J. Phys. Chem. A **2007,** *111,* 495−504

Measurements of the $^{12}C/^{13}C$ Kinetic Isotope Effects in the Gas-Phase Reactions of Light Alkanes with Chlorine Atoms

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Received: July 21, 2006; In Final Form: November 10, 2006

The carbon kinetic isotope effects (KIEs) of the reactions of several light non-methane hydrocarbons (NMHC) with Cl atoms were determined at room temperature and ambient pressure. All measured KIEs, defined as the ratio of the Cl reaction rate constants of the light isotopologue over that of the heavy isotopologue ($^{Cl}k_{12}/^{Cl}k_{13}$) are greater than unity or normal KIEs. For simplicity, measured KIEs are reported in per mil according to $^{Cl}\epsilon = (^{Cl}k_{12}/^{Cl}k_{13} - 1) \times 1000‰$ unless noted otherwise. The following average KIEs were obtained (all in ‰): 10.73 ± 0.20 (ethane), 6.44 ± 0.14 (propane), 6.18 ± 0.18 (methylpropane), 3.94 ± 0.01 (*n*-butane), 1.79 ± 0.42 (methylbutane), 3.22 ± 0.17 (*n*-pentane), 2.02 ± 0.40 (*n*-hexane), 2.06 ± 0.19 (*n*-heptane), 1.54 ± 0.15 (*n*-octane), 3.04 ± 0.09 (cyclopentane), 2.30 ± 0.09 (cyclohexane), and 2.56 ± 0.25 (methylcyclopentane). Measurements of the $^{12}C/^{13}C$ KIEs for the Cl atom reactions of the C_2-C_8 *n*-alkanes were also made at 348 K, and no significant temperature dependence was observed. To our knowledge, these $^{12}C/^{13}C$ KIE measurements for alkanes + Cl reactions are the first of their kind. Simultaneous to the KIE measurement, the rate constant for the reaction of each alkane with Cl atoms was measured using a relative rate method. Our measurements agree with published values within ±20%. The measured rate constant for methylcyclopentane, for which no literature value is available, is $(2.83 \pm 0.11) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, 1σ standard error. The $^{Cl}\epsilon$ values presented here for the C_2-C_8 alkanes are an order of magnitude smaller than reported methane $^{Cl}\epsilon$ values (*Geophys. Res. Lett.*, **2000**, *27*, 1715), in contrast to reported $^{OH}\epsilon$ values for methane (*J. Geophys. Res. (Atmos.)*, **2001**, *106*, 23, 127) and C_2-C_8 alkanes (*J. Phys. Chem. A*, **2004**, *108*, 11537), which are all smaller than 10‰. This has important implications for atmospheric modeling of saturated NMHC stable carbon isotope ratios. ^{13}C-structure reactivity relationship values ($^{13}C-SRR$) for alkane−Cl reactions have been determined and are similar to previously reported values for alkane−OH reactions.

Introduction

Over the past decade, the usefulness of stable carbon isotope ratio ($\delta^{13}C$) measurements to investigate the chemistry of atmospheric nonmethane hydrocarbon (NMHC) has been demonstrated.[1−9] The majority of these investigations have dealt specifically with the OH radical chemistry of NMHC, which are on a global average the most important atmospheric reactions of NMHC. It has been established, however, that the use of carbon isotopes in the methane budget should include Cl-atom chemistry due to the relatively large carbon kinetic isotope effect ($^{12}C/^{13}C$ KIE) of the Cl reaction[10−14] in comparison to that of the OH reaction.[15,16] This is in spite of the small impact of chlorine chemistry on the overall atmospheric loss of methane.

Similarly, to quantify the impact of Cl-atom chemistry on the $\delta^{13}C$ of NMHC, accurate $^{12}C/^{13}C$ KIEs for Cl atom reactions must be known. It is understood that reactions with Cl atoms play a key role in the oxidation of NMHC at high latitudes during polar sunrise conditions.[17−22] As well, there is some evidence that elevated Cl-atom concentrations in the marine boundary layer may contribute to chemical removal of hydrocarbons from coastal environments.[23−26] Depending on the magnitude of the Cl reaction KIEs, however, chlorine chemistry could also have an impact on NMHC $\delta^{13}C$ in regions with low concentrations of Cl atoms. $^{12}C/^{13}C$ KIE measurements for the OH reactions of many NMHC have been reported,[4,27,28] but to our knowledge, there are no published $^{12}C/^{13}C$ KIEs for the reactions of saturated NMHC with Cl atoms. Here we present the first KIE measurements for the reactions of Cl atoms with saturated NMHC.

Unlike hydrogen isotope effects that can generate substantial KIEs ($k_H/k_D > 2$),[1] $^{12}C/^{13}C$ KIEs for saturated NMHC with natural abundance isotope ratios are typically less than 10‰. Nevertheless, these carbon KIEs for the reactions of hydrocarbons without artificial enrichment or depletion of ^{13}C can be determined with very good precision, typically ±0.5‰, using gas chromatography and combustion coupled with isotope ratio mass spectrometry (GCC-IRMS).[29] The KIE measurement technique used in this work allows for very precise determination of small isotope effects with ϵ values in the low per mil range by directly and simultaneously measuring change in NMHC concentration and isotope ratios. This eliminates the large uncertainty that is introduced by comparing separate measurements of labeled and unlabeled isotopologue reaction rate coefficients.

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10.1021/jp064634p CCC: $37.00 © 2007 American Chemical Society
Published on Web 12/29/2006

Experimental Method

The technique used for measuring Cl reaction $^{12}C/^{13}C$ KIEs is very similar to the technique for measuring OH reaction $^{12}C/^{13}C$ KIEs, described in detail in a previous publication by our group,[29] and required only a few modifications to generate Cl atoms rather than OH radicals. Hydrocarbons of interest ($\geq$97% purity grade from Sigma-Aldrich, Air Products, and Matheson Gas) with naturally occurring isotope abundances were injected into a 30 L PTFE reaction chamber filled with synthetic air (Air Products, 99.9%) to generate concentrations between 50 and 450 parts per million by volume (ppmV). The reaction chamber was housed in a modified drying oven that could regulate the temperature to within $\pm$3 K between room temperature and 473 K. Chlorine atoms were generated by photolyzing molecular Cl_2 (Sigma-Aldrich, $\geq$99.5% purity) injected into the reaction chamber using between 1 and 12 fluorescent lights mounted on the back of the drying oven and emitting in the ultraviolet range, $\lambda_{max} = 350$ nm. An automated system sampled 5 mL aliquots of the reaction chamber contents, which were separated using gas chromatography, converted to CO_2 on a combustion interface, and finally analyzed using an isotope ratio mass spectrometer (GCC-IRMS).

Samples were separated on an HP1 column (Agilent Technologies, 60 m, 0.32 mm i.d., 5 μm film thickness) and, using two-dimensional chromatography when necessary for further separation of the C_2 and C_3 hydrocarbons, on a PoraPlot Q column (Chromatographic Specialties, 60 m, 0.32 mm i.d.). The GC temperature programming varied depending on the hydrocarbons being separated, with all programs beginning at 243 K. An electronic pressure control unit adjusted the column head pressure with the temperature to maintain a constant 1.5 mL min^{-1} flow of helium carrier gas (Air Products, 99.995%). A small portion of the GC effluent, approximately 0.3 mL min^{-1}, was diverted to a Saturn 2000 ion trap mass spectrometer for peak identification and for verification of peak purity. The remaining portion of the GC effluent passed through a combustion interface for quantitative conversion of all carbon species to carbon dioxide, followed by a Nafion permeation dryer for water removal. Approximately 0.4 mL min^{-1} of the dried gas was then transferred through an open split interface into the ion source of a Finnigan MAT 252 IRMS for stable carbon isotope ratio measurement.

