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Kinetics of isotope exchange between ozone and CO_2 and production of the ^{17}O anomaly in CO_2

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We present results from direct laboratory measurements of the triple oxygen isotopic composition of CO_2 irradiated in CO_2-O_2 mixtures at pressures and CO_2:O_2 ratios similar to those in the stratosphere (67-133 hPa, CO_2/O_2=0.0021). The measured ^{17}O anomaly in CO_2 is accurately reproduced by a complete kinetics model in which the relative rate coefficients for ozone formation derived from experiments of Mauersberger and co-workers and the O+O_2 isotope exchange rates calculated from statistical thermodynamics are the only isotope effects included. The combined measurement and model results provide clear evidence that the ^{17}O anomaly in CO_2 is due to statistical or near-statistical isotope exchange with $O(^1D)$ and that there cannot be significant non-mass-dependent isotope effects in O_3 photolysis or in the CO_2+$O(^1D)$ isotope exchange reaction. The model slightly overpredicts $\delta^{18}O$ and $\delta^{17}O$, which may be due to small errors in the O_3 formation rate coefficients or their pressure or temperature dependence or to mass-dependent isotope effects in other reactions such as CO_2+$O(^1D)$. Implications of these results for stratospheric CO_2 are explored through further kinetics modeling.