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Examination of the mechanism of the oxidation of aromatic compounds in the atmosphere

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Aromatic compounds, emitted from a range of sources, contribute substantially to the formation of ozone and of secondary organic aerosols in the troposphere. There are substantial uncertainties in the mechanisms. The current version of the master chemical mechanism (MCM v3.1) significantly overestimates ozone formation and underestimates the concentration of OH, in comparisons with measurements made at the EUPHORE chamber in Valencia. The major reaction channels, which follow addition of OH to the aromatic, involve addition of O_2 to form a peroxy radical, with subsequent reaction to form a phenol + HO_2, or to form a bridged peroxy radical. The yields of phenol and of some of the carbonyl compounds resulting from the bridged compound, are well established experimentally, and provide good constraints in the development of mechanisms.

The systems have proved difficult to study experimentally and this contribution uses high level ab initio methods to explore the potential energy surface of the reaction of benzene and toluene with OH, and the subsequent reaction of the adduct with O_2. The calculations are based on density functional theory (DFT) to determine the geometries of stable intermediates and of transition states, coupled with higher level G3 methods to refine the surface parameters at these geometries. The calculations have been used to carry out transition state theory initial estimates of the rates of the reaction channels and these estimates have been further refined using full master equation calculations to determine the rates under atmospheric pressure and temperature conditions. The results have then been tuned, within the uncertainties of the theoretical methods, to available experimental data on the elementary reactions to obtain optimised surfaces. These surfaces have been employed to investigate a range of potential reactions that could help to resolve the disagreement between MCMv3.1 and the chamber data. A

full assessment of the atmospheric implications of the final results will be given.