

The Hydrogen Kinetic Isotope Effects of the Reactions of *n*-Alkanes with Chlorine Atoms in the Gas Phase

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Abstract. The stable-hydrogen kinetic isotope effects (KIEs) for a series of *n*-alkanes in reaction with chlorine atoms in the gas phase were studied in a 25-L PTFE reaction chamber at 298 K. The time dependence of both the stable hydrogen isotope ratios and the concentrations was determined using a gas chromatography pyrolysis isotope ratio mass spectrometry (GC-P-IRMS) system. The following KIE values, in per mil (‰), were obtained: 39.6 ± 2.7 (*n*-butane), 28.2 ± 0.9 (*n*-pentane), 24.6 ± 1.0 (*n*-hexane), 24.0 ± 1.2 (*n*-heptane), 17.9 ± 3.3 (*n*-octane), 15.1 ± 0.7 (*n*-nonane), and 14.9 ± 1.8 (*n*-decane). The errors given are the ±1σ standard errors. These measured values were used to derive structure-reactivity relationships (SRRs), which allow for the calculation of the KIEs for the reaction of *n*-alkanes with Cl atoms. The results of the calculations agree with the measurements within few per mil or better. The site specific stable hydrogen isotope fractionation effects for methyl groups are approximately a factor of 3 larger than those for methylene group, a finding which is qualitatively similar to site-specific stable hydrogen isotope effects reported in literature for reactions of alkanes with the OH radical. Because *n*-alkanes with close to natural isotope ratios (i.e. neither artificially labeled, nor enriched or depleted) were used, the KIE data are directly applicable to atmospheric studies. Based on these KIE values, the impact of Cl-atom reactions of the stable hydrogen isotope ratio on alkanes are estimated for different levels of Cl-atom concentrations. On average in the troposphere, the impact of Cl-atom reactions of the stable hydrogen isotope ratio of *n*-alkanes will be small. However, in regions of the troposphere with high concentrations of Cl atoms, such as the tropospheric ozone depletion episodes during polar sunrise, the impact of Cl-atom reactions is substantial.

Key words: stable isotope ratios, kinetic isotope effects, non-methane hydrocarbons, deuterium, tropospheric Cl atoms

1. Introduction

The removal of non-methane hydrocarbons (NMHCs) from the troposphere is almost exclusively determined by oxidation reactions. While OH and O₃ are major

oxidants during daylight hours and NO_3 can play a role in nighttime chemistry, in the last decade evidence has been mounting concerning reactive chlorine and its effect on the tropospheric chemistry of marine (Finlayson-Pitts, 1993; Finlayson-Pitts *et al.*, 1989; Keene *et al.*, 1993; Oum *et al.*, 1998; Singh and Kasting, 1988) and Arctic (Ariya *et al.*, 1998; Spicer *et al.*, 2002) environments. Chlorine atoms are strong oxidants of non-methane hydrocarbons, having reaction rates with *n*-alkanes that often exceed those of the analogous reactions with the OH radical by two orders of magnitude (Aschmann and Atkinson, 1995; Atkinson, 1997; Atkinson and Aschmann, 1985; Atkinson *et al.*, 1997; Wallington *et al.*, 1988). Estimates of chlorine atom concentrations in the troposphere are in the range of 10^3 – 10^6 Cl atoms cm^{-3} in the marine boundary layer (Allan *et al.*, 2001; Chang *et al.*, 2004; Spicer *et al.*, 1998), 10^3 – 10^5 Cl atoms cm^{-3} in the Arctic during ozone depletion episodes (Ariya *et al.*, 1998; Boudries and Bottenheim, 2000; Ramacher *et al.*, 1999; Röckmann *et al.*, 1999), and in the range of 10^3 Cl atoms cm^{-3} or less on a global average (Maben *et al.*, 1995; Rudolph *et al.*, 1996, 1997a; Singh *et al.*, 1996).

It has been shown that measurements of stable isotope ratios of atmospheric NMHCs can be used to further understanding of the sources, sinks, and distributions of tropospheric NMHCs (Anderson *et al.*, 2003; Czapiewski *et al.*, 2002; Goldstein and Shaw, 2003; Iannone *et al.*, 2003; Rudolph *et al.*, 1997b, 2000, 2002, 2003; Rudolph and Czuba, 2000; Saito *et al.*, 2002; Schmidt *et al.*, 2004; Thompson *et al.*, 2003; Tsunogai *et al.*, 1999). Recently, the stable hydrogen kinetic isotope effects (KIEs) for reactions of NMHCs, including *n*-alkanes, with OH have been measured in a series of laboratory experiments (Iannone *et al.*, 2004). There are also several studies of the effect of deuterium labeling on rate constants for the reaction of several alkanes with OH radicals (Tully *et al.*, 1986; Droege and Tully, 1986) and the reaction of unsaturated compounds with Cl atoms (Stutz *et al.*, 1997, 1998). However, to our knowledge, there are no published studies of the kinetic isotope fractionation associated with the reactions of saturated hydrocarbons with Cl atoms in the gas phase except for KIE studies of the methane + Cl reaction by Tyler *et al.* (2000) and Saueressig *et al.* (1996) and of perdeuterated *n*-butane by Stutz *et al.* (1998). Here, measurements of the stable hydrogen KIEs for the reactions of several *n*-alkanes with Cl atoms are presented.

Based on these results, the impact of Cl-atom reactions on the stable hydrogen isotope ratios of atmospheric *n*-alkanes is estimated for different scenarios, and the possibility to use stable hydrogen isotope ratios for quantifying tropospheric Cl-atom concentrations is discussed. Furthermore, the results are used to derive structure–reactivity relationships which allow for the prediction of the hydrogen KIEs for reaction of *n*-alkanes with Cl atoms.

2. Experiment

The methodology was similar to the procedure described by Anderson *et al.* (2003) for measurements of KIEs for reactions of hydrocarbons with the OH radical. The

method is a relative rate measurement, which compares the loss rate of hydrocarbon molecules containing no D atom with the loss rate of molecules containing one D atom. The Cl-atom induced changes in concentration and stable hydrogen isotope ratio in a chemical reactor were measured as a function of time, and the KIEs were determined from the dependence between concentration and isotope ratio. The concentration and stable isotope ratio measurements were made by gas chromatography coupled on-line via a pyrolysis interface to an isotope ratio mass spectrometer. The experiments were made using commercially available hydrocarbons, which were neither artificially labeled nor enriched or depleted in D.

