

New insights on H₂-O₂ dynamic behavior. Effects of several bath gases.

P. Sabia¹, M.V. Manna^{1,2}, M. de Joannon¹, R. Ragucci¹

1. Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

3. University Federico II, Napoli, Italy

Introduction

The oxidation process of H₂ and O₂ systems have received a lot of attention because of it represents the first step for the development of complex kinetic schemes within the idea of their construction in a hierarchical structure. Recently updated kinetic mechanisms for the H₂-O₂ system have been proposed by several authors. In this work, new experimental tests have been run for a lean H₂-O₂ mixture in several bath gas (CO₂, N₂, H₂O and Ar) in a Jet Stirred Flow Reactor, in order to test the performance of recently proposed kinetic schemes in different environments. While the capability to predict experimental data of updated detailed schemes is satisfactory when the diluent is N₂, for the other bath gases some discrepancies occur, thus highlighting the role of third-body reactions and the lack of a deep knowledge of the third-body collisional efficiencies for several bath gas.

In addition, instabilities have been experimentally detected, with temperature oscillations within the control volume. An analysis of Rates of Reactions suggests that CO₂ and H₂O may suppress instabilities because of their high third body collisional efficiency.

Methodology

The oxidation process of a lean H₂-O₂ mixture was studied in a JSFR. This reactor enables to systematically study the dependence of the chemical species distribution as a function of a range of combustion parameters, such as fuel mixture composition and temperature. It consists of a fused silica sphere of 113 cm³. The main flow is composed of oxygen and diluent. It passes through a quartz tube located within two cylindrical electrically heated ceramic fiber ovens. It subsequently mixes with the secondary flow, composed by fuel and diluent, in a premixing chamber. Then the pre-mixed mixture enters the reactor through four nozzles of 1 mm diameter located at its center. To detect and follow accurately the temperature changes during gaseous reactions, a type R thermocouple (40 µm bead size) was used.

Experiments were performed setting the follow operative conditions: inlet temperature 400-800 K, pressure 1.2 atm, dilution level 94 % using nitrogen as diluent agent, residence time 0.5 s, equivalence ratio (ϕ) was set equal to 0.5.

To provide a detailed chemical analysis, the outlet stable species O₂, N₂, H₂ were analyzed by gas chromatography (μ -GC AGILENT). In addition, O₂ was also analyzed by an oxygen analyzer supplied by ADEV s.r.l.. Gas outlet flow was cooled down to 1-2 °C by a chiller to condense water and obtain concentrations on a dry base. The experimental results obtained in the JSFR were simulated using the PSR code of the CHEMKIN PRO software package [1]. Three different detailed gas-phase chemical kinetic models were used (tab. 1).

Kinetic mechanism	Number of Reactions	Number of Species	Ref.
Davis (2016)	44	15	2
Polimi (2018)	33	14	3
Aramcomech (2006)	40	16	4

Tab. 1. Kinetic mechanisms and details.

Experimental tests and simulations

Tests were performed for hydrogen/oxygen/nitrogen mixtures, changing the mixture inlet temperature (T_{in}) and for a fixed equivalence ratio ($\phi = 0.5$).

For mixture diluted in N_2 , the temperature starts increasing for $T_{in} > 850$ K (Fig. 1). For $T_{in} > 890$ K, temperature oscillations establish, while for $T_{in} > 930$ K the oxidation occur through a steady state. All the considered kinetic mechanisms well predict the system behavior. Small discrepancies can be recognized among the kinetic schemes, in particular the reactivity predicted by the “DAVIS” mechanism is slightly higher at low temperatures.

