Removal of Laughing Gas N_2O by Singlet CH_2: A Theoretical Study

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Laughing gas (N_2O) reacts *extremely slowly* with highly reactive common oxidants such as OH, NO_3, and O_3. Subsequently, N_2O can be transported to the stratosphere where it can react with singlet O-atom to yield NO, which then degrades the ozone layer. Because of this, N_2O is currently the most important ozone-depleting substance being emitted. N_2O is often produced in combustion, especially when nitrogen oxide reduction devices are used. Therefore, it is of interest to examine the removal N_2O by singlet CH_2. We have studied this process using high accuracy thermochemistry mHEAT-345(Q) calculations, followed by two-dimensional master equation simulations to predict product yields and rate constants. Two distinctive mechanisms including an addition/elimination (major) and an O-abstraction (minor) pathway have been characterized. The calculated results show that the reaction is very fast with a negative temperature dependence: decreasing from about 10^{-10} cm^3/s at 100 K to about 10^{-11} cm^3/s at 1000 K. In addition, the predicted reaction products are: 98% for CH_2N + NO and 2% for CH_2O + N_2, which are almost pressure- and temperature-independent. While CH_2 is not present in the atmosphere of the Earth, the reaction is potentially important in planetary atmospheres. Moreover, it seems likely that similarly fast destruction of N_2O might occur via reactions with Criegee intermediates and related species.

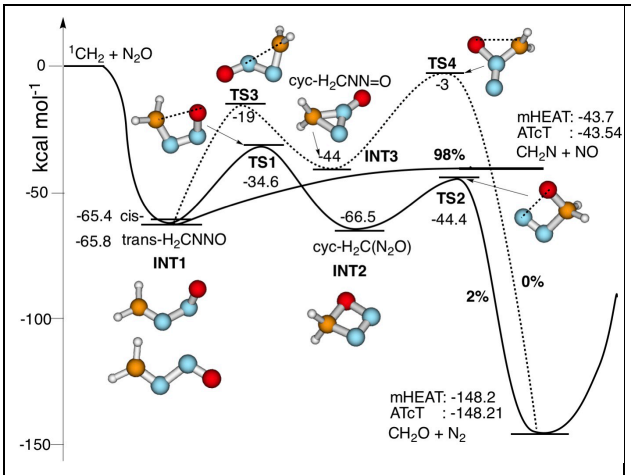

Fig. 1: Potential energy surface for an addition/elimination mechanism constructed using mHEAT-345(Q) method.

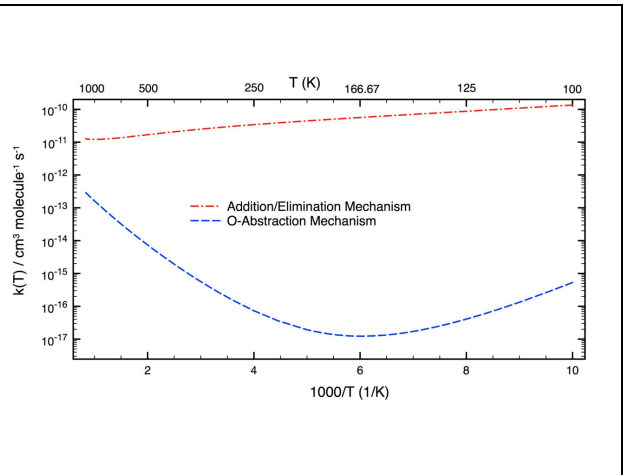

Fig. 2: Calculated rate constants of both addition/elimination and O-abstraction mechanisms as a function of temperature.