



Kinetic Isotope Effects, VOC's, and Atmospheric Chemistry

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Abstract

The focus of this research is to use stable isotopes as a new tool in understanding free radical chemistry in the atmosphere on a timescale of hours. This will be accomplished using ^{13}C as an indirect isotopic tracer of the reaction of isoprene with OH. This reaction is associated with a substantial kinetic isotope effect ($\text{KIE} = 1.007$). Modeling results indicate that the diurnal course in isotopic composition of ambient isoprene and its primary oxidation products, methacrolein (MACR) and methyl vinyl ketone (MVK), will provide valuable insights into atmospheric oxidation in forested locales.

A series of laboratory chemical kinetics experiments will be carried out to determine the kinetic isotope effects associated with the different degradation pathways of isoprene and other biogenic volatile organic compounds (BVOC's). In addition, field samples will be taken to characterize diurnal and seasonal patterns in $\delta^{13}\text{C}$ of selected BVOC's. Work thus far has focused on instrumentation development and modeling.

Introduction

Globally, emissions of biogenic volatile organic compounds (BVOC's) have been estimated to exceed those from anthropogenic sources by as much as an order of magnitude [*Guenther et al.*, 1995; *Mueller*, 1992]. This, combined with the high reactivity of plant-produced volatile organic compounds, has led to the realization that emissions by terrestrial ecosystems have significant impacts on tropospheric chemistry at both a regional and global scale [*Goldstein et al.*, 1998; *Guenther et al.*, 1995]. Isoprene (C₅H₈) is the dominant BVOC emitted by vegetation, and globally represents the single largest known reactive hydrocarbon source to the atmosphere. Isoprene chemistry is therefore particularly important in determining the oxidizing capacity of the lower troposphere, and could play a role in biosphere feedbacks to climate change [*Shallcross and Monks*, 2000].

The primary daytime sink for isoprene is reaction with the hydroxyl radical (Figure 1), a reaction which, in the presence of NO_x, is coupled with ozone (O₃) production. Thus it has been found that isoprene oxidation can control the ozone production efficiency in many rural and semi-rural settings [*Hirsch et al.*, 1996]. In the absence of OH, chemical loss of isoprene is believed to occur via reaction with ozone or nitrate radical (NO₃). Isoprene oxidation can also impact reactive nitrogen speciation and transport through formation of peroxyacetyl nitrate (PAN) and related compounds [*Carter*, 1996; *Carter and Atkinson*, 1996].

Introduction

The hydroxyl radical is the most important oxidant in the Earth's atmosphere, determining the lifetime of many greenhouse gases such as methane and ozone depleting gases such as methyl halides. Currently, our best estimates of globally-averaged OH concentrations are based on inversion of global atmospheric measurements of the anthropogenic pollutant methylchloroform combined with knowledge of its production and emission [*Montzka et al.*, 2000]. On regional scales, similar techniques have been employed using shorter-lived gases such as anthropogenically-emitted hydrocarbons [*Goldstein et al.*, 1998].

Using Gas Chromatography Combustion Isotope Ratio Mass Spectrometry (GCC-IRMS), Rudolph *et al.* [1999] have demonstrated that the reaction of isoprene with OH is associated with a substantial ^{13}C isotopic fractionation ($\text{KIE} = 1.007 \pm 0.001$). This raises the possibility of using stable isotopes of volatile organic compounds to quantify free radical chemistry in the atmosphere and represents a new approach to studying atmospheric oxidation in general.

