UNIVERSITY OF COPENHAGEN

Trends in Peroxy Radical Hydrogen Shift Rate Constants

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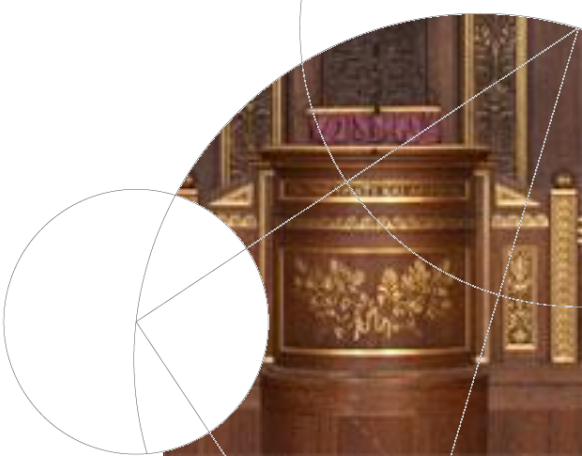
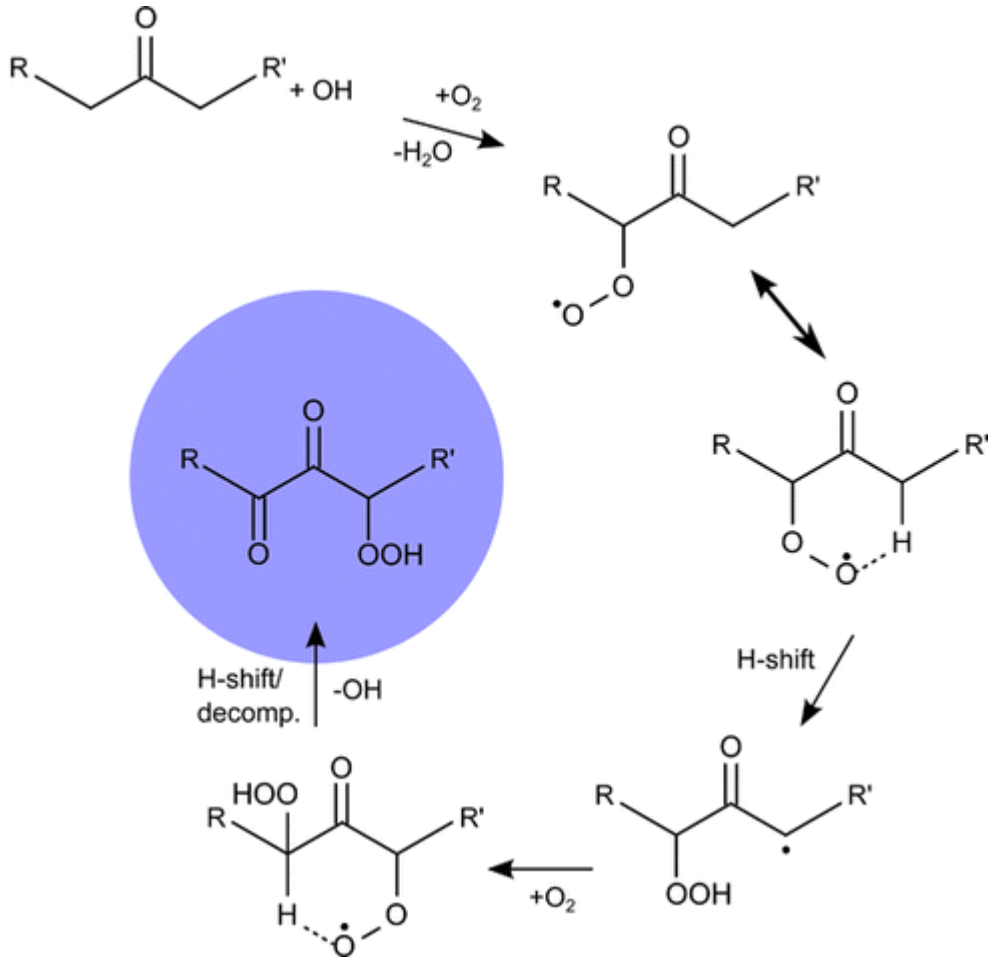
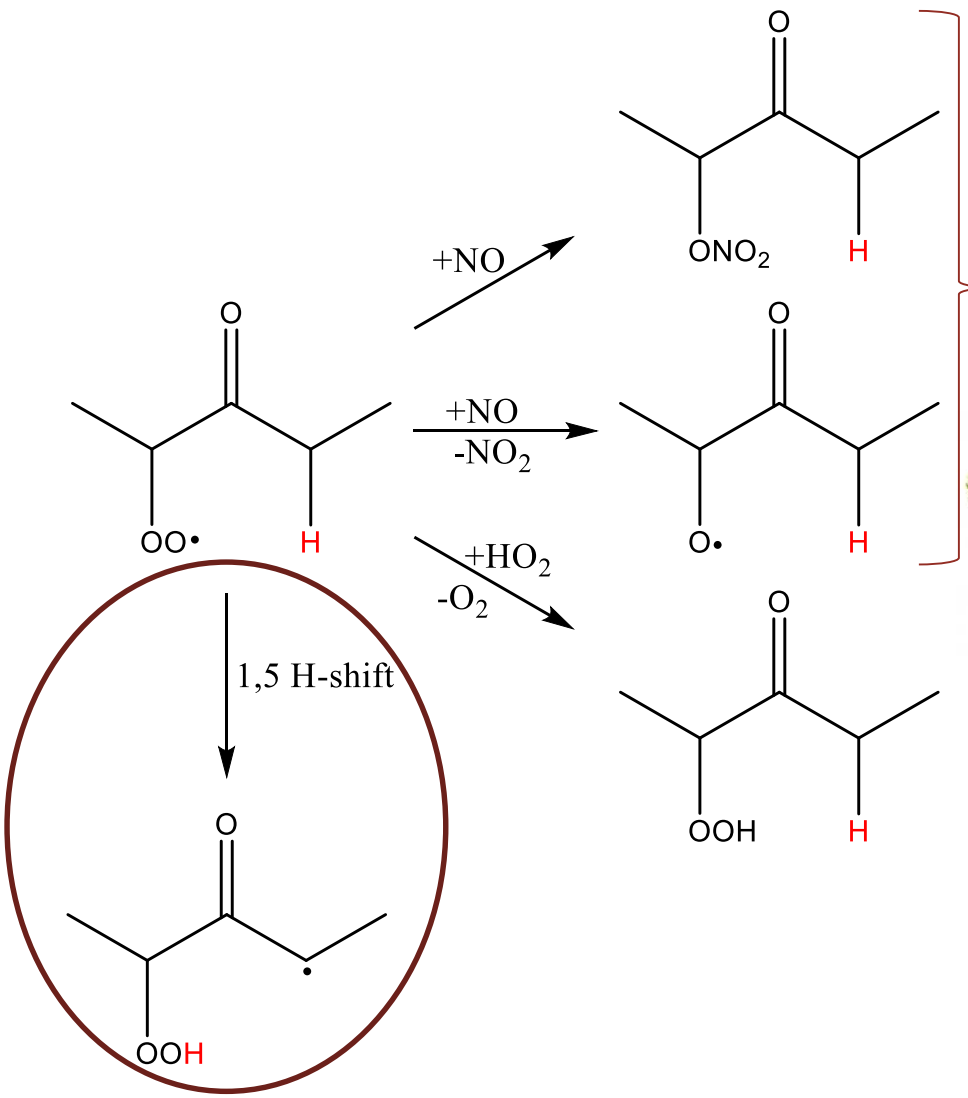


