

The reaction between NaOH and H

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In a previous study [1], we reported the rate constants of NaO and NaOH with several atmospheric constituents. We found that the NaO + H₂O and NaOH + CO₂ reactions have a large impact on the underside of the meteoric Na layer in the terrestrial mesosphere, shifting the modelled peak 2 km higher than observed by ground based lidar. A role of the NaOH + H → NaO + H₂ reaction recycling active sodium from the NaOH reservoir was then proposed, suggesting that the reaction could be a factor of 5-10 faster than derived from highly uncertain extrapolation of previous measurements between 1800 and 2200 K. Here we report the first study of this reaction under atmospherically relevant conditions. We have found the rate constant to be $k(\text{NaOH} + \text{H}) = (4 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, showing no temperature dependence in the 190 K - 300 K temperature range beyond experimental uncertainty, and essentially in agreement with the previous measurements in hydrogen-rich flames [2]. This higher rate constant brings the modelled Na layer peak in agreement with lidar observations.

The flame-inhibiting properties of Na have been known for many decades, and were proposed to occur via the sequence Na + OH (+ M) → NaOH followed by NaOH + H → Na + H₂O, which catalyzes the recombination of H and OH to H₂O. The rate coefficient for Na + OH + He has been measured previously at 653 K by us [3]. A satisfactory RRKM fit predicts $k(\text{Na} + \text{OH} + \text{N}_2, 300 - 2400 \text{ K}) = 2.7 \times 10^{-29} (300 / T)^{1.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, in excellent agreement with the estimate between 1800 and 2200 K obtained from flames seeded with Na [2]. This implies that the mechanism for flame inhibition by Na is now fully confirmed.

Finally, we will show using theoretical trajectory calculations that the unexpectedly slow, yet *T*-independent, rate coefficient for NaOH + H is explained by severe constraints in the angle of attack that H can make on NaOH to produce H₂O.

References

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