

# Analysis of $\text{NH}_2 + \text{H}_2\text{O}_2 \rightleftharpoons \text{NH}_3 + \text{HO}_2$ and $\text{NH}_2\text{O} + \text{O}_2 \rightleftharpoons \text{HNO} + \text{HO}_2$ Kinetics and Modeling of $\text{NH}_3$ Oxidation Experiments at High Pressures

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## Abstract text

The pulsed laser photolysis / laser-induced fluorescence method has been used to generate amidogen radicals from  $\text{NH}_3$  precursor at 193 nm. The methodology has been detailed elsewhere.<sup>1</sup> Time-resolved LIF measurements were made on the reaction of  $\text{NH}_2$  with  $\text{H}_2\text{O}_2$  to obtain the second-order rate constant  $k = 2.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 412 K. There are no prior measurements for comparison. To check this value and to enable reliable extrapolation to other temperatures, the potential energy surface has been explored using CCSD(T)-F12/aug-cc-pVQZ energies at M06-2X/6-311+G(2df,2p) geometries. Entrance and exit complexes are noted, as well as barriers to H-atom abstraction of around  $14 \text{ kJ mol}^{-1}$ . There are two distinct configurations of the transition state which can interconvert via low-barrier torsions. Accordingly the kinetics were analyzed with multi-structural canonical variational transition state theory<sup>2</sup> and the small curvature multidimensional tunneling model, which yield results within about a factor of 2 of experiment. The impact of different treatments of zero-point vibrational energy is discussed.

Ammonia oxidation experiments were conducted in a laminar flow reactor at high pressure (30 bar and 100 bar) and temperatures of 450-900 K under oxidizing and stoichiometric conditions. Quartz and alumina tubes were used to check for surface effects. Details of the apparatus may be found elsewhere.<sup>3</sup> The data were interpreted in terms of a detailed chemical kinetic model. The products were  $\text{N}_2$  and  $\text{N}_2\text{O}$ , while  $\text{NO}$  and  $\text{NO}_2$  concentrations were below the detection limit even under oxidizing conditions. A new chemical mechanism was constructed and the agreement between experimental results and the modelling work was satisfactory.

The reaction  $\text{NH}_2\text{O} + \text{O}_2$  has the largest positive sensitivity coefficient in the model.  $\text{NH}_2\text{O}$  is a significant intermediate species as shown by a reaction path analysis and is favored by the excess of  $\text{O}_2$  in oxidizing conditions. This oxidation reaction was analyzed via *ab initio* methods based on CCSD(T)/CBS results. Out-of-plane bending for the pyramidal  $\text{NH}_2\text{O}$  species has a low barrier of  $17 \text{ cm}^{-1}$ . Its reaction with oxygen yields  $\text{HO}_2$  radicals, which are converted to more reactive OH by the reaction  $\text{NH}_2 + \text{HO}_2$ .

## References

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