

The carbon kinetic isotope effects of ozone-alkene reactions in the gas-phase and the impact of ozone reactions on the stable carbon isotope ratios of alkenes in the atmosphere

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[1] The kinetic isotope effects (KIEs) for several ozone-alkene reactions in the gas phase were studied in a 30 L PTFE reaction chamber. The time dependence of the stable carbon isotope ratios and the concentrations were determined using a gas chromatography combustion isotope ratio mass spectrometry (GCC-IRMS) system. The following average KIE values were obtained: 18.9 ± 2.8 (ethene), 9.5 ± 2.5 (propene), 8.7 ± 1 (1-butene), 8.1 ± 0.4 (*E*-2-butene), 7.9 ± 0.4 (1,3-butadiene), 6.7 ± 0.9 (1-pentene), 7.3 ± 0.2 (*Z*-2-pentene), 6.7 ± 0.7 (cyclopentene), 6.1 ± 1 (isoprene), 5.0 ± 0.7 (1-hexene), 5.6 ± 0.5 (cyclohexene), and 4.3 ± 0.7 (1-heptene). These data are the first of their kind to be reported in the literature. The ozone-alkene KIE values show a systematic inverse dependence from alkene carbon number. Based on the observed KIEs, the contribution of ozone-alkene reactions to the isotopic fractionation of alkenes in the atmosphere can be estimated. On average this contribution is generally small compared to the impact of reaction with OH radicals. However, when OH-concentrations are very low, e.g. during nighttime and at high latitudes in winter, the contribution of the ozone reaction dominates and under these conditions the ozone-alkene reaction will have a clearly visible impact on the stable carbon isotope ratio of atmospheric alkenes.

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1. Introduction

[2] Studies of the stable isotope composition of CH₄, CO and CO₂, have been shown to be useful for the understanding of the sources, sinks, and distributions of these gases [Lowe *et al.*, 1994; Brenninkmeijer *et al.*, 1995; Ciais *et al.*, 1995, 1997]. More recently it has been shown that isotope ratio measurements can also be used to better understand the atmospheric chemistry of non-methane hydrocarbons (NMHCs). Following the development of a method to

measure the stable carbon isotope ratio of NMHCs at atmospheric concentrations [Rudolph *et al.*, 1997], studies of the stable carbon isotope ratios of ambient NMHCs have ensued [Tsunogai *et al.*, 1999; Rudolph *et al.*, 2000; Saito *et al.*, 2002]. This has led to the development of the “Isotopic Hydrocarbon Clock” concept [Rudolph and Czuba, 2000]. Any interpretation of stable carbon isotope measurements of NMHCs in the atmosphere will require the knowledge of the isotope fractionation associated with their atmospheric reactions. The most important atmospheric reaction of NMHCs is with OH radicals and the kinetic isotope effects (KIEs) for some of the most relevant NMHC-OH reactions have been published recently [Rudolph *et al.*, 2000]. Generally for most alkanes and aromatic hydrocarbons, no other atmospheric reactions contribute significantly to their atmospheric removal. However, alkenes also react with ozone. Consequently this reaction will have an impact on the stable carbon isotope ratio of alkenes in the atmosphere. The magnitude of this impact will depend not only on the contribution of this reaction to the removal of alkenes from the atmosphere, but also on the KIE. The contribution of the ozone-alkene reaction to the atmospheric loss of alkenes can be calculated from measured ozone concentrations and the rate constants for these reactions. However, we cannot reliably determine the change in stable carbon isotope ratios due to alkene-ozone reactions without knowledge of the KIE for these reactions.

[3] Measurements of rate constants for the gas-phase reactions of alkenes with ozone have been performed for many decades [Atkinson, 1994; Atkinson, 1997] but no measurements of the KIEs of these reactions are known to us. In this paper we present measurements of the stable carbon KIEs for the reaction of alkenes with ozone. The results of these measurements are used to estimate the impact of this reaction on the stable carbon isotope ratio of atmospheric alkenes. This impact is compared with the effect of processing due to reaction with OH for different atmospheric conditions.

