J. Phys. Chem. A 2003, 107, 6191−6199

Method for Measuring Carbon Kinetic Isotope Effects of Gas-Phase Reactions of Light Hydrocarbons with the Hydroxyl Radical

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Received: January 30, 2003; In Final Form: May 26, 2003

A technique for the accurate measurement of the carbon kinetic isotope effects (KIEs) of the reactions of light non-methane hydrocarbons (NMHC) with OH radicals in the gas phase is presented. The method uses a variant of established relative rate techniques, which has been optimized for measurements of KIEs. The instrumentation consists of three basic components: (1) a gas-phase reaction chamber, (2) a gas chromatograph (GC) for separating the components of the reaction mixture, and (3) an isotope ratio mass spectrometer coupled on-line to the GC. Using this technique, measurements of hydroxyl radical reaction KIEs with C_2−C_9 saturated and unsaturated hydrocarbons having rate constants between 10^{-11} and 10^{-13} cm^3 molecule^{-1} s^{-1} are achievable. This method has been used successfully to measure the carbon KIE for the reactions of OH with a wide range of hydrocarbons in the gas phase.

1. Introduction

Measurements of isotope effects can be used to gain better insight into the fundamentals of chemical reaction as well as to study complex chemical and physical systems ranging from sedimentary rocks, crude oil, natural gas reservoirs, and marine and terrestrial plants to planetary atmospheres and outer space. Studies of the kinetic isotope effect (KIE) of gas-phase reactions of organic compounds have been conducted to study the mechanisms of these reactions as well as to provide an understanding of the process, which is needed to interpret stable isotope ratio measurements of organic compounds in the atmosphere. Examples for the use of studies of isotope effects to gain insight into reaction mechanisms are measurements of rate constants for reactions of deuterium-labeled and unlabeled light non-methane hydrocarbons (NMHC) with OH radicals[1−5] and with Cl atoms.[6] The possibility to use stable carbon and hydrogen isotope ratio measurements to identify sources for atmospheric trace gases, to constrain budgets of important atmospheric trace gases, and to differentiate between mixing processes and chemical reactions in the atmosphere[7−12] has triggered studies of kinetic isotope effects for gas-phase reactions of organic compounds with a natural abundance or close to a natural abundance of stable isotopes. Here the most widely studied reaction type is the reaction with OH radicals, the most important removal process for organic compounds in the atmosphere.[13]

In the past, most of KIE studies of gas-phase reactions of organic compounds were conducted by performing separate measurements of the rate constants for isotopically labeled and unlabeled compounds.[1−6] The advantage of this procedure is that no additional instrumentation is required. The disadvantage is that uncertainties of the rate constant measurements propagate into the uncertainty of the isotope effects, which results in significant uncertainties of the KIEs. In favorable cases,[1−5] the relative uncertainties of the KIEs are in the range of 5−10% of the measured rate constants; in less favorable cases,[6] the relative uncertainty of the KIE may be as high as 25%. Although this is sufficient for studies of reactions with large isotope effects, such as differences in rate constants between unlabeled and artificially deuterated organic compounds, this approach is of limited use for measurements of very small isotope effects (e.g. for stable carbon isotope effects or for reactions of organic compounds without artificial labeling). In these cases, the KIE often is very close to unity, and determining a very small isotope effect from the ratio of individually measured absolute rate constants can result in uncertainties larger than the studied effect.

For measurements of very small KIEs, relative rate methods are more suitable.[10,14,15] Saueressig et al.[15] report measurements of the stable carbon and stable hydrogen KIEs for reactions of methane with the OH radical of 1.0039 ± 0.0004 and 1.294 ± 0.018, respectively. Rudolph et al.[10] report measurements of KIEs for reactions of NMHC with the OH radical with uncertainties in the range of ±0.001 and less. In the paper by Rudolph et al.,[10] a very brief description of the methodology, which is based on a relative rate method combined with gas chromatography coupled on-line to isotope ratio mass spectrometry, is given. Here we present a detailed description and characterizations of the instrumentation, the experimental procedure, and the data evaluation for high-precision measurements of KIEs for gas-phase reactions of NMHC.

2. Experimental Procedure

Our procedure for KIE measurement is a modification of the method used for measuring relative reaction rates of NMHC−OH reactions in which reactants are irradiated inside a flexible PTFE reaction chamber in the presence of an alkyl nitrite and NO.[16−19] The setup for the technique consists of a reaction chamber, automated sampling procedure, cryogenic concentra-

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10.1021/jp034256d CCC: $25.00

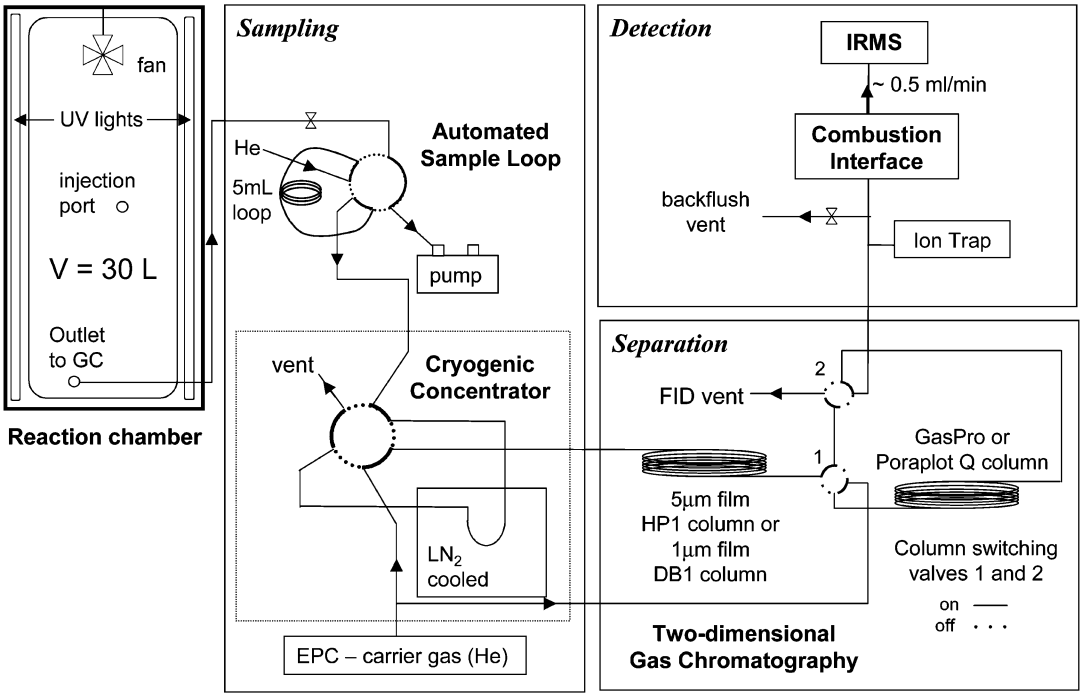

Figure 1. Diagram of the instrumentation for kinetic isotope effect studies.

tor, gas chromatograph, combustion interface, and isotope ratio mass spectrometer (GCC-IRMS) (Figure 1). Changes in hydrocarbon concentration and the stable carbon isotope ratio in the reaction chamber are monitored as a function of time. The KIE is determined from the dependence between concentration and the stable carbon isotope ratio of the studied NMHC.

