Laboratory Studies of the Hydrogen Kinetic Isotope Effects (KIES) of the Reaction of Non-Methane Hydrocarbons with the OH Radical in the Gas Phase

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Abstract. The hydrogen kinetic isotope effects (KIEs) of the reactions of 15 non-methane hydrocarbons (NMHCs) with the OH radical were measured at 298 ± 2 K. The measurements were made using NMHCs without artificial isotopic labeling or enrichment. The following average hydrogen KIE values, in per mil (‰), were obtained: 29.8 ± 2.1 (toluene), 51.6 ± 2.1 (*n*-butane), 97.3 ± 12.5 (*i*-butane), 63.2 ± 5.9 (cyclopentane), 10.5 (*p*-xylene), 26.8 ± 3.5 (ethylbenzene), 65.9 ± 7.0 (*n*-pentane), 79.5 ± 9.6 (cyclohexane), 52.8 ± 5.0 (*n*-hexane), 38.9 ± 7.8 (*n*-heptane), 33.4 ± 3.1 (*n*-octane), 29.6 ± 1.6 (*n*-nonane), and 29.0 ± 5.3 (*n*-decane). The KIEs for reactions of two alkenes (cyclohexene and 1-heptene) could not be determined accurately due to interference from reaction with ozone, but nevertheless the results clearly show that the KIEs for reaction of alkenes with OH are significantly lower than those for saturated hydrocarbons. The KIEs for reaction of alkanes are smaller than isotope effects reported in literature for the reactions of NMHCs artificially labeled with deuterium. The main reason for this difference is the reduced probability for reaction at a labeled site for compounds with close to natural deuterium abundance, although some impact of secondary isotope effects cannot be ruled out. Still, the KIEs for NMHCs with natural or close to natural abundance of deuterium are of sufficient magnitude to allow determination of the extent of chemical processing of hydrocarbons in the atmosphere using methods analogous to stable carbon KIE studies. Furthermore, it is shown that combining stable hydrogen and stable carbon isotope ratio data has the potential to also provide valuable information regarding the stable isotope ratios of emissions, and specifically to test one of the key assumptions of the stable isotope hydrocarbon clock, the absence of significant variations of the stable isotope ratio for the emitted NMHCs.

Key words: stable isotope ratios, kinetic isotope effects, non-methane hydrocarbons, deuterium, tropospheric OH radicals.

1. Introduction

The reaction of non-methane hydrocarbons (NMHCs) with OH radicals is the primary atmospheric removal mechanism for most light hydrocarbons (Ehhalt, 1999; Rudolph, 2002). Ambient measurements of the stable carbon isotope ratios of NMHCs have recently become a valuable tool for understanding the atmospheric chemistry of NMHCs (Rudolph *et al.*, 1997, 2000, 2003; Rudolph and Czuba, 2000; Tsunogai *et al.*, 1999; Saito *et al.*, 2002). Specifically, it has been demonstrated that measurements of stable carbon isotope ratios are useful for establishing the average photochemical ages of NMHCs in air ($t_{av} \cdot [\mathrm{OH}]_{av}$) as well as estimating average OH-radical concentrations. Rudolph and Czuba (2000) developed the theoretical concept which describes the dependence between the stable carbon isotope ratio and the average photochemical age, the so-called stable isotope hydrocarbon clock equation:

$$\delta^{13}\mathrm{C} = t_{av} \cdot [\mathrm{OH}]_{av} \cdot {}^{\mathrm{OH}}k \cdot {}^{\mathrm{OH}}\varepsilon^{13\mathrm{C}} + {}^{0}\delta^{13}\mathrm{C}\,. \tag{1}$$

Here, $\delta^{13}\mathrm{C}$ and ${}^{0}\delta^{13}\mathrm{C}$ represent observed and emitted carbon delta values for the studied hydrocarbon; t_{av} represents the average age of the compound; ${}^{\mathrm{OH}}k$ is the rate constant for the reaction with the OH radical; $[\mathrm{OH}]_{av}$ represents the average OH-radical concentration; and ${}^{\mathrm{OH}}\varepsilon^{13}\mathrm{C}$ represents the carbon KIE for the reaction of the studied compound with the OH radical in the following form:

$${}^{\mathrm{OH}}\varepsilon^{13\mathrm{C}}(‰) = \left(\frac{{}^{\mathrm{OH}}k_{12\mathrm{C}}}{{}^{\mathrm{OH}}k_{13\mathrm{C}}} - 1\right) \cdot 1000\,. \tag{2}$$

Here, $k_{12\mathrm{C}}$ is the rate constant for reaction of the NMHC containing only $^{12}\mathrm{C}$ atoms with OH, $k_{13\mathrm{C}}$ is the rate constant for the same reaction of the NMHC containing a $^{13}\mathrm{C}$ atom. Rudolph *et al.* (2000) and very recently Saito *et al.* (2002) demonstrated that this concept can successfully be applied to studies of NMHCs in the troposphere.

Stable hydrogen isotope ratios can potentially be used for the same purpose. An equation analogous to Equation (1) can be written to describe the dependence between observed and emitted hydrogen delta values ($\delta\mathrm{D}$ and ${}^{0}\delta\mathrm{D}$, respectively), the hydrogen KIE for reaction of the studied compound with OH radicals (using ${}^{\mathrm{OH}}\varepsilon^{\mathrm{D}}\,(‰) = (k_{\mathrm{H}}/k_{\mathrm{D}} - 1) \cdot 1000$, analogous to ${}^{\mathrm{OH}}\varepsilon^{13\mathrm{C}}$), and the average photochemical age:

$$\delta\mathrm{D} = t_{av} \cdot [\mathrm{OH}]_{av} \cdot {}^{\mathrm{OH}}k \cdot {}^{\mathrm{OH}}\varepsilon^{\mathrm{D}} + {}^{0}\delta\mathrm{D}. \tag{3}$$