Oxidation Chemistry and Kinetic Isotope Effects

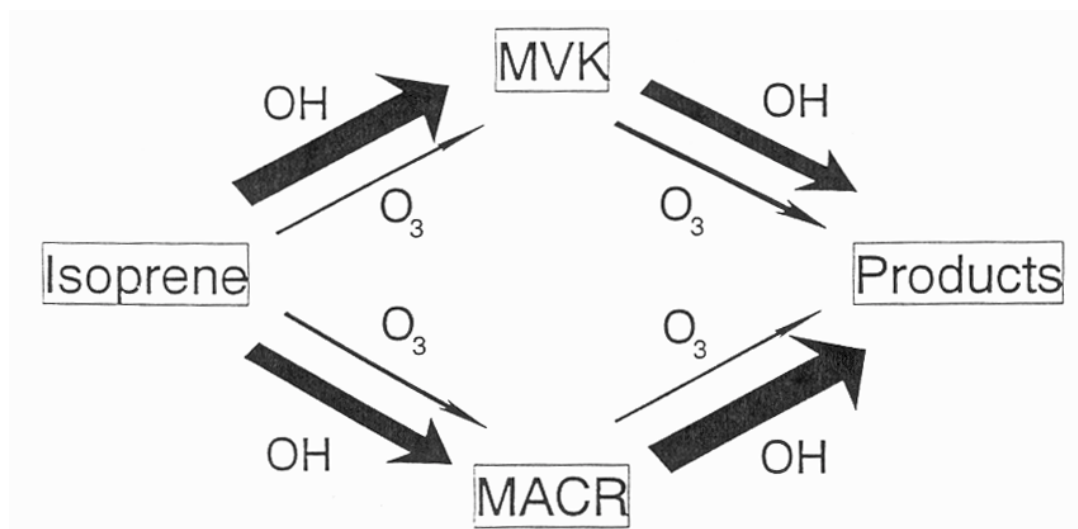
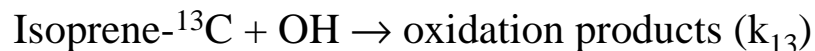
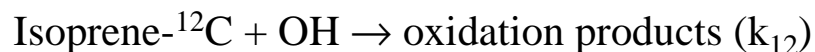


Figure 1. Diagram illustrating the dominant daytime reaction pathways for isoprene and its oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) by OH and ozone. Arrow sizes are proportional to the relative reaction rates. From Montzka *et al.* [1993].



$$\text{Kinetic Isotope Effect (KIE)} = k_{12}/k_{13} = 1.007$$

Oxidation Chemistry and Kinetic Isotope Effects

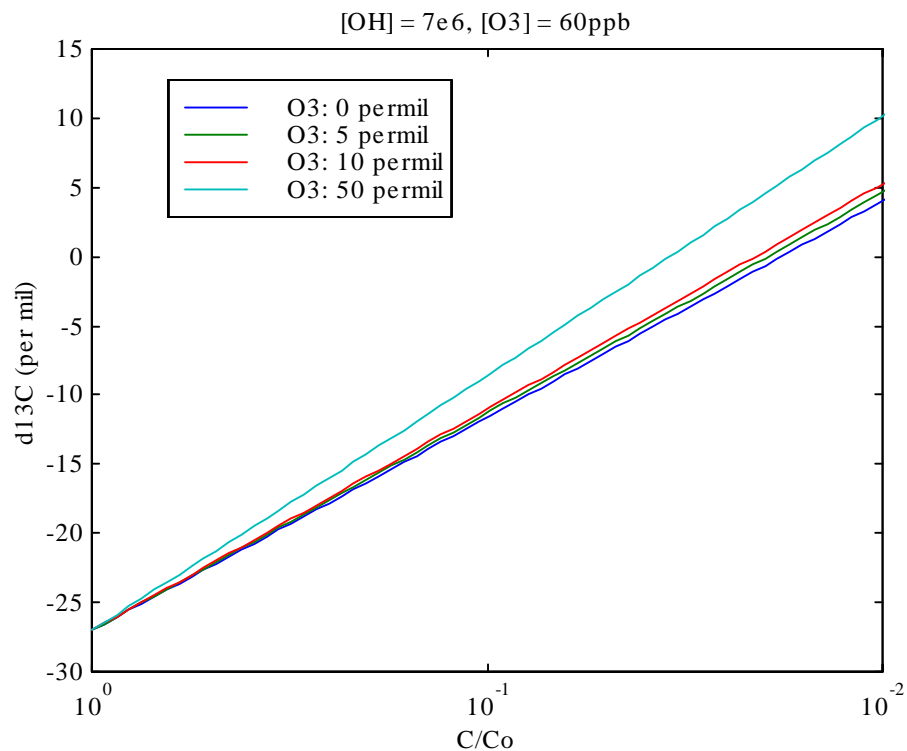


Figure 2. Isotopic composition ($\delta^{13}\text{C}$) of isoprene during the course of reaction with OH, as a function of the fraction of isoprene remaining (C/C_0). The residual isoprene becomes more and more enriched in ^{13}C as OH reacts preferentially with lighter ^{12}C -containing molecules. Different lines correspond to different KIE values for the isoprene + ozone reaction (currently unknown).

Modeling Results

We have predicted the diurnal course of isoprene concentrations and $\delta^{13}\text{C}$ over a forest using a simple box model (see Figure 3).

