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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

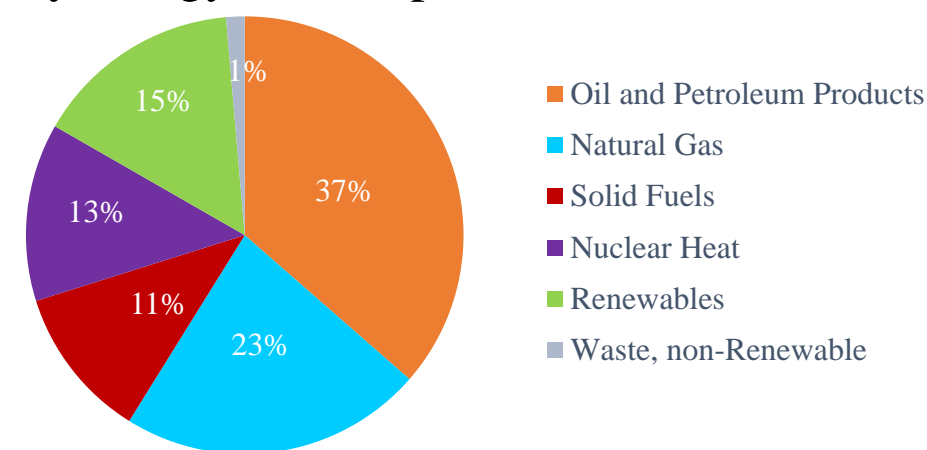
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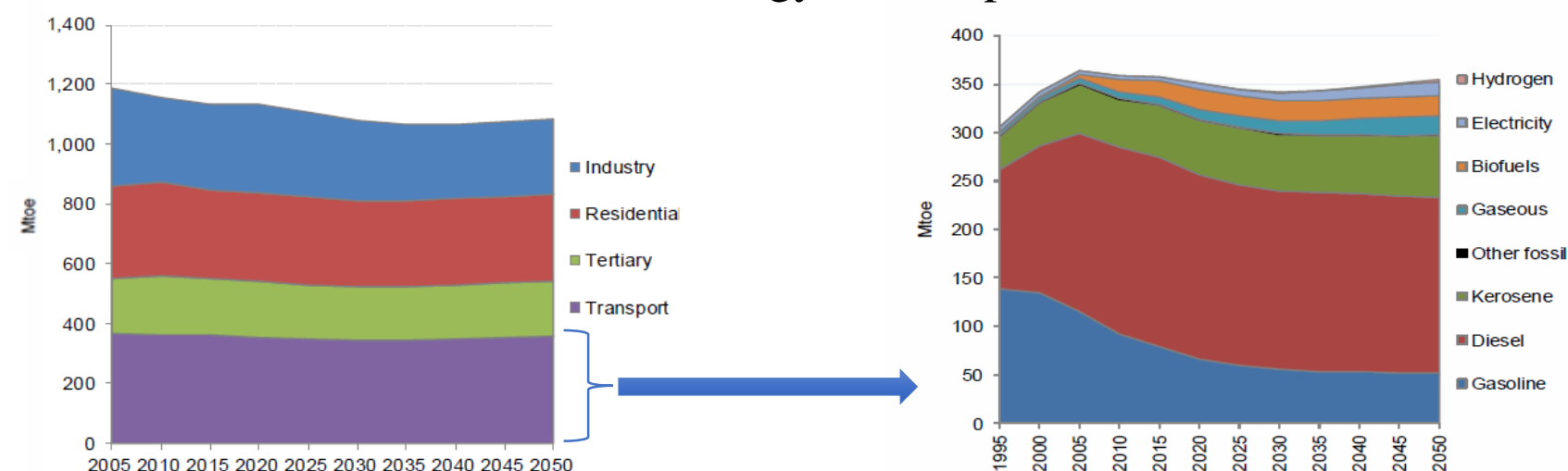
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1. Combustion (in internal combustion engines)