Prior to the reaction initiation, between two and four measurements were made of the contents of the reaction chamber to establish stability in concentration and stable carbon isotope ratio of the hydrocarbons. From these measurements, the mean relative standard deviation of the individual hydrocarbon concentration values was 1.4%, with all values lower than 5.0%. The mean standard deviation of the stable carbon isotope ratio ($\delta^{13}C$) values was 0.14‰, and all values were lower than 0.4‰. However, in four separate experiments, the initial concentration of a single hydrocarbon species, specifically propane, *n*-butane, methylbutane, and *n*-hexane, was higher than the dynamic range of the isotope ratio measurement on the IRMS. For these measurements, the initial concentrations of the compounds could be measured by the $^{12}C^{16}O_2$ mass 44 Faraday cup of the IRMS, but due to the limited dynamic range of the mass 45 and 46 signals, necessary for quantification of the ^{13}C signal, the initial $^{13}C/^{12}C$ measurements were not reliable. For these four experiments, the variability of the $\delta^{13}C$ of the other NMHC in each experiment was relied on to verify isotopic stability within the reaction chamber prior to reaction, and the initial isotope ratio data point for the KIE analysis was taken from a subsequent data point once the measurements fell within the IRMS dynamic range. Each reaction chamber measurement took approximately 1.5−2 h, depending on details of the GC separation. Measurements were made until less than 50% of the original hydrocarbon concentration remained. Following the initiation of the Cl atom reaction, at least three additional measurements of the reaction chamber contents were made.

From the traces generated by the IRMS software, stable carbon isotope ratios and hydrocarbon concentrations were determined. For hydrocarbons without artificial enrichment of ^{13}C, the abundance of the ^{12}C atoms in the sample is effectively proportional to the hydrocarbon concentration and could therefore be used directly to monitor the change of hydrocarbon concentration with time. The KIE, defined as the ratio of the rate constants for the species containing only ^{12}C atoms and those containing a ^{13}C atom, k_{12}/k_{13}, was determined from the slope of the linear least-squares fit of the relationship between concentrations and isotope ratios described by Anderson et al.[29] as:

$$\ln\left(\frac{^{12}C_t}{^{12}C_0}\right) = \frac{k_{12}/k_{13}}{1 - k_{12}/k_{13}} \times \ln\left(\frac{^{13}C_t/^{12}C_t}{^{13}C_0/^{12}C_0}\right) \qquad (1)$$

where C_t and C_0 are the abundances of carbon atoms at time t and $t = 0$, respectively. The experimental uncertainty for an individual experiment is determined from the uncertainty in the slope of eq 1 using an average of the pre-reaction-initiation measurements as the value for $t = 0$. For the compounds with initial concentrations that exceeded the IRMS linear range for isotope ratio measurement, the first data point that was within the linear range following the reaction initiation was used as the value for $t = 0$.

To verify that reaction with Cl atoms was the primary loss mechanism within the reaction chamber, the relative loss rates of each hydrocarbon in comparison to a reference hydrocarbon, selected from the other hydrocarbons in the experiment, were determined for each experiment. From this loss rate and the literature rate coefficient for the reference hydrocarbon, an experimental rate constant for each hydrocarbon was determined for comparison against literature values. For the experiments performed at 348 K, literature rate constant data is only available for propane and *n*-butane, for which the reported values are independent of temperature over the ranges 200−700 K and 290−600 K, respectively.[30]

Results and Discussion

In seven experiments with between two and six hydrocarbons each, the Cl reaction $^{12}C/^{13}C$ KIEs for 12 light alkanes were measured at 298 $\pm$ 3 K and atmospheric pressure. In two experiments containing C_6−C_8 *n*-alkanes, *o*-xylene was also present and was used as a reference compound. As well, the KIEs for the reactions of the *n*-alkanes from C_3−C_8 with Cl atoms were measured in one experiment at 348 $\pm$ 3 K, also at atmospheric pressure. A summary of the KIE measurements is given in Table 1.

For each compound, the experimental rate constant was determined relative to a reference compound. The measured rate coefficients and the reference hydrocarbon for each measurement are also shown in Table 1. The KIE results from all room-temperature experiments were averaged for each hydrocarbon and are reported in Table 2, with the uncertainty reported as the error of the mean KIE for each hydrocarbon with more than one measurement. The more conservative mean KIE value is reported rather than an error-weighted average KIE, as the uncertainties derived from the regression plots of eq 1 are

TABLE 1: Carbon Kinetic Isotope Effects for the Reactions of Light-Saturated Nonmethane Hydrocarbons with Cl Atoms Measured at 100 kPa Total Pressure in Air

alkane	temp, K	$^{\mathrm{Cl}}\epsilon$,[a] ‰	R^2	$10^{10}\,{}^{\mathrm{Cl}}k$,[b] cm^3 molecule^{-1} s^{-1}
ethane	299	10.59 ± 0.13	0.999	0.47 ± 0.03[c]
	300	10.88 ± 0.48	0.987	0.49 ± 0.12[c]
propane	295	6.22 ± 0.17	0.997	1.33 ± 0.03[d]
	299	6.53 ± 0.03	1.000	1.76 ± 0.11[e]
	300	6.59 ± 0.14	0.997	1.68 ± 0.11[e]
	348	6.04 ± 0.11	0.997	1.28 ± 0.08[f]
methylpropane	298	6.18 ± 0.18	0.995	1.38 ± 0.05[g]
n-butane	295	3.95 ± 0.15	0.996	2.11 ± 0.06[h]
	295	3.94 ± 0.10	0.997	2.07 ± 0.02[d]
	348	4.84 ± 0.14	0.996	2.23 ± 0.14[c]
methylbutane	298	1.79 ± 0.42	0.859	1.93 ± 0.07[g]
n-pentane	295	3.10 ± 0.19	0.993	2.64 ± 0.06[h]
	295	3.34 ± 0.11	0.997	2.59 ± 0.03[d]
	348	2.91 ± 0.11	0.986	3.05 ± 0.20[c]
cyclopentane	298	3.04 ± 0.09	0.996	3.05 ± 0.06[i]
cyclohexane	298	2.30 ± 0.09	0.992	3.83 ± 0.12[g]
methylcyclopentane	298	2.56 ± 0.25	0.955	2.82 ± 0.11[j]
n-hexane	295	2.46 ± 0.06	0.999	3.16 ± 0.07[h]
	295	2.68 ± 0.09	0.995	3.41 ± 0.12[k]
	299	1.13 ± 0.06	0.995	3.18 ± 0.50[l]
	301	1.80 ± 0.34	0.933	3.39 ± 0.48[l]
	348	1.55 ± 0.13	0.947	4.18 ± 0.28[c]
n-heptane	295	1.90 ± 0.08	0.995	3.55 ± 0.22[f]
	295	2.55 ± 0.15	0.989	3.55 ± 0.04[d]
	299	1.93 ± 0.20	0.948	3.61 ± 0.57[l]
	301	1.84 ± 0.46	0.888	3.31 ± 0.52[l]
	348	1.58 ± 0.13	0.949	4.56 ± 0.31[c]
n-octane	295	1.59 ± 0.07	0.996	4.03 ± 0.09[h]
	295	1.18 ± 0.09	0.976	3.68 ± 0.07[d]
	299	1.60 ± 0.24	0.902	3.91 ± 0.62[l]
	301	1.78 ± 0.22	0.970	3.65 ± 0.57[l]
	348	1.91 ± 0.13	0.962	4.42 ± 0.31[c]

[a] Error shown is calculated from the standard error in the plot of eq 1. [b] Experimental rate constant calculated using literature rate constants and uncertainties for the reference compound[29,31−33] and the standard error of the relative rate analysis. [c] Propane used as reference compound. [d] *n*-Hexane used as reference compound. [e] Ethane used as reference compound. [f] *n*-Butane used as reference compound. [g] Cyclopentane used as reference compound. [h] *n*-Heptane used as reference compound. [i] Methylpropane used as reference compound. [j] Cyclohexane used as reference compound. [k] *n*-Octane used as reference compound. [l] *o*-Xylene used as reference compound.

generally smaller than the errors derived from the reproducibility of the measurements. Also reported in Table 2 are the average rate constants determined from the relative rate analyses along with published rate constants. Although the hydrocarbon concentrations used in the experiments were significantly higher than ambient concentrations, the measured first-order reaction rate coefficients at these concentrations are consistent with reported measurements.

