Mechanistic considerations for N-X bond fragmentation of pyridinium salts

2024.01.18

Literature Seminar

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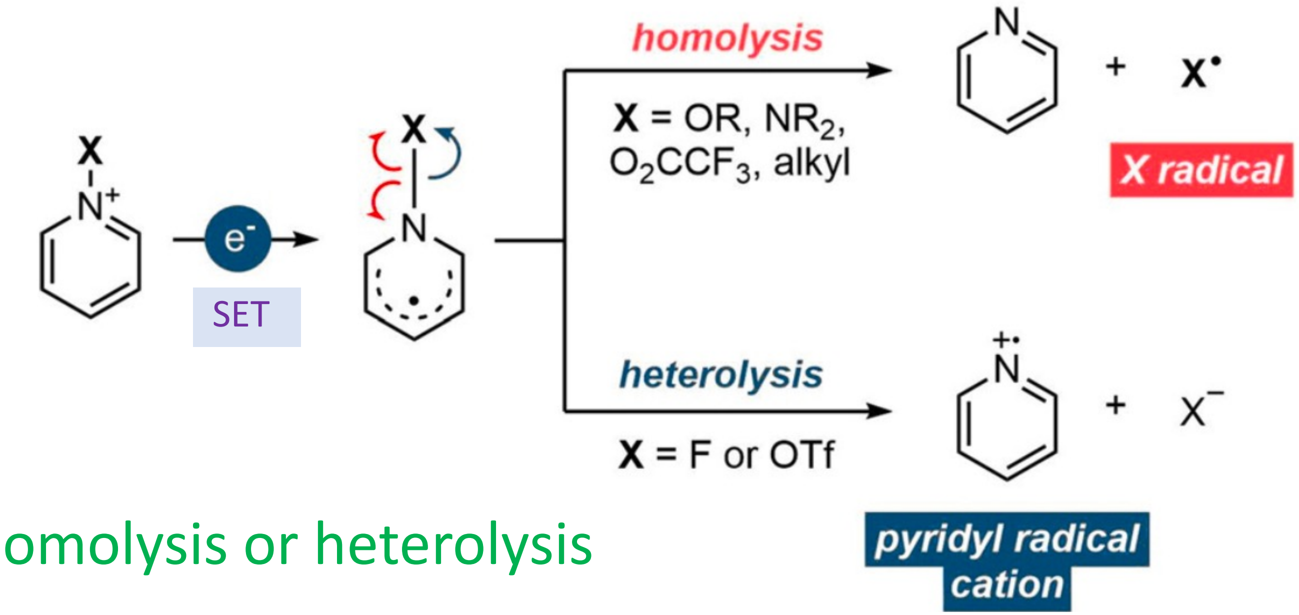
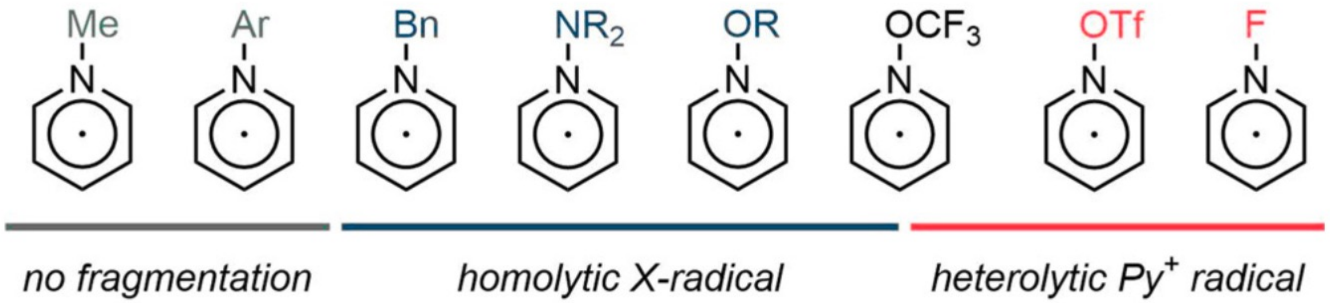
Contents

Fragmentation of pyridinium ion via single electron reduction

Pyridinium salts: Redox-Active Functional Group Transfer Reagents



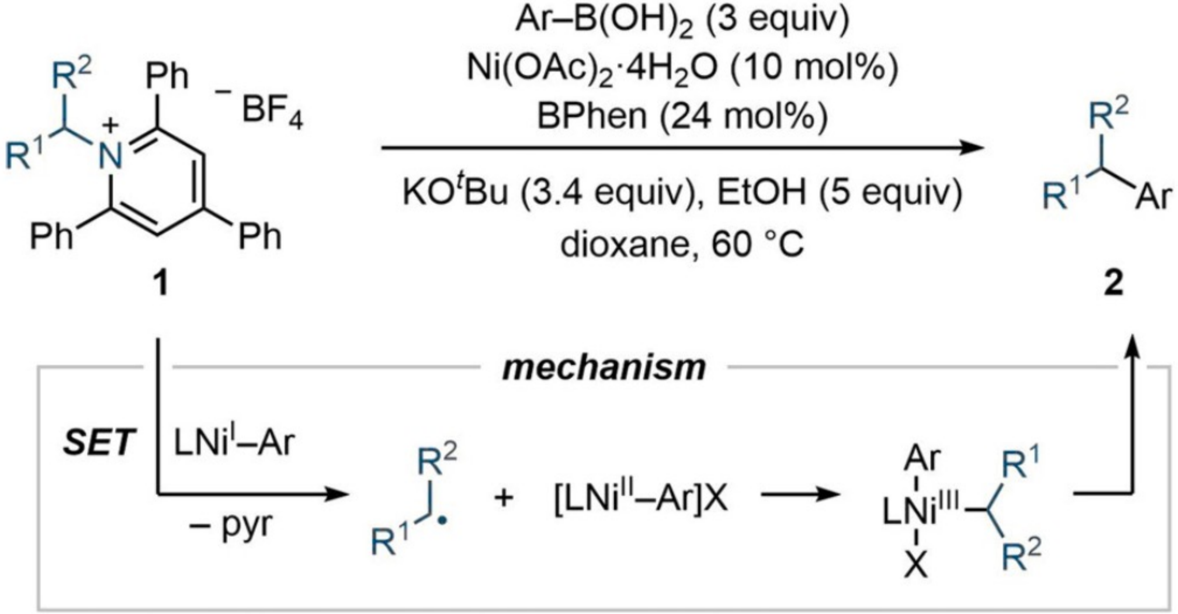
fragmentation = homolysis or heterolysis



S. L. Rössler, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 9264–9280

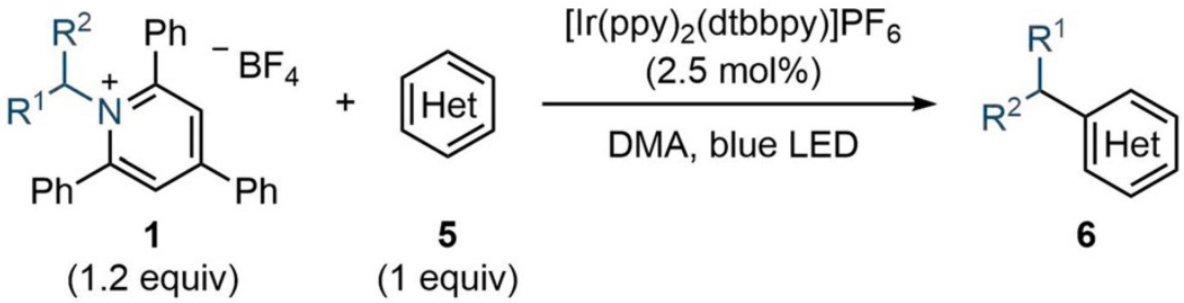
N-C bond fragmentation via homolytic cleavage

Ni catalysis



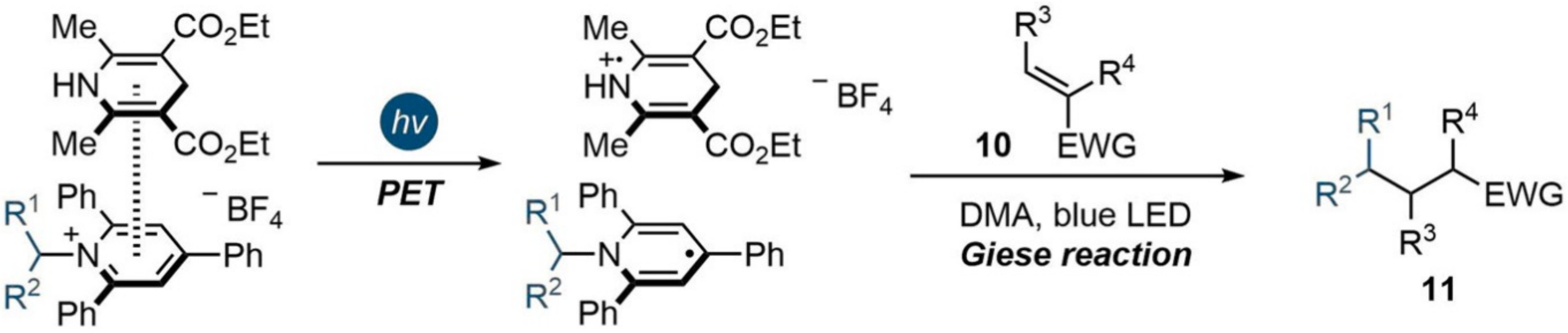
C. H. Basch, et al. *J. Am. Chem. Soc.* **2017**, *139*, 15, 5313−5316

