Termolecular reaction H + O$_2$ + M -> HO$_2$ + M

Studying the pressure dependence

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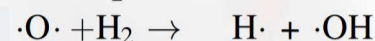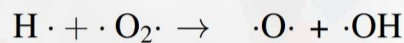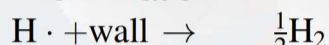## 1 - The problem in a hydrogen combustion mechanism

Initiation
$$H_2 \rightarrow H\cdot + H\cdot$$

Propagation
$$\cdot OH + H_2 \rightarrow H\cdot + H_2O$$

Ramification
$$H\cdot + \cdot O_2\cdot \rightarrow \cdot O\cdot + \cdot OH$$
$$\cdot O\cdot + H_2 \rightarrow H\cdot + \cdot OH$$

Termination
$$H\cdot + wall \rightarrow \tfrac{1}{2}H_2$$
$$H\cdot + \cdot O_2\cdot + M \rightarrow HO_2\cdot + M$$

The pressure dependence of the termolecular reaction $H + O_2 + M \rightarrow HO_2 + M$ is one of the main sources of uncertainty when modelling hydrogen combustion chemistry.

This reaction is initiated by a $H + O_2$ collision giving a long lived excited HO_2^* radical that can react to products, $O + OH$, which is endothermic, dissociate back to reactants, $H + O_2$, or be stabilized by collision.

The long-lived nature of this excited HO_2^* radical is a result of its electronic structure. At collinear and perpendicular geometries this radical correlates with a hydrogen atom in a $2p$ state. Leading to the fact that the dissociation back to $H + OH$ has energy barriers in these directions.

Being a termolecular reaction, it cannot be studied using normal classical trajectory programs. We have adapted the program MReaDy to study this reaction at 1500 K 2000 K and 2500 K at pressures of 10, 20 and 50 atm.
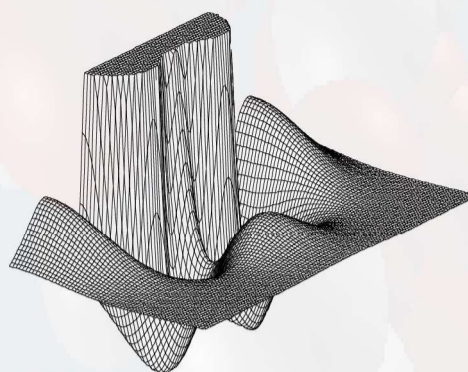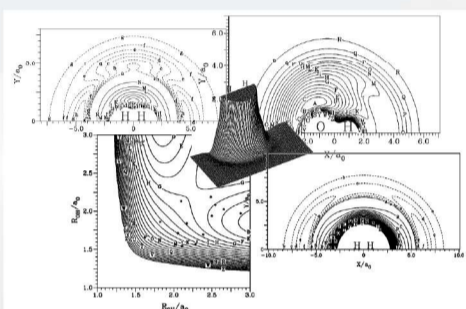

HO$_2$ Potential Energy Surface. Energy profile for a hydrogen atom around an oxygen diatomic at its equilibrium geometry. Once the hydrogen atoms approaches the O$_2$ molecule it stays in a trap with small exit channels.

In these calculations we model a mixture of H atoms and O$_2$ molecules and only consider as reactive collisions those forming the HO_2^* radical. All other collisions are considered as non-reactive, i.e., only transfer energy between partners.

With this program we can take into account the energy transfer by collision. Following the HO2* radicals formed, we are able to evaluate its stabilization which has been defined when a radical is not colliding wit another system and his internal energy is bellow 0.19157 E_{rmh}, corresponding to the classical energy of dissociation.

To keep constant the number of particles and energy, every time that the HO_2^* radical is stabilized or reacts to give H + OH products, they are removed and replaced by an H atom and a O$_2$ molecule wit the same total energy. This allow us to keep a N,V,E (microcanonical) ensemble.

2 - The MReaDy program

The Verlet algorithm
$$\vec{x}_{n+1} = 2\vec{x}_n - \vec{x}_{n-1} + \vec{a}_n \Delta t^2$$

$$\vec{v}_n = \frac{\vec{x}_{n+1} - \vec{x}_{n-1}}{2\Delta t}$$

Molecules in a 3D periodic system.

