The stable carbon kinetic isotope effects of the reactions

of isoprene, methacrolein, and methyl vinyl ketone with

ozone in the gas phase

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Abstract

The stable-carbon kinetic isotope effects (KIEs) for the gas-phase reactions of isoprene, methacrolein (MACR), and methyl vinyl ketone (MVK) with ozone were studied in a 25 L reaction chamber at (298 ± 2) K and ambient pressure. The time dependence of both the stable-carbon isotope ratios and the concentrations was determined using a gas chromatography combustion isotope ratio mass spectrometry (GCC-IRMS) system. The volatile organic compounds (VOCs) used in the KIE experiments had natural-abundance isotopic composition thus KIE data obtained from these experiments can be directly applied to atmospheric studies of isoprene chemistry. All $^{13}C/^{12}C$ KIEs reported herein are as per mille ε values, where $\varepsilon = (KIE - 1) \times 1000$‰, and $KIE = k_{12}/k_{13}$. The following average stable-carbon KIEs were obtained: (8.40 ± 0.11) ‰ (isoprene), (7.67 ± 0.28) ‰ (MACR), and (7.87 ± 0.08) ‰ (MVK). The stable-carbon KIE values of three 1-alkenes, which were used as reference compounds for relative rate experiments, were also determined: (5.48 ± 0.09) ‰ (1-heptene), (4.67 ± 0.17) ‰ (1-octene), and (4.59 ± 0.56) ‰ (1-nonene). The ε values for the reactions of isoprene and 1-heptene with ozone agree with measurements in a previous study, but the values presented here have a substantially improved accuracy. The ε values for 1-octene and 1-nonene reactions with ozone have not been measured before and closely follow the $1/N_C$ dependence (where N_C represents the number of carbon atoms in the alkene) observed in previous studies. MACR and MVK had ε values that were somewhat below the expected range of values predicted by the $1/N_C$ dependence found for alkenes.

1. Introduction

Isoprene, C_5H_8, is the single most important volatile organic compound (VOC) emitted by vegetation. Estimated global annual biogenic emissions of isoprene are ~500 Tg yr^{-1}, roughly four times that of monoterpenes and comparable to the sum of all other non-methane hydrocarbons (NMHCs) (Guenther, 1999). Furthermore, the emission rate of isoprene exceeds that of all anthropogenic non-methane hydrocarbons and is, on a global average, of a magnitude comparable to that of methane.

The atmospheric oxidation of isoprene is initiated by reaction with OH radicals, ozone, NO_3, or Cl atoms. During daytime hours, when isoprene emissions from plants are at their highest levels, the reaction with OH radicals dominates. Isoprene is also present in the troposphere during nighttime hours and undergoes reaction with ozone and NO_3, important nighttime oxidants (Stroud et al., 2002).

Methacrolein (MACR, 2-methyl-2-propenal), methyl vinyl ketone (MVK, 3-buten-2-one), formaldehyde, and 3-methylfuran have been shown to be the main reaction products of both the OH- and O_3-initiated oxidation of isoprene, and are measured in significant quantities in forested areas (Montzka et al., 1993, 1995; Warneke et al., 2001). MACR and MVK are subsequently removed from the atmosphere through their reactions with OH radicals (Chuong and Stevens, 2004) and ozone. Lower rate constants for MACR and MVK removal result in longer atmospheric lifetimes compared with isoprene, which allows for the accumulation of MVK and MACR, formed by the oxidation of isoprene, in the atmosphere. Combined with the time dependence of isoprene emissions and atmospheric mixing, this results in a complex dependence between isoprene and MVK and MACR mixing ratios, which is difficult to understand based on measurements of mixing ratios alone.

Recently it has been shown that studies of stable carbon isotope ratios of atmospheric volatile organic compounds (VOCs) can be used to obtain additional constraints on the processes determining the atmospheric VOC concentrations (Rudolph et al., 2000; Goldstein and Shaw, 2003; Rudolph and Czuba, 2000; Saito et al., 2002). However, quantitative applications of stable isotope ratio measurements require knowledge of the isotope fractionation effects associated with the key reactions. To our

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knowledge, there are no published measurements of the KIEs for reaction of MVK and MACR with ozone and only one publication which presents KIE measurements for the reaction of isoprene with ozone (Iannone et al., 2003).

In this paper, we present and discuss measurements of the stable carbon KIEs for the gas-phase reactions of isoprene, MACR and MVK and some 1-alkenes with ozone. The measurements were made using VOCs without artificial enrichment or depletion of ^{13}C and thus are directly applicable to atmospheric reactions.

2. Experimental

The experimental techniques used in this study are similar to the methods to measure stable carbon isotope KIEs described previously in the literature (Anderson et al., 2003, 2004; Rudolph et al., 2000; Iannone et al., 2003). KIE experiments are similar in concept to relative rate (RR) experiments. In typical RR experiments, a reaction is carried out in a chamber and reactant concentrations are measured as a time series. Rate constants are determined through comparison of the relative loss rates of two reacting compounds and previously reported rate constants for one of the compounds, the reference compound. KIE experiments use a similar experimental procedure except that, in addition to concentration measurements, stable isotope ratios are obtained in each measurement. In the case of carbon KIE experiments, the procedure is a measurement of the relative rate for the reaction of molecules containing only ^{12}C atoms over the reaction of molecules containing a ^{13}C atom.

In this study two types of experiments were performed: (1) RR experiments measuring concentration only, and (2) KIE experiments measuring concentration and stable carbon isotope ratios. Several common components were shared amongst the RR and KIE experiments: a reaction chamber kept in the dark, an ozone generator, a sampling system which obtains samples of reaction mixture and transfers them to the GC, and a detection system. For the RR experiments a GC-FID instrument was used for VOC measurements, for the KIE studies a GCC-IRMS system. The 25 L reaction chamber was made of a fluorinated ethylene propylene (FEP) Teflon film of 0.05 mm thickness (DuPont Polymer Products Department, Wilmington, Delaware). Several Teflon ports integrated into the chamber walls allowed for the injection of VOCs and the transfer of gases to and from the chamber via 1/8 inch Teflon lines. A fan inside the chamber ensured that compounds were well-mixed. The ozone generator consisted of a 7 cm length, 3 mm i.d. quartz tube irradiated by an Hg-discharge (Pen-ray) lamp (Ultra Violet Products, Upland, CA) attached to the reaction chamber via a 1/8 inch Teflon tubing. The reaction of alkenes in the reaction chamber with O_3 was carried out by flowing synthetic air through the ozone generator and admitting the O_3/air mixture into the reaction chamber at rates between 5.0–15 mL min^{-1}. Any radical

species formed during the photolysis were scrubbed from the O_3/air mixture using an in-line 16 cm long Pyrex tube filled with Raschig rings, which was placed between the ozone generator and the reaction chamber.

The reaction chamber was placed in a temperature controlled housing maintained at (298 ± 2) K that allows for reactions to take place in the dark. Sampling was performed through the use of a six-port switching valve equipped with a 10 mL sampling loop. A pump downstream of the six-port valve was used to fill the sample loop with air from the reaction chamber mixture after flushing the transfer lines and the sample loop at a rate of 100 mL min^{-1} for 30 s. Upon valve-switching, the helium carrier gas transferred the 10 mL sample to the GC column.