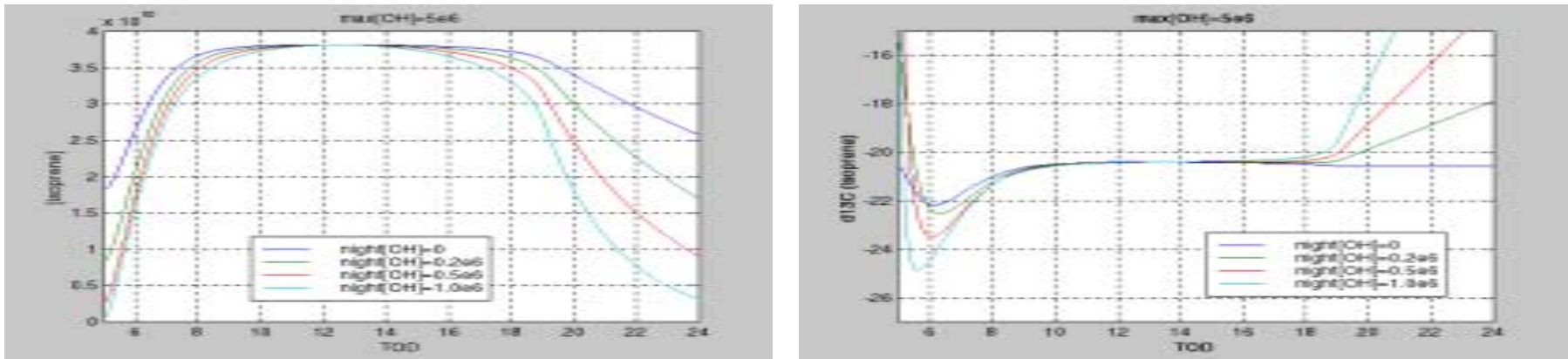


Figure 3: Modeled diurnal trends in isoprene concentration and $\delta^{13}\text{C}$ for different levels of OH at night. Concentration units are molec/cm³; $\delta^{13}\text{C}$ is in per mil (‰). The model assumes diurnally-varying OH concentrations (maximum = 5×10^6 molec/cm³ at noon) and isoprene emissions (maximum = 2×10^{12} molec/cm²s), constant O₃ (60 ppb), and a constant boundary layer height. $\delta^{13}\text{C}$ of freshly emitted isoprene is taken as -27‰ .

Modeling Results

Whereas the concentration of isoprene is sensitive to the source strength, the isotopic composition of atmospheric isoprene is not. The isotopic composition of isoprene should therefore provide an excellent measure of the oxidative processing of isoprene. For example, the diurnal course of $\delta^{13}\text{C}$ of isoprene should be highly sensitive to the extent of OH chemistry that occurs at night. After emissions cease in the evening, if the nighttime decay is due to hydroxyl radical, the residual isoprene will become progressively more and more depleted in ^{13}C as OH reacts preferentially with ^{12}C -containing molecules (Figure 6). For simplicity, the above model assumed no NO_3 chemistry, and that no fractionation occurs for the reaction of isoprene with ozone. In reality, the contribution to $\delta^{13}\text{C}$ from both of these factors will need to be determined.

A similar model could describe the expected concentration and isotopic composition for the primary oxidation products of isoprene, MVK and MACR. However, the isotopic composition of MVK and MACR would reflect isotope effects associated with their photochemical production from isoprene, as well as their photochemical loss processes. The reaction of isoprene with OH is 3.5 and 5 times faster than that for MACR and MVK, respectively. The reaction of isoprene with O_3 is 12 and 3 times faster than that for MACR and MVK, respectively. The reaction of MACR and MVK with NO_3 is extremely slow (lifetimes of order weeks to years), and thus should not be an important loss process. Thus, the isotopic signature of the combined loss processes for isoprene, MVK, and MACR should provide a useful set of constraints for quantifying the magnitude of NO_3 and OH oxidation in the atmosphere.

Further Research

We will measure the fractionation associated with atmospheric oxidation and formation processes for isoprene, MACR, and MVK and, thus, develop a novel method for studying the oxidative properties of the atmosphere on a time scale of hours. Laboratory experiments will also be designed to test the use of stable carbon isotopes as proxies to quantify the oxidation chemistry and budgets of other volatile organic compounds (VOCs), such as methylbutenol and acetone. These experiments will lay the foundation for future field measurements of $\delta^{13}\text{C}$ of selected VOCs in the atmosphere.

The laboratory experiments will require:

- 1) quantifying the KIE of the VOC + O₃ reactions;
- 2) quantifying the KIE of the VOC + NO₃ reaction;
- 3) quantifying the KIE of the VOC + OH reaction.

