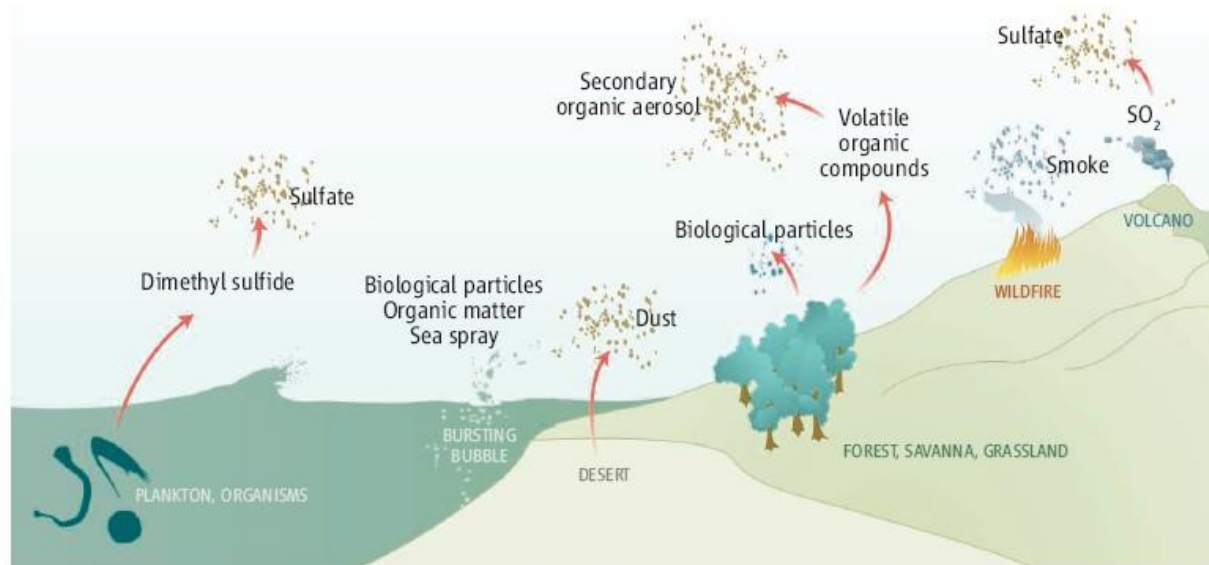


Structure-Reactivity Analyses for Epoxide, Organosulfate, and Organonitrate Reactions Relevant to Secondary Organic Aerosol Composition



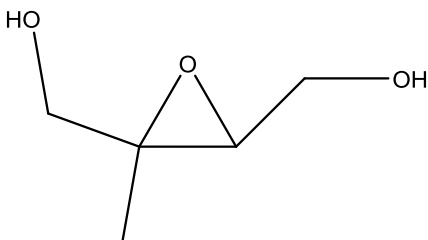
Epoxide Intermediates Explain SOA Composition

ENVIRONMENTAL
Science & Technology

2013

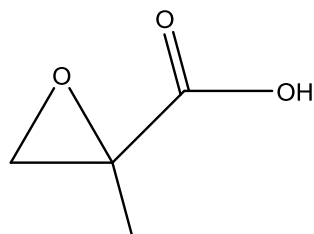
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Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor

Sri Hapsari Budisulistiorini,[†] Manjula R. Canagaratna,[‡] Philip L. Croteau,[‡] Wendy J. Marth,[†] Karsten Baumann,[§] Eric S. Edgerton,[§] Stephanie L. Shaw,^{||} Eladio M. Knipping,[⊥] Douglas R. Worsnop,[‡] John T. Jayne,[‡] Avram Gold,[†] and Jason D. Surratt^{*,†}



Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides 2013

Ying-Hsuan Lin^a, Haofei Zhang^{a,1}, Havalva O. T. Pye^b, Zhenfa Zhang^a, Wendy J. Marth^a, Sarah Park^a, Maiko Arashiro^a, Tianqu Cui^a, Sri Hapsari Budisulistiorini^a, Kenneth G. Sexton^a, William Vizuete^a, Ying Xie^b, Deborah J. Luecken^b, Ivan R. Piletic^b, Edward O. Edney^b, Libero J. Bartolotti^c, Avram Gold^a, and Jason D. Surratt^{a,2}

^aDepartment of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599; ^bNational Exposure Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27711; and ^cDepartment of Chemistry, East Carolina University, Greenville, NC 27858

PNAS

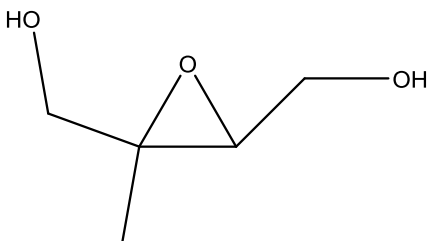
Epoxide Intermediates Explain SOA Composition

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PCCP



PAPER

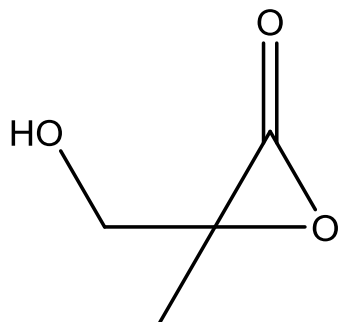
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Cite this: *Phys. Chem. Chem. Phys.*,
2015, 17, 17914