The reactions were carried out at atmospheric pressure in a 25-L reaction chamber made of a PTFE film (0.13-mm thickness). A newly fabricated reaction chamber was used in order to avoid interference from contamination which can build up on the walls of the chamber during use in experiments. The reaction chamber was placed in a temperature-controlled housing (298 ± 2 K) which also allowed for irradiation with up to twelve individually-controlled linear fluorescent, blacklight phosphor (emitting at $\lambda_{\text{max}} = 356$ nm) lamps (manufactured by Osram Sylvania Canada). The reaction chamber was filled twice with 25 L of synthetic air and pumped out completely in order to remove any impurities from the chamber, then filled again with 25 L of synthetic air. Seven *n*-alkanes were injected via syringe through a septum of a Teflon port on the chamber wall: *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane to create mixing ratios in the range of 150–500 ppm in the reaction chamber. The concentration and stable hydrogen isotope ratio of the NMHCs were measured by continuous-flow isotope ratio mass spectrometry (CF-IRMS) coupled with a gas chromatograph via a pyrolysis interface (GC-P-IRMS) (Brenna *et al.*, 1997).

Several series of 2–5 measurements, covering periods ranging from 2 to 8 h, were made with a variety of NMHCs in the reaction chamber, but in the absence of any reactant to test the stability of the concentration and stable hydrogen isotope ratio values. The standard deviation of the δ D measurements for all these measurements was 2.9‰, the average relative standard deviation for the concentration measurements was 2%. Similarly, before starting the chlorine reactions, two measurements were taken over a period of ~ 2 h. For these two pre-reaction measurements, the average standard deviation of the stable hydrogen isotope ratios was 2.7‰, comparable to the average repeatability of the δ D measurements. The only outlier in these isotope ratio measurements was *n*-octane, here the standard deviation was 7.8%. There was no systematic change in concentration between the two successive measurements; the average relative decrease was below 1%. However, the two pre-reaction concentration measurements made exhibited a larger than usual unsystematic variability. On average, the relative standard deviation of the concentration measurements was 8%. This was mainly due to the high variability of the *n*-butane, *n*-hexane and *n*-decane concentration measurements, which had relative standard deviations between 12% and 16%. A possible

reason for this above average variability of the concentration may be incomplete mixing of the injected NMHCs inside the chamber prior to the first pre-reaction measurement. The relative decrease in concentration between two consecutive measurements during the experiments was 38% and the change in δD was 8.6%. These systematic changes are substantially higher than the observed random variations.

After injecting 2–3 mL of chlorine gas, the UV lights were activated for a period of 20 min, initiating the photolysis of the chlorine molecules and producing Cl atoms. Typically every 2 h, a 5-cm³ sample was taken from the reaction chamber and analyzed, 2–3 mL of Cl₂ were injected, and the UV lights were activated for 20 min. The short irradiation times were sufficient to completely photolyse the injected Cl₂. The interval between two successive measurements is determined by the time needed for the GC-C-IRMS analysis. Six samples were analyzed in this way. For each sample, the transfer lines and the sampling loop were flushed with 70 mL of the reaction chamber mixture. The 5-cm³ sample was then transferred to a liquid-nitrogen cooled cryofocussing trap at 93 K. The trap was then flash-heated and the adsorbed hydrocarbons were injected into a gas chromatograph. The *n*-alkanes were separated on a Varian 3400 Gas Chromatograph equipped with a 60 m × 5 μm film × 0.32 mm ID HP-1 column (Agilent Technologies). The temperature program used was: –30 °C held for 2 min, increasing 2 °C min⁻¹ until the final temperature of 180 °C, held for 20 min. Helium was used as the carrier gas at a flow rate of 1.5–2.0 cm³ min⁻¹. The GC effluent was transferred to a pyrolysis furnace at 1723 K where the hydrogen of the alkanes was quantitatively converted to H₂/HD gas. The temperature and the residence time (>300 ms) of the gas passed through the furnace were high enough to quantitatively convert all hydrocarbons including the CH₄ reference gas (Burgoyne and Hayes, 1998). The pyrolyzed GC flow was then passed through a tubular Nafion® dryer for water removal before entering the open split of a Finnigan DeltaPlus XL Isotope Ratio Mass Spectrometer (manufactured by Thermo Electron (Bremen) GmbH). H₂ and CH₄ reference gases were automatically injected at the beginning and end of every measurement; H₂ was introduced through a separate open split and CH₄ was injected via a 4-way bypass valve between the column and the pyrolysis furnace. Both the H₂ and CH₄ gas standards are traceable to Vienna Standard Mean Ocean Water (V-SMOW), and they provided the reference points for which the δD values of the studied *n*-alkanes were determined. Ion-current ratios were corrected for the formation of H₃⁺ ions in the IRMS source before starting the experiment (Sessions *et al.*, 2001a, b). The experiment was continued until the concentrations of the *n*-alkanes were depleted to <25% of their initial values.

IRMS traces were evaluated using Isodat NT Version 1.1 software (Thermo Electron (Bremen) GmbH). The software allows the user to perform manual peak integrations to evaluate peaks not properly integrated by the auto-integration routine. Stable hydrogen isotope ratios are expressed as the ratio D/H and are usually presented as per mil delta values, δ (‰), relative to the absolute D/H ratio of

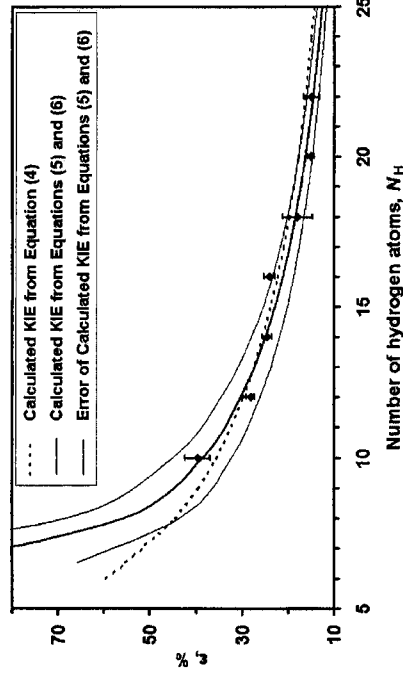


Figure 1. Example plot for determination of the *n*-pentane + Cl KIE value from the dependence between concentration and stable hydrogen isotope ratio (Equation (2)).

