Electrochemical Alcohol Oxidation Mediated by Nitroxyl Radicals

Literature Seminer (2017/5/20)

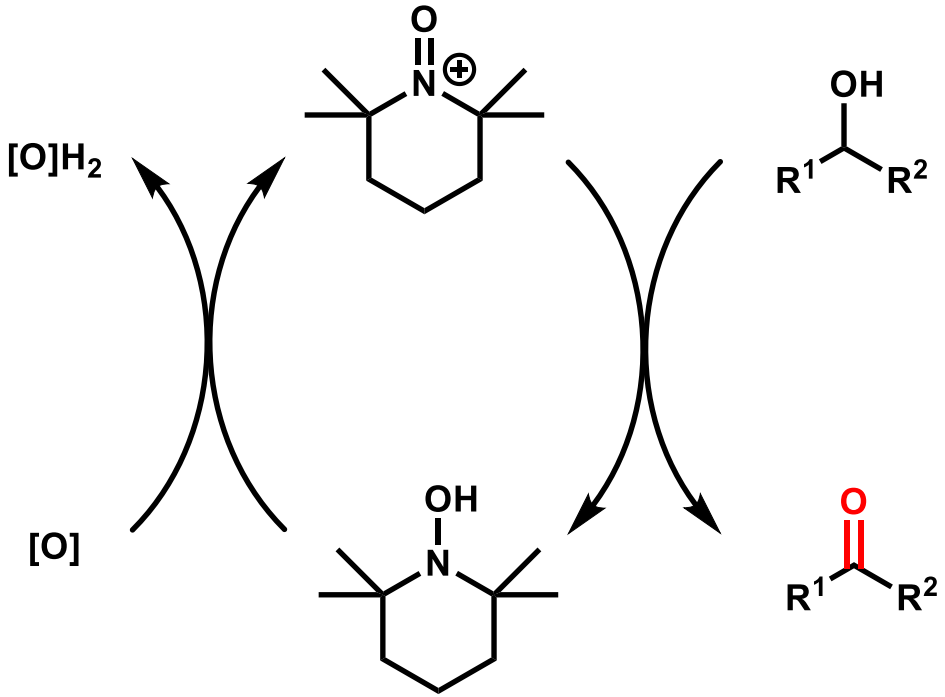
D3 Satoshi Hashimoto

Nitroxyl Radicals

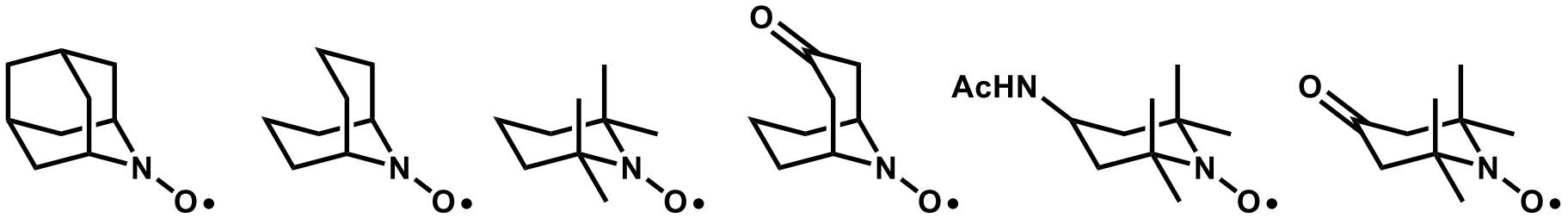
Chemical oxidation of TEMPO:

Oxidants

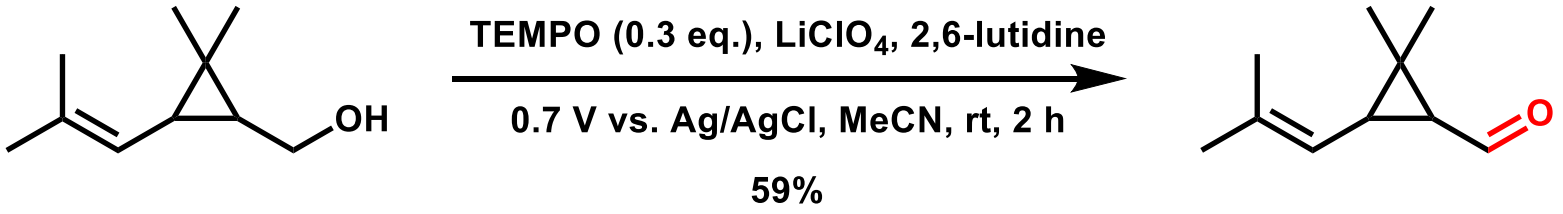
NaOCl
Br_2
$PhI(OAc)_2$



Nitroxyl redox potentials ($E_{1/2}$)

