Reactions of OH Radicals with Volatile Organic Compounds

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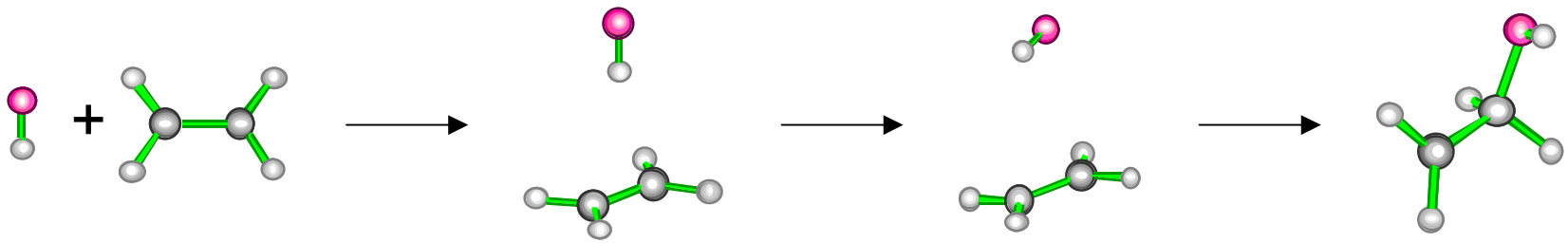

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Oxidation of VOCs in the Troposphere

- Oxidation of VOCs plays a central role in atmospheric chemistry, leading to ozone production and a cascade of secondary aerosol formation.

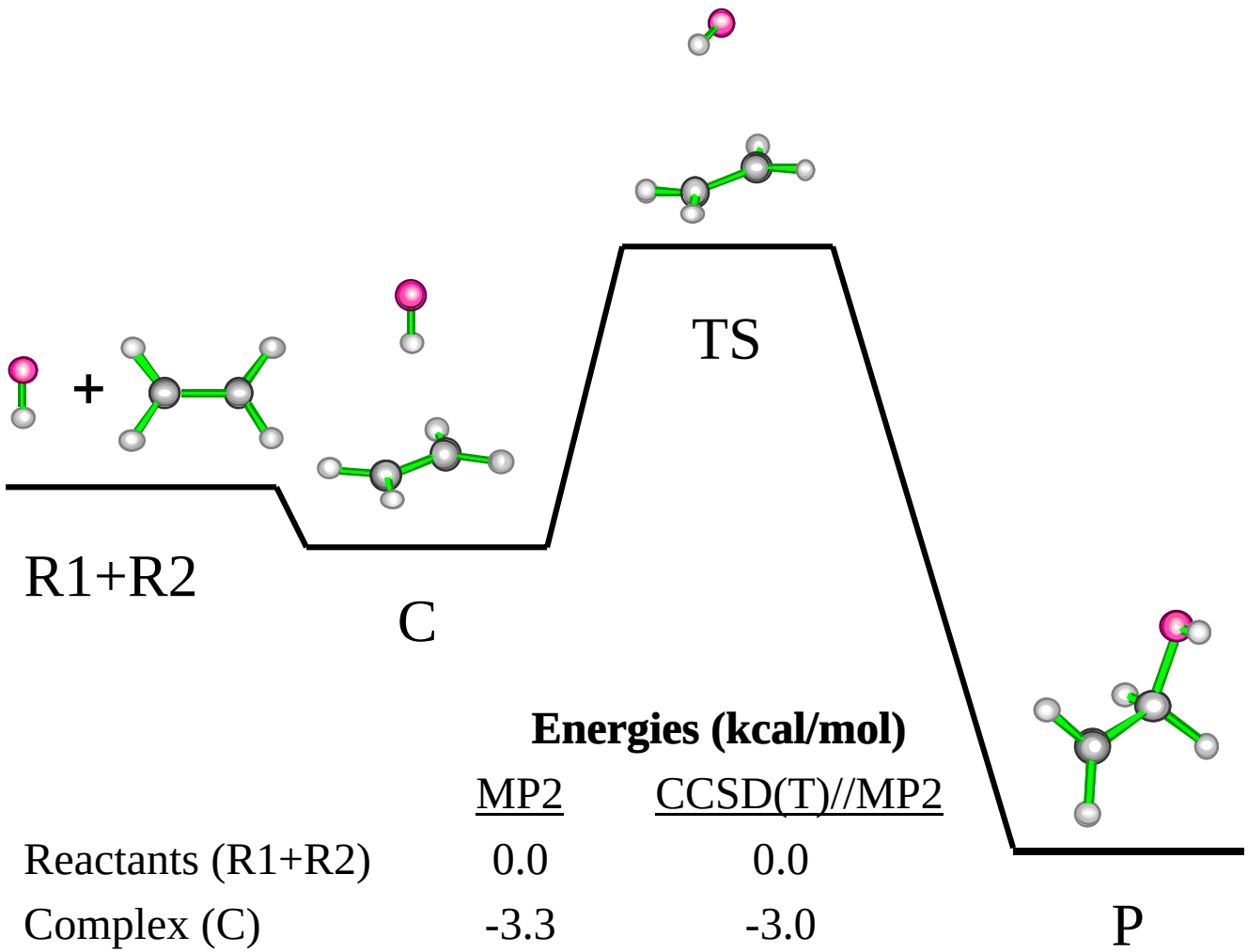
- Oxidation reactions involving radicals are difficult to study both experimentally and theoretically. Typically, radical reactions are very fast, complicating the identification of important reaction pathways and intermediates. Obtaining accurate rate constants from first-principles for radical reactions (with small or negative activation barriers) is computationally challenging.