The unreacted hydrocarbons in samples taken from the reaction chamber are separated on a gas chromatograph, after which a quantitative combustion step converts all hydrocarbons to CO_2, followed by isotopic analysis on an isotope ratio mass spectrometer (IRMS). The gas chromatographic separation is necessary to differentiate between reactants and products, but it also allows the study of several hydrocarbons in one experiment. In our experiments, we use NMHC without artificial labeling.

2.1. Reaction Chamber. Synthetic air, ppm-level hydrocarbon reactants, isopropyl nitrite, and NO are introduced into a PTFE reaction chamber (0.13-mm wall thickness) of approximately 30-L volume suspended in a box with dimensions of 1.3 m × 0.5 m × 0.3 m. The isopropyl nitrite used in our experiments was prepared by the synthesis described by Noyes.[20] The hydrocarbons were 97+% grade chemicals from Sigma Aldrich, Air Products, and Matheson Gas. A fan on the top of the box and a vent near the bottom of the box allow ambient temperature to be maintained inside the reaction chamber, typically 295 ± 4 K. Four fluorescent "black lights" emitting in the wavelength range from 320 to 400 nm are mounted on the inside corners of the box. OH radicals are generated by the photolysis of isopropyl nitrite in the presence of ppm levels of NO according to the following reaction sequence:

$$(CH_3)_2HCONO + h\nu \rightarrow (CH_3)_2HCO + NO$$

$$(CH_3)_2HCO + O_2 \rightarrow (CH_3)_2CO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

The reaction chambers are replaced after three experiments to avoid the accumulation of reaction products on the inner walls of the chambers. Prior to use in an experiment, new reaction chambers are filled with synthetic air and placed horizontally on a laboratory bench for at least 8 h. Only chambers that experience no visual loss of air are used in the KIE experiments.

The reaction chamber is equipped with several ports, which are connected to a series of valves and a diaphragm pump. This allows the emptying and filling of the chamber with gases without opening it to ambient air. Similarly, gaseous and liquid reactants are added directly to the reaction chamber through an injection port in the PTFE chamber.

Before the start of the experiments, the reaction chamber was emptied using a diaphragm pump and refilled with synthetic air (Air Products, 99.9%) three times. At this point, analyses of the air in reaction chambers previously used for an experiment showed less than ppb levels of hydrocarbons and low ppb levels of acetone, a product from the isopropyl nitrite photolysis from the previous experiment. After filling the chamber with air for the third time, we added NO and hydrocarbons. At least three measurements of the stable carbon isotope ratios and concentrations, so-called "stability measurements", were made before starting the reaction to verify that the concentration and isotope ratio remained unchanged in the absence of OH radicals.

2.2. Sampling. Samples were taken from the reaction chamber and analyzed at approximately 2-h intervals. The samples are taken from the reaction chamber by an automated sample loop located between the reaction chamber and a diaphragm pump (Figure 1). A needle valve located between the six-port sampling valve and the pump controls the flow rate of air being pumped from the reaction chamber via a $^1/_8$ in. Teflon line through a six-way valve and a sample loop of 5-mL volume to the pump. Prior to sampling the connection lines, the valve and sample loop were flushed for 2 min at a flow rate of 35 mL/min. A pressure gauge is located next to the sample loop to verify that the pressure inside the sample loop remains constant and close to ambient throughout the sampling procedure. This allows us to keep variations of the injected sample size below 1.5%. The contents of the sample loop is quantitatively transferred to a cryogenic trap through a $^{1}/_{8}$ in. stainless steel line maintained at 353 K in a He (Air Products, 99.995%) flow of approximately 10 mL/min.

Prior to injection onto the first separation column, the hydrocarbons are focused in the cryogenic trap (8 cm × $^{1}/_{16}$ in. stainless steel tube) at 93 K. The trap is connected to a second six-port valve. After sufficient time for the transfer of the analytes from the sample loop to the cryogenic trap, typically between 5 and 7 min, the six-port valve is rotated and the trap is flash-heated to inject the analytes onto the GC. The desorbed sample is transferred by a flow of helium controlled by an electronic pressure control (EPC) unit onto the GC columns. The operation of the sample loop as well as of the cryogenic trap is fully automated, and the timing is controlled electronically.

2.3. Gas Chromatographic Separation. The gas chromatograph (Varian 3600) is equipped with two columns in a configuration that allows selective transfer from one column to the other as well as selection of the effluent of either column for transfer to the detection system. The first column is either a DB-1 column (60 m, 0.32-mm i.d., 1-μm film thickness) or an HP1 column (Agilent Technologies, 60 m, 0.32-mm i.d., 5-μm film thickness), and the second column is a GSC-GasPro porous layer open tubular column (60 m, 0.32-mm i.d.) or a Poraplot Q column (60 m, 0.32-mm i.d.). The column selection, temperature program, and timing of column switching depend on the hydrocarbons being studied. The carrier gas is helium at a flow rate maintained at approximately 1.5 mL/min throughout the temperature program by an electronic pressure-control unit that adjusts the column head pressure as a function of column temperature.

2.4. Detection. Approximately 0.3 mL/min of the column effluent is transferred to a Saturn 2000 ion trap mass spectrometer for peak identification and peak purity verification. A piece of deactivated fused-silica capillary tubing (1.0 m × 0.1-mm i. d.) determines the flow rate to the ion trap. The remainder of the effluent is transferred to a combustion interface (Finnigan MAT) that quantitatively converts hydrocarbons to carbon dioxide and water. The design of the interface follows that developed by Matthews and Hayes.[21] The interface is composed of a thin ceramic tube with three wires (copper, nickel, and platinum) inside, previously exposed to pure oxygen while at 823 K, thus creating an oxidizing environment at 1223 K that is capable of quantitatively oxidizing hydrocarbons to carbon dioxide and water. Depending on the amount of NMHC in the analyzed samples, the interface has to be regenerated regularly by flushing with pure oxygen; in our experiments, this was done approximately once every 30−35 runs between subsequent KIE experiments. After the removal of water with a Nafion permeation dryer, approximately 0.4 mL/min of the carrier gas is transferred via an open split to the ion source of the isotope ratio mass spectrometer (Finnigan MAT 252). Masses 44 ($^{12}C^{16}O_2$), 45 ($^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$), and 46 ($^{12}C^{18}O^{16}O$) are continually monitored, and the data are stored in digitized form for subsequent evaluation of the chromatograms. From each of the digitized chromatograms, the areas of the mass 44, 45, and 46 peaks for each compound are determined using a commercial software package (ISODAT) and manual definitions of the mass-44 peak boundaries and baseline. The area of the mass-44 peak, representing the ^{12}C content in the analyzed compound, is used for the concentration measurement. The $^{13}C/^{12}C$ ratio is calculated by an algorithm in the ISODAT software from the mass-$^{45}/_{44}$ ratio, correcting for ^{17}O with the procedure outlined by Santrock et al.[22]