All liquid VOCs were obtained from Sigma-Aldrich with the following stated purities: isoprene (99%), MACR (95%), MVK (99%), 1-heptene (97%), 1-octene (98%), 1-nonene (98%), and 1-decene (94%). Pure gases had the following stated purities: synthetic air (99.96%, Praxair) and CO (99.997%, Messer).

The GC-FID measurements were performed with a SiCHROMAT gas chromatograph (Siemens AG, Munich, Germany) equipped with a 15 m $\times$ 5.0 μm film $\times$ 0.53 mm i.d. RTX-5 column (Restek Corporation, Bellefonte, PA). The GC temperature started with an isothermal period of 303 K held for 5.00 min, then the temperature was increased at a rate of 5.00 K min^{-1} until the final temperature of 393 K was reached, which was held for 7.00 min. Helium carrier gas (99.9995%, Messer) was split at a ratio of 1:20 before entering the GC column. The flow rate through the column was 7 mL min^{-1}. A PE Nelson 900 Series Interface (PerkinElmer Life and Analytical Sciences, Inc., Boston, MA) connected to a PC with dedicated PE Nelson software was employed for peak evaluation. Each VOC peak was integrated by manually defining the peak boundaries.

The GCC-IRMS system consisted of: (1) a cryofocussing system, (2) an Agilent 6890 Gas Chromatograph equipped with a 60 m $\times$ 5 μm film $\times$ 0.32 mm i.d. DB-1 column (Agilent Technologies), (3) a combustion interface, (4) a water trap, and (5) an Isoprime Isotope Ratio Mass Spectrometer

(IRMS) (GV Instruments, Manchester, UK; formerly Micromass). A schematic of the system is provided as Figure 1.

A cryotrap (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany) was used to concentrate the VOCs at 163 K prior to injection onto the GC column. After injection, a capillary trap was used to focus the VOCs at the top of the column at 213 K. The GC temperature program used was: 303 K held for 7.50 min, increased at a rate of 4.00 K min^{-1} until the final temperature of 373 K was reached, and held for 35 min.

The organic compounds eluting from the column were converted to carbon dioxide and water in an oxidation interface. This interface consisted of a quartz tube packed with CuO particles (0.1–0.5 mm) held at 1123 K. The water resulting from VOC combustion was removed by a water trap which consisted of a coiled capillary cooled with liquid nitrogen to 173 K. The He gas stream containing $^{12}CO_2$ and $^{13}CO_2$ enters the source of the IRMS through an open split. Reference gas (CO_2 with $\delta^{13}C_{V-PDB} = -4.62‰$) was injected at the beginning and end of every measurement.

A series of measurements was carried out to determine the effect of wall losses on MACR and MVK mixing ratios. A mixture of MACR and MVK in synthetic air was generated inside the chamber via syringe-injection of the liquid VOCs. Over a period of 45.5 h, samples were taken at intervals of 1.5 h from the reaction chamber and analyzed by GC-FID.

Two sets of reactions were studied in the relative rate experiments: (1) the reactions of O_3 with MACR and MVK, and (2) the reaction of O_3 with isoprene. In one set of experiments, MACR, MVK, and the reference compounds 1-heptene and 1-decene were introduced into the reaction chamber containing a 1×10^4 ppm mixture of CO gas in synthetic air. In another set of experiments, isoprene was studied; here, the reference compounds were 1-heptene, 1-octene, and 1-decene. Initial VOC mixing ratios were in the range of 10–18 ppmV. Reaction chambers were replaced after every two experiments to avoid interference due to contaminating species which can accumulate on the chamber walls.

Before initiating the O_3 reaction, 2–4 measurements were conducted in order to monitor the stability of the VOC mixing ratios and for the KIE experiments also the stable carbon isotope ratios in the

absence of ozone. If the relative change of the peak areas between individual measurements for each compound was below 2%, the system was considered adequately stable and the reaction with O_3 was then carried out. In the KIE studies, an additional requirement for stability was a change in stable carbon delta value no greater than 1‰. The air/O_3 stream was admitted to the chamber for defined periods depending upon the desired rate of reactant depletion. RR and KIE measurements were taken at regular intervals of ~1 h and continued until the reactant VOCs were depleted to <25% of their initial concentrations.

In the analysis of RR experiments, the change in reactant concentration, $\ln([HC]_0/[HC]_t)$, is plotted against the change in concentration of a reference compound, $\ln([ref]_0/[ref]_t)$. Such plots are linear, with the slope determined by the ratio of the reaction rates k_{HC}/k_{ref}. Slopes obtained from linear regression analyses are multiplied with the literature rate constants of the reference compound, k_{ref}, to obtain rate constants, k_{RR}.

For the KIE experiments, IRMS traces were evaluated using MassLynx v4.0i software (GV Instruments). From integrated peak data, concentrations and isotope ratios of the reactant alkenes were obtained. Stable carbon isotope ratios are expressed as the ratio $^{13}C/^{12}C$. Carbon isotope ratios are usually presented as per mille difference values, $\delta^{13}C$(‰), relative to the absolute ratio of the internationally accepted reference standard V-PDB (Vienna Pee Dee Belemnite):

$$\delta^{13}C = \left(\frac{([^{13}C]/[^{12}C])_s - ([^{13}C]/[^{12}C])_{\text{V-PDB}}}{([^{13}C]/[^{12}C])_{\text{V-PDB}}} \right) 1000‰ \,. \tag{1}$$

The KIE value is the ratio of rate constants for two isotopologues participating in the same reaction. For the studies presented here, the KIE is defined as,

$$\text{KIE} = \frac{k_{12}}{k_{13}} \tag{2}$$

where k_{12} is the rate constant for the reaction of a studied compound (i.e. isoprene, MACR, or MVK) containing solely ^{12}C species and k_{13} is the rate constant for the same reaction if the compound has one ^{13}C atom. It should be noted that in the absence of artificial ^{13}C enrichment, due to the low natural

abundance of ^{13}C, for NMHCs with a low number of C atoms, the fraction of isotopologues with more than one ^{13}C atom is very small and can be neglected without creating measurable bias. KIE values were obtained from the slope of a linearized dependence between isotope ratios and concentrations (or peak areas) at different times:

$$\ln\left(\frac{[^{12}C]_{s,t}}{[^{12}C]_{s,0}}\right) = \frac{k_{12}/k_{13}}{1-k_{12}/k_{13}}\ln\left(\frac{\delta^{13}C_t + 1000}{\delta^{13}C_0 + 1000}\right). \tag{3}$$

The KIE can be calculated from the slope as

$$KIE = \frac{slope}{1+slope}. \tag{4}$$

For the sake of convenience, KIE values are presented as per mille epsilon values, $\varepsilon(‰)$:

$$\varepsilon = \left(k_{12}/k_{13} - 1\right)1000‰. \tag{5}$$

Due to the low abundance of ^{13}C and the small change of isotope ratios within the experiments the ratios of the peak areas for the mass-44 signal of the IRMS are valid approximations for the ratios of the ^{12}C isotopologue concentrations in Equation (3).

3. Results and Discussion

3.1. Wall loss and relative rate experiments

GC peak area analyses over a 45.5 h period indicated first-order loss rates of $(1.25 \pm 0.07) \times 10^{-6}$ s^{-1} and $(7.86 \pm 0.07) \times 10^{-7}$ s^{-1} for MACR and MVK, respectively. Since the difference between the loss rates of $(0.46 \pm 0.1) \times 10^{-7}$ s^{-1} is substantial, these decreases in concentration are most likely primarily due to wall losses and not leaks of the reaction chamber. For the typical duration of the RR and KIE experiment of 8–10 hours, such wall losses would contribute about 4% and 2.5% to the loss of MACR and MVK, respectively. Since these changes in concentration due to wall loss are much smaller than that due to reaction with ozone, the bias from these loss reactions is small compared to other sources of uncertainty. Therefore no corrections for wall losses were made.