In addition to the general possibility of using stable hydrogen isotope ratios to study atmospheric processing of NMHCs, the combination of stable hydrogen and stable carbon isotope ratio measurements will allow us to address the key uncertainty in the stable isotope hydrocarbon clock equation, namely uncertainty and variability of the stable isotope ratio of emissions. Combining Equations (1) and (3) results in a linear dependence between stable hydrogen and stable carbon isotope ratios which is valid for atmospheric NMHCs as long as the assumption of uniform stable isotope ratios of the emissions is justified.

$$\delta\mathrm{D} = \left(\frac{\mathrm{OH}_{\varepsilon}\mathrm{D}}{\mathrm{OH}_{\varepsilon}13\mathrm{C}}\right) \cdot (\delta^{13}\mathrm{C} - {}^{0}\delta^{13}\mathrm{C}) + {}^{0}\delta\mathrm{D}. \tag{4}$$

The slope of this linear function depends only on the KIEs for reaction of the studied NMHC with OH, and will therefore allow one to clearly distinguish between the influence of atmospheric processing and source variability. However, the possibility to use δD measurements for this purpose depends, among other factors, on the magnitudes of the carbon and hydrogen kinetic isotope effects.

Recently, the stable carbon KIEs for reactions of NMHCs with OH and other reactants of relevance for the atmosphere have been studied in several series of laboratory experiments (Iannone *et al.*, 2003; Rudolph *et al.*, 2000; Anderson *et al.*, 2003). There are also several studies of the effect of deuterium-labeling on the rate constants for reaction of several alkanes with OH radicals (Tully *et al.*, 1986a, b; Droege and Tully, 1986a, b, 1987). The reported deuterium isotope effects are substantial and suggest that they are of sufficient magnitude to allow for the usage of stable hydrogen isotope ratio measurements in studies of the atmospheric processing of NMHCs. However, these studies were performed using compounds where all hydrogen atoms at a given carbon atom were substituted by deuterium atoms. To our knowledge, no measurements of the stable hydrogen KIEs of NMHCs with close to natural deuterium abundance, which would be directly applicable to atmospheric studies, have been published to date. In this paper, we present laboratory measurements of stable hydrogen KIEs for the reaction of several light alkanes, alkenes and aromatic compounds with the OH radical. The results of these measurements are used to investigate the possibility of using stable hydrogen isotope ratio measurements for studies of the atmospheric processing of NMHCs.

2. Experiment

The experimental technique used to measure stable hydrogen isotope KIEs was very similar to the methods described by Rudolph *et al.* (2000), Anderson *et al.* (2003), and Iannone *et al.* (2003), therefore, only a brief description of the method is given here. In principle the procedure is a measurement of the relative rate for the reaction of molecules containing only ^{1}H atoms over the reaction of molecules containing a deuterium atom. In a reaction chamber, changes in the hydrocarbon concentration and stable hydrogen delta value were measured as a function of time and the KIEs are determined from the dependence between concentration and δD. In our experiments, we used hydrocarbons without artificial enrichment or depletion of deuterium and therefore close to natural deuterium/hydrogen ratios.

The reactions were carried out in reaction chambers ($\sim$25 L) made of PTFE foil of 0.13-mm thickness. Generally, the reaction chamber was replaced after two experiments. The reaction chamber was placed in a temperature-controlled housing which also allowed irradiation with up to twelve fluorescent lamps. The lamps used in these experiments had an emission maximum at 350 nm. All experiments were conducted at 298 ± 2 K.

The reaction chamber was filled with a mixture of NMHCs (typically 5 to 8 per experiment with mixing ratios between 150 ppm and 400 ppm per NMHC), and 400–600 ppm NO in synthetic air. Injections of liquid-phase isopropyl nitrite (IPN), were carried out after every measurement to compensate for the consumption of IPN. The resulting mixing ratio of IPN was in the range of 500–1000 ppm. IPN was synthesized in the laboratory using a procedure based on the synthesis of alkyl nitrites described by Noyes (1943). Gas-phase hydrocarbons *n*-butane (99.85%), and *i*-butane (99%) were purchased from Matheson Tri-Gas and Aldrich Chemical Company, respectively; and the liquid-phase hydrocarbons toluene (99.5+%), cyclopentane (99+%), *p*-xylene (99+%), ethylbenzene (99%), cyclohexene (99+%), *n*-pentane (99+%), cyclohexane (99.5%), *n*-hexane (99+%), 1-heptene (97%), *n*-heptane (99%), *n*-octane (98%), *n*-nonane (99%), and *n*-decane (99+%) were obtained from Aldrich Chemical Company. NO (1% mixture in N_2) was obtained from Air Products. All chemicals were neither artificially enriched nor depleted in ^{2}H and were used as purchased without further purification.

Prior to starting the experiments by turning on the lamps, the stability of the concentrations and stable hydrogen isotope ratios was verified. Experiments were only conducted if in the absence of light the relative changes in the concentrations were below 2% and the change in the delta values of the NMHCs was below 5‰ over a period of 3 h. Following the stability measurements, IPN was injected into the reaction chamber, and the lights were activated (5–20 min) to initiate OH production.

The change in concentration and stable hydrogen isotope ratio resulting from reaction of the NMHCs with OH was monitored by continuous-flow isotope ratio mass spectrometry (CF-IRMS) coupled with a gas chromatograph via a pyrolysis interface (GC-P-IRMS). At regular intervals, typically every hour, samples of 5 cm^3 were taken from the reaction chamber and analyzed. The NMHCs taken from the chamber air were cryogenically concentrated at 93 K in a cryofocussor trap. Subsequently the NMHCs were analyzed on a Varian 3400 Gas Chromatograph equipped with a 60 m × 5 μm film × 0.32 mm ID polymethyl siloxane (HP-1) column (Agilent Technologies). The temperature program used was: –30 °C initial temperature held for 2.00 min, increasing the temperature 2.50 °C min^{-1} until the final temperature of 180 °C was reached and then held for 20 min. The carrier gas was helium with a flow rate of 1.5–2 cm^3 min^{-1}.

