REACTION MECHANISM AND KINETICS OF THE GAS PHASE REACTIONS OF METHANE SULFONAMIDE WITH Cl RADICALS AND THE FATE OF $CH_2S(=O)_2NH_2$ RADICAL[a]

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Methane sulfonamide ($CH_3S(=O)_2NH_2$, MSAM) is an important trace compound detected for the first time in ambient air over the Red Sea and the Gulf of Aden.[b,c] The average mixing ratios of this compound were found to be in the range of 20 – 50 ppt with a maximum value of 60 ppt.[b,c] The energetics and rate coefficients for its reactions with Cl radical and in presence of atmospheric oxygen ($^3O_2$) to form various products have not been reported. In the present work, we investigated the atmospheric oxidation mechanism and energetics of the reaction of MSAM with Cl radicals using high level quantum chemistry calculations. The MSAM + Cl radical reaction mainly proceeds by H-abstraction paths. Abstraction of H-atom from the methyl group of MSAM by Cl radical to form $CH_2S(=O)_2NH_2$ radical + HCl products was found to be dominant compared to other possible paths. The barrier height for this reaction was found to be 4.8 kcal mol^{-1} above the energy of the starting reactants at the CCSD(T)/aug-cc-pV(T+d)Z//M06-2X/aug-cc-pV(T+d)Z level. The rate coefficients were calculated for all possible H-atom abstraction paths associated with the MSAM + Cl radical using canonical variational transition state theory (CVT) with a small curvature tunneling (SCT) approximation in the temperatures between 200 and 300 K. The rate coefficient data, atmospheric lifetime of MSAM, branching ratios and thermodynamic parameters associated with the MSAM + Cl radical reaction are discussed. In addition, the atmospheric fate of the major product (i.e., the $CH_2S(=O)_2NH_2$ radical) with respect to its interaction with $^3O_2$ to form the RO_2 radical adduct (R = -$CH_2S(=O)_2NH_2$) using the same level of theory was also investigated. The formed RO_2 radical adduct proceeds through various multichannel pathways in the presence of HO_2 radical to form several greenhouse gases and environmental pollutants including SO_2, CO_2, CO, HC(O)OH and HNO_3 as final products.

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[b]Edtbauer, A. et al. Atmos. Chem. Phys. 2020, 20, 6081.

[c]Berasategui, M. et al. Atmos. Chem. Phys. 2020, 20, 2695.