2015

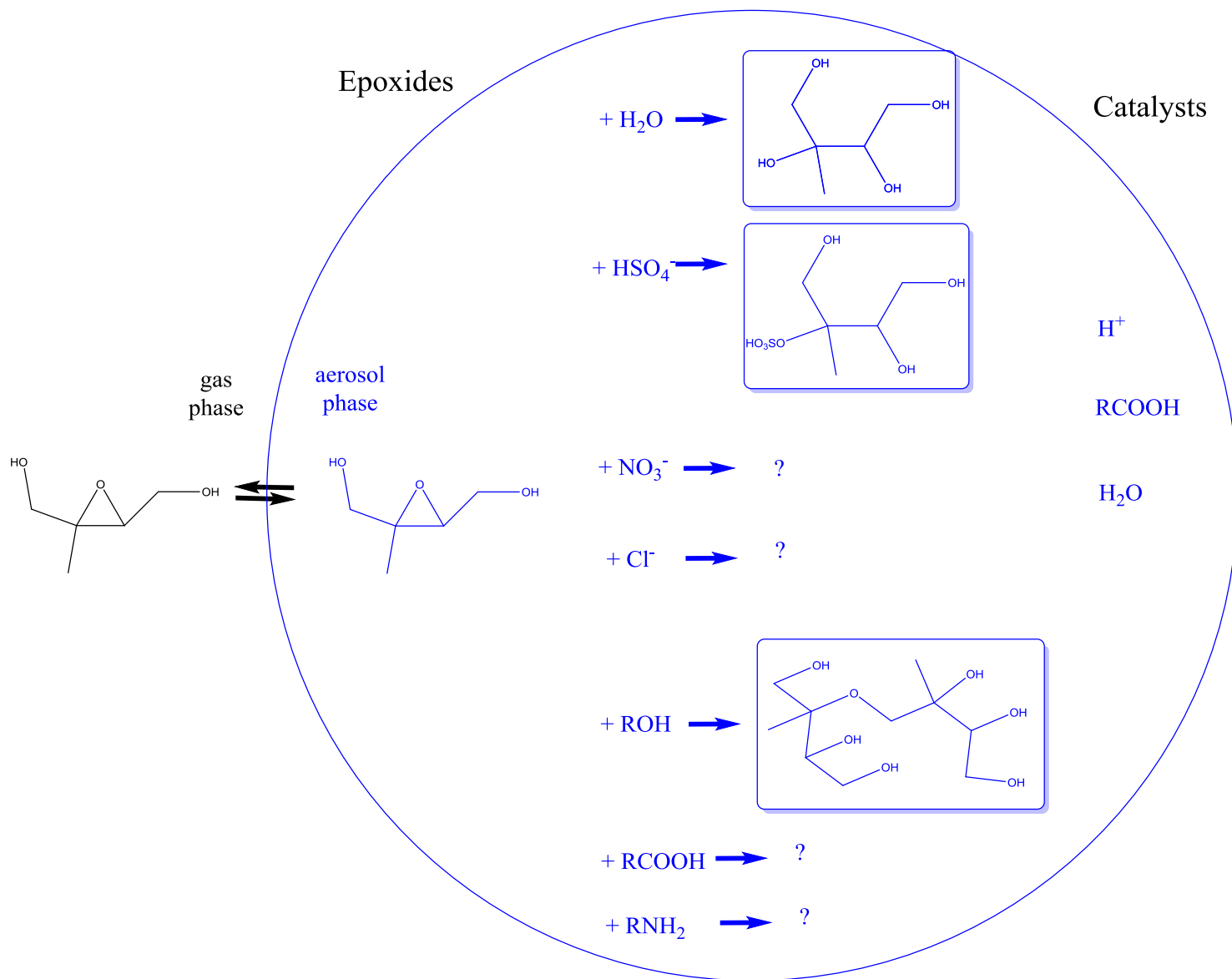


Mechanism of the hydroxyl radical oxidation of methacryloyl peroxyoxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere[†]

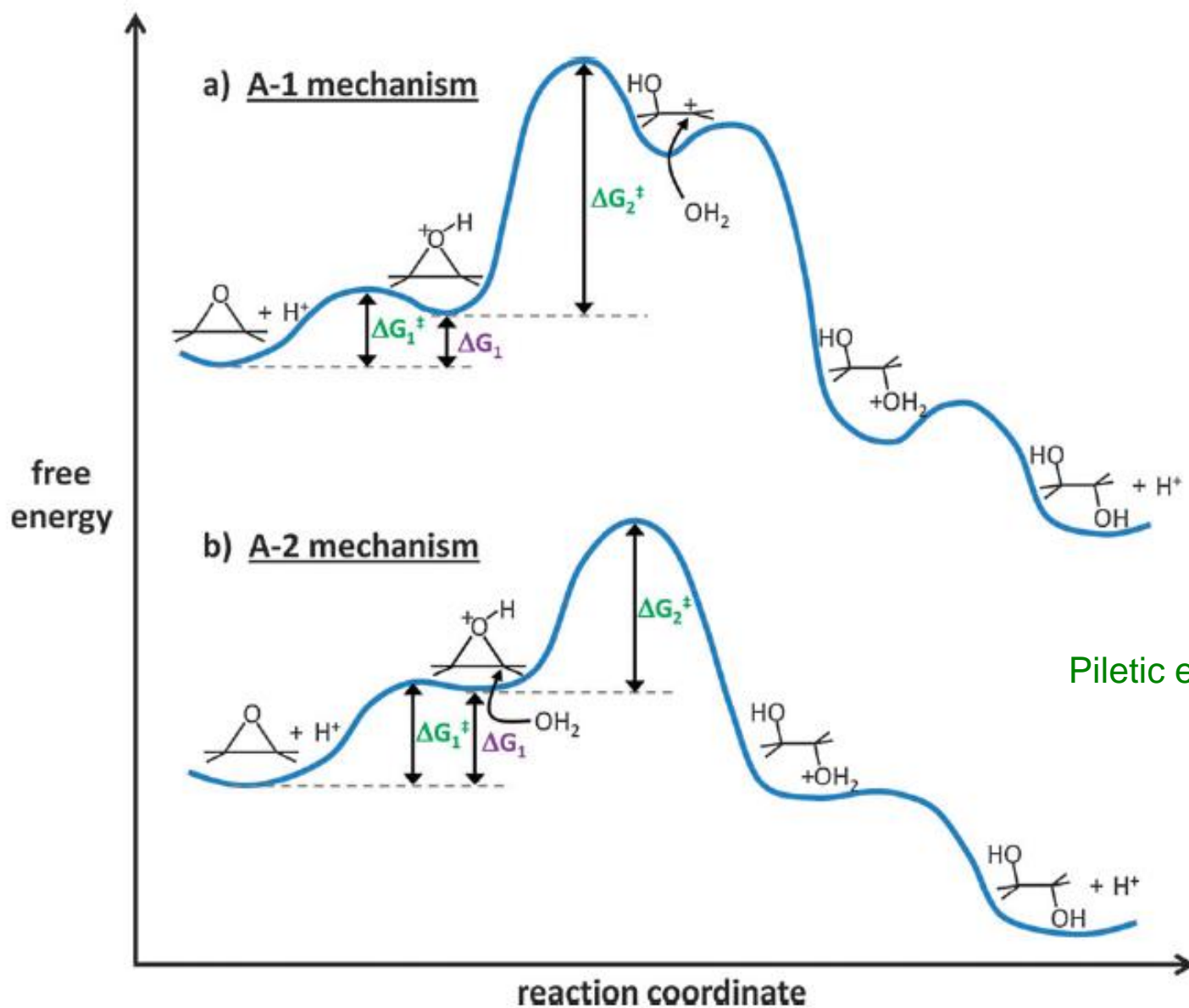
Tran B. Nguyen,^{*,a} Kelvin H. Bates,^b John D. Crouse,^a Rebecca H. Schwantes,^a Xuan Zhang,^a Henrik G. Kjaergaard,^c Jason D. Surratt,^d Peng Lin,^e Alexander Laskin,^e John H. Seinfeld^{b,f} and Paul O. Wennberg^{a,f}