The isotope ratio measurements are calibrated using an on-line open-split injection of reference CO_2. The CO_2 reference gas is added twice for 20 s each at the beginning and end of each analysis. The open-split reference gas is checked for stability prior to and immediately following each analysis by off-line comparison to an aliquot of the same reference gas. The off-line reference gas is calibrated between KIE experiments by comparison with two carbonate standards that can be traced to the primary international standard Vienna PeeDee Belemnite (VPDB).

2.5. Calculation of the Kinetic Isotope Effect. From the stored chromatograms, the mass-44 peaks for each compound are integrated manually at least three times using slightly different but realistic peak boundary conditions. These repeat evaluations are used to determine the concentrations and stable carbon isotope ratios as well as the uncertainties originating from the peak evaluation procedure and the baseline noise.

The kinetic isotope effect, k_{12}/k_{13}, is obtained from the dependence between the stable carbon isotope ratio, $^{13}C/^{12}C$, and the measurements of the ^{12}C isotope obtained from the mass-44 data. k_{12} and k_{13} are the rate constants for the reaction of hydrocarbons with only ^{12}C atoms and the reaction of hydrocarbons containing a ^{13}C atom, respectively. The relation can be described by the following function:

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

or

$$\ln(^{12}C_t) = \frac{k_{12}/k_{13}}{1-(k_{12}/k_{13})^*}\ln(^{13}C_t/^{12}C_t) - \frac{k_{12}/k_{13}}{1-(k_{12}/k_{13})^*}\ln(^{13}C_0/^{12}C_0) + \ln(^{12}C_0) \qquad (2)$$

where C_0 and C_t correspond to the abundance of carbon atoms at time zero and t, respectively. A plot according to eq 1 for a specific hydrocarbon should form a straight line with a zero y-axis intercept and a slope of $(k_{12}/k_{13})/(1-(k_{12}/k_{13}))$. Equation 2 also describes a straight line with a slope of $(k_{12}/k_{13})/(1-(k_{12}/k_{13}))$ but with a nonzero y-axis intercept of $-(k_{12}/k_{13})/(1-(k_{12}/k_{13}))^*\ln(^{13}C_0/^{12}C_0) - \ln(^{12}C_0)$. In both cases, the KIE is calculated from the slope of a linear least-squares fit, and the experimental uncertainty for an individual experiment can be determined from the uncertainty in the slope. Figure 2 shows examples for five separate KIE experiments used to study the reaction of toluene with OH radicals.

The use of the ratio $^{13}C_t/^{12}C_t$ in eq 1 or 2 takes advantage of the fact that isotope ratio mass spectrometry measurement allows very reproducible and accurate measurements of this ratio. This is required because the changes in stable carbon isotope ratios are generally very small. For the same reason, the stable carbon isotope ratio is usually expressed as the relative difference between the sample and a reference in permill.

$$\delta^{13}C\ (‰) = \frac{(^{13}C/^{12}C - {}^{13}C_{ref}/^{12}C_{ref})}{(^{13}C_{ref}/^{12}C_{ref})} \times 1000 \qquad (3)$$

Here, C_{13} and C_{12} denote the atomic abundance of the different isotopes in the studied compound, and C_{ref} denotes the abundance in the standard. This equation allows the conversion of stable carbon isotope ratios expressed as $\delta^{13}C$ values, the conventional way to present stable isotope ratios,

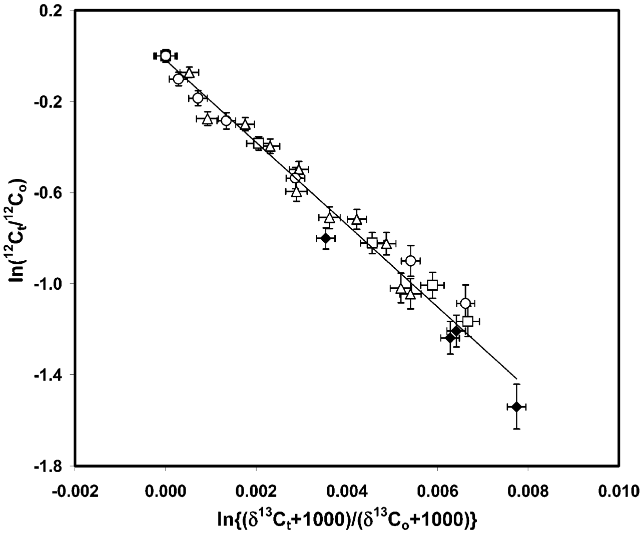

Figure 2. Example of a plot according to eq 1 for the reaction of toluene with OH radicals. Results from five different experiments are shown. Each symbol represents a different experiment. The error bars were calculated from the standard deviation of the initial concentration and isotope ratio measurements as well as a 0.2‰ absolute error for each isotope ratio measurement and a 2% relative error for each concentration measurement. A linear regression of all toluene−OH data is shown, with slope = −180.7 ± 4.9 corresponding to a KIE of 5.56 ± 0.15‰.

into concentration ratios ($^{13}C/^{12}C$). Although the reference point is of no importance for the determination of KIEs according to eq 1 or 2, all $\delta^{13}C$ results presented in this paper are given relative to VPDB in order to be defined on an internationally accepted scale.

Isotope fractionation effects are often very small and therefore are, similar to stable isotope ratios, for the sake of convenience, often expressed as a relative difference ($^{OH}\epsilon$) of the reaction rate constants in permill:

$$^{OH}\epsilon(‰) = \frac{(^{OH}k_{12} - {}^{OH}k_{13})}{^{OH}k_{13}} \times 1000 = (^{OH}k_{12}/^{OH}k_{13} - 1) \times 1000 \quad (4)$$

In the literature, isotope effects are also often expressed as a fractionation factor (α). The relation between k_{12}, k_{13}, α, and ϵ (in permill) is

$$k_{12}/k_{13} = \alpha^{-1} = 1 + (\epsilon/1000) \quad (5)$$

Because our studies concentrate on measurements of very small isotope effects, we use ϵ (in permill) as the most convenient way to express such small effects.