For compounds with multiple KIE measurements, the variability in the measurements was within the experimental uncertainties of the method, with the exception of the *n*-hexane KIE. The KIE for the reaction of *n*-hexane with Cl was measured four times at room temperature. The mean and the standard error of the KIE for *n*-hexane + Cl was (2.02 ± 0.40)‰, while the range of KIEs measured is 1.54‰. The lowest KIE observed (1.13 ± 0.06)‰ was from an experiment where the initial concentration of *n*-hexane was above the dynamic range of the isotope ratio measurement capability of the IRMS such that the isotope ratio measurements made prior to the reaction initiation were unreliable. However, the variability of the isotope ratios for the remainder of the hydrocarbons within the experiment were well within acceptable limits for these measurements, as discussed by Anderson et al.[29] Therefore, it is unlikely that in this experiment the *n*-hexane isotope ratio measurements have larger uncertainties than usual. Furthermore, this value was tested for outlier status using the Q-test, but did not qualify as an outlier from a purely statistical standpoint. Similarly, the experimental rate constant determined for *n*-hexane from this experiment was in agreement with the literature value within an uncertainty of ±20%. Thus, all measured KIE values for the room-temperature reaction of *n*-hexane with Cl atoms were used for the calculation of the mean KIE.

Relative Rate Analysis. From 26 measurements of the room-temperature experimental rate constants for the reactions of alkanes with Cl atoms, all were in agreement with the literature rate constants to within ±20%. Thus we are confident that in all our experiments the primary loss mechanism for each hydrocarbon was due to reaction with Cl atoms.

For the reaction of methylcyclopentane with Cl atoms, there is no known published rate constant. Our rate constant, measured relative to cyclohexane,[34] is (2.82 ± 0.11) × 10^{-10} cm^3 molecule^{-1} s^{-1}. The uncertainty in the rate constant is the 1σ standard error calculated from the standard error in the plot of the relative loss rates and the uncertainty in the literature rate constant for the reaction of cyclohexane with chlorine atoms. By using the group rate constants discussed by Atkinson,[35] the

TABLE 2: Summary of the Carbon Kinetic Isotope Effects and Rate Constants for the Reactions of Nonmethane Hydrocarbons with Cl Atoms at 298 ± 3 K and 100 kPa Total Pressure in Air

alkane	average $^{\mathrm{Cl}}\epsilon$,[a] ‰	$^{\mathrm{OH}}\epsilon$,[b] ‰	$10^{10}\,{}^{\mathrm{Cl}}k_{\mathrm{literature}}$, cm^3 molecule^{-1} s^{-1}	$10^{10}\,{}^{\mathrm{Cl}}k_{\mathrm{experimental}}$,[c] cm^3 molecule^{-1} s^{-1}
ethane	10.73 ± 0.20	8.57 ± 1.95	0.593 ± 0.035[e]	0.48 ± 0.01
propane	6.44 ± 0.14	5.46 ± 0.35	1.4 ± 0.1[e]	1.59 ± 0.23
methylpropane[d]	6.18 ± 0.18	8.45 ± 1.49	1.30 ± 0.01[f]	1.38 ± 0.05
n-butane	3.94 ± 0.01	5.16 ± 0.67	2.1 ± 0.1[e]	2.09 ± 0.03
methylbutane[d]	1.79 ± 0.42	2.91 ± 0.43	1.96 ± 0.02[f]	1.93 ± 0.07
n-pentane	3.22 ± 0.17	2.85 ± 0.79	2.51 ± 0.02[f]	2.62 ± 0.03
cyclopentane[d]	3.04 ± 0.09	1.84 ± 0.13	3.3 ± 0.1[g]	3.05 ± 0.06
n-hexane	2.02 ± 0.40	2.20 ± 0.07	3.06 ± 0.03[f]	3.20 ± 0.15
cyclohexane[d]	2.30 ± 0.09	4.46 ± 0.51	3.1 ± 0.1[h]	3.83 ± 0.12
methylcyclopentane[d]	2.56 ± 0.25	1.77 ± 0.53	3.0 ± 1.5[i]	2.82 ± 0.11
n-heptane	2.06 ± 0.19	1.96 ± 0.26	3.65 ± 0.07[f]	3.50 ± 0.13
n-octane	1.54 ± 0.15	2.13 ± 0.39	4.1 ± 0.1[f]	3.82 ± 0.18

[a] Uncertainty reported is the error of the mean KIE value for compounds with more than one KIE measurement, and the uncertainty from the standard error of the plot of eq 1 for compounds with only one measurement. [b] For comparison, the reported KIEs for reaction with OH radicals at 298 ± 3 K are included.[27] [c] Average experimental $^{\mathrm{Cl}}k$ value and 1σ standard error of the rate constants determined using relative rate analysis for compounds measured more than once. [d] Errors given are the errors derived from the slope of the relative rate plots as only one measurement was made. [e] Atkinson et al.[30] [f] Hooshiyar and Niki.[31] [g] Wallington et al.[33] [h] Aschmann and Atkinson.[34] [i] Calculated using group rate constants as described by Atkinson.[35]

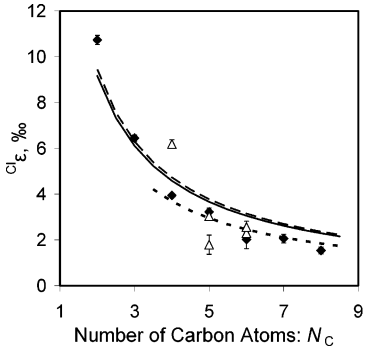

Figure 1. Plot of the $^{12}C/^{13}C$ KIEs for the reactions of saturated NMHC with Cl atoms. The solid curve is the N_C^{-1} linear least-squares fit determined using all the alkane KIE data, and the dashed and dotted curves are the N_C^{-1} linear least-squares fits using all the *n*-alkane data and the *n*-alkane data with four or more carbon atoms, respectively. The error bars are the error of the mean KIE for compounds with more than one KIE measurement and the standard error in the plot of eq 1 for compounds with only one KIE measurement.

rate constant for this reaction can be estimated. Although there are recommended ring strain factors for the OH radical reactions of cyclic alkanes, there are no recommended ring strain factors for Cl atom reactions of three-, four-, or five-membered rings. By using the literature rate constant for the reaction of cyclopentane with Cl atoms, 3.25×10^{-10} cm^3 molecule^{-1} s^{-1},[33] the measured rate constant for methylcyclopentane from this work, 2.82×10^{-10} cm^3 molecule^{-1} s^{-1}, and published group rate constants for hydrogen atom abstraction from primary, secondary, and tertiary carbon atoms by a chlorine atom,[35] we estimate a five-membered ring strain factor F_5 of 1.02. This is close enough to unity to estimate that ring strain has no effect on this rate constant. Without considering ring strain, the calculated rate constants for cyclopentane and methylcyclopentane of 2.90×10^{-10} and 3.02×10^{-10}, respectively, both in cm^3 molecule^{-1} s^{-1}, are both within ±15% of the experimentally determined rate constants.