photoredox catalysis



F. J. R. Klauck, et al. *Angew. Chem. Int. Ed*. **2017**, *56*, 12336−12339

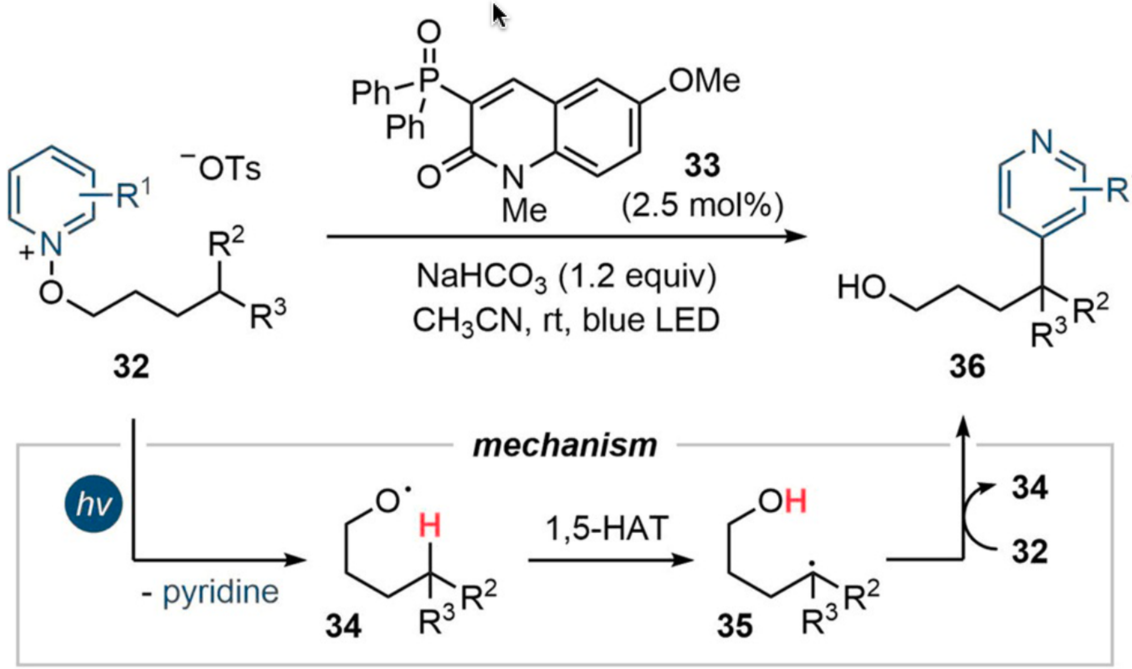
EDA complex



J. Wu, et al. *Angew. Chem. Int. Ed*. **2019**, *58*, 5697−5701

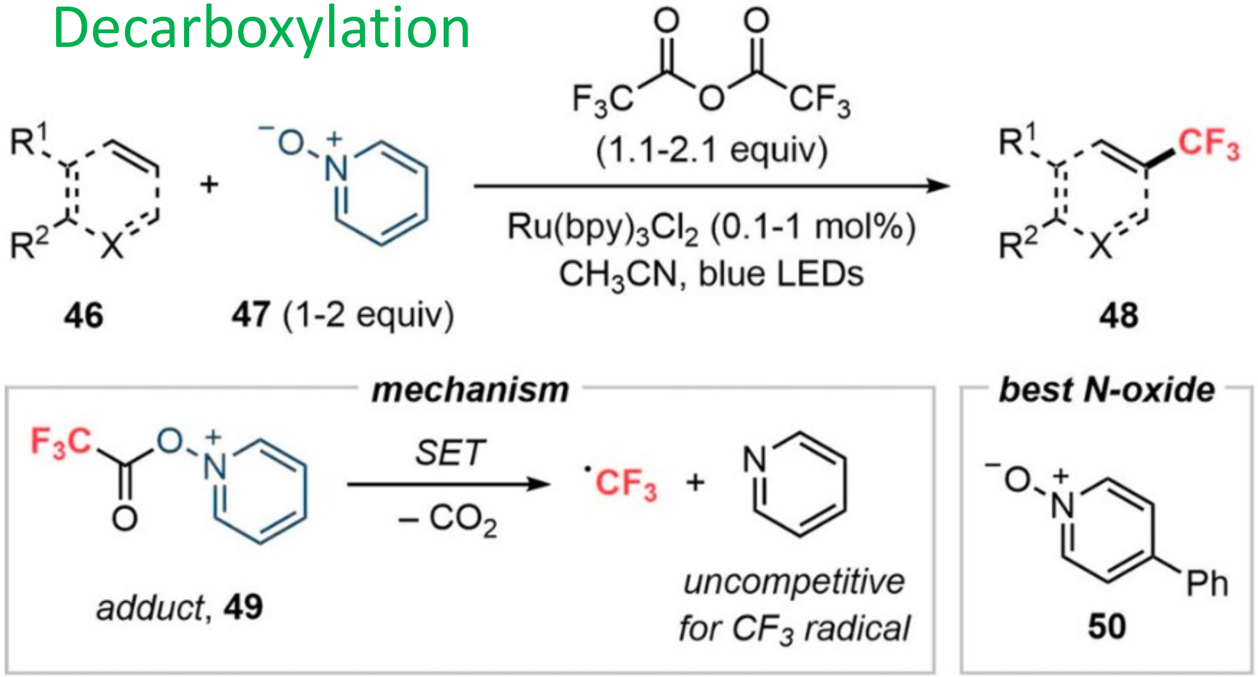
N-O bond fragmentation via homolytic cleavage

Radical translocation



I. Kim, et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 15517-15522

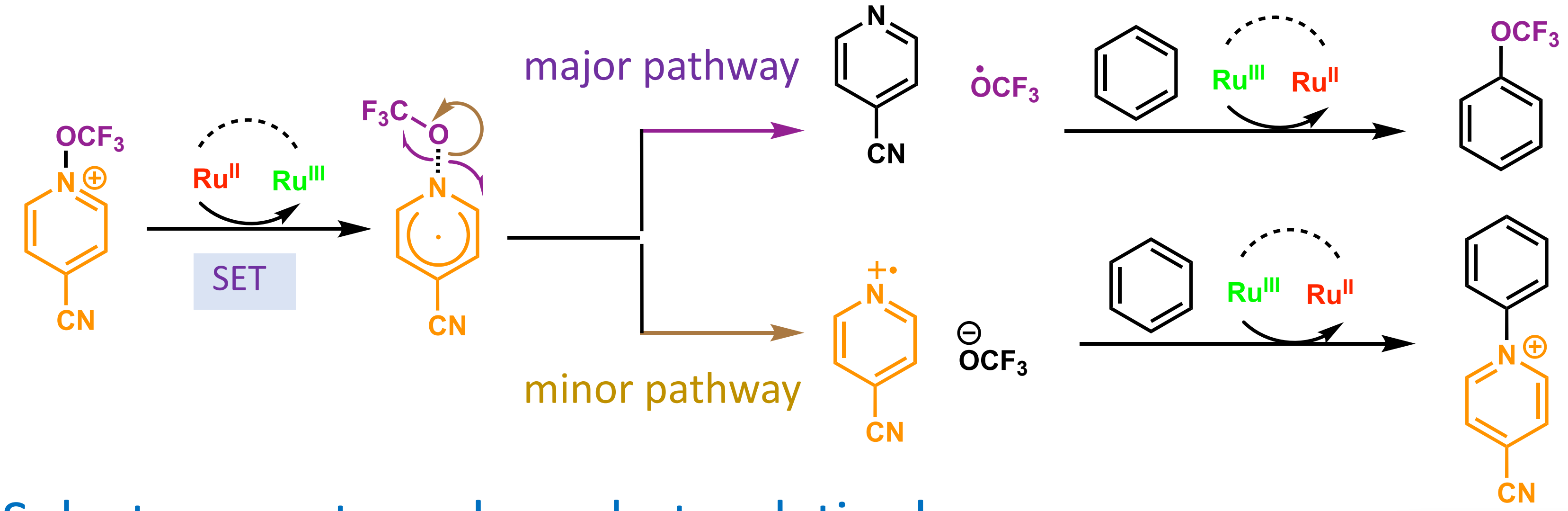
Decarboxylation



J. W. Beatty, et al. *Nat. Commun.* **2015**, *6*, 7919

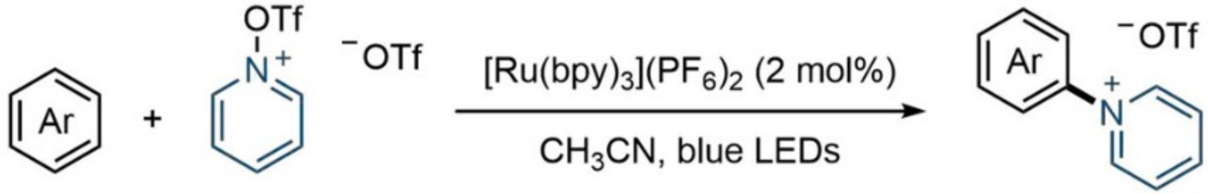
Photocatalytic generation of pyridyl radical cation via heterolytic cleavage

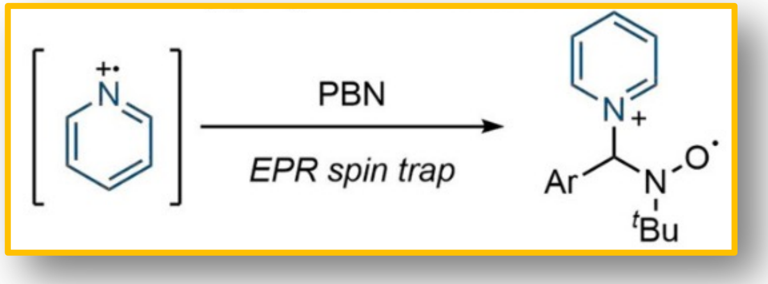
Heterolytic cleavage as a minor competing pathway



B. J. Jelier, et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 13784-13789

Select reagents undergo heterolytic cleavage

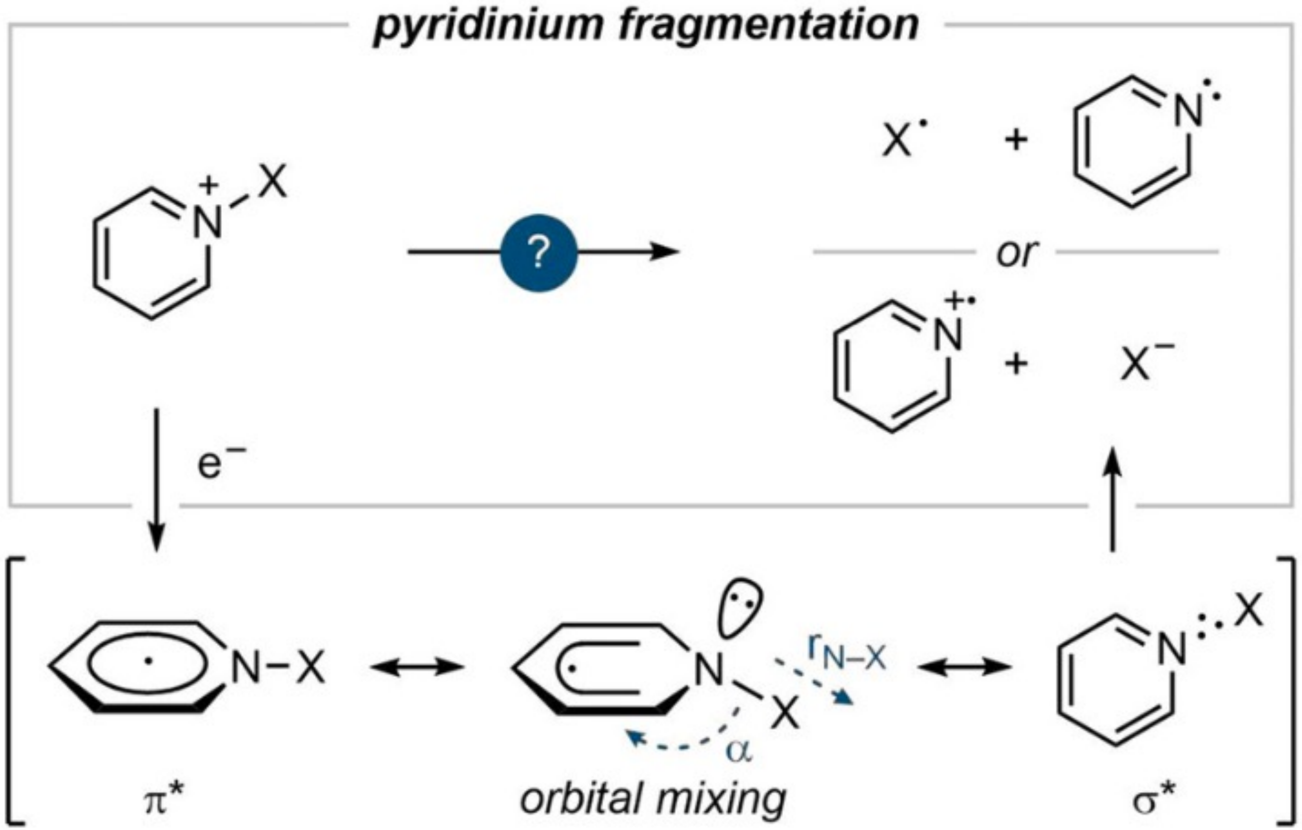




High-energy trifloxy radical is not generated

S. L. Rössler, et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 526–531

Postulated mechanism of pyridinium fragmentation



Keywords

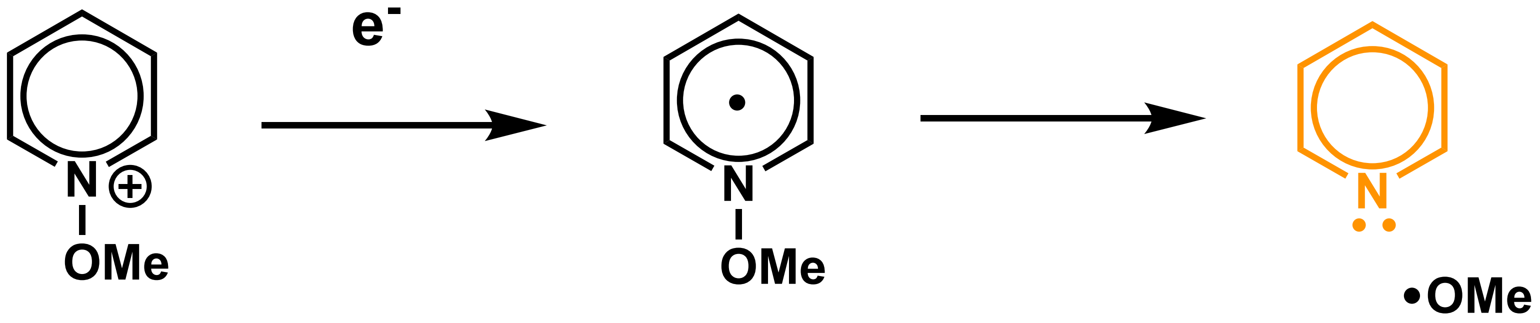
- orbital mixing
- three electron N∴X bond

