

Prediction of photolysis processes in numerical models: A new MCM/GECKO-A protocol

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Chemical mechanisms are essential for our understanding of air quality and climate change, which have a significant impact on society and economy. To study fundamental chemical processes and assess the quality of simplified mechanisms for large-scale science and policy modeling, a benchmark mechanism is needed. A widely used benchmark mechanism is the Master Chemical Mechanism (MCM, <http://mcm.leeds.ac.uk>; Jenkin *et al.*, 1997; Saunders *et al.*, 2003). With about 17,000 reactions, current research focus is on the automation of mechanism construction and the design/update of a protocol for mechanism self-generation within the GECKO-A framework (Aumont *et al.*, 2005).

Some of the largest uncertainties in chemical mechanisms derive from photolysis reactions, owing to uncertainties in laboratory-measured absorption cross sections and, in particular, quantum yields for single compounds and in the methodologies applied to estimate photolysis parameters for species without experimental data. In order to calculate photolysis parameters for the new MCM/GECKO-A mechanism construction protocol, we have updated and extended the TUV5.2 photolysis model (Madronich and Flocke, 1997) to 147 species and ca. 240 photochemical pathways. The MCM/GECKO-A methodology for determining the photolysis rates for species with unknown photochemical data is also updated with the aid of the extended TUV model. Recent laboratory studies allow us to develop new relationships for several compound classes with absorbing functional groups (chromophores) including carbonyls, organic nitrates and hydroperoxides. Experimental data is also used to validate the new photolysis protocol in box model simulations.

However, limitations still exist, in particular for compounds containing multiple chromophores. Data is extremely scarce for these compounds despite their relevance for the degradation of organic compounds in the atmosphere, photochemical production of ozone and other secondary pollutants including secondary organic aerosol. Model simulations have been carried out to investigate the influence of different choices of photolysis parameters in the newly developed protocol and the effects on atmospheric chemistry in different environments.

References

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