Carbon Number Dependence of KIEs. A plot of the mean KIEs against the number of carbon atoms N_C is shown in Figure 1. On the basis of the assumption that the probability of a reaction occurring at the ^{13}C atom is inversely proportional to N_C and that the isotope fractionation is independent of the reaction site, the KIEs for all measured alkane−Cl reactions can be described as $^{Cl}\epsilon = (18.3 \pm 1.2)‰ \times N_C^{-1}$ with an R^2 value of 0.846. The same relationship for only the *n*-alkane data gives a similar dependence of $^{Cl}\epsilon = (18.9 \pm 1.3)‰ \times N_C^{-1}$ with an R^2 value of 0.923. As shown in Figure 1, these curves give a reasonable first-order description of the measured Cl reaction KIEs, but they overestimate KIEs for $N_C > 3$ and neglect potential differences between reactions at primary, secondary, and tertiary carbon atoms. A third relationship for the carbon number dependence of the C_4-C_8 *n*-alkanes, $^{Cl}\epsilon = (14.7 \pm 0.8)‰ \times N_C^{-1}$ with an R^2 value of 0.891, is also included in Figure 1. Considering the difference between the constant for the latter relationship and that of the relationship that includes all the *n*-alkane data, it appears that the reactions with ethane and propane may have Cl-atom reaction mechanisms that fall between those of methane and the remainder of the *n*-alkanes. This may be simply due to the difference of primary and secondary carbon atoms, which is discussed in the following section.

^{13}C-Structure Reactivity Relationship. A better description of the alkane−Cl KIE values was made using an approach based on the structure reactivity relationship (SRR) for the reactions of Cl atoms with alkanes described by Greiner[36] and later modified by Atkinson,[35] similar to the ^{13}C and H/D structure reactivity relationships for the reactions of OH radicals and Cl atoms with alkanes described previously.[27,37−41] Atkinson discussed the use of SRR for approximating the rate constants of the reactions of Cl atoms with alkanes using the group rate constants $k_{1°} = 3.5 \times 10^{-11}$, $k_{2°} = 9.3 \times 10^{-11}$, and $k_{3°} = 6.8 \times 10^{-11}$, all in cm^3 molecule^{-1} s^{-1},[35] for the H-atom abstraction by a Cl atom from a primary, secondary, and tertiary carbon atom, respectively, along with individual substituent factors $F(X) = 1.00$, $F(Y) = F(Z) = 0.79$, where substituents are $X = -CH_3$, $Y = -CH_2-$ and $Z = >CH-$. For example, the rate constant for the reaction of propane with Cl atoms is:

$$k = F(Y)k_{1°} + F(X)F(X)k_{2°} + F(Y)k_{1°} \tag{2}$$

which can be simplified to:

$$k = 2Fk_{1°} + k_{2°} \tag{3}$$

where $F = F(Y) = F(Z) = 0.79$. In analogy to this, the rate constants k_{12} for propane can be written using the following:

$$k_{12} = 2Fk_{1°12} + k_{2°12} \tag{4}$$

Similarly, the rate constant k_{13} for the reaction of a Cl atom with a molecule containing one ^{13}C atom can be written as the sum of the products of probabilities for each carbon atom being labeled and the resultant rate constant for that particular possibility determined using the appropriate group rate constants. The probability that one hydrocarbon molecule contains more that one ^{13}C atom is very low and therefore can be ignored without introducing any significant error. We also assume that the ^{13}C atom is randomly distributed between the carbon atoms of the heavier isotopologue. Strictly speaking, this is a simplification, as fractionation during the formation processes as well as during reactions in the atmosphere may lead to nonrandom distribution. However, it has been shown that the error introduced by this assumption depends on the extent of site-specific isotope enrichment and the magnitude of site-specific KIEs.[39] Because of the small isotope effects observed for ^{13}C, it can be expected that, for molecules without artificial enrichment or depletion of ^{13}C, such effects will be well within the uncertainties in the $^{12}C/^{13}C$ KIE measurements at this time. Therefore, again using propane as an example, the rate constant k_{13} for reaction of Cl atoms with propane containing ^{13}C is:

$$k_{13} = {}^{2}/_{3}(Fk_{1°13} + Fk_{1°12} + k_{2°12}) + {}^{1}/_{3}(k_{2°13} + 2Fk_{1°12}) \tag{5}$$

It is assumed that the F factors are independent of the mass of the carbon atom. The ^{13}C-specific group rate constants for the reactions of Cl atoms with saturated hydrocarbons can be estimated from our measured KIEs. The difference between the rate constants for labeled and unlabeled compounds can be derived from our experimental results, $k_{13} - k_{12} = -k_{12}\epsilon/(1000 + \epsilon)$. For propane, combining eqs 4 and 5, replacing $k_{1°13} - k_{1°12}$ with $\Delta_{1°13}$, and $k_{2°13} - k_{2°12}$ with $\Delta_{2°13}$, gives:

$$k_{13} - k_{12} = -k_{12}\epsilon/(1000 + \epsilon) = ({}^{1}/_{3})(2F\Delta_{1°13} + \Delta_{2°13}) \tag{6}$$

With the same approach used by Anderson et al.,[27] it is assumed that the group rate constants $k_{1°}$, $k_{2°}$, and $k_{3°}$ discussed by Atkinson[32] are $k_{1°12}$, $k_{2°12}$, and $k_{3°12}$ for reactions at ^{12}C atoms and that the rate constant k derived from the SRR method is the rate constant k_{12} for the reaction of Cl atoms with a hydrocarbon containing only ^{12}C atoms. This is a simplification because, typically, rate constants are determined using com-

TABLE 3: ^{13}C−SRR Values for the Reactions of Hydrocarbons with Cl Atoms at 298 K and 100 kPa Total Pressure in Air

hydrocarbon or hydrocarbon group	$10^{13}\ {}^{\mathrm{Cl}}\Delta_{1°13}$, cm^3 molecule^{-1} s^{-1}	$10^{13}\ {}^{\mathrm{Cl}}\Delta_{2°13}$, cm^3 molecule^{-1} s^{-1}	$10^{13}\ {}^{\mathrm{Cl}}\Delta_{3°13}$, cm^3 molecule^{-1} s^{-1}
ethane	-6.3 ± 0.1		
propane	-12.1 ± 1.2^{a}		
C_4−C_8 *n*-alkanes	-3.8 ± 5.0	-7.8 ± 2.2	
cyclopentane		-15.8 ± 0.7	
cyclohexane		-11.3 ± 0.6	
methylpropane			-17 ± 1^{b}
methylbutane			$10 \pm 5^{a,b}$
methylcyclopentane			$-8 \pm 8^{a,b}$
average[c]	-6.0 ± 0.1	-13.2 ± 0.6	-16 ± 1

[a] Calculated using the average ${}^{\mathrm{Cl}}\Delta_{2°13}$ value. [b] Calculated using the average ${}^{\mathrm{Cl}}\Delta_{1°13}$ value. [c] Determined using error-weighted averaging.

pounds with natural carbon isotope ratios, which means that they contain about 1.1% ^{13}C atoms. However, because the carbon KIEs are small in comparison to the rate constants for the individual isotopologues, the relative difference between k_{12} and the measured value for natural abundance compounds is approximately 0.01%, which is more than an order of magnitude lower than typical uncertainties of experimental rate constants. Rate constants determined for natural abundance NMHC, such as literature rate constants, are therefore valid approximations for k_{12}. From eq 6 and similar relations for other hydrocarbons or hydrocarbon groups,[27] the group rate constants $k_{1°13}$, $k_{2°13}$, and $k_{3°13}$ for reactions at primary, secondary, and tertiary ^{13}C atoms can be derived using measured KIEs and known literature rate constants.

