



Computational chemistry in the generation of detailed kinetic models for the combustion of hydrocarbon

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Computational chemistry in the generation of detailed kinetic models for the combustion of hydrocarbons

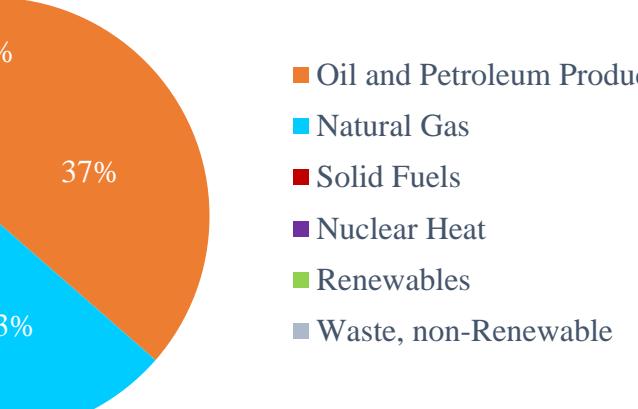
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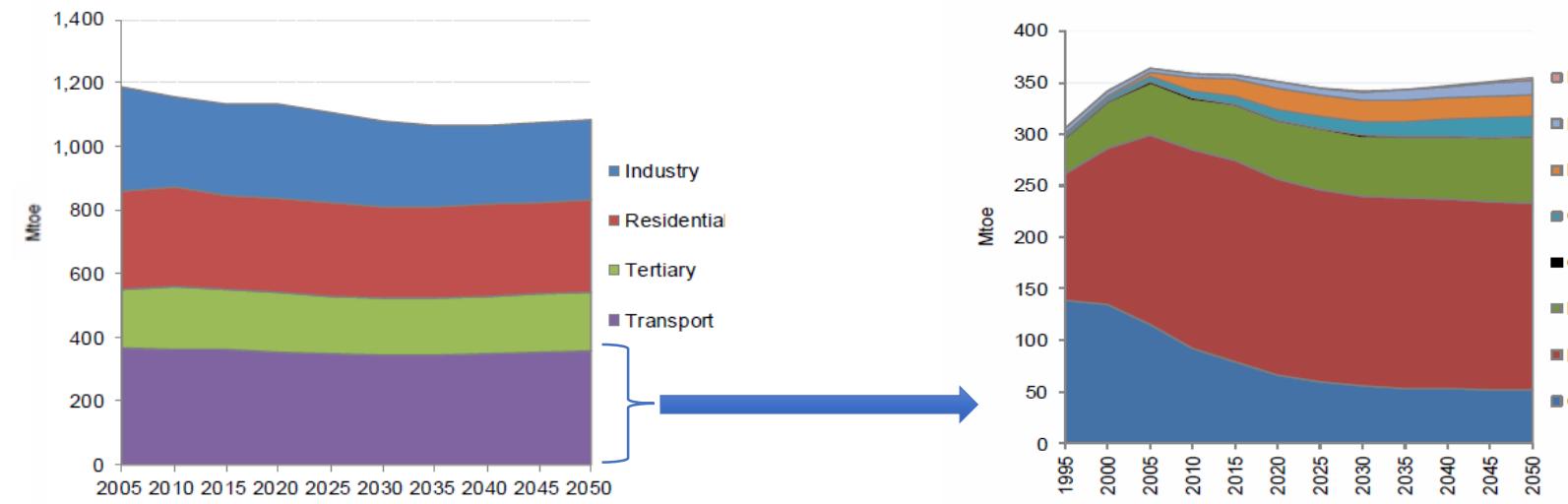
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1. Combustion (in internal combustion engines)

70% of total primary energy consumption mix in EU (2019)



