

Photochemical Quantum Yields of Enol Production

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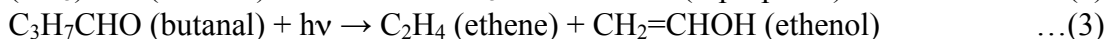
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Atmospheric models are unable to reproduce the observed concentration of organic acids in the troposphere, frequently under-estimating their concentration by a factor of two. Recently, we proposed that collision-induced keto-enol photo-tautomerization of small aldehydes and ketones might provide a source of the missing acids.¹ Enols are predicted to be short-lived in the troposphere, reacting quickly with OH radicals. Recent computational studies indicate that they will readily form organic acids.²

In this presentation we will present wavelength and pressure dependent quantum yields for the production of enols from various photochemical and photophysical sources:



where M represents any collision partner, typically N₂. Quantum yields for photo-tautomerization (1 and 2) are typically 1-10%, depending on wavelength and pressure, with larger quantum yields found at longer wavelength and modest pressure. Shorter wavelengths favour bond dissociation pathways, and higher pressure favours collisional relaxation into the keto well rather than isomerization into the enol well. Quantum yields for the Norrish Type-II process, (3), are much larger; up to 40% under some conditions.

We will also show preliminary data on the formation of 1-propenol from photo-tautomerisation of propanal, and photochemical (Norrish Type-II) formation of larger enols from longer aldehydes and ketones. These results indicate that enol production should be ubiquitous in the atmosphere and an important source of reactive species, whose atmospheric fate is not yet properly determined.

References

- (1) Clubb, A.E.; Jordan, M.J.T.; Kable, S.H.; Osborn, D.L. *J. Phys. Chem. Lett.* **2012**, 3, 3522-3526.
- (2) So, S.; Wille, U.; da Silva, G. *Env. Sci. & Tech.* **2014**, 48, 6694–6701.