

OXYGEN ISOTOPE STUDIES IN O + CO REACTION: ENERGY CONSTRAINTS IN SYMMETRY SELECTIVE FRACTIONATION, S. K. Bhattacharya and M. H. Thiemens, Chemistry Dept., B-017, Univ. of Calif., San Diego, La Jolla, California.

Now that chemically produced mass independent isotopic fractionations have been observed, two important goals exist which must be met to establish relevance of such processes in the early solar system. First, the specific physico-chemical mechanisms must be determined and second, isotopic fractionation in reactions involving astronomically relevant molecules must be studied. For oxygen, the most relevant molecule is CO. Thiemens and Meagher (1) have demonstrated a mass independent fractionation in CO₂ produced from discharge in CO, however the fractionation mechanism associated with the chemistry of CO₂ formation was not clear. It was speculated that, if oxygen atoms were present, a mass independent effect may occur through $O + CO \rightarrow OCO$, a reaction which could be subject to a symmetry selective fractionation (2).

The present experiment has been designed to provide a source of oxygen atoms which may be energetically and eventually isotopically characterized and which react with ground state CO of known isotopic composition. Briefly, ozone is produced by discharge in oxygen at a pressure of 30 torr in a 5L spherical glass reaction vessel, trapped on a cold trap (77K) at the bottom and the residual oxygen removed. Ozone is warmed to room temperature, a small (~20 μmoles) aliquot removed for isotopic analysis and the remaining ozone is recondensed. Carbon monoxide is then admitted to the reaction vessel at a pressure of 300 torr and ozone is brought to room temperature. The gas mixture is then photolyzed with a Hg continuum lamp driven by a microwave generator which dissociates O₃ molecule into an oxygen molecule and atom, the latter eventually reacting with CO. The CO does not absorb light. Following complete ozone dissociation, the product CO₂, formed strictly by $O + CO$, is cryogenically separated and reacted overnight with BrF₅ at 850°C to convert the CO₂ to CF₄ and O₂. The product O₂ and CF₄ are separated and the isotopic composition of O₂ determined. The yields are determined at each stage to ensure completeness of the reactions.

Preliminary results indicate that the isotopic composition of the product CO₂ lies approximately midway between the CO and a mass fractionation line which passes through the O₃ isotopic composition. The present experiments generated O₃ which is enriched in ¹⁷O,¹⁸O, compared to the CO. A line in a δ¹⁷O vs δ¹⁸O plot, defined by the isotopic composition of the CO and CO₂, intersects the O₃ mass fractionation line (10-15)% lighter in δ¹⁸O than the starting O₃ composition. The isotopic composition of the oxygen atoms is not known, and ¹⁸O + ³²O₂ isotopic exchange occurs in the present experiments, though to an unknown extent since competition with $O + CO \rightarrow CO_2$ varies with extent of reaction.

Irrespective of the extent of exchange, the results suggest that the fractionation is not via symmetry selection since ¹⁷O,¹⁸O mass independent enrichment of CO₂ should occur with CO₂ δ-values greater than the bulk composition of the O and CO. The present experiments are most consistent, with simple quantitative addition of oxygen atoms with CO, though subject to defining the O atom composition more precisely. If there is no symmetry effect observable, then the model of Heidenreich and Thiemens (2) has been further defined. That model requires that the symmetry reaction occur via inverse predissociation. That specific process occurs by overlap of the energy of the reaction pair with the diffuse bands of the polyatomic product molecule. Since these bands exist above the dissociation energy of the product molecule, the total energy of the collisional pair must exceed that level. For the

O₃ experiments, the oxygen atoms in all situations, UV and discharge, always possessed sufficient energy such that the O₃^{*} intermediate always had energy in excess of the O₃ dissociation energy (1.0eV). In the present experiments, the oxygen atom has less than 0.5eV energy; thus the energy of the CO₂^{*} intermediate is well below its diffuse band limit (5.4eV), and its formation would not be subject to the symmetry lifetime constraints described by Heidenreich and Thiemens (2). For the CO discharge experiments (1), the CO is vibrationally excited, and sufficient energy is available for CO₂^{*} to be produced via inverse predissociation.

In summary, the reaction of oxygen atoms with CO produces CO₂ with an isotopic composition which appears to be midway between the CO and a presumed O-atom isotopic composition. Further experiments with varying O atom isotopic composition will help to resolve the fractionation process. The results provide further support of the symmetry mechanism which requires that the process occur via inverse predissociation.

REFERENCES

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- (2) J. E. Heidenreich and M. H. Thiemens (1986). J. Chem. Phys. 84, 2129.