Transport sector: 31 % of the total energy consumption in 2019



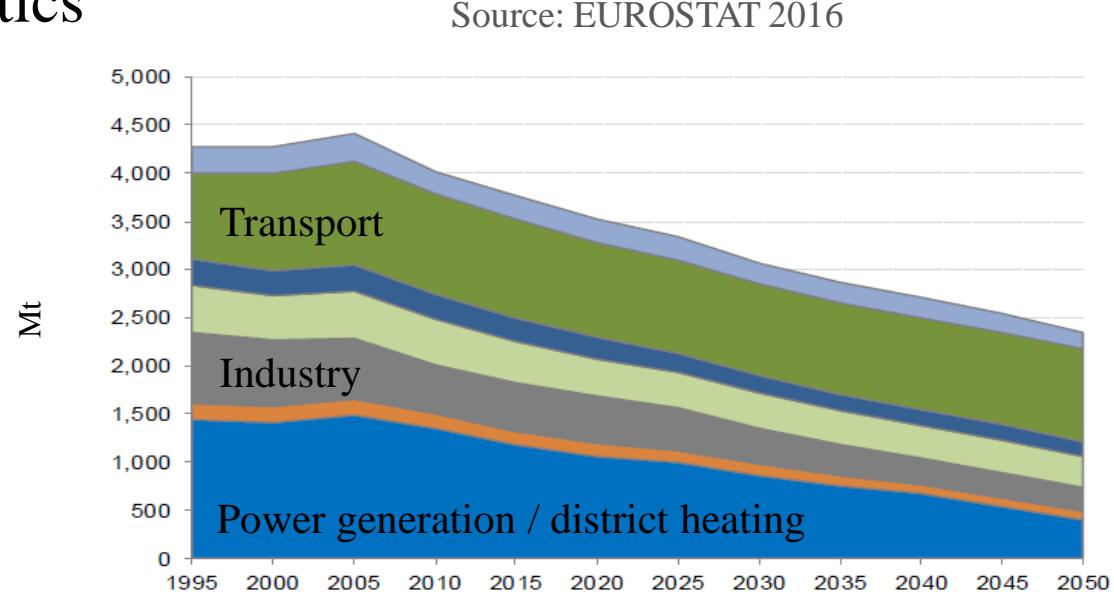
Source: EUROSTAT 2019

2. Combustion Issues

Economic and geopolitics

Environment / Health:

CO₂ emissions



Regulated pollutants (road transport, Euro VI):

CO, Total Hydrocarbons (THC), Non-Methane Hydrocarbons (NMHC), NO_x, Particulate Matter (PM)

Secondary pollutants: ozone

Unregulated pollutants: oxygenated compounds (alcohol, aldehydes, ...)

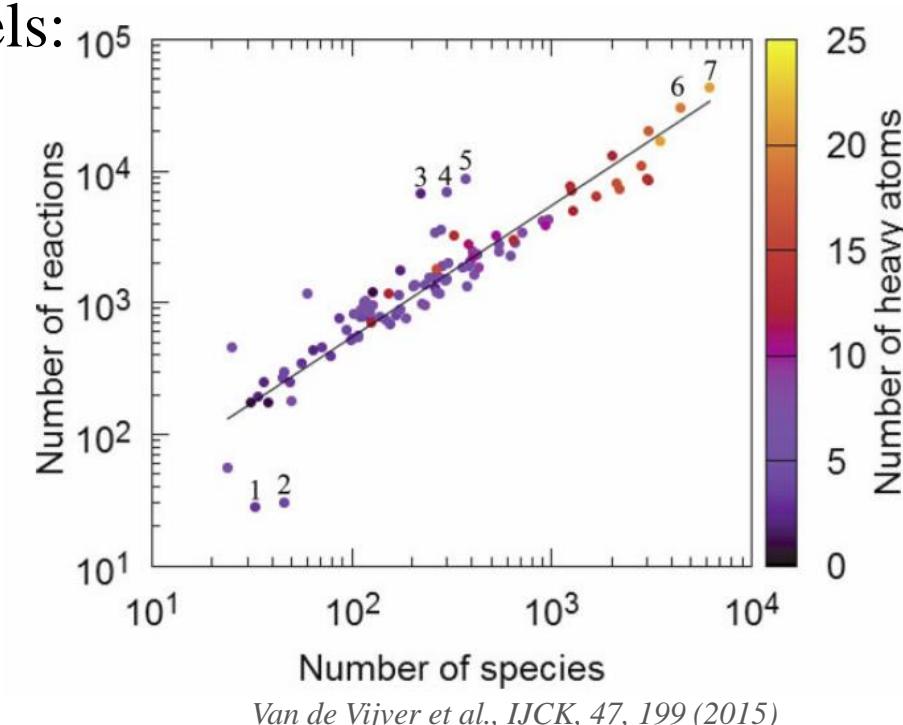
3. Combustion Kinetics

Kinetic models to understand:

- Complex behaviors (ignition, NTC, ...)
- Reactivity (fuel conversion, heat release)
- Products / pollutants formation