Autoxidation



Crounse *et al*. JPCL 2013

Hydrogen Shift Reactions

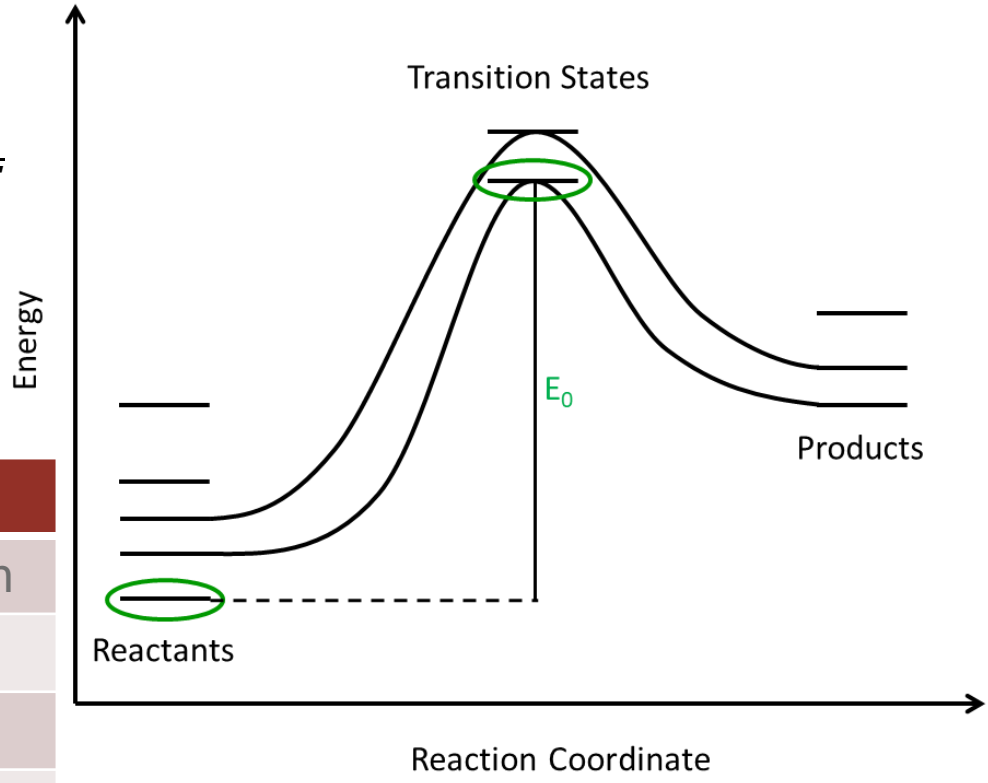


Pseudo first-order rate constants

	Pristine	Urban
$\sim 10^{-3}$ s^{-1}	(10 ppt)	~ 1 s^{-1} (10 ppb)
$\sim 10^{-2}$ s^{-1}	(40 ppt)	$\sim 10^{-3}$ s^{-1} (4 ppt)

Multi-Conformer Transition State Theory

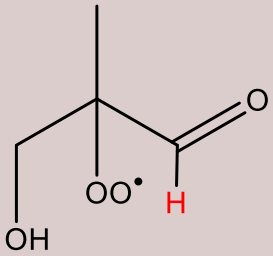
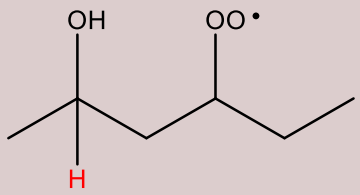
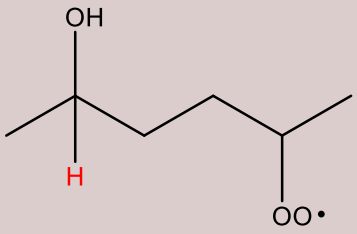
$$k = \kappa \frac{k_B T}{h} \frac{\sum_{i=1}^{TS\ conformers} e^{\frac{-\Delta E_i}{k_B T}} Q_{TS,i}}{\sum_{j=1}^{R\ conformers} e^{\frac{-\Delta E_j}{k_B T}} Q_{R,j}} e^{\frac{-E_0}{k_B T}}$$



Method	Action
MMFF	Conformer Search
B3LYP/6-31+G(d)	Optimization
2 kcal/mol cutoff	
ωB97X-D/aVTZ	Optimization Frequencies
CCSD(T)-F12a/VDZ-F12	Single point energy