MReaDy[1] uses accurate PESs, reactive and nonreactive, and concurrently integrates the equations of motion of the chemical species present in the system.
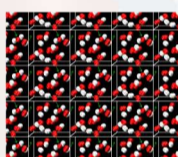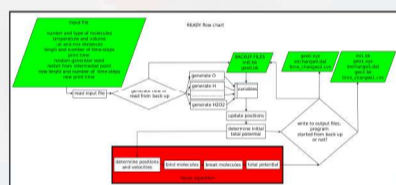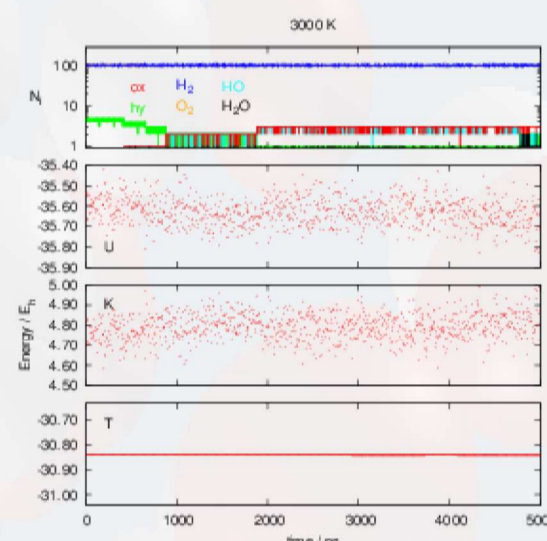
In the absence of accurate PESs, non-reactive collisions are treated using pair-additive repulsive potentials in order to account for the energy transfer between colliding partners.

H$_2$($^1\Sigma$)	H$_2$($^3\Sigma$)	O$_2$($^3\Sigma$)	O$_2$($^1\Delta$)
HO($^2\Pi$)	HO$_2$(^{2}A")	H$_2$O($\tilde{X}^1$A')	H$_2$O(^{3}A")
O$_3$(^{1}A$_1$)	H$_3$	H$_4$(^{1}B$_1$)	H$_2$O$_2$(^{1}A)
H$_2$O$_2$(^{3}A)	O$_4$(^{3}A)	H$_3$O	HO$_3$(^{2}A)

Flow chart for the generical MReaDy. Alterations are implemented according to the simulation's requirements.

Table representing the full agrupa script, attributing the reaction probabilities and respective PES after a collision. (n.r. - non reactive).
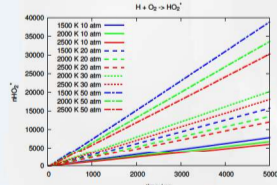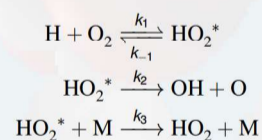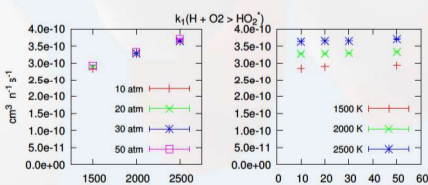

Example of a simulation showing the time evolution of a mixture of 100 H$_2$, 100 O$_2$ and 5 H. Below the potential, kinetic and the total energy, showing the system's total energy conservation[2].