3. Results and Discussion

The procedure and instrumentation for KIE measurements described above consists of several steps and require the adjustment and optimization of a substantial set of experimental parameters to obtain reproducible and accurate results. In this section, we will describe the tests and their results, which were conducted to verify the proper operation of the instruments and the accuracy of the results. Furthermore, the influence of key parameters on the reproducibility and accuracy of the measurements will be discussed.

3.1. Stability. Several tests that did not require the measurement of stable carbon isotope ratios were performed. Their main purpose was to determine the long-term stability of NMHC in the reaction chambers in the absence of OH radicals. Four reaction chambers were tested under different conditions. The NMHC concentration measurements required for these tests were all performed on a GC (HP5890 II) with a dual FID system using the same reaction chamber housing, automatic sampling, cryogenic trapping, and GC column assembly described in section 2 and used for the KIE measurements. A summary of the results from these tests is presented in Table 1. The tests were performed at 298 ± 4 K.

As an example, data collected during the second test in Table 1 is shown in Figure 3. The variability between subsequent measurements is less than ±1.5%, most likely because of temperature and pressure fluctuations in the sample loop. Typically, for these tests, there were small overall decreases in the concentrations with time, with larger compounds usually experiencing a higher rate of loss. This suggests that either diffusional loss through the walls of the chamber or adsorption to the walls of the chamber or a combination of these effects was occurring. Because the results indicate systematic differences between compounds of different molecular weight and the changes for low molecular weight compounds are very small, a dilution with air from outside the chamber seems unlikely.

The first two test series and the fourth show that there is typically no more than an overall change of ±0.25%/h in the hydrocarbon concentration when the lights are off or the hydroxyl radical initiators isopropyl nitrite and NO are not present. The results from the third test show concentration changes similar to the first two tests despite irradiation in the absence of isopropyl nitrite and NO.

The remaining tests were similar to the first four tests. In all eight tests, averaging 28 h in duration, the average overall rate of change for all species was −0.04%/h, with average 10th and 90th percentiles of variability in concentration measurements of −2.0 and +0.5% respectively. Differences in losses between tests may be due to differences in the leak-tightness of the PTFE seals on individual chambers but can also result from minor differences in the history of the surface of the PTFE reaction chambers.

The stability tests demonstrated that the reaction initiation did not occur until such time as both isopropyl nitrite and NO were present and the UV lights were turned on. For chambers that did experience a hydrocarbon concentration change of greater than ±1%/h over a 15-h period, either a systematic loss or a large random instability can be observed within the first three measurements. Thus, for each KIE experiment, three stability runs were made to ensure concentration stability and reaction chamber integrity prior to the start of a reaction, and experiments were conducted only if the observed changes in concentration and the stable isotope ratio were within the expected uncertainty of the measurement technique (±2% and ±0.2 ‰ respectively).

3.2. Reaction Conditions. From eq 1 or 2, it is obvious that the error of a KIE derived from the dependence between the stable carbon isotope ratio and concentration will depend on the change in concentration during the experiment. However, because of the small dynamic range of the stable carbon isotope ratio measurements, the actual concentration range is limited. The practical working range of the IRMS for these measurements is between approximately 0.3 and 500 ng of carbon per compound. For the 5-cm^3 sample, which we used for the measurement of the stable carbon isotope ratios, this corresponds to a concentration range of approximately 0.1 to 200 ppm depending on the molecular weight of the NMHC. At the lower

TABLE 1: Summary of Reaction Chamber Stability Tests Performed Using the GC-FID System

experimental conditions	duration, h	compound	initial concentration, ppm V	average rate of change, %/h	percentile of concentration change	
					10th	90th
chamber: SEP00_01, no UV lights	7	ethane	67	−0.07 ± 0.07	−0.67	−0.06
		methylbutane	53	−0.07 ± 0.03	−0.74	−0.24
		n-heptane	12	−0.11 ± 0.04	−1.10	−0.26
		benzene	10	−0.16 ± 0.07	−1.89	−0.80
		toluene	6	−0.11 ± 0.11	−1.78	−0.07
chamber: SEP00_01, no UV lights	22.7	ethane	64	−0.02 ± 0.01	−0.33	0.41
		methylbutane	51	−0.07 ± 0.01	0.40	1.63
		n-heptane	10	−0.08 ± 0.01	−1.35	0.28
		benzene	9	−0.11 ± 0.01	−1.96	0.28
		toluene	4	−0.15 ± 0.01	−3.04	−0.01
chamber: SEP00_01, UV lights on first 25h, then off for remainder of reaction chamber test	44.9	ethane	44	0.02 ± 0.01	−0.12	2.02
		ethene	29	−0.10 ± 0.02	−5.00	−0.01
		methylbutane	45	0.02 ± 0.01	−1.88	0.65
		n-heptane	8	−0.08 ± 0.01	−3.76	−0.08
		benzene	13	−0.07 ± 0.01	−3.53	−0.12
		toluene	5	−0.20 ± 0.01	−8.36	−1.05
chamber: SEP00_01, no UV lights, NO and isopropyl nitrite present	21	ethane	34	−0.05 ± 0.02	−0.98	0.57
		ethene	21	−0.04 ± 0.02	−0.54	1.20
		methylbutane	34	−0.04 ± 0.02	−0.65	0.77
		n-heptane	6	0.21 ± 0.03	−0.15	3.72
		benzene	13	0.25 ± 0.04	−0.09	4.26
		toluene	6	−0.19 ± 0.03	−3.42	0.19
chamber: JUN01_01, no UV lights	22.6	ethane	93	−0.06 ± 0.01	−1.08	−0.04
		propane	151	−0.08 ± 0.02	−1.23	−0.01
chamber: JUN01_04, no UV lights	14.1	ethane	309	0.15 ± 0.09	−0.08	3.31
		propane	186	−0.11 ± 0.06	−1.03	0.96
chamber: SEP01_10, no UV lights	18.2	ethane	81	−0.08 ± 0.29	−7.31	−0.21
		propane	75	0.11 ± 0.15	−6.21	−0.41
		n-butane	50	−0.01 ± 0.04	−1.65	−0.24
chamber: SEP01_10, MeCl added at 51.4 h, no UV lights	70.5	ethane	22	−0.01 ± 0.01	−1.58	0.02
		propane	20	0.00 ± 0.01	−1.92	−0.18
		methyl chloride	14	−0.07 ± 0.02	−1.64	−0.72
		n-butane	13	0.00 ± 0.00	−1.24	−0.56