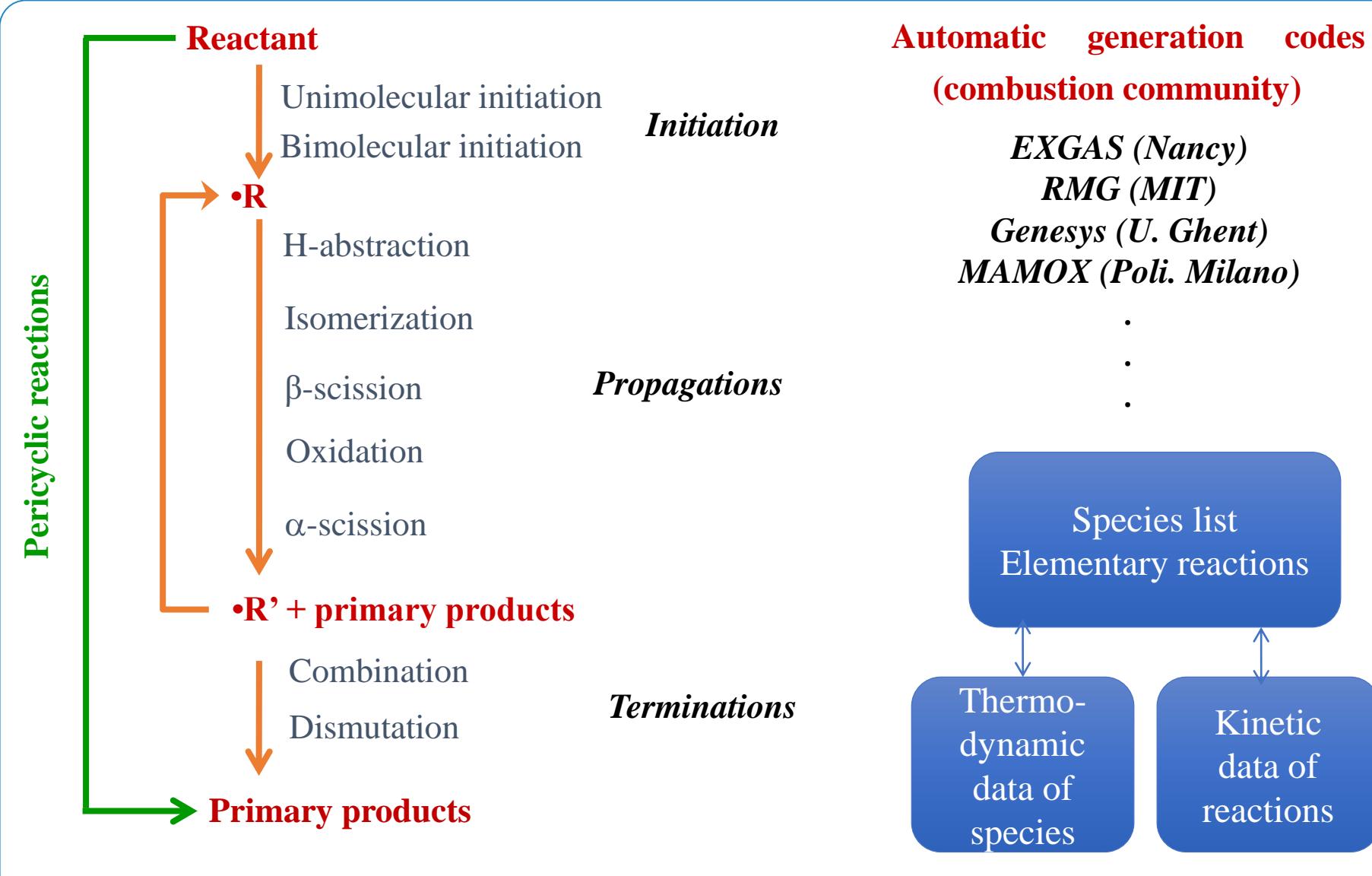
Detailed Chemical Kinetic Models:

- Chain reaction mechanism
- Composed of elementary reactions
 - Thermodynamic data for each species
 - Kinetic data for each reaction
- Size of mechanisms grows with molecular size

