4.012 A protocol for the prediction of photolysis processes in numerical models.

Early Career Scientist

Presenting Author:
Peter Brauer, Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, YO10 5DD, UK, peter.brauer@york.ac.uk

Co-Authors:
Andrew R. Rickard, Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, YO10 5DD, UK; National Centre for Atmospheric Research, University of York, York, YO10 5DD, UK
Sasha Madronich, Atmospheric Chemistry Observations and Modeling, National Center for Atmospheric Research, Boulder, Colorado 80307, USA
Michael E. Jenkin, Atmospheric Chemistry Services, Okehampton, Devon, EX20 4QB, UK
Mathew J. Evans, Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, YO10 5DD, UK; National Centre for Atmospheric Research, University of York, York, YO10 5DD, UK

Abstract:

Chemical mechanisms are essential for our understanding of air quality and climate change, which have a significant impact on society and economy. A benchmark mechanism is needed to study fundamental chemical processes and assess the quality of simplified mechanisms for large-scale modeling. A widely used benchmark mechanism is the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk). With ~17,000 reactions, a current research focus is on the automation of the mechanism generation process and the design/update of a protocol for mechanism self-generation.
Photolysis processes contribute to some of the largest uncertainties in the mechanism. This comprises both uncertainties in laboratory measured cross sections and quantum yields for single compounds and in the methodology for estimating photolysis parameters for species without laboratory measurements. We have extended the TUV5.2 photolysis model to include 147 species leading to 240 photochemical pathways.

The extended TUV model is used to update the MCM methodology for determining the photolysis rates for compounds without laboratory measurements. Recent laboratory studies allow us to provide new relationships for some classes of compounds including carbonyls, organic nitrates and hydroperoxides. However, for compounds with multiple absorbing functional groups (chromophores) the laboratory dataset is extremely limited (6 compounds in the current database). These oxidized materials play a central role in the atmospheric degradation of organics and so in the production of secondary organic material and ozone; however, the lack of laboratory data makes the evaluation of their photolysis extremely difficult. We present modeling simulations of the impact of different choices of newly developed parameterizations of the photolysis of these compounds and their effects on the chemistry in different airmasses.