

The reaction of molecular oxygen with excited formaldehyde; a new atmospheric source of HO₂?

Meredith Jordan^a, Paolo Sebastianelli^b, Keiran Rowell^a, Maggie Corrigan^a, Blair Welsh,^b Scott Kable^b

^aSchool of Chemistry, The University of Sydney, Sydney, NSW, Australia;

^bSchool of Chemistry, The University of NSW, Sydney, NSW, Australia

MJ: Meredith.jordan@sydney.edu.au, PS: Paolo Sebastianelli p.sebastianelli@unsw.edu.au,

KR: k.rowell@unsw.edu.au, MC: mcor3140@uni.sydney.edu.au, BW: blair.welsh@unsw.edu.au,

SK: s.kable@unsw.edu.au

Atmospheric chemistry is driven by radicals. In particular, the HO₂ and OH radicals are involved in oxidation of all atmospheric carbon species to CO₂. Near the Earth's surface, molecules such as carbonyls absorb ultraviolet (UV) solar photons and dissociate into radicals, which can then react with atmospheric molecular oxygen, O₂, to form HO₂ and OH. Despite their importance, the ability of current atmospheric chemistry models to predict OH and HO₂ concentrations is relatively poor. OH can be underestimated in forested regions and HO₂ in polluted regions, each by an order of magnitude.¹ This underprediction suggests additional OH and/or HO₂ sources that are not included in our current understanding of atmospheric chemistry. Here we propose that reaction of molecular oxygen with, not the radical fragments, but with excited 'parent' carbonyl molecules constitutes a new HO₂ source.

We examine reaction of the simplest carbonyl, formaldehyde, H₂CO, with O₂:



where the excited H₂CO* species is formed following absorption of a near-UV photon and the O₂ has a triplet, , ground state. Three excited H₂CO species can potentially react with O₂: (i) the initially excited singlet state, S₁, (ii) the lowest energy triplet state, T₁, which can be accessed via S₁ → T₁ intersystem crossing, and (iii) highly vibrationally excited ground state H₂CO molecules, S₀*, which are formed following non-radiative relaxation from an electronic excited state. Electronic structure theory calculations are used to investigate the energetic feasibility of these reactions. The reactions of S₀ H₂CO with the and excited states of O₂ are also considered. These states can be formed during oxygen quenching of T₁ H₂CO, a process analogous to triplet-triplet annihilation.

Rate coefficients for the various reactions are predicted using RRKM theory or Barker and coworkers' semi-microcanonical transition state theory.² These are used within master equation models to assess the importance of (R1) and to simulate recent experimental results. The atmospheric implications of (R1) are also discussed.

References

1. D. Stone, L. K. Whalley and D. E. Heard, "Tropospheric OH and HO₂ radicals: Field measurements and model comparisons" *Chem. Soc. Rev.* **41**, 6348–6404 (2012). doi.org/10.1039/C2CS35140D
2. A. Maran Zana, J. R. Barker and G. Tonachini, "Master equation simulations of competing unimolecular and bimolecular reactions: application to OH production in the reaction of acetyl radical with O₂" *Phys. Chem. Chem. Phys.* **9**, 4129–4141(2007). doi.org/10.1039/B705116F