The hydrocarbons in the GC effluent were passed through a pyrolysis furnace at 1723 K, where they were converted to an H_2/HD gas. The temperature and residence time (>300 ms) of gases that passed through the pyrolysis furnace were high enough to effect the quantitative conversion of all hydrocarbons including the CH_4 reference gas (Burgoyne and Hayes, 1998). The pyrolyzed GC flow then passed through a tubular Nafion® dryer to remove water and then entered the open split of the Finnigan DeltaPlus XL Isotope Ratio Mass Spectrometer (IRMS). At the beginning and end of every IRMS measurement, H_2 reference gas was automatically injected through a separate open split, and CH_4 reference gas was automatically injected via a 4-way bypass valve between the column and the pyrolysis furnace. These gas standards, of known hydrogen isotopic composition, provided the basis for which the δD values of the studied NMHCs were determined. Ion-current ratios were corrected for the formation of H_3^+ ions in the IRMS between experiments (Sessions *et al.*, 2001a, b). Since these experiments relied on relative data, absolute delta values, and hence the need for accurate calibrations with reference materials, were not strictly required. Typically, each experiment continued until the concentrations of the NMHCs were depleted to about 50–30% of their initial values.

IRMS traces were evaluated using Isodat NT Version 1.1 (Finnigan) software, and manual peak integrations were performed to evaluate peaks not integrated appropriately by the auto-integration routine. From these integrations, concentration and isotope ratio data of the NMHCs under study were obtained.

The measured stable hydrogen isotope ratios are the ratio of the deuterium-atom signal (HD) over the hydrogen-atom signal [H_2]. Due to the very low D over H ratio in NMHCs with close to natural D abundance, the number of NMHC molecules with more than one D atom can be neglected and consequently the measured [HD]/[H_2] ratio is proportional to the ratio of the concentrations of deuterium labeled over unlabeled molecules in the studied NMHC. The in-house CH_4 standard, which was injected both at the beginning and end of every measurement is traceable to V-SMOW and the stable hydrogen isotope ratios given here are presented as isotope ratios in delta notation as per mil (‰) values relative to the [D]/[H] ratio of V-SMOW ($R_{\text{V-SMOW}}$):

$$\delta D_{\text{V-SMOW}} = \left(\frac{R - R_{\text{V-SMOW}}}{R_{\text{V-SMOW}}}\right) \cdot 1000‰\,. \tag{5}$$

The following equation (e.g., Rudolph *et al.*, 2000) allows one to calculate the hydrogen KIE value from the dependence between measured delta values, δD, and concentrations, [H] at time t and at the beginning of the experiment ($t = 0$):

$$\text{KIE} = \frac{k_H}{k_D} = \frac{\ln([H]_t/[H]_0)}{\ln([H]_t/[H]_0) + \ln\left[\dfrac{\delta D_t + 1000}{\delta D_0 + 1000}\right]} \tag{6}$$

Rearrangement of Equation (6) gives

$$\ln([H]_t/[H]_0) = \left(\frac{k_H/k_D}{1 - k_H/k_D}\right) \ln\left[\frac{\delta D_t + 1000}{\delta D_0 + 1000}\right] \tag{7}$$

and the KIE, k_H/k_D, is calculated from the slope of the linear regression according to Equation (7). In this paper, only results from experiments with a correlation coefficient (R^2) greater than 0.95 are presented.

Table I. Hydrogen KIE values for reaction of NMHC with OH-radicals

NMHC	Number of hydrogen atoms	Average KIE value,[a] ‰
Toluene	8	29.8 ± 2.1 (2)
n-Butane	10	51.6 ± 2.1 (2)
i-Butane	10	97.3 ± 12.5 (2)
Cyclopentane	10	63.2 ± 5.9 (3)
p-Xylene	10	10.5 (1)
Ethylbenzene	10	26.8 ± 3.5 (2)
Cyclohexene	10	11.1 (1)[b]
n-Pentane	12	65.9 ± 7.0 (3)
Cyclohexane	12	79.5 ± 9.6 (2)
n-Hexane	14	52.8 ± 5.0 (4)
1-Heptene	14	23.4 (1)[b]
n-Heptane	16	38.9 ± 7.8 (4)
n-Octane	18	33.4 ± 3.1 (4)
n-Nonane	20	29.6 ± 1.6 (2)
n-Decane	22	29.0 ± 5.3 (3)

[a] The number of measurements conducted is given in brackets; the error given is the error of the mean value where more than one measurement was made.
[b] These values represent a combination of reaction with OH and O_3, see text for details.

The hydrogen KIE values are presented here as per mil epsilon values, ${}^{\mathrm{OH}}\varepsilon^{\mathrm{D}}(‰)$:

$$ {}^{\mathrm{OH}}\varepsilon^{\mathrm{D}}(‰) = \left(\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} - 1\right) \cdot 1000 \,. \tag{8} $$

3. Results

The data obtained from 10 experiments using, in total, 15 different NMHCs is summarized as Table I. The relative errors are generally less than 20%, and for all NMHCs except for *i*-butane, the uncertainty of the average KIE is less than 10‰. Similar to the carbon KIEs for reaction of NMHCs with OH radicals, all measured hydrogen KIEs are normal kinetic isotope effects: Molecules containing the heavier isotope react slower than molecules containing only the light isotope.

Because UV radiation ($\lambda_{\max} = 350$ nm) was used to initiate the production of OH radicals, there is the possibility that ozone could be generated, stemming from the photolysis of NO_2. For unsaturated compounds this can potentially cause bias due to their reaction with ozone. In the case of aromatic hydrocarbons it is extremely unlikely that this bias can be of any significance. The OH-radical concentration in the reaction chamber is typically in the range of 10^8 radicals cm^{-3}. The rate constants for the ozone reaction of the aromatic compounds studied here are approximately ten orders of magnitude smaller than the corresponding OH-radical rate constants. Consequently ozone concentrations below 10^{17} molecules cm^{-3}, which corresponds to mixing ratios of several thousand ppm, will have little impact on the studied aromatic compounds. The accumulation of several thousand ppm of ozone in the reaction chamber can be ruled out. However, in the case of alkenes the situation is less favorable. Due to their higher reactivity towards ozone, a recognizable interference due to ozone reaction would only require ozone mixing ratios in the range of some ppm. Although the presence of an excess of NO will reduce the ozone concentration due to the reaction $NO + O_3 \rightarrow NO_2 + O_2$, in our reaction system ozone mixing ratios of some ppm cannot be ruled out for the photo-stationary state between NO_2 photolysis and the NO-ozone reaction.

