

Hydrogen combustion: mixture rules and rate constants. A case study on the multicomponent pressure dependence of $\text{H}+\text{O}_2+\text{M}=\text{HO}_2+\text{M}$

M. Primi, T. Dinelli, M. Lea Casagrande, L. Pratali Maffei, A. Cuoci,
M. Pelucchi, C. Cavallotti

matteo.primi@polimi.it

*Dept. Chemistry, Materials, and Chemical Engineering, Politecnico di Milano
Piazza Leonardo da Vinci, 32, Milano, Italy

Abstract

Hydrogen combustion has recently been the subject of considerable interest because of its perspective use as energy vector. It has though been shown that the mixture rules used to determine rate constants of termolecular reactions currently implemented in most kinetic simulation software are physically inconsistent when used in the fall-off regime. Also, there is considerable uncertainty in the dependence on the bath gas of the rate constants of some key termolecular reactions. In this context, we developed an approach to study hydrogen reactivity whose final aim is the full a priori revision of the elementary kinetics of hydrogen combustion chemistry. Specifically, we present an efficient and accurate implementation of a method for determining the rate constants of termolecular reactions, we apply it to the study of the $\text{H}+\text{O}_2+\text{M}\rightarrow\text{HO}_2+\text{M}$ reaction both for single and multiple colliders, and we investigate its impact on kinetic simulations. First, the contribution of intermolecular energy transfer to the reactive process is determined using a 1D master equation model with the collisional kernel described using the single exponential energy transfer model and recombination fluxes computed using Variable Reaction Coordinate Transition State Theory. The energy transfer parameters of the collisional model are then fitted for several colliders (Ar, He, N₂, H₂, CO₂, H₂O) through regression over a large set of experimental rate constants, by interfacing the master equation simulator MESS to a non-linear regression software. Finally, a physically consistent mixture model is implemented for the first time in a kinetic simulator, the OpenSmoke software, and kinetic simulations are performed to study model performances. The simulation results show that the impact of the new sets of rate constants so determined can be significant in some combustion environments.

Introduction

In the last decades, the use of hydrogen has gained significant interest for replacing traditional carbon-based fuels either alone, mixed with CO, CO₂, and H₂O, or as a primary component of synthetic gas. It is particularly suitable for high-temperature, energy-intensive industrial processes [1], as well as for the decarbonization of

heavy/long-distance transport [2]. Furthermore, blending hydrogen with natural gas for household heating and distributing it through existing pipeline systems is already a viable option [3]. However, the utilization of hydrogen blends in commercial applications has been limited due to several technical challenges, which include blowout, flashback, autoignition, combustion dynamics, and environmental impact. A great accuracy in describing hydrogen reactivity is the first fundamental step in overcoming these challenges. Currently, two main issues limit the accuracy of hydrogen kinetics in systems with a high number of pressure-dependent termolecular reactions, as it happens in atmospheric and combustion chemistry. Firstly, within existing kinetic mechanisms, termolecular reactions are expressed as a function of a reference reaction with a specific collider (usually Argon), and the rates with other colliders are obtained by means of corrective parameters, the third body efficiencies. However, these parameters are often determined through fitting of complex sets of data, with the consequence that they can vary substantially even between similar kinetic mechanisms, leading to non-unambiguous results. Secondly, Burke [4] has demonstrated that the mixture rules used to determine rate constants currently implemented in most kinetic simulation software are physically inconsistent when used in the fall-off regime.

This work aims to develop an efficient and accurate approach to be used to address these methodological shortcomings. Reporting the case study of $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ reaction, the proposed method has been applied to determine the rate constants of termolecular reactions, both for single and multiple colliders, and its impact has been evaluated through kinetic simulations.

Methods

The proposed approach is implemented in two separate and consecutive steps, as shown in Figure 1. The first has the purpose of determining accurately the energy transfer parameters of different colliders and consequently the rate constant in the presence of a single bath gas. In the second one, the rate constants so determined are used to estimate mixture dependent rate parameters using for this purpose the physically consistent mixture rules proposed by Burke et al. [5] to properly describe multicollider systems.

In the first step of this approach, high pressure rate constants are determined using the ab initio transition state theory based master equation approach (AI-TST-ME) as implemented in EStokTP [6]. In particular, the rate constant for the $\text{H} + \text{O}_2$ recombination reaction is determined using Variable Reaction Coordinate Transition State Theory (VRC-TST) determining energies as a function of the transitional coordinates at the CASPT2 level using a cc-pVDZ basis set and a full valance active space. The interaction potential was corrected for geometry relaxation and basis set effects.