OH Reaction with Ethylene

- The OH + C_2H_4 reaction is the simplest prototype of reactions of OH with unsaturated hydrocarbons, such as isoprene and terpenes, which are important in the troposphere.

- The goal of studying this prototypical reaction is to understand the level of theory (electronic structure and dynamics) needed to accurately predict rate constants for these reactions

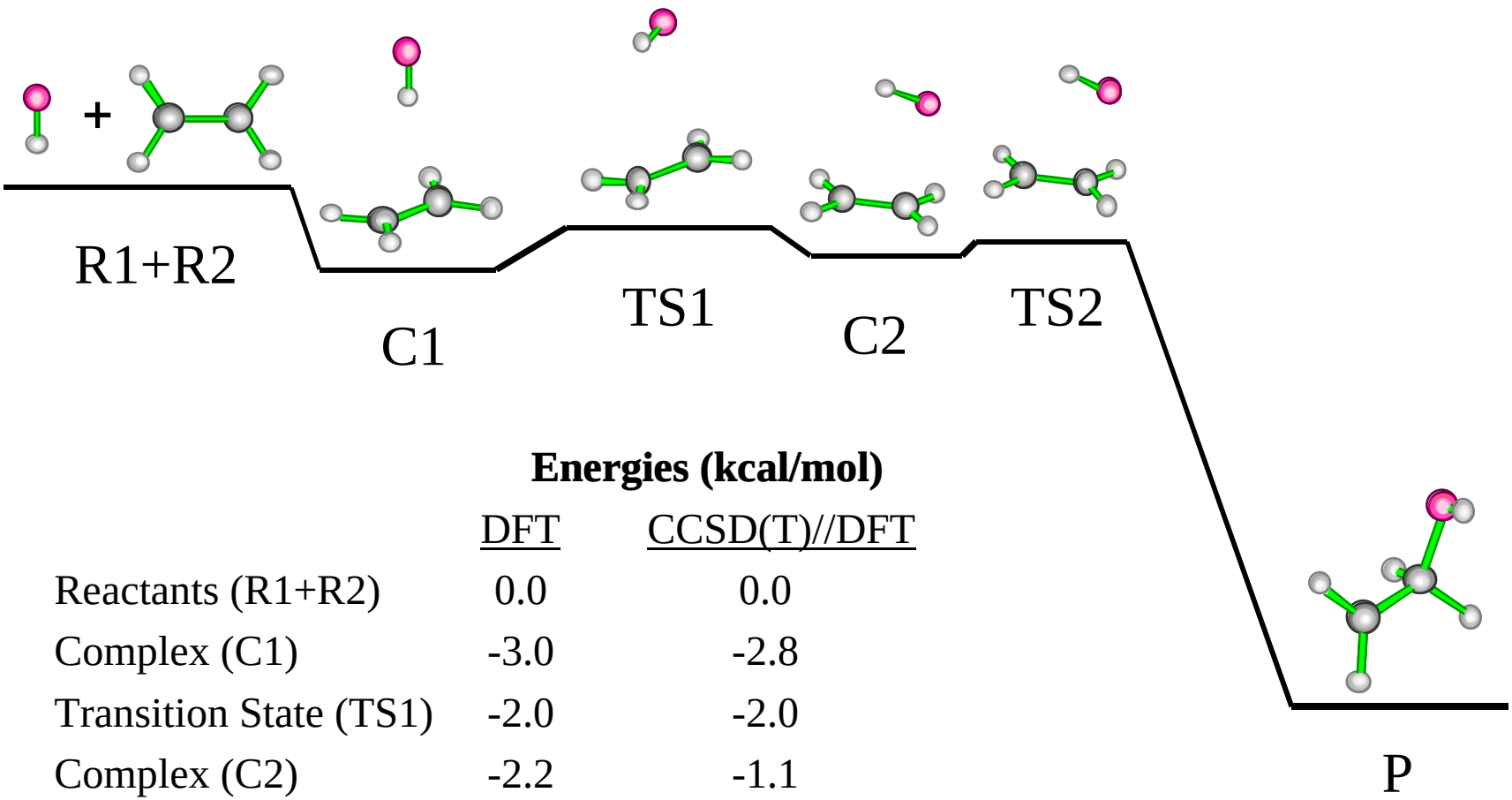
OH + C_2H_4 Reaction Path Schematic MP2/cc-pVDZ



