



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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Isoprene, C₅H₈, 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). 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. Recently it has been shown that stable carbon isotope measurements can be very valuable for obtaining detailed insight into the atmospheric chemistry of VOCs. However, an essential prerequisite for the interpretation of such measurements is the knowledge of the isotope effects associated with the atmospheric VOC loss and formation processes.

The stable-carbon kinetic isotope effects (KIEs) for the gas-phase reactions of isoprene, as well as those of the two main products of isoprene oxidation, 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 ¹³C/¹²C isotope fractionation associated with MACR and MVK production during the ozonolysis of isoprene was also measured. Preferential ¹³C-atom fractionation during isoprene ozonolysis causes different amounts of lighter and heavier MACR and MVK isotopomers to form. 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. All 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.