V-SMOW:

$$\delta D = \left(\frac{(D/H)_{\text{sample}} - (D/H)_{\text{V-SMOW}}}{(D/H)_{\text{V-SMOW}}} \right) 1000\text{‰} \quad (1)$$

The KIE can be expressed as k_H/k_D the ratio of rate constants for two isotopologues participating in the same reaction. This value is obtained from the slope of a linear dependence between experimentally derived isotope ratios and concentrations at time t and $t = 0$:

$$\ln \left(\frac{H_t}{H_0} \right) = \frac{k_H/k_D}{1 - k_H/k_D} \ln \left(\frac{\delta D_t + 1000}{\delta D_0 + 1000} \right) \quad (2)$$

Figure 1 demonstrates the use Equation (2) for the determination of the *n*-pentane + Cl KIE value. Since for most reactions of hydrocarbons the difference between k_H and k_D is small, KIE values are often presented as per mil (‰) epsilon values, ϵ :

$$\epsilon = (k_H/k_D - 1)1000\text{‰} \quad (3)$$

The pure gases and chemicals used in this study had the following stated purities: synthetic air (99.999%), obtained from Air Products; and chlorine gas (99.999%) and *n*-butane (99.85%), both obtained from Matheson Tri-Gas. *n*-Pentane (99+%), *n*-hexane (99+%), *n*-heptane (99%), *n*-octane (98%), *n*-nonane (99%), and *n*-decane (99+%) were obtained from Aldrich Chemical Company. All were used without further purification.

3. Results and Discussion

The KIE data are summarized in Table I. The errors reported are based on the errors of the least-squares fits to the measured data. The relative errors are less than 10% for all *n*-alkanes studied except *n*-octane (18.4%) and *n*-decane (12.1%).

Table I. Measured stable hydrogen kinetic isotope effects (KIEs) of selected gas-phase Cl + *n*-alkane reactions

<i>n</i> -Alkane	No. H atoms (N_H)	No. Data points ^a	R^2 Value	ϵ (%) ^b
<i>n</i> -Butane	10	7	0.9769	39.6 ± 2.7
<i>n</i> -Pentane	12	7	0.9947	28.2 ± 0.9
<i>n</i> -Hexane	14	7	0.9923	24.6 ± 1.0
<i>n</i> -Heptane	16	7	0.9874	24.0 ± 1.2
<i>n</i> -Octane	18	6	0.8824	17.9 ± 3.3
<i>n</i> -Nonane	20	6	0.9925	15.1 ± 0.7
<i>n</i> -Decane	22	6	0.9598	14.9 ± 1.8

^aNumber of data points used for the linear regression.

^bError given is the $\pm 1\sigma$ standard error derived from the error of the linear regression.

Table II. Rate constants relative to *n*-hexane for reactions of chlorine atoms with *n*-alkanes at 298 K

<i>n</i> -Alkane	Literature rate constant, 10^{-10} cm ³ molecule ⁻¹ s ⁻¹	Relative rate literature ^a	Relative rate experiment ^b	Rate constant derived from experimental relative rate ^c , 10^{-10} cm ³ molecule ⁻¹ s ⁻¹
<i>n</i> -Butane	2.15 ± 0.15 ^d	0.705	0.620 ± 0.029	1.89 ± 0.22
<i>n</i> -Pentane	2.50 ± 0.03 ^e	0.820	0.837 ± 0.046	2.55 ± 0.17
<i>n</i> -Heptane	3.65 ± 0.07 ^e	1.197	1.156 ± 0.046	3.52 ± 0.21
<i>n</i> -Octane	4.09 ± 0.12 ^e	1.341	1.435 ± 0.094	4.38 ± 0.41
<i>n</i> -Nonane	4.29 ± 0.13 ^f	1.407	1.544 ± 0.103	4.71 ± 0.46
<i>n</i> -Decane	4.87 ± 0.19 ^f	1.597	1.616 ± 0.108	4.83 ± 0.52

^a $k_{\text{ref}}(\text{Cl} + n\text{-hexane}) = (3.05 \pm 0.03) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ (Hooshiyar and Niki, 1995).

^bError given is the $\pm 1\sigma$ standard error derived from the error of the linear regression.

^cRelative to the *n*-hexane rate constant reported by Hooshiyar and Niki (1995), the error given is the $\pm 1\sigma$ standard error derived by error propagation from the experimental relative rate and the error of the reaction rate constant of the reference compound (*n*-hexane).

^dTyndall *et al.* (1997).

^eHooshiyar and Niki (1995).

^fAschmann and Atkinson (1995).

To verify that losses of *n*-alkanes were due solely to the Cl reaction, a relative-rate analysis was performed (Table II). Within the experimental uncertainties of approximately 10%, the relative rates for Cl + *n*-butane, *n*-pentane, *n*-octane, *n*-heptane, *n*-nonane and *n*-decane derived in our experiments (relative to *n*-hexane) were all in agreement with literature values.

The measured KIE systematically depends on the number of hydrogen atoms (N_H) in the molecule. A reasonable description of the dependence between the n -alkane + Cl ϵ values ($Cl\epsilon$) and N_H is given by:

$$Cl\epsilon = \left(\frac{357 \pm 13}{N_H} \right) \% \quad (4)$$

This inverse dependence on N_H is similar to dependencies observed for OH + n -alkane carbon and hydrogen KIEs (Rudolph *et al.*, 2000; Iannone *et al.*, 2004).