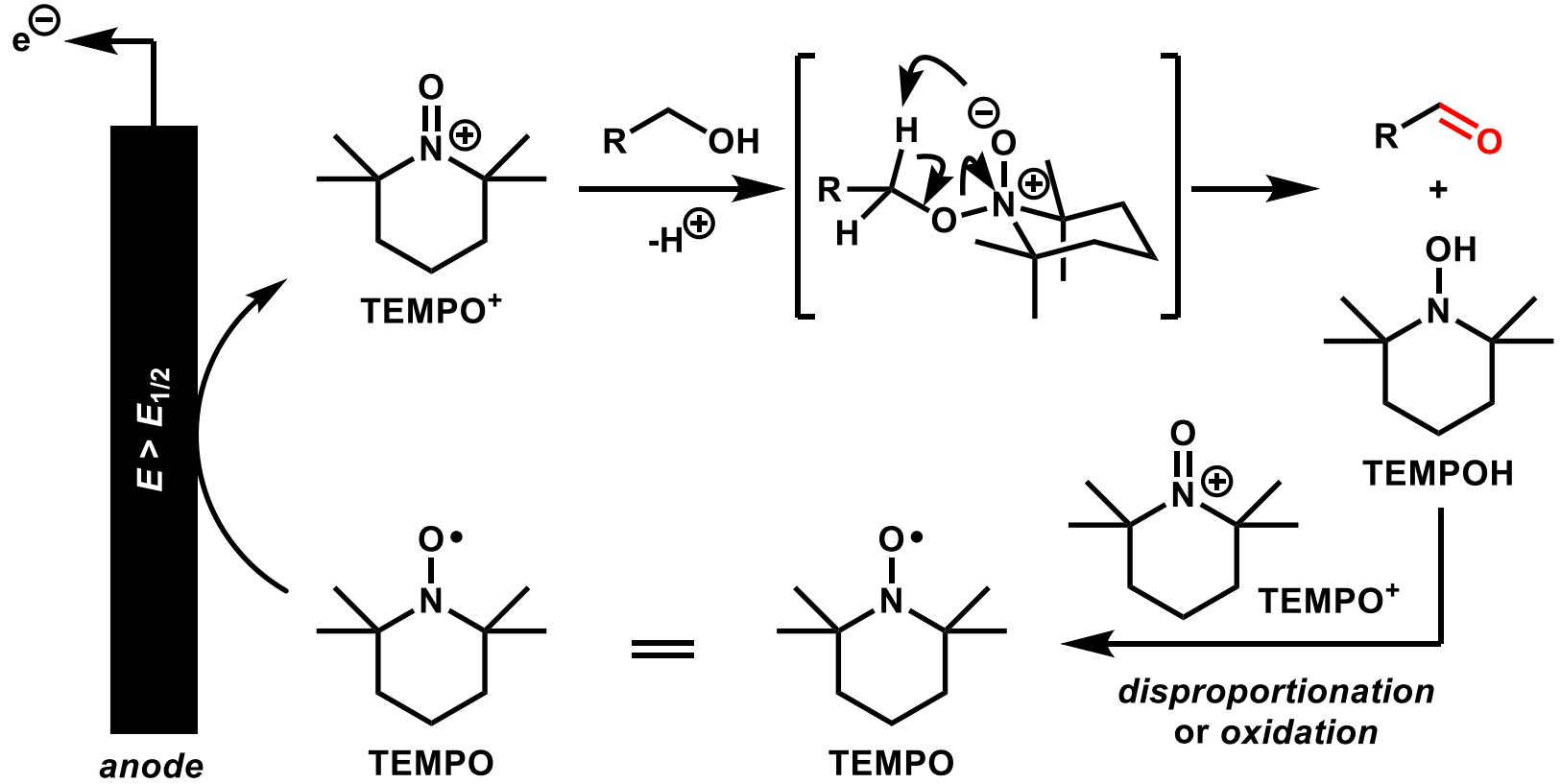


Electrochemical Oxidation with TEMPO



Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492.

Proposed mechanism:



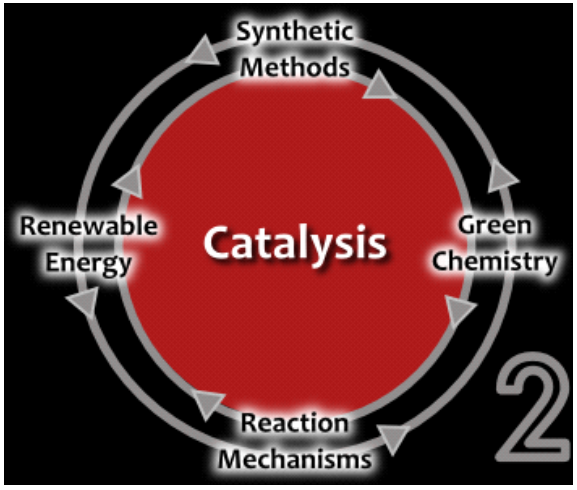
Prof. Shannon S. Stahl

B.S. Chemistry (1992)
University of Illinois at Urbana-Champaign, Urbana, IL

Ph.D. Chemistry (1997)
NSF Predoctoral Fellow
California Institute of Technology, Pasadena, CA
Advisor: Prof. John E. Bercaw
Mechanistic Studies of Alkane Activation by Platinum(II) Complexes

NSF Postdoctoral Fellow (1997-1999)
Massachusetts Institute of Technology, Cambridge, MA
Advisor: Prof. Stephen J. Lippard
Mechanistic Enzymology of Soluble Methane Monooxygenase

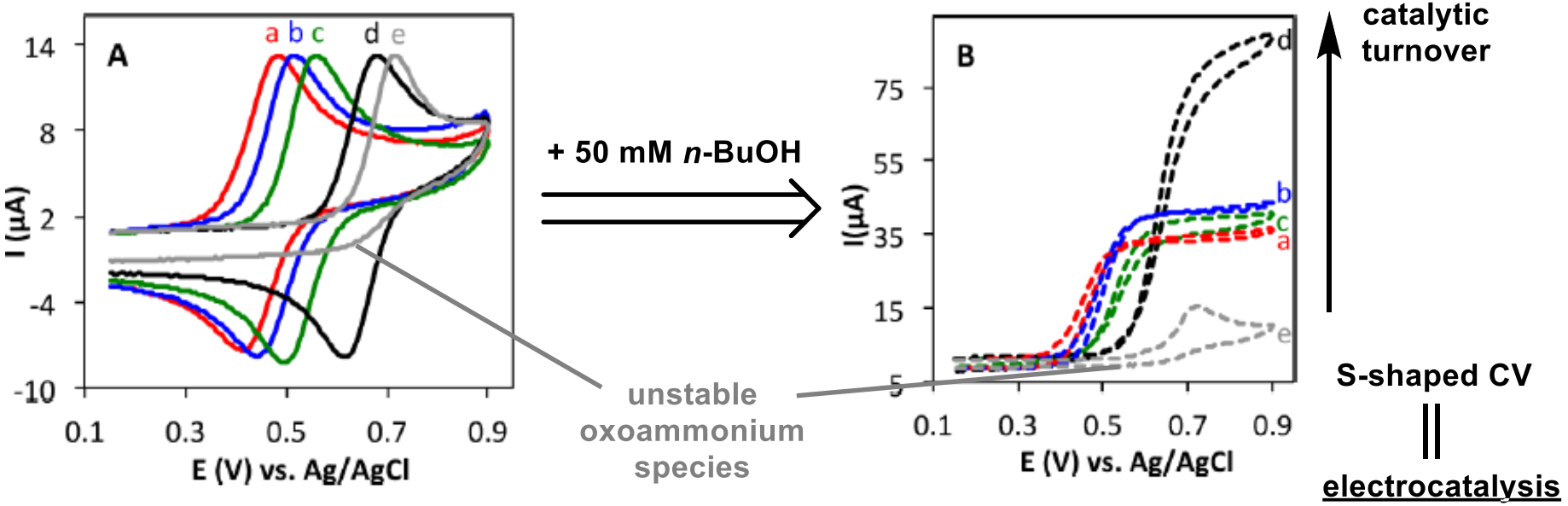
Professor of Chemistry
University of Wisconsin - Madison