Indeed, the observed relative rate for the reaction of 1-heptene versus toluene is 4.7, whereas the relative rate expected from published rate constants for the OH-radical reaction (Table II) is only 2.9. Since for alkanes and aromatic compounds the observed relative rates on average differ only by approximately 10% from those calculated using published OH-radical reaction rate constants (Table II), this indicates that approximately 40% of the removal of 1-heptene is due to reaction with ozone. The KIE for the reaction of 1-heptene with ozone is $(9.2 \pm 1.8)‰$ (R. Iannone, unpublished results). Based on this, we estimate that the true KIE for the reaction of 1-heptene with the OH-radical is approximately 30‰. Although this value has a substantial uncertainty, it is still significantly smaller than the KIE for the reaction of an alkane with the same number of hydrogen atoms.

In the case of cyclohexene we estimate that a considerably larger fraction of the observed concentration decrease, about 80%, is due to reaction with ozone; a consequence of the higher reactivity of cyclohexene towards ozone (Table II). It is therefore not surprising that the experimental KIE of 11.1‰ for cyclohexene is very close to the KIE of $(9.5 \pm 0.7)‰$ for reaction of cyclohexene with ozone (R. Iannone, unpublished results). The small contribution of the OH-reaction to the observed KIE does not allow the calculation of a meaningful true KIE for the reaction of cyclohexene with OH. Nevertheless, this indicates that the KIE for the OH-reaction of cyclohexene is considerably smaller than the KIEs found for saturated hydrocarbons. E.g. a KIE of 50‰ for the OH-reaction would result in a combined ozone and OH-reaction KIE of approximately 18‰, significantly higher then the observed value of 11.1‰.

Two general features are obvious from the results shown in Table I. The hydrogen KIEs for saturated NMHCs are significantly higher than those for unsaturated NMHCs and, within each of these two groups, the KIEs decrease with increasing number of hydrogen atoms.

Table II. Summary at rate constants for the OH + NMHC and O_3 + NMHC reactions in this study at 298 K

NMHC	k_{OH}, 10^{-12} cm^3 molecule^{-1} s^{-1}	k_{OH}, cm^3 molecule^{-1} s^{-1}
Toluene	6.0^{a}	1.50×10^{-22} ^{d}
Cyclopentene	57^{b}	6.55×10^{-16} ^{e}
n-Butane	2.44^{c}	9.88×10^{-24} ^{f}
i-Butane	2.19^{c}	2.04×10^{-23} ^{f}
Cyclopentane	5.02^{c}	
p-Xylene	14.3^{a}	4.0×10^{-22} ^{d}
Ethylbenzene	7.1^{a}	
Cyclohexene	67.7^{c}	7.45×10^{-17} ^{e}
n-Pentane	4.0^{b}	
Cyclohexane	7.21^{c}	
n-Hexane	5.45^{c}	
1-Heptene	40^{c}	9.4×10^{-18} ^{g}
n-Heptane	7.0^{c}	
n-Octane	8.7^{c}	
n-Nonane	10.0^{c}	
n-Decane	11.2^{c}	

[a] Atkinson (1997); [b] Rogers (1989); [c] Atkinson (1994); [d] Pate *et al.* (1976); [e] Greene and Atkinson (1992); measured 296 ± 2 K; [f] Schubert and Pease (1956); [g] Grosjean and Grosjean (1995); measured at 288 K.

Within a homologous series such as the *n*-alkanes (Figure 1), the KIE systematically depends on the number of hydrogen atoms in the molecule. Although there is some variability, as a first approximation, the KIEs for *n*-alkanes can be described by KIE (*n*-alkane) $= (640 \pm 43)‰/N_H$, where N_H is the number of hydrogen atoms. To some extent other alkanes follow this dependence, though there are deviations for *i*-butane and cyclohexane. Similarly, the stable hydrogen KIE reported for the reaction of methane with OH is 294‰ (Saueressig *et al.*, 2001). This is about 70% higher than one would expect from extrapolation of the *n*-alkane KIEs but within 20% of the value expected from extrapolation of the *i*-butane and cyclohexane KIEs. This indicates that details of the structure of the *n*-alkane may have a visible impact on the magnitude of the KIE.

This inverse dependence on number of hydrogen atoms is very similar to the carbon number dependence of the carbon KIEs found for these reactions (Rudolph *et al.*, 2000), although the magnitude of the carbon and hydrogen KIEs differs. The reason for this dependence is the marginal impact of isotopically heavy atoms on the rate of reaction if they are remote from the reaction site of the molecule. Due to the low abundances of the heavier isotopes of hydrogen (0.0115 atom %)

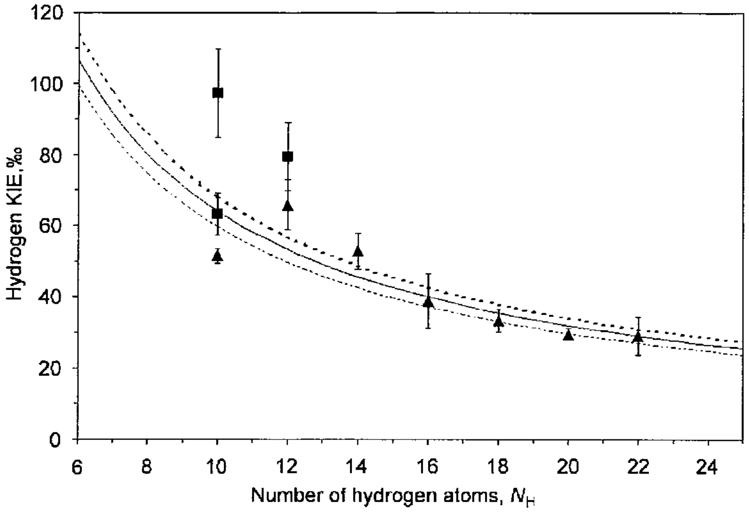

Figure 1. Dependence between the hydrogen KIE for reaction of alkanes with OH radicals and number of hydrogen atoms (N_H) within the studied molecule. Measured KIEs for *n*-alkanes are shown as triangles, the solid line is a least squares fit to an inverse dependence between KIE and number of hydrogen atoms (KIE = (640 ± 43)‰/N_H; the dashed lines represent the uncertainty of the least squares fit. The squares represent the KIEs for other alkanes (*i*-butane, cyclopentane and cyclohexane).

