable carbon isotope ratio due to solely OH-radical reaction ($\varepsilon = 5.95 \pm 0.28$) (Anderson *et al.*, 2004b) would be 14‰, whereas the change in isotope ratio due to only Cl-atom reaction ($\varepsilon = 2.89 \pm 0.31$) would be 7‰.

The change of the stable carbon isotope ratio of hydrocarbon z due to reaction with oxidants i and j can be described using the following general equation, similar to the equation used by Iannone *et al.* to describe the contributions by OH and O_3 reactions (Iannone *et al.*, 2003):

$$\delta_z - {}^0\delta_z = t \times ({}^i k_z \cdot [i]_{av} \cdot {}^i \varepsilon_z + {}^j k_z \cdot [j]_{av} \cdot {}^j \varepsilon_z) \quad (11)$$

where δ_z and ${}^0\delta_z$ are the average ambient stable isotope ratio and the average stable isotope ratio of the emission for hydrocarbon z , t is the average age of hydrocarbon z , and $[i]_{av}$ and $[j]_{av}$ are the average concentrations over time t according to:

$$[i]_{av} = \frac{\int_0^t [i] dt}{t} \quad (12)$$

Thus, assuming only reaction with OH and Cl, the relative impact of the reaction with Cl atoms on the overall isotope ratio change is dependent on the magnitude of the KIEs, the

rate constants and the atmospheric concentration of Cl atoms and OH radicals. The percentage of the overall isotope ratio change of a hydrocarbon z due to reaction with Cl atoms, $\Delta\delta^{13}\text{C}_{\text{Cl}}/\Delta\delta^{13}\text{C}_{\text{total}}$ (%) where $\Delta\delta^{13}\text{C}_{\text{Cl}} + \Delta\delta^{13}\text{C}_{\text{OH}} = \Delta\delta^{13}\text{C}_{\text{total}} = \delta_z - {}^0\delta_z$, depends on the ratio of the concentrations of the Cl atoms and OH radicals, $[\text{Cl}]/[\text{OH}]$ such that:

$$\frac{\Delta\delta^{13}\text{C}_{\text{Cl}}}{\Delta\delta^{13}\text{C}_{\text{total}}} = \frac{{}^{\text{Cl}}\epsilon_z \cdot {}^{\text{Cl}}k_z \cdot [\text{Cl}]/[\text{OH}]}{{}^{\text{Cl}}\epsilon_z \cdot {}^{\text{Cl}}k_z \cdot [\text{Cl}]/[\text{OH}] + {}^{\text{OH}}\epsilon_z \cdot {}^{\text{OH}}k_z} \times 100\% \quad (13)$$

For most hydrocarbons, because the magnitude of the KIEs for reactions with Cl atoms and OH radicals are similar, the impact of chlorine atom reactions will be insignificant under continental background conditions where Cl-atom concentrations are less than 10^2 cm^{-3} (Figure 2) and OH-radical concentrations are 10^5 cm^{-3} or greater. However, as previously discussed, under Polar sunrise conditions and in the marine boundary layer Cl atom concentrations may reach concentrations as high as 10^5 cm^{-3} . With a typical average OH radical concentration of 10^6 cm^{-3} , it is thus plausible that the ratio of Cl atoms to OH radicals may exceed 0.1. Table IV shows the percentage impact of the Cl-atom reaction on the overall change in stable carbon isotope ratio for $[\text{Cl}]/[\text{OH}]$ ratios ranging from 0.0001 to 0.1 using Equation (13) for saturated and unsaturated hydrocarbons where KIE data is available for both OH and Cl reactions.

