Geophysical Research Abstracts
Vol. 13, EGU2011-14119, 2011
EGU General Assembly 2011

Atmospheric Oxidation of Carbonyl Sulfide and Associated Isotope Effect

Johan A. Schmidt (1), Matthew S. Johnson (1), and Sebastian Danielache (2)

(1) Department of Chemistry, University of Copenhagen, Copenhagen, Denmark, (2) Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan

Carbonyl Sulfide (OCS) is the most abundant sulfur containing compound in the atmosphere. The main sinks for OCS in the atmosphere are reactions with HO and O(^{3}P) and photolysis, with HO oxidation being the dominant sink [1]. Despite it's importance there have only been a few studies of this reaction. Experimental studies limited to low pressures (p5 mbar) determined the reaction rate to be pressure independent with a rate of ca. k=2*10-15cm3s-1[2]. We present an ab initio theoretical study of the HO+OCS reaction. In the low pressure range (p10 mbar) we find that reaction is dominated by a pressure independent channel (b) where HO attacks the terminal S atom leading to SOH and CO. In this pressure range we calculate the rate to be k=2.4*10-15cm3s-1, in excellent agreement with experiments. Our study predicts that as the pressure is increased a complex forming channel (a) becomes important. Channel (a) is pressure dependent and exceeds channel (b) at pressures above ∼500 mbar. At 1 bar we predict the overall rate to be k=6*10-15cm3s-1 or 3 times greater than previously known. In addition we have calculated the kinetic isotope effect. At low pressures where channel (b) dominates we predict the ^{34}S KIE to be about 20 permil and at higher pressures when channel (a) dominates the KIE is about 10 permil.

[1] E. Kjellstrom, J. Atm. Chem., 29, (1998), 151.
[2] B.-M. Cheng and Y.-P. Lee, Int. J. Chem. Kinet., 18, (1986), 1303