S. L. Rössler, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 9264–9280

Contents

1. Examples of N-X bond fragmentation
2. Theoretical background
3. Model calculation

Single electron reduction & fragmentation



pyridinium ion

pyridyl radical

pyridine & methoxy radical

Step 1

Single electron reduction

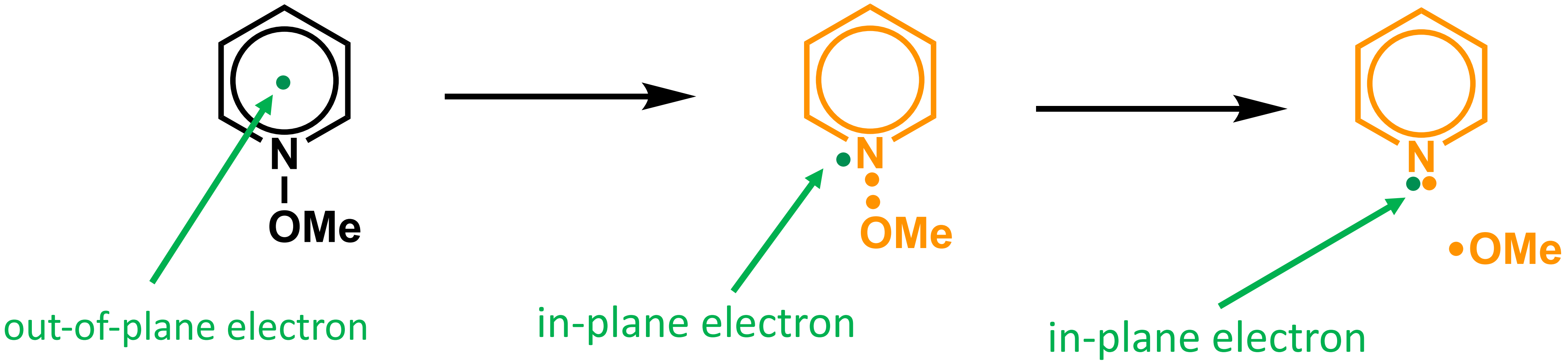
π^* orbital of pyridinium ion receives an electron from donor.

Step 2

N-O bond fragmentation

→ today's topic

How can we obtain pyridine ?

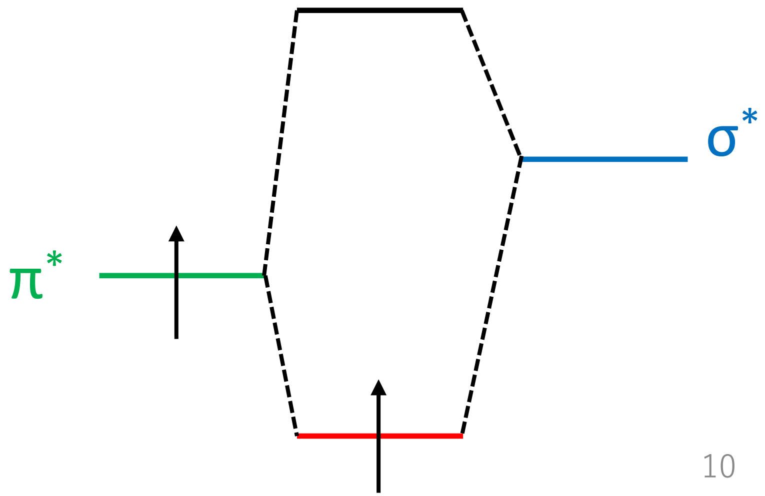


An electron must be transferred from out-of-plane to in-plane before fragmentation.

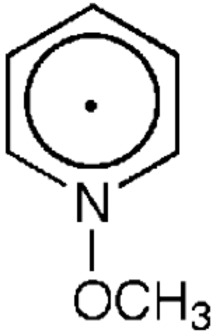
→ Orbital mixing

π^* & σ^* are orthogonal

→ N-O bond bending

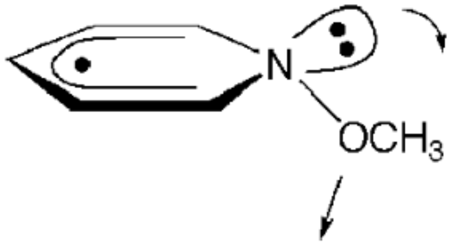


N-O bond bending



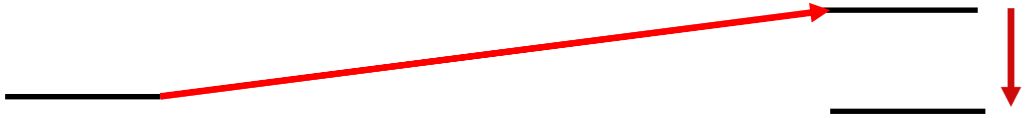
planar radical

no orbital mixing



N-O bond bending

orbital mixing

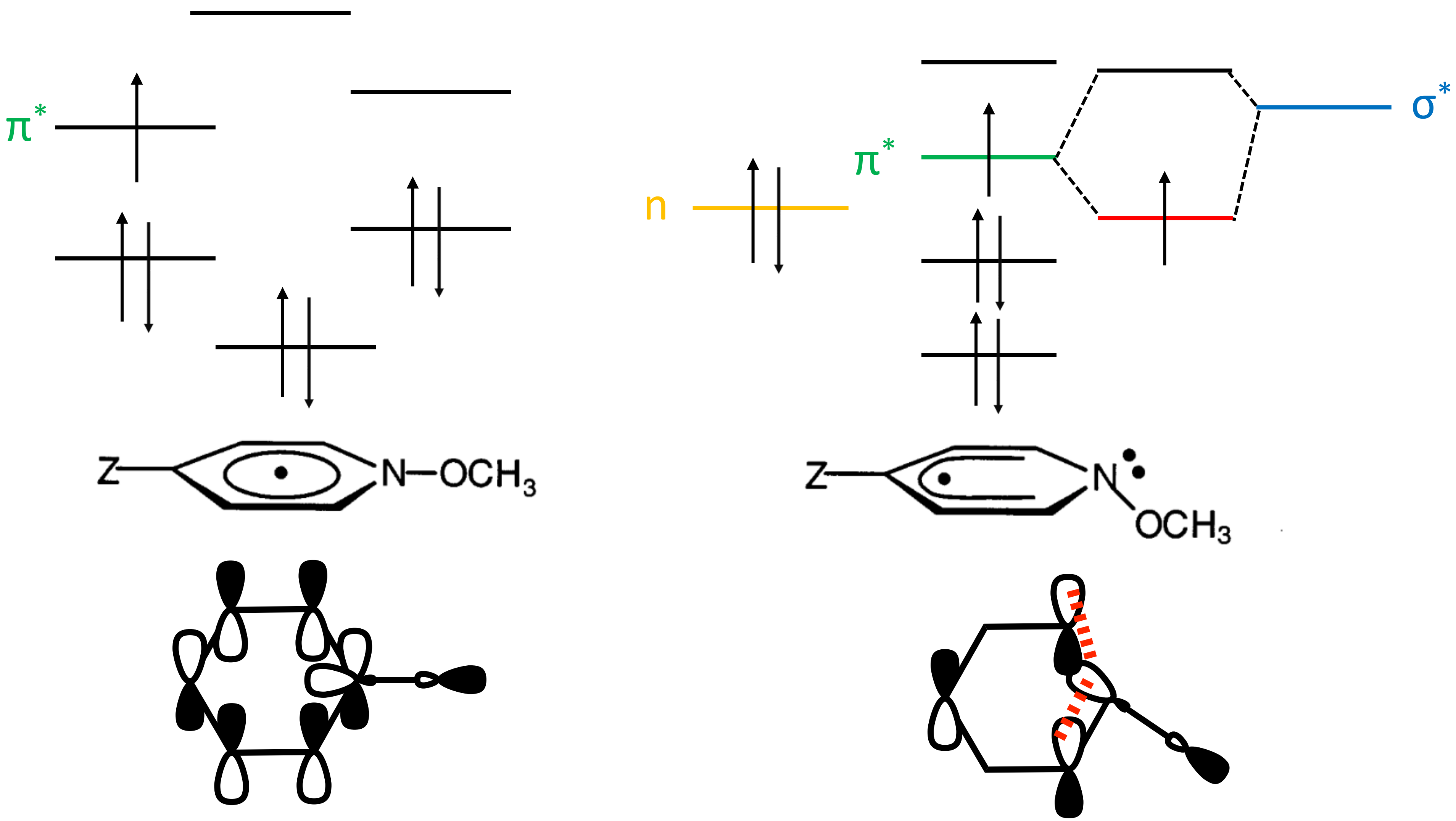


climb

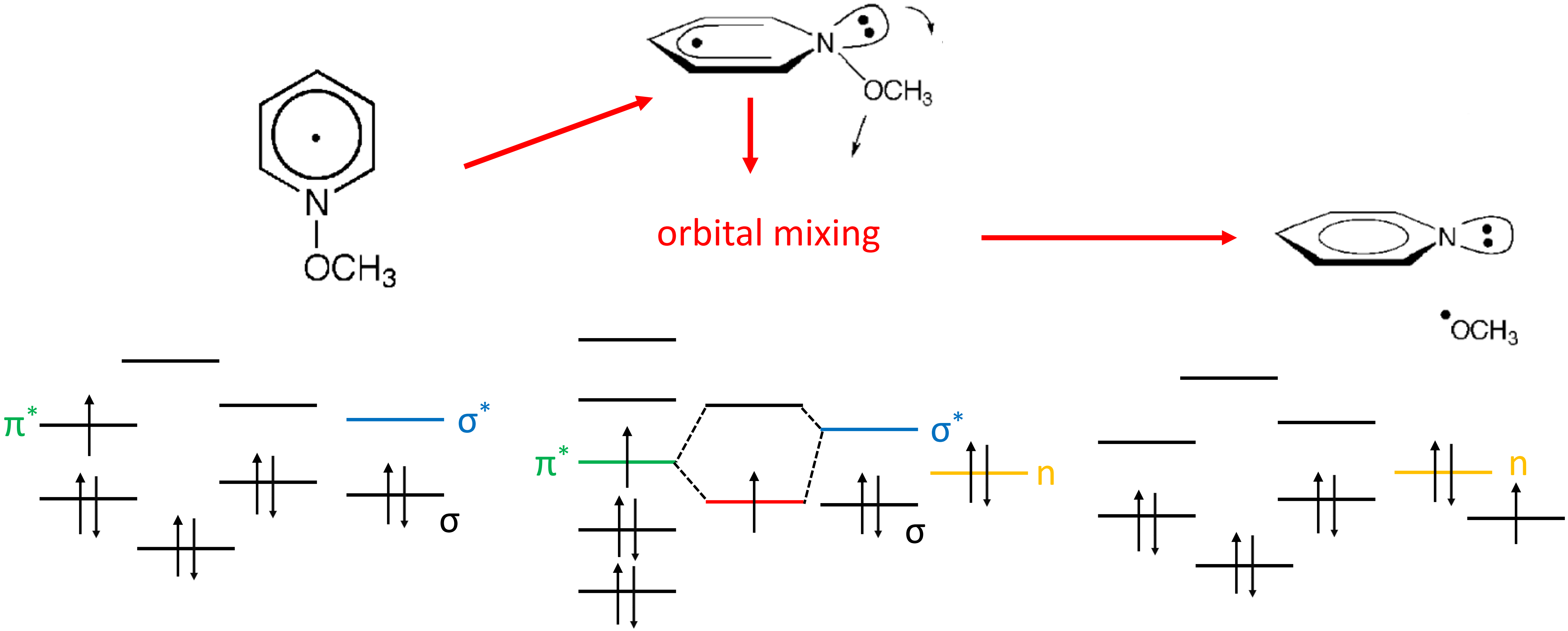
E

π^* & σ^* mixing lowers energy

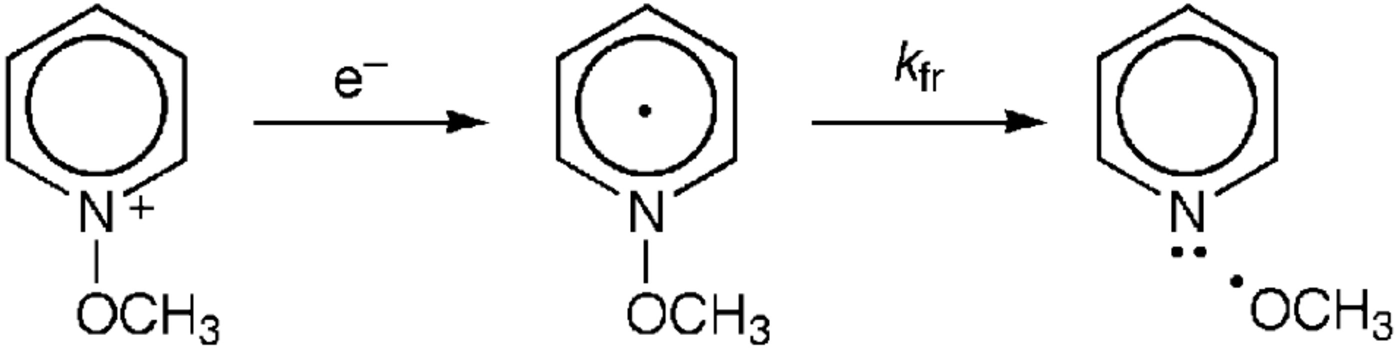
Representative configurations involved in fragmentation



Configuration changes in fragmentation



Short summary



π^* orbital of pyridinium ion receives an electron from donor.