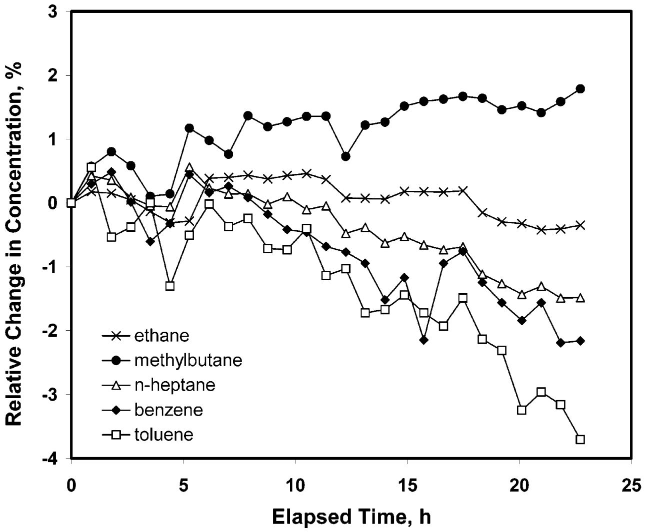

Figure 3. Example of the time dependence of hydrocarbon concentrations in the absence of OH radicals.

end of the range, the signal-to-noise ratio of the IRMS contributes substantially to the uncertainty of the stable carbon isotope ratio measurements. For our kinetic studies, we therefore considered only measurements where the analyzed sample contained at least 10 ng of carbon for the studied compound, corresponding to a concentration of about 3 ppm. These limitations result in a useful dynamic range of less than 2 orders of magnitude. To avoid a further reduction of the concentration range available for the experiments, the initial hydrocarbon concentrations in the reaction chamber are adjusted to generate a signal close to but not exceeding the upper limit of the dynamic range.

Consequently, the rate of decrease of the NMHC concentrations and thus the OH-radical concentration had to be adjusted to ensure that reliable stable carbon isotope ratios were possible throughout the duration of the experiment. The duration of an experiment is determined by the number of data points required to determine the KIE according to eq 1 or 2 and the time needed for each GC analysis of NMHC concentrations in the reaction chamber. The time required for one measurement of NMHC concentrations and stable carbon isotope ratios was in the range of 2 h, depending on the studied compounds. On the basis of experience, five to seven data points were sufficient to determine the KIE according to eq 1 or 2. Consequently, the overall time for one experiment is in the range of 10−15 h, not including the necessary time for setting up the experiments. Optimally, the change in NMHC concentration during this period should be a factor of 10 to 20, a compromise between the limited dynamic range of the IRMS and the possibility of deriving the KIE accurately from the dependence between the isotope ratio and concentration. Consequently, the product of OH-radical concentration and the rate constant for the studied reaction should be around 1×10^{-4} to 2×10^{-4} s^{-1}. By choosing appropriate isopropyl nitrite concentrations and irradiation

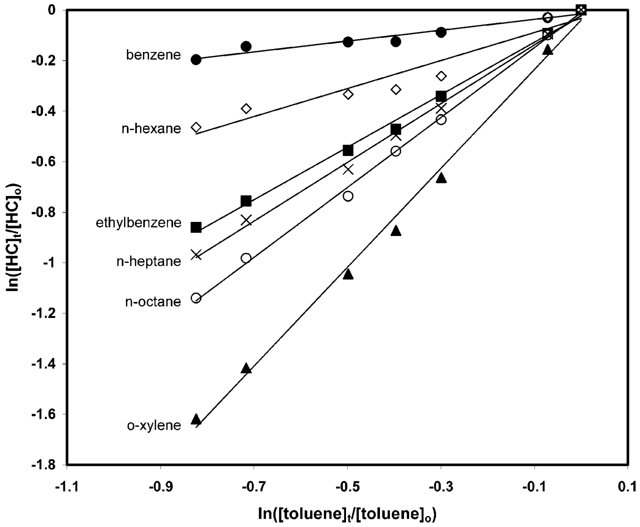

Figure 4. Relative rate plot for reaction for the seven hydrocarbons with OH radicals using toluene as a reference.

conditions depending on the reactivity of the NMHC, this was achieved. However, it should be noted that for NMHC with very low reactivity toward the OH radical this is not always possible, which results in reduced accuracy for KIE measurements of unreactive NMHC.

The initial concentrations of isopropyl nitrate varied between 100 and 1000 ppm. Similarly, the number of lights and the period of irradiation between successive measurements were adjusted. Additional isopropyl nitrite was added to the reaction chamber after each measurement to maintain sufficient levels of OH in the reaction chamber without having a large excess of isopropyl nitrite in the chamber at any given time. In experiments with compounds having different reactivities, the amount of isopropyl nitrite added during the experiment was often increased over the course of the reaction. This resulted in lower OH-radical levels at the beginning of an experiment and higher OH concentrations toward the end of the experiment. This allowed us to study compounds with different reactivity in one experiment. It should be noted that isopropyl nitrate was added as a pure substance. Consequently, the resulting dilution of the NMHC in the reaction chamber was below 1‰. This dilution effect is small compared to the uncertainty of the concentration measurements; therefore, no correction of the NMHC concentrations was made.

Depending on the reactivity of the NMHC, concentrations at the end of an experiment were between 5 and 70% of the initial concentrations. For the more reactive hydrocarbons, a decrease of 95% of the initial concentration was usually possible within approximately 16 h, whereas for less reactive species, sometimes only 25−30% of the initial hydrocarbon concentration had reacted in this time period. For ethane, over 30 h was required to achieve a 30% decrease in the initial concentration.

3.3. Reaction Rate Analyses. In most experiments, several different NMHCs were studied simultaneously. This not only increases the number of KIE determinations that can be made in one experiment but also allows for verification that the change in NMHC concentration is indeed due to reaction with OH radicals only. This was done for each experiment by determining whether a relative rate analysis is in agreement with rate constants from the literature. Figure 4 shows an example of the relative loss rates for an experiment in which hydroxyl radicals were reacted with seven hydrocarbons. In this example, toluene is used as a reference. Apart from *n*-hexane and benzene, for which the R^2 values are 0.927 and 0.943, respectively, all R^2 values are greater than 0.995. Apart from *n*-hexane, the experimental relative rate constants are within the literature uncertainties (Table 2).