From several experiments using GC-FID and GCC-IRMS detection, relative rate constants were evaluated relative to the 1-alkenes, using rate constants reported by Grosjean and Grosjean (1995) and Protczak and Trzeszczynski (2002). Uncertainties for the experimental rate constants were determined through error analysis using Gaussian error propagation, taking into account both the errors of the literature rate constants and the errors in linear regression slopes from the experimental data. Table 1 provides a comparison between the average experimentally-determined (k_{RR}) and published (k_{lit}) rate constants. Examples for relative rate plots from an experiment studying isoprene are given in Figure 2. Linear regressions of all RR plots yielded high r^2 values, most of which were above 0.99.

With the exception of MACR, all of our rate constants are well within the range of published rate constants and their uncertainties. The average k_{RR} value for MACR, $(1.9 \pm 0.12) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, is about 50–75% higher than the four rate constants for this reaction reported by Grosjean et al. (1993) [$(1.02 \pm 0.05) \times 10^{-18}$], Grosjean and Grosjean (1998) [$(1.08 \pm 0.21) \times 10^{-18}$], Atkinson et al. (1981) [$(1.12 \pm 0.13) \times 10^{-18}$], and Neeb et al. (1998) [$(1.30 \pm 0.14) \times 10^{-18}$], all in units of cm^3 molecule^{-1} s^{-1}. That our experimental rate constant for MACR is higher than other reported values, with

rate constants for all other VOCs in agreement with literature, suggests that there are additional processes removing MACR. It has been reported that OH radicals can be produced at significant yields from the reaction of O_3 with alkenes (Paulson et al., 1999; Atkinson et al., 1992; Atkinson et al., 1995). Although the addition of 1×10^4 ppmV CO to the chamber reduces the steady state OH radical concentration (Gutbrod et al., 1997), there still will be competitions between VOCs and CO for reaction with OH radicals since for practical reasons we limited the concentration of CO. A comparison of rate constant ratios $^{O3}k/^{OH}k$ for the studied VOCs (Table 2) reveals that MACR has the lowest ratio, and thus experiences the highest relative contribution to VOC loss due to OH radicals.

3.2. Correction of KIEs for interfernce by OH-reactions

The carbon delta values and peak areas from each measurement were plotted according to Equation (3). From the slope of this linear dependence, the KIE values were determined according to Equation (4). Figure 3 provides an example for one experiment studying the MVK + O_3 reaction. Typically, 4–5 GCC-IRMS measurements were conducted after the introduction of ozone to the reaction chamber. All r^2 values for the slope determined by Equation (3) were above 0.995.

As mentioned previously, there is strong evidence that at least for one of the studied VOCs the loss rate is influenced by reaction with OH radicals. Therefore all $^{O3}\varepsilon$ values derived from the slope according to Equation (3) were corrected for interferences with OH radicals by using the following equation:

$$^{O_3}\varepsilon_i = \frac{^{O_3}\varepsilon_{i,obs} - {^{OH}F_i} \cdot {^{OH}\varepsilon_i}}{1 - {^{OH}F_i}} \tag{6}$$

where $^{O3}\varepsilon_{i,obs}$ represents KIEs for the particular reaction of VOC i with O_3 determined from Equation (5), $^{OH}\varepsilon_i$ represents the KIE for the corresponding VOC + OH reaction, and $^{OH}F_i$ is the fraction of VOC i consumed by OH radicals.

The determination of $^{OH}F_i$ requires knowledge of the OH-radical and O_3 concentrations. Since both

the OH-radical and the O_3 concentration can vary with time during the experiments, [OH] and [O_3] were determined for each measurement interval. Values for [O_3] were determined indirectly through the loss of 1-octene, the VOC with the highest $^{O3}k/^{OH}k$ value (Table 2) and thus the least amount of interference due to OH of all VOCs studied. The average ozone [O_3]$_n$ concentration for the interval between two measurements was calculated from the following equation.

$$[O_3]_n = \frac{-\ln\left([\text{1-octene}]_n / [\text{1-octene}]_{n-1}\right)}{^{O_3}k_{\text{1-octene}}\Delta t} \tag{7}$$

Where [1-octene]$_n$ represents concentrations for measurement point n, [1-octene]$_{n-1}$ is the concentration for the previous measurement, $^{O3}k_{\text{1-octene}}$ is the rate constant for the 1-octene + O_3 reaction and Δt represents the difference in times between the measurement n and $n-1$.

Estimates of OH-radical concentrations were determined in two ways: (1) a steady-state approximation based on the formation of OH due to ozone-alkene reactions and loss of OH from reactions with CO and VOCs; and (2) differences between the loss rates of VOCs calculated from the ozone concentration and observations for the VOCs with lowest $^{O3}k/^{OH}k$ ratio and thus the largest impact of OH interference.

The steady-state calculations used the following equation:

$$[OH]_n = \frac{[O_3]_n \sum_i {}^{O_3}k_i \cdot {}^{OH}y_i \cdot [\text{VOC}_i]_n}{{}^{OH}k_{CO} \cdot [CO] \sum_i {}^{OH}k_i \cdot [\text{VOC}_i]_n} . \tag{8}$$

Here, $^{O3}k_i$, $^{OH}y_i$, and [VOC$_i$]$_n$ represent the O_3 rate constant, OH yield, and concentration, respectively, for every VOC undergoing reaction; $^{OH}k_{CO}$ and [CO] represent the CO + OH rate constant and CO concentration; and, $^{OH}k_i$ represents the rate constant for the reaction of VOC i with OH radicals. The second estimate of OH was calculated using,

$$[OH]_n = \frac{1}{\Delta t} \frac{{}^{O_3}k_{MACR}}{{}^{OH}k_{MACR}} \left[\frac{\ln\left([\text{1-octene}]_n / [\text{1-octene}]_{n-1}\right)}{{}^{O_3}k_{\text{1-octene}}} - \frac{\ln\left([\text{1-octene}]_n / [\text{1-octene}]_{n-1}\right)}{{}^{O_3}k_{MACR}} \right] \tag{9}$$

where [1-octene]$_n$/[1-octene]$_{n-1}$ and [MACR]$_n$/[MACR]$_{n-1}$ represent ratios of 1-octene and MACR concentrations at the current sampling time over that of the previous; $^{O3}k_{MACR}$, $^{OH}k_{MACR}$, and $^{O3}k_{\text{1-octene}}$

represent rate constants for the reactions of MACR with O_3 and OH and 1-octene with O_3, respectively.

With the exception of the first time interval in each experiment, both methods for OH estimation agreed to within 10% of each another. Since MACR was not included in some of the experiments, [OH] concentrations based on Equation (8) were used to determine $^{OH}F_{i,n}$, the relative contribution of OH-reactions to the loss of compound i for interval n:

$$^{OH}F_{i,n} = \frac{^{OH}k_i[OH]_n}{^{OH}k_i[OH]_n + {}^{O_3}k_i[O_3]_n}.$$ (10)

Using the correction given in Equation (6), $^{O3}\varepsilon_i$ was calculated for every VOC i using the mean of all $^{OH}F_{i,n}$ values determined from Equation (10) for each experiment. Uncertainties for $^{O3}\varepsilon_i$ were determined from propagated errors of $^{OH}F_i$, $^{O3}\varepsilon_{obs}$, and $^{OH}\varepsilon_i$. Table 3 provides a summary of $^{O3}\varepsilon_i$ values for all studied VOCs and data used for the corrections.