and carbon (1.07 atom %) (Rosman and Taylor, 1998), the molecules studied here effectively never contain more than one atom of the heavier isotope. Thus for a molecule which contains an atom of the heavy isotope of carbon or hydrogen the probability that this heavy atom is located in the vicinity of the reaction site decreases with the number of carbon or hydrogen atoms.

Similar to the KIEs for reactions of saturated NMHCs, the KIEs for unsaturated hydrocarbons can also be approximated by an inverse dependence on the number of hydrogen atoms of the studied compounds, KIE (unsaturated) = (214 ± 93)‰/N_H. Although the measured hydrogen KIEs for unsaturated compounds have a substantial uncertainty, it is obvious that, on average, hydrogen KIEs for unsaturated NMHCs are a factor of approximately three smaller than those for saturated compounds. This is consistent with the different mechanisms for reaction of saturated and unsaturated NMHCs with the OH radical. Saturated NMHCs react exclusively by hydrogen-atom abstraction. Unsaturated NMHCs, on the other hand, mainly react via addition of the OH radical to a double bond. Reactions occurring directly at the H atom, such as abstraction, have larger hydrogen KIEs than addition reactions. Zero-point energy effects (ZPEs) in abstraction reactions lead to substantial D/H fractionation due to the relative energy requirements for the scissions of C–H versus C–D bonds via reaction with the OH radical.

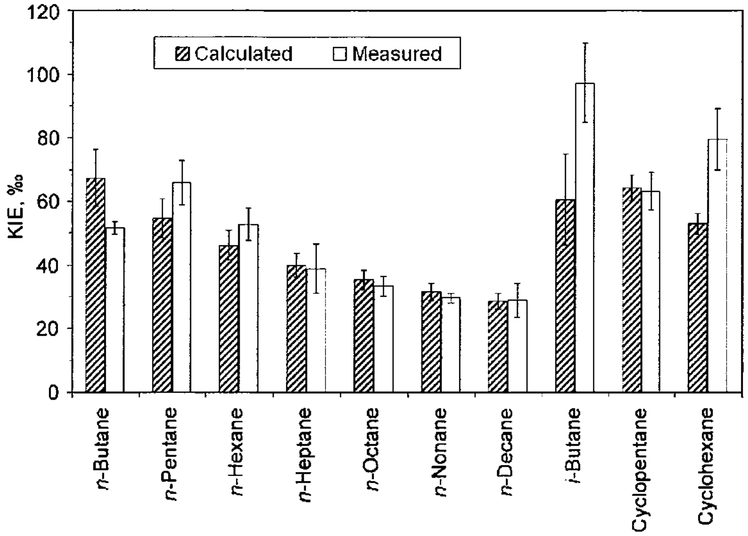

Figure 2. Comparison of calculated and measured hydrogen KIEs for the reaction of NMHCs with OH radicals. The calculations are based on the site specific reactivities published by Tully *et al.* (1986a) and Droege and Tully (1986b).

During addition of OH to a double bond a C–O bond is formed, and because neither O–H nor C–H bonds are formed or disrupted, these isotope effects are secondary. However, it should be noted that, to some extent, unsaturated compounds also react with OH radicals via abstraction. Although this is only a small contribution to the overall reaction, it can be expected that the hydrogen KIE resulting from abstraction is significantly higher than the KIE due to addition and therefore may still have an impact on the overall hydrogen KIEs for some unsaturated compounds.

To our knowledge there are no published measurements of stable hydrogen KIEs for reactions of NMHCs with close to natural isotope abundance. However, Tully *et al.* (1986a), and Droege and Tully (1986a, b) determined the OH-reactivities of hydrogen and deuterium atoms attached to primary, secondary, and tertiary carbon atoms from measurements of the rate constants of deuterium-labeled and natural-abundance NMHCs. Based on these site-specific rate constants, the KIEs for NMHCs with any known abundance and distribution of deuterium labeling can be calculated. The results of such calculations for NMHCs with close to natural deuterium abundance and a uniform distribution of the deuterium atoms are shown in Figure 2 together with the results of our measurements.

In general, the calculated and measured kinetic isotope effects agree well. The only exceptions are *i*-butane and cyclohexane. But even for these two compounds, the discrepancy between calculation and measurement is only slightly larger than the statistical 1σ uncertainty of the differences. This suggests that secondary isotope effects are of minor importance for the reaction of alkanes with the OH radical.

However, for all studied *n*-alkanes and cycloalkanes, the reaction, and therefore also the KIE, is dominated by attack of the OH radical on a methylene-group hydrogen or deuterium atom. The only studied compound where reaction at primary or tertiary carbon atoms plays a major role is *i*-butane; a too limited basis for general conclusions. When using those site-specific reactivities for reactions at primary or secondary carbon atoms published by Droege and Tully (1986a) for propane, the calculated kinetic isotope effects for *n*-alkanes and cycloalkanes are only a few percent larger than the results of the calculations in Figure 2, which were based on reactivities derived for n-butane (Droege and Tully, 1986b). We therefore think it is justified to use the general dependence between structure and KIE to derive first order estimates of hydrogen KIEs for reaction of alkanes with OH, which have not been studied experimentally. Specifically, for experimental reasons our measurements did not include ethane and propane and we estimate that their KIEs are approximately 150‰ and 90‰, respectively. Although there are still some uncertainties in our overall understanding of the stable hydrogen KIEs for reaction of NMHCs with the OH radical it is sufficient to justify a deeper look into the possibility of using stable hydrogen isotope studies of NMHCs to improve our understanding of the atmospheric chemistry of NMHCs.