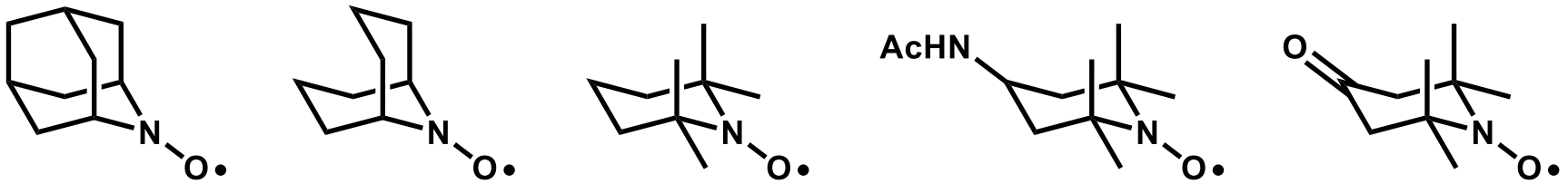
Research Interest
Development of Useful Synthetic Methods and
The Elucidation of Mechanistic Prinsiple
• Aerobic oxidation catalyst
• Catalysis for soler energy conversion

Contents

Cyclic Voltammograms of Nitroxyl Radicals



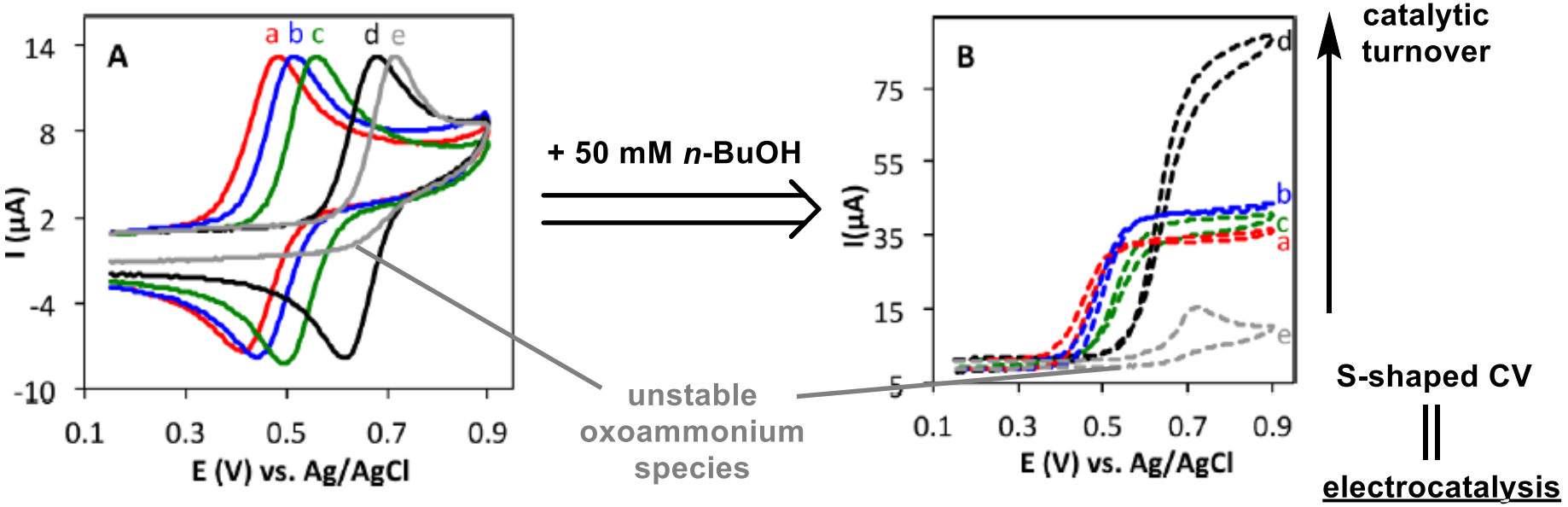
a: AZADO, b: ABNO, c: TEMPO, d: ACT, e: 4-oxo-TEMPO; HCO_3^-/CO_3^{2-} electrolyte (pH 10)



	AZADO	ABNO	TEMPO	4-acetamido-TEMPO	4-oxo-TEMPO
$E_{1/2}$	0.45 (V)	0.48	0.53	0.65	0.69

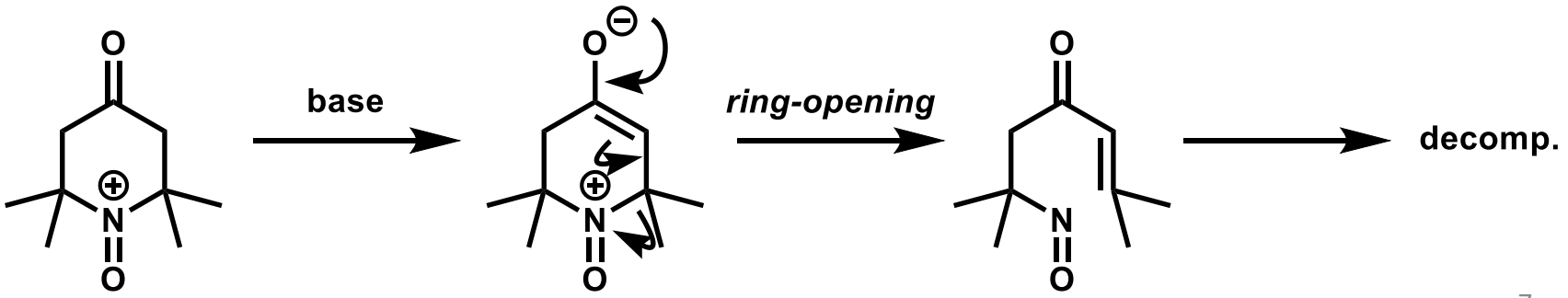
Iwabuchi, Y. *et al. Tetrahedron Lett.* **2012**, *53*, 2070.

Cyclic Voltammograms of Nitroxyl Radicals



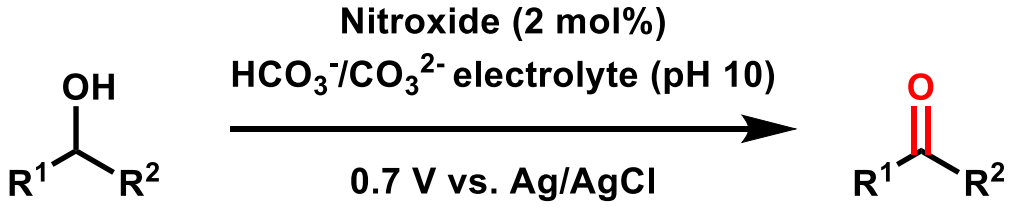
a: AZADO, **b: ABNO**, **c: TEMPO**, **d: ACT**, e: 4-oxo-TEMPO; HCO_3^-/CO_3^{2-} electrolyte (pH 10)

The Instability of 4-oxo-TEMPO$^+$

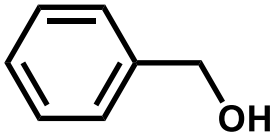
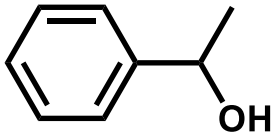
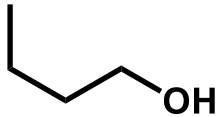
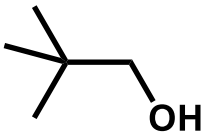
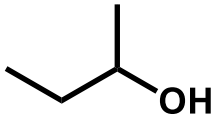


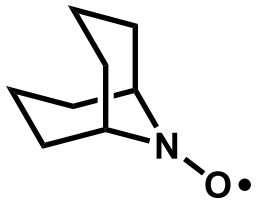
Sen, V. D.; Golubev, V. A. *Russ. J. Org. Chem.* **2011**, *47*, 869.