For most hydrocarbons, the reaction with Cl atoms has little impact on the overall change in stable carbon isotope ratio from chemical reaction when the ratio of Cl atoms to OH radicals is less than 0.001. For light alkenes, there may be an additional impact on $\delta^{13}\text{C}$ due to reaction with ozone (Iannone *et al.*, 2003); this would further decrease the relative importance of the Cl reaction for the overall isotope ratio change. For ethane,

however, even at a $[\text{Cl}]/[\text{OH}]$ ratio of 0.001 the reaction with Cl accounts for almost one-quarter of the overall isotope change. For $[\text{Cl}]/[\text{OH}]$ values closer to the levels possible at Polar sunrise and in early morning marine boundary layers, the impact of the reactions with Cl atoms can be significant for all of the hydrocarbons studied. This indicates that both reactions with Cl and OH should be considered when interpreting isotope ratio data from these types of locations.

6. Conclusions

The $^{12}\text{C}/^{13}\text{C}$ -KIEs in all studied reactions of unsaturated hydrocarbons with chlorine atoms are normal KIEs. For the reactions of aromatic hydrocarbons with Cl atoms, the measured KIEs are all significantly lower than the previously reported KIEs in the reactions of aromatic hydrocarbons with OH radicals. The aromatic-Cl KIEs are similar in magnitude to previously reported KIEs for the reactions of alkanes with OH radicals when comparing compounds with the same numbers of carbon atoms. This is consistent with the knowledge that Cl-reactions of aromatic hydrocarbons occur via hydrogen atom abstractions from an alkyl group rather than via additions to the aromatic ring. It would be interesting to contrast the KIEs reported here for the reactions of alkylbenzenes with Cl against the KIE for benzene + Cl. However, because the rate coefficient for the latter is on the order of $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Shi and Bernhard, 1997), the KIE measurement method used in this work is not suitable for this reaction.

The measured carbon KIEs for the reactions of alkenes with Cl atoms do not have the N_{C}^{-1} dependence that has been observed in all other measured hydrocarbon-radical reactions studied to date. There are strong indications of inverse effects for individual steps of the reaction sequence resulting from the stabilization of the intermediate in the reaction mechanism. However, these effects are smaller in magnitude than the sum of the normal KIE components. Due to the pressure-dependent competition between the stabilization and decay of the intermediate, the impact of the inverse effect is largest for the KIE of ethene + Cl, for which the reaction is below the high-pressure limit under tropospheric conditions. The impact of the inverse effect on the overall KIE decreases with increasing alkene mass. This is compatible with the decrease of the high-pressure

limit for the addition reaction of alkenes with increasing carbon number. A pressure of one atmosphere of air is close to the high pressure limit for alkene-Cl reactions. For heavier alkenes the high-pressure limit is reached at one atmosphere. With increasing carbon number there is also an increasing contribution of abstraction and addition-elimination channels to the overall reaction. This is in contrast to the $^{12}\text{C}/^{13}\text{C}$ -KIEs for the reactions of alkenes with OH radicals. For these reactions the addition pathway dominates under tropospheric conditions. Furthermore, for the addition of OH to carbon-carbon double bonds, the high-pressure limit is reached for tropospheric conditions. The differences in the carbon number dependence of the KIEs between reactions of alkenes with Cl-atoms and OH-radicals are therefore fully compatible with our understanding of the reaction mechanisms.

Because the KIE for the reaction of ethene + Cl was on the order of 1.01, and not near 1.4, we conclude that for unlabeled ethene the transition state has a symmetry number of 2, which is the case if the Cl atom in the transition state is positioned symmetrically to the two carbon atoms, not yet predisposed to reaction at either atom. This conclusion also applies to the transition states of the ethene-OH and benzene-OH reactions, as the KIEs for these reactions are also not large with respect to the potential changes in symmetry.

Reactions of light NMHC with Cl atoms can have a significant impact on the stable carbon isotope ratios of these compounds in regions where the Cl atom to OH ratio reaches levels of 0.01 or greater, which is possible in both arctic and marine environments. These reactions may not have a large impact on the average stable carbon isotope ratio for long-lived species in marine environments where episodes of elevated Cl

atoms are short in comparison to the lifetime of the species. In arctic conditions at Polar sunrise, however, the impact on the isotope ratios of both long-lived and short-lived species could be significant. Thus, for more accurate interpretation of stable carbon isotope data in these regions, both OH and Cl chemistry should be taken into account. More importantly, due to the differences between the $^{12}\text{C}/^{13}\text{C}$ -KIEs for the reactions of unsaturated hydrocarbons with Cl atoms and OH radicals, particularly for the aromatic compounds which are relatively unaffected by O_3 chemistry, we predict that based on the KIEs reported in this work, isotope ratio measurements will be a valuable indicator for differentiating between Cl and OH chemistry.