In the case of the hydrogen KIEs for reaction of alkanes with OH, it has been shown that a structure-reactivity relationship (SRR) exists with different isotope fractionation for reactions occurring at primary (1°), secondary (2°), or tertiary (3°) carbon atoms (Droege and Tully, 1986; Tully *et al.*, 1986; Iannone *et al.*, 2004); the terms primary, secondary, and tertiary refer to the number of other carbon atoms attached to the carbon atom of interest (e.g. a primary, or 1° , C atom has 1 other carbon atom attached to it). Similarly, the KIEs for reactions with Cl atoms can be derived from the contributions of primary and secondary H-atom (H atoms attached to primary and secondary carbons, respectively) abstraction to the rates of reaction of the undeuterated (k_H) and deuterated (k_D) NMHCs under the assumption of a random distribution of one D atom in the deuterated alkane. We consider only the case of a single D atom within the deuterated alkane because the probability of the occurrence of two or more D atoms in a single molecule is extremely low given that the natural abundance of the 2H isotope is 0.0115 atom %. For the reaction of n -alkanes with four or more carbon atoms, the SRR derived by Atkinson (1997) can be written in the form:

$$k_H = N_{1^\circ H} F_{1^\circ} k_{1^\circ H} + N_{2^\circ H} F_{2^\circ} k_{2^\circ H} \quad (5)$$

and

$$k_D = \left(\frac{N_{1^\circ H}}{N_H} \right) [F_{1^\circ} k_{1^\circ D} + (N_{1^\circ H} - 1) F_{1^\circ} k_{1^\circ H} + N_{2^\circ H} F_{2^\circ} k_{2^\circ H}] \\ + \left(\frac{N_{2^\circ H}}{N_H} \right) [(F_{2^\circ} k_{2^\circ D} + (N_{2^\circ H} - 1) F_{2^\circ} k_{2^\circ H} + N_{1^\circ H} F_{1^\circ} k_{1^\circ H})] \quad (6)$$

Here, $N_{1^\circ H}$, $N_{2^\circ H}$, and N_H represent the numbers of primary, secondary, and total H atoms in the selected n -alkane, respectively; F_{1° and F_{2° are average correction factors reflecting the effect of different alkyl groups adjacent to the selected n -alkane's methyl (RCH₃) and methylene carbon atoms (R₂CH₂), respectively; $k_{1^\circ H}$ and $k_{2^\circ H}$ are site-specific reaction rate constants at 298 K for the abstraction of primary and secondary hydrogen atoms; and $k_{1^\circ D}$ and $k_{2^\circ D}$ are site-specific reaction rate constants at 298 K for the abstraction of primary and secondary deuterium atoms. The values for $k_{1^\circ H}$ and $k_{2^\circ H}$ can be derived from the carbon atom based group rate constants of $k_p^* = 3.50 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for methyl groups

and $k_s^* = 9.30 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for methylene groups (Atkinson, 1997) through dividing by the number of hydrogen atoms in each group,

$$k_{1^\circ\text{H}}^* = \frac{k_p^*}{3} \quad (7a)$$

and

$$k_{2^\circ\text{H}}^* = \frac{k_s^*}{2} \quad (7b)$$

The resulting values are $1.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{1^\circ\text{H}}$ and $4.65 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{2^\circ\text{H}}$.

Following the suggestion of Atkinson (1997), we use a correction factor of $F = 0.79$ for all non-methyl groups ($-\text{CH}_2-$, $-\text{CH}-$, and $>\text{C}<$) attached to the site of interest and no correction ($F = 1.00$) for methyl (CH_3-) groups attached to the site of interest. We assume that F values are identical for H and D atoms at the same site ($F_{1^\circ\text{H}} \equiv F_{1^\circ\text{D}}$ and $F_{2^\circ\text{H}} \equiv F_{2^\circ\text{D}}$). For all n -alkanes, the following expression can be written for the average correction factor F_{1° , since for all n -alkanes, with the exception of ethane, the two $-\text{CH}_3$ groups are each only adjacent to one $-\text{CH}_2-$ group and consequently F_X is identical for all hydrogen atoms attached to a primary carbon ($F_X = F = 0.79$):

$$F_{1^\circ} \equiv \frac{\sum_i F_{X_i}}{N_{1^\circ\text{H}}} = F = 0.79 \quad (8)$$

The index i represents the hydrogen atoms attached to a methyl group. The general expression for the average structure-specific correction factor for secondary H atoms, F_{2° , is:

$$F_{2^\circ} \equiv \frac{\sum_j F_{X_j} F_{Y_j}}{N_{2^\circ\text{H}}} \quad (9)$$

where the index j stands for the hydrogen atoms attached to methylene carbon atoms. For n -alkanes where $N_C \geq 4$ (n -butane and higher)) we obtain for $\sum_j F_{X_j} F_{Y_j}$:

$$\sum_j F_{X_j} F_{Y_j} = 4F + 2F^2(N_C - 4) = 4F + F^2(N_H - 10) \quad (10)$$

Equation (10) can be derived from the consideration that, in n -alkanes with four or more C atoms, there are two types of $-\text{CH}_2-$ groups: two that are adjacent to a $-\text{CH}_3$ and a $-\text{CH}_2-$ group, and those that are adjacent to two $-\text{CH}_2-$ groups. The first group, which consists of four hydrogen atoms, constitutes the first term of Equation (10), and the second group is represented by the second term. The second part of Equation (10) also uses the general relation between the number of carbon atoms and hydrogen atoms in an n -alkane ($N_C = (N_H - 2)/2$). It should be noted that for $N_C = 4$ (n -butane), the second term of Equation (10) disappears since there are no methylene groups with two $-\text{CH}_2-$ groups attached).