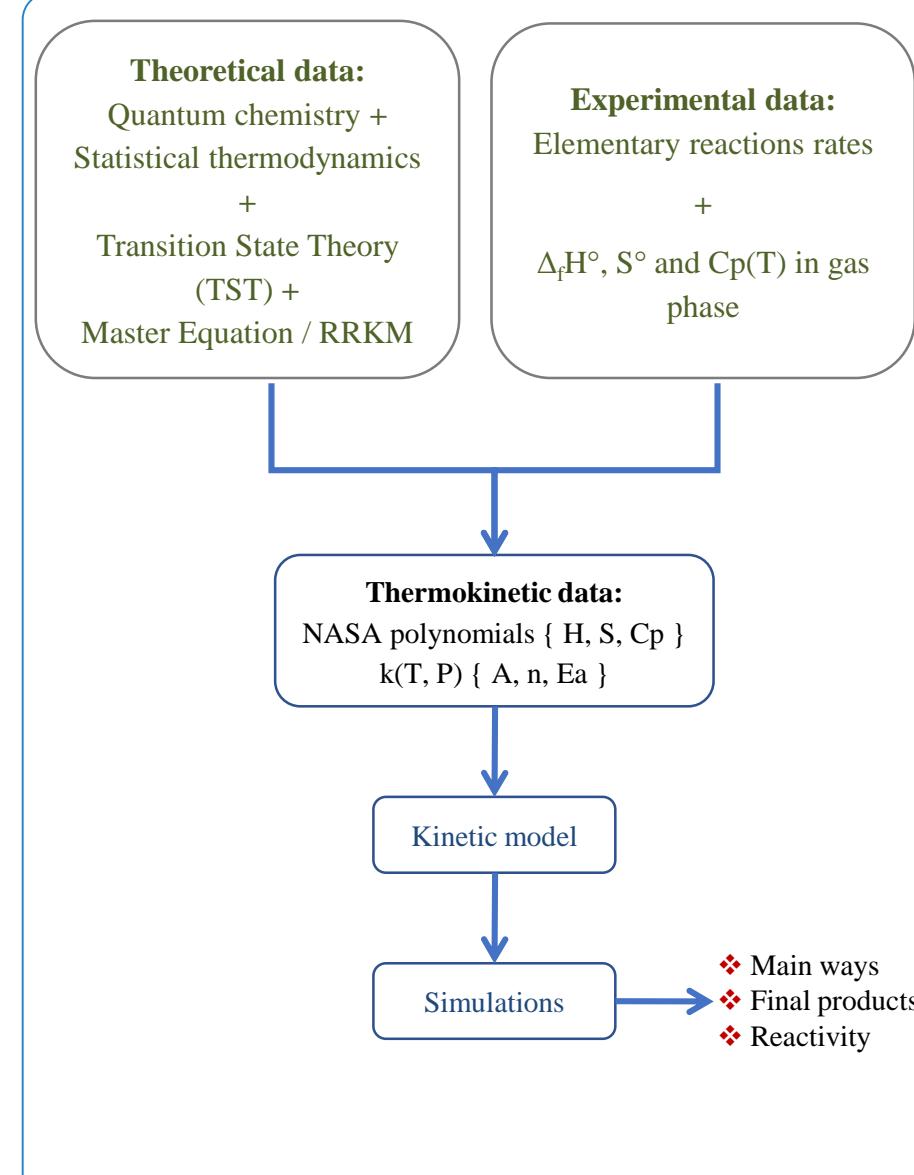


Van de Vijver et al., IJCK, 47, 199 (2015)

4. Reaction Mechanism



5. Computational methodology



Quantum Chemical calculations: Gaussian 09, MOLPRO

Benchmark (DFT, ab initio, composite methods, ...)

Thermokinetic data : TST

1D tunnelling corrections (asymmetric Eckart)