The group ^{13}C−SRR values $\Delta_{1°13}$, $\Delta_{2°13}$, and $\Delta_{3°13}$ were determined using the method described in detail previously[27] and are summarized in Table 3. From the KIE results for the reaction of ethane with Cl atoms, $k_{13} - k_{12} = \Delta_{1°13}$ and k_{12} taken from literature, the ^{13}C−SRR value was determined directly as $(-6.3 \pm 0.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, with the uncertainty determined from the uncertainties in ${}^{\mathrm{Cl}}\epsilon_{\mathrm{ethane}}$ and the literature rate constant ${}^{\mathrm{Cl}}k_{\mathrm{ethane}}$. From the KIE results for the C_4−C_8 *n*-alkanes, ${}^{\mathrm{Cl}}\Delta_{1°13}$ and ${}^{\mathrm{Cl}}\Delta_{2°13}$ were determined using the general equation derived by Anderson et al.:[27]

$$-k_{12}\epsilon/(1000+\epsilon) = N_{\mathrm{C}}^{-1}[2F\Delta_{1°13} + (2F - 4F^2)\Delta_{2°13}] + F^2\Delta_{2°13} \quad (7)$$

From a linear least-squares fit to the measured KIE data, $\Delta_{1°13} = (-3.8 \pm 5.0) \times 10^{-13}$ and $\Delta_{2°13} = (-7.8 \pm 2.2) \times 10^{-13}$, both in units of cm^3 molecule^{-1} s^{-1}, were derived from the standard errors of the slope and *y*-intercept. The large uncertainty of this $\Delta_{1°13}$ value is attributed to the small contribution of the methyl groups to the overall reactivity of *n*-alkanes with four or more carbon atoms.

From the KIEs for the Cl reactions of cyclopentane and cyclohexane, $\Delta_{2°13}$ values were determined to be $(-15.8 \pm 0.7) \times 10^{-13}$ and $(-11.3 \pm 0.6) \times 10^{-13}$, both cm^3 molecule^{-1} s^{-1}, respectively. For propane, because eq 6 contains both $\Delta_{1°13}$ and $\Delta_{2°13}$, the average $\Delta_{2°13}$ $(-13.2 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} was used to determine $\Delta_{1°13}$ at $(-8.7 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The uncertainty was determined using the uncertainties in ${}^{\mathrm{Cl}}\epsilon_{\mathrm{propane}}$ and ${}^{\mathrm{Cl}}k_{\mathrm{propane}}$, as well as the uncertainty in the average $\Delta_{2°13}$ value. The average $\Delta_{2°13}$ and $\Delta_{1°13}$, $(-6.4 \pm 0.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, were then used to determine values for $\Delta_{3°13}$ from the Cl reaction KIEs for alkanes with tertiary carbon atoms. The $\Delta_{3°13}$ values were calculated as $(-17 \pm 1) \times 10^{-13}$, $(10 \pm 5) \times 10^{-13}$, and $(-8 \pm 8) \times 10^{-13}$, all in cm^3 molecule^{-1} s^{-1} from the KIE values for methylpropane, methylbutane, and methylcyclopentane, respectively. The resultant error-weighted average $\Delta_{3°13}$ is $(-16 \pm 1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

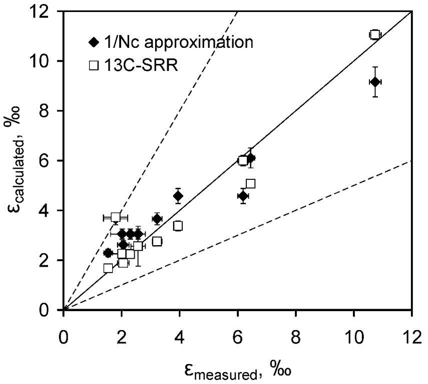

Figure 2. Comparison of the measured and calculated ^{12}C/^{13}C KIEs for the reactions of chlorine atoms with saturated hydrocarbons. The calculated KIEs are determined using the N_{C}^{-1} approximation ϵ (‰) = $(18.3 \pm 1.3) \times N_{\mathrm{C}}^{-1}$ and the average ^{13}C−SRR values reported in Table 3 with the $\Delta_{2°13}$ value from cyclopentane. A comparison of the cyclopentane KIE values is excluded as by definition the calculated value is the experimental value. The solid line is the $y = x$ line, and the dotted lines show the $y = 0.5x$ and $y = 2x$ lines.

The high uncertainty in the $\Delta_{3°13}$ value calculated using the methylcyclopentane KIE is due in part to the uncertainty of the KIE measurement, but also the small contribution of the reaction at the tertiary carbon atom to the overall rate constant, contributing approximately 14% to the overall rate constant. As well, there is poor agreement between the $\Delta_{3°13}$ values determined from methylpropane and methylbutane. It is clear from the uncertainties in the experimental data and the R^2 value from the KIE determination that the methylbutane KIE is far more uncertain than the methylpropane KIE. Error-weighted averaging leads to a $\Delta_{3°13}$ value with a relative small uncertainty, but this is predominantly based on one measurement with a small uncertainty.

A comparison of the measured ^{12}C/^{13}C KIEs for the reactions of Cl atoms with saturated hydrocarbons against the KIEs determined using the N_{C}^{-1} approximation and the ^{13}C−SRR values is shown in Figure 2. With the only exception being the KIE for the reaction of Cl atoms with methylbutane from both calculation methods, the calculated values are all within ±50% of the measured values, which is the acceptable tolerance suggested by Atkinson[32] for SRR-determined rate constants. The average percent deviations between measured KIEs and KIEs calculated using ^{13}C−SRR values or the N_{C}^{-1} approximation are (-4 ± 11)% and (16 ± 26)%, respectively.

Site-Specific Isotope Fractionation. By using each of the average ^{13}C−SRR values and the SRR $k_{1°}$, $k_{2°}$, and $k_{3°}$ values from Atkinson[35] as the values for $k_{1°12}$, $k_{2°12}$, and $k_{3°12}$, respectively, the site-specific isotope fractionation can be expressed as relative difference similar to the ϵ terminology for KIEs: $\epsilon_{1°} = (18.6 \pm 0.3)$‰, $\epsilon_{2°} = (14.4 \pm 0.7)$‰, and $\epsilon_{3°} =$

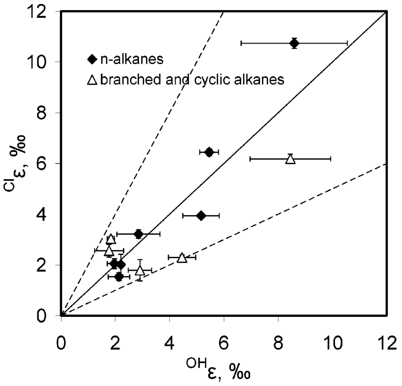

Figure 3. Comparison of the $^{12}C/^{13}C$ KIEs for the reactions of Cl atoms (this work) and OH radicals[20] with saturated C_2-C_8 NMHC. Error bars are the errors of the mean KIE for compounds with more than one measurement and the standard error in the least-squares regression line of eq 1 for compounds with only one measurement. The solid line shows the relationship $y = x$, and the dotted lines show the relationships $y = 2x$ and $y = {}^1/_2x$.

TABLE 4: Group Kinetic Isotope Effects and Group Rate Constants for Cl and OH Reactions with Saturated Hydrocarbons at 298 K and 100 kPa Total Pressure in Air

group[a]	$^{Cl}\epsilon$, ‰	$10^{11}\,{}^{Cl}k$,[b] cm^3 molecule^{-1} s^{-1}	$^{OH}\epsilon$,[c] ‰	$10^{13}\,{}^{OH}k$,[d] cm^3 molecule^{-1} s^{-1}
methane	65 ± 5[e]	0.01	3.9 ± 0.4	0.064
primary	18.6 ± 0.3	3.5	18.7 ± 5.2	1.4
secondary	14.4 ± 0.7	9.3	10.5 ± 0.7	9.3
tertiary	23.6 ± 1.6	6.8	14.4 ± 3.2	19.5

[a] Group from which a hydrogen atom is abstracted. [b] From Atkinson[35] and Atkinson et al.[42] [c] Methane + OH KIE from Saueressig et al.[16] Other group KIEs from Anderson et al.[27] [d] From Atkinson[35] and Atkinson and Arey.[43] [e] Average methane + Cl KIE from Tyler et al.,[13] Saueressig et al.,[14] and Crowley et al.,[10] with 2σ standard deviation uncertainty.