2. Experimental

2.1. Instrumentation

[4] Figure 1 shows a schematic diagram of the experimental set-up. Experiments were carried out at 298 ± 2 K and ambient pressure in a 30 L collapsible PTFE reaction chamber. This chamber was housed in a dark enclosure to prevent any possible bias of the measured KIEs due to light induced reactions. Ozone was generated as a mixture in O₂ by passing

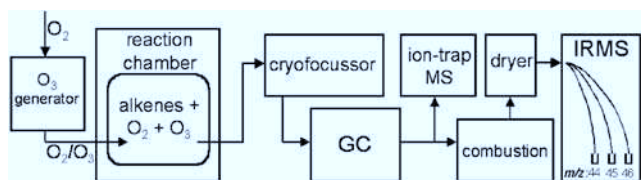


Figure 1. Schematic diagram of experiment set-up for measuring ozone-alkene kinetic isotope effects.

oxygen through an ozone generator, which consisted of a 4 mm i.D., approximately 20 cm long quartz tube irradiated by a Hg-discharge lamp (Pen-ray lamp from Ultra Violet Products). The O_2/O_3 stream was admitted to the reaction chamber typically at a flow rate of 2–6 mL/min continuously throughout the entire experiment. The steady state ozone mixing ratio in the reaction chamber was always well below 1 ppm; during most experiments between a few ppb and 0.2 ppm. The concentration and stable carbon isotope composition of the alkenes was measured at regular intervals by gas chromatography combined with on-line combustion and isotope ratio mass spectrometry (GCC-IRMS). The sample injection consisted of several steps: (1) cooling the cryofocussing trap to 93 K with liquid nitrogen, (2) flushing the transfer lines with the sample from the reaction chamber, (3) transferring the sample to the stainless steel trap in the cryofocussing trap where the sample VOCs were adsorbed and the air gases were vented, and (4) flash-heating the adsorbed VOCs and subsequent injection into the gas chromatograph.

[5] A Varian 3600 Gas Chromatograph equipped with two columns (to allow for two-dimensional gas chromatography in certain cases where additional separation is necessary) was used to separate the sample components. The two columns used in this study were: (1) a 60 m $\times$ 5 μ m film $\times$ 0.32 mm i.D. HP-1 column (Agilent Technologies), and (2) a 60 m $\times$ 0.32 mm i.D. Poraplot Q column.

[6] After the separation step, the GC effluent was split between a combustion interface (80%), where all organic compounds were quantitatively converted to CO_2 and H_2O , and a Varian Saturn 2000 ion-trap mass spectrometer (20%). The combustion interface consisted of nickel, platinum and copper wires housed in a thin ceramic tube at 1223 K. The combustion interface was regularly regenerated by flushing with oxygen at 823 K. The combustion effluent stream was dried by passing it through a tubular Nafion membrane surrounded by a flow of dry helium. The CO_2 from combustion was introduced to a Finnigan MAT 252 Isotope Ratio Mass Spectrometer (IRMS) via an open split at ~ 0.4 mL/min.

2.2. Procedure

[7] Mixtures of gaseous alkenes of comparable reactivity (~ 30 ppm per alkene) and cyclohexane (3000 ppm) were prepared inside the 30 L chamber using dry synthetic air as the diluent gas. The cyclohexane was used to scavenge OH generated from the ozone-alkene reaction. The concentration of cyclohexane was sufficient to limit the contribution of OH-reactions to the loss of alkenes to 6% or less and the resulting bias for the measured KIEs was always below 0.1‰. The alkenes were injected into the reaction chamber by a syringe through a septum installed in one of the ports of the reaction chamber. Liquid hydrocarbons (Aldrich) with stated purities of 95% or better and were used without further purification. A fan inside the chamber ensured that

its contents were rapidly mixed. Before any measurements were taken, the chamber contents were allowed at least 5 minutes to undergo mixing, thereby reducing any concentration gradients. Prior to starting the reactions by adding ozone, several measurements were carried out to ensure that the system was stable. Experiments were only conducted if the relative change in the concentrations was below 2% and the change in the delta values of the alkenes was below 0.5‰ over three consecutive measurements.

[8] While adding ozone to the reaction chamber, a measurement was performed approximately every 2 h to determine the concentrations and stable carbon isotope ratios of the studied alkenes. This was repeated until all alkenes were depleted to $\leq 30\%$ of their initial concentration.

2.3. Data Evaluation

[9] The carbon isotope peaks were evaluated using the commercial FINIGAN software package. Manual peak integrations were performed to evaluate peaks not integrated appropriately by the software routine. From the peak areas, concentration and isotope ratio data of the alkenes under study were obtained.