1D-HR approach for hindered rotors from relaxed scans

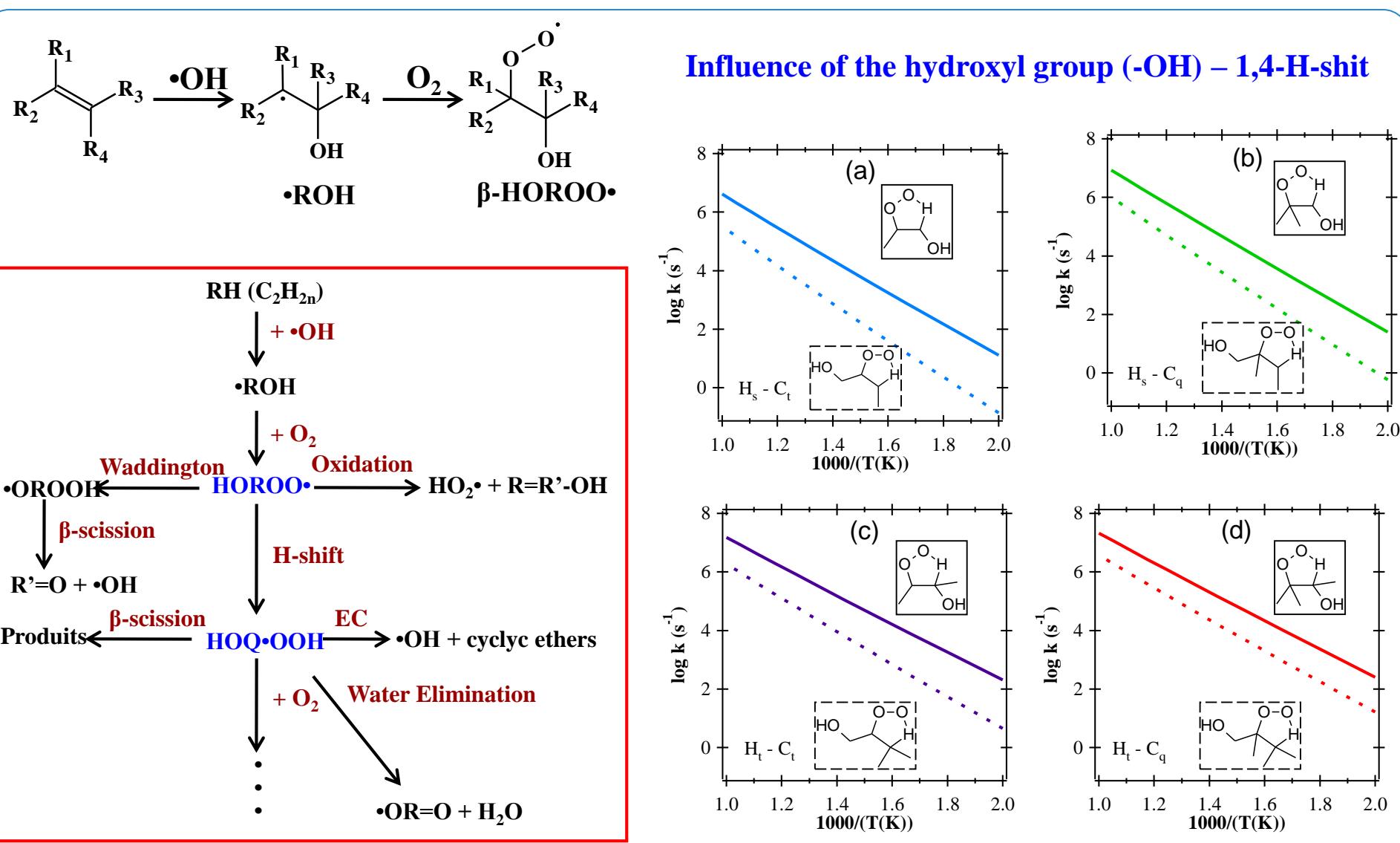
Pressure effects: RRKM/ME

<Delta_E_down> = 250 * (T/300)^0.85 (cm^-1) in N₂

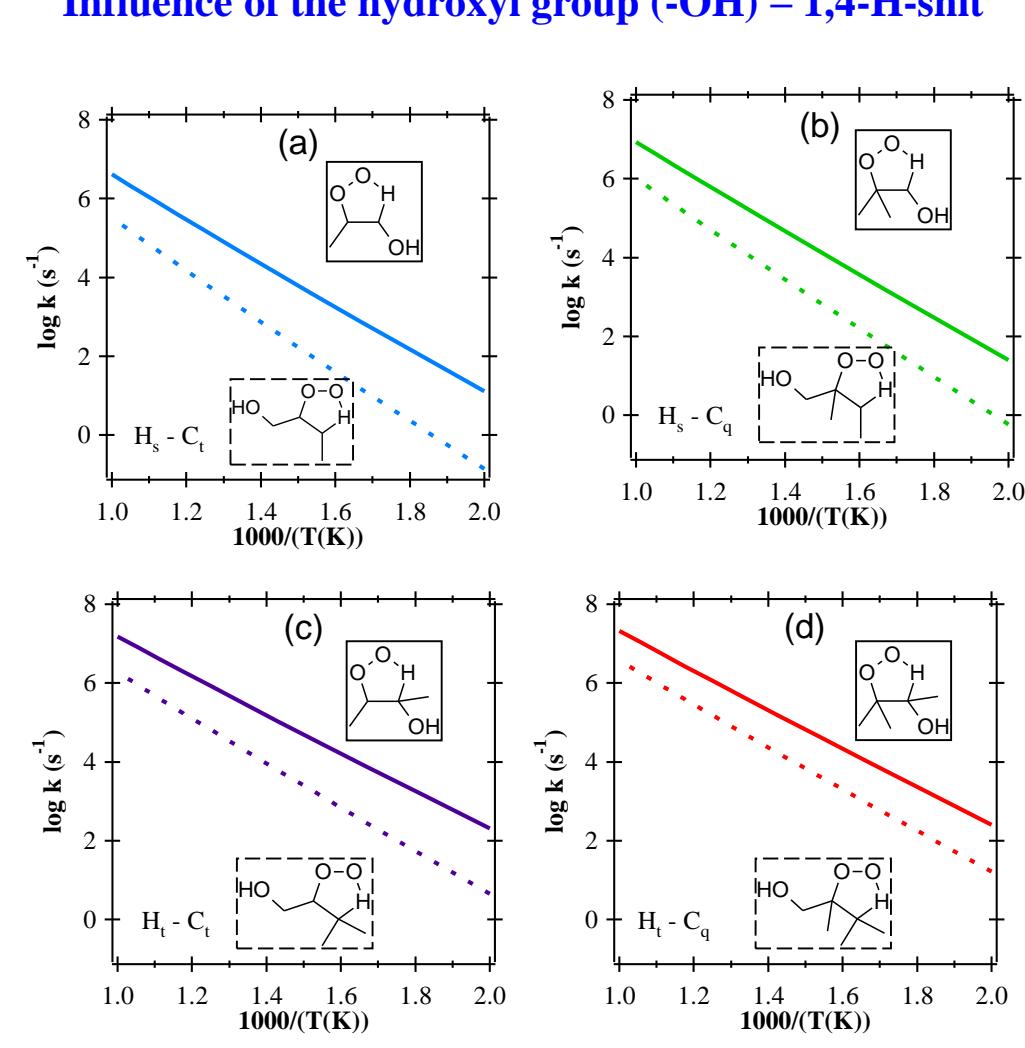
1D tunnelling corrections (asymmetric Eckart)

1D-HR approach for hindered rotors from relaxed scans

6. Example: Unimolecular decomposition of beta-HOROO• radicals



Influence of the hydroxyl group (-OH) – 1,4-H-shift



Proposition of a tabulation method based on different transition state models

Reference TS group1	TS-substitution	k = AT^n exp(-E/RT)		
		A	n	E
	R ₁ , R ₂ , R ₃ = H	1.35×10 ⁻³	4.55	26985
	R ₁ = Alkyl radical; R ₂ , R ₃ = H	9.48×10 ⁻¹	3.73	26469
