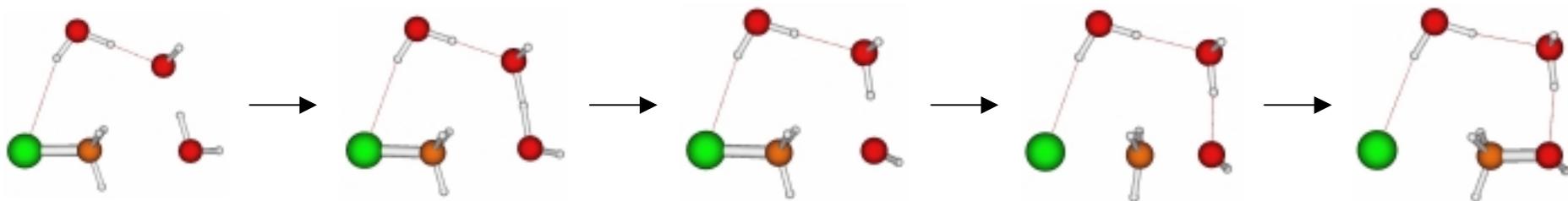


# Reactions of OH<sup>-</sup> with Chlorinated Methanes

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# Experimental Kinetics for $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$



## Gas-Phase $\text{S}_{\text{N}}2$ Reaction Rates

Bohme & Raksit JACS 106, 3447 (1984)



$m$	$k$ ( $\text{M}^{-1}\text{s}^{-1}$ )
0	$9 \times 10^{11}$
1	$4 \times 10^{11}$
2	$< 1 \times 10^9$
3	$< 6 \times 10^8$

## Gas-Phase PT Reaction Thresholds

Hierl et al., JPC 99, 15655 (1995)



$m$	$E_{\text{tr}}$ (kcal/mol)
0	9
1	37
2	53

Microsolvation leads to large decreases in reaction rates and large increases in reaction energies

# Experimental Kinetics for $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$

Nucleophilic sub. ( $\text{S}_{\text{N}}2$ ):  $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n \rightarrow \text{CH}_{(4-n)}\text{Cl}_{(n-1)}\text{OH} + \text{Cl}^-$

Proton transfer (PT):  $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n \rightarrow \text{CH}_{(3-n)}\text{Cl}_n^- + \text{H}_2\text{O}$

## Solution-Phase Reaction

$\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$  (T=373 K)

## $\text{S}_{\text{N}}2$ Reaction Rates ( $\text{M}^{-1}\text{s}^{-1}$ )

$\text{OH}^- + \text{CH}_3\text{Cl}$  (T=298 K)

$n$	$k$ ( $\text{M}^{-1}\text{s}^{-1}$ )	Reaction	Gas phase <sup>a</sup>	Aqueous phase <sup>b</sup>
1	$2.4 \times 10^{-2}$	$\text{S}_{\text{N}}2$	$9.6 \times 10^{11}$	$6.3 \times 10^{-6}$
2	$1.6 \times 10^{-4}$	$\text{S}_{\text{N}}2$		
3	0.3	PT		
4	$<10^{-5}$	$\text{S}_{\text{N}}2$		

<sup>a</sup> Olmstead & Brauman JACS 99, 4219 (1977)

<sup>b</sup> Bathgate & Moelwyn-Hughes JCS 2642 (1959)