4. Consequences for Atmospheric Observations of Stable Hydrogen Isotope Ratios and Their Interpretation

Potentially, the large hydrogen KIEs make δD measurements of NMHCs a powerful tool to study chemical processing in the atmosphere since the magnitude of the change in δD is proportional to the KIE (see Equations (1) and (3)). However, the magnitude of the KIE is not the only factor determining the usefulness of δD values for studies of the atmospheric chemistry of NMHCs. It has been mentioned previously that variability or uncertainty of the δD value of NMHC emissions is one of the key uncertainties in the use of Equations (1) or (3) to quantify average atmospheric processing of NMHCs.

No studies of the δD values of NMHC emissions are known to us, but the stable hydrogen isotope ratios of petroleum have been studied in great detail (e.g., Yeh and Epstein, 1981). For most NMHCs, the dominant sources are due to usage, consumption, and processing of petroleum derived products and Rudolph *et al.* (2002) found that the δ^{13}C values for many NMHCs emitted into the atmosphere are very close to the average δ^{13}C value of crude oil. Therefore a first approximation of the variability of the δD value of NMHC emissions can be obtained from the δD values of crude oil.

The variability of the stable hydrogen isotope ratio of crude oil observed by Yeh and Epstein (1981) corresponds to a standard deviation of approximately ±20‰. This is approximately an order of magnitude higher than the variability they reported for stable carbon isotope ratios. To some extent this reduces the advantage of the large hydrogen KIEs to quantify photochemical processing using Equation

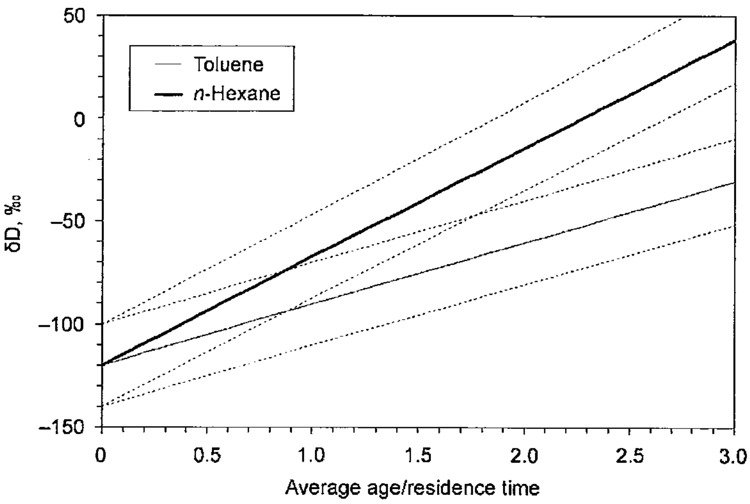

Figure 3. Change in stable hydrogen isotope ratio as function of average photochemical age for toluene and hexane. The photochemical age is given in multiples of atmospheric residence time ($\tau = (k_{\mathrm{OH}} \cdot [\mathrm{OH}]_{av})$ to eliminate the dependence on the rate constant and average OH-radical concentration. The dotted lines give the uncertainty range resulting from errors in the KIEs and the uncertainty of the stable hydrogen isotope ratio of the emissions.

(3). Nevertheless, δD measurements can be a sensitive tool to study atmospheric processing by OH radicals, and two examples are shown in Figure 3. In the case of *n*-hexane and other light alkanes (not shown in Figure 3), a time period which corresponds to less than one third of their average atmospheric lifetime will result in changes of δD which are higher than the expected variability of emissions. Based on an average OH concentration of 10^6 radicals cm^{-3}, this corresponds to approximately one day. In the case of toluene and other aromatic compounds the situation is less favourable due to the lower hydrogen KIEs for the reaction of this group of compounds with OH. Nevertheless, it can be expected that for these compounds, OH-processing exceeding the equivalent of one atmospheric lifetime will change δD by a value exceeding the uncertainty of the source composition.

The uncertainty of the stable isotope ratio of NMHC emissions is the key limitation in the use of stable isotope ratios to determine the photochemical age of atmospheric NMHCs. Other sources of uncertainty are measurement errors, and errors of the KIEs and the reaction rate constants. However, these other sources of uncertainty depend on the accuracy of experimental data and therefore can, at least in principle, be reduced by improving experimental methods.

In the absence of variations of the stable carbon isotope ratio in NMHC emissions, a well-defined and unambiguous dependence between δD and δ^{13}C exists as formulated in Equation (4). Examples for different NMHCs are shown in Figure 4. The stable isotope ratios of NMHC emissions used in these calculations are based