(23.6 ± 1.6)‰. As there were no literature uncertainties provided for the SRR k values for reactions at specific types of carbon atoms, the uncertainties in the above site-specific fractionation effects take into account only the uncertainties in the average $^{13}C-SRR$ values.

Comparison of OH- and Cl-Reaction KIEs. In contrast to the OH and Cl reactions of methane, where $^{Cl}\epsilon$ is more than an order of magnitude larger than $^{OH}\epsilon$,[10−16] the KIEs for the OH and Cl reactions of alkanes are similar, as shown in Figure 3. A least-squares regression of all measured NMHC-reaction KIEs gives $^{Cl}\epsilon$ (‰) = $(0.95 \pm 0.17) \times {}^{OH}\epsilon + (0.04 \pm 0.80)$ with an R^2 of 0.749. Although there is some scatter and some of the data have significant experimental errors, in general, $^{Cl}\epsilon$ and $^{OH}\epsilon$ differ by less than a factor of 2. Likewise, the constants describing the average carbon number dependence of the KIEs for the OH and Cl reactions of n-alkanes, (18.9 ± 1.3)‰ and (16.6 ± 1.0)‰,[27] respectively, are very similar. The difference of 2.3‰ is statistically not significant. Even for ethane, the second-lightest member of the alkanes, the value of $^{OH}\epsilon$ is well within a factor of 2 of $^{Cl}\epsilon$, although there is substantial uncertainty in the measured OH reaction KIE. This clearly shows that there is a significant difference in group isotope fractionation between reactions of methane and reactions of saturated NMHC.

In Table 4, the site-specific isotope fractionation effects for the reaction of alkanes with Cl atoms are compared with previously reported site-specific fractionation for alkane−OH reactions, including the values for OH and Cl reactions with methane. Also included in Table 4 are the group rate constants. The isotope fractionations at primary carbon atoms by reaction with OH and Cl are essentially identical. The abstractions of a hydrogen atom from a secondary carbon atom by both OH and Cl have smaller effects than abstractions from a primary carbon atom, with a slightly larger fractionation by the Cl reaction than by the OH reaction. There is a more significant difference in the group isotope fractionation values for abstraction from a tertiary carbon atom, again with a larger fractionation due to hydrogen abstraction by a Cl atom. It should be kept in mind, however, that the number of KIE measurements used to determine the tertiary group KIE values is quite small.

Although the rate constants for the OH and Cl reactions with saturated NMHC are 2 orders of magnitude apart, the KIEs are overall quite similar in magnitude. This, while not surprising given that both reactions occur as hydrogen abstraction reactions, emphasizes the difference between the reactions with methane and NMHC. Significant theoretical work has been done to calculate the $^{12}C/^{13}C$ KIEs in the OH and Cl reactions with methane, confirming experimental results that demonstrate that Cl + methane KIE is a factor of 10 greater than the OH + methane KIE.[10−16] Gupta et al.[11] attribute the 10-fold difference in the KIEs to the differences in the geometries in the transition states of the reactions. They calculate that the lengthening $H_3C\cdot\cdot\cdot HX$ bond, where X is −OH or −Cl, is approximately 0.2 Å longer in the more productlike $H_3C\cdots H\cdots Cl$ transition state than in the $H_3C\cdots H\cdots OH$ transition state. This is in agreement with the fact that the methane + Cl reaction is endothermic, while the OH reaction is slightly exothermic. The longer $H_3C\cdots HCl$ bond results in more movement of the carbon atom, producing a tunneling factor for the KIE that is an order of magnitude greater than that of the OH reaction transition state.

Unlike the endothermic methane + Cl reaction, the reactions of alkanes with Cl atoms are slightly exothermic,[44] which corresponds with their KIEs that are on the order of 1−10‰. The similarity between the KIEs for reactions of alkanes with Cl atoms and OH radicals also suggests that the sum of varying inverse and normal effects contributing to the overall KIEs have magnitudes such that, when combined, result in similar KIEs. To examine these KIEs and to understand the differences in the group isotope effects, we use transition state theory (TST).[45]

On the basis of TST, the bimolecular reaction rate constant k is:

$$k = (\kappa T/h) \times \exp(\Delta S^{\ddagger}/R) \times \exp(-\Delta H^{\ddagger}/RT) \qquad (8)$$

for the formation of the transition state from the reactants, where κ and h are Boltzmann's and Planck's constants, respectively, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$, the standard entropy and standard enthalpy, respectively, R is the ideal gas constant, and T is the absolute temperature. Equation 8 can be written for k_{12} and k_{13}:

$$k_{12} = (\kappa \mathrm{T}/h) \times \exp(\Delta S_{12}{}^{\ddagger}/R) \times \exp(-\Delta H_{12}{}^{\ddagger}/RT) \qquad (9a)$$

$$k_{13} = (\kappa \mathrm{T}/h) \times \exp(\Delta S_{13}{}^{\ddagger}/R) \times \exp(-\Delta H_{13}{}^{\ddagger}/RT) \qquad (9b)$$

Thus, the KIE is:

$$\mathrm{KIE} = k_{12}/k_{13} = \exp(\Delta\Delta S^{\ddagger}/\mathrm{R}) \times \exp(-\Delta\Delta H^{\ddagger}/\mathrm{RT}) \qquad (10)$$

such that $\Delta\Delta S^{\ddagger} = \Delta S_{12}{}^{\ddagger} - \Delta S_{13}{}^{\ddagger}$ and $\Delta\Delta H^{\ddagger} = \Delta H_{12}{}^{\ddagger} - \Delta H_{13}{}^{\ddagger}$. For a large $\Delta\Delta H^{\ddagger}$ where the difference in the zero-point energies (ZPEs) ΔE_0 between the two isotopologues and their transition states is large, the KIE will be substantial. This is the case for many measured H/D-KIEs for alkane−OH reactions.[37,38,41] In these situations, small differences between $\Delta S_{12}{}^{\ddagger}$ and $\Delta S_{13}{}^{\ddagger}$ can be ignored. However, for reactions where ΔE_0 is small, the overall KIE will be small, and contributions from differences in the reaction entropies can be significant. On the basis of fundamental statistical mechanics, the reaction entropy can be considered to be the sum of the individual entropy partition functions:

$$S = S_{\mathrm{tran}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + S_{\mathrm{elec}} \tag{11}$$

such that each entropy partition function can be investigated individually to estimate the impact of each degree of freedom and the overall impact on the KIE from the entropy term.

Because eq 10 involves the differences in $\Delta S^{\ddagger}$ for hydrocarbons containing a ^{13}C atom from those with only ^{12}C atoms, the electronic entropy partition function S_{elec} need not be considered, as the isotopologues are electronically identical. Similarly, the other entropy partition functions must be considered in light of the differences between the isotopologues, which allows for the elimination of all partition functions that are not affected by replacing one ^{12}C atom with a ^{13}C atom.

The translational entropy partition function S_{tran} of an ideal gas is:

$$S^{\ddagger}_{\mathrm{tran}} = 37.0 + \frac{3}{2} R \ln\left(\frac{M}{40}\right) + \frac{3}{2} R \ln\left(\frac{T}{298}\right) + R \ln(n) \tag{12}$$

where M is the molecular weight in amu, and n is the number of optical isomers. Thus, for the carbon KIE, differences between the translational entropy partition functions for the isotopologues are dependent on the molecular masses of the entire molecules, and not on the reaction site, such that:

$$\exp(\Delta\Delta S^{\ddagger}_{\mathrm{tran}}/R) = \left(\frac{M_{12,\mathrm{TS}} M_{13}}{M_{13,\mathrm{TS}} M_{12}}\right)^{3/2} \tag{13}$$

For ethane−OH and −Cl reactions, this gives a contribution to the overall KIE in eq 10, regardless of the reaction site, of 1.0178 and 1.0268, respectively. Here we use the actual ratio of k_{12}/k_{13} rather than an ϵ value in per mil. This is not insignificant compared to the measured KIEs. For reactions with propane and butane, the $\exp(\Delta\Delta S^{\ddagger}_{\mathrm{tran}}/R)$ term for reactions with Cl atoms contributes progressively smaller factors of 1.0151 and 1.0097, respectively, and for reactions with OH radicals 1.0094 and 1.0058, respectively.