[10] Stable carbon isotope ratios are defined as ratio of the number of carbon-13 atoms over the number of the carbon-12 atoms ($^{13}C/^{12}C$) in the sample. The isotope ratio measurements were made relative to a standard traceable to the internationally accepted Vienna Pee Dee Belemnite scale and are presented in delta notation as per mil (‰) values relative to this scale:

$$\delta^{13}C = \left[\left(\frac{^{13}C/^{12}C}{^{13}C/^{12}C} \right)_{\text{sample}} - \left(\frac{^{13}C/^{12}C}{^{13}C/^{12}C} \right)_{\text{ref.}} \right] \cdot 1000\text{‰} \quad (1)$$

Here, ^{13}C and ^{12}C represent the abundance of different isotopes in the sample and the reference. The following equation represents the KIE, the ratio of the rate constant for molecules containing only ^{12}C (k_{12}) over the rate constant for molecules containing a ^{13}C atom (k_{13}), as function of isotope ratios and concentrations at time t and at $t = 0$:

$$k_{12}/k_{13} = \ln \left(\frac{^{12}C_t/^{12}C_0}{^{12}C_t/^{12}C_0} \right) / \left\{ \ln \left(\frac{^{12}C_t/^{12}C_0}{^{12}C_t/^{12}C_0} \right) + \ln \left[\frac{(\delta^{13}C_t + 1000)}{(\delta^{13}C_0 + 1000)} \right] \right\} \quad (2)$$

This equation can be rearranged to form an equation that allows determining the KIE from the slope of a linear dependence between concentration and stable carbon isotope ratio of the studied compound:

$$\ln \left(\frac{^{12}C_t/^{12}C_0}{^{12}C_t/^{12}C_0} \right) = k_{12}/k_{13} / (1 - k_{12}/k_{13}) \cdot \ln \left[\left(\frac{^{13}C_t/^{12}C_t}{^{13}C_0/^{12}C_0} \right) / \left(\frac{^{13}C_0/^{12}C_0}{^{13}C_0/^{12}C_0} \right) \right] \quad (3)$$

Similar to using δ values to express stable carbon isotope ratios, KIE values can be represented in epsilon notation as per mil (‰) values:

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

3. Results and Discussion

[11] Figure 2 provides an example of a linear plot of the dependence between concentration and stable carbon iso-

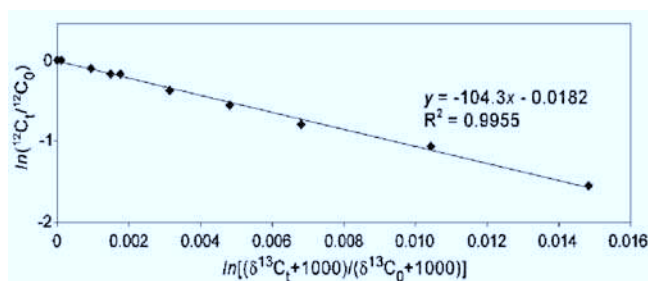


Figure 2. Plot of experimental data for the determination of the 1-butene KIE value. The KIE is determined from the slope of the linear regression according to $\text{KIE} = \text{slope}/(\text{slope} + 1)$.

tope ratio as defined by (3). The data obtained from a total of 10 experiments studying 14 alkenes are summarized in Table 1. The KIE values of terminal alkenes show an inverse dependence on carbon number (Figure 3). Within the uncertainties of the measurements, the KIEs for other alkenes studied fall on the same curve, but the range of carbon numbers studied for non-terminal alkenes is small and the shape of the curve is determined predominantly by the terminal alkenes.

[12] For compounds only reacting with OH the change in isotopic composition relative to the source composition can be calculated by the following equation [Rudolph and Czuba, 2000]:

$$\delta_z = t_{av} \cdot {}^{\text{OH}}k_z \cdot [\text{OH}] \cdot {}^{\text{OH}}\epsilon_z + {}^0\delta_z \quad (5)$$