	R ₁ , R ₃ = H; R ₂ = Alkyl radical	2.77×10 ⁻¹	3.77	23992
	R ₁ , R ₂ = Alkyl radical; R ₃ = H	1.43×10 ³	2.76	24752
	R ₁ = H; R ₂ , R ₃ = Alkyl radical; R ₃ = H	1.52×10 ³	2.64	22082
	R ₁ , R ₂ , R ₃ = Alkyl radical	6.12×10 ³	2.47	21089
Reference TS Group2	TS-substitution	k = AT^n exp(-E/RT)		
		A	n	E
	R ₁ , R ₂ , R ₃ = H	9.28×10 ³	2.46	21874
	R ₁ = Alkyl radical; R ₂ , R ₃ = H	1.76×10 ³	2.69	21498
	R ₁ , R ₂ = Alkyl radical; R ₃ = H	1.19×10 ⁶	1.94	22261
	R ₁ , R ₂ = H; R ₃ = Alkyl radical	1.92×10 ⁵	2.03	20190
	R ₁ , R ₃ = Alkyl radical; R ₂ = H	2.85×10 ⁵	2.00	19560
	R ₁ , R ₂ , R ₃ = Alkyl radical	3.01×10 ⁶	1.75	20103

* see at Phys. Chem. Chem. Phys., 2016, 18, 12231