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



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



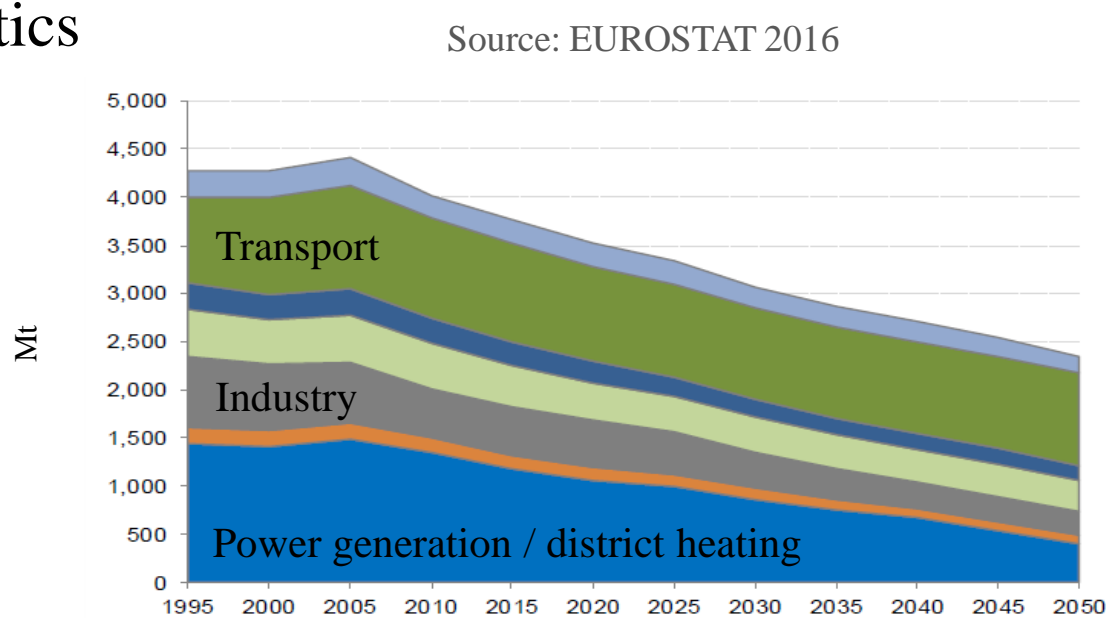
Source: EUROSTAT 2019

2. Combustion Issues

Economic and geopolitics

Environment / Health:

CO₂ emissions



Source: EUROSTAT 2016

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, ...)