SOA as Chemical Reactor

Nucleophiles

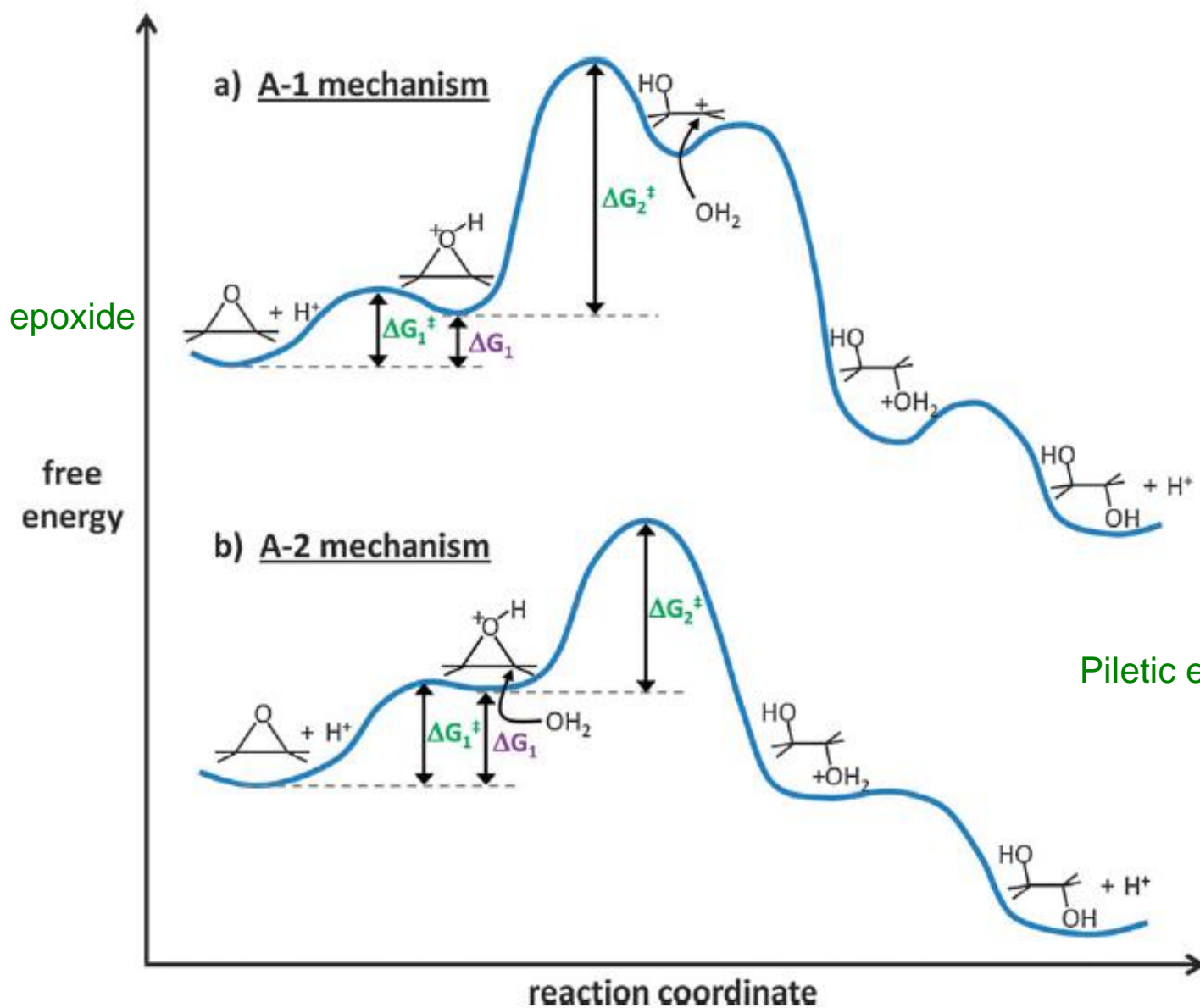


Nucleophilic Addition Mechanisms



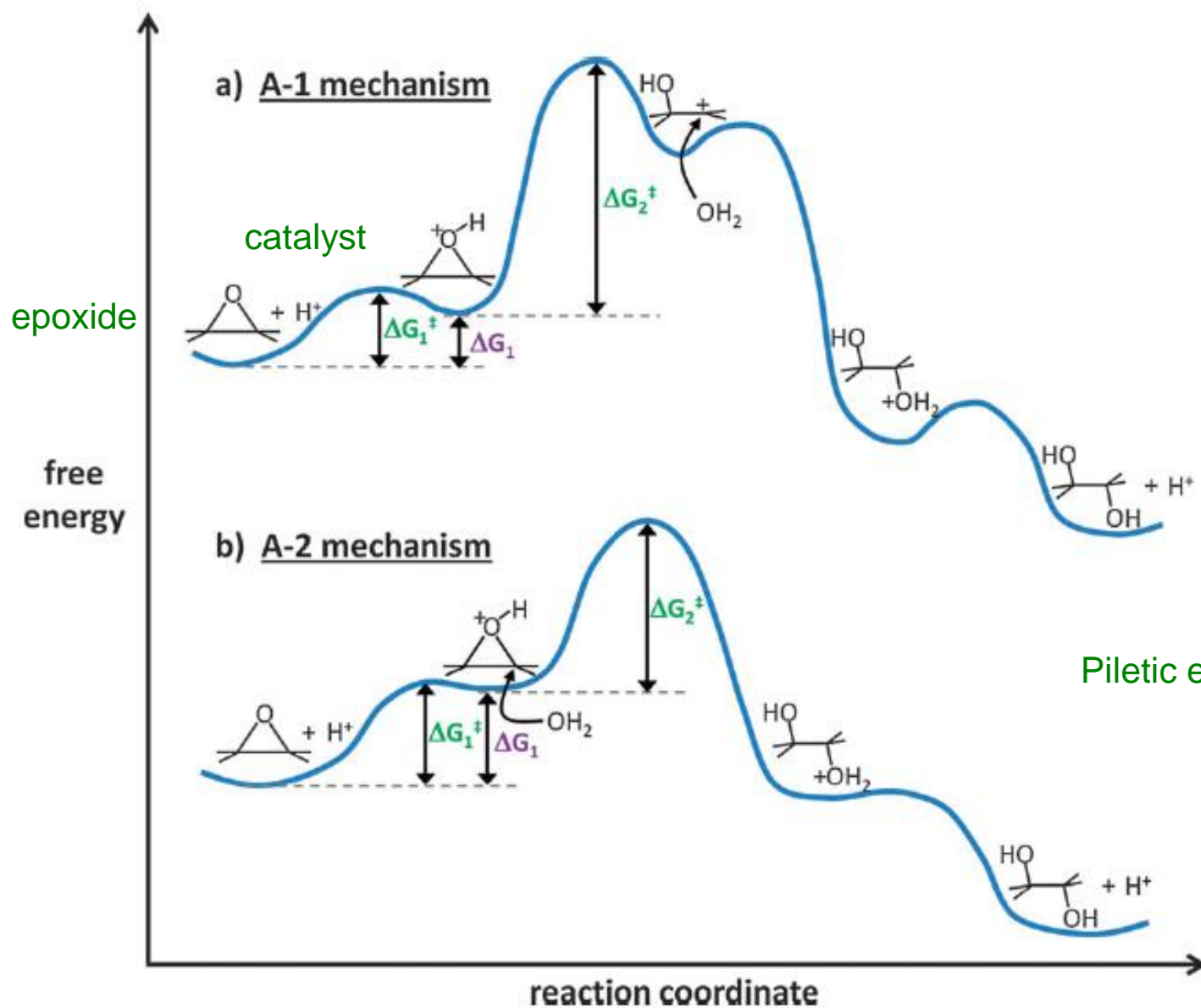
Piletic et al., *PCCP*, 2013

Nucleophilic Addition Mechanisms



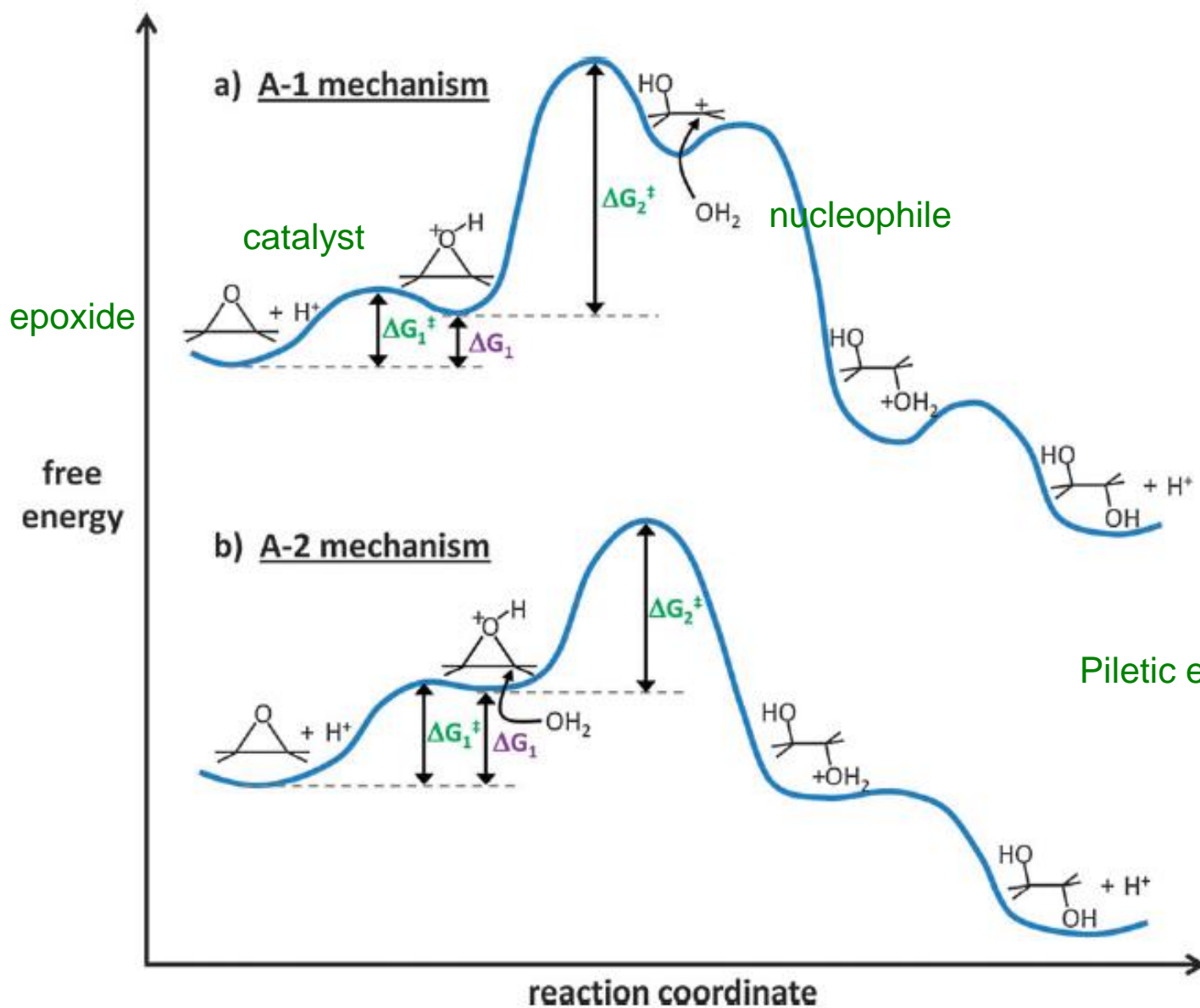
Piletic et al., *PCCP*, 2013

Nucleophilic Addition Mechanisms



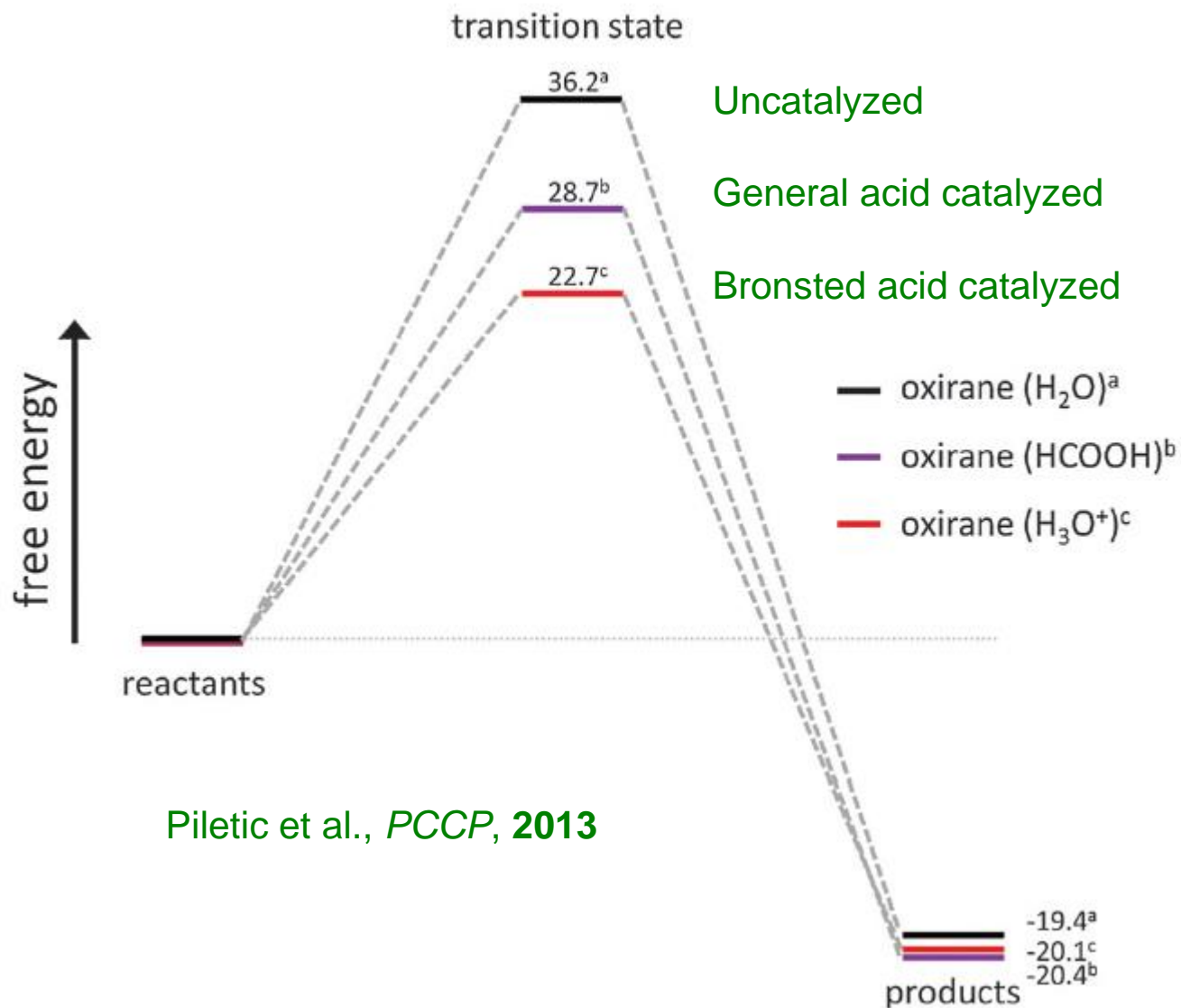
Piletic et al., *PCCP*, 2013

Nucleophilic Addition Mechanisms

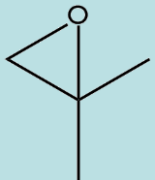
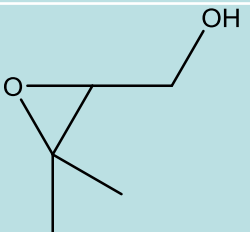
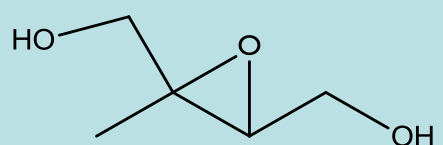
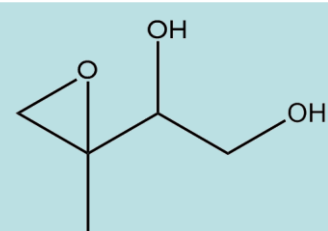
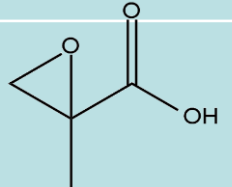


Piletic et al., *PCCP*, 2013

Acid Catalysis: Bronsted vs. General