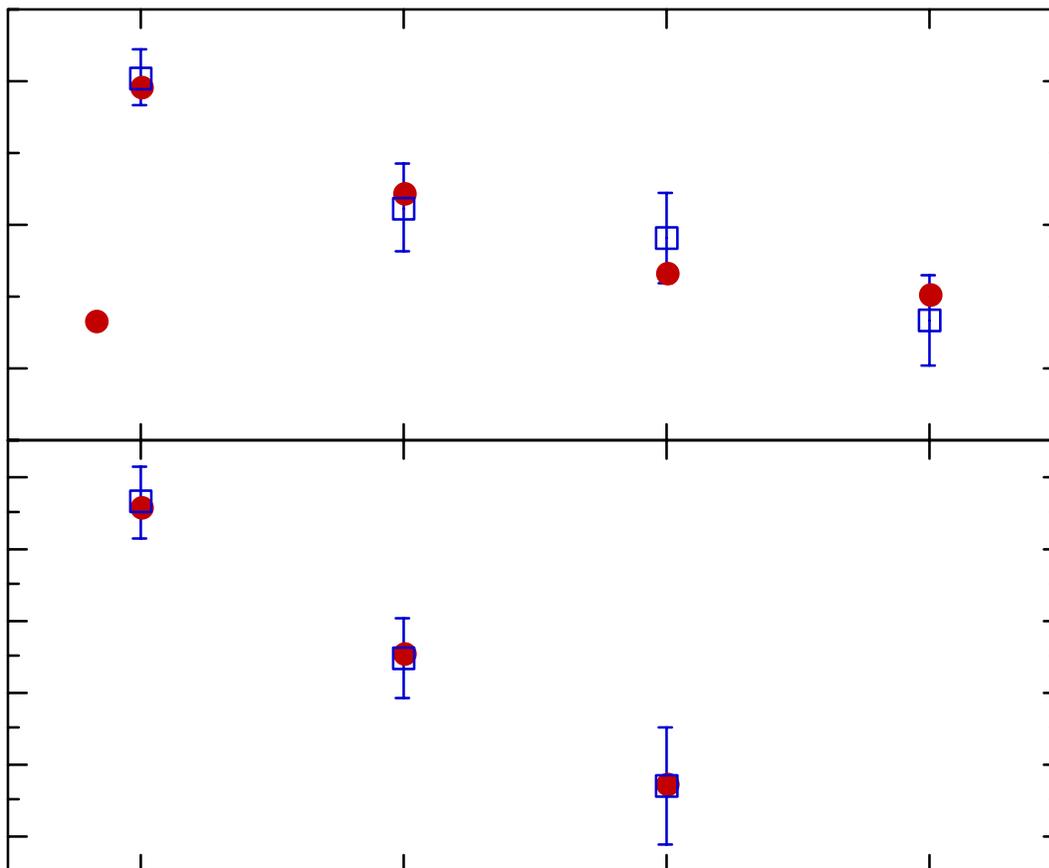
Mabey & Mill JPC Ref Data 7, 383 (1978)

- Large variation in reaction rates with number of chlorine atoms, and change in reaction mechanism for  $n=3$  (PT vs.  $\text{S}_{\text{N}}2$ )
- Bulk solvation leads to change in rate constant by **17 orders of magnitude**

## Benchmarking of Electronic Structure Methods

- Computed reaction enthalpies are compared to experimental values ( $\Delta H_{\text{rxn}}$ )
- We compute  $\Delta H_{\text{rxn}}(0 \text{ K})$  by adding zero-point energy differences to  $\Delta E_{\text{rxn}}$  from harmonic frequencies at MP2/aug-cc-pvdz level of theory
- The experimental values of  $\Delta H_{\text{rxn}}(0 \text{ K})$  are computed using experimental  $\Delta H_f^0(0 \text{ K})$  for the reactant and product species