Replacing $\Delta_{1^{\circ}} = k_{1^{\circ}D} - k_{1^{\circ}H}$ and $\Delta_{2^{\circ}} = k_{2^{\circ}D} - k_{2^{\circ}H}$, Equation (6) can be written as,

$$k_D = \left(\frac{N_{1^{\circ}H}}{N_H}\right)[F_{1^{\circ}}\Delta_{1^{\circ}} + N_{1^{\circ}H}F_{1^{\circ}}k_{1^{\circ}H} + N_{2^{\circ}H}F_{2^{\circ}}k_{2^{\circ}H}] + \left(\frac{N_{2^{\circ}H}}{N_H}\right)[F_{2^{\circ}}\Delta_{2^{\circ}} + N_{2^{\circ}H}F_{2^{\circ}}k_{2^{\circ}H} + N_{1^{\circ}H}F_{1^{\circ}}k_{1^{\circ}H}] \quad (11)$$

Factoring out the $F_{1^{\circ}}\Delta_{1^{\circ}}$ and $F_{2^{\circ}}\Delta_{2^{\circ}}$ terms,

$$k_D = \left(\frac{N_{1^{\circ}H}}{N_H}\right)[N_{1^{\circ}H}F_{1^{\circ}}k_{1^{\circ}H} + N_{2^{\circ}H}F_{2^{\circ}}k_{2^{\circ}H}] + \left(\frac{N_{2^{\circ}H}}{N_H}\right)[N_{1^{\circ}H}F_{1^{\circ}}k_{1^{\circ}H} + N_{2^{\circ}H}F_{2^{\circ}}k_{2^{\circ}H}] + \left(\frac{N_{1^{\circ}H}}{N_H}\right)F_{1^{\circ}}\Delta_{1^{\circ}} + \left(\frac{N_{2^{\circ}H}}{N_H}\right)F_{2^{\circ}}\Delta_{2^{\circ}} \quad (12)$$

The sum of the first two terms in Equation (12) is equivalent to Equation (5) since, for any n -alkane, $N_H = N_{1^{\circ}H} + N_{2^{\circ}H}$. Thus, Equation (12) reduces to,

$$k_D = k_H + \left(\frac{N_{1^{\circ}H}}{N_H}\right)F_{1^{\circ}}\Delta_{1^{\circ}} + \left(\frac{N_{2^{\circ}H}}{N_H}\right)F_{2^{\circ}}\Delta_{2^{\circ}} \quad (13)$$

Substituting Equations (8) and (9) and (10) into (13),

$$k_D = k_H + \left(\frac{\sum_i F_{X_i}}{N_H}\right)\Delta_{1^{\circ}} + \left(\frac{\sum_j F_{X_j}F_{Y_j}}{N_H}\right)\Delta_{2^{\circ}} \quad (14)$$

With $\sum_i F_{X_i} = 6F$ and $\sum_j F_{X_j}F_{Y_j} = 4F + F^2(N_H - 10)$ we obtain:

$$k_D = k_H + \left(\frac{6F}{N_H}\right)\Delta_{1^{\circ}} + \left(\frac{4F + F^2(N_H - 10)}{N_H}\right)\Delta_{2^{\circ}} \quad (15a)$$

or

$$k_D = k_H + \left(\frac{6F}{N_H}\right)\Delta_{1^{\circ}} + \left(\frac{4F - 10F^2}{N_H}\right)\Delta_{2^{\circ}} + F^2\Delta_{2^{\circ}} \quad (15b)$$

Factoring out N_H^{-1} ,

$$k_D - k_H = \left(\frac{1}{N_H}\right)[6F\Delta_{1^{\circ}} + (4F - 10F^2)\Delta_{2^{\circ}}] + F^2\Delta_{2^{\circ}} \quad (15c)$$

Equation (3) can be rearranged into the following form, isolating k_D :

$$k_D = k_H \left(1 + \frac{\varepsilon}{1000\%}\right)^{-1} \quad (3b)$$

Substituting Equation (3) into (15c),

$$\frac{-k_H\varepsilon}{1000 + \varepsilon} = \left(\frac{1}{N_H}\right)[6F\Delta_{1^{\circ}} + (4F - 10F^2)\Delta_{2^{\circ}}] + F^2\Delta_{2^{\circ}} \quad (16)$$

Estimates for $\Delta_{1^{\circ}}$ and $\Delta_{2^{\circ}}$ were derived from the linear dependence between $\frac{-k_{\text{H}}}{1000+\epsilon}$ and $1/N_{\text{H}}$ in Equation (16) by a least-squares fit using the experimentally derived KIE ϵ values. Values for k_{H} were obtained from Equation (5). The value $\Delta_{2^{\circ}}$ can be determined from the y-intercept, which corresponds to $F^2\Delta_{2^{\circ}}$, and then, $\Delta_{1^{\circ}}$ can be calculated from the slope of $6F\Delta_{1^{\circ}} + (4F - 10F^2)\Delta_{2^{\circ}}$. Using the values from Equations (7a) and (7b) for $k_{1^{\circ}\text{H}}$ and $k_{2^{\circ}\text{H}}$, and the definitions $\Delta_{1^{\circ}} = k_{1^{\circ}\text{D}} - k_{1^{\circ}\text{H}}$ and $\Delta_{2^{\circ}} = k_{2^{\circ}\text{H}} - k_{2^{\circ}\text{D}}$, we obtain $(4.6 \pm 2.6) \times 10^{-12}$ and $(3.3 \pm 0.1) \times 10^{-11}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{1^{\circ}\text{D}}$ and $k_{2^{\circ}\text{D}}$, respectively. The large error of $k_{1^{\circ}\text{D}}$ is due to the dominance of the reaction at methylene groups for the studied *n*-alkanes. Using these estimates for $k_{1^{\circ}\text{D}}$ and $k_{2^{\circ}\text{D}}$, the ratio of Equations (5) and (6) can now be calculated to obtain the KIEs for *n*-alkane + Cl reactions. The calculated k and KIE ϵ values for the *n*-alkanes studied are summarized in Table III. When experimental values for k_{H} (see Table II) are used in Equation (16) instead of values calculated from Equation (5) to derive $k_{1^{\circ}\text{D}}$ and $k_{2^{\circ}\text{D}}$, the calculated KIE ϵ values are about 1% lower, but the differences between measured and experimental values are still within the uncertainties of the experimental and calculated ϵ values.