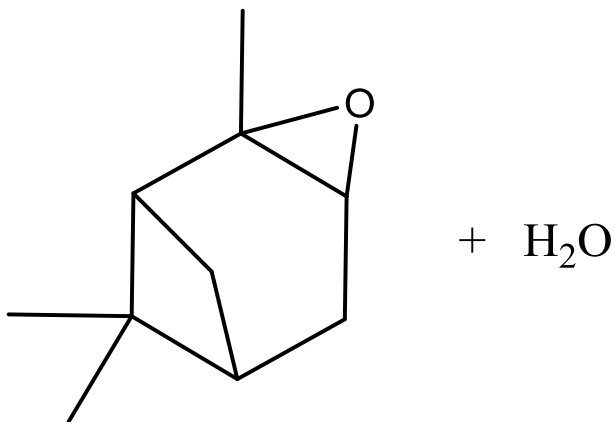
Bronsted-Acid Catalyzed

epoxide	k (M ⁻¹ s ⁻¹)
2-methyl-1,2-epoxypropane 	8.7 (Minerath et al. <i>ES&T</i> , 2008)
2,3-MBO epoxide 	0.41 (Mael et al. <i>JPC A</i> , 2015)
IEPOX-4 	0.036 (Darer et al. <i>ES&T</i> , 2012)
IEPOX-1 	0.0079 (Darer et al. <i>ES&T</i> , 2012)
MAE 	0.0000591 (Birdsall et al. <i>ACP</i> , 2014)

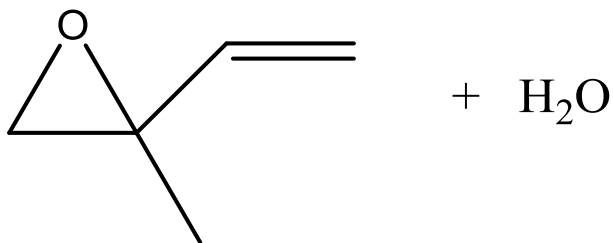
Structure-Reactivity Conclusions

- Tertiary nucleophilic addition most common, but primary nucleophilic addition is observed for MAE - indicates A-2 mechanism dominance
- Neighboring OH groups reduce the rate constant – these electron withdrawing groups destabilize the A-2 transition state species (make the epoxide C more electropositive) and raise the effective activation energy