N-O bond bending is important for π^* & σ^* orbital mixing.

Orbital mixing is impossible when planar radical.

Contents

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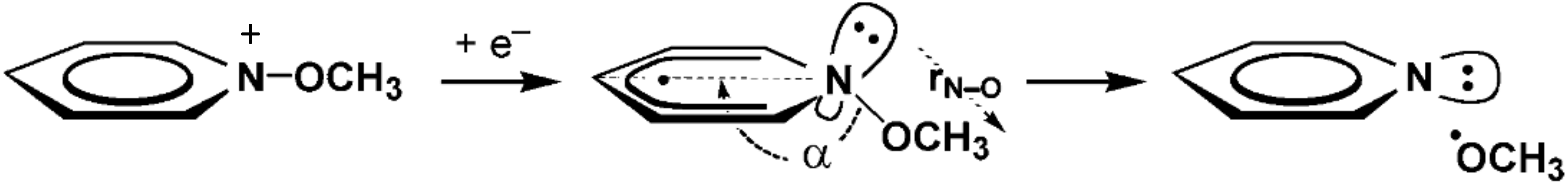
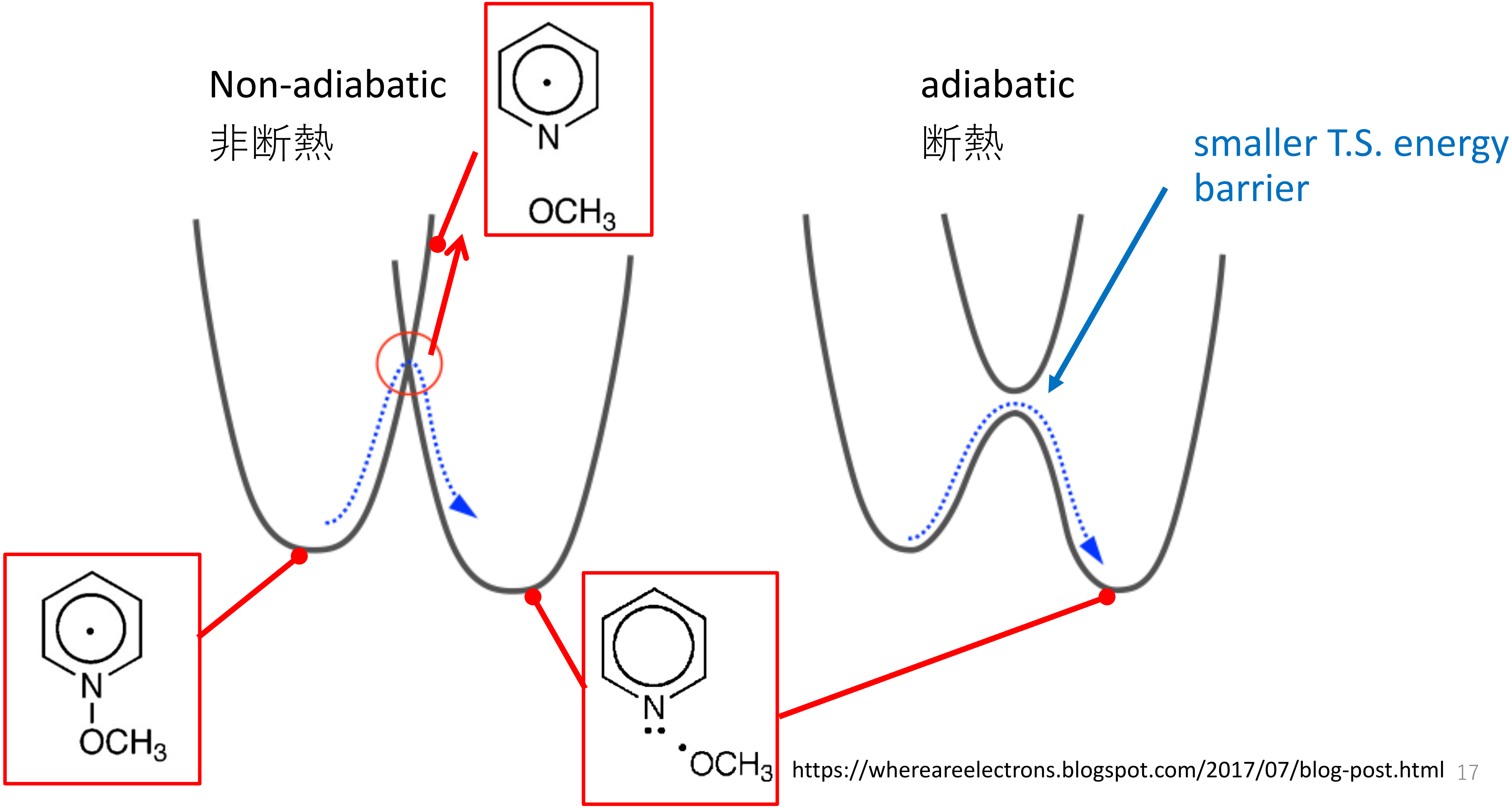
Model



N-O out of plane bending angle α

N-O bond length r

Fragmentation is adiabatic



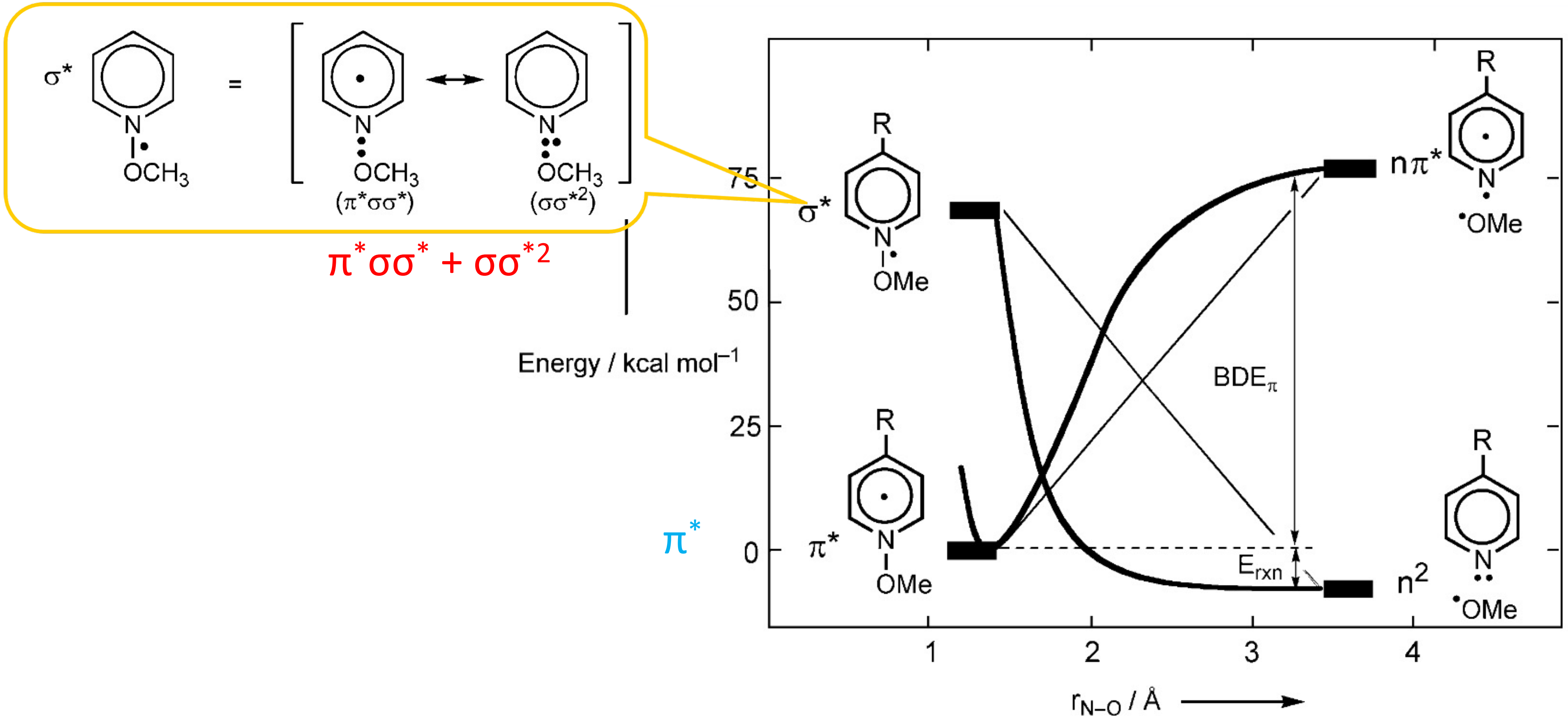
Non-adiabatic
非断熱

adiabatic
断熱

smaller T.S. energy barrier

https://whereareelectrons.blogspot.com/2017/07/blog-post.html

Energy correlation diagram



$\pi^*\sigma\sigma^* + \sigma\sigma^{*2}$

$n\pi^*$

π^*

n^2

Assumed a single mixed σ^* state that changes character between $\pi^*\sigma\sigma^*$ & $\sigma\sigma^{*2}$.

Fragmentation occurs from $\sigma\sigma^{*2}$.

