Mechanism optimization P^4: progress, promises and possible pitfalls

Tamás Turányi

Institute of Chemistry, Eötvös University (ELTE), Budapest, Hungary
Tel.: +36 1 372 2500 ext. 1109, Fax: +36 1 372 2592, E-mail: turanyi@chem.elte.hu

Traditionally, direct and indirect chemical kinetic measurements have been distinguished. In direct measurements, the reaction conditions are selected in such a way that the measured signal depends mainly on the rate parameters of a single reaction step, thus a rate coefficient can be determined from it directly. In the indirect measurements, the experimental results depend on the rate parameters of several elementary reactions and these data can be interpreted via simulations using a detailed reaction mechanism.

Determination of rate parameters of gas phase elementary reactions is usually based on direct measurements. The rate parameters obtained in many independent direct measurements are then used in reaction mechanisms, which are tested against the results of indirect experiments, like time-to-ignition or laminar flame velocity measurements. Unfortunately, the rate coefficients determined in direct measurements have large uncertainty (about ±30%), therefore further adjustment of the rate parameters is needed to reproduce the results of indirect measurements.

The systematic, mathematical approach to the determination of rate parameters to reproduce a large set of indirect measurements is call mechanism optimization. The first articles on mechanism optimization were published by Frenklach *et al.* and the methodology was significantly developed further by Wang *et al.* The methods of these authors were summarized in their recent articles [1], [2].

An improved methodology for mechanism optimization has been developed recently [3] that takes into account both the direct and indirect measurements. All rate parameters in a detailed mechanism (Arrhenius parameters, third body efficiencies, enthalpies-of-formation, parameters of pressure dependence etc.) can be fitted. The method has been used for the determination of the rate parameters of two important elementary reactions of the hydrogen combustion system [3] and of the cyclohexane and 1-hexene decomposition reactions [4].

The lecture reviews the main features of the optimization algorithms suggested in the literature. The *progress* made in our Laboratory is detailed. This methodology offers *promises* for the improvement of the detailed combustion mechanisms of basic fuels and the determination of rate parameters from shock tube experimental data. However, the mechanism optimization methodology has also several *possible pitfalls*, which will also be enumerated.

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