# Comparison of Experimental and Calculated Reaction Enthalpies

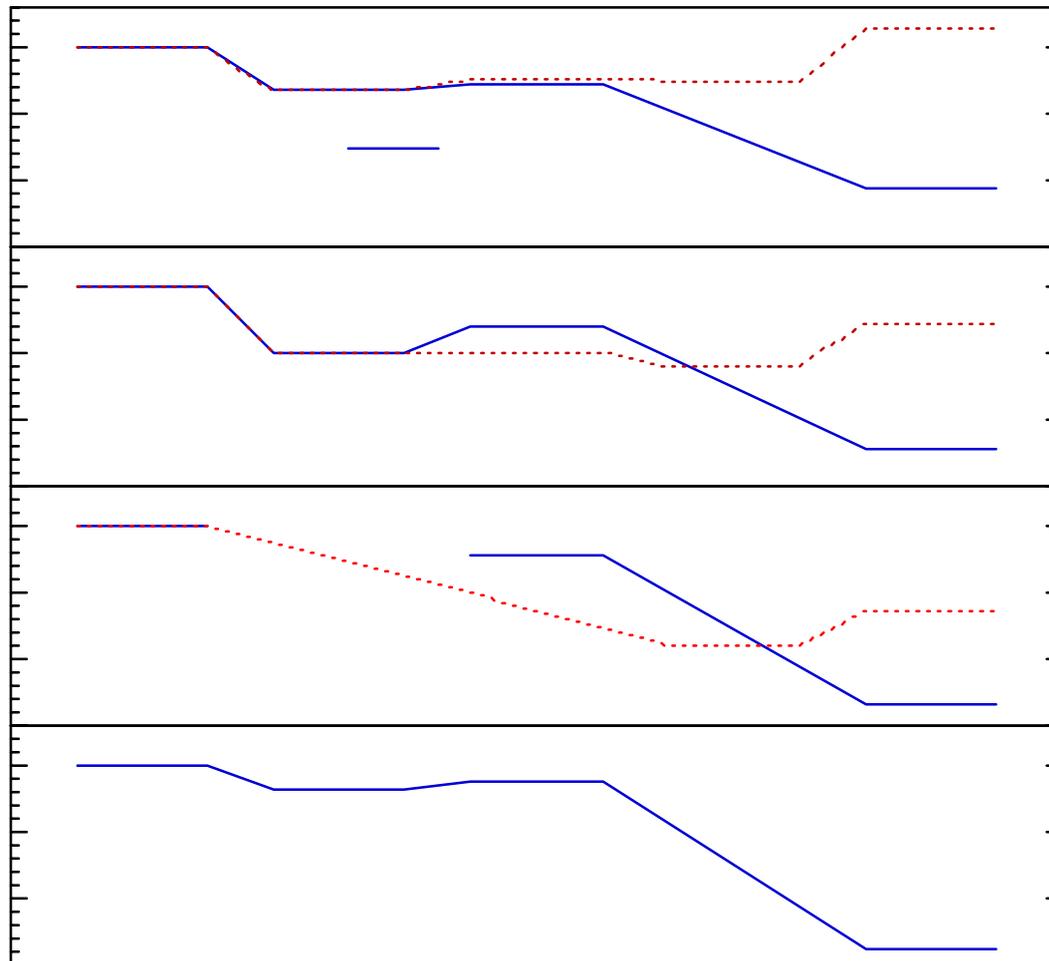


All computed values are within experimental error bars

