

Kinetic Studies of the Reactions of NH₂ Radicals with H₂S and SO₂: Differing Roles for Bound Intermediates

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Amino radicals are key intermediates in the production of nitrogen oxides in combustion. Sulfur in fuels can have an impact on the extent of NO_x formation, and the reactions



have been investigated as part of an effort to establish a mechanism for interactions between sulfur and nitrogen species.

Ground-state NH₂ was generated by pulsed photolysis of NH₃ precursor at 193 nm, and monitored by time-resolved laser-induced fluorescence at 570.3 nm, in the presence of excess molecular reactant in an Ar bath gas. For reaction 1, experiments were conducted over 298 – 550 K and at pressures from 9 to 25 mbar, and pressure-dependent kinetics were observed close to the low-pressure limit, with $k_0 \approx 1.2 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ which did not vary significantly with temperature. This contrasts with a prior study where fall-off was observed at very low pressures (1). The high-pressure limit was estimated from the removal rate constant of vibrationally-excited (0,1,0) NH₂ (detected via LIF at a wavelength of 531.8 nm) as approximately $1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results are rationalized in terms of RRKM theory and an NH₂-SO₂ binding energy of about 75 kJ mol⁻¹, which was computed via coupled-cluster theory extrapolated to the complete basis set limit. Possible subsequent chemistry of this adduct is discussed.

Reaction 2 was investigated over 295 – 820 K. The rate constant was observed to be independent of pressure and temperature, with $k_2 \approx 4.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The removal rate constant for excited NH₂ (0,1,0) is approximately $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The potential energy surface indicates a weakly bound adduct between NH₂ and H₂S in the entrance channel, and its influence on the unexpectedly slow kinetics is explored via RRKM theory. The adduct is not stable enough to be a final sink for NH₂ and a modest barrier to formation of NH₃ + SH is characterized by *ab initio* methods. The results are contrasted with the behavior of the analogous OH + H₂S system (2).

References

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