TABLE 2: Relative Rate Constants at Room Temperature for the Reaction of OH Radicals with Selected Hydrocarbons at 760 Torr Total Pressure in Air

			$10^{12} \times {}^{OH}k_{HC}$, $cm^3\,molecule^{-1}\,s^{-1}$	
hydrocarbon	${}^{OH}k_{HC}/{}^{OH}k_{toluene}$[a]	R^2	literature	this work
n-hexane	0.555 ± 0.069	0.927	5.61 ± 1.40[23]	3.24 ± 0.41
benzene	0.215 ± 0.024	0.944	1.17 ± 0.06[24]	1.25 ± 0.14
n-heptane	1.16 ± 0.03	0.996	7.20 ± 1.80[23]	6.79 ± 0.18
n-octane	1.38 ± 0.03	0.998	8.72 ± 1.70[23]	8.08 ± 0.16
ethylbenzene	1.04 ± 0.03	0.996	7.5 ± 2.6[25]	6.07 ± 0.18
o-xylene	1.96 ± 0.06	0.996	12.2 ± 1.9[26]	11.43 ± 0.34

[a] ${}^{OH}k_{toluene} = (5.84 \pm 0.84) \times 10^{12}$ cm^3 molecule^{-1} s^{-1}.[26]

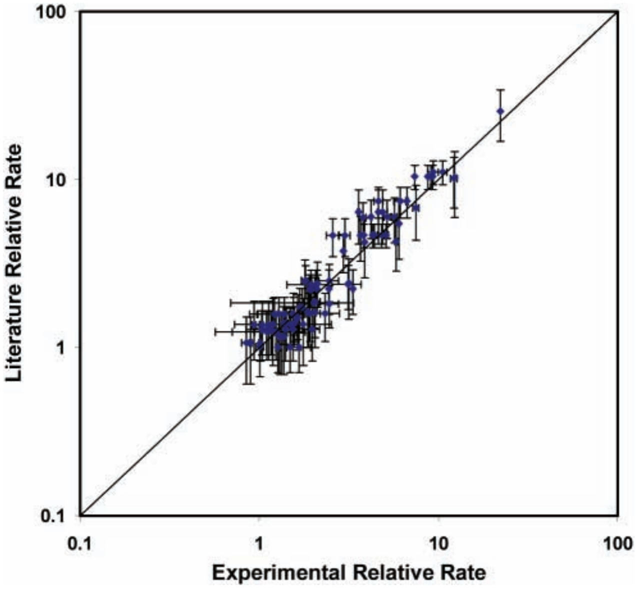

Figure 5. Plot of the literature relative rate of ${}^{i}k_{OH}/{}^{j}k_{OH}$ versus the experimental relative rate for 92 comparisons between compounds in 7 experiments. The solid line shows the expected dependence for perfect agreement between literature data and our measurements. The errors of the literature values are calculated from the uncertainties in the literature rate constants, and the errors of the experimental data are derived from the uncertainties in the linear regressions of the relative rate plots.

From seven experiments performed in 2001 containing three to eight hydrocarbons each, ${}^{i}k_{OH}/{}^{j}k_{OH}$ was determined for every combination of species. To avoid pairs of compounds being considered twice, ${}^{i}k_{OH}$ is defined as the larger rate of the two rate constants. In Figure 5, these experimentally derived ratios were compared to the ratio of the literature rate constants. Within the uncertainty of the data points, nearly all values fall on the $x = y$ line, which indicates nearly perfect agreement between relative rate constants derived from our measurements and published rate constants. The average relative error in the literature relative rates is 29%. On average, the difference between literature and experimental relative rates is 7.4%, well within the uncertainty of the literature data.

3.4. Kinetic Isotope Effects. As mentioned above, the KIEs can be determined from least-squares fits to eq 1 or 2. Although in principle the results should be identical, the weight given to the individual data points is different, thus the results may differ slightly. Using eq 1 assumes that the initial concentrations and stable carbon isotope ratios (${}^{12}C_0$ and${}^{13}C_0/{}^{12}C_0$) are precisely known. Under these conditions, the KIEs derived using eq 1

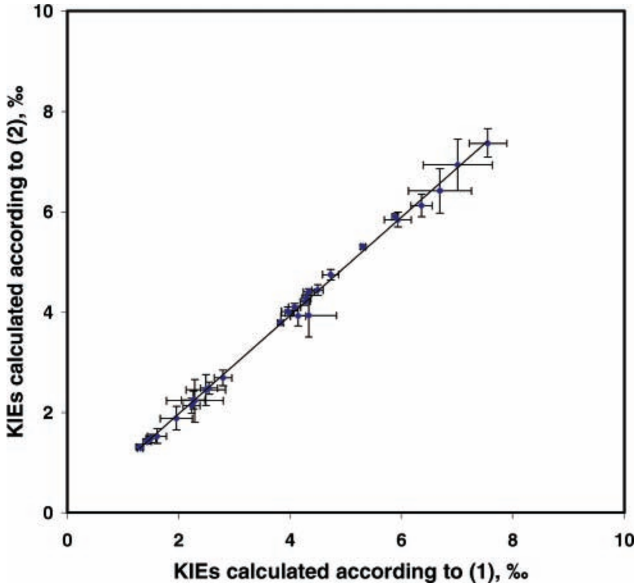

Figure 6. Comparison of KIEs calculated from experimental data using eqs 1 and 2 for six separate experiments. The slope of the linear regression is 0.9835, and the R^2 value is 0.9983.

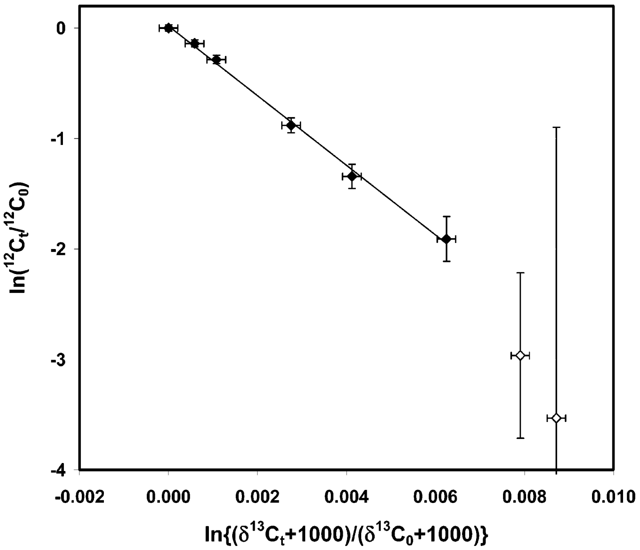

Figure 7. Plot according to eq 1 for 1,2,4-trimethylbenzene measurements from a single experiment. Closed symbols represent data points used in the KIE calculation. Data points with open symbols were eliminated from the calculation because of high uncertainty in the concentrations. A linear regression to the data points used in the KIE determination is shown. The result of the linear fit is $y = -315.67x + 0.0185$, $R^2 = 0.9969$.

have higher accuracy and give better estimates than those derived from eq 2. However, errors in the initial values will result in biased KIEs. This can be avoided if eq 2 is used. But in this case, two parameters have to be fitted to the data, which will increase the uncertainty of the derived KIE.