In contrast to the translational partition function, the rotational partition function for a complex nonlinear labeled molecule, which is comprised of both external and internal rotations, depends not only on the mass of the molecule but also on the labeled position. For the transition state, the internal and external rotational components are dependent on both the labeled site and the reaction site. For molecules with several carbon atoms, this creates a very complex situation that cannot be easily reduced to differences in site labeling.

For a complex nonlinear molecule, the rotational entropy partition function is the sum of the external and internal rotations. The external component[45] is:

$$S^{\ddagger}_{\mathrm{rot-ext}} = 11.5 + \frac{R}{2} \ln\left(\frac{{I_{\mathrm{M}}}^3}{\sigma_{\mathrm{e}}}\right) + \frac{3}{2} R \ln\left(\frac{T}{298}\right) \tag{14}$$

where σ_{e} is the external symmetry number of the molecule and ${I_{\mathrm{M}}}^3$ is the product of the three principle moments of inertia, I^a, I^b, and I^c, the effective moments of inertia of the rotations about the a-, b-, and c- principle inertial axes, respectively. The differences between the changes in the external rotational entropy partition functions for the stable carbon isotopologues is therefore 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:

$$\exp(\Delta\Delta S^{\ddagger}_{\mathrm{rot-ext}}/R) = \left(\frac{{}^{13}{I_{\mathrm{M}}}^3 \times {}^{12}{\mathrm{I}_{M,TS}}^3 \times {}^{12}\sigma_{\mathrm{e}} \times {}^{13}\sigma_{e,TS}}{{}^{12}{I_{\mathrm{M}}}^3 \times {}^{3}{I_{\mathrm{M,TS}}}^3 \times {}^{13}\sigma_{\mathrm{e}} \times {}^{12}\sigma_{\mathrm{e,TS}}}\right)^{1/2} \tag{15}$$

In general, for hydrocarbons, the ratio ${}^{13}{I_{\mathrm{M}}}^3/{}^{12}{I_{\mathrm{M}}}^3$ is greater than unity, and significant in terms of per mil effects. The ratio is estimated to be 1.03 for ethane, 1.04 for propane, and 1.05 for n-butane. For the transition state, the external rotation component depends on both the labeled site or isotopomer and the reaction site, making the calculation even more complex. An estimate of the average impact may be derived by employing a two-atom model, assuming two spheres with masses ^{12}M or ^{13}M for the alkane component of the transition state and the mass of the radical for the radical component. The average ratio of the moments of inertia of the transition states will be slightly smaller than those of the reactants due to increased overall mass and decreased sensitivity to one amu differences such that ${}^{13}{I_{\mathrm{M}}}^3/{}^{12}{I_{\mathrm{M}}}^3 > {}^{13}{I_{\mathrm{M,TS}}}^3/{}^{12}{I_{\mathrm{M,TS}}}^3$. This results in overall normal KIE contributions according to eq 15.

The contribution to the overall KIE from the vibrational entropy partition function is unity for strong bonds with vibration frequencies ν where $\kappa T \ll hc\nu$.[45] For weaker bonds where κT is not $\ll hc\nu$, such as the newly formed HCl or HOH bonds in the transition state, the contribution may be significant. For each vibrational degree of freedom, the vibrational entropy partition function is:

$$S^{\ddagger}_{\mathrm{vib}} = R \ln[(1 - e^{-hc\nu/\kappa T})^{-1}] + R \tag{16}$$

where ν is the frequency of the vibration in cm^{-1}. Thus, the entropy contribution to the KIE function can be written for each of these weaker vibration frequencies ν_i:

$$\exp(\Delta\Delta S^{\ddagger}_{\mathrm{vib}}/R) = \frac{[1 - \exp(-hc^{12}\nu_i/\kappa T)][1 - \exp(-hc^{13}\nu_{i,\mathrm{TS}}/\kappa T)]}{[1 - \exp(-hc^{13}\nu_i/\kappa T)][1 - \exp(-hc^{12}\nu_{i,\mathrm{TS}}/\kappa T)]} \tag{17}$$

Although all bonds with carbon atoms contribute to the vibrational partition function, it is only from ν_i values of the degenerate weak bonds formed in the transition state that the vibration frequencies will contribute significantly to the overall KIE. For reactions of alkanes, Donahue and co-workers estimated that the primary impact is due to the vibration frequencies of the newly formed CHO and CHCl bends, 300 cm^{-1} and 250 cm^{-1}, respectively.[46,47] Assuming that these frequencies are for the ^{12}C bends, the ^{13}C bend frequencies can be determined using Teller−Redlich theory:[48] ${}^{13}\nu = {}^{12}\nu \times \sqrt{12/13} = 288$ cm^{-1} and 240 cm^{-1}. Thus, the vibration entropy partition function contributes factors of approximately $1 - 0.0356\, {N_{\mathrm{C}}}^{-1}$ and $1 - 0.0409\, {N_{\mathrm{C}}}^{-1}$ for reactions of alkanes with OH radicals and Cl atoms, respectively.

Of course, changes in vibration frequencies also result in changes in zero-point energies. Using the estimated vibration frequency for the degenerate ^{13}CHCl and ^{13}CHCl bends of 288 cm^{-1} and 240 cm^{-1}, the changes in zero-point energies would result in KIE contributions of approximately 1.0485 and 1.0585 for a hydrogen-atom abstraction from a ^{13}C atom by a Cl atom

TABLE 5: Estimated Stable Carbon KIE Contributions for the Reactions of Light Alkanes with Cl Atoms and OH Radicals

KIE contribution	alkane	OH_{298}	Cl_{298}	Cl_{348}
ΔZPE^a	ethane	1.0293	1.0243	1.0207
	propane	1.0195	1.0162	1.0138
	n-butane	1.0146	1.0121	1.0104
$\exp(\Delta\Delta S^{\ddagger}_{vib}/R)$	ethane	0.9822	0.9795	0.9774
	propane	0.9881	0.9864	0.9850
	n-butane	0.9911	0.9898	0.9887
ZPE and $S_{vib}{}^b$	ethane	1.0109	1.0033	0.9976
	propane	1.0074	1.0023	0.9986
	n-butane	1.0056	1.0018	0.9990
$\exp(\Delta\Delta S^{\ddagger}_{tran}/R)$	ethane	1.0178	1.0268	1.0268
	propane	1.0094	1.0151	1.0151
	n-butane	1.0058	1.0097	1.0097
$\exp(\Delta\Delta S^{\ddagger}_{rot-ext}/R)^c$	ethane	1.009	1.006	1.006
	propane	1.017	1.015	1.015
	n-butane	1.023	1.021	1.021

[a] Calculated using only the newly formed CHO and CHCl bends, with estimated $^{12}CHO = 300\ cm^{-1}$ and $^{12}CHCl = 250\ cm^{-1}$.[46,47] The overall zero-point energy contribution to the KIE, including the weakened C−H bonds, would be slightly closer to unity. [b] Combined stable carbon isotope effects of the contributions from the zero-point energy differences of the newly formed bonds and the vibrational entropy functions. [c] Estimated as described in the text.

and an OH radical, respectively. Accounting for the N_C^{-1} probability of the reaction occurring at the labeled carbon atom for ethane + Cl, this would result in a zero-point energy contribution to the overall KIE of approximately 24‰. However, the combined calculated isotope effects due to the differences in vibration frequencies for both entropy and enthalpy contributions for ethane, propane, and butane are all closer to unity, with values of 1.0033, 1.0023, and 1.0018, respectively, for Cl atom reactions, and 1.0110, 1.0074, and 1.0056, respectively, for OH radical reactions.