Figure 2 shows a comparison of the experimental results with calculations based on Equation (4) and the SRR (Equations (5) and (6)). The SRR gives estimations of KIE ϵ values that are, on average, within $\pm 3\%$ of the experimental ϵ values,

Table III. Summary of values required for the calculation of ϵ values based on structure-reactivity relationships

<i>n</i> -Alkane	N_{H}	$N_{2^{\circ}\text{H}}^{\text{a}}$	$F_{2^{\circ}}^{\text{b}}$	k Values ^c , 10^{-11} cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$		ϵ (%)	
				k_{H}^{d}	k_{D}^{e}	Calculated ^f	Measured
<i>n</i> -Butane	10	4	0.79	20.2	19.5 ± 0.01	38.6 ± 6.3	39.6 ± 2.7
<i>n</i> -Pentane	12	6	0.73	26.0	25.3 ± 0.01	30.3 ± 4.2	28.2 ± 0.9
<i>n</i> -Hexane	14	8	0.71	31.8	31.1 ± 0.01	24.9 ± 3.0	24.6 ± 1.0
<i>n</i> -Heptane	16	10	0.69	37.6	36.9 ± 0.01	21.1 ± 2.3	24.0 ± 1.2
<i>n</i> -Octane	18	12	0.68	43.4	42.7 ± 0.01	18.4 ± 1.8	17.9 ± 3.3
<i>n</i> -Nonane	20	14	0.67	49.2	48.5 ± 0.01	16.3 ± 1.5	15.1 ± 0.7
<i>n</i> -Decane	22	16	0.67	55.0	54.3 ± 0.01	14.6 ± 1.3	14.9 ± 1.8

^aFor all *n*-alkanes, $N_{1^{\circ}\text{H}}$ always equals 6 and $N_{2^{\circ}\text{H}} = N_{\text{H}} - 6$.

^b $F_{1^{\circ}}$ is always 0.79 for *n*-alkanes according to Equation (8).

^c k values for specific H- and D-atom sites are (all in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{1^{\circ}\text{H}} = 1.17 \times 10^{-11}$, $k_{2^{\circ}\text{H}} = 4.65 \times 10^{-11}$, $k_{1^{\circ}\text{D}} = (4.60 \pm 2.64) \times 10^{-12}$, and $k_{2^{\circ}\text{D}} = (3.33 \pm 0.08) \times 10^{-11}$. Errors of $k_{1^{\circ}\text{D}}$ and $k_{2^{\circ}\text{D}}$ are derived from the errors of the slope and y-intercept, respectively, of Equation (16).

^dValues for k_{H} are calculated using Equation (5).

^eThe error of k_{D} is the $\pm 1\sigma$ standard error derived from the errors of $k_{1^{\circ}\text{D}}$ and $k_{2^{\circ}\text{D}}$.

^fThe calculation is based on the ratio of Equations (5) and (6), and the subsequent use of Equation (3). The error given is the $\pm 1\sigma$ standard error derived from the error of k_{D} .

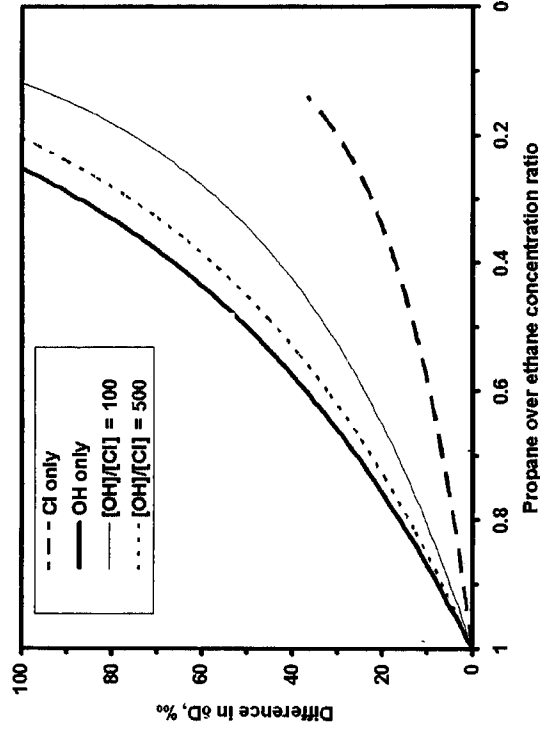


Figure 2. Plot of hydrogen KIE (ϵ) values for Cl + *n*-alkane reaction against hydrogen number (N_H). Also shown are estimates of the KIE using Equations (4), (5) and (6). The errors shown are the $\pm 1\sigma$ standard errors.

and with the exception of *n*-heptane, all measured ϵ values agree within their 1σ error with the SRR calculations. The results of calculations based on Equation (4) are similar for the range of studied compounds, although compared to the SRR and the experimental values, the simple $1/N_H$ dependence (Equation (4)) somewhat underestimates the KIE for *n*-butane and gives slightly higher values for the heavier *n*-alkanes. Significant differences are observed for extrapolations to ethane and propane. The KIEs for ethane and propane calculated from Equations (5) and (6) are $(112 \pm 38)\%$ and $(56 \pm 12)\%$, respectively. The results obtained from Equation (4) are only $(60 \pm 13)\%$ and $(45 \pm 13)\%$, respectively. The large errors in the calculated ethane and propane ϵ values using Equations (5) and (6) are largely due to the 57% error in k_{1D} which has a larger effect for *n*-alkanes with fewer 2° H atoms.

The ratios of k_H/k_D are 2.5 for methyl and 1.4 for methylene groups. Qualitatively, this decrease in the k_H/k_D ratio is similar to the findings for the reaction of alkanes with the OH radical (Droege and Tully, 1986; Tully *et al.*, 1986) where the ratios for k_H over k_D change in the order of $1^\circ > 2^\circ > 3^\circ$. Qualitatively this may be explained by the increase in stability of the radical, which is formed by the abstraction of a hydrogen atom from the hydrocarbon. Quantitatively, the kinetic isotope effect values are approximately a factor of two lower for the reactions with Cl atoms than for the reactions with OH radicals with *n*-alkanes having four or more carbon atoms.