In our experiments, averages of the initial concentrations and their uncertainties can be derived from the measurements made prior to the start of the reaction. In most experiments performed, the relative standard deviations for the concentration measurements were less than ±2%, and the uncertainties of the isotope ratio measurements were below ± 0.2‰. These uncertainties are small, and we therefore used eq 1 to determine the KIEs from the measurements. A comparison of results from five different experiments (KIEs for seven different compounds) derived by using a fit to eq 2 showed no statistically significant differences (Figure 6) from results determined using a fit to eq 1.

In our fit procedures, we used a simple one-way regression that does not consider the individual errors of the data points. However, we determined the uncertainty of each data point to avoid the inclusion of data points with very large uncertainties into the fit procedure. Typically, large errors were observed only for measurements at very low concentrations. This large uncertainty can be explained primarily by the less favorable signal-to-noise ratio for these measurements, but data points at low concentrations can also be biased by overlaps of their chromatographic peaks with small, unidentified contaminants or reaction products or by wall effects. An example is shown in Figure 7. Although the two data points at low concentrations statistically are not outliers, it is obvious that the inclusion of data points with such large errors will have an adverse effect on the overall quality of the fit. Such data points were therefore excluded from the fit. Using error-weighting fit procedures would also drastically reduce the impact of such data points on the fit results. However, this would rely entirely on the estimated statistical errors, which do not include potential uncertainties due to wall effects or peak overlaps.

3.5. Reproducibility. *3.5.1. Isotope Ratios.* The reproducibility of isotope ratio measurements depends largely on the signal-to-noise ratio for the mass-45 ion current and thus also on the area of the integrated peak. We determined the noise-limited uncertainty of δ^{13}C by repeatedly integrating the same peak using slightly different but always realistic peak boundary and baseline definitions. Peaks with an area of less than 0.1 V·s have an uncertainty of >±2‰. Peaks within the range of 0.1−0.5 V·s have uncertainties of ca. ±1‰, peaks with areas between 0.5 and 1.0 V·s have uncertainties of ca. ±0.5‰, and peaks with areas of >1.0 V·s have uncertainties of ca. ±0.2‰. These results are based on the evaluation of more than 100 peaks for each of the size ranges. The results are valid only for well-resolved peaks. For obvious reasons, peaks that are not completely resolved from neighboring peaks have larger uncertainties.

The relative uncertainty in the concentrations derived from the mass-44 signal is approximately 2%. For the concentration range studied here, this error is independent of the signal size because the random noise of the mass-44 signal is always negligible compared to the signal. In addition to signal-to-noise ratio effects, however, the completeness of the separation from neighboring peaks is an important factor affecting the reproducibility of the peak integration.

3.5.2. Kinetic Isotope Effects. As pointed out above, ideally the turnover of the reactants should be in the range of ≥90% to make optimum use of the available dynamic range of the IRMS. The amount of reactant consumed depends on the duration of the experiment, the concentration of the reaction partner, namely, the OH radical, and the rate constant for the reaction. The parameters that can be modified in the experiments are the duration of the reaction and the concentration of the OH radical. However, both parameters have upper limits. The maximum duration of an experiment is limited not only by practical considerations but also by the fact that increasing the duration of the experiments increases the risk of reactant loss due to interaction with walls, diffusion through the chamber walls, or leakage. To some extent, increasing the photon flux and the isopropyl nitrite concentration can increase the OH-radical concentration. However, at high OH-radical concentrations, the radical loss rate is determined by radical−radical recombination reactions and thus increases with the second order of the OH-radical concentration. This limits the maximum OH-

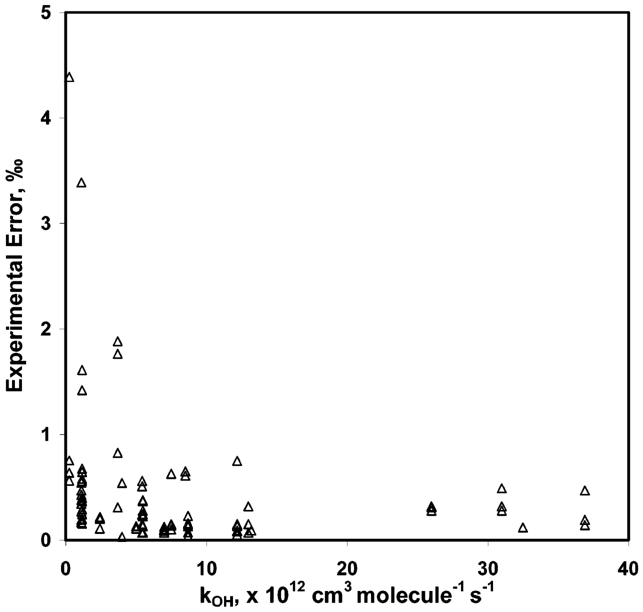

Figure 8. Plot of experimental uncertainties in the KIE measurement against the reaction rate coefficient for 21 different hydrocarbon−OH reactions.

radical concentration that can be achieved under realistic conditions. Consequently, for NMHC with low reactivity toward OH radicals, we expect that the uncertainty of KIE measurements will be larger than for more reactive compounds. Indeed, this is clearly visible in the results of our measurements. Figure 8 shows the experimental errors for 93 measurements of 21 different hydrocarbon−OH reaction KIEs. For hydrocarbons with reaction rate coefficients greater than 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, the average experimental uncertainty in the KIE measurement was ±0.22‰, and the hydrocarbons with slower reaction rate coefficients had an average experimental uncertainty of ±0.74‰. By grouping the hydrocarbons into sets with similar reaction rate coefficients for these experiments, the experiments were targeted to have durations between 14 and 20 h, with the only exceptions being for hydrocarbons with very slow reaction rate coefficients. For this reason, the average experimental uncertainty is fairly constant over a large k_{OH} range, with higher errors only for the slowest reactions.

The separation between reactants and the reaction products also plays a crucial role in the reproducibility of the KIE measurements. Over the course of an experiment, a large number of reaction products build up inside the reaction chamber, most of which contain carbon and contribute to the carbon dioxide signal on the IRMS. Even with the use of 2D separation, it can sometimes be difficult to fully separate some of the compounds of interest from the reaction products. For isotope ratio measurements by GC-IRMS, incomplete separation has a very significant adverse impact on the quality of the measurements, predominantly because of the small shifts in retention time for isotopically labeled compounds. Thus, even minor peaks located close to a large peak can cause errors in the $\delta^{13}C$ value of the larger peak by more than ±10‰. Although an analysis of the ion trap mass spectra generally allows us to identify overlaps, it does not allow us to correct the resulting errors in stable isotope ratio measurements.