3.3. Comparison with previously published data

To our knowledge there are no previously published KIE values for the reactions of MVK, MACR, 1-octene, and 1-nonene with ozone, only for isoprene and 1-heptene are literature data available for comparison. The new KIE for isoprene is with (8.40 ± 0.11) ‰ somewhat higher than the previously reported value of (6.1 ± 1.0) ‰ (Iannone et al, 2003). This value is an average of four measurements ranging from 4.0–7.8‰, resulting in a 95% confidence interval of 2.84–7.79‰. The measurements reported here have a 95% confidence interval of 7.96–8.84‰. Although statistically the difference between the two measurements is not highly significant, the new results have important implications. It has been mentioned previously that KIE values are important for the quantitative interpretation of atmospheric isotope ratio measurements. The new KIE does not only increase the predicted change of the $\delta^{13}C$ values of atmospheric isoprene resulting from reaction with ozone, the substantially reduced uncertainty also reduces the uncertainties of these predictions. There is also a more theoretical implication. While the previously reported value suggested that the KIE for the reaction of isoprene fits

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well into the semi-empirical relationship between KIE and number of carbon atoms derived by Iannone et al. (2003) for reactions of alkenes with ozone, the new KIE is (1.4±0.3) ‰ higher than the prediction.

Similar to the new KIE for isoprene reaction, the KIE measured for *n*-heptene in this study is somewhat higher than a previously reported value. Iannone et al. (2003) reported a stable carbon $^{O3}\varepsilon$ value for 1-heptene of (4.3±0.7) ‰. Although the new value is within the range of the 95% confidence limit of the previously published value (2.41‰–5.65‰), the newer average value of (5.48 ± 0.09) ‰, which was based on 10 experiments, has a substantially lower uncertainty with a smaller 95% confidence interval (4.93–6.03‰).

3.4. *Dependence of KIEs on carbon number and molecular mass*

Iannone et al. (2003) have fitted their alkene + O_3 KIE data to a simple inverse dependence on carbon number which requires determination of only one parameter from the experimental data:

$$^{O_3}\varepsilon = \frac{(34.3 \pm 1.7)\,‰}{N_C} \tag{12}$$

where N_C represents the number of carbon atoms of the individual 1-alkene. Replacing the 1-heptene and adding the 1-octene and 1-nonene $^{O3}\varepsilon$ values from this investigation to the previously published C_2–C_6 1-alkene data, changes the parameter in the N_C^{-1} dependence to (34.9±1.5) ‰. Including all available KIE data for reactions of unsaturated VOC with ozone results in a value of (34.0±1.0) ‰. Excluding MVK and MACR gives a value of (34.4±1.0) ‰ and excluding dienes as well as MVK and MACR results in a fit parameter of (34.5±1.0) ‰. Using only the data from this paper a fit parameter of (34.9±2.1)‰ is obtained. Thus overall our new measurements support the findings of Iannone et al. (2003) that a N_C^{-1} dependence presents a robust first order estimate of the KIEs, with experimental data and predictions generally in agreement within the uncertainty of the measurements.

However, as has been mentioned above, the KIE measurements presented in this paper have in general a substantially better reproducibility than the previously reported measurements. Therefore

these new data can be used to look at the minor differences between measurements and predictions in more detail. Figure 4 shows a comparison between observations and predictions. The differences are small, but nevertheless statistically significant at the 2σ level. Overall, predictions based on an inverse carbon number dependence underestimate the KIEs for alkenes and overestimate the KIEs for MVK and MACR. Increasing the fit parameter in Equation (12) to a value of 40‰ would decrease the discrepancy between measurement and prediction to less than 0.5‰ for isoprene and the heavy alkenes. However, this increases the discrepancy between prediction and observation for MVK and MACR to about 2‰. Figure 4 shows a comparison between observations and a fit of the measurements to an inverse molecular mass dependence.

$$^{O_3}\varepsilon = \frac{(550 \pm 8)\,\text{‰}}{MM} \tag{13}$$

The theoretical basis for the dependence of KIEs on N_C^{-1} is based on the simplification that the isotope effect resulting from substitution of one carbon atom in a C=C double bond is independent of the functional groups which are connected to the double bond. Among other simplifications, this does not explicitly consider isotope effects depending only on molecular mass, such as changes in translational degrees of freedom or, in the framework of collision theory, the collision frequency. However, it should be noted that due to the proportionality of carbon number and molecular mass for alkenes, any function based on a dependence on carbon number will to some extent also be able to describe a dependence on molecular mass. MVK and MACR have a larger molecular mass than alkenes with the same carbon number. Molecular mass dependent isotope effects based on changes in collision frequency or translational partition functions decrease with increasing molecular mass. Qualitatively this is consistent with the observation that an inverse carbon number dependence derived for alkenes will overestimate the KIEs for reactions of MVK and MACR. Only considering the mass dependence of the collision frequency, or the loss of one translational degree of freedom in the transition state, predicts that the KIE for reaction of MVK and MACR with ozone will be 1.2‰ lower than the KIE for an alkene with the same carbon number as MVK or MACR. This is a small effect, but similar in magnitude to the

differences between the KIEs for MACR or MVK and predictions derived from the alkene reaction KIEs.

The predictions based on Equation (13) agree extremely well with the experimental data (Figure 4). To some extent this may be fortuitous since the number of data points is small. The values for inverse molecular mass only cover a small range. In this case a simple one parameter fit often results in a very good approximation for more complex dependencies. It also has to be considered that for 1-alkenes and, with a marginal deviation also for isoprene, molecular mass is proportional to carbon number. Thus the good agreement between fit to an inverse molecular mass dependence and observations does not imply the existence of a generally valid inverse molecular mass dependence of the KIEs. It is more realistic to interpret Equation (13) as a function which combines the established inverse carbon number dependence with some smaller mass dependent contributions into a simple parameterization, which provides a good approximation for a limited range of data.

A comparison of predictions based on Equation (13) with the data of Iannone et al. (2003) shows a small, but consistent over-prediction of the measurements. Since the inverse carbon number dependence of the KIE derived by Iannone et al. (2003) was based on studies of alkenes and a few dienes and cycloalkenes it can be converted into an inverse mass dependence using the approximation $MM = 14 \cdot N_C$:

$$^{O_3}\varepsilon = \frac{(14 \cdot 34.3 \pm 14 \cdot 1.7)\text{‰}}{MM} = \frac{(480 \pm 24)\text{‰}}{MM} \tag{13}$$

This function under-predicts the results from this paper by 0.6‰ to 1‰ (Figure 5). Although these differences are close to the combined uncertainties of measurements and predictions, the consistent under-prediction of all observations indicates the existence of a small, but nevertheless systematic bias between the two data sets for ozone-alkene reaction KIEs.

4. Conclusions

The results of this new data set of KIEs for gas-phase reactions of unsaturated VOC with ozone support the findings of Iannone et al. (2003) that a dependence on the inverse of carbon number allows a useful, first order estimate of KIEs. However, a more detailed comparison shows some discrepancies between predictions based on the inverse carbon number dependence derived by Iannone et al. (2003) and our new measurements. The new measurements of the KIEs for reactions of isoprene and heavy 1-alkenes are consistently higher than the predictions. Similarly, the new KIEs for the reactions of isoprene and 1-heptene, are slightly higher than the previously reported values. These findings indicate that there is a small, but consistent bias between the two data sets.

