

Tools for evaluating the MCM using chamber experiments coupled with modeling

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Several developments have been made to the MCM and to the tools available on the MCM website, as part of EUROCHAMP and with other European and national research funding. These developments will be described, within the context of one of the aims of JRA2, to facilitate the use of chambers in the evaluation of chemical mechanisms.

1. The IUPAC and MCM websites have been directly linked to facilitate the automatic updates of rate data and channel yields on the MCM, derived from the IUPAC evaluated database. That database itself is being extended significantly.
2. A FORTRAN open source box model has been constructed for use with chamber data. It incorporates a facility for extracting the current MCM mechanisms for the species under investigation and the appropriate inorganic chemistry, and for constructing the chamber auxiliary mechanism. It contains a new method for constraining the model to measured data (concentrations, photolysis rates etc). A graphical interface has been constructed which facilitates the setting of the initial and constraining parameters, and the use of MCM website analysis tools, such as rate of production analysis. The development, which will be continued in EUROCHAMP 2, obviates the need to use commercial integration packages and provides a model which is closely linked to the aims of EUROCHAMP.
3. A retro-extraction tool has been developed that enables the sources of a given species to be traced, as a function of time, within MCM experiment comparisons. Examples of its application, e.g. to the formation of glyoxal throughout a toluene oxidation experiment, will be shown. The tool is valuable in sensitivity analyses of the mechanism and should be particularly useful in conjunction with high and low resolution PTR-TOF-MS experiments.
4. Electronic structure / master equation analyses have been applied to benzene oxidation and the energies of key turning points on the potential energy surface optimized. Recent work includes analysis of the effects of changes in temperature and pressure to facilitate further optimization of the mechanism in indoor chambers and in pulsed laser photolysis and discharge flow experiments.
5. One of the aims of EUROCHAMP2 is the development of an electronic lab notebook for use in chamber / model comparisons. The plans will be briefly outlined.