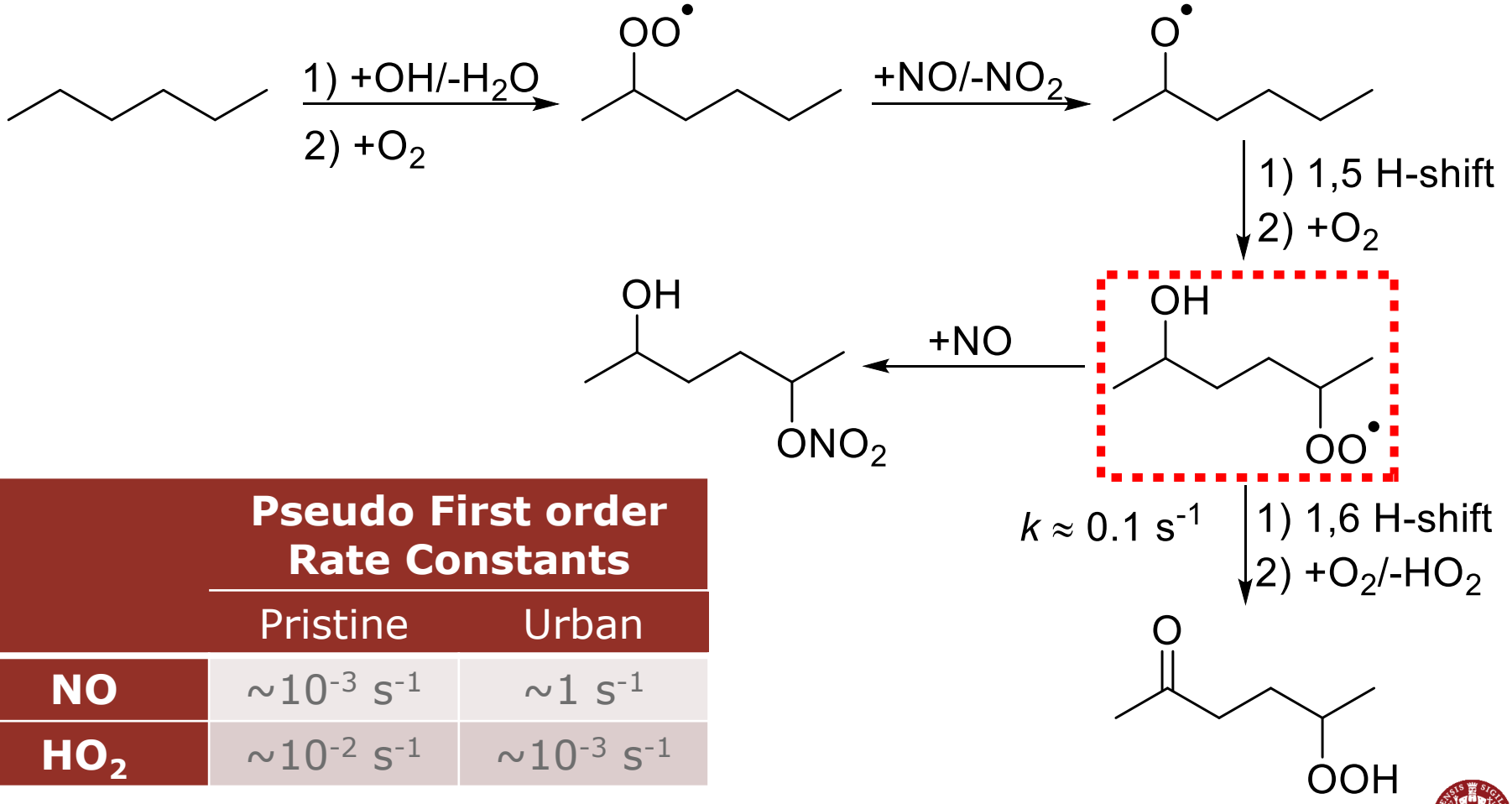
Møller *et al.* JPC A 2016

Reactions with Experimental Rate Constants

Reactant				
Theory	S,R	0.48 s^{-1}	0.13 s^{-1}	0.30 s^{-1}
	S,S		0.11 s^{-1}	0.055 s^{-1}
Experiment		0.5 s^{-1}	0.048 s^{-1}	0.14 s^{-1}

Crounse *et al.* JPC A 2012
Møller *et al.* JPC A 2016
Praske *et al.* PNAS 2018

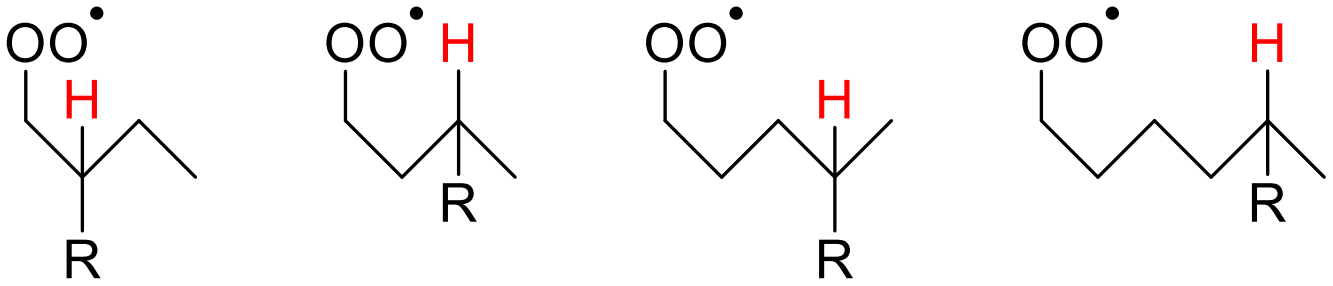
Oxidation of Gasoline Emissions



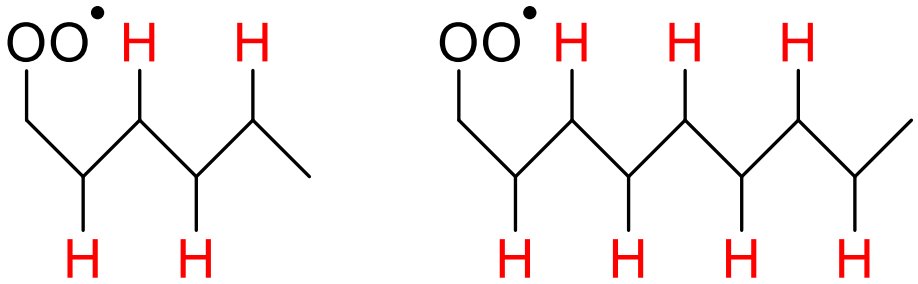
	Pseudo First order Rate Constants	
	Pristine	Urban
NO	~10^{-3} s^{-1}	~1 s^{-1}
HO_2	~10^{-2} s^{-1}	~10^{-3} s^{-1}