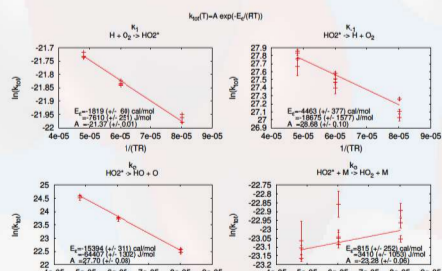## 3 - Results from adapted MReady for the formation of the HO$_2$ radical (a termolecular process)
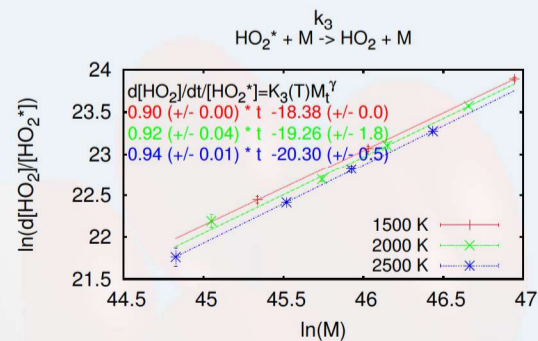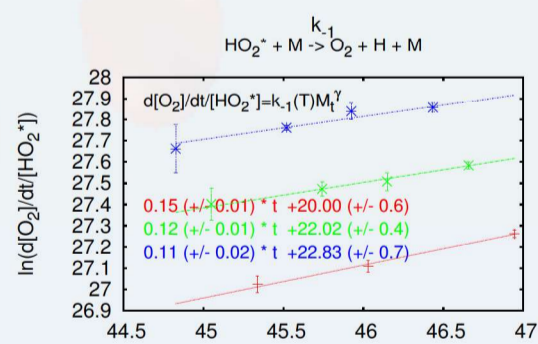
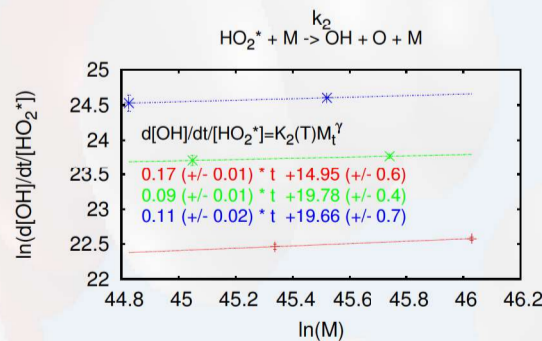Looking for the pressure dependence of the system:

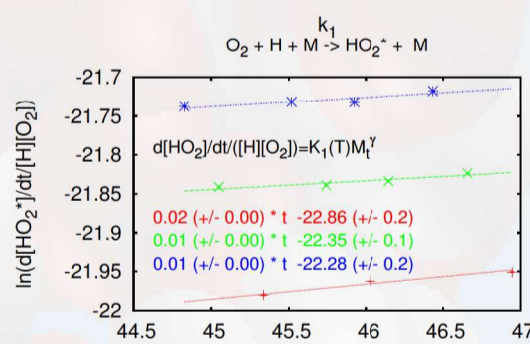$$H + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HO_2^*$$
$$HO_2^* \xrightarrow{k_2} OH + O$$
$$HO_2^* + M \xrightarrow{k_3} HO_2 + M$$

Formation of the HO$_2^*$ complex.

Histograms of the HO$_2^*$ complex collisions

Activation Energy.

k$_1$: O$_2$ + H + M -> HO$_2^*$ + M

d[HO$_2$]/dt/([H][O$_2$])=K$_1$(T)M$_t^\gamma$

0.02 (+/- 0.00) * t -22.86 (+/- 0.2)
0.01 (+/- 0.00) * t -22.35 (+/- 0.1)
0.01 (+/- 0.00) * t -22.28 (+/- 0.2)

k$_{-1}$: HO$_2^*$ + M -> O$_2$ + H + M

d[O$_2$]/dt/[HO$_2^*$]=k$_{-1}$(T)M$_t^\gamma$

0.15 (+/- 0.01) * t +20.00 (+/- 0.6)
0.12 (+/- 0.01) * t +22.02 (+/- 0.4)
0.11 (+/- 0.02) * t +22.83 (+/- 0.7)

k$_2$: HO$_2^*$ + M -> OH + O + M

d[OH]/dt/[HO$_2^*$]=K$_2$(T)M$_t^\gamma$

0.17 (+/- 0.01) * t +14.95 (+/- 0.6)
0.09 (+/- 0.01) * t +19.78 (+/- 0.4)
0.11 (+/- 0.02) * t +19.66 (+/- 0.7)

k$_3$: HO$_2^*$ + M -> HO$_2$ + M

d[HO$_2$]/dt/[HO$_2^*$]=K$_3$(T)M$_t^\gamma$

0.90 (+/- 0.00) * t -18.38 (+/- 0.0)
0.92 (+/- 0.04) * t -19.26 (+/- 1.8)
0.94 (+/- 0.01) * t -20.30 (+/- 0.5)

Kinetic plots.

References and Acknowledgement

[1] César Mogo and João Brandão.
The READY program: Building a global potential energy surface and reactive dynamic simulations for the hydrogen combustion.
Journal of Computational Chemistry, 35(17):1330–1337, 2014.

[2] César Mogo and João Brandão.
N-dimensional switch function for energy conservation in multiprocess reaction dynamics.
Journal of Computational Chemistry, 37(16):1521–1524, 2016.

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