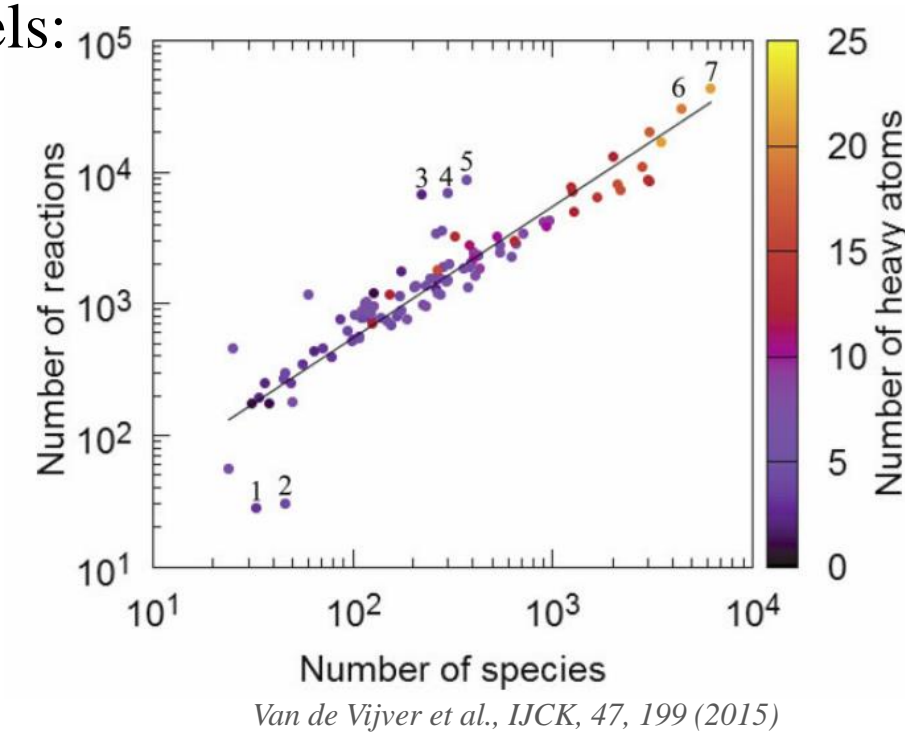
3. Combustion Kinetics

Kinetic models to understand:

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

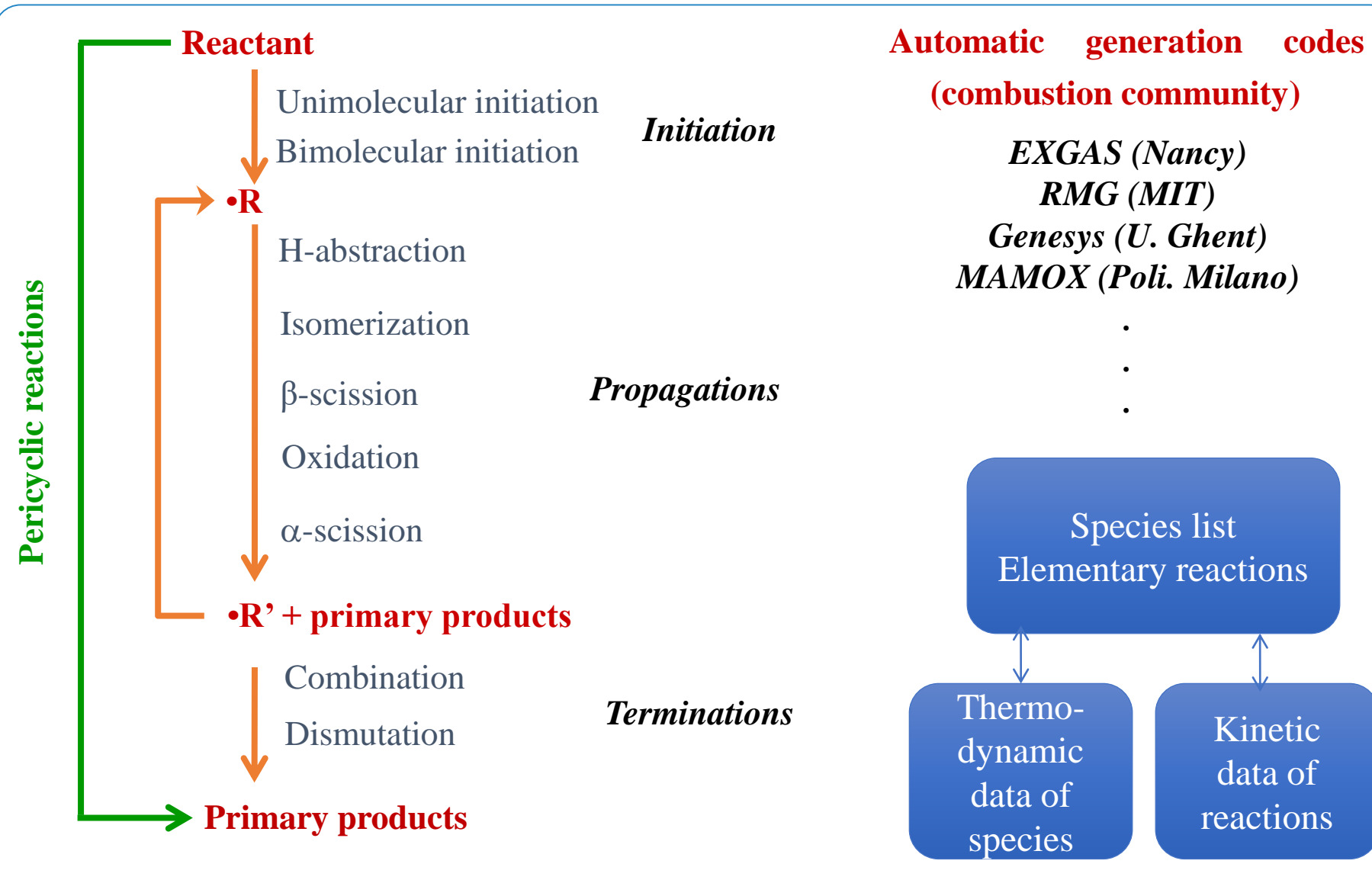
Detailed Chemical Kinetic Models:

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

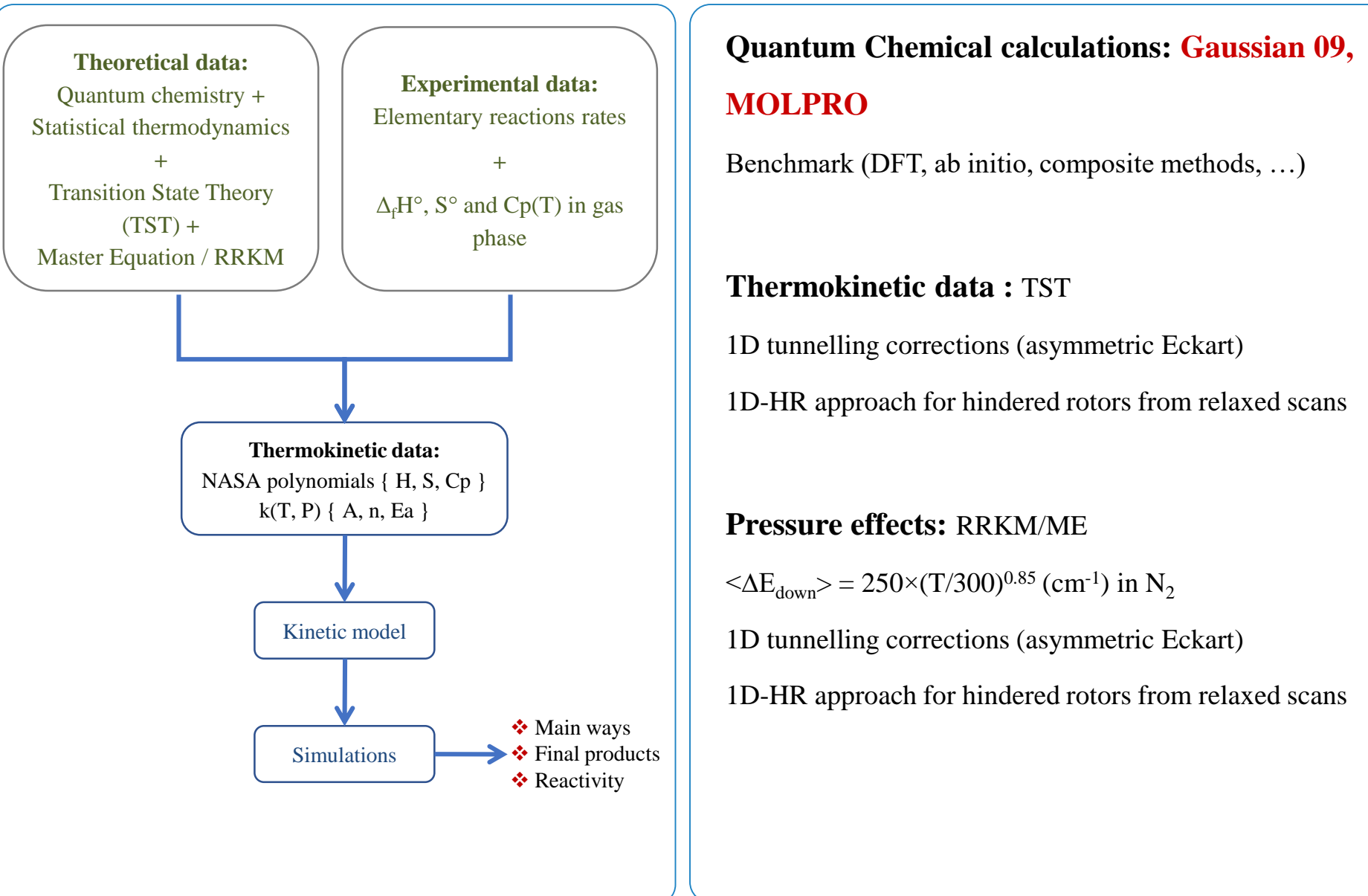


Van de Vijver et al., *IJCK*, 47, 199 (2015)

