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Modelling of the photooxidation of toluene: conceptual ideas for validating detailed mechanisms

V. Wagner[1], M. E. Jenkin[2], S. M. Saunders[1,*], J. Stanton[1], K Wirtz[3], and M. J. Pilling[1]

[1]School of Chemistry, University of Leeds, Leeds LS2 9JT, UK
[2]Imperial College, Silwood Park, Ascot, Berkshire SL5 7PY, UK
[3]Centro de Estudios Ambientales del Mediterraneo, C. Charles R. Darwin 14, 46980 Paterna, Spain
[*]present address: School of Earth and Geographical Science, University of Western Australia, 6009, Western Australia

Abstract. Toluene photooxidation is chosen as an example to examine how simulations of smog-chamber experiments can be used to unravel shortcomings in detailed mechanisms and to provide information on complex reaction systems that will be crucial for the design of future validation experiments. The mechanism used in this study is extracted from the Master Chemical Mechanism Version 3 (MCM v3) and has been updated with new modules for cresol and g-dicarbonyl chemistry. Model simulations are carried out for a toluene-NO_x experiment undertaken at the European Photoreactor (EUPHORE). The comparison of the simulation with the experimental data reveals two fundamental shortcomings in the mechanism: OH production is too low by about 80%, and the ozone concentration at the end of the experiment is over-predicted by 55%. The radical budget was analysed to identify the key intermediates governing the radical transformation in the toluene system. Ring-opening products, particularly conjugated g-dicarbonyls, were identified as dominant radical sources in the early stages of the experiment. The analysis of the time evolution of radical production points to a missing OH source that peaks when the system reaches highest reactivity. First generation products are also of major importance for the ozone production in the system. The analysis of the radical budget suggests two options to explain the concurrent under-prediction of OH and over-prediction of ozone in the model: 1) missing oxidation processes that produce or regenerate OH without or with little NO to NO_2 conversion or 2) NO_3 chemistry that sequesters reactive nitrogen oxides into stable nitrogen compounds and at the same time produces peroxy radicals. Sensitivity analysis was employed to identify significant contributors to ozone production and it is shown how this technique, in combination with ozone isopleth plots, can be used for the design of validation experiments.

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