Here, δ_z and ${}^0\delta_z$ represent observed and emitted carbon delta values for compound z ; t_{av} represents the average age of compound z ; ${}^{\text{OH}}k_z$ is the rate constant for the reaction of OH with compound z ; $[\text{OH}]$ represents the average OH concentration; and ${}^{\text{OH}}\epsilon_z$ represents the KIE for the reaction of OH with compound z . This equation adequately describes isotope fractionation for alkanes and aromatic compounds, since reaction with OH is by far the dominant loss mechanism for these compounds. However, it potentially gives a biased estimate of the fractionation alkenes undergo. In the case of alkenes, (5) must be modified to include a term for the ozone reaction:

$$\delta_z = t_{av} \cdot {}^{\text{OH}}k_z \cdot [\text{OH}] \cdot {}^{\text{OH}}\epsilon_z + t_{av} \cdot {}^{\text{O}_3}k_z \cdot [\text{O}_3] \cdot {}^{\text{O}_3}\epsilon_z + {}^0\delta_z \quad (6)$$

The second term in (6) represents the contribution of the ozone-alkene reaction toward changing the isotopic com-

Table 1. KIE Values for Ozone-Alkene Reactions

Alkene	KIE, ‰
Ethene	18.85 ± 2.80 (2)
Propene	9.49 ± 2.47 (4)
1-Butene	8.70 ± 0.96 (3)
<i>E</i> -2-Butene	8.05 ± 0.35 (3)
1,3-Butadiene	$7.91 \pm 0.35^{\text{a}}$ (1)
1-Pentene	6.72 ± 0.87 (3)
<i>Z</i> -2-Pentene	$7.32 \pm 0.15^{\text{a}}$ (1)
Cyclopentene	6.68 ± 0.73 (3)
Isoprene	6.05 ± 0.99 (4)
1-Hexene	5.04 ± 0.69 (5)
Cyclohexene	5.64 ± 0.54 (5)
1-Heptene	4.31 ± 0.69 (3)

^aIn cases where only one measurement was made, the error was derived from the uncertainty of the slope of the linear regression according to (3).

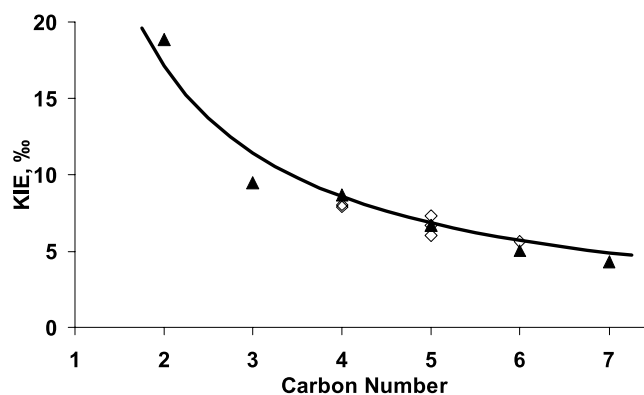


Figure 3. Plot of carbon KIE values for ozone-alkene reactions versus carbon number. Terminal alkenes are shown as full triangles, other alkenes as open diamonds. Also shown is a fit to an inverse dependence on carbon number (N_C), $\text{KIE} = (34.3 \pm 1.7)\text{‰}/N_C$.

position of atmospheric alkenes. Although ${}^{\text{O}_3}\epsilon_z$ values are of comparable magnitude to ${}^{\text{OH}}\epsilon_z$ values, ozone-alkene rate coefficients are, on average, six orders of magnitude lower than those of the corresponding OH-alkene rate constants. On the other hand in the troposphere ozone concentrations are very often orders of magnitude higher than OH-concentrations.

[13] Based on (6) the change in stable carbon isotope ratio of alkenes can be calculated as a function of time and the concentrations of ozone and OH. As an example the time dependence of the stable carbon isotope ratio of isoprene is shown for three different conditions in Figure 4. The conditions are chosen such that they represent to some extent typical conditions for the unpolluted lower troposphere at mid northern latitudes ($[\text{OH}] = 1.0 \times 10^6$ radicals cm^{-3} , $[\text{O}_3] = 30$ ppb), urban conditions ($[\text{OH}] = 1.0 \times 10^6$ radicals cm^{-3} , $[\text{O}_3] = 100$ ppb) and nighttime conditions ($[\text{OH}] = 1.0 \times 10^3$ radicals cm^{-3} , $[\text{O}_3] = 30$ ppb). For the isotopic composition of the source we use $-27.7 \pm 0.5\text{‰}$, the average composition of isoprene emissions from vege-