Praske *et al*. PNAS 2018

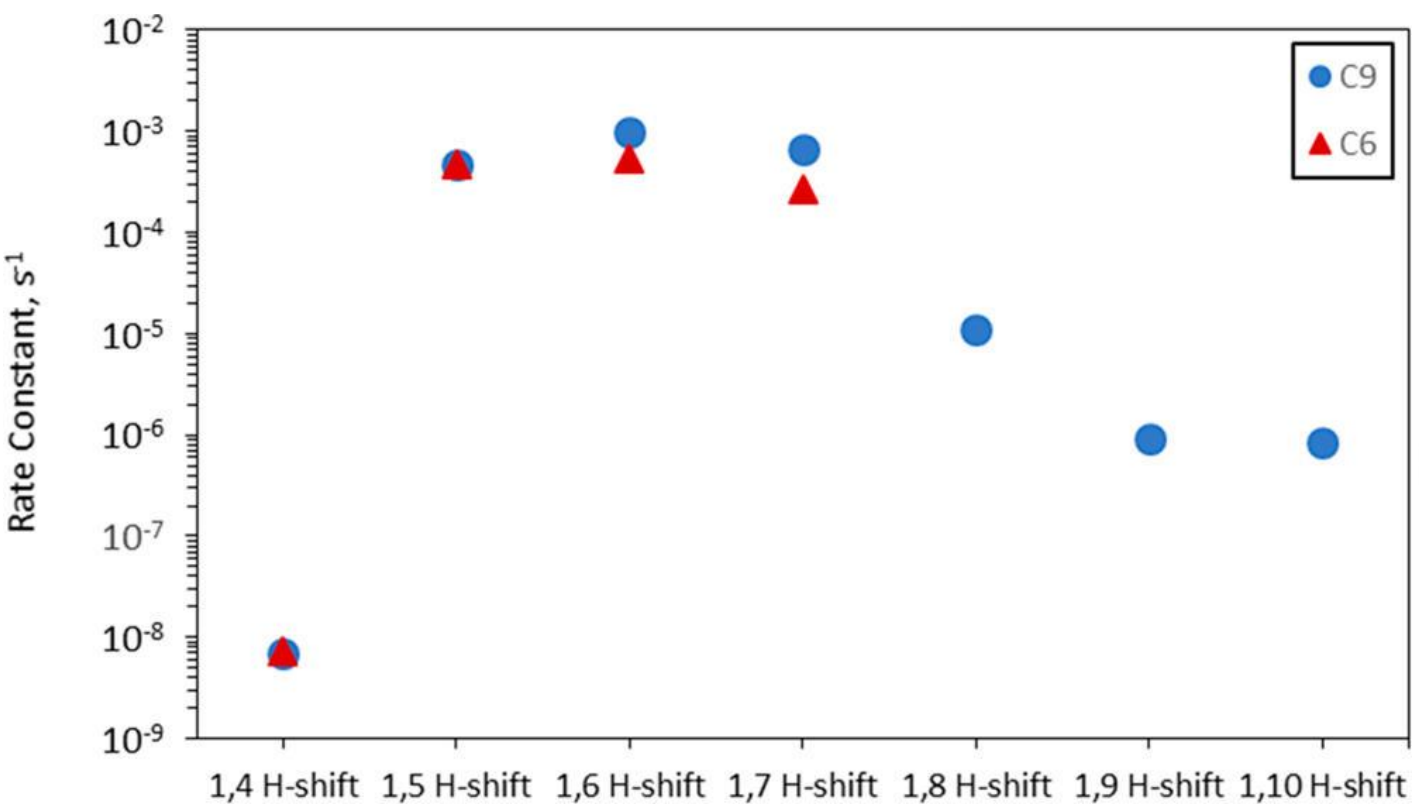
Systematic Set of Reactions

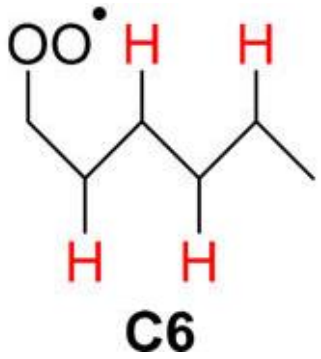


R: C=O, C=C, OH, OCH_3, OOH, CH_3, H, ONO_2, F

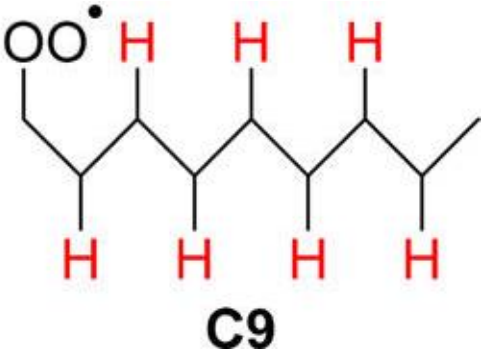


Effect of Size on H-shifts



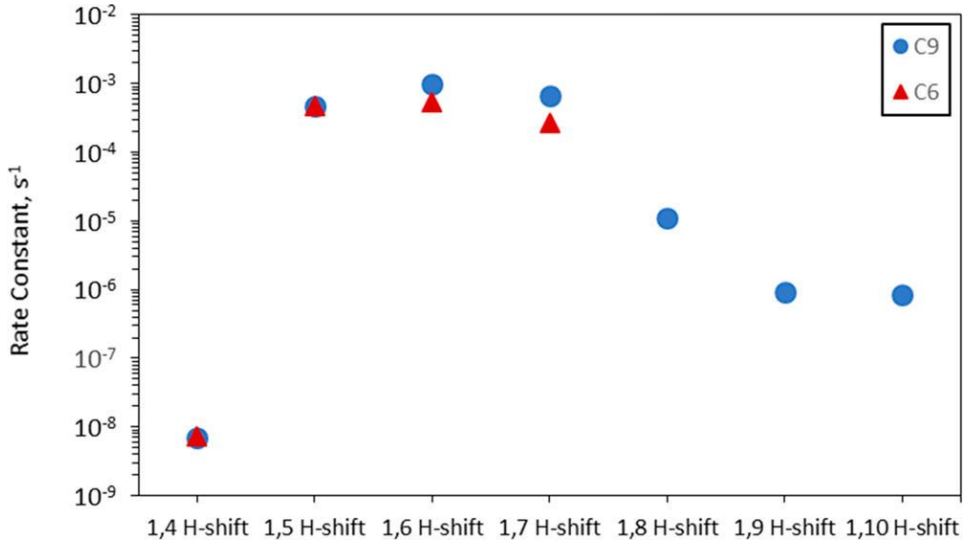