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Figure 1. Plot of the mean carbon kinetic isotope effects (KIEs) for the reactions of Cl atoms with unsaturated hydrocarbons against the inverse of the number of carbon atoms, N_C . Error bars show the error of the KIE as shown in Table 2. The curves are reported carbon KIE least squares best-fits for sets of different reaction types: alkane-OH (Anderson *et al.*, 2004a); alkane-Cl KIEs (Anderson *et al.*, submitted 2006); alkene-OH (Anderson *et al.*, 2004a); alkene-O₃ (Iannone *et al.*, 2003); and aromatic-OH (Anderson *et al.*, 2004b).

Figure 2. The rate of change of stable carbon isotope ratios of four unsaturated hydrocarbons due to reaction with Cl atoms at three different Cl-atom concentrations in units of atoms cm⁻³. Also shown is the rate of change of the isotope ratio for these hydrocarbons due to reaction with 10⁵ OH radicals cm⁻³.

Table I. Measurements of the carbon kinetic isotope effects in the reactions of unsaturated hydrocarbons with Cl atoms at 298 ± 3 K and 100 kPa total pressure in air.

Hydrocarbon	Reaction Temperature, K	Cl_ϵ , ^a ‰	R^2	$10^{11}k$, ^b $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$
Ethene	298	5.65 ± 0.34	0.983	10.0 ± 1.2^c
Propene	298	5.69 ± 0.12	0.998	27.9 ± 4.1^d
Propene	299	5.44 ± 0.22	0.994	24.7 ± 6.0^e
1-Butene	299	5.93 ± 1.16	0.868	32.6 ± 4.2^c
1-Pentene	299	4.86 ± 0.63	0.937	42.2 ± 5.0^c
Cyclopentene	299	3.75 ± 0.14	0.996	73.2 ± 8.8^c
Toluene	299	2.67 ± 0.19	0.964	6.5 ± 0.5^f
Toluene	301	3.11 ± 0.18	0.997	6.9 ± 0.6^f
Ethylbenzene	299	2.05 ± 0.09	0.988	11.2 ± 0.8^f
Ethylbenzene	301	2.29 ± 0.02	1.000	11.7 ± 0.8^f
<i>o</i> -Xylene	299	2.23 ± 0.07	0.995	13.4 ± 1.2^g
<i>o</i> -Xylene	301	1.46 ± 0.22	0.977	12.8 ± 1.1^g

^aError shown is calculated from the standard error in the plot of Equation (1).

^bExperimental rate constant calculated using literature rate constants and uncertainties for the reference compound (Atkinson and Aschmann, 1985; Coquet and Ariya, 2000; Ezell *et al.*, 2002; Fantechi *et al.*, 1998; Shi and Bernhard, 1997; Smith *et al.*, 2002; Stutz *et al.*, 1998; Wallington *et al.*, 1989) and the standard error of the relative rate analysis.

^cPropene used as reference compound.

^dEthene used as reference compound.

^e1-Butene used as reference compound.

^f*o*-Xylene used as reference compound.

^gToluene used as reference compound.

Table II. Summary of the carbon kinetic isotope effects in the reactions of unsaturated hydrocarbons with Cl atoms, OH radicals and O₃ at 298 ± 3 K and 100 kPa total pressure in air.