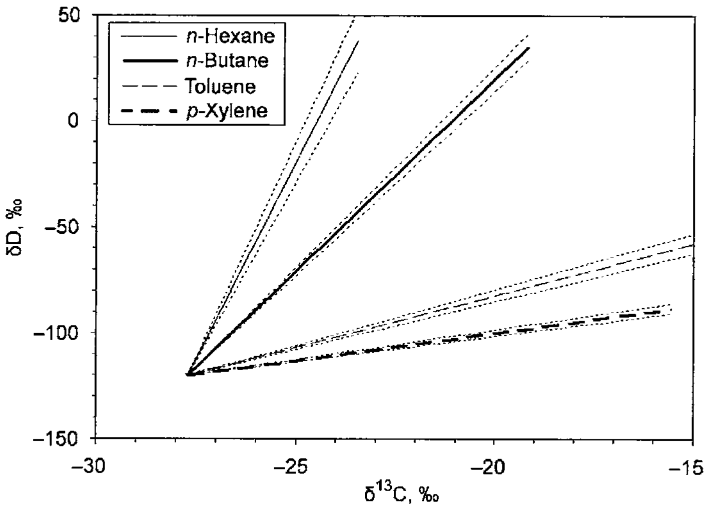

Figure 4. Dependence between stable hydrogen and carbon isotope ratios of NMHCs in the atmosphere resulting from reaction with OH radicals according to $\delta D = ({}^{OH}\varepsilon^{D}/{}^{OH}\varepsilon^{13C}) \cdot (\delta^{13}C - {}^{0}\delta^{13}C) + {}^{0}\delta D$ (4). The hydrogen KIEs (${}^{OH}\varepsilon^{D}$) are taken from this work, the carbon KIEs (${}^{OH}\varepsilon^{13C}$) from Rudolph *et al.* (2000) and Anderson *et al.* (2003). The stable isotope ratios of the emissions are –27.7‰ for carbon and –120‰ for hydrogen. The thin lines show the uncertainties of δD resulting from errors of the KIEs.

on an average stable carbon isotope ratio of –27.7‰ (Rudolph *et al.*, 2002) and a stable hydrogen isotope ratio of –120‰ (Yeh and Epstein, 1981). The uncertainty estimates shown in Figure 4 are based on the errors of the hydrogen and carbon KIEs for the reaction of NMHCs with OH radicals. Based on these uncertainty estimates, small changes in the stable isotope ratios of emissions will be clearly visible as deviations from the predicted ideal behaviour. Combining measurements of stable carbon and stable hydrogen isotope ratios will greatly reduce uncertainties in photochemical ages of NMHCs derived from isotope ratio measurements.

However, this does not necessarily allow one to distinguish the influence of the different factors. Measurements of stable hydrogen and stable carbon isotope ratios of atmospheric NMHCs will provide two constraints for each NMHC, but the atmospheric observations will depend on three factors: (1) the stable carbon isotope ratio of the emissions, (2) the stable hydrogen isotope ratio of the emissions, and (3) the average photochemical age. Obviously, this problem cannot be solved without introducing additional constraints. Such additional constraints can be obtained by using NMHCs with only a weak dependence between δD and $\delta^{13}C$ such as *n*-hexane or *p*-xylene (Figure 4). This opens up the possibility to correct for the impact of atmospheric aging on either stable carbon or stable hydrogen ratios of atmospheric NMHCs. We can rearrange Equation (4) to determine the stable isotope ratios of emissions from atmospheric measurements:

$$^{0}\delta\mathrm{D} = \delta\mathrm{D} - \left(\frac{\mathrm{OH}_{\varepsilon}{}^{\mathrm{D}}}{\mathrm{OH}_{\varepsilon}{}^{13\mathrm{C}}}\right) \cdot (\delta^{13}\mathrm{C} - {}^{0}\delta^{13}\mathrm{C}) \tag{9a}$$

or

$$^{0}\delta^{13}\mathrm{C} = \delta^{13}\mathrm{C} - \left(\frac{\mathrm{OH}_{\varepsilon}{}^{13\mathrm{C}}}{\mathrm{OH}_{\varepsilon}{}^{\mathrm{D}}}\right) \cdot (\delta\mathrm{D} - {}^{0}\delta\mathrm{D}). \tag{9b}$$

Uncertainty in stable carbon isotope ratios of emissions ($\Delta^{0}\delta^{13}\mathrm{C}$) results in uncertainties of the corrected stable hydrogen isotope ratio ($\Delta^{0}\delta\mathrm{D}$) according to the following equation:

$$\Delta^{0}\delta\mathrm{D} = \left(\frac{\mathrm{OH}_{\varepsilon}{}^{\mathrm{D}}}{\mathrm{OH}_{\varepsilon}{}^{13\mathrm{C}}}\right) \cdot \Delta\delta^{13}\mathrm{C}\,. \tag{10a}$$

Or in case of stable carbon isotope ratios:

$$\Delta^{0}\delta^{13}\mathrm{C} = \left(\frac{\mathrm{OH}_{\varepsilon}{}^{13\mathrm{C}}}{\mathrm{OH}_{\varepsilon}{}^{\mathrm{D}}}\right) \cdot \Delta\delta\mathrm{D}\,. \tag{10b}$$

Obviously, the uncertainty of stable isotope ratios of emissions derived from the previous equations will depend on the ratio of the stable carbon KIE over the stable hydrogen KIE. If there is no kinetic isotope effect, the atmospheric measurement will represent the isotope ratio of the emissions and thus could be directly used for source identification or source apportionment purposes. However, our KIE measurements show that ignoring the impact of atmospheric processing may result in substantial bias for stable isotope ratios derived from atmospheric observations.

A schematic example based on the KIEs of *p*-xylene is shown in Figure 5. The extrapolation of an observed δD to values consistent with δ^{13}C values which are within the expected composition of emissions (broken vertical lines in Figure 5) constrains the stable hydrogen isotope ratio of the sources (dark shaded range in Figure 5). In this example, the range of the thus derived stable hydrogen isotope ratio is substantially smaller than the variability observed for crude oil, the parent material for many NMHCs in the atmosphere.

The use of stable isotope ratios to study photochemical processing is based on an approximation and the validity of this approximation depends on the following condition (Rudolph and Czuba, 2000):

$$\frac{\tau}{\Delta\tau} \gg \ln\left(\frac{^{0}\mathrm{c}}{\mathrm{c}}\right). \tag{11}$$

Here, τ is the atmospheric residence time of the studied compound; $\Delta\tau$ is the difference in residence time between molecules containing a heavy isotope of hydrogen or carbon and those containing only the light isotope; and $^{0}\mathrm{c}/\mathrm{c}$ describes