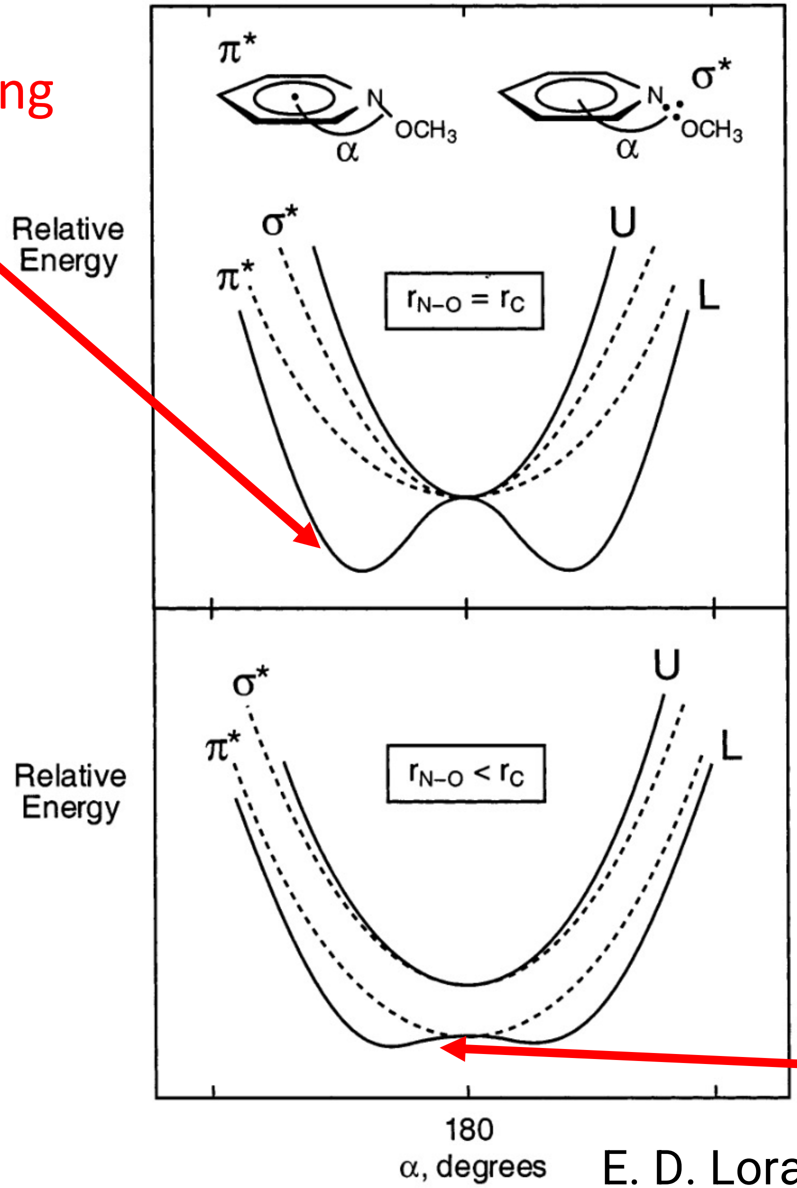
E. D. Lorance, and I. R. Gould. *J. Phys. Chem. A* **2005**, *109*, 12, 2912−2919

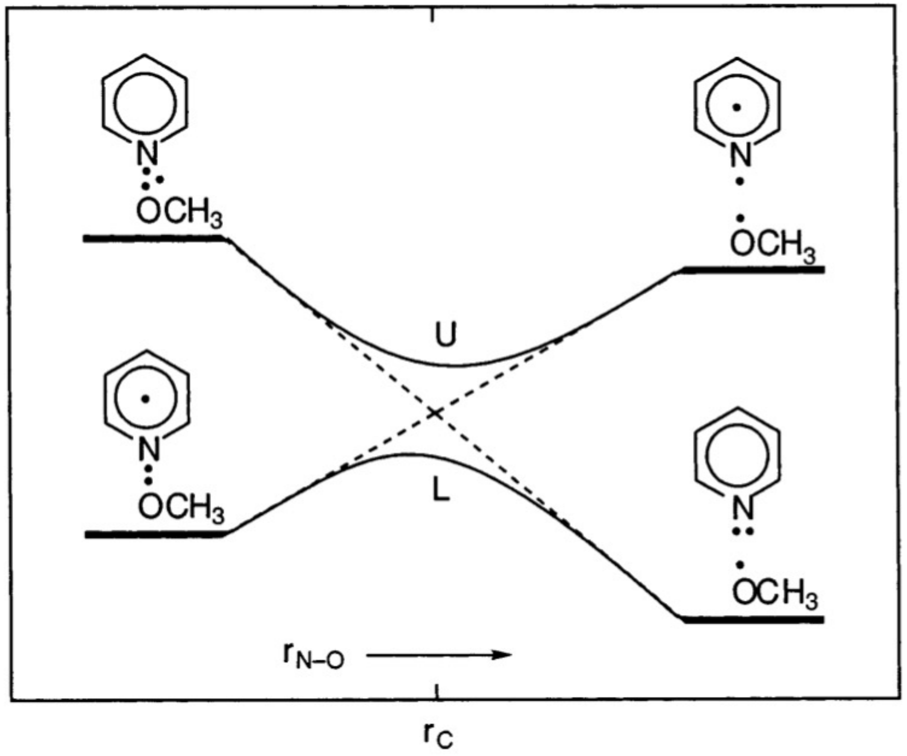
Radical states formed by orbital mixing

extensive mixing

$r_{N\text{-}O} = r_c$

$r_{N\text{-}O} < r_c$





Orbital mixing becomes more extensive with increasing bond length & decreasing angle

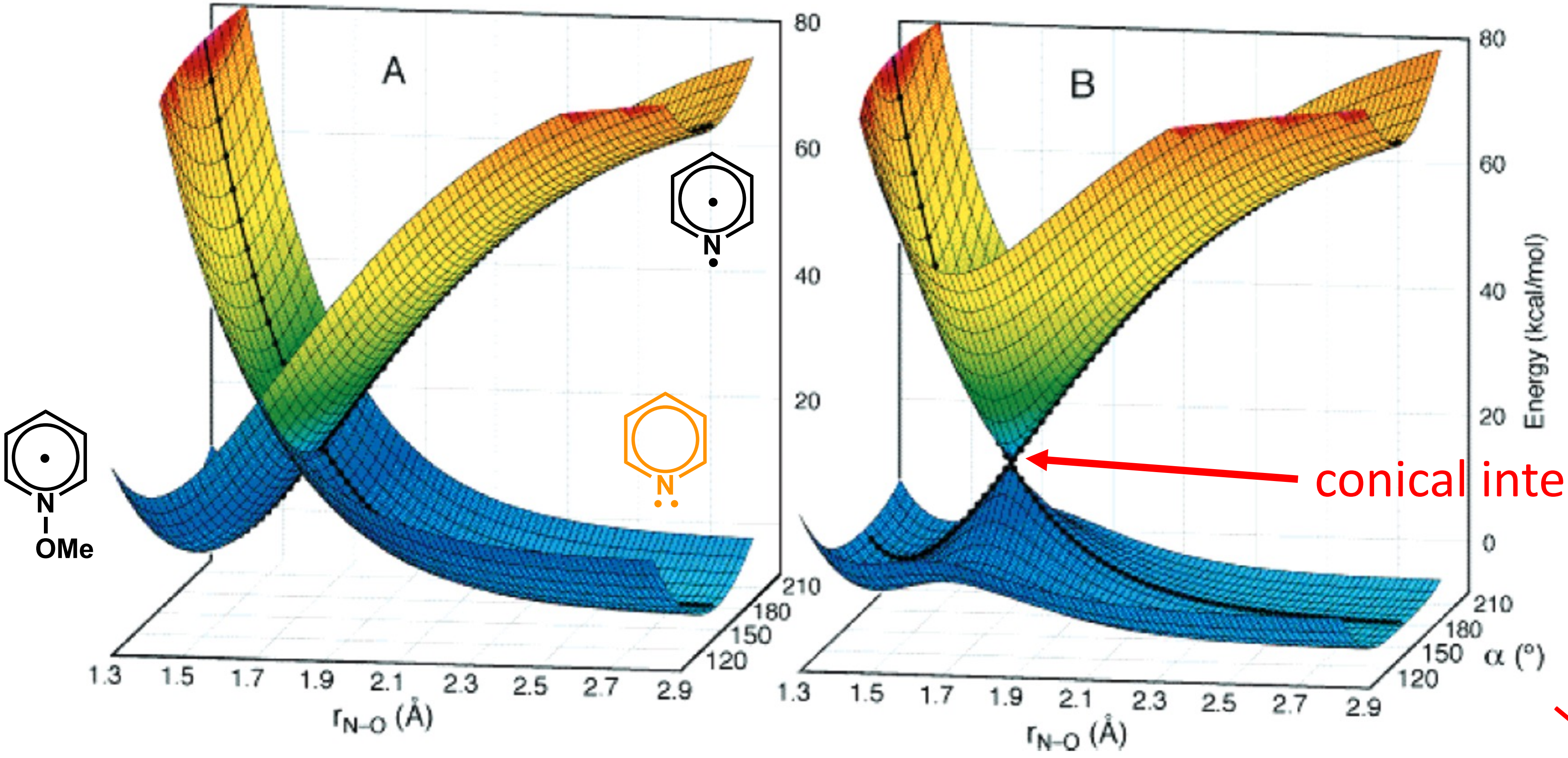
small effect of orbital mixing

E. D. Lorance, et al. *J. Am. Chem. Soc.* **2002**, *124*, 51, 15225−15238

Energy potential surface

A: diabatic surfaces

B: adiabatic surfaces



Energy ↑

conical intersection

bond angle →

bond length →

bond length →

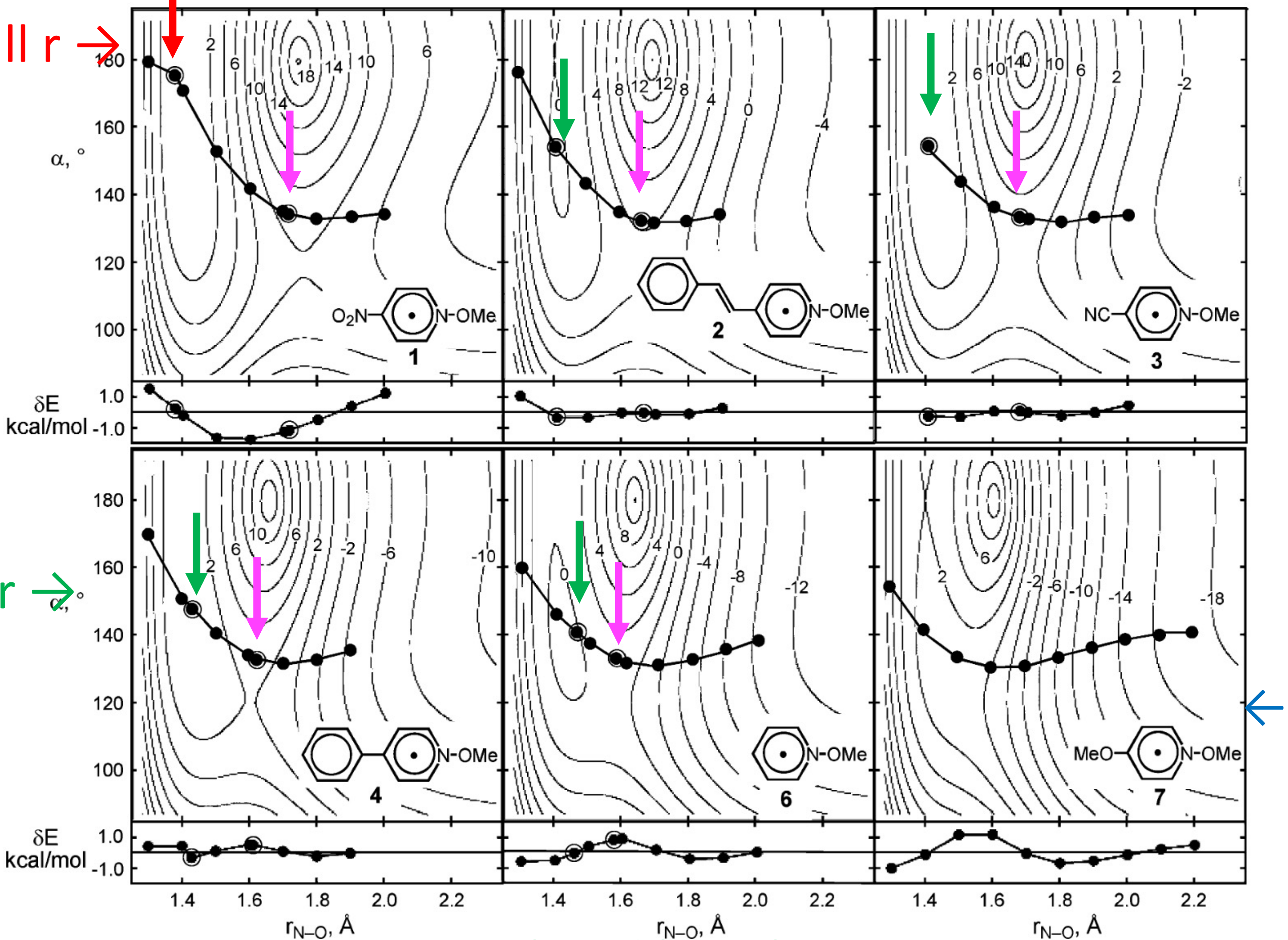
E. D. Lorance and I. R. Gould. *J. Phys. Chem. A* **2005**, *109*, 12, 2912−2919

Contour plots

radical

T.S.

