

Using a molecular reactor to study ter-molecular processes

Theoretical and Computational Chemistry Research Group

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Dynamical Methods for COld Molecular collisions, DyMCom

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Termolecular reactions

Termolecular processes are difficult to study by theoretical methods as they require the presence of three particles in the same region at the same time.

Although rare, termolecular reactions can play an important role in many chemical processes.

They usually involve a initial collision of two species, forming a “collision complex” that lives enough time to collide with the third molecule.

The global reaction rate should depend on:

- Probability of formation of the “collision complex”
- Average lifetime of this complex
- Probability of reaction with the third reactant.

The $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$ reaction at low temperatures

The removal of a hydrogen atom from a methanol molecule by the hydroxyl radical producing water and hydroxymethyl or methoxy radicals has been suggested to be a possible source for the presence of methoxy radicals detected in interstellar space.

The experimental results display a peculiar behaviour:

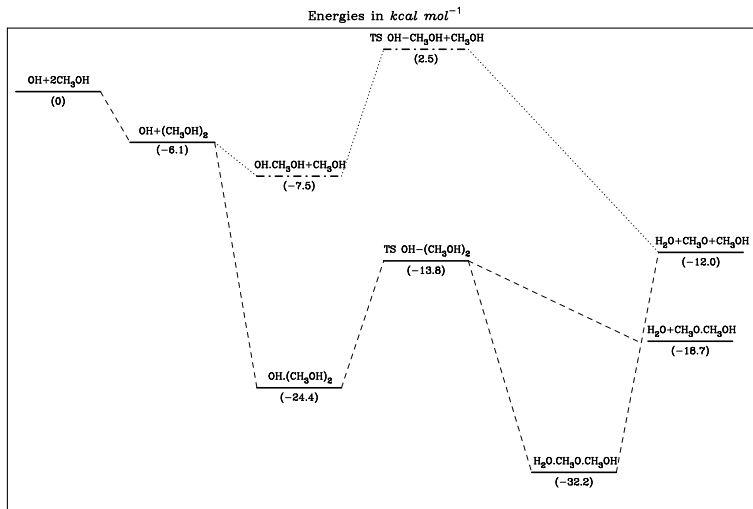
- At temperatures above 200 K the formation of hydroxymethyl radical, CH_2OH , dominates with a thermal rate constant that increases with temperature;
- However at temperatures below 200 K the product CH_3O dominates, but the thermal rate constant decreases with temperature, halving its value when temperature increases from 50 K to 200 K.

The $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$ reaction, a termolecular process?

To explain the low temperature behaviour, Siebrand *et al.* studied the role of the presence of the methanol dimer on this process.

This careful work, extensively debated in the WG1 and WG2 meeting of the COST CM1401 “Our Astrochemistry history” held at Ciudad Real in december 2017, states that under the low temperatures of the supersonic Laval nozzle beam, there coexist a mixture of methanol monomers and dimers, which have a binding energy of $6.1 \text{ kcal mol}^{-1}$. The collision of the hydroxyl radical with the dimer would dissociate it forming a stable $\text{CH}_3\text{OH} \cdots \text{OH}$ complex. This stable complex would react, by tunnelling, producing the methoxy radical.

Octávio Roncero has published a different explanation not involving the formation of such dimer.

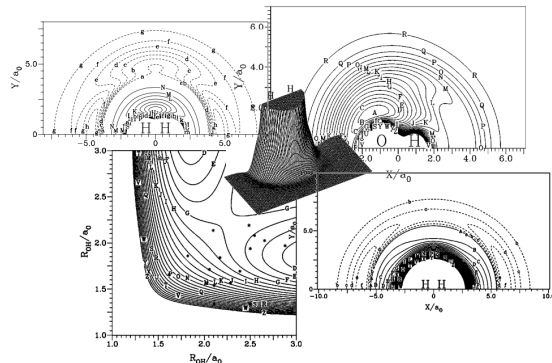
Energy diagram for the $\text{OH} + 2\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O} + \text{CH}_3\text{OH}$ 

Evolution of the reaction

Building a molecular reactor with multiple Potential Energy Surfaces

Molecular modeling of chemical processes has become a strategy to incorporate different elementary reactions in studies of complex reactive processes.

Using all the necessary Potential Energy Surfaces in one calculation, we can integrate the equations of motion of all the atoms present in the mixture and follow the different reactions that take place in the bulk.