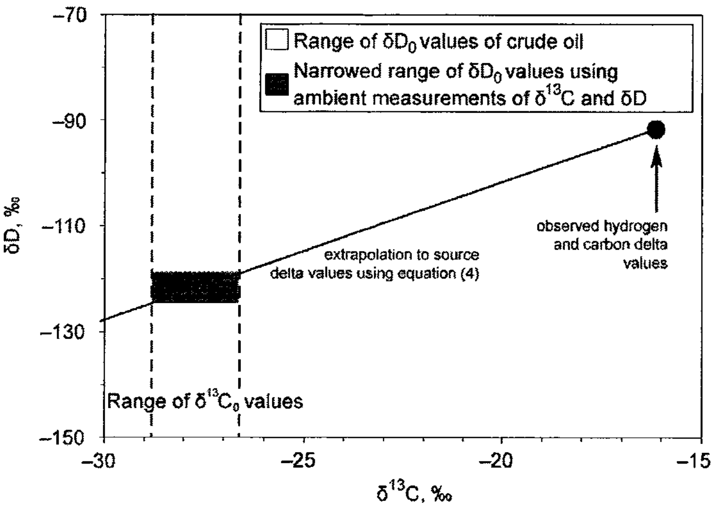

Figure 5. Schematic presentation of the possibility to correct ambient stable isotope ratio observations for atmospheric processing of *p*-xylene by OH radicals. The solid circle represents the hypothetical result of a measurement, the solid line shows the dependence between stable hydrogen and stable carbon isotope ratios predicted by Equation (4), and the broken line gives the uncertainty range for the stable carbon isotope ratios of aromatic hydrocarbon emissions reported by Rudolph *et al.* (2002). The dark grey shaded area gives the range of stable hydrogen isotope ratios of emissions, which would be compatible with an observation of the chosen δD and $\delta^{13}C$. For comparison, the variability of the stable hydrogen isotope ratio of crude oil (Yeh and Epstein, 1981) is shown as a light grey shaded area.

the change in concentration due to chemical removal of the studied compound. It has been shown that for stable carbon isotope studies, the condition (11) is met for all circumstances that can be realistically expected in the atmosphere. However, as mentioned above, hydrogen KIEs for reaction of NMHCs with OH are significantly larger than the corresponding carbon KIEs and therefore $\tau/\Delta\tau$ will be smaller. The largest hydrogen KIEs we measured is approximately 100‰ (Table I), equivalent to a value of ten for $\tau/\Delta\tau$. Using condition (11), this corresponds to a concentration change of about four orders of magnitude. This is still sufficient to cover the relevant range of atmospheric concentrations of alkanes, which are typically between some ppt and several ppb (Rudolph, 2002).

Another potential source of bias is the dependence of the isotope effects on the site of deuterium substitution. This can cause enrichment of deuterium at one site relative to another site during the atmospheric degradation of NMHCs by OH. Combined with the site specific probability for reaction with OH-radicals this will result in small, but not necessarily negligible changes in the overall reactivity of the deuterium-containing compounds and thus of the KIE. For example, the reaction of *n*-alkanes with the OH radical will cause a preferential enrichment of deuterium at the methyl groups. Since the the kinetic isotope effect is smaller for *n*-alkanes labeled at the methylene group compared to those labeled at the methyl group, the average KIE will change depending on the extent of labeling at the different sites. Based on the site specific reactivity studies of Tully *et al.* (1986a), and Droege and Tully (1986a, b), we calculate that a deuterium enrichment of 100‰ at the secondary carbon atoms of n-butane or n-pentane will change the overall KIE for reaction with OH radicals by approximately 1‰. For heavier n-alkanes the effect will be even smaller. A similar enrichment of deuterium at the tertiary carbon atom of i-butane results in a change of nearly 7‰, which is still in the range of the uncertainties of measured KIEs, but already a potentially relevant contribution to the overall uncertainties of photochemical age estimates based on stable hydrogen isotope measurements of NMHCs.

5. Summary and Conclusions

Based on the measured stable hydrogen kinetic isotope effects for reaction of NMHCs with OH radicals, we expect substantial changes in δD values from chemical processing in the atmosphere. We predict that in many cases these changes will be larger than the uncertainty in the stable hydrogen isotope ratio of emissions. Therefore, measurements of δD will be useful in the study of the atmospheric processing of NMHCs, similar to measurements of δ^{13}C. In the case of hydrogen KIEs, by far the largest effects are found for saturated compounds, whereas in the case of carbon, the KIEs for reactions of unsaturated hydrocarbons are higher.

Combining measurements of stable hydrogen and stable carbon isotope ratios of atmospheric NMHCs has much potential to reduce uncertainties in calculations of photochemical processing. Specifically, this will allow one to recognize errors resulting from variability of stable isotope ratios of emissions. Furthermore, it is predicted that concurrent measurements of stable carbon and hydrogen isotope ratios of atmospheric NMHCs will also provide information of the isotope ratios of the emissions and will thus be useful for source identification.

Presently there is no published method for measurements of the δD of atmospheric NMHCs. Existing methods for measurement of δ^{13}C of atmospheric NMHCs (Rudolph *et al.*, 1997, 2000; Tsunogai *et al.*, 1999; Saito *et al.*, 2002) could be modified; though the much lower isotope ratios for D compared to ^{13}C will require larger samples to obtain an adequate signal-to-noise ratio at the IRMS collectors. However, this problem is, to some extent, compensated by the larger hydrogen KIEs. For saturated hydrocarbons in the atmosphere, measurements of the stable hydrogen isotope ratios with approximately 10‰ precision will be sufficient to quantify the impact of atmospheric reactions on their stable hydrogen isotope ratios.

Finally it has to be mentioned that potentially other atmospheric processes than the studied reaction with OH-radicals can contribute to a change in δD or δ^{13}C. Although the reaction with OH-radicals is by far the most important loss process for the NMHC studied here, there exist conditions where other reactions can be relevant. For example, for alkenes reaction with ozone and at night under specific conditions, the reaction with the NO_3 radical can be relevant, and, during polar sunrise at high northern latitudes, Cl-atom reactions have a substantial impact on the removal of alkanes from the lower troposphere. Obviously, these reactions potentially can create a bias for the interpretation of stable isotope ratios of atmospheric NMHCs. On the other hand, depending on the magnitude of the KIEs for these reactions, isotope ratio measurements may provide a more detailed insight into the relative importance of these reactions.

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