Turnover Frequencies of Nitroxides for Oxidation

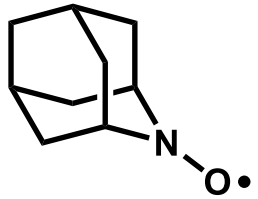


TOF(h^{-1}) of various nytroxides for oxidation of alcohols

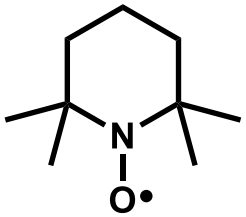
	 *1° benzylic*	 *2° benzylic*	 *1° aliphatic*	 *hindered 1° aliphatic*	 *2° aliphatic*
ABNO	**1088**	**238**	**588**	**337**	**87**
AZADO	**1128**	**358**	**488**	**298**	**78**
TEMPO	**853**	**118**	**568**	**198**	**18**
ACT	**1228**	**378**	**708**	**388**	**73**



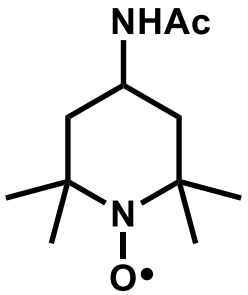
ABNO



AZADO



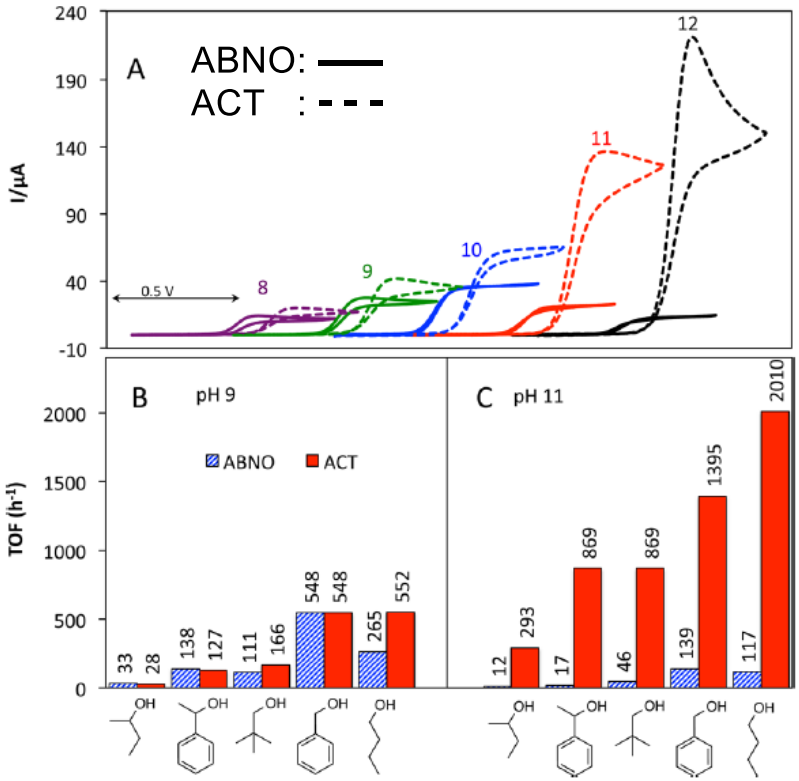
TEMPO



ACT

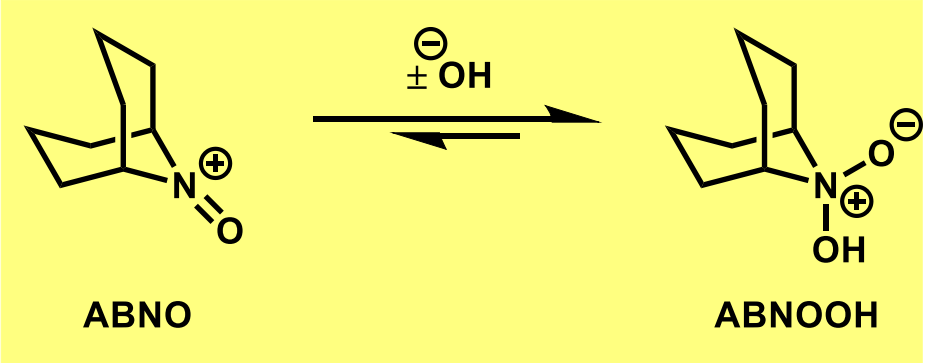
pH Effect on Electrocatalytic Oxidation of Alcohols

CVs of ABNO and ACT at different pH

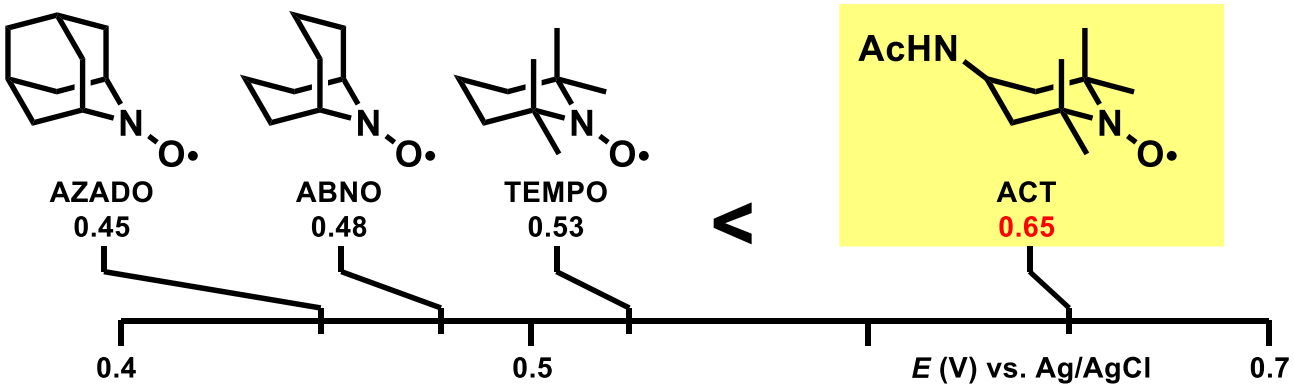


(A) Cyclic voltammograms
50 mM 1-BuOH at various pH values
(B,C) TOFs for oxidation of various alcohols
1 mM nitroxides, 50 mM alcohols in aqueous HCO_3^-/CO_3^{2-} buffer

Formation of ABNOOH inhibits electrocatalytic oxidation of ABNO in basic condition.