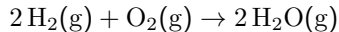
The Multiprocess Reaction Dynamics Program (MReaDy)

- Each atom should be assigned to a molecule in a defined electronic state (PES).
- At each step the distances between the atoms are checked in order to define if any molecular system should be split (a collision terminate) or if new species (collisions) should be considered.
- The PES of the new molecular system is randomly defined respecting its probability according to the Wigner-Vitmer spin/symmetry rules.
- In addition to the forces defined by the PESs, intermolecular interactions between the present molecules should also be considered.

Although time consuming, modeling a multi-process reaction dynamics using classical dynamics has shown to be able to reproduce complex reactions from first principles and to study the rate of the collisional stabilization of the HO₂ molecule

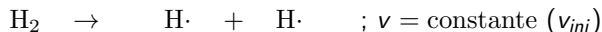
Hydrogen combustion mechanism

The hydrogen combustion does not occur in a single step

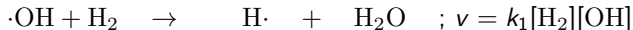


This process involves a lot of elementary reactions. A simple mechanism is:

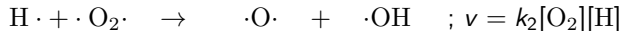
Initiation



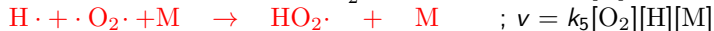
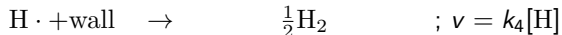
Propagation



Ramification

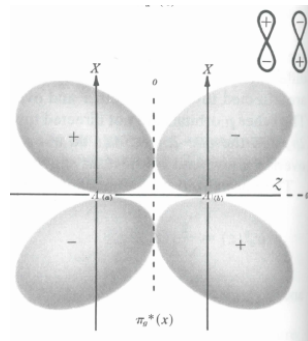
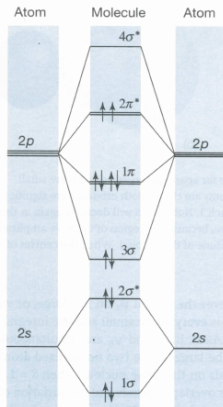


Termination



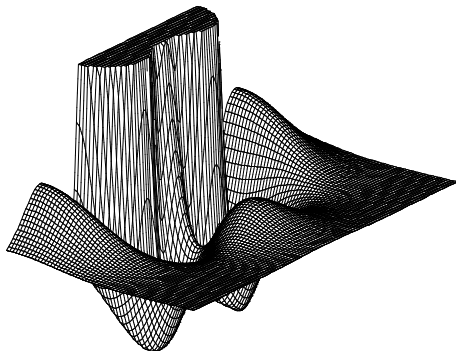
Hydrogen combustion

Remembering general chemistry ideas



At collinear and perpendicular geometries, the π_g^* molecular orbitals of O₂ (${}^3\Sigma_g^-$) only correlate with a hydrogen atom in a 2p state. By this way, the dissociation back to H + O₂ has energy barriers in these directions.

One view of the HO₂ Potential Energy Surface



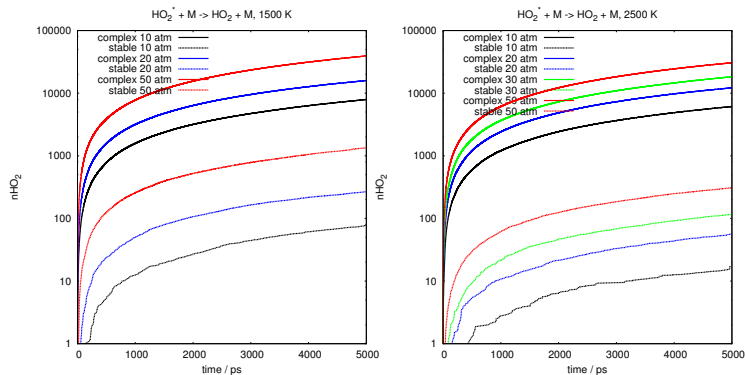
Energy profile for a hydrogen atom around an oxygen diatomic at its equilibrium geometry.

Once the hydrogen atoms approaches the O₂ molecule it stays in a trap with small exit channels.