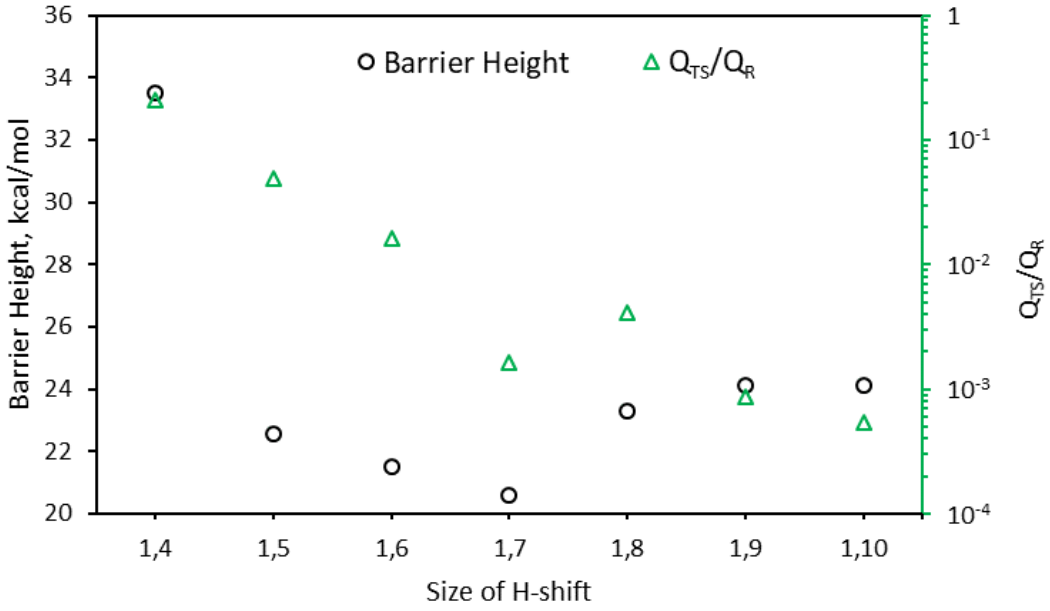
C6

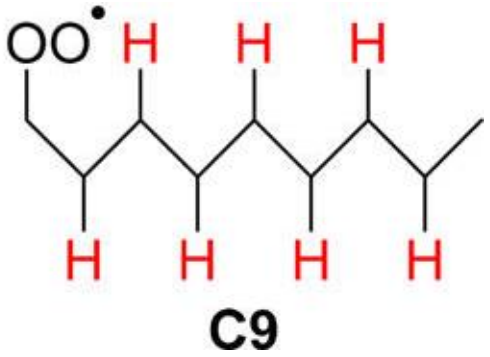


C9

Effect of Size on H-shifts

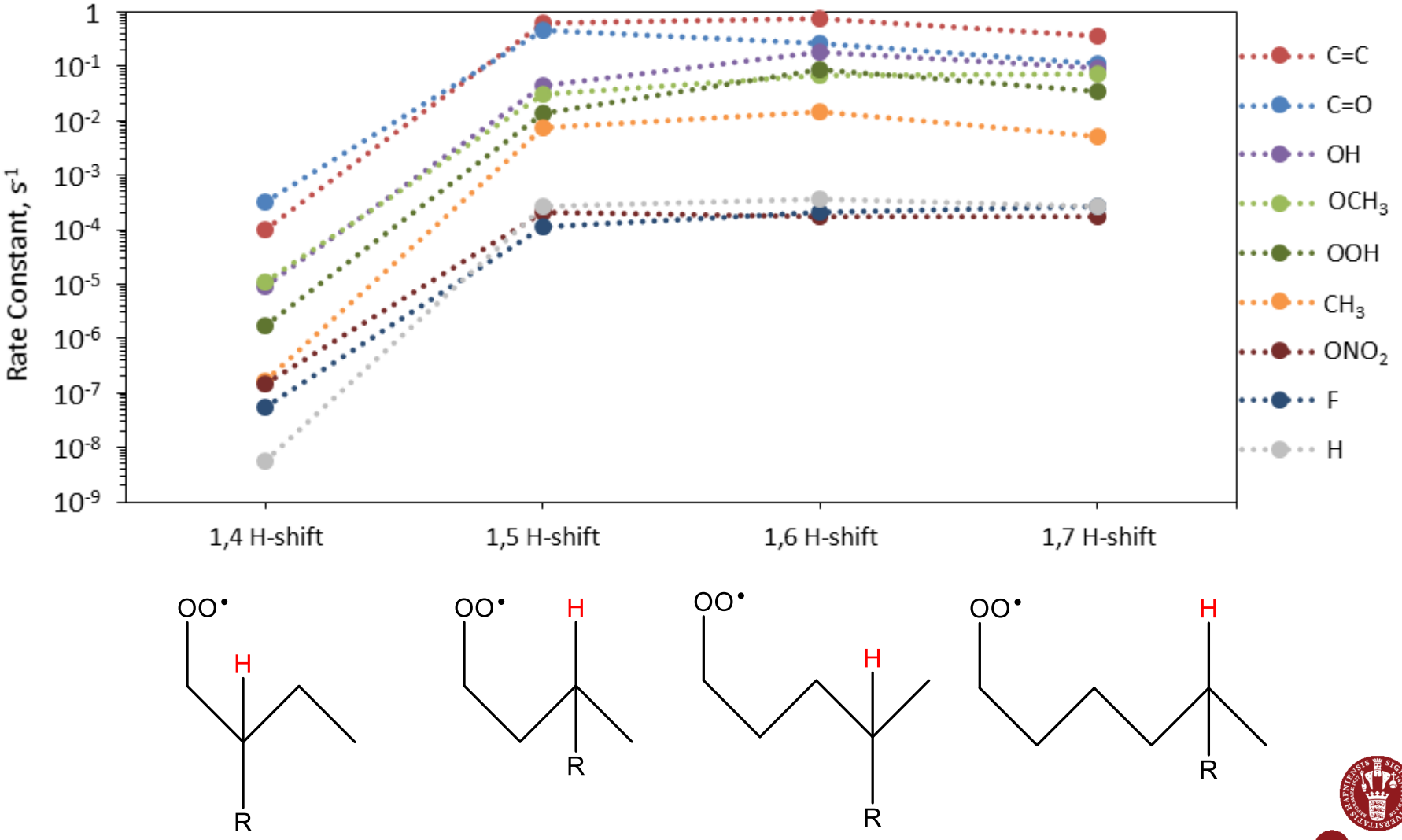




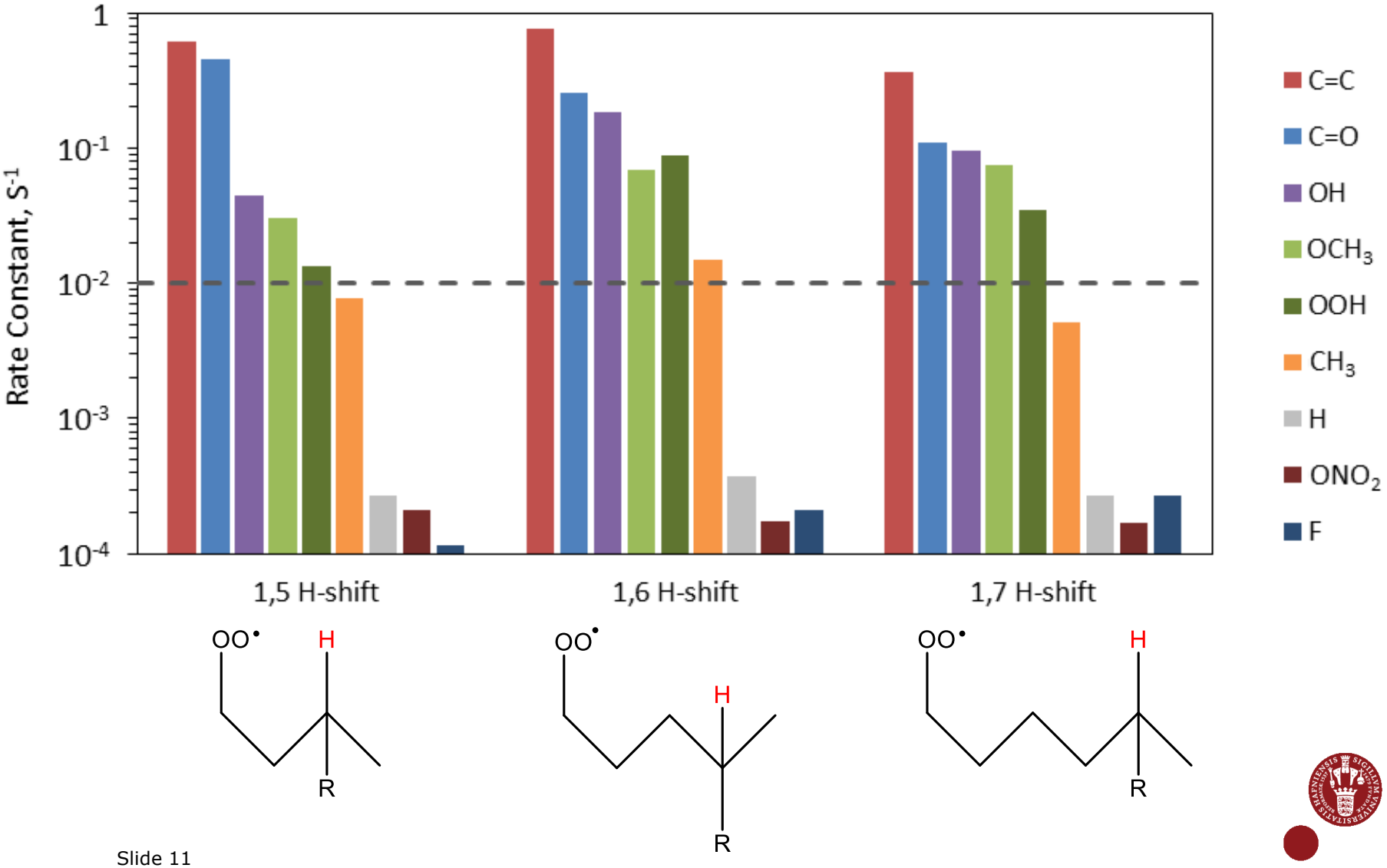


C9

Effect Functional Groups

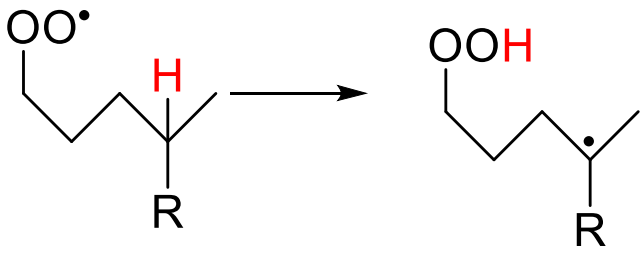


Effect of Functional Groups



Conclusions

- Unsubstituted 1,5; 1,6 and 1,7 H-shifts have rate constants of ~10^{-3} s^{-1}



R : $\underbrace{C{=}C > C{=}O}_{>\times 400} > \underbrace{OH \sim OCH_3 \geq OOH}_{>\times 50} > \underbrace{CH_3}_{>\times 20} > \underbrace{H}_{\equiv 1} \sim \underbrace{ONO_2 \sim F}_{\sim\times 1}$

- Substituted 1,5 to 1,7 H-shifts are often faster than 0.01 s^{-1} and need to be considered in atmospheric oxidation mechanisms

Acknowledgements

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The Kjaergaard Group

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