In contrast to this, the KIEs for reaction of MVK and MACR are lower than the values predicted by the inverse carbon number dependence. In view of the positive deviation for alkenes and the very good reproducibility of the measurements, it is very unlikely that this is due to experimental errors. MVK and MACR have a molecular mass, which is 25% larger than that of alkenes with four carbon atoms. Molecular mass dependent contributions to isotope effects are smaller for molecules of higher mass. Therefore qualitatively the findings are consistent with a small, but measurable contribution from molecular mass dependent effects to the overall KIE. However, since for all VOCs studied to date (except MACR and MVK) the molecular mass is effectively proportional to the number of carbon atoms, a quantitative separation of mass dependent and carbon number dependent contributions to the KIEs is not yet possible. Nevertheless, the results of this study strongly suggest that the molecular mass dependent effects are of sufficient magnitude to be studied with the presently available experimental methods.

The presently published carbon KIE measurements for gas-phase reactions of VOC were predominantly motivated by their usefulness for the interpretation of measurements of isotope ratios of atmospheric VOCs. Although the tropospheric oxidation of isoprene, MACR, and MVK via O_3 in most cases is a less significant loss process than OH-radical oxidation, the studied VOCs are sufficiently

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long-lived to survive into nighttime hours where mixing ratios of O_3 are significantly large and OH is minimal. For daytime hours, where isoprene emissions from vegetation are at peak levels, the reaction of these VOCs with OH radicals will be the dominant loss processes, and, the dominant production process for MACR and MVK. For this reason, a more complete picture of the isotopic fractionation of isoprene, MACR and MVK would require both their KIE measurements for the OH-radical reaction and concurrent measurements of mixing ratios and carbon isotope ratios of these VOCs in ambient samples.
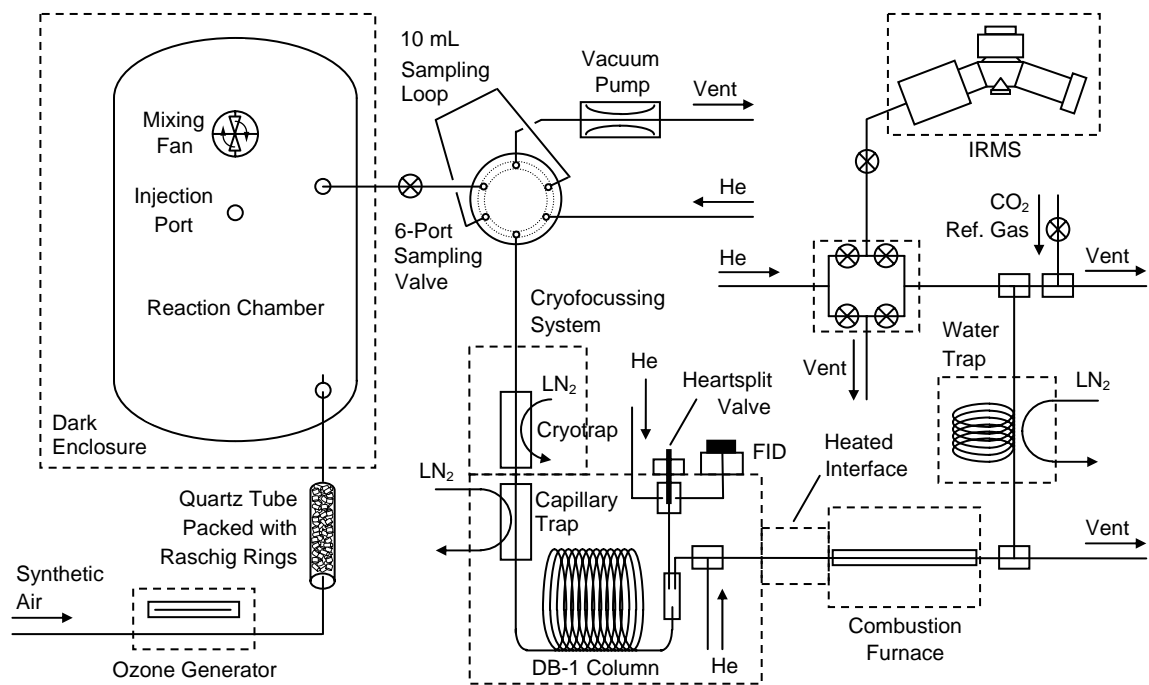
Acknowledgements