Hydrocarbon	Average Cl ε, ^a ‰	OH ε, ‰	O ₃ ε, ^b ‰	Cl ^c $k_{\text{experimental}}$, 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹	Cl ^d $k_{\text{literature}}$, 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
Ethene	5.65 ± 0.34	18.6 ± 2.9 ^e	18.9 ± 2.8	10.0 ± 1.2	9.9 ± 1.1 ^f
					9.3 ± 0.6 ^g
					12.1 ± 0.7 ^h
					10.4 ± 1.5 ⁱ
Propene	5.56 ± 0.18	11.70 ± 0.19 ^j	9.5 ± 2.5	26.3 ± 2.2	23 ± 3 ^f
					27.6 ± 0.6 ^g
					32.2 ± 1.3 ^h
					24.4 ± 0.7 ^k
					26.4 ± 2.1 ^l
					26.8 ± 3.2 ⁱ
1-Butene	5.93 ± 1.16	7.40 ± 0.32 ^j	8.7 ± 1.0	32.6 ± 4.2	22 ± 3 ^f
					35.2 ± 0.7 ^g
					33.8 ± 4.8 ^l
					30.3 ± 7.3 ⁱ
1-Pentene	4.86 ± 0.63		6.7 ± 0.9	42.2 ± 5.0	48 ± 8 ^g
					39.7 ± 3.6 ^l
					44.0 ± 6.1 ⁱ
Cyclopentene	3.75 ± 0.14		6.7 ± 0.7	73.2 ± 8.8	
Toluene	2.89 ± 0.31	5.95 ± 0.28 ^m		6.7 ± 0.3	5.9 ± 0.5 ⁿ
					5.6 ± 1.3 ^p
					6.1 ± 2.0 ^q
					5.9 ± 0.3 ⁱ
Ethylbenzene	2.17 ± 0.17	4.34 ± 0.28 ^m		11.5 ± 0.4	10.9 ± 0.3 ^r
					13.4 ± 0.6 ^r
					12.2 ± 1.8 ⁱ
<i>o</i> -Xylene	1.85 ± 0.54	4.27 ± 0.05 ^m		13.1 ± 0.5	12 ± 1 ^h
					15 ± 1 ⁿ
					13.5 ± 2.1 ⁱ

^aUncertainty shown is the error of the mean KIE value for compounds with two KIE measurements, and the uncertainty from the standard error of the plot of Equation (1) for compounds with only one KIE measurement.

^bIannone *et al.*, (2003)

^cMean ^{Cl}*k* value with 1σ standard error of the *k* values determined using relative rate analysis for compounds measured more than once. For identification of the reference substances used in the relative rate measurements see Table I.

^dFor comparison, literature rate constants for the reaction with Cl atoms are included.

^eAnderson *et al.*, (2004a).

^fStutz *et al.*, (1998).

^gCoquet and Ariya, (2000).

^hWallington *et al.*, (1989).

ⁱMean literature rate constant with 1σ standard error.

^jRudolph *et al.*, (2000).

^kAtkinson and Aschmann, (1985).

^lEzell *et al.*, (2002).

^mAnderson *et al.*, (2004b).

ⁿShi and Bernhard, (1997).

^pFantechi *et al.*, (1998).

^qSmith *et al.*, (2002).

^rChadwick *et al.*, (2001).

Table III. Comparison of the rate constants and carbon kinetic isotope effects for the reactions of Cl atoms and OH radicals with C₇ and C₈ alkane and aromatic hydrocarbons.

Hydrocarbon	^{Cl} ε, ‰	10 ¹⁰ ^{Cl} <i>k</i> , cm ³ molecule ⁻¹ s ⁻¹	^{OH} ε, ‰	10 ¹² ^{OH} <i>k</i> , ^g cm ³ molecule ⁻¹ s ⁻¹
<i>n</i> -Heptane	2.06 ± 0.33 ^a	36.5 ± 0.7 ^b	1.96 ± 0.26 ^e	6.8 ± 1.4
Toluene	2.89 ± 0.31	5.9 ± 0.3 ^c	5.95 ± 0.28 ^f	5.6 ± 1.1
<i>n</i> -Octane	1.54 ± 0.26 ^a	41.0 ± 0.1 ^b	2.13 ± 0.39 ^e	8.1 ± 1.6
Ethylbenzene	2.17 ± 0.17	12.2 ± 1.8 ^d	4.34 ± 0.28 ^f	7.0 ± 1.8
<i>o</i> -Xylene	1.85 ± 0.54	13.5 ± 2.1 ^c	4.27 ± 0.05 ^f	13.6 ± 3.4