In addition to the differences in the zero-point energies of the newly formed bonds, there would also be a small influence from the differences in the zero-point energies of the weakened $^{12}C-H$ and $^{13}C-H$ bonds. These would have inverse effects, smaller than the normal effects from the new CHCl or CHO bends, but the extent to which these vibration frequencies are changed during the formation of the transition states is unknown. However, analysis of the temperature dependence of these reactions provides a means for elucidating this information, as shown in the next section.

Table 5 shows a summary of the estimated isotope effects due to one degree of freedom from each enthalpy component and the ZPE contribution of the newly formed CHO or CHCl bend for reactions with ethane, propane, and *n*-butane. The estimated contributions are all relatively small and of similar magnitudes, such that the KIEs are not highly dominated by any particular component. In general, because alkane−OH and alkane−Cl KIEs are influenced by both reaction enthalpies and reaction entropies, and because some of these contributions are dependent on site-labeling while others are not, it is clear that attempting to predict overall $^{12}C/^{13}C$ KIEs using site-specific isotope effects will not provide highly reliable estimates but rather only a general approximation.

Temperature Dependence. As shown in Table 5, because of the ZPE differences of the newly formed CHCl bends over the given reaction temperatures, a reduction of the isotope effect is predicted. Only a very small increase in the inverse kinetic isotope effect due to the vibrational partition function is calculated over the temperature range. The combined temperature dependence of these two effects changes their overall impact for the reaction with ethane, propane, and butane from 1.0033, 1.0023, and 1.0018, respectively, to 0.9977, 0.9986, and 0.9990. This suggests significant temperature dependence in the isotope effects, strongest for the reaction of Cl atoms with ethane.

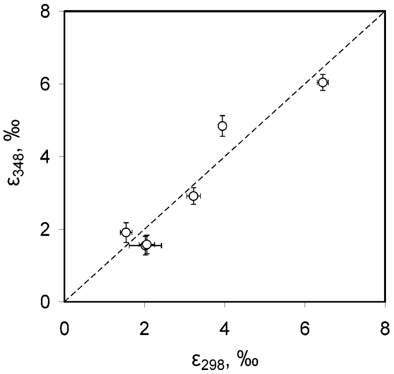

Figure 4. Comparison of the $^{12}C/^{13}C$ KIEs for the reactions of C_3-C_8 *n*-alkanes with Cl atoms at 298 and 348 K. Error bars show the error in the mean KIE for the KIEs measured at room temperature and the uncertainty determined using the standard error in the plot of eq 1 for the KIEs measured at 348 K. Also shown is the $y = x$ line.

A comparison of the KIEs measured at 348 K for the reactions of C_3-C_8 *n*-alkanes with Cl atoms to the KIEs measured at 298 K is shown in Figure 4. With only one KIE measurement for each *n*-alkane at 50 K above ambient temperature, there is overall very little indication for a significant change in the KIEs. A linear least-squares fit to the data gives the relationship ϵ_{348} (‰) = (0.99 ± 0.07) × ϵ_{298} with an R^2 value of 0.900. There is no predicted temperature dependence for the other entropy contributions to the isotope effect to explain the discrepancy between the predicted and measured temperature dependence. Thus, either the vibration frequency estimated by Donahue et al.[47] for the newly formed CHCl bend is an overestimate or other vibration frequencies contribute to the ZPE such that the overall predicted temperature dependence from ZPEs is relatively small.

Conclusions

The carbon kinetic isotope effects for the reactions Cl atoms and NMHC with natural ^{13}C abundance are small in comparison to the KIE for the reaction of Cl atoms with methane; the largest isotope effect is found for ethane, for which the reaction of the heavier isotopologue is less than 11‰ slower than for the light isotopologue. The kinetic isotope effects decrease with increasing carbon number and a first-order estimate can be obtained from a simple inverse dependence on carbon number. Although this simple approach does not allow prediction of the observed differences between *n*-alkanes and branched alkanes or cyclic and noncyclic alkanes with identical carbon number, it provides a good first approximation of the *n*-alkanes with four or more carbon atoms.

A better description of the measured carbon KIEs can be derived from site-specific isotope effects, similar to the SRR concept used for calculating rate constants. Although there are still several NMHC where predictions and experimental observations differ significantly, this method allows predictions of KIEs with better accuracy than a simple inverse carbon number dependence. One limitation of the isotope SRR concept is the relatively small number of available KIE measurements, which results in uncertainties of derived site-specific KIEs as well as the necessity to limit the number of carbon mass dependent parameters in the isotope SRR. It is expected that such uncertainties arising from the limited number of experimental data can be reduced when new measurements become available. A more fundamental problem is that the overall KIEs for reactions of alkanes result from contributions due to changes in zero-point energy as well as translational, rotational, and vibrational partition functions. The contributions from these different effects are very often of similar magnitude, although sometimes of different direction. Conceptually, the isotope−SRR concept in its present form is primarily suited to describe the influence of changes in ZPE and vibration frequency dependent partition functions. Differences in translational partition functions depend only on molecular mass and are independent of the reaction site. Rotational partition functions depend in a complex way on changes in mass, ^{13}C-labeled site, and reaction site. These effects are not directly included in the isotope−SRR concept and thus the use of site-specific isotope effects may not be sufficient for an empirical description or require somewhat different parameter sets than conventional SRR.

^{12}C/^{13}C KIEs for the reactions of alkanes from C_2-C_8 with Cl atoms and OH radicals are very similar in magnitude. This is in contrast to the order of magnitude difference found between $^{OH}\epsilon_{methane}$ and $^{Cl}\epsilon_{methane}$. The largest KIE difference for the saturated NMHC is for the reactions with ethane, where ϵ for the Cl reaction is nearly twice as large as that of the OH reaction. This suggests that ethane represents a transition between methane and other alkanes. This is also supported by the significant difference between the carbon number dependence determined from all the *n*-alkane data and the dependence that includes only data for *n*-alkanes with four or more carbon atoms.

The reported KIE measurements for the reactions of Cl atoms with saturated NMHC provide a valuable constraint on the previously unknown impact of chlorine chemistry on ambient NMHC δ^{13}C measurements. Because the OH- and Cl-reaction carbon KIEs are of the same order of magnitude, the relative impact of Cl- and OH-reactions can be approximated using the overall reactivity of saturated NMHC to each oxidant. Thus, in regions where the overall reactivity to Cl atoms is minimal, the impact of chlorine chemistry on δ^{13}C can be reasonably ignored. Likewise, in regions where concentrations of Cl atoms reach 10^4 cm^{-3} or higher, the relative reaction rates with Cl and OH reactions become comparable and modeling and interpretation of ambient δ^{13}C in these regions should take into account fractionation due to both types of chemistry. It should also be noted that because the KIEs for the OH and Cl reactions are similar and relatively small, stable carbon isotope signatures of saturated NMHC are not a particularly sensitive tool for differentiating between OH and Cl chemistry. Thus measurement of the stable carbon isotope ratios of saturated NMHC is less promising for the elucidation of tropospheric Cl atom chemistry than isotope ratio studies for unsaturated hydrocarbons.[49] For the interpretation of tropospheric measurements of the stable carbon isotope ratios of NMHC, the most important consequence of our findings is that, in general, reactions with Cl atoms will have a very limited impact on the measured isotope ratio. Possible exceptions are conditions with a dominating influence of Cl atom chemistry such as ozone depletion episodes in the boundary layer during polar sunrise.

Acknowledgment. We sincerely thank D. Ernst and A. Chivulescu at the Science and Technology Branch, Environment Canada, for technical support and isotope standard preparation. This research was supported financially by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Foundation for Climate and Atmospheric Sciences (CFCAS).

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