Max difference = 2.5 kcal/mol, mean unsigned difference = 1.0 kcal/mol

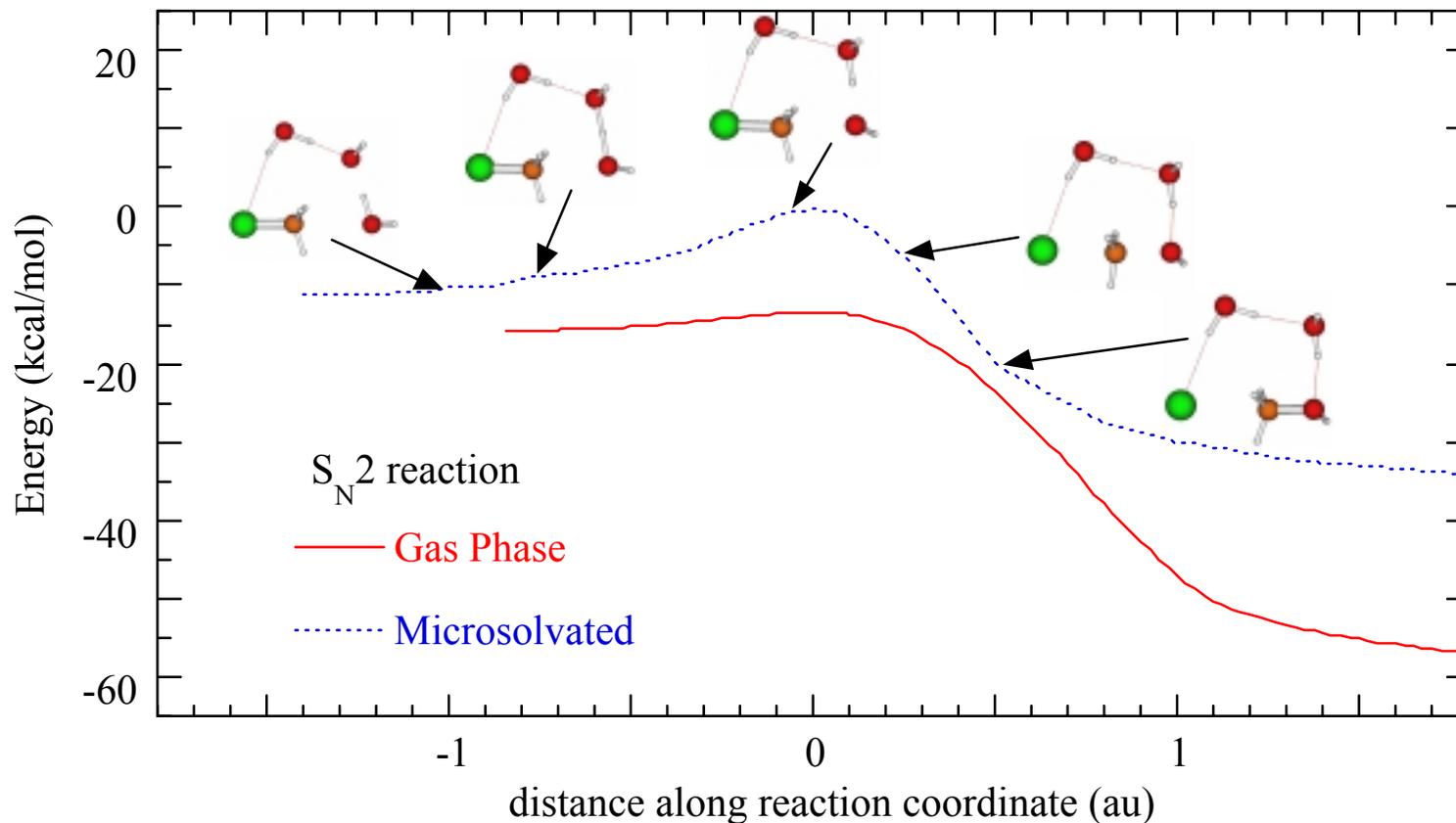
# Reaction Energetics for $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$