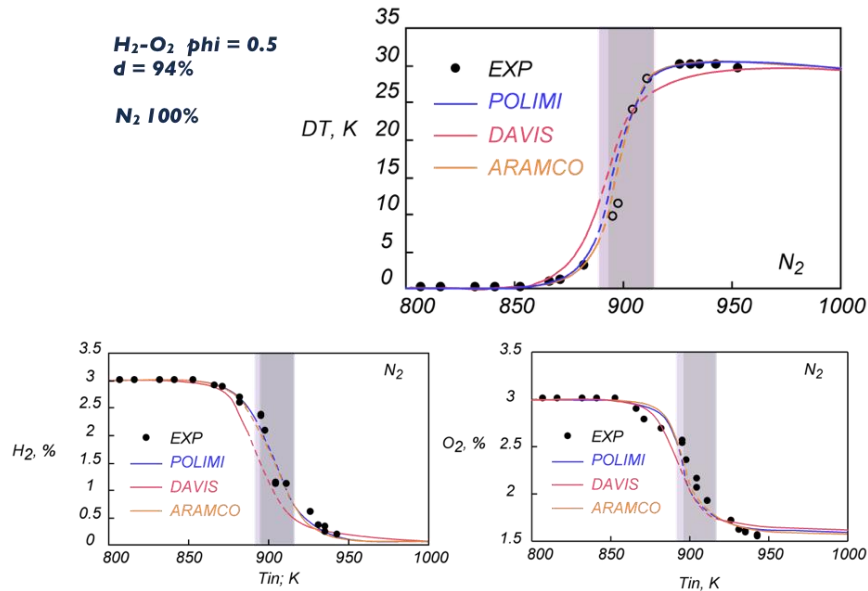


Figure 1. Experimental profiles of Temperature, H_2 , O_2 for a lean ($\Phi=0.5$) H_2/O_2 mixture diluted in N_2 at 94%.

For mixture diluted in CO_2 (Fig. 2), the temperature starts increasing for $T_{in} > 930$ K, then it slowly increases up to the steady condition. No temperature oscillations are detected for this system.

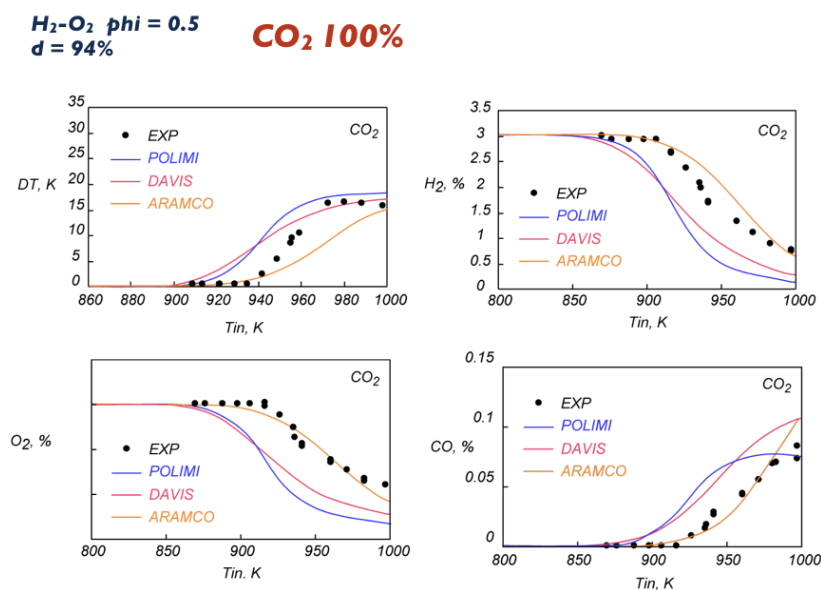


Figure 2. Experimental profiles of Temperature, H_2 , O_2 and CO for a lean ($\Phi=0.5$) H_2/O_2 mixture diluted in CO_2 at 94%.

The considered kinetic mechanisms do not properly reproduce the experimental data, and predictions are different among the kinetic schemes. The “DAVIS” and “POLIMI” ones behave similarly, while the “ARAMCO” one shows a lower reactivity. The experimental data lay in-between the numerical predictions.

Fig. 3 shows the experimental data and the numerical predictions for Temperature, H_2 and O_2 for a lean ($\Phi = 0.5$) H_2/O_2 mixture diluted in H_2O and N_2 (30% -70%) at 94%. For this case, the temperature starts increasing for $T_{in} > 915$ K, then it slowly increases up to the steady condition. No temperature oscillations are detected for this system. The considered kinetic mechanisms do not properly behave similarly and predict a reactivity slightly higher with respect to the experimental data, and predictions are different among the numerical results.

