EuroSciCon

Euroscicon Conference on
Physical Chemistry and Analytical Separation Techniques

October 08-09, 2018
Amsterdam, Netherlands

J Org Inorg Chem 2018 Volume: 4
DOI: 10.21767/2472-1123-C6-018

QUANTUM RATE COEFFICIENTS FOR THE O + O2 EXCHANGE REACTION

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Molecular oxygen O_2 is the most important molecule on earth's atmosphere and stratospheric ozone O_3 protects us from the UV radiation. The abundance of ^{16}O being 99.8%, O_2 and O_3 exclusively formed from it are dominant, thereby giving a reference for any process involving oxygen. A strong enrichment of O_3 (~10%) in both ^{18}O and ^{17}O (mass-independent fractionation-MIF) has been observed decades ago and was reproduced in laboratory experiments. Although this phenomenon remains globally unexplained, the three-body recombination O + O_2 + M —> O_3 + M is believed to be the main process leading to this enrichment. At sufficiently low pressures, it can be partitioned into two steps: the formation of O3 in a highly excited rovibrational state, from reaction O + O_2—> O_3* (step 1), and its subsequent stabilization by collision with an energy absorbing partner M (say N_2), O_3* + M —> O_3 + M (step 2). Thus, the efficiency of the exchange reaction O + O_2 —> O_3* —> O_2 + O, involving O_3* as an intermediate, is one of the key parameters to understand ozone formation. We have shown that this reaction, initiated by step 1, is very fast with three identical 16O atoms involved due to a quantum permutation symmetry effect. Consequently, it competes ferociously with step 2 described above, the latter becoming in this way much less effective. We have reproduced experimentally observed negative temperature dependence for this reaction rate constant when ^{18}O is involved, along with other groups. We will sum up results of a computationally intensive full-quantum investigation of the dynamics of the 16O + $^{32}O_2$, ^{18}O + $^{32}O_2$ and ^{17}O + $^{32}O_2$ processes supported by an accurate global potential energy surface for the O_3 ground state. Our study based on a time independent quantum mechanical approach demonstrates that all approximate theoretical simulation techniques and calculations previously reported for this process result in considerable inaccuracies, especially because of the neglect of the quantum symmetries such as the nuclear spin symmetry due to the three (or two) identical atoms, ^{16}O or ^{18}O.

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