



The kinetic isotope effects for reactions of non-methane hydrocarbons with the OH-radical and other reactants of atmospheric relevance

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During the past years methods for measuring the stable isotope ratios of non-methane hydrocarbons (NMHC) in the atmosphere have become available. Such measurement can be extremely valuable for the identification and quantification of NMHC sources as well as for the determination of the extent of photochemical processing of the investigated hydrocarbons in the atmosphere. However, the quantitative evaluations of such stable isotope ratio measurements require knowledge of the kinetic isotope effects (KIEs) for their atmospheric reactions. We studied the carbon and hydrogen KIEs for reaction of alkanes, alkenes and aromatic hydrocarbons with the OH-radical, the most important atmospheric reactant for NMHC. To some extent also reactions with ozone and the Cl-atom were investigated. Most of the KIE measurements were conducted at room temperature ($298 \pm 4\text{K}$), but for several reactions also the temperature dependence of the KIE was investigated.

The KIEs were measured in a 30 L PTFE reaction chamber at ambient pressure using gas chromatography coupled with online combustion and isotope ratio mass spectrometry (GCC-IRMS). For all experiments NMHC with natural isotope abundance were used in order to allow direct application of measured KIEs to the interpretation of atmospheric isotope ratio measurements. The principle of the procedure is a relative rate study determining the loss rate of the unlabeled hydrocarbon relative to that of a hydrocarbon with one atom replaced by the heavier isotope (^{13}C or D). The method allows measurements of stable carbon KIEs with uncertainties in the range of 0.1-1

per mil; for stable hydrogen KIEs the uncertainty is in the range of 5 per mil.

The results show obvious dependence between chemical structure of the hydrocarbon and magnitude of the kinetic isotope effects. For most of the reaction types studied it was possible to develop structure-reactivity relationships, which allow useful first order calculations of KIEs. Based on the magnitude of the KIEs we conclude that stable hydrogen isotope ratios of atmospheric alkanes as well as stable carbon isotope ratios of unsaturated hydrocarbon can be substantially affected by atmospheric reactions and are thus promising tools for studying atmospheric processing of NMHC. In contrast to this we estimate that measurements of stable hydrogen isotope ratios of alkenes and stable carbon isotope ratios of heavy alkanes will be useful for source apportionment studies.