The only saturated hydrocarbon with close to natural deuterium abundance for which the KIE for reaction with Cl atoms has been published is methane. The structure-specific reactivities for primary and secondary H and D atoms do not allow a quantitative comparison using Equations (5) and (6), but, qualitatively, the recently reported values for this reaction of $(474 \pm 26)\%$ (Tyler *et al.*, 2000) and $(508 \pm 41)\%$ (Saueressig *et al.*, 1996) are compatible with our finding of increasing stable hydrogen isotope fractionation effects with decreasing degrees of substitution of the carbon atom to which the reacting hydrogen atom is attached. Stutz *et al.* (1998) reported the ratio for the reaction of *n*-butane relative to perdeuterated *n*-butane (*n*-C₄D₁₀). Their value of 1.4 ± 0.2 , or $(400 \pm 200)\%$, is in close agreement with the value of 1.36 ± 0.06 , or $(360 \pm 60)\%$, which can be calculated from the SRR described above. Similarly, their rate constant of $(1.6 \pm 0.1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ for reaction of *n*-C₄D₁₀ with Cl atoms is in good agreement with the value of $(1.49 \pm 0.13) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ we calculate using the values derived for $k_{1^{\circ}\text{D}}$ and $k_{2^{\circ}\text{D}}$.

4. Impact of Cl + *n*-Alkane Reactions on the Stable Hydrogen Isotope Ratios of Tropospheric *n*-Alkanes

The change in isotope ratios of hydrocarbons undergoing reaction with OH radicals in the troposphere relative to the source composition can be calculated through the following equation (Rudolph and Czuba, 2000):

$$\delta_z = t_{av} [\text{OH}]_{av} {}^{\text{OH}}k_z \varepsilon_z + {}^0\delta_z \quad (17)$$

Here, δ_z and ${}^0\delta_z$ represent observed and emitted hydrogen delta values for compound *z*; t_{av} represents the average age of compound *z*; ${}^{\text{OH}}k_z$ is the rate constants for the reaction of OH with *z*; $[\text{OH}]_{av}$ represents the average OH concentration and ${}^{\text{OH}}\varepsilon_z$ is the KIE value for the reaction of OH with *z*. Although this dependence has originally been derived for stable carbon isotope effects, it has recently been shown that stable hydrogen isotope ratios of NMHCs may be used for the same purpose (Iannone *et al.*, 2004). The applicability of Equation (17) depends on, among other factors, the condition that reaction with OH radicals is the only relevant tropospheric loss mechanism. Although reaction with OH is by far the most important loss reaction for alkanes in the troposphere, there is strong evidence that under certain conditions, e.g. polar sunrise (Jobson *et al.*, 1994; Ariya *et al.*, 1998; Ramacher *et al.*, 1999), reaction with Cl atoms contributes to the removal of NMHCs. Two important questions arise: Is there a possible bias for OH processing quantified using Equation (17), and can isotope ratio measurements be used to identify a possible impact of Cl reactions on the atmospheric removal of alkanes?

Equation (17) can be modified to include the contribution of Cl atoms on δ_z :

$$\delta_z - {}^0\delta_z = t_{av} [\text{OH}]_{av} {}^{\text{OH}}k_z \varepsilon_z + t_{av} [\text{Cl}]_{av} {}^{\text{Cl}}k_z \varepsilon_z \quad (18)$$

This equation allows for the determination of the total change in the stable isotope ratios of atmospheric *n*-alkanes, as well as separate calculations of the contributions from reactions with Cl ($\delta_{z+Cl} = t_{av}[Cl]_{av} k_z^{Cl} \epsilon_z$) and OH ($\delta_{z+OH} = t_{av}[OH]_{av} k_z^{OH} \epsilon_z$). As a measure for the relative importance of the reaction with Cl atoms the following ratio (R_{Cl}) may be used:

$$R_{Cl} \equiv \frac{\delta_{z+Cl}}{\delta_{z+Cl} + \delta_{z+OH}} = \frac{[Cl]_{av} k_z^{Cl} \epsilon_z}{[Cl]_{av} k_z^{Cl} \epsilon_z + [OH]_{av} k_z^{OH} \epsilon_z} \quad (19)$$

Examples for R_{Cl} values are summarized in Table IV for different Cl-atom and OH-radical concentrations. At a concentration of 10^3 Cl atoms cm^{-3} and for an average tropospheric OH concentration of 10^6 radicals cm^{-3} the impact of Cl-atom reactions is small. Based on the indirect estimates of upper limits for the average tropospheric Cl-atom concentration by Rudolph *et al.* (1996) and Singh *et al.* (1996) in the range of some 10^3 atoms cm^{-3} , we conclude that on average the impact of Cl-atom reactions on the stable hydrogen isotope ratio of tropospheric *n*-alkanes is negligible.

However, under specific conditions, Cl-atom concentration significantly exceeding 10^3 Cl atoms cm^{-3} are found (Ariya *et al.*, 1998; Chang *et al.*, 2004; Spicer *et al.*, 1998, 2002; Ramacher *et al.*, 1999). Under these conditions, the impact of Cl-atom reactions will be visible in the stable hydrogen isotope ratio of *n*-alkanes. Especially during polar sunrise, where low OH-radical concentrations and high Cl-atom levels can be found, a very significant impact from the Cl-atom reaction is to be expected.

Although Equation (18) allows for the determination of the contribution of the different reactions to the change in hydrogen isotope ratios if the reactant concentrations are known, it does not allow for the differentiation between Cl-atom and OH-radical reactions from isotope-ratio measurements alone. Furthermore, the use of Equation (18) to quantify photochemical processing requires that the

Table IV. Contribution of Cl-atom reactions to the change of stable hydrogen isotope ratios of *n*-alkanes due to chemical reactions in the troposphere for different Cl-atom and OH-radical concentrations^a

[Cl], atoms cm^{-3}	[OH], radicals cm^{-3}	R_{Cl}		
		Ethane (%)	<i>n</i> -Butane (%)	<i>n</i> -Hexane (%)
1×10^3	1×10^6	13	7	3
1×10^4	1×10^6	60	42	23
1×10^5	1×10^6	94	88	74
1×10^3	1×10^5	60	42	23
1×10^4	1×10^5	94	88	74

^aBased on the rate constants published by Atkinson (1997), the k_z^{OH} values published by Iannone *et al.* (2004), and the ϵ_z^{Cl} values from this paper.