Energies (kcal/mol)

	MP2	CCSD(T)//MP2
Reactants (R1+R2)	0.0	0.0
Complex (C)	-3.3	-3.0
Transition State (TS)	7.5	-1.2
Products (P)	-31.1	-26.1

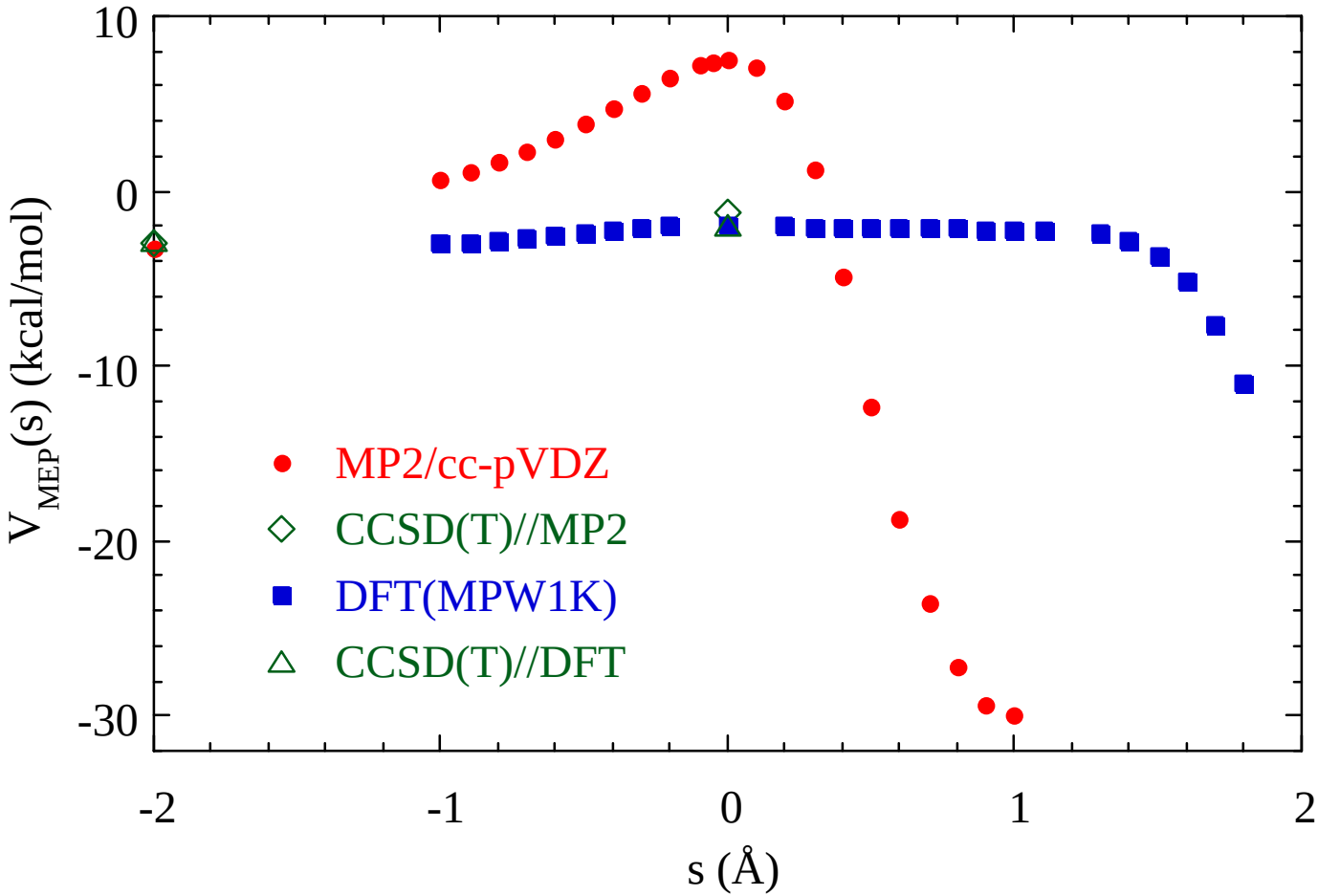
OH + C_2H_4 Reaction Path Schematic DFT (MPW1K)



Energies (kcal/mol)

	DFT	CCSD(T)//DFT
Reactants (R1+R2)	0.0	0.0
Complex (C1)	-3.0	-2.8
Transition State (TS1)	-2.0	-2.0
Complex (C2)	-2.2	-1.1
Transition State (TS2)	-2.2	-1.0
Products (P)	-33.6	-26.3

Energies Along OH + C_2H_4 Minimum Energy Path



- Spin contamination in the MP2 method is high, and spin projected methods yield more reasonable energetics, but are not quantitative
- DFT with MPW1K functional of Fast et al. provides good description of the reaction energetics