Fig. 1. Schematic of the system used for carbon kinetic isotope effect (KIE) experiments. Shut-off valves are denoted by the ⊗ symbol. The heartsplit valve in the open position can be used to divert column eluate to the FID; for all experiments this valve remained closed (i.e. all column flow proceeded toward the combustion furnace).
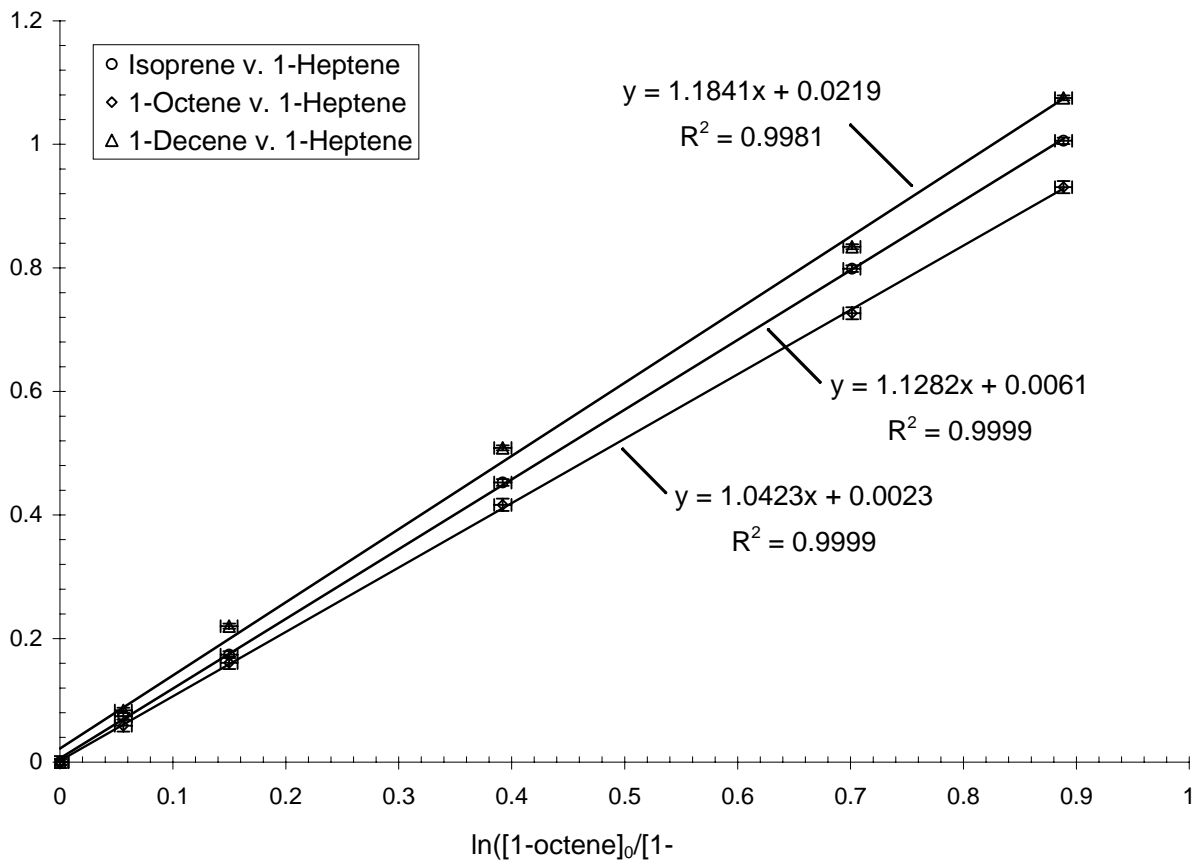
Fig. 2. Example of relative rate plot for the reaction of isoprene, 1-heptene and 1-decene with O_3 using 1-octene as the reference compound.
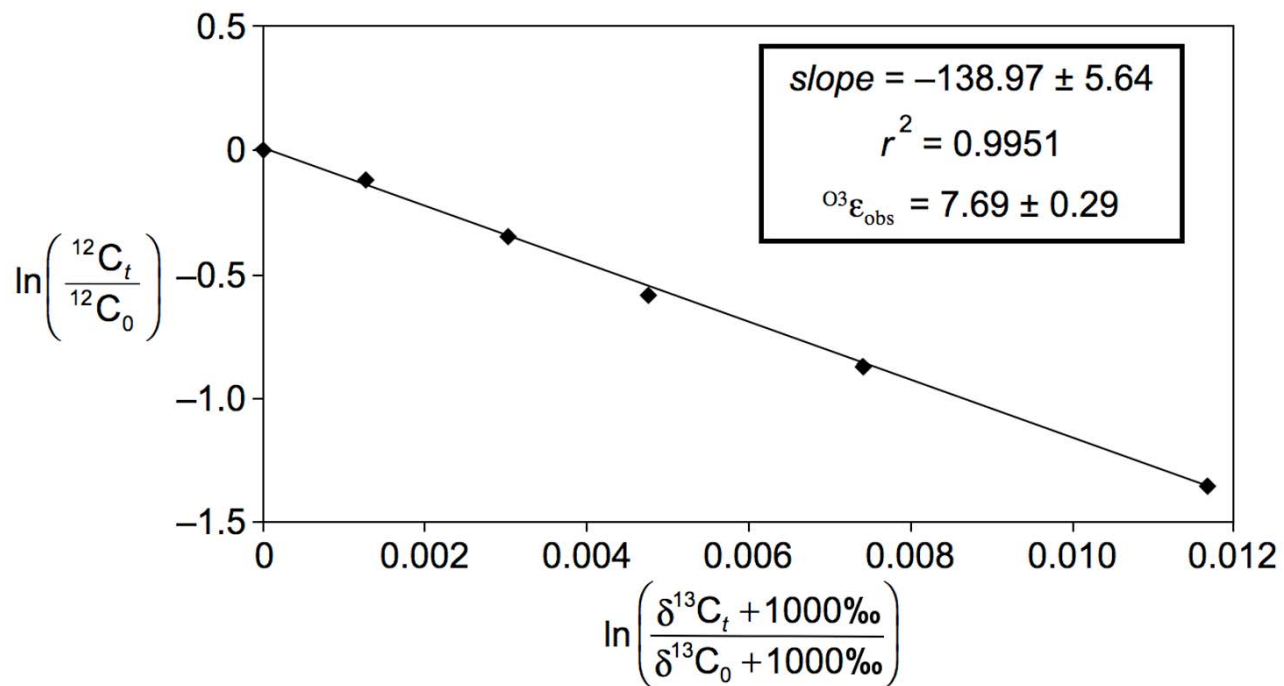
Fig. 3. Example plot for the determination of the $^{O3}\varepsilon_{obs}$ value of the MVK + O_3 reaction from the dependence between concentration and stable carbon isotope ratio formulated in Equation (3).
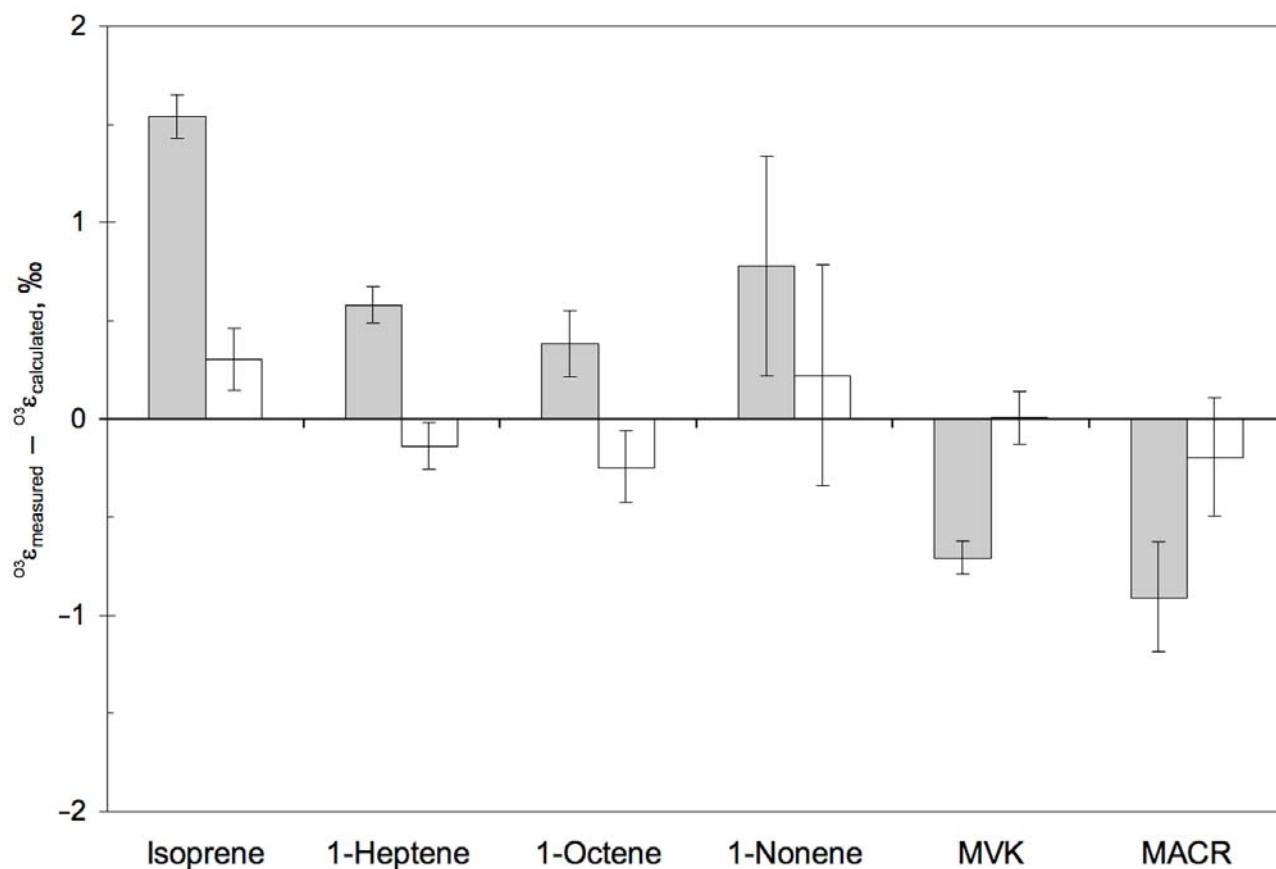
Fig. 4. Comparison between measured $^{O3}\varepsilon$ values and calculations. Grey bars are based on a fit of the data from this paper to a N_C^{-1} dependence ($^{O3}\varepsilon = ((34.9\pm2.1)\ ‰ \cdot N_C^{-1})$). The open bars are based on a dependence of the KIE on the inverse of molecular mass ($^{O3}\varepsilon = (550\pm8)\ ‰ \cdot MM^{-1}$). The error bars show the uncertainties resulting from the errors of the measurements and the fit parameters.