$-NO_2$: large α & small r →



bond angle ↑

-Ph : small α & large r →

← -OMe : barrierless

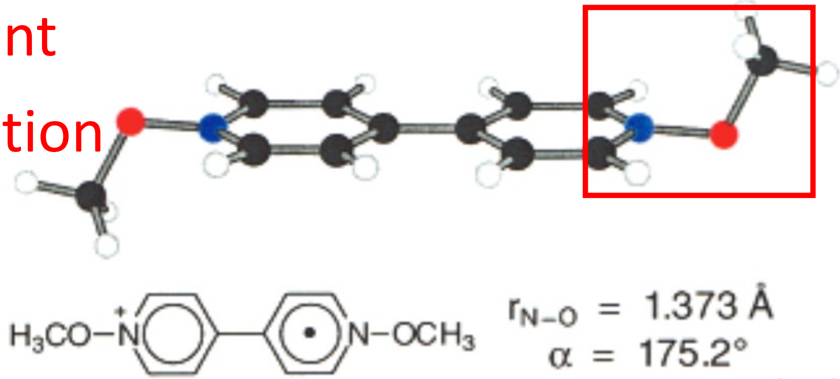
bond length →

E. D. Lorance and I. R. Gould. *J. Phys. Chem. A* **2005**, *109*, 12, 2912−2919

Bent conformations of minimized radical structures

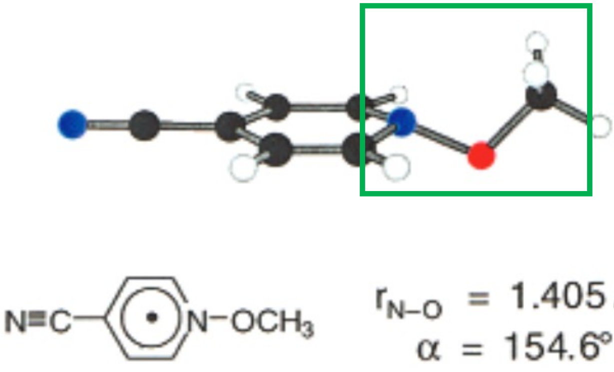
EWG: hardly bent

slow fragmentation



2

r_{N-O} = 1.373 Å
α = 175.2°
k_{fr} = 4.0×10^{4} s^{-1}



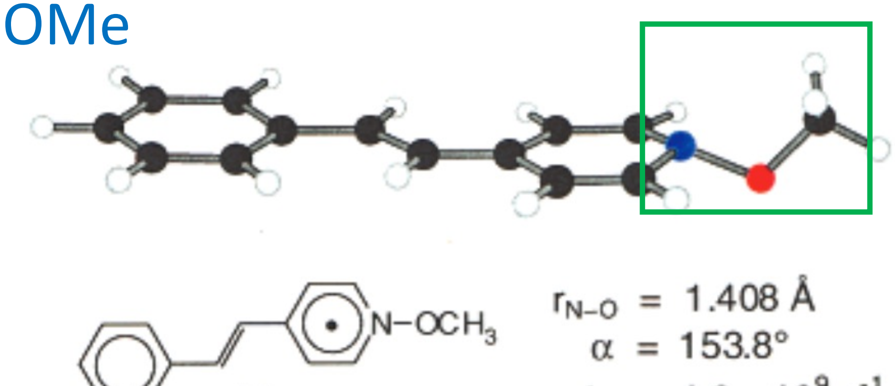
3

r_{N-O} = 1.405 Å
α = 154.6°
k_{fr} = 1.2×10^{10} s^{-1}

reaction rate:

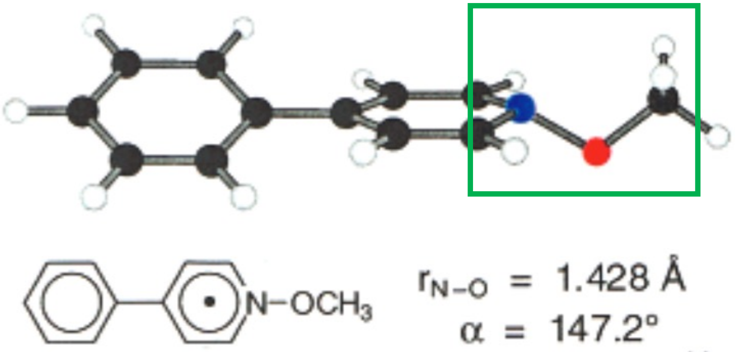
-NO_2 < -Ph < -OMe

delocalizing group : bent



10

r_{N-O} = 1.408 Å
α = 153.8°
k_{fr} = 4.6×10^{9} s^{-1}



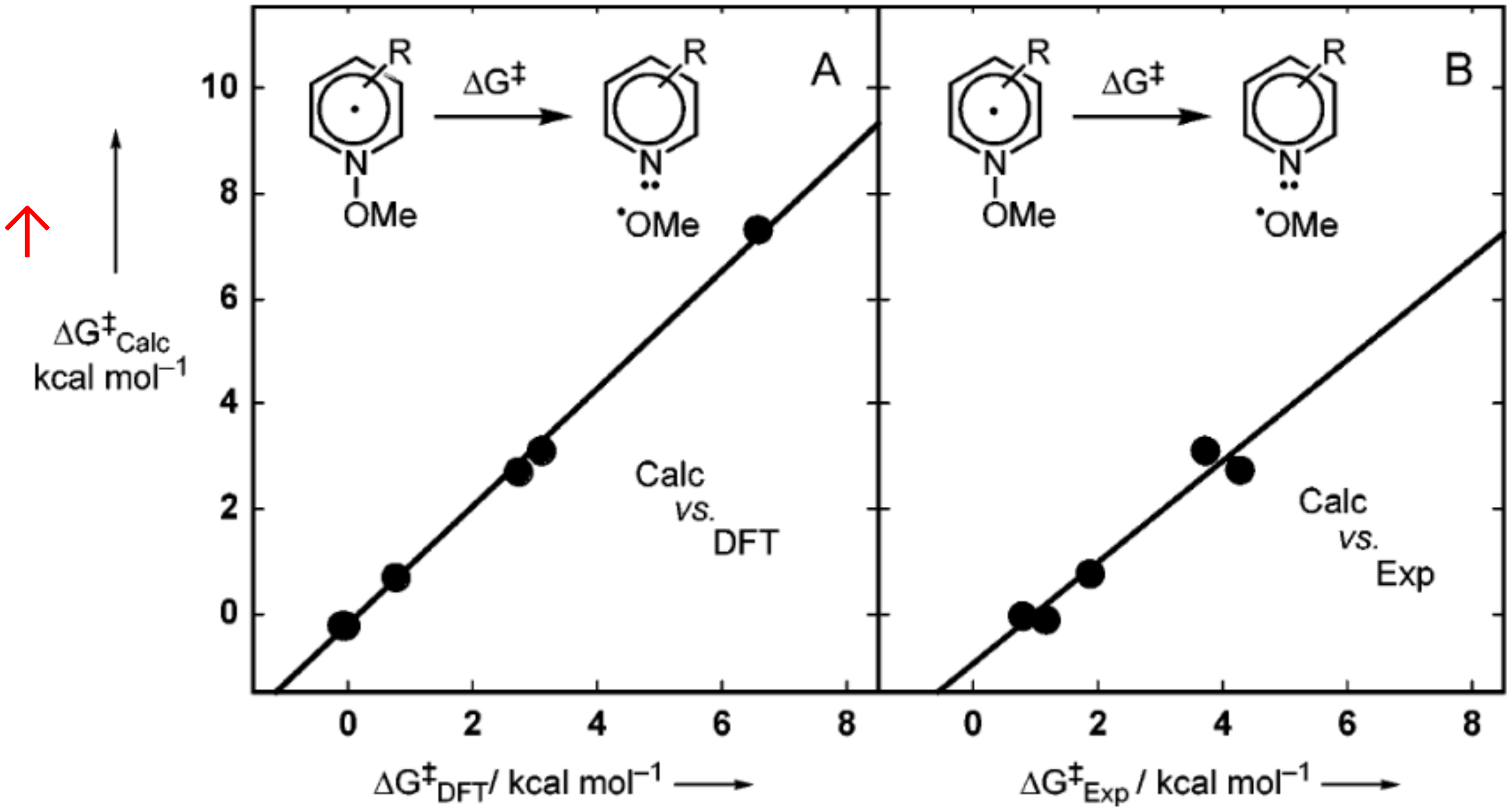
1

r_{N-O} = 1.428 Å
α = 147.2°
k_{fr} = 2.7×10^{11} s^{-1}

E. D. Lorance, et al. *J. Am. Chem. Soc.* **2002**, *124*, 51, 15225−15238

The validation of model calculation

Calculation ↑



DFT →

Experiment →

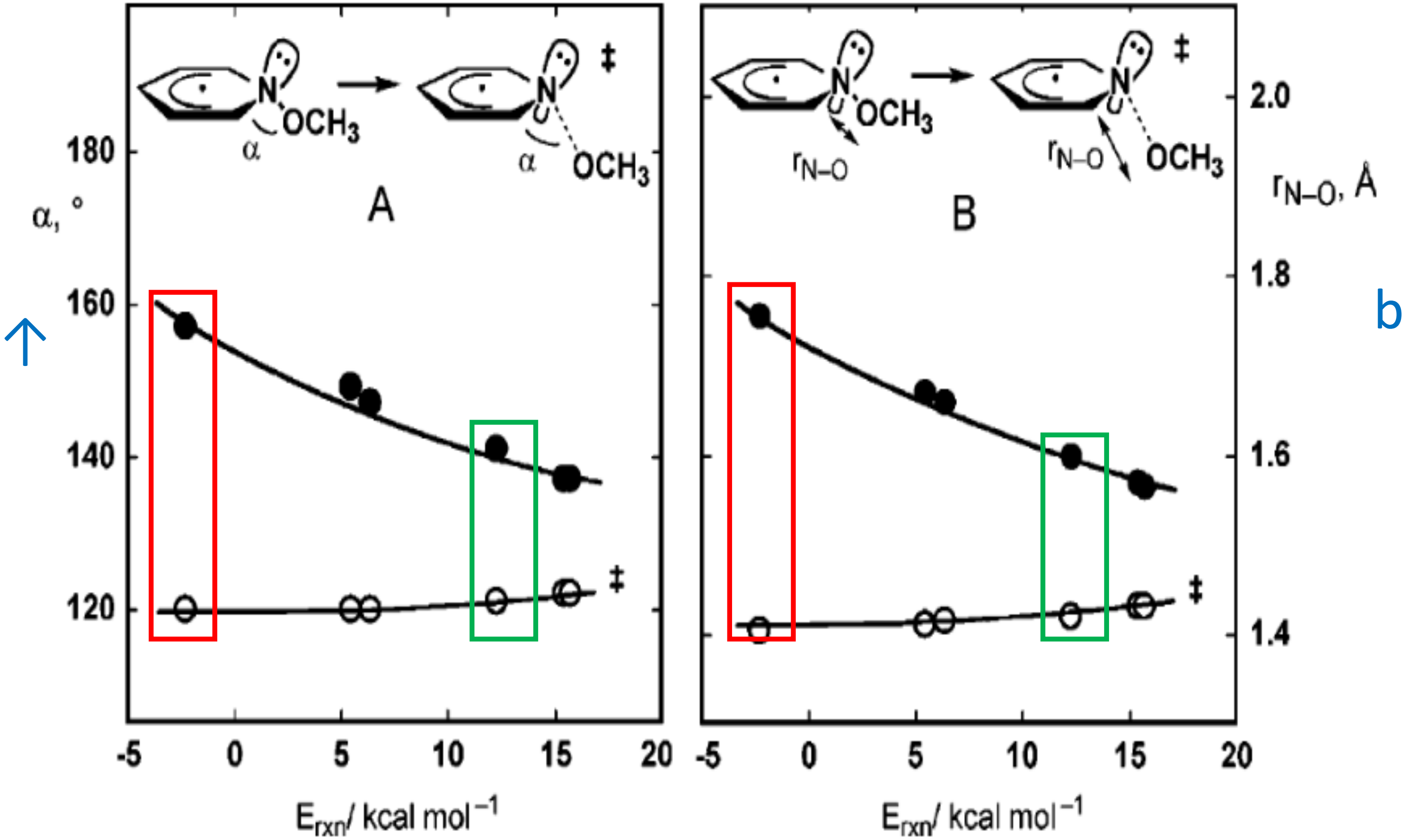
Activation free energies

Model vs DFT : good agreement (left)

