

# Dissociative recombination of metal oxide ions with electrons

David Bones and John Plane\*

<sup>1</sup> School of Chemistry, University of Leeds. Leeds. UK

\* Corresponding author: j.m.c.plane @leeds.ac.uk

Modelling the temporal and spatial extent of the metal layers in the mesosphere, and understanding the lifetimes of sporadic *E* layers which affect radio communications with space, requires knowledge of the rate coefficients of dissociative recombination of metal oxide ions with electrons. In this study, the dissociative recombination (DR) of  $\text{FeO}^+$  and  $\text{CaO}^+$  has been measured for the first time. Curiously, almost no DR reactions involving metallic species have been studied previously, in spite of their importance in atmospheric, combustion and plasma processes.

The kinetic measurements are made in a flowing afterglow system with a Langmuir probe to measure the absolute electron concentration. Metal oxide ions are produced by pulsed laser ablation of a solid target, and then introduced into an argon ion/electron plasma. The relative concentration of metal oxide ions  $\text{MO}^+$  is measured by a quadrupole mass spectrometer as a function of flow rate (3 – 5 slm), which is inversely proportional to the reaction time of the  $\text{MO}^+$  ions with the electrons in the plasma (2.1 to 3.5 ms).

Charge transfer reactions between argon ions and neutral molecules complicate the analysis. A kinetic model describing gas-phase chemistry and diffusion to the reactor walls was fitted to the experimental data to extract the DR rate coefficients. This yields a DR rate coefficient at 298 K of  $k(\text{FeO}^+ + \text{e}^-) = (5.5 \pm 1.0) \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the quoted uncertainty is at the  $2\sigma$  level.  $\text{Fe}^+$  ions in the lower thermosphere are oxidized by  $\text{O}_3$  to  $\text{FeO}^+$ , and this DR reaction is shown to provide a more important route for neutralizing  $\text{Fe}^+$  below 110 km than the radiative/dielectronic recombination of  $\text{Fe}^+$  with electrons. The experimental system was first validated by measuring two other DR reaction rate coefficients:  $k(\text{O}_2^+ + \text{e}^-) = (2.0 \pm 0.4) \times 10^{-7}$  and  $k(\text{N}_2\text{O}^+ + \text{e}^-) = (3.3 \pm 0.8) \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which are in good agreement with the recent literature.<sup>1</sup> The new rate coefficient better predicts the underside and the maximum density (at 95 km) of the  $\text{Fe}^+$  layer. The  $\text{CaO}^+ + \text{e}^-$  reaction is about a factor of 2 slower, which explains the unexpectedly high concentration of  $\text{Ca}^+$  to  $\text{Fe}^+$  in the lower thermosphere, measured by rocket-borne mass spectrometry.<sup>2</sup>

## References

- (1) Bones, D.; Plane, J. M. C.; Feng, W., *J. Phys. Chem. A*, DOI:10.1021/acs.jpca.1025b04947.
- (2) Kopp, E., *J. Geophys. Res.-Atmos.* **1997**, *102*, 9667-9674.