CCSD(T)/CBS



# Effects of microsolvation on reaction energetics for $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$ , $n=1-4$

MP2/aVDZ



- Barrier height for microsolvated reaction about equal to asymptotic reactant energy
- Reaction involves proton transfer from water to  $\text{OH}^-$

# Effects of chlorination and microsolvation on reaction rate constants for $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$ , $n=1-4$

**Rate constants ( $10^9 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )  
for  $\text{OH}^- + \text{CH}_{(4-n)}\text{Cl}_n$   
 $\text{S}_\text{N}2$  reaction at 300 K**

**Rate constants ( $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )  
for  $\text{OH}^-(\text{H}_2\text{O})_m + \text{CH}_3\text{Cl}$   
 $\text{S}_\text{N}2$  reaction at 300 K**

n	<u>Rate constant</u>		$R_{\text{CO}}$ (Å)	$\mu$ (D)
	Calc.	Exp.		
1	6.5	1.5	12	1.9
2	7.1		12	1.6
3	17		10	1.0
4	78		10	0.0

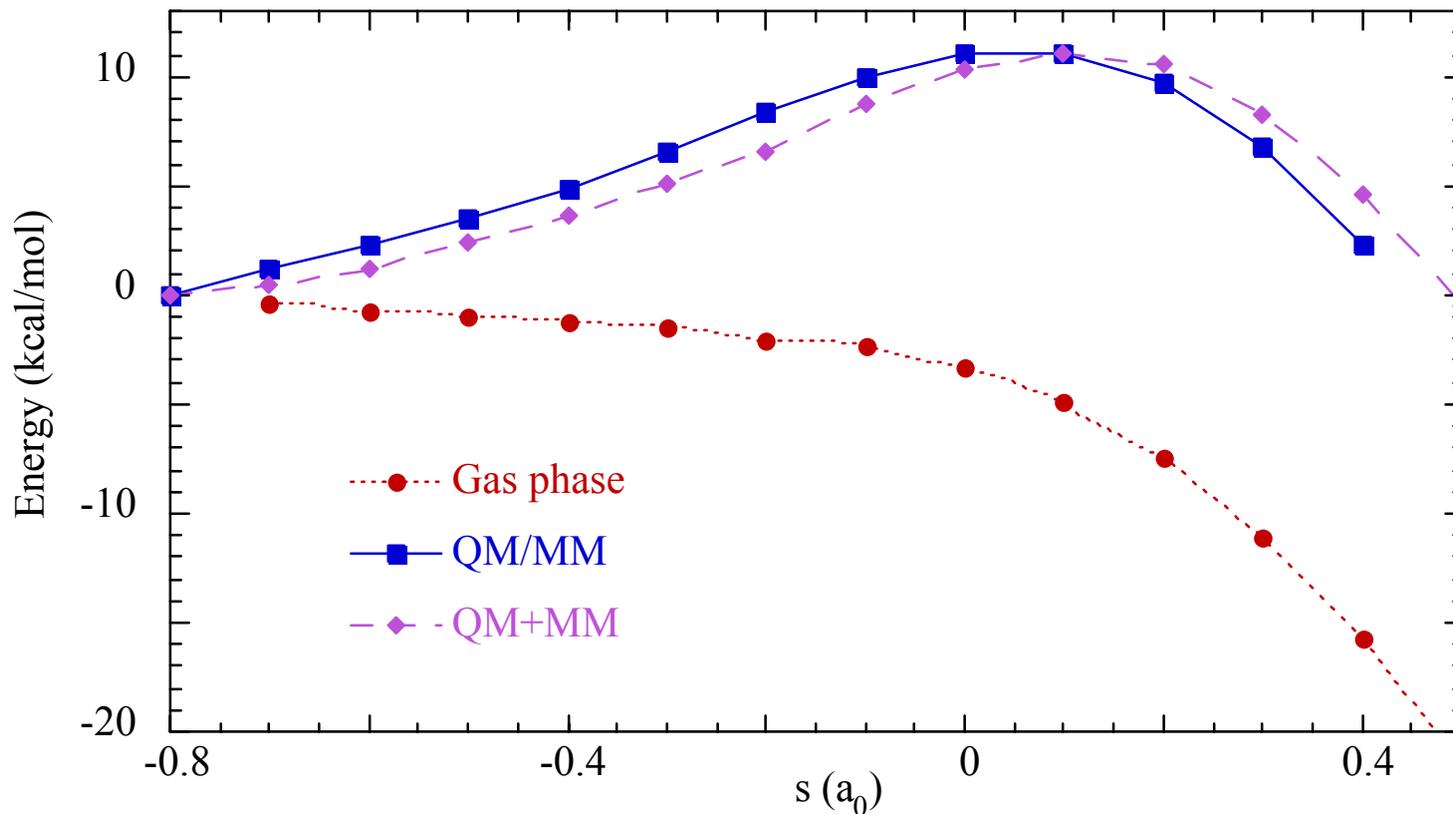
m	<u>Transition State</u>		
	Asymp.	Interior	Exp.
0	$6.5 \times 10^{-9}$	$1.1 \times 10^{-1}$	$1.5 \times 10^{-9}$
1	$5.2 \times 10^{-9}$	$9.6 \times 10^{-10}$	$6.0 \times 10^{-10}$
2	$4.8 \times 10^{-9}$	$5.8 \times 10^{-16}$	$< 2.0 \times 10^{-12}$

- Experimental studies only for  $\text{CH}_3\text{Cl}$  reactions; n dependence shows interesting trends, e.g., proton transfer channel becomes accessible for  $n=3$
- Interior transition state becomes dynamical bottleneck for  $m=1$

# Bulk solvation effects on the $\text{OH}^- + \text{CH}_3\text{Cl}$ $\text{S}_\text{N}2$ reaction

(with M. Dupuis)

QM= SCF/6-31G\* along MEP/aVDZ MEP



- QM+MM: gas-phase QM calculation for cluster + MM simulation of solvation of electrostatic model of cluster
- QM+MM  $\approx$  QM/MM  $\Rightarrow$  self-consistent treatment of solute polarization not important for this system

# Summary

- Levels of electronic structure calculations have been benchmarked and applied to reaction energetics for gas-phase and microsolvated reactions of OH<sup>-</sup> with chlorinated methanes
- Barriers and reaction energies for both S<sub>N</sub>2 and PT reactions increase with microsolvation
- Proton transfer channel becomes energetically more favorable compared to the S<sub>N</sub>2 channel as number of chlorine atoms on methane increases - experimental studies of the dependence of branching ratios on number of chlorine atoms would be interesting
- Water molecules can directly participate in the reaction (e.g., proton transfer between OH<sup>-</sup> and water) and can qualitatively change the features of the potential energy surface (e.g., intermediate complex and saddle point for PT reaction disappears) - explicit treatment of water molecules in electronic structure calculations is necessary
- Dynamical bottlenecks for gas-phase S<sub>N</sub>2 reactions are in the entrance channel; rate constants do not provide a probe of the regions of the PES controlling the rate constant in bulk - better experimental determination of rate constants for microsolvated reactions would provide more direct benchmarks of our approach to condensed phase reactions