The field measurements will require:

- 4) preconcentrating a sufficient amount of isoprene and other compounds of interest from ambient air;
- 5) measuring the $\delta^{13}\text{C}$ of isoprene emitted from selected ecotypes, and its dependence on parameters such as temperature and light;
- 6) measuring $\delta^{13}\text{C}$ of isoprene and other VOCs, and their diurnal variation, in conjunction with other ongoing measurements at a forested site.

Instrumentation

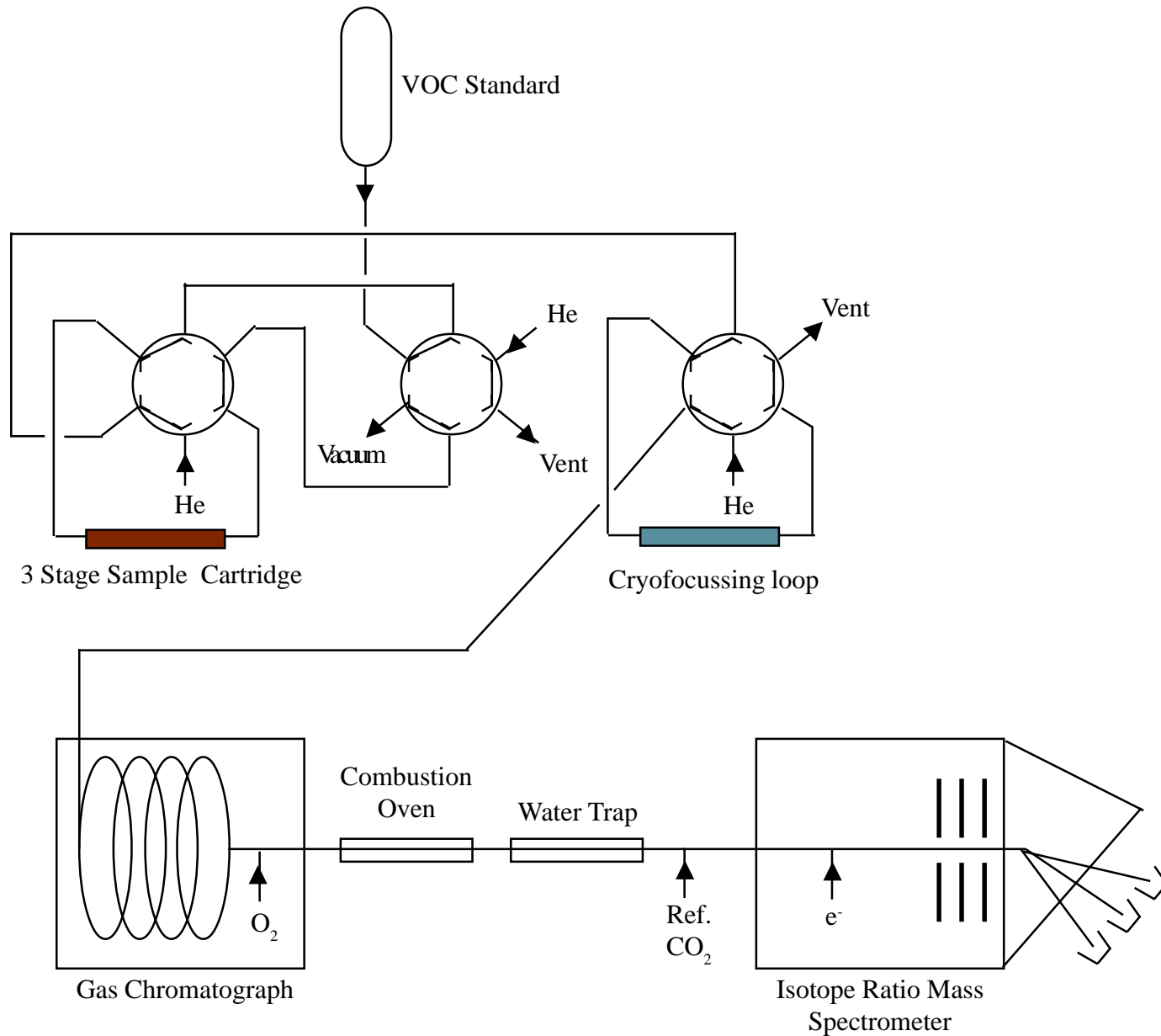


Figure 4. Preconcentration and GCC- IRMS setup.

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