^aAnderson *et al.*, (Anderson *et al.*, submitted 2006)

^bHooshiyar and Niki, (Hooshiyar and Niki, 1995)

^cShi and Bernhard, (Shi and Bernhard, 1997)

^dChatwick *et al.*, (Chadwick *et al.*, 2001)

^eAnderson *et al.*, (Anderson *et al.*, 2004a)

^fAnderson *et al.*, (Anderson *et al.*, 2004b)

^gAtkinson and Arey, (Atkinson and Arey, 2003)

Table IV. Dependence of the relative impact on the stable carbon isotope ratios of nonmethane hydrocarbons due to reaction with Cl atoms on the ratio of Cl atoms to OH radicals.

Hydrocarbon	$\Delta\delta^{13}\text{C}_{\text{Cl}}/\Delta\delta^{13}\text{C}_{\text{total}}$, ^{a,b} %			
	[Cl]/[OH] = 0.0001	[Cl]/[OH] = 0.001	[Cl]/[OH] = 0.01	[Cl]/[OH] = 0.1
Ethane	2.9 ± 0.9	23 ± 6	75 ± 8	97 ± 9
Propane	1.5 ± 0.3	13 ± 3	60 ± 7	94 ± 8
Methylpropane	0.45 ± 0.12	4.3 ± 1.1	31 ± 6	82 ± 5
<i>n</i> -Butane	0.66 ± 0.16	6.2 ± 1.4	40 ± 6	87 ± 7
Methylbutane	0.33 ± 0.14	3.2 ± 1.3	25 ± 9	77 ± 24
<i>n</i> -Pentane	0.74 ± 0.28	6.9 ± 2.4	43 ± 9	88 ± 7
<i>n</i> -Hexane	0.53 ± 0.16	5.1 ± 1.4	35 ± 9	84 ± 23
<i>n</i> -Heptane	0.56 ± 0.14	5.3 ± 1.3	36 ± 7	85 ± 11
<i>n</i> -Octane	0.36 ± 0.10	3.5 ± 1.0	27 ± 6	78 ± 11
Cyclopentane	1.1 ± 0.3	9.8 ± 2.3	52 ± 7	92 ± 6
Cyclohexane	0.23 ± 0.05	2.2 ± 0.5	19 ± 4	69 ± 7
Methylcyclopentane	0.77 ± 0.59	7.2 ± 5.3	44 ± 28	89 ± 61
Ethene	0.04 ± 0.01	0.35 ± 0.07	3.4 ± 0.7	26 ± 4
Propene	0.04 ± 0.01	0.41 ± 0.08	4.0 ± 0.8	29 ± 5
1-Butene	0.06 ± 0.02	0.56 ± 0.17	5.3 ± 1.6	36 ± 10
Toluene	0.05 ± 0.01	0.51 ± 0.13	4.9 ± 1.2	34 ± 7
Ethylbenzene	0.09 ± 0.03	0.86 ± 0.27	8.0 ± 2.4	47 ± 11
<i>o</i> -Xylene	0.05 ± 0.02	0.47 ± 0.19	4.5 ± 1.8	32 ± 12

^aCalculated using Cl-reaction KIE values from this work, literature OH-reaction KIE values (Anderson *et al.*, 2004a; Anderson *et al.*, 2004b; Rudolph *et al.*, 2000), literature Cl-reaction KIE values (Anderson *et al.*, submitted 2006), and literature rate constant data (Aschmann and Atkinson, 1995; Atkinson and Arey, 2003; Atkinson, 1997; Chadwick *et al.*, 2001; Coquet and Ariya, 2000; Hooshiyar and Niki, 1995; Shi and Bernhard, 1997; Stutz *et al.*, 1998; Wallington *et al.*, 1989).

^bUncertainties are the standard deviations determined using the reported uncertainties in the literature data and in the KIEs from this work.