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

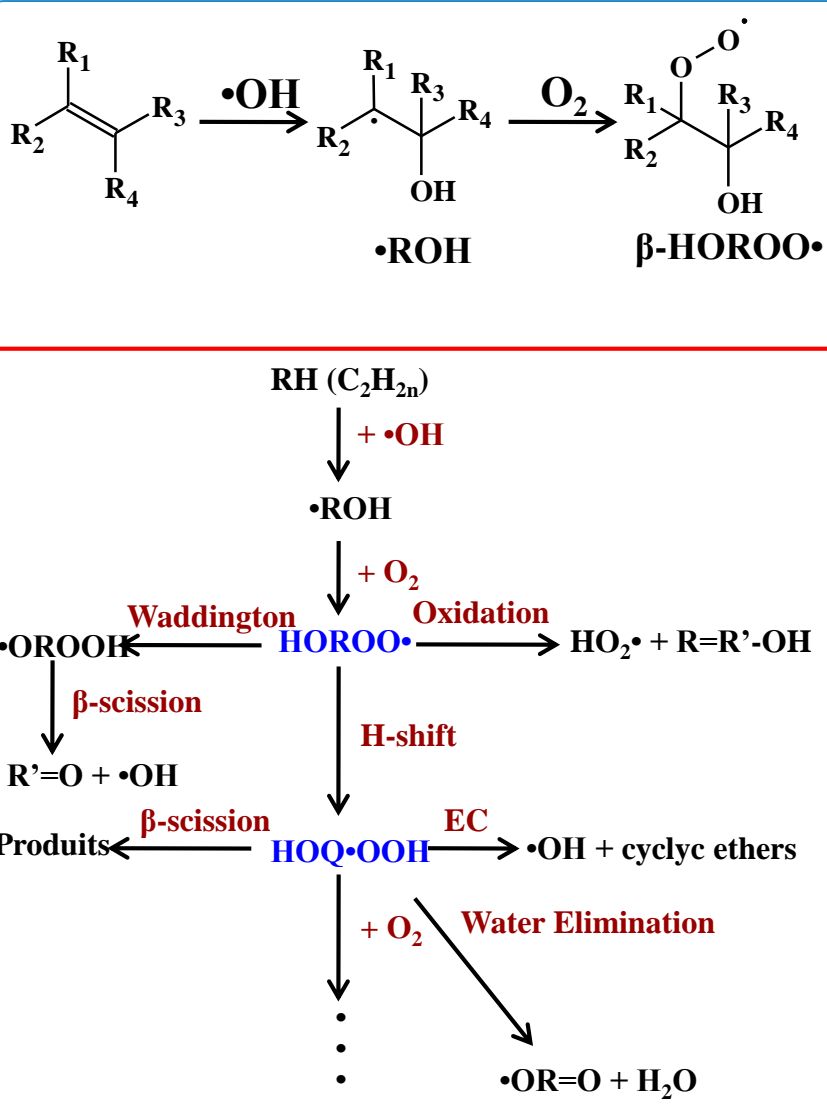
Pressure effects: RRKM/ME

$\langle \Delta E_{down} \rangle = 250 \times (T/300)^{0.85}$ (cm⁻¹) in N₂

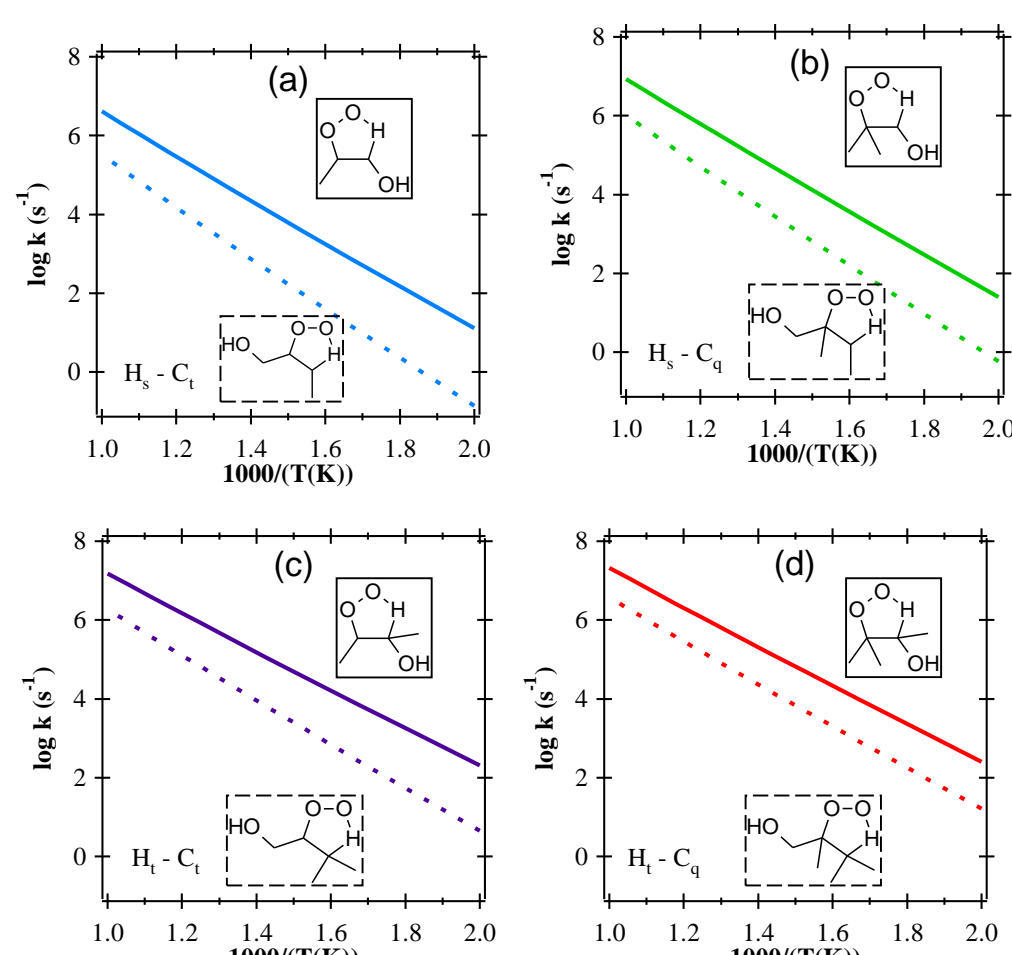
1D tunnelling corrections (asymmetric Eckart)

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

Reaction class: 1,4 H-shift of beta-HOROO• radicals*					
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;	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	22661
		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