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Measurements and kinetics modeling of the O_2/CO_2 dependence of the oxygen-17 isotope anomaly in carbon dioxide

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Ozone formed in the atmosphere and the laboratory is not only unusually enriched in the heavy rare isotopes of oxygen for the small difference in masses for ^{17}O and ^{18}O relative to ^{16}O, but the enrichments are also non-mass-dependent, with a ^{17}O anomaly of $\Delta^{17}O \approx 40$ per mil (where $\Delta^{17}O = \ln^{17}O - 0.52 \times \ln^{18}O$). Unusual kinetic isotope effects in the three-body ozone formation reaction were determined to be the source of the anomalous oxygen isotopic composition (Janssen et al., 1999, Mauersberger et al.,1999). Theoretical work has suggested that the observed non-mass-dependent enrichments emerge from dynamically driven, non-statistical effects resulting from the short lifetime of the rovibrationally excited O_3* complex or its collisional stabilization to stable O_3, particularly for the symmetric over the asymmetric isotopologues (e.g., Gao and Marcus 2001). Stratospheric CO_2 also has an anomalous oxygen isotopic composition that is thought to be transferred from ozone by photolysis to form $O(^1D)$ followed by the $O(^1D)+CO_2$ isotope exchange reaction, although some have postulated that an additional anomalous isotope effect must also exist in at least one of the other reactions for this system (e.g., Shaheen et al. 2007). To further investigate the anomalous isotopic compositions ofCO_2, we have conducted additional photochemical experiments measuring the enrichments of ^{17}O and ^{18}O in CO_2 relative to O_2 in irradiated mixtures of O_2 and CO_2. We then compared these and previous results from other laboratories with a photochemical kinetics model using both measured and derived kinetic isotope effects in ozone formation. Our model can quantitatively predict the enrichments and ^{17}O anomaly in both ozone and CO_2 without additional non-mass-dependent isotope effects for pressures and O_2/CO_2 mixing ratios relevant to the stratosphere. However, the model cannot predict the relative enrichments or isotope anomaly in CO_2 for our or previous experiments at low O_2/CO_2 ratios, so a number of additional hypothetical mechanisms that have isotope effects with possible O_2/CO_2dependences were introduced into the model. While including some of these mechanisms does result in a decrease in the relative enrichments in CO_2 as the O_2/CO_2 ratio decreases, none of the mechanisms in the model can predict the large change observed experimentally. While the underlying mechanism(s) of the O_2/CO_2 dependence thus remains an open question, the model results also point to additional measurements of the pressure and bath gas dependence of isotope effects in both ozone formation and other reactions in this system that could help to resolve the model-measurement discrepancies at higher pressures and at low O_2/CO_2 ratios.

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