Fig. 5. Dependence of KIEs for reaction of ozone with unsaturated VOC on molecular mass. Data from this paper are shown as triangles, data from Iannone et al. (2003) are presented as circles. The solid line shows the dependence $^{O3}\varepsilon = (550\pm8)$ ‰ $\cdot$ MM^{-1} and the broken line shows an inverse mass dependence derived from the inverse carbon number dependence by Iannone et al. (2003) by using $MM = 14 \cdot N_C$.
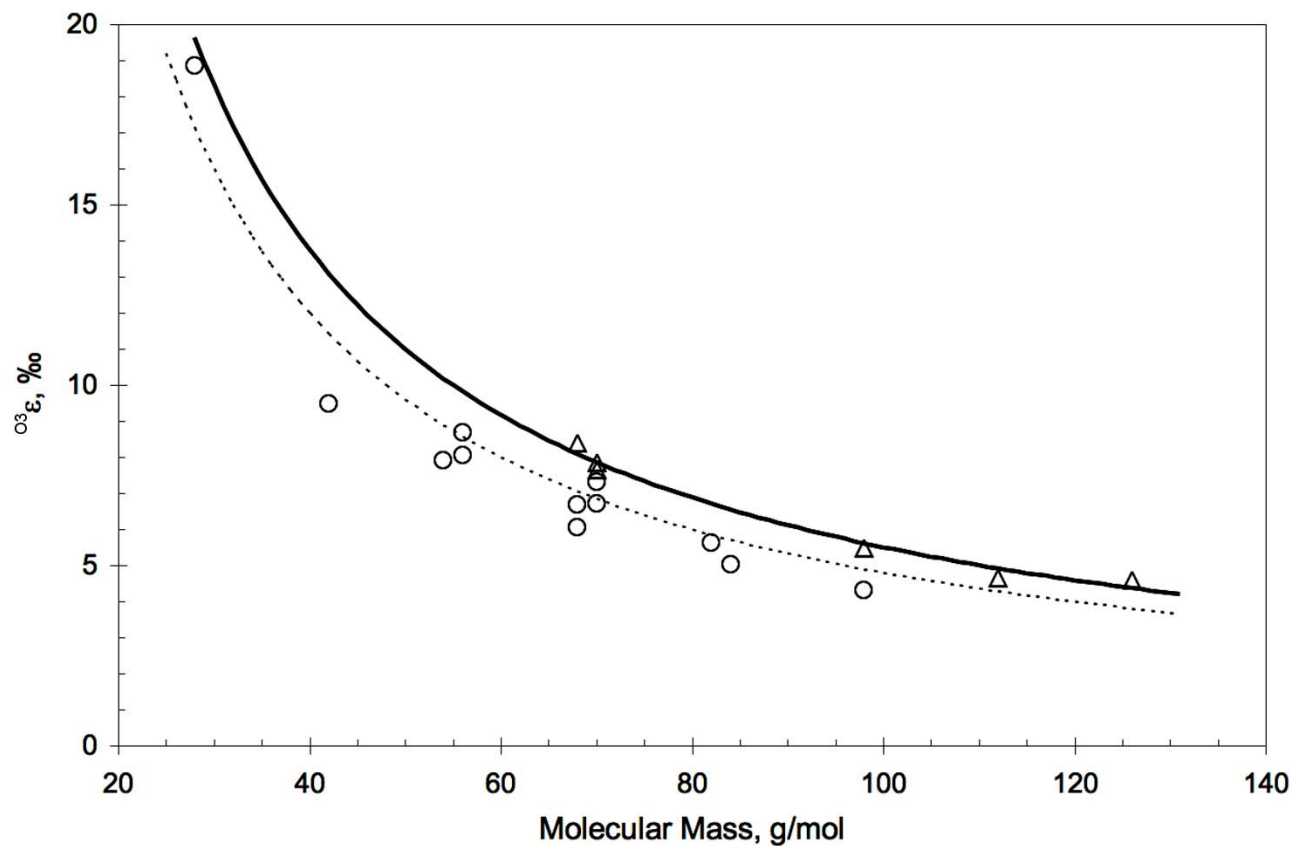
Table 1

Comparison between mean ozone-alkene relative rate constants from the GC-FID and GCC-IRMS studies of this investigation and literature rate constants (298 K)

Studied Alkene	Rate Constant, 10^{-18} cm^3 molecule^{-1} s^{-1}	Reference
MACR	1.02 ± 0.05	Grosjean et al., 1993.
	1.08 ± 0.21	Grosjean and Grosjean, 1998.
	1.12 ± 0.13	Atkinson et al., 1981.
	1.30 ± 0.14	Neeb et al., 1998.
	1.15 ± 0.18	Treacy et al., 1992.
	1.95 ± 0.35	This work, GC-FID
	1.96 ± 0.23	This work, GCC-IRMS
MVK	4.72 ± 0.09	Grosjean et al., 1993.
	5.84 ± 0.41	Grosjean and Grosjean, 1998.
	5.40 ± 0.60	Neeb et al., 1998.
	4.77 ± 0.57	Atkinson et al., 1981.
	4.22 ± 0.63	Treacy et al., 1992.
	4.37 ± 0.76	This work, GC-FID
	4.88 ± 0.10	This work, GCC-IRMS
Isoprene	11.9 ± 0.9	Klawatsch-Carrasco et al., 2004.
	12.1 ± 0.3	Avzianova and Ariya, 2002.
	12.2 ± 0.3	Greene and Atkinson, 1992.
	12.5 ± 1.2	Treacy et al., 1992.
	10.1 ± 1.3	This work, GC-FID
	12.1 ± 0.4	This work, GCC-IRMS
1-Heptene	9.4 ± 0.4	Grosjean and Grosjean, 1995.
	8.5 ± 1.0	This work, GC-FID
	11.7 ± 0.4	This work, GCC-IRMS
1-Octene	12.5 ± 0.4	Grosjean and Grosjean, 1995.
	8.4 ± 0.8	This work, GC-FID
	10.1 ± 0.4	This work, GCC-IRMS
1-Nonene	11.5 ± 3.9	Protczak and Trzeszczynski, 2002.
	11.2 ± 0.5	This work, GCC-IRMS
1-Decene	8.0 ± 1.4	Protczak and Trzeszczynski, 2002.
	11.4 ± 0.5	This work, GC-FID

Table 2

Rate constants and OH yields for the studied VOCs

Compound	^{O3}k, 10^{-18} cm³ molecule⁻¹ s⁻¹	^{OH}k,[a] 10^{-11} cm³ molecule⁻¹ s⁻¹	$^{O3}k/^{OH}k$, 10^{-7}	^{OH}y
Isoprene	12.8 ± 3.2	10.1 ± 2.5	1.27	0.35[b]
MACR	1.08 ± 0.21	3.35 ± 0.84	0.32	0.82[c]
MVK	5.84 ± 0.41	1.88 ± 0.47	3.11	0.36[c]
1-Heptene	9.40 ± 0.38	3.95 ± 0.16	2.38	0.27[d]
1-Octene	12.5 ± 4.0	3.80[e]	3.29	0.18[d]
1-Nonene	11.5 ± 3.9	3.65[f]	3.11	0.17[g]

[a]All VOC + OH rate constants taken from Atkinson (1997) unless noted otherwise.