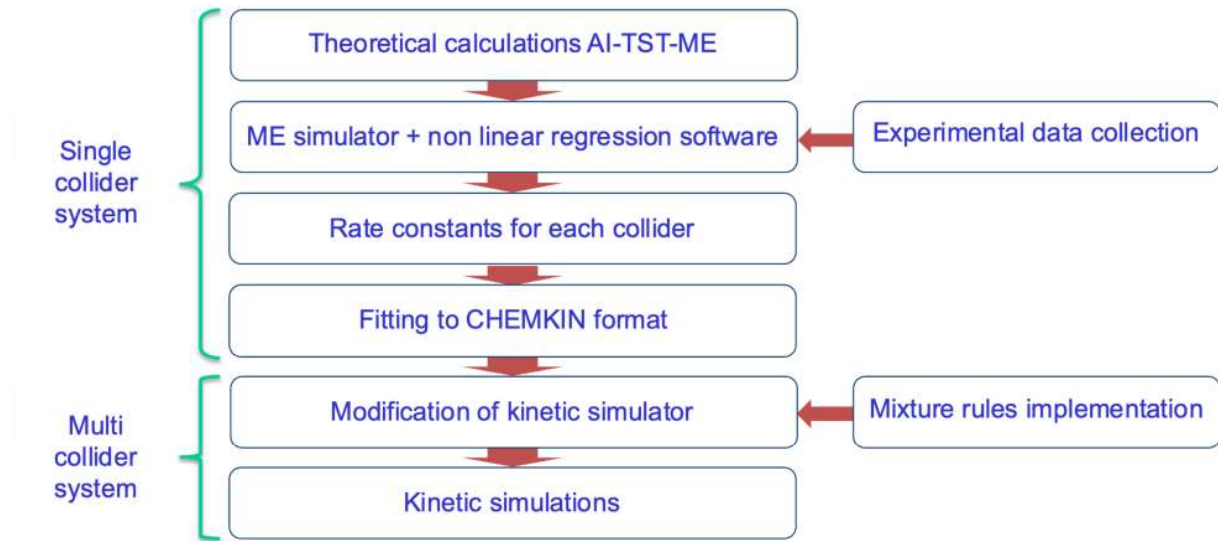


Figure 1. Method conceptual scheme

Afterward, a 1D master equation model was used with the collisional kernel described using the single exponential energy transfer model and recombination fluxes computed using VRC-TST. The master equation used in this work has the following expression:

$$\frac{dn(E)}{dt} = \sum_{i=1}^M Z_i [M_i] \sum_{E^l=0}^{\infty} (P_i(E, E^l)n(E^l) - P_i(E^l, E) \cdot n(E)) - k(E)n(E) \quad (1)$$

where the subscript i refers to the i th component of the mixture, Z_i is the collision frequency between the reactant and the third body M_i , whose concentration is indicated as $[M_i]$, while $k(E)$ is the microcanonical decomposition rate constant of the reactant with energy E . Finally, $P_i(E, E^l)$, also known as collisional kernel, represents the probability that a reactant with energy E^l moves to energy E due to a collision with an i th mixture component. In this work, the single exponential energy transfer model is exploited and is expressed as:

$$P_i(E, E^l) = \frac{1}{N(E^l)} e^{\left(\frac{-E^l-E}{\alpha_i}\right)} \quad E \leq E^l \quad (2)$$

Where $N(E^l)$ is a normalization constant so that the integral of P_i over all energy states is equal to 1 and α_i is the average energy transferred per down collision. The last one is a semi-empirical parameter that depends on the collider, expressed as:

$$\alpha_i = \alpha_0 \left(\frac{T}{298 K}\right)^n \quad (E \leq E^l), \quad (3)$$

where α_0 and n are parameters that must be defined for each investigated collider. For this purpose, a regression over more than 500 experimental data has been performed by coupling the master equation solver MESS [7] with a non linear regression software. Eight possible species (Ar, N₂, H₂, CO₂, H₂O, O₂, He, Kr) were investigated as bath gas, representing an exhaustive list of strong and weak colliders.

Once the energy transfer parameters have been determined, rate constants for each individual collider were calculated at pressures up to 100 bar and at temperatures between 300 and 2500 K. Then, the rate constants were fitted and expressed in the modified Arrhenius form that is suitable for implementation in kinetic mechanisms that use the ChemKin format, as is the case for OpenSMOKE++ [8]. For the sake of simplicity, pressure dependence is accounted for using the PLOG ChemKin format, though other methods have been implemented in OpenSMOKE++.

Finally, the linear mixture rule algorithm proposed by Burke et al. [5] was implemented in OpenSMOKE++. This algorithm can briefly be explained as follows: first the reduced pressure, defined as the ratio between the low and high-pressure limit rate constants multiplied by the total concentration is determined and used as a quantitative measure of the width of the falloff regime. Then, the contributions of each collider to the rate constant are estimated at the same reduced pressure rather than absolute pressure as in traditional linear mixture rules. Therefore, rate constants for weak and strong colliders are more similar than values evaluated at the absolute pressure. Finally, the rate constant is determined as a linear sum of the rate constants of each component at the same reduced pressure weighted by their fractional contributions to the reduced pressure [5].

To test the impact of the implemented approach, some kinetic simulations were performed inserting the $\text{H}+\text{O}_2+\text{M}\rightarrow\text{HO}_2+\text{M}$ rate constant calculated with the systematic approach described above in the CRECK hydrogen mechanism and simulating hydrogen laminar flame speeds.