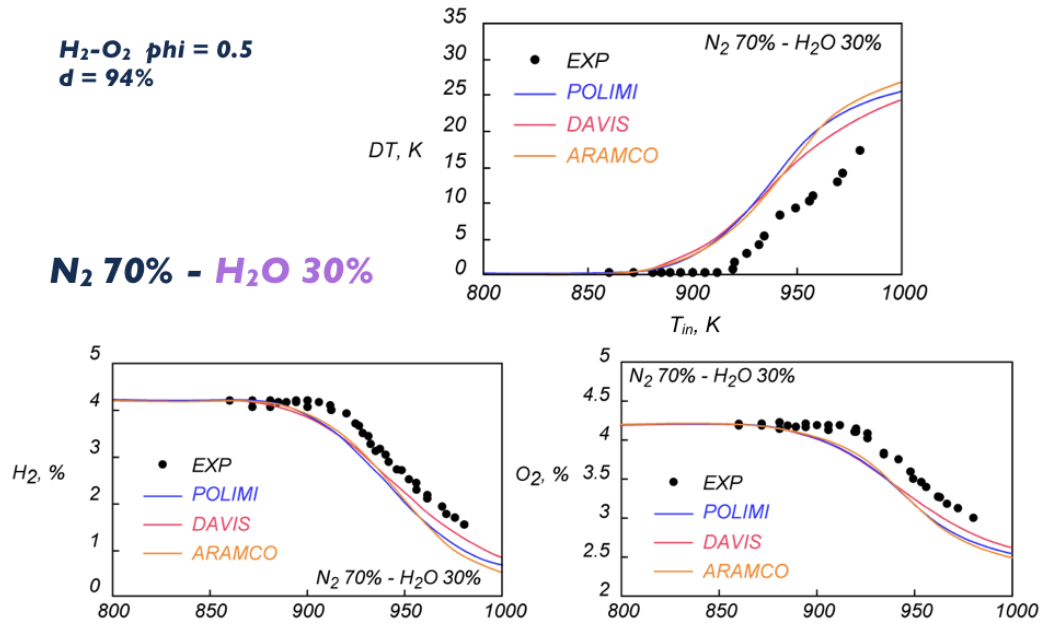


Figure 3. Experimental profiles of Temperature, H_2 and O_2 for a lean ($\Phi=0.5$) H_2/O_2 mixture diluted in H_2O and N_2 (30% -70%) at 94%.

Experimental tests and simulations

In order to highlight the reactions that lead to system instabilities, Reaction Rate analyses have been realized. Figure 4 reports the RR analyses for the mixture the H_2-O_2 diluted in N_2 . The low temperature branching mechanism is composed by the formation of HO_2 radicals ($H + O_2 + M = HO_2 + M$), recombination to H_2O_2 ($HO_2 + HO_2 = H_2O_2 + O_2$) and its decomposition ($H_2O_2 (+M) = OH + OH (+M)$) with the production of OH radicals.

As the system approaches the dynamic behavior, the reaction rate of reaction $H + HO_2 = OH + OH$ becomes equal to $HO_2 + HO_2 = H_2O_2 + O_2$, thus providing for OH radicals by a kinetic pathways relatively faster than the global reaction rate of the low temperature branching kinetic mechanism. Thus the reactivity of the system increases.

After the dynamic regimes, the relative importance of the reaction $H + HO_2 = OH + OH$ is dampened by the reaction $H + O_2 = OH + O$, that provides for the radical pool necessary to sustain the H_2 oxidation.

During the instabilities, the RR of such two reactions changes with temperature, thus leading to oscillating behaviors.

In the case of systems diluted in H_2O or CO_2 the reaction rate of the reaction $H + O_2 + M = HO_2 + M$ is increased by the third molecular effect of such species thus the reaction rate of $H + HO_2 = OH + OH$ is slowed down, thus it cannot behave as alternative branching mechanism.