- COOH groups are extremely good electron withdrawing groups, and raise the effective activation energy even higher

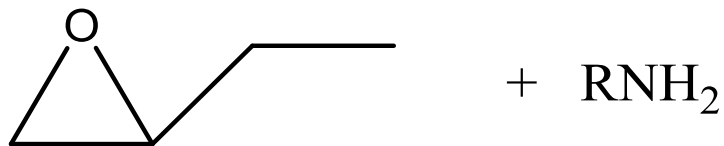
General Acid Catalyzed Reactions



Bleier et al. *JPC A*, 2013



Minerath et al. *ES&T*, 2009



Stropoli et al. *JPC A*, 2015

Which Nucleophiles Dominate?

Nucleophilicity (the donation of electrons to form a new bond) is affected by four factors:

- 1) **Charge** – the more negative, the better
- 2) **Electronegativity/Lone Pairs** – the less electronegative the atoms and the more lone pairs, the better
- 3) **Solvent** – polar solvents (water) can complicate analysis
- 4) **Steric hindrance** – the less bulky, the better

Nucleophilicity scale definition:

$$\frac{\textit{nucleophile nucleophilic strength}}{\textit{water nucleophilic strength}} = \frac{(Y_{\textit{nuc product}}/X_{\textit{nucleophile}})}{(Y_{\textit{hydrolysis product}}/X_{\textit{H2O}})}$$

Relative Nucleophilicities: Inorganic Ions

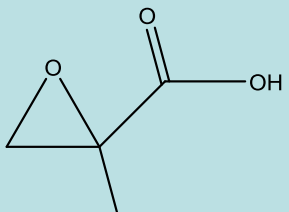
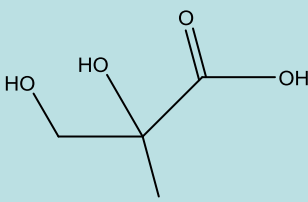
1,2-epoxyisoprene reaction (Minerath et al. *ES&T*, 2009):

nucleophile	relative nucleophilicity
H ₂ O	1 (by definition)
NO ₃ ⁻	7.0
HSO ₄ ⁻	8.8
Cl ⁻	31
Br ⁻	60
I ⁻	140

Charge and Solvent effect: stronger H-bonding with solvent H₂O of strong acid conjugate bases and smaller halides hinders nucleophilicity, but all negative ions stronger than H₂O

