Reaction kinetics of Ca, Mg and Fe atoms with $O_2(a^1\Delta_g)$

John Plane,[1*] Charlotte Whalley,[1] Laura Soriano,[1] Andrew Goddard,[1] David Glowacki,[2] and Al Viggiano[3]

[1] University of Leeds, Leeds, UK
[2] University of Bristol, Bristol, UK
[3] Air Force Research Laboratory, Kirtland AFB, NM, USA
* Corresponding author: j.m.c.plane@leeds.ac.uk

The first excited state of molecular oxygen, $O_2(a^1\Delta_g)$, is produced in the mesosphere-lower thermosphere (MLT) region of the earth's atmosphere by photolysis of O_3 at wavelengths shorter than 320 nm. $O_2(a)$ is comparatively long-lived in the MLT. The quenching life-time is more than 4 hours, much longer than the phosphorescence lifetime of 72 minutes for emission at 1.27 μm in the infra-red. The rate of O_3 photolysis in the MLT is $\sim 8 \times 10^{-3}$ s^{-1}, so that during daytime the steady-state ratio $[O_2(a)]/[O_3]$ is about 30. Since $O_2(a)$ contains almost 1 eV of electronic excitation compared with ground-state $O_2(X^3\Sigma_g^-)$, it has the potential to be significantly more reactive although it is not a radical species.

This paper describes the kinetics of $O_2(a)$ reacting with Ca, Mg and Fe atoms, which are produced in the MLT by meteoric ablation. A new method[1] for producing $O_2(a)$ cleanly and at significant concentrations was employed: Cl_2 was bubbled through a chilled alkaline solution of H_2O_2, forming $O_2(a)$ with a yield of between 16 and 26%. The absolute concentration of $O_2(a)$ was determined from the weak O_2(a-X) emission at 1270 nm, using an InGaAs photodiode detector calibrated against a radiometric standard. The flow of $O_2(a)$ was then injected into a fast flow tube for kinetic measurements. Metal atoms were produced in the flow tube using two methods: thermal evaporation (Ca and Mg), and pulsed laser ablation of an Fe target. The metal atom concentrations at the downstream end of the tube were monitored by laser induced fluorescence. The following results were obtained:

Reaction	Bimolecular Rate Coefficient cm^3 $molecule^{-1}$ s^{-1}	Termolecular Rate Coefficient cm^6 $molecule^{-2}$ s^{-1}
Mg + $O_2(a)$	$< 2.4 \times 10^{-14}$	$(1.8\pm0.2) \times 10^{-30}$
Ca + $O_2(a)$	$(2.7\pm1.0) \times 10^{-12}$	$(2.9\pm0.2) \times 10^{-28}$
Fe + $O_2(a)$	$(1.1\pm0.1) \times 10^{-13}$	$< 2.4 \times 10^{-31}$

Surprisingly, the reactions of the three metals with $O_2(a)$ exhibit completely different behaviour, which was explained using electronic structure calculations and RRKM theory. Ca + $O_2(a)$ mostly occurs via recombination to produce $CaO_2(^1A_1)$, with a rate coefficient that is ~80 times larger than for the reaction Ca + $O_2(X)$. There is also limited switching through a conical intersection between the reactant singlet and product triplet surfaces, leading to the bimolecular products CaO + O. The reaction Mg + $O_2(a)$ occurs exclusively by recombination on a singlet surface, producing $MgO_2(^1A_1)$. The rate coefficient is ~4000 times larger than for the reaction Mg + $O_2(X)$. Fe + $O_2(a)$ produces FeO + O, although with a probability of only ~ 0.1%. There is no evidence for recombination, suggesting that this reaction proceeds mostly by near-resonant electronic energy transfer, producing $O_2(X)$ and $Fe(a^5F)$ (the lowest-lying excited state of Fe).

References

(1) Midey, A.; Dotan, I.; Viggiano, A. A. *J. Phys. Chem. A*, **2008**, 112, 3040–3045.