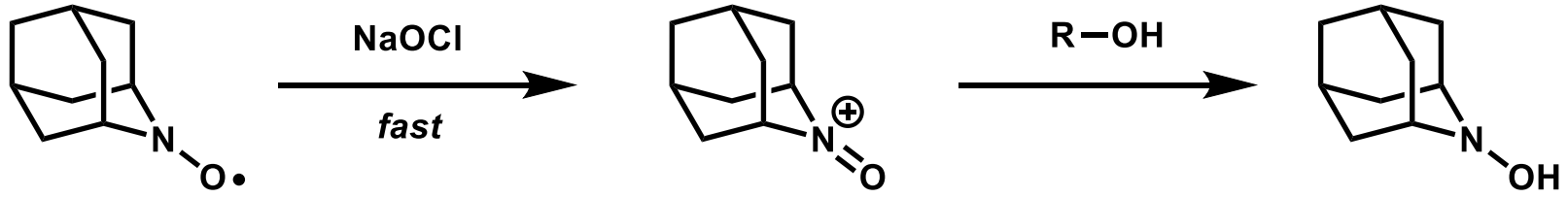


Why ACT Activity Is Enhanced?

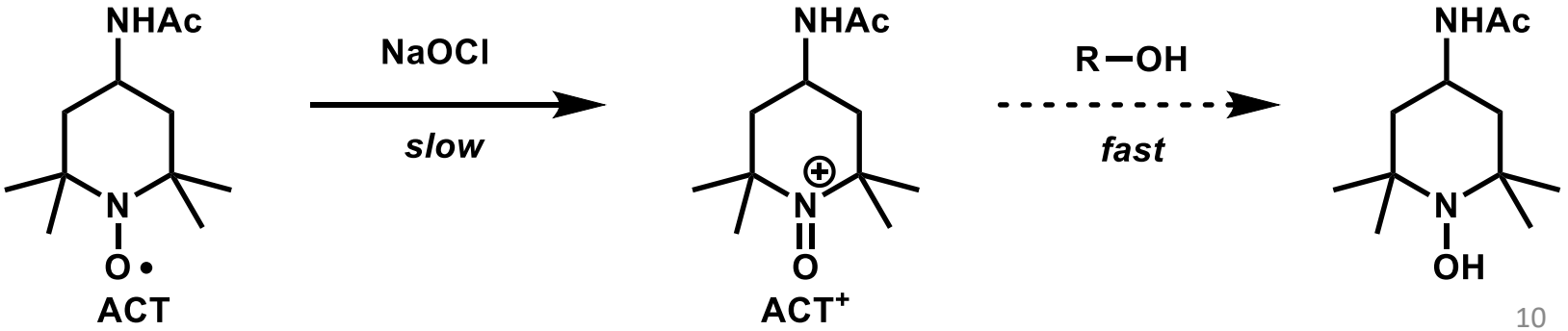


High activity arises from high redox potential?

Active chemical oxidation of AZADO by NaOCl

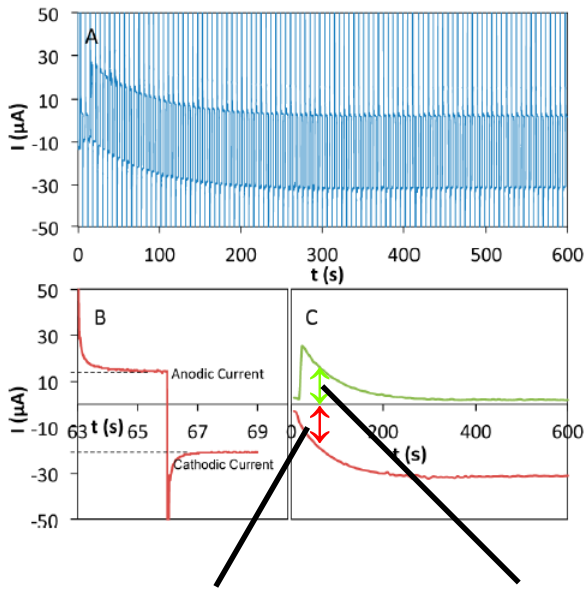


Sluggish chemical oxidation of ACT by NaOCl



Cyclic Chronoamperometry for Concentration Profiles

Cyclic Chronoamperogram



(A) Representative cyclic chronoamperometric data for the oxidation of TEMPO by NaOCl.

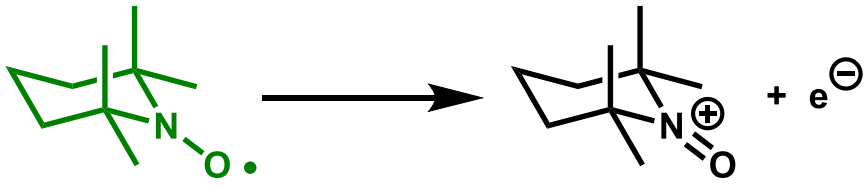
(B) Expansion of the oxidation and reduction current from a single cycle in plot (A), obtained from potential step $E_{1/2}$±0.18 V.

(C) Plots of the faradaic anodic(+) and cathodic(-) current at each step in plot (A). Initial concentrations: 5.0 mM TEMPO, 0.2 M NaOCl, 0.12 M $NaHCO_3$. Pulse width = 3s

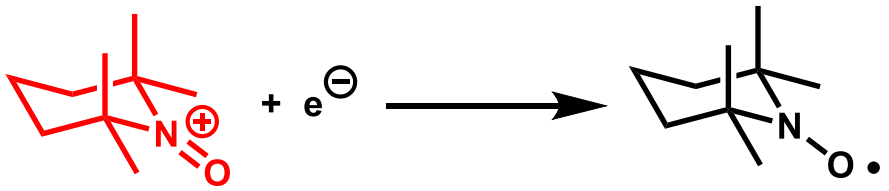
Cathodic current proportional to [oxoammonium] concentration

Anodic current proportional to [nitroxyl] concentration

Anode:

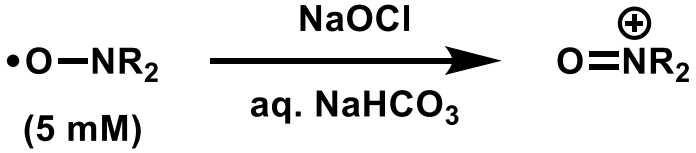


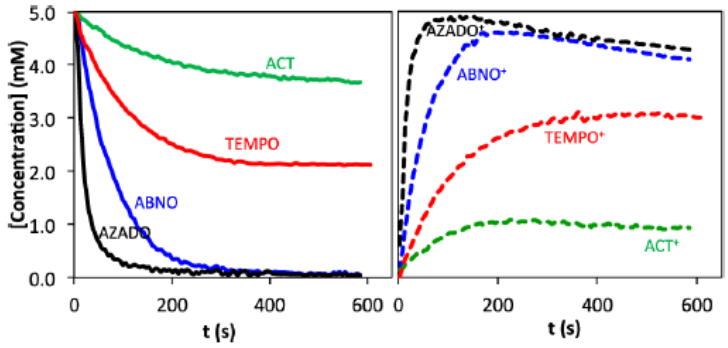
Cathode:



Concentration Profiles of Nitroxyl and Oxoammonium Species

• profile of nitroxyls in the presence of NaOCl:



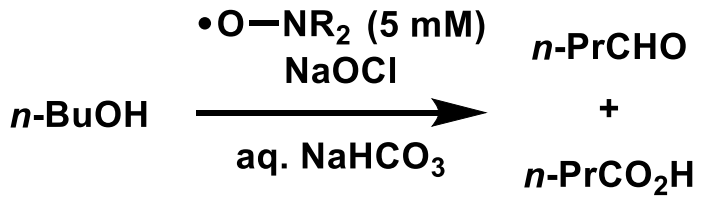


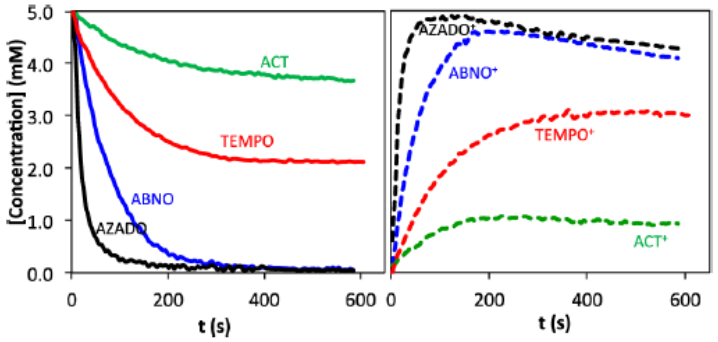
The relative rates match the redox potentials.
AZADO > ABNO > TEMPO > ACT

(0.45) (0.48) (0.53) (0.65)

Oxidation of ACT is 60- and 7-fold slower than AZADO and ABNO.

• profile of nitroxyls in the oxidation of *n*-BuOH:





[nitroxyl] + [oxoammonium] = 5 mM

Steady-state concentration

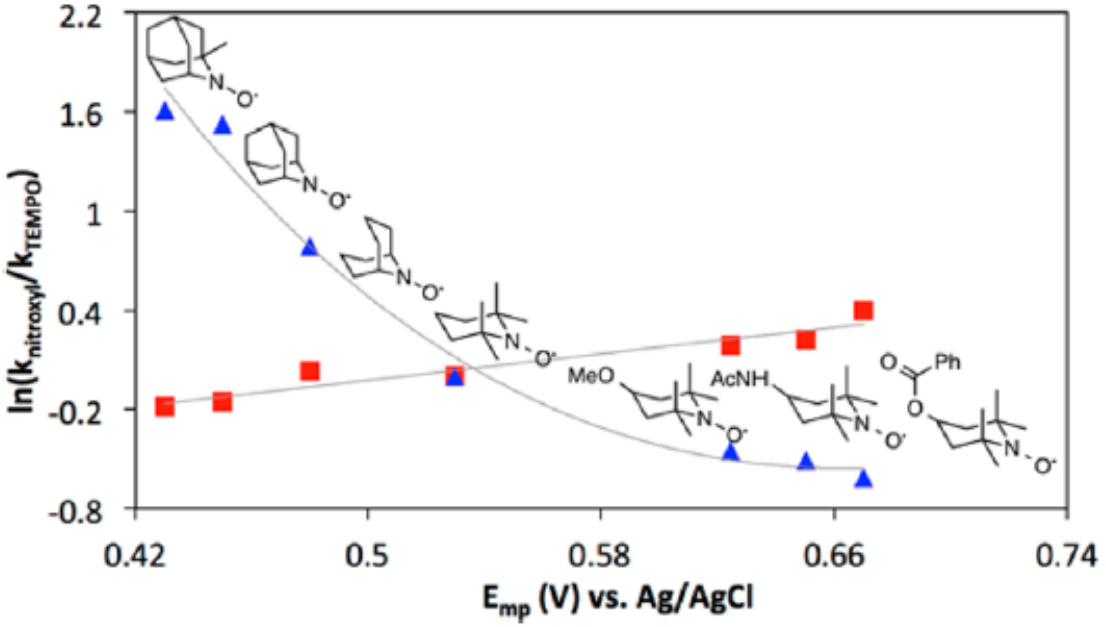
$AZADO^+$, $ABNO^+$ ~100%

$TEMPO^+$ ~60%

ACT^+ ~20%

Poor activity of ACT with NaOCl is because of slow formation of oxoammonium species.

Short Summary

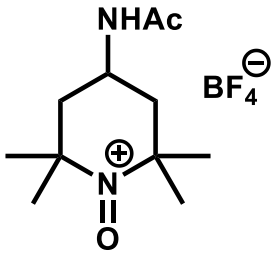


Linear-free-energy correlations for nitroxyl-catalyzed oxidation of *n*-BuOH with NaOCl (blue triangles) or electrochemical conditions (red squares).

NaOCl-driven reaction: nitroxyls with lower E_{mp} are more-effective catalysts

Electrocatalytic reaction: E_{mp} could overcome steric effects in catalytic activity

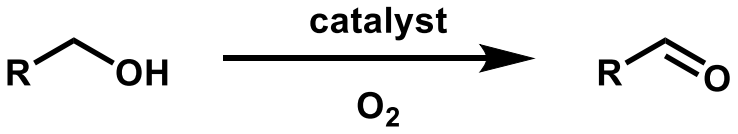
Widespread use of ACT as electrocatalyst or stoichiometric use of ACT+ (Bobbitt's salt) will be expected.