Relative Nucleophilicities: Alcohols and Acids

MAE reaction (Birdsall et al. *ACP*, 2014):

nucleophile	relative nucleophilicity
CH_3COOH	0.4
MAE 	0.6
2-MG 	0.8 total = 0.4 (carboxylic acid) + 0.4 (primary alcohol)
H_2O	1 (by definition)
CH_3OH	3.1
HSO_4^-	11

All OH groups have similar nucleophilicity, weaker than HSO_4^-

Relative Nucleophilicities: Amines

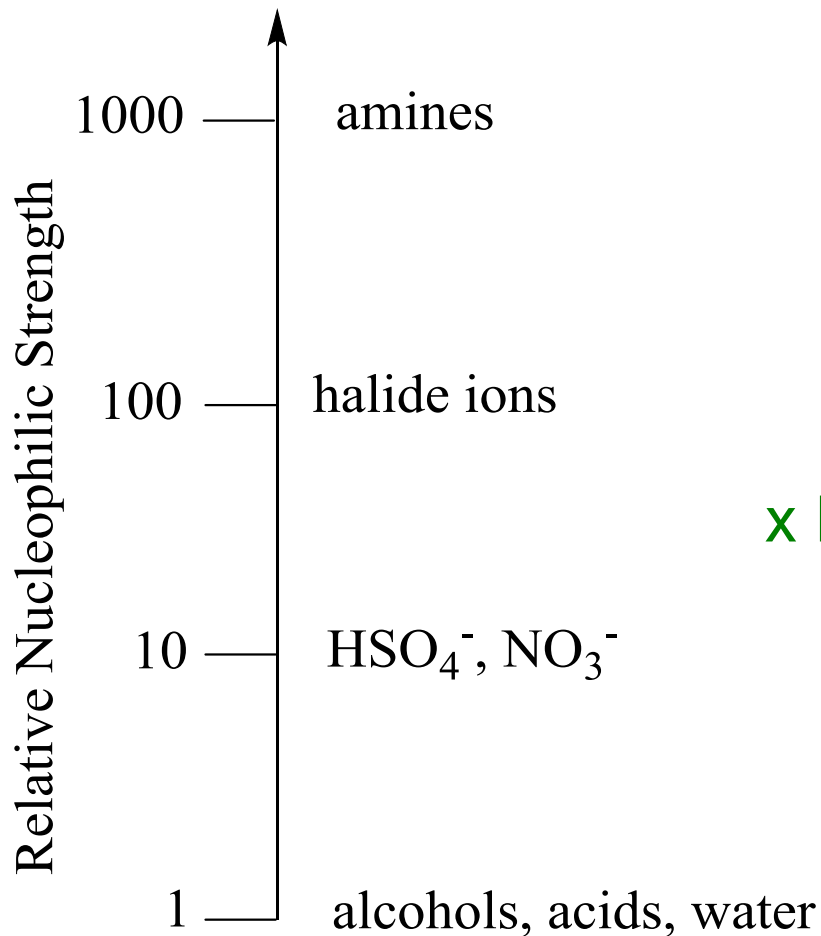
1,2-epoxybutane reaction (Stropoli et al. *JPC A*, 2015):

nucleophile	relative nucleophilicity
H ₂ O	1 (by definition)
HSO ₄ ⁻	20
t-butyl amine	3000

Electronegativity/Lone Pair Effect: Nitrogen has lower electronegativity than oxygen, but has a lone pair, unlike carbon, which combines to make amines very strong nucleophiles – organic amines especially strong because alkyl groups are electron donating

Protonated amines are very weak nucleophiles – most atmospheric amines are protonated at SOA pH's

