



## **Kinetic isotope effect (KIE) measurements of isoprene, methacrolein, and methyl vinyl ketone in reaction with OH radicals and ozone in the gas phase**

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Isoprene is an important VOC which has the highest emission rate by plants. Compared to monoterpenes and several thousand other compounds emitted by plants, the estimated global annual biogenic emissions of isoprene is  $\sim 500$  Tg/yr, roughly four times that of monoterpenes and near that of all other VOCs. The atmospheric oxidation of isoprene is initiated by reaction with OH radicals, ozone,  $\text{NO}_3$ , and Cl atoms. The OH + isoprene reaction is, however, the dominant loss since high isoprene emissions and the production of OH coincide during daytime hours. Methacrolein (MACR) and methyl vinyl ketone (MVK) are major reaction products of both the OH- and  $\text{O}_3$ -initiated oxidation of isoprene. MACR and MVK are subsequently removed from the atmosphere through their reactions with OH radicals and ozone, although at rates slower than the reactions of isoprene with OH and  $\text{O}_3$ .

Recently, the stable carbon and hydrogen kinetic isotope effects (KIEs) for reactions of VOCs, particularly *n*-alkanes, alkenes and simple aromatic compounds such as benzene, toluene, and the xylenes, have been studied through the use of a gas chromatography–combustion–isotope ratio mass spectrometry (GCC-IRMS) system. Measured KIEs in natural abundance studies of a variety of important tropospheric oxidation reactions have been used to further the understanding of the sources, sinks, and distributions of tropospheric VOCs.

The stable-carbon kinetic isotope effects (KIEs) for the gas-phase reactions of isoprene, MACR, and MVK with ozone were studied in a 25-L reaction chamber at  $(298 \pm 2)$  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 KIEs associated with production of MACR and MVK from the reaction of isoprene with ozone were also studied. The 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. The KIEs are reported as per mille  $\varepsilon$  values where  $\varepsilon$  (permil) =  $(\text{KIE} - 1) \times 1000$ , and  $\text{KIE} = k_{12}/k_{13}$ . The following average stable-carbon KIE  $\varepsilon$  values (all in units of permil) for the VOC + OH reactions were obtained:  $6.56 \pm 0.12$  (ISO),  $5.88 \pm 0.08$  (MACR), and  $6.78 \pm 0.14$  (MVK). For the VOC + O<sub>3</sub> reactions, the following  $\varepsilon$  values (also in units of permil) were obtained:  $8.15 \pm 0.10$  (ISO),  $7.18 \pm 0.28$  (MACR), and  $7.77 \pm 0.08$  (MVK). The stable-carbon KIE values of three 1-alkene + O<sub>3</sub> reactions were also determined (permil):  $5.44 \pm 0.09$  (1-heptene),  $4.75 \pm 0.14$  (1-octene),  $4.55 \pm 0.37$  (1-nonene). Numerical model calculations of the isoprene + O<sub>3</sub> reaction, using site-specific  $\varepsilon$  values determined in this study, predicted mixing ratios and stable carbon delta values for isoprene, MACR and MVK that were in agreement with the experimental results.