Bobbitt' salt

Contents

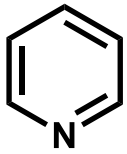
Representative Catalyst System for Aerobic Oxidation



Noble-metal catalysts

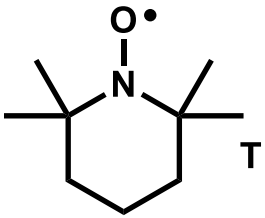
$(py)_2Pd(OAc)_2$,

py =



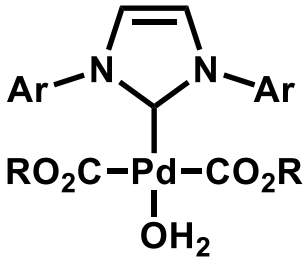
***Uemura* (1999)**

$RuCl_2(PPh_3)_3$/TEMPO



TEMPO

***Sheldon* (2001)**



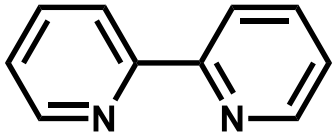
***Sigman* (2004)**

Cu-based catalysts

CuCl/TEMPO

***Semmelhack* (1984)**

(bpy)$CuBr_2$/TEMPO/KO*t*-Bu



bpy

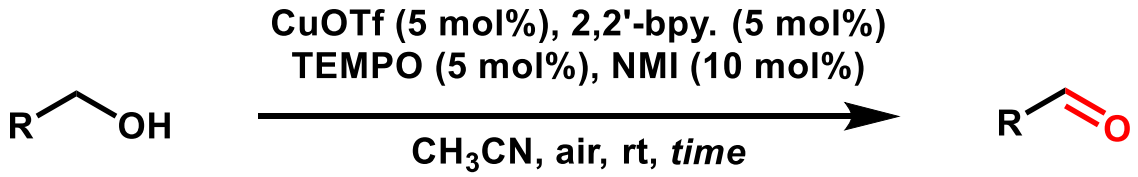
***Sheldon* (2003)**

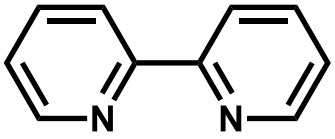
(bpy)$Cu(OTf)_2$/TEMPO/DBU

***Koskinen* (2009)**

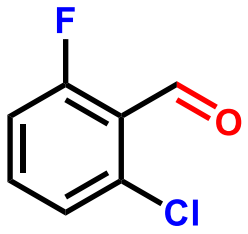
1) Uemura, S. *et al. J. Org. Chem.* **1999**, *64*, 6750. 2) Sheldon, R. A. *et al. J. Am. Chem. Soc.* **2001**, *123*, 6826. 3) Sigman, M. S. *et al. J. Am. Chem. Soc.* **2004**, *126*, 9724. 4) Semmelhack, M. F. *et al. J. Am. Chem. Soc.* **1984**, *106*, 3374. 5) Sheldon, R. A. *et al. Chem. Commun.* **2003**, 2414. 6) Koskinen, A. M. P. *et al. Chem.-Eur. J.* **2009**, *15*, 10901.

Cu/TEMPO Catalyst System for Aerobic Oxidation Developed by Stahl

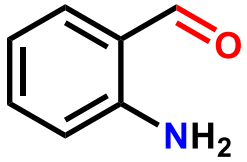




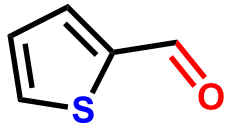
2,2'-bpy.



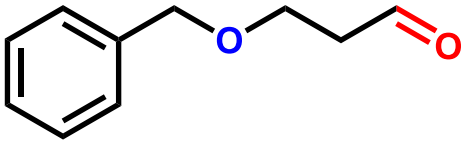
3 h, >98%



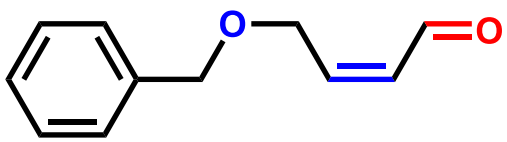
3 h, >98%



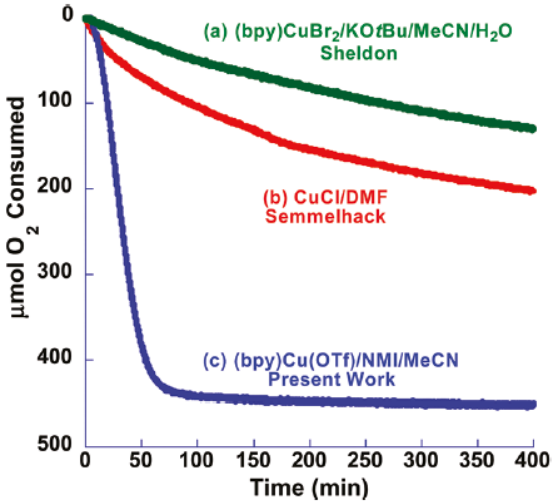
3 h, 83%



5 h, >98%



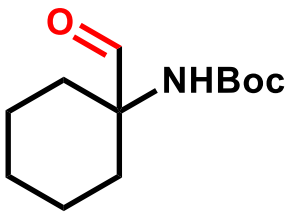
1.5 h, >98%
19:1 *Z*:*E*



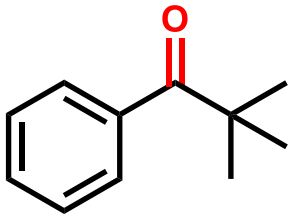
comparison of gas-uptake kinetic profiles
(using O_2 instead of air)

Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 16901.

Cu/ABNO Catalyst System for Aerobic Oxidation



90%



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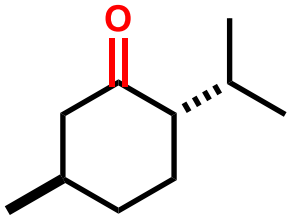

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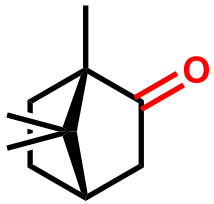
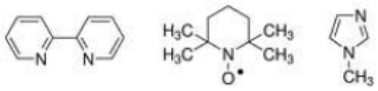
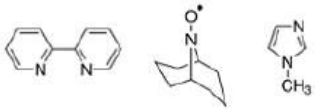


77%[a]