[b]Average of 7 values reported in the literature by Gutbrod et al., 1997; Lewin et al., 2001; Rickard et al., 1999; Marston et al., 1998; Paulson et al., 1998; Neeb and Moortgat, 1999; and Zhang et al., 2002.

[c]Value taken from the Master Chemical Mechanism (MCMv3) (Jenkin et al., 2003).

[d]Atkinson et al. (1995).

[e]Grosjean and Williams (1992).

[f]Rate constant estimated by extrapolation from C_7–C_8 1-alkene literature rate constants.

[g]Estimated from a linear dependence of C_4–C_7 1-alkene y_{OH} values taken from Atkinson et al. (1995) against carbon number.

Table 3

Summary of stable carbon $^{O3}\delta$ values for the reactions of isoprene, MACR, MVK, and C_7–C_9 1-alkenes with ozone at (298 ± 4) K

Compound and Experiment	VOC Loss During Experiment, %[a]	$^{OH}F_i$ Mean Value[b]	Correction for $^{O3}\varepsilon_i$, ‰	$^{O3}\varepsilon_i$, ‰[c]
Isoprene[d]				
KIE-04	74.5	0.14 ± 0.01	+0.23	8.17 ± 0.19
KIE-05	94.3	0.10 ± 0.02	+0.22	8.72 ± 0.23
KIE-06	84.8	0.10 ± 0.02	+0.16	8.22 ± 0.26
KIE-17	74.3	0.14 ± 0.01	+0.25	8.38 ± 0.21
KIE-18	75.1	0.12 ± 0.01	+0.23	8.51 ± 0.16
			Mean:	8.40 ± 0.11[e]
			95% Confidence Interval:	7.96–8.84
MACR[d]				
KIE-11	71.8	0.37 ± 0.05	+0.81	8.06 ± 0.41
KIE-13	60.1	0.36 ± 0.04	+0.79	8.10 ± 0.37
KIE-14	41.7	0.37 ± 0.04	+0.48	7.17 ± 0.21
KIE-21	66.1	0.41 ± 0.02	+0.74	7.36 ± 0.30
			Mean:	7.67 ± 0.28[e]
			95% Confidence Interval:	6.74–8.61
MVK[d]				
KIE-11	92.1	0.10 ± 0.02	+0.10	7.79 ± 0.68
KIE-12	96.9	0.09 ± 0.02	+0.12	8.15 ± 0.30
KIE-13	93.3	0.09 ± 0.02	+0.10	7.83 ± 0.18
KIE-14	75.4	0.10 ± 0.01	+0.10	7.74 ± 0.24
KIE-21	96.0	0.12 ± 0.01	+0.12	7.86 ± 0.15
			Mean:	7.87 ± 0.08[e]
			95% Confidence Interval:	7.56–8.19
1-Heptene[f]				
KIE-04	70.0	0.08 ± 0.01	+0.01	5.16 ± 0.55
KIE-05	91.7	0.06 ± 0.01	+0.02	5.37 ± 0.48
KIE-06	97.7	0.05 ± 0.01	+0.02	5.33 ± 0.42
KIE-17	69.4	0.08 ± 0.01	+0.03	5.44 ± 0.63
KIE-18	70.6	0.07 ± 0.01	+0.02	5.18 ± 0.62
KIE-11	93.2	0.08 ± 0.01	+0.08	6.04 ± 0.39
KIE-12	97.9	0.07 ± 0.01	+0.02	5.35 ± 0.35
KIE-13	95.8	0.07 ± 0.01	+0.03	5.49 ± 0.38
KIE-14	92.9	0.08 ± 0.01	+0.04	5.55 ± 0.43
KIE-21	74.4	0.09 ± 0.01	+0.05	5.87 ± 0.45
			Mean:	5.48 ± 0.09[e]
			95% Confidence Interval:	4.93–6.03

Table 3 (Continued)

Compound and Experiment	VOC Loss During Experiment, $\%^a$	$^{OH}F_i$ Mean Value[b]	Correction for $^{O3}\varepsilon_i$, ‰	$^{O3}\varepsilon_i$, ‰[c]
1-Octene[f]				
KIE-06	82.9	0.04 ± 0.01	-0.02	3.98 ± 0.60
KIE-17	71.5	0.06 ± 0.00	-0.01	4.28 ± 0.38
KIE-18	72.5	0.05 ± 0.01	0.02	4.74 ± 0.32
KIE-11	94.1	0.06 ± 0.01	$+0.06$	5.44 ± 0.36
KIE-12	97.5	0.05 ± 0.01	$+0.02$	4.84 ± 0.37
KIE-13	96.4	0.06 ± 0.01	$+0.01$	4.56 ± 0.33
KIE-14	93.8	0.05 ± 0.01	$+0.01$	4.53 ± 0.36
KIE-21	76.4	0.06 ± 0.01	$+0.02$	4.98 ± 0.34
			Mean:	4.67 ± 0.17^e
			95% Confidence Interval:	3.80–5.54
1-Nonene[f]				
KIE-04	73.3	0.06 ± 0.01	$+0.04$	4.59 ± 0.56

[a]Initial concentrations were (all in units of 10^{14} molecules cm^{-3}) 3.6, 4.4, 4.5, 2.6, 2.3, and 2.1 for isoprene, MACR, MVK, 1-heptene, 1-octene, and 1-nonene.

[b]Average contribution of OH radicals to the overall reactant VOC loss determined by mean value of Equation (10), using the Equation (8) estimate of [OH] for every time interval.

[c]Uncertainty estimates for individual $^{O3}\varepsilon_i$ values were determined by the propagated errors of $^{OH}F_i$, $^{O3}\varepsilon_{obs,i}$, and $^{OH}\varepsilon_i$.

[d] $^{OH}\varepsilon_i$ values of (6.56 ± 0.12) ‰ (isoprene), (5.88 ± 0.08) ‰ (MACR), and (6.78 ± 0.14) ‰ (MVK), required for the corrections of $^{O3}\varepsilon_{obs,i}$ using Equation (11), were unpublished results from a similar study.

[e]Uncertainty was determined by the standard error: $\sigma(n - 1)^{-0.5}$, where σ represents the standard deviation of the averaged $^{O3}\varepsilon_i$ values, and n represents the number of $^{O3}\varepsilon$ values included in the calculation of the mean.

[f] $^{OH}\varepsilon_{av}$ values of (5.04 ± 0.23) ‰ (1-heptene), (4.41 ± 0.20) ‰ (1-octene), and (3.92 ± 0.18) ‰ (1-nonene) were estimated from the following inverse dependence of 1-alkene + OH KIEs (Rudolph et al., 2000; Anderson et al., 2004) toward carbon number (N_C): $^{OH}\varepsilon$(1-alkene) $= (35.3 \pm 1.6)N_C^{-1}$.

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