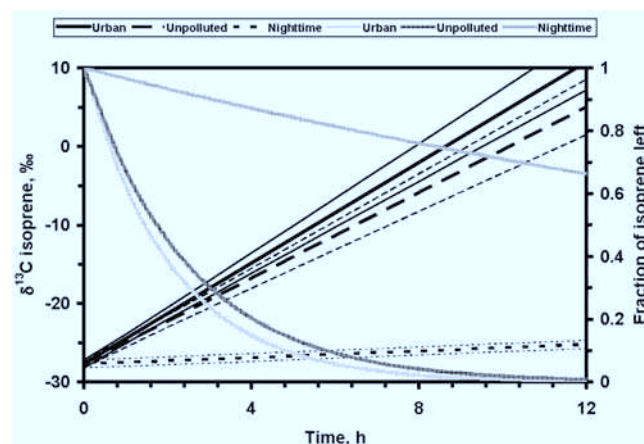


Figure 4. Temporal development of the stable carbon isotope ratio of isoprene for typical urban, unpolluted, and nighttime conditions (details see text). The thin lines represent the uncertainties derived from the uncertainties of the KIE and the stable isotope ratio of the emissions. Also shown is the fraction of isoprene left (grey lines).

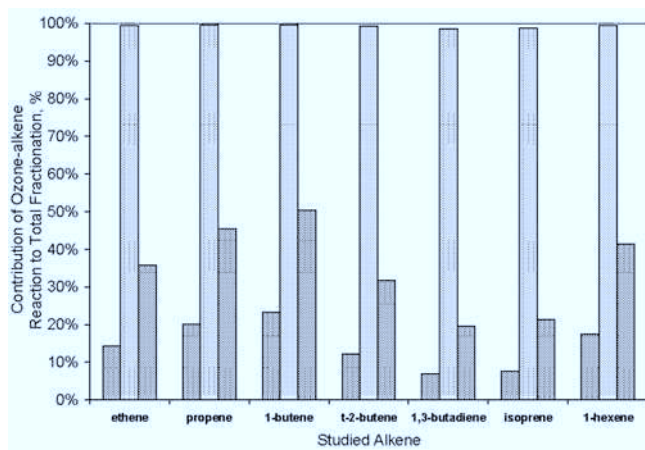


Figure 5. Relative contribution of the ozone-alkene reaction to the total stable carbon isotope fractionation of alkenes in the atmosphere under different conditions. Concentrations typical of three different conditions (see also Figure 4) are used for the comparison: Average, (left bar), nighttime (center bar), and urban (right bar). The reaction rate constants for the calculations are taken from Atkinson [1994, 1997], the KIEs for reaction with OH and ozone from Rudolph *et al.* [2000] and this work, respectively.

tation reported by Rudolph *et al.* [2003]. The reaction rate constants are taken from Atkinson [1994, 1997]; the KIEs for the reactions of isoprene with OH and ozone are $6.9 \pm 0.8\text{‰}$ [Rudolph *et al.*, 2000] and $6.1 \pm 1.0\text{‰}$ (this work), respectively.

[14] The results shown in Figure 4 are based on the assumption that the concentrations of OH and ozone do not vary with time. Although these are somewhat unrealistic assumptions, the results shown in Figure 4 give some idea about the average change since (6) defines the dependence between average processing and stable isotope ratio [Rudolph and Czuba, 2000]. Consequently, the time scale in Figure 4 can also be interpreted as the average extent of processing of the studied compound.

[15] For average and urban conditions the rate of change of the stable carbon isotope ratios is in the range of several per mil per hour. Such changes exceed the variability of the emissions and the uncertainty of stable carbon isotope ratio measurements, which are typically in the range of 0.5 to 2 per mil [Rudolph *et al.*, 1997, 2003]. However the changes during the night, which are nearly entirely due to reaction with ozone, are considerably lower, although not negligible. Consequently changes in ozone concentration have only a small impact on the stable carbon isotope ratio during daytime. Obviously, during daytime, the OH reaction generally dominates the change in stable carbon isotope ratios.

[16] This is not specific for isoprene; during daytime the reaction with OH nearly always has a substantially larger impact on the stable carbon isotope ratio than reaction with ozone. However, as shown in Figure 5, for some compounds and at high ozone concentrations the reaction with ozone can contribute between 30% and 50% to the overall change in stable carbon isotope ratio.

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