The magnitude of the KIE does not have a significant effect on the reproducibility of the KIE measurement. However, it should be noted that, because the absolute error is more or less independent of the magnitude of the KIE, the relative uncertainty of a KIE will be lower for larger KIEs.

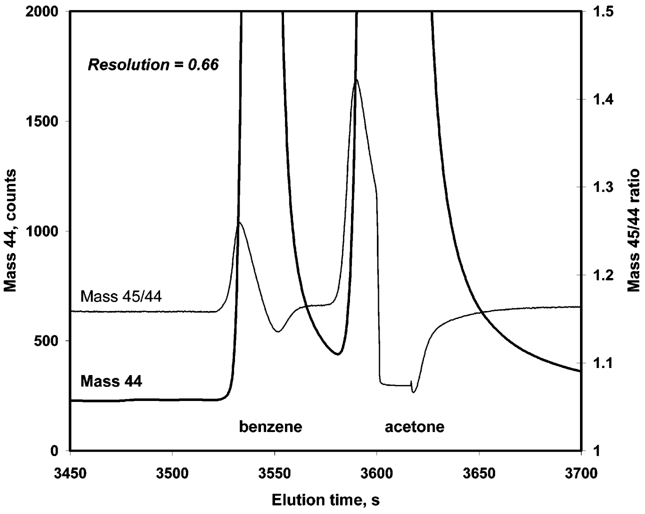

Figure 9. Example of a chromatogram showing the separation between benzene and acetone. The ratio trace, mass-$^{45}/_{44}$, shows the offset that occurs because of differing elution times of isotopically labeled compounds.

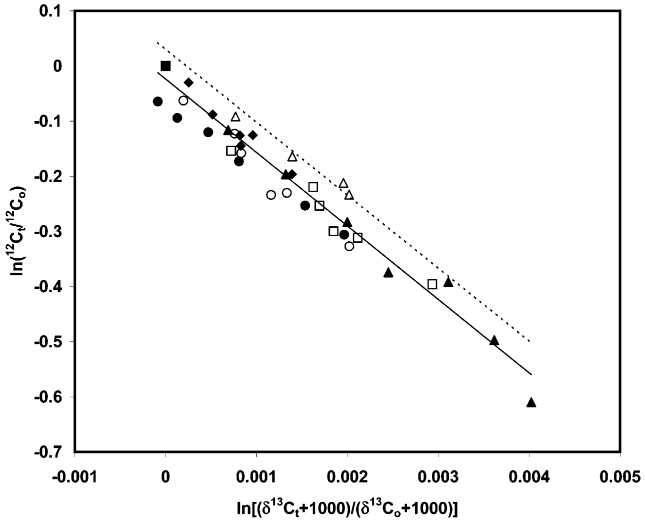

Figure 10. Plot according to eq 1 for benzene measurements from six experiments. The solid line is the linear regression for these measurements, and the dashed line shows the results from Rudolph et al.[10]

Benzene, with moderate reactivity toward OH radicals, less than ideal separation from acetone (Figure 9), and an average KIE value, is an ideal candidate for critically studying the reproducibility and accuracy of the measurements. Figure 10 shows six separate experiments from this work for benzene−OH reactions at 298 ± 5 K in comparison to the KIE reported by Rudolph et al.[10] They report a KIE for the benzene−OH reaction at 315 ± 3 K of 8.19 ± 1.46‰. The average of all of the individually calculated KIEs from our work is 7.47‰ with a standard deviation (1σ) of 0.91‰. If the data from all six experiments is combined and the slope of the data is used to calculate the KIE, the result is 7.56 ± 0.28‰. The small difference between the two KIE averages is consistent with different numbers of data points for individual experiments and thus a different weighting for some of the experiments, but either way, the results are consistent with the literature data.

Conclusions

The described methodology allows accurate measurements of small KIEs for reactions of organic compounds in the gas phase. Measurement uncertainty is generally less than 1‰, and under optimum conditions, the reproducibility of the KIEs is better than 0.3‰. These uncertainties are more than adequate for the interpretation of measurements of stable carbon isotope ratios in atmospheric NMHC. The reproducibility of the measurements is also sufficient to allow the use of KIE measurements to gain more detailed insight into the mechanisms of the reactions.

Studying several NMHCs simultaneously in one experiment allows us to test the experimental procedure by comparing observed relative rate constants with data from the literature. One of the disadvantages is the relatively long duration of the KIE measurements. In the present setup, the duration of one gas chromatographic analysis of the hydrocarbon concentrations in the reaction chamber is about 2 h. This is mainly due to the simultaneous study of several NMHCs in one experiment, which results in a complex mixture of NMHCs and NMHC reaction products. Obviously, the time required for one analysis of the NMHCs in the reaction chamber can be substantially reduced if only one compound is studied in a given experiment.

Another limitation is inherent in the methodology. Because the procedure is based on measuring the change in the stable isotope ratio and concentration of the residual NMHC, the accuracy of the KIE measurement strongly depends on the turnover of the studied compounds. Depending on the reactivity of the compounds and the achievable concentration of the reactant, in our case the OH radical, a minimum time is required to achieve a turnover that will allow us to determine the concentration and isotope ratio changes with sufficient accuracy. For compounds with rate constants in the range of $\geq 10^{-12}$ cm^3 molecule^{-1} s^{-1}, this does not create any serious limitations because OH-radical concentrations high enough to obtain a substantial depletion of the studied compound within less than 1 day are achievable. For less reactive compounds, the limited extent of processing results in the reduced accuracy of the KIE measurements. To some extent, increasing the duration of the experiment can increase the accuracy of the measurement; however, practical problems, such as the accumulation of the products of isopropyl nitrate photolysis, limit the actual useful time span of an experiment.

Until now, this method has been primarily used for studies of the carbon KIE for reactions of NMHC with the OH radical, but it is obvious that with minor modifications a wide range of other gas-phase reactions of organic compounds can be studied. Possible examples are reactions of organic compounds with ozone, halogen atoms, and NO_3 radicals or photolytic decomposition. Furthermore, the methodology can be readily adopted to study other stable isotopes. Commercial interfaces are available to combine GC separations with hydrogen, oxygen, or nitrogen stable isotope ratio mass spectrometry.

Finally, it should be mentioned that the presented method is not limited to studying compounds without artificial labeling. Obviously, using such substances is very cost-efficient because it allows for the use of readily available, inexpensive chemicals. Nevertheless, our method can be directly applied to artificially labeled compounds, which opens the possibility of using position-specific labeling to determine position-specific KIEs. Combined with the possibility of accurately measuring small KIEs, this would provide valuable additional insight into the details of the gas-phase reactions of volatile organic compounds.

Acknowledgment. We thank the Natural Science and Engineering Research Council (NSERC) for financial assistance.

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