variability of the stable isotope ratio of the hydrocarbon is small compared to the change in δD due to photochemical processing for the studied air masses. This is similar to one of the most critical problems of the use of hydrocarbon concentration ratios to demonstrate the existence of significant Cl-atom concentrations in the troposphere. The evidence for tropospheric Cl-atom reaction induced removal of NMHCs is based mainly on the ratios of hydrocarbon concentrations and their change with time (Jobson *et al.*, 1994; Ariya *et al.*, 1998; Ramacher *et al.*, 1999). Under the assumption that the hydrocarbons in an air mass have been subjected to the same photochemical history, the concentration ratios of two NMHCs can be described by the following equation:

$$\ln \left(\frac{c_1}{c_2} \right)_t = \ln \left(\frac{c_1}{c_2} \right)_0 \left\{ (k_{Cl}^2 - k_{Cl}^1) \int_0^t [Cl] dt + (k_{OH}^2 - k_{OH}^1) \int_0^t [OH] dt \right\} \quad (20)$$

Here, c_1 and c_2 are the concentrations of two NMHCs, k^1 and k^2 represent rate constants for the reactions of hydrocarbon 1 and 2 with Cl atoms and OH radicals, and [Cl] and [OH] are the Cl and OH concentrations, respectively. Hydrocarbon ratios are used to reduce the impact of the mixing of air masses with different NMHC concentrations. Since the rate constants for reaction with Cl and OH differ substantially between individual NMHCs, the change of the concentration ratio, c_1/c_2 , with time will depend on the relative importance of OH-radical or Cl-atom processing of the NMHCs. Although in several cases (Jobson *et al.*, 1994; Ariya *et al.*, 1998; Ramacher *et al.*, 1999) this approach has been used successfully to present a very strong case for an important contribution from Cl reactions to the tropospheric removal of NMHCs, the validity of Equation (20) depends on the assumptions of a representative average concentration ratio $(\frac{c_1}{c_2})_0$ for $t = 0$, that is, at the time of emission into the atmosphere. Combining isotope ratio measurements and hydrocarbon concentration ratios can be used to greatly reduce the uncertainties in the interpretation of the indirect evidence for tropospheric Cl-atom processing of NMHCs. This is demonstrated in Figure 3 using the ratios of propane over ethane concentrations as an example. Shown is the dependence of the difference in stable hydrogen isotope ratios between propane and ethane on the concentration ratio of ethane over propane. There is a clear distinction between Cl-atom and OH-radical induced changes of the NMHC concentration ratios. For example, in the case of the Cl reaction only, a change in the propane over ethane concentration ratio of a factor of two results in an increase of the difference of stable isotope ratios of less than 15%. For OH-radical processing, the corresponding change exceeds 50%. Such changes most likely will exceed the uncertainties caused by the variability of the stable hydrogen isotope ratios of NMHC emissions (Iannone *et al.*, 2004). Nevertheless, correlated changes in the stable isotope ratio and NMHC concentration ratios of emissions might still cause biased results. However, such correlated changes are not very likely. Furthermore, different NMHCs have different rate constants and KIEs, thus, the study of different NMHCs can be used to further reduce the probability of bias. For most tropospheric conditions, OH-radical concentrations

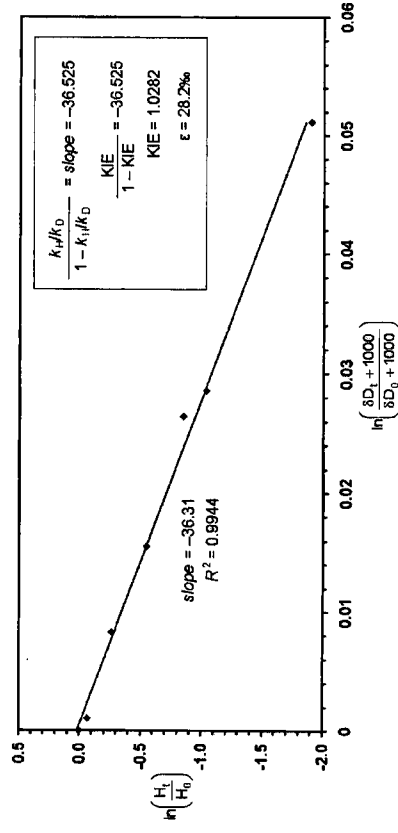


Figure 3. Calculated dependence of the difference in stable hydrogen isotope ratios between propane and ethane on the concentration ratio of ethane over propane. The calculations are based on the room temperature rate constants recommended by Atkinson (1997), and the KIEs from this work and Iannone *et al.* (2004).

will exceed those of Cl atoms by orders of magnitude (Singh and Kasting, 1988; Rudolph *et al.*, 1996; Singh *et al.*, 1996). Obviously, under these conditions the relative influence of Cl-atom reactions will be reduced. Nevertheless, even for Cl-atom concentrations two orders of magnitude below the OH-radical concentration, the dependence between NMHC concentration ratio and stable hydrogen isotope ratio clearly differs from that for OH-radical reactions only (Figure 3).

5. Summary and Conclusions

The measured KIEs for reaction of *n*-alkanes with Cl atoms can be approximated combining the SRR derived by Atkinson (1997) with site-specific rate constants of $k_{1^{\circ}\text{D}} = (4.60 \pm 2.64) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction at deuterium atoms in methyl groups, and $k_{2^{\circ}\text{D}} = (3.33 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for deuterium in methylene groups. In general, the KIEs for reactions of *n*-alkanes with Cl atoms are smaller than those for OH-radical reactions, but qualitatively the results suggest that, similar to the findings for OH reactions, the stable hydrogen isotope fractionation effects increase with a decreasing degree of substitution of the carbon atom to which the reacting hydrogen atom is attached (i.e. tertiary to secondary to primary sites).

In general, a major impact of Cl reactions on the stable hydrogen isotope ratio of *n*-alkanes in the troposphere is not expected. Exceptions are conditions where high Cl-atom concentrations can be found, such as tropospheric ozone depletion episodes during polar sunrise. Under these conditions we predict that the change in stable hydrogen isotope ratio will be significantly different from conditions dominated by OH-radical reactions. Potentially, this can be used to eliminate the potential

bias from variations in NMHC emission ratios, which is associated with the use of hydrocarbon concentration ratios to identify contributions from Cl-atom reactions to the tropospheric removal of NMHCs.

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