Stahl試薬

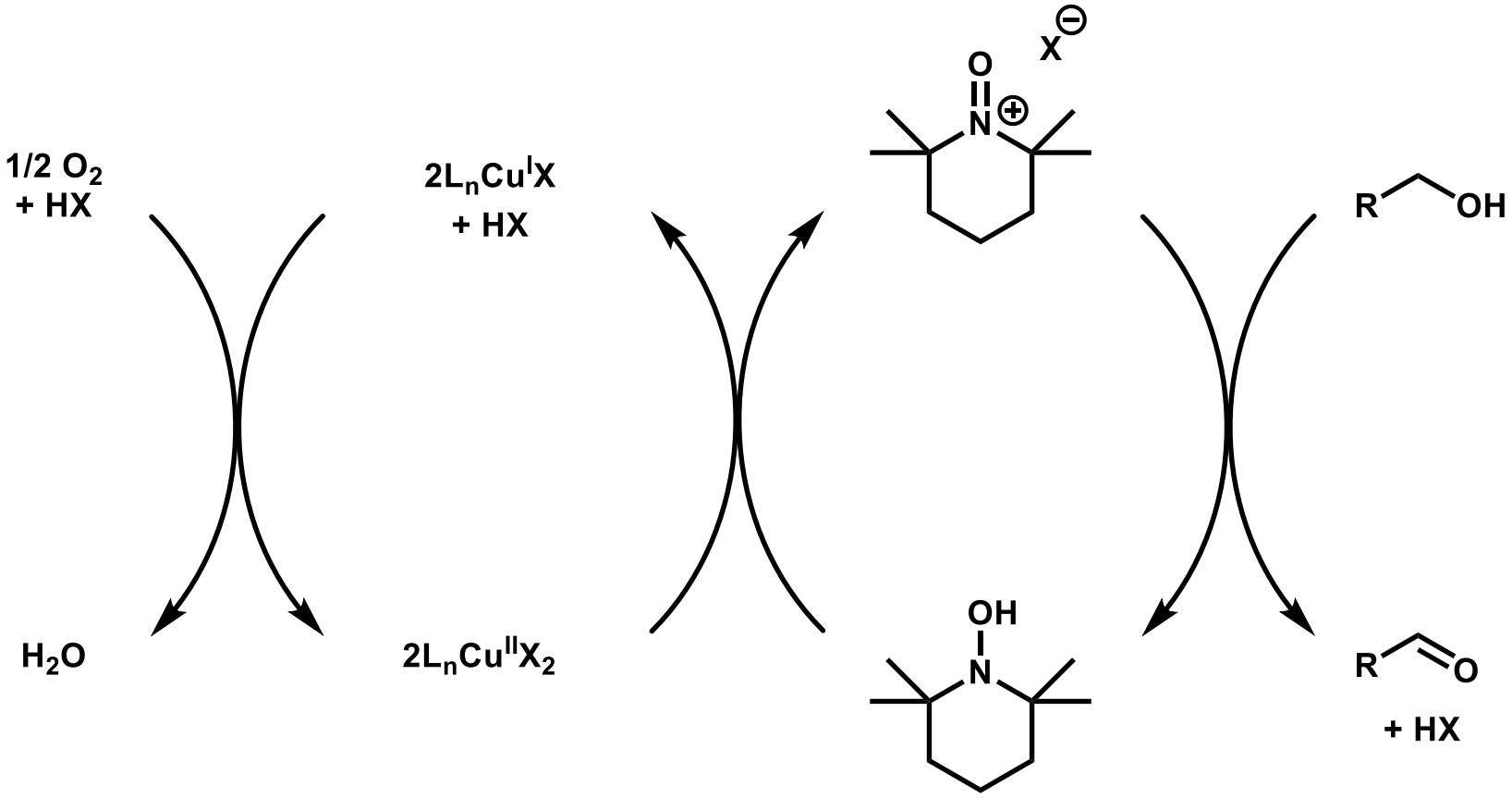
製品詳細

製品番号	構造式	製品名
796549		Stahl Aerobic Oxidation TEMPO solution, 0.2 M in acetonitrile
796557		Stahl Aerobic Oxidation ABNO solution, 0.04M ABNO in Acetonitrile

[a] Reaction performed at 70 °C with O_2 balloon.

Steves, J. E.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 15742.

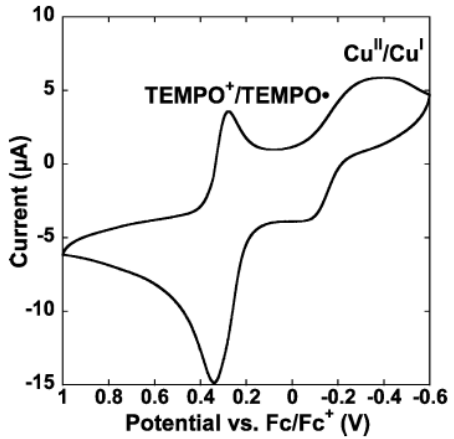
Proposed Reaction Mechanism by Semmelhack



Semmelhack, M. F.; Schmid, C. R.; Cortés, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374.

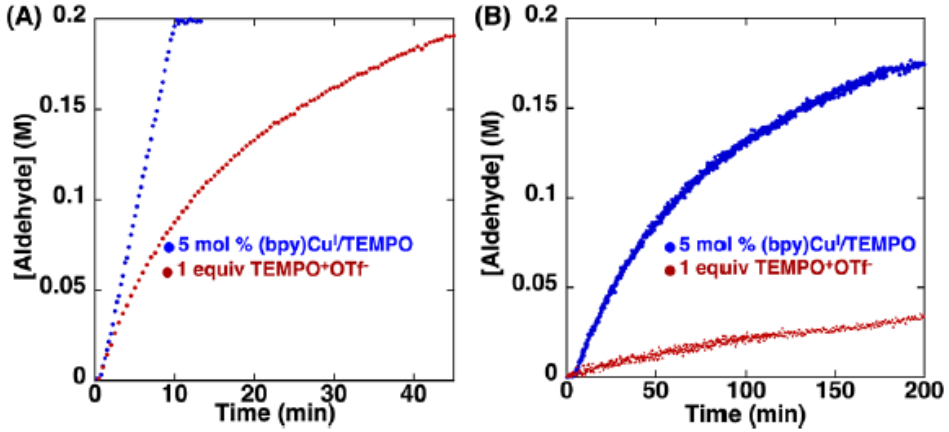
Analysis of Oxoammonium-Mediated Oxidation Pathway

Cyclic voltammogram



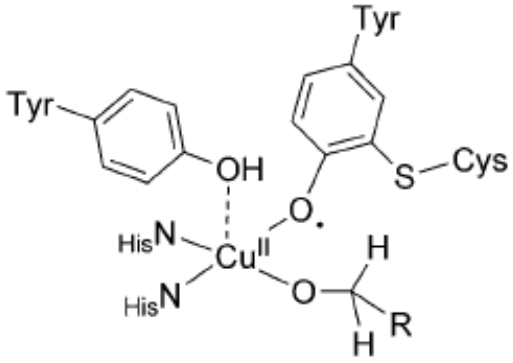
Conditions: 2.5 mM Cu^{I}(OTf), 2.5 mM bpy., 2.5 mM TEMPO, 5 mM NMI, 500 mM $LiClO_4$ 100 mV/s scan rate

Formation of aldehyde in the oxidation