Results and discussion

The energy transfer parameters obtained from the regressions are reported in Table 1. The total number of rate constants used for the regression is 130 for Ar, taken from six different works, and measured between 298 to 2053 K and at pressures comprised between 0.01 and 950 bar. Differently, 15 works were considered for N₂, collecting 134 experimental rate constants between 298-1908 K and 26 Torr and 950 bar. Regarding H₂O, regression was performed on 84 rate constants from six works, measured between 298 and 1375 K and at pressures from 0.03 and 45 bar. The 39 rate constants used for the regression for O₂ were measured at 0.009-0.04 bar and from 298 to 700 K, whereas 4 experimental data sets were considered for CO₂, consisting of 26 rate constants measured at 1-17 bar from 800 to 1300 K. Concerning H₂, the regression was performed on 23 rate constants measured at 298 K and from 0.09 to 0.8 bar. The data used for Kr are also at room temperature but were measured between 0.09 and 0.16 bar. Lastly, 105 rate constants from 6 works were used for the regression concerning He, with experimental data measured between 298 and 700 K and at pressures from 0.005 to 900 bar. All regressions performed have a correlation index higher than 0.95, which was considered as the minimum acceptable value. Regressions over CO₂ and H₂ have the lowest correlation index, respectively 0.957 and 0.966. It is assumed that this is mainly related to the limited temperature and pressure ranges in which experimental measurements are available. To the best

of our knowledge, we have found in the literature only one other estimate of the collision parameters of these colliders for this reaction [9], which are found to be in reasonable agreement with those determined in this work.

Table 1. Energy transfer parameters calculated for different colliders and correlation index of the regression.

Collider	α_0	n	Correlation index
Ar	33.3	1.048	0.985
He	27.4	1.005	0.990
N ₂	49.0	0.927	0.988
O ₂	36.6	0.952	0.996
H ₂	36.4	0.943	0.966
CO ₂	52.5	1.493	0.957
H ₂ O	158.1	1.394	0.978
Kr	30.9	1.000	0.974

The rate constant in the CRECK Syngas (H₂/CO) mechanism (version 2003, March 2020) [10][11],[12] were updated with new values determined for the H+O₂+M→HO₂+M rate constant and used to simulate the laminar flame speeds measured by Sun and Li [13] in hydrogen-air mixtures. It was found that the flame speed is lowered with the updated model, which leads to a better agreement with the experimental data. The main impact of the updated rates is found in the operating conditions where the system is sensitive to the H+O₂+M→HO₂+M reaction, thus at pressures of 1-2 bar and temperatures below 1000 K.

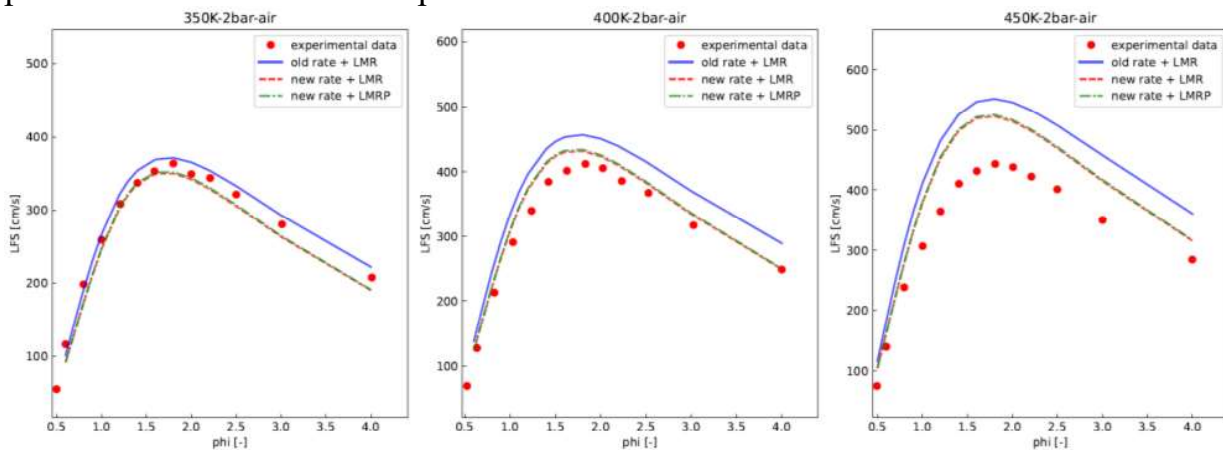


Figure 2. Comparison between LFS predicted using the updated and reference CRECK syngas models with experimental data [13]

Conclusions

Effective collisional parameters and proper dependence of rate constant from mixture composition were determined using a new approach for the H+O₂ reaction. Their inclusion in kinetic simulations allowed to improve the agreement with experimental data for what concerns laminar flame speed in some combustion

environments. Future developments include the extension of the new method to other key termolecular reactions in hydrogen combustion and the investigation of mixtures formed by both weak and strong colliders.

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