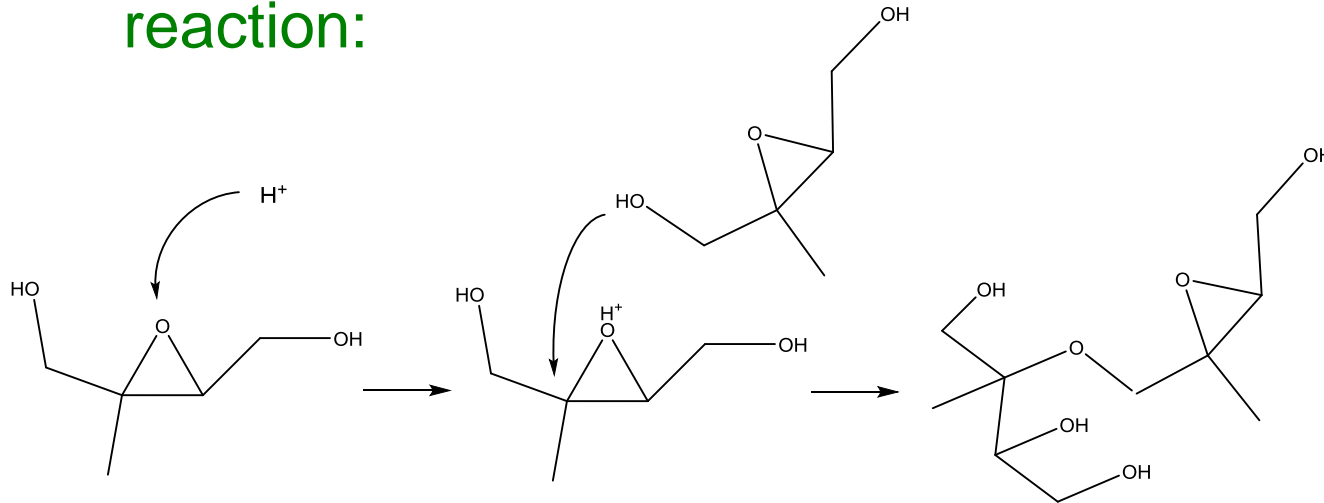
Nucleophilicity Scale



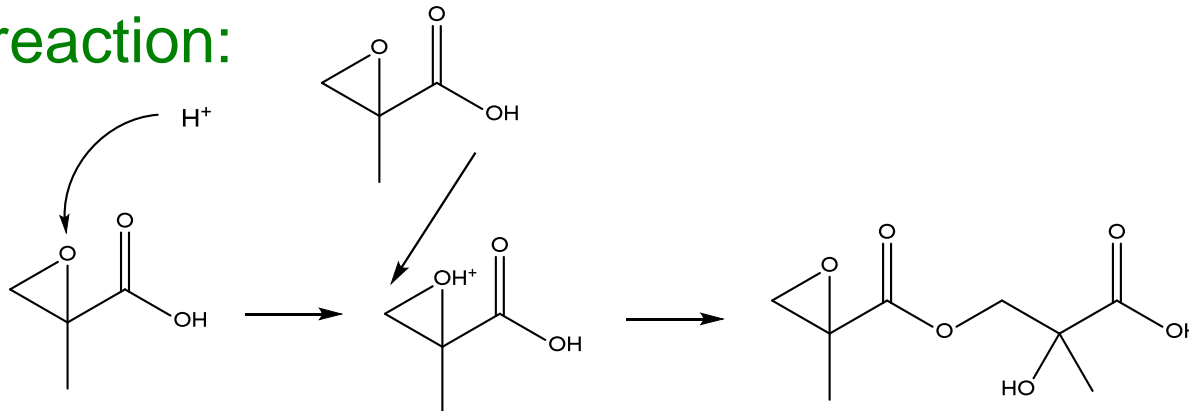
$$\text{Relative SOA Reactivity} = [\text{Nucleophile}]_{\text{SOA}} \times \text{Relative Nucleophilic Strength}$$

Oligomerization is a Nucleophilic Addition Reaction

Oligomerization of IEPOX is an **alcohol** nucleophilic addition reaction:

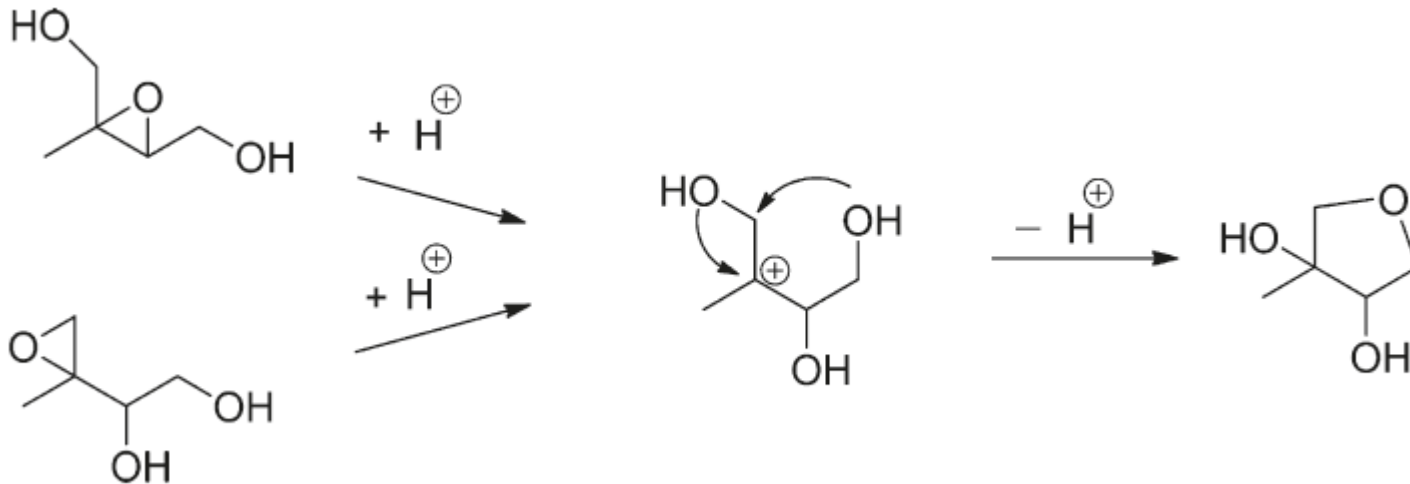


Oligomerization of MAE is an **acid** nucleophilic addition reaction:



Isomerization Is a Unimolecular Nucleophilic Addition Reaction

THF-like isomerization products observed from IEPOX (Lin et al. *ES&T*, 2012):



Because ring closing reactions are relatively slow, isomerization will dominate only when stronger nucleophiles are in low concentration (i.e., low SOA liquid water content)

Metastability of Organonitrates and Halides: Nucleophilic Substitution

Organic halides have generally not been detected in ambient SOA and organonitrates have been shown to be susceptible to hydrolysis (Boone et al. *ES&T*, **2015**).

Relative nucleophilic substitution efficiency is predicted by leaving group properties (potential leaving groups in SOA: halides and NO_3^-) and structure at reactive site (tertiary structure best stabilizes intermediate).

Leaving group property is proportional to weak base property because the weak bases are able to take on extra electron density as they “leave”: Cl^- and NO_3^- are excellent leaving groups.

Structure-Reactivity Tools for Predicting SOA Reactions

All Major Classes of Epoxide Reactions (Hydrolysis, Organosulfate Formation, Oligomerization, and Isomerization) Can Be Interpreted as Nucleophilic Addition Reactions.

Relative Rates of Nucleophilic Addition to Epoxides Depend on Catalysts, Epoxide Carbon Substitution Structure, Relative Nucleophilicity, and Nucleophile Concentrations.

Water Nucleophilic Substitution for Rates Depend on Leaving Groups, Carbon Substitution Structure, Liquid Water Content.

Acknowledgements

Emily Minerath '09, Madeline Schultz '10,
Neil Cole-Filipiak '10, Alison O'Connor '12,
Kevin Hu '12, Adam Darer '12, Dylan Bleier,
Adam Birdsall '13, Cassandra Zentner '13,
Michael Jacobs '14, Alex Watanabe '14,
Corina Miner '16, Liora Mael '16,
Santino Stropoli '18



National Science Foundation
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