Model vs Experiment : good agreement (right)

E. D. Lorance and I. R. Gould. *J. Phys. Chem. A* **2005**, *109*, 12, 2912−2919

Relationships of exothermicity with bond angle and bond length



bond angle ↑

bond length ↑

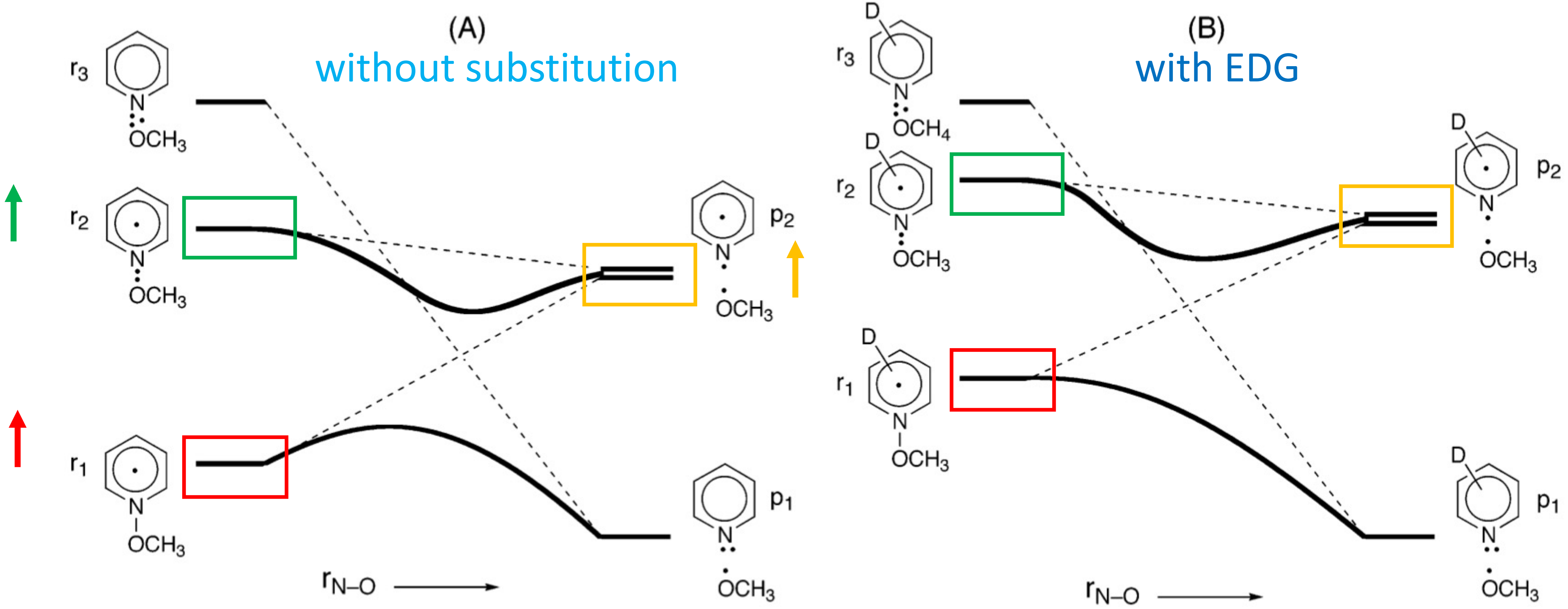
exothermicity →

(α, r) at T.S. are similar among different structures, while those at radical minimum are not.

Slow reaction has a radical minimum that is far apart from T.S. & it is an endothermic reaction.

E. D. Lorance and I. R. Gould. *J. Phys. Chem. A* **2005**, *109*, 12, 2912−2919

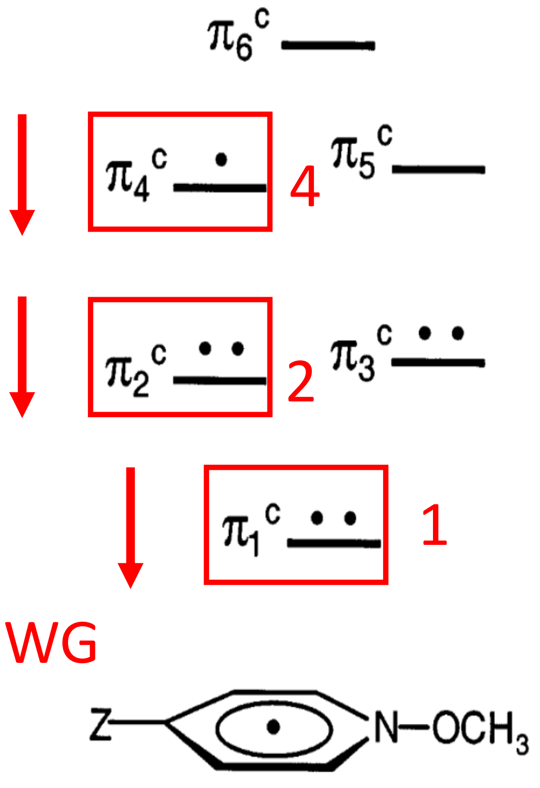
Substitutional effect: general discussion



EDG raises the energies of configurations in which π^* is occupied. (B)

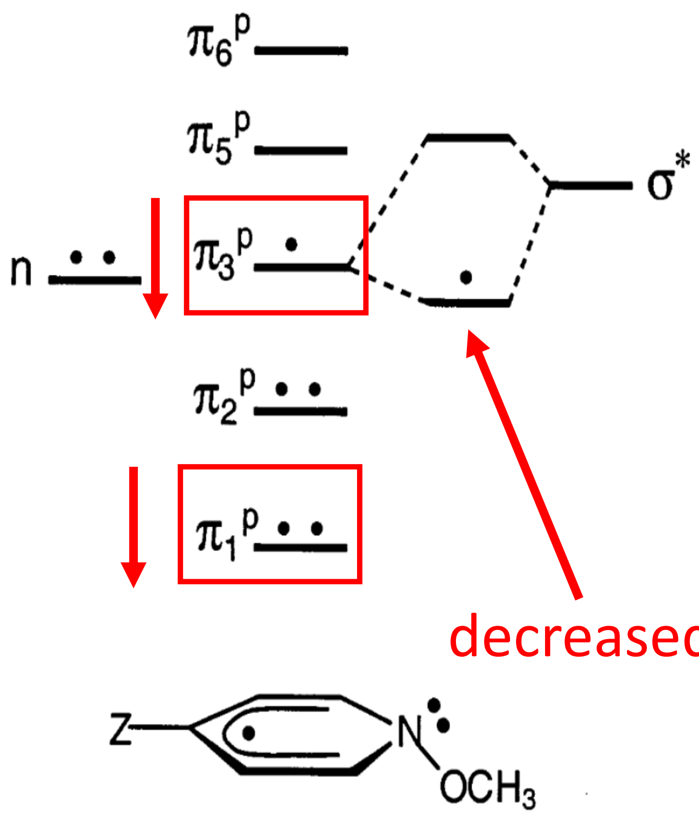
E. D. Lorance, W. H. Kramer, and I. R. Gould. *J. Am. Chem. Soc.* **2004**, 126, 43, 14071−14078

Effect of electron-withdrawing groups



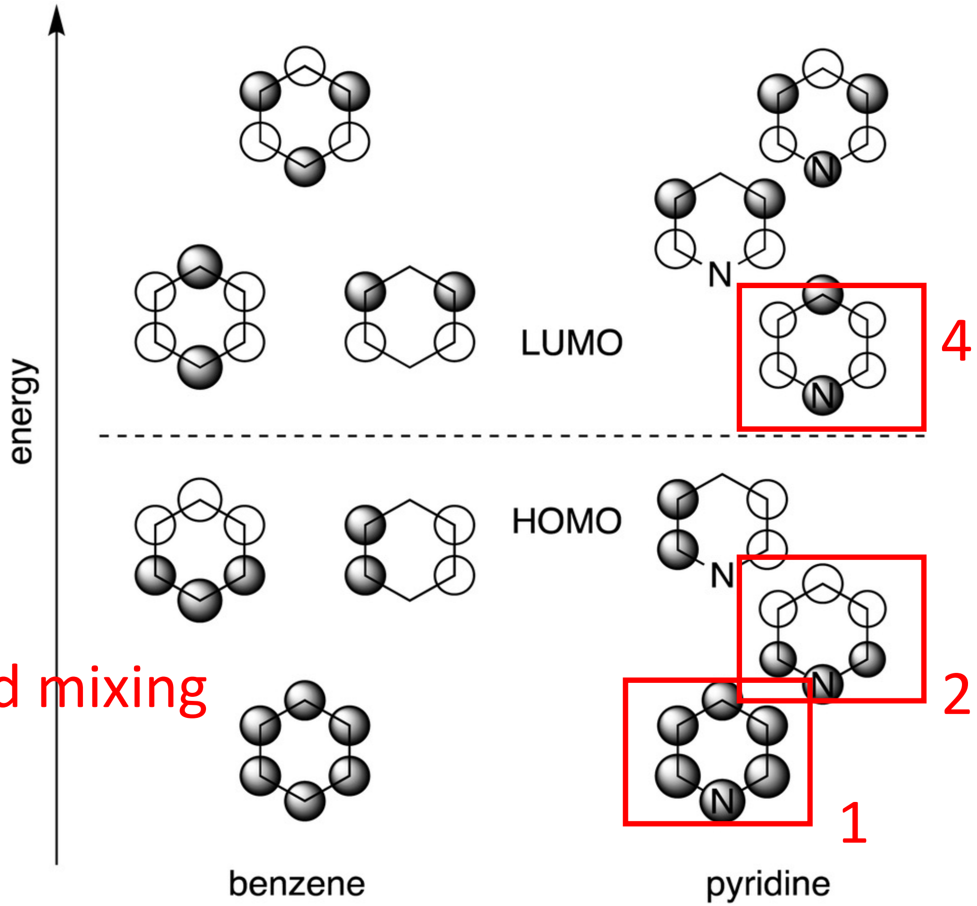
Z = EWG

more stabilized



less stabilized

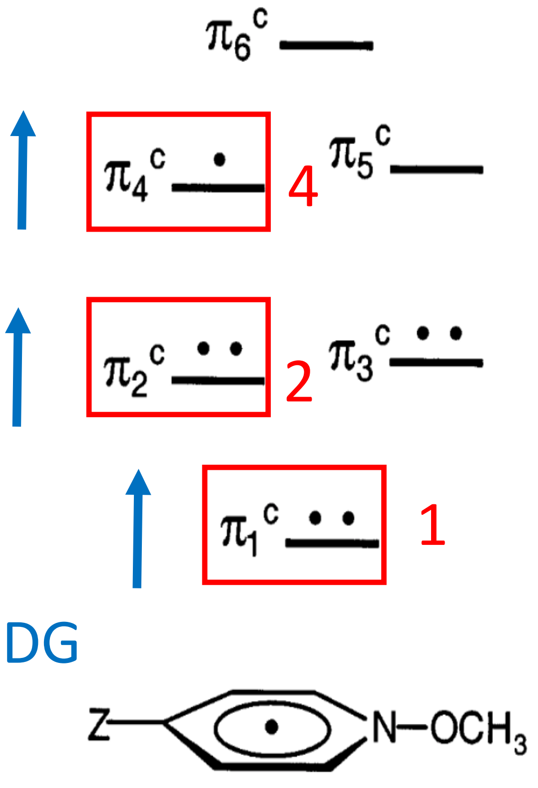
decreased mixing



EWG makes fragmentation slower.