Building a molecular reactor to study the $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$

- We fill the reaction box with H atoms and O₂ diatomics, randomly generated according to the temperature and pressure of the experiment.
- Consider only the ground HO₂ PES.
- All the other collisions are considered as non-reactive. For those electronic states we do not have PES, they are build from pairwise interaction fitted to high spin interactions.
- We consider a collision whenever we enter the ground state HO₂ PES.
- A complex has been formed if the HO₂* **potential energy** is 0.2 eV lower than the H+O₂ dissociation energy.
- A radical HO₂* is considered stabilized if its **internal energy** is lower than the H+O₂ dissociation energy.
- To keep constant the number of reactants, each stabilized radical is replaced by reactants with the same **total energy**.

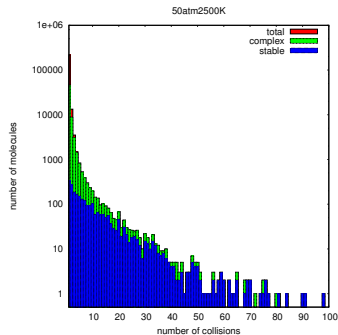
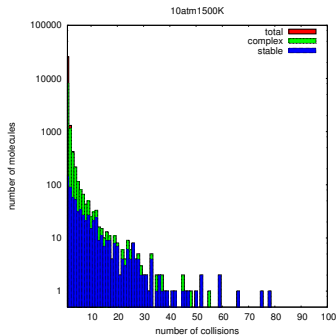
Complex formation and stabilization of the HO₂* radical



Formation and stabilization of the HO₂ radical at pressures of 10 atm, 20 atm and 50 atm at temperatures of 1500 K and 2500 K.

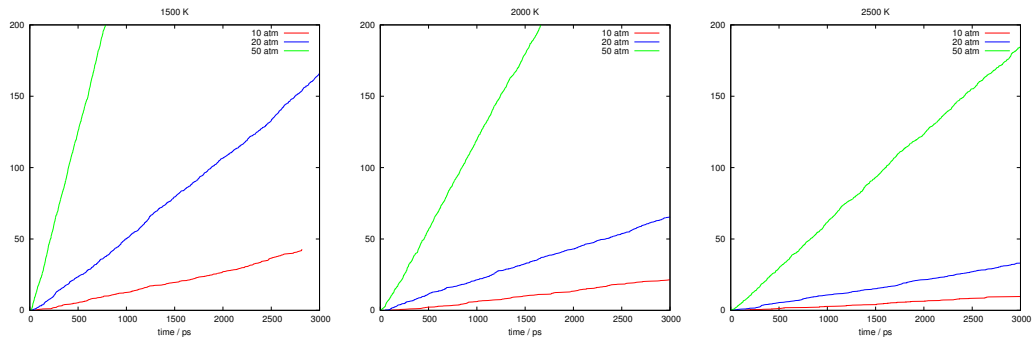
The number of HO₂* complex formed depends mainly on the pressure but the formation of stable radical is higher at lower temperatures.

Number of collisions to stabilize the HO₂



Each HO₂^{*} experiment a lot of collisions before its internal energy becomes lower than the classical dissociation energy, $-0.19157 E_h$.

Rate of formation of stable HO₂



Stabilization of the HO₂^{*} radical at different temperatures and pressures. The slope of these lines give us the rate of stabilization.

At each temperature, higher pressures result in higher number of stable HO₂ radicals.
Increasing the temperature, lowers the stabilization rates.

HO₂* average lifetime and stabilization velocity

T / K	P / atm	life time / fs	$v_{form.}(HO_2^*) / ns^{-1}$
1500	10	1795 ± 84	0.01594E12 ± 2.7E7
	20	1638 ± 43	0.05453E12 ± 3.0E7
	50	1397 ± 35	0.26407E12 ± 3.9E7
2000	10	1197 ± 83	0.00726E12 ± 2.8E7
	20	1131 ± 51	0.02234E12 ± 2.1E7
	30	1115 ± 59	0.04941E12 ± 2.8E7
	50	1022 ± 34	0.12124E12 ± 2.4E7
2500	10	931 ± 110	0.00321E12 ± 2.5E7
	20	844 ± 18	0.01123E12 ± 1.5E7
	30	805 ± 39	0.02342E12 ± 1.7E7
	50	785 ± 25	0.06186E12 ± 1.6E7

Thanks for your attention