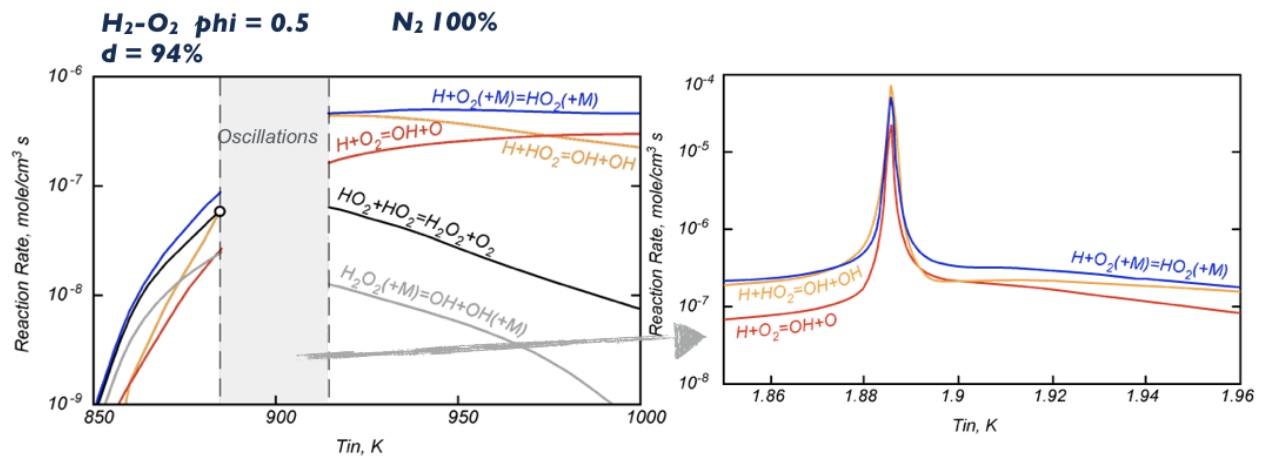


Figure 4. RR analyses for the mixture the H_2 - O_2 diluted in N_2 .

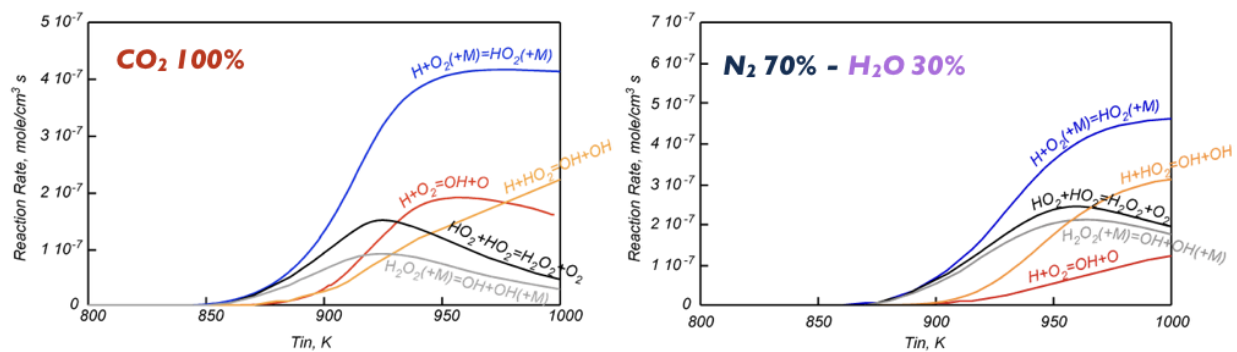


Figure 5. RR analyses for the mixture the H_2 - O_2 diluted in CO_2 and H_2O .

Conclusions

The present work experimentally characterizes the oxidation process of diluted and pre-heated hydrogen/oxygen mixtures in a perfectly stirred reactor. Several bath gases bath gas (CO_2 , N_2 , H_2O and Ar) are used to dilute the reference mixture. Several updated kinetic mechanisms are used to simulate the experimental data. While their capability to predict experimental data is satisfactory for the diluent is N_2 , some discrepancies occur for the other bath gases, thus highlighting the lack of a deep knowledge of the third-body collisional efficiencies. In addition, instabilities have been experimentally detected, with temperature oscillations within the control volume. An analysis of Rates of Reactions suggests that CO_2 and H_2O may suppress instabilities because of their high third body collisional efficiency.

References

- [1] CHEMKIN-PRO 15131, Reaction Design: San Diego, 2013
- [2] "DAVIS": <http://ignis.usc.edu/Mechanisms/H2-CO/h2-co.html>
- [3] "POLIMI": (<http://creckmodeling.chem.polimi.it/menu-kinetics/menu-kinetics-detailed-mechanisms/menu-kinetics-h2-co-mechanism>)
- [4] "ARAMCO" : <http://www.nuigalway.ie/c3/aramco2/frontmatter.html>