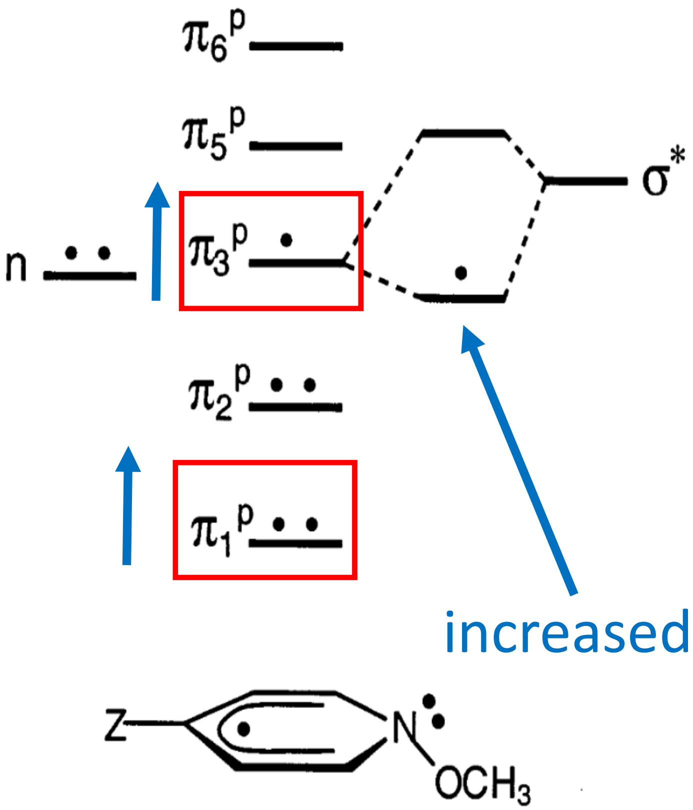
E. D. Lorance, et al. *J. Am. Chem. Soc.* **2002**, *124*, 51, 15225−15238

Effect of electron-donating groups



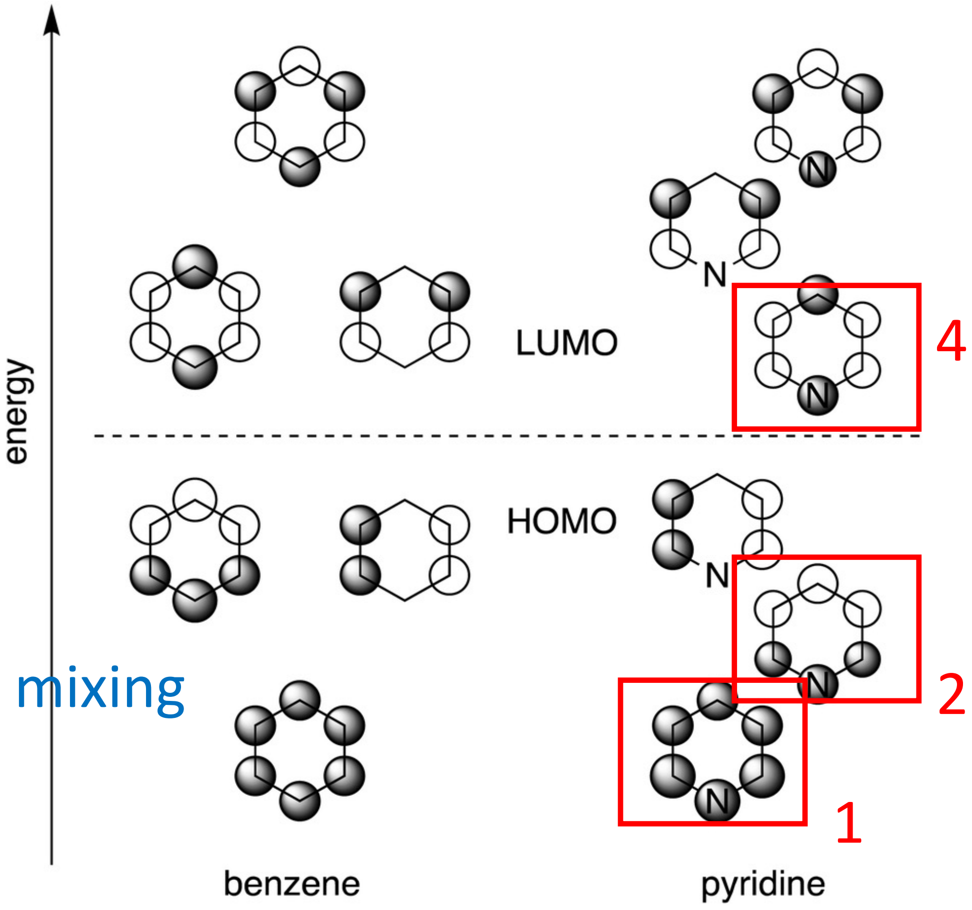
Z = EDG

more destabilized



less destabilized

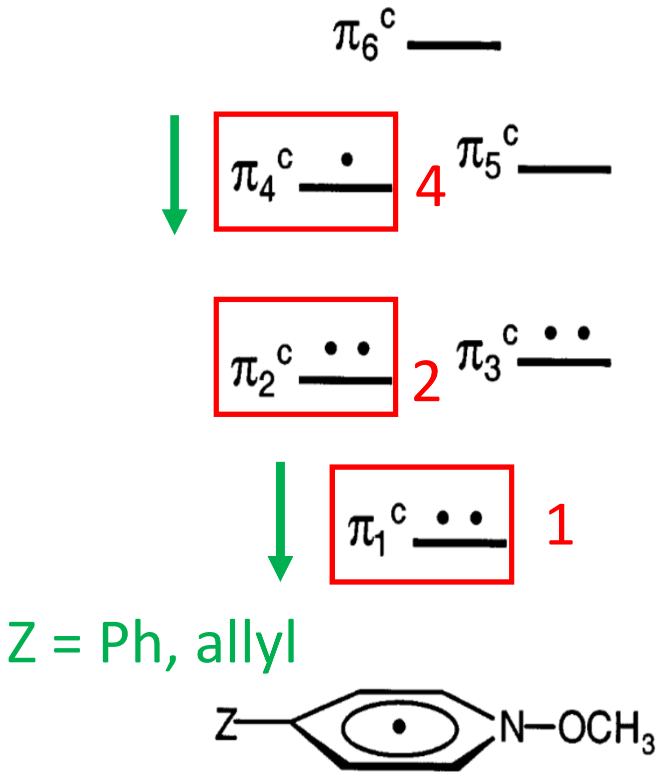
increased mixing



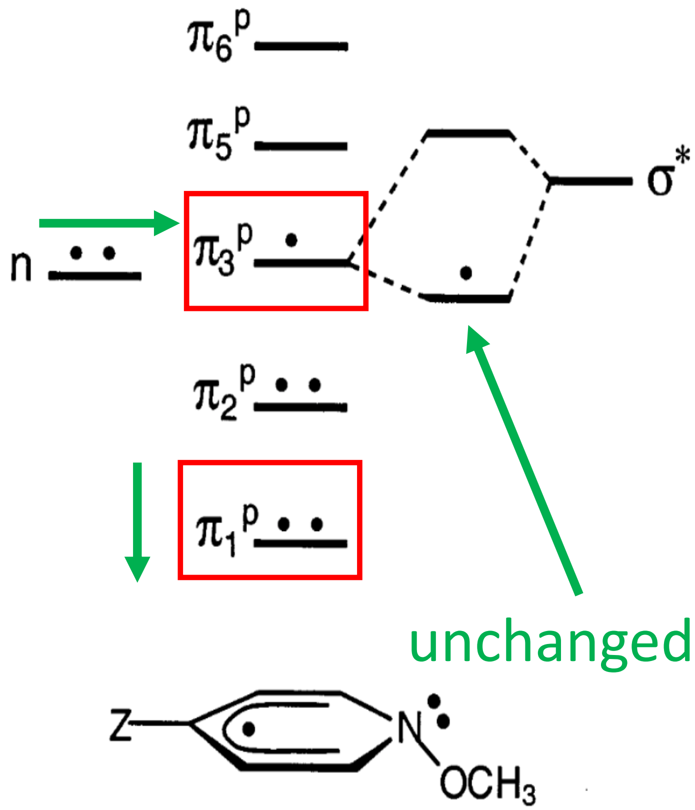
EDG makes fragmentation faster.

E. D. Lorance, et al. *J. Am. Chem. Soc.* **2002**, *124*, 51, 15225−15238

Effect of delocalizing groups

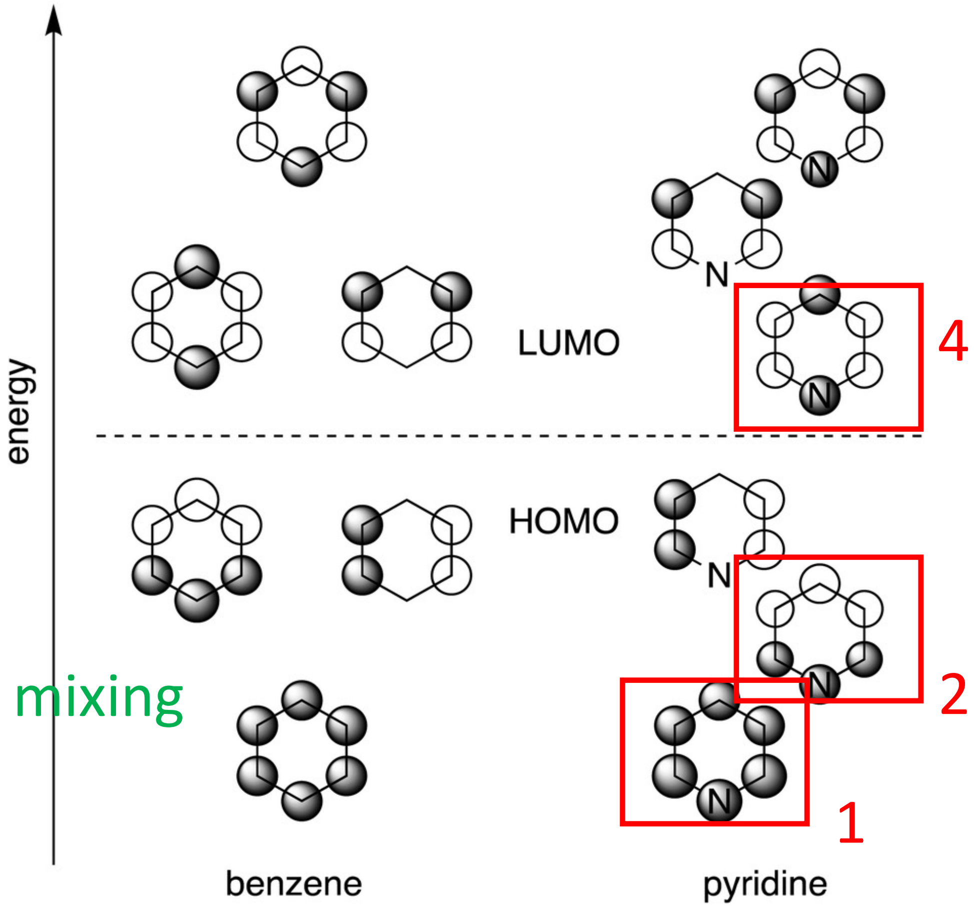


more stabilized



unchanged mixing

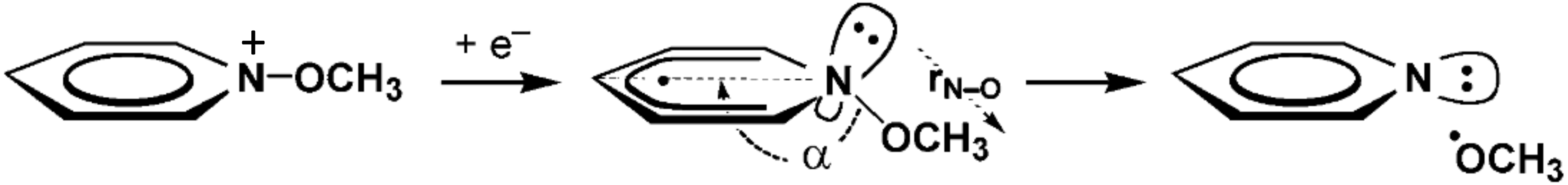
less stabilized



Delocalizing group makes fragmentation slower.

E. D. Lorance, et al. *J. Am. Chem. Soc.* **2002**, *124*, 51, 15225−15238

Summary



N-O bond bending is important for π^* & σ^* orbital mixing.

Fragmentation occurs from three electron N∴X bond.

Conformations at T.S. are similar among different pyridyl radicals.

Fast fragmentation reaction

- occurs when pyridyl radical has EDG(s)
- is highly exothermic
- has radical minimum whose conformation is close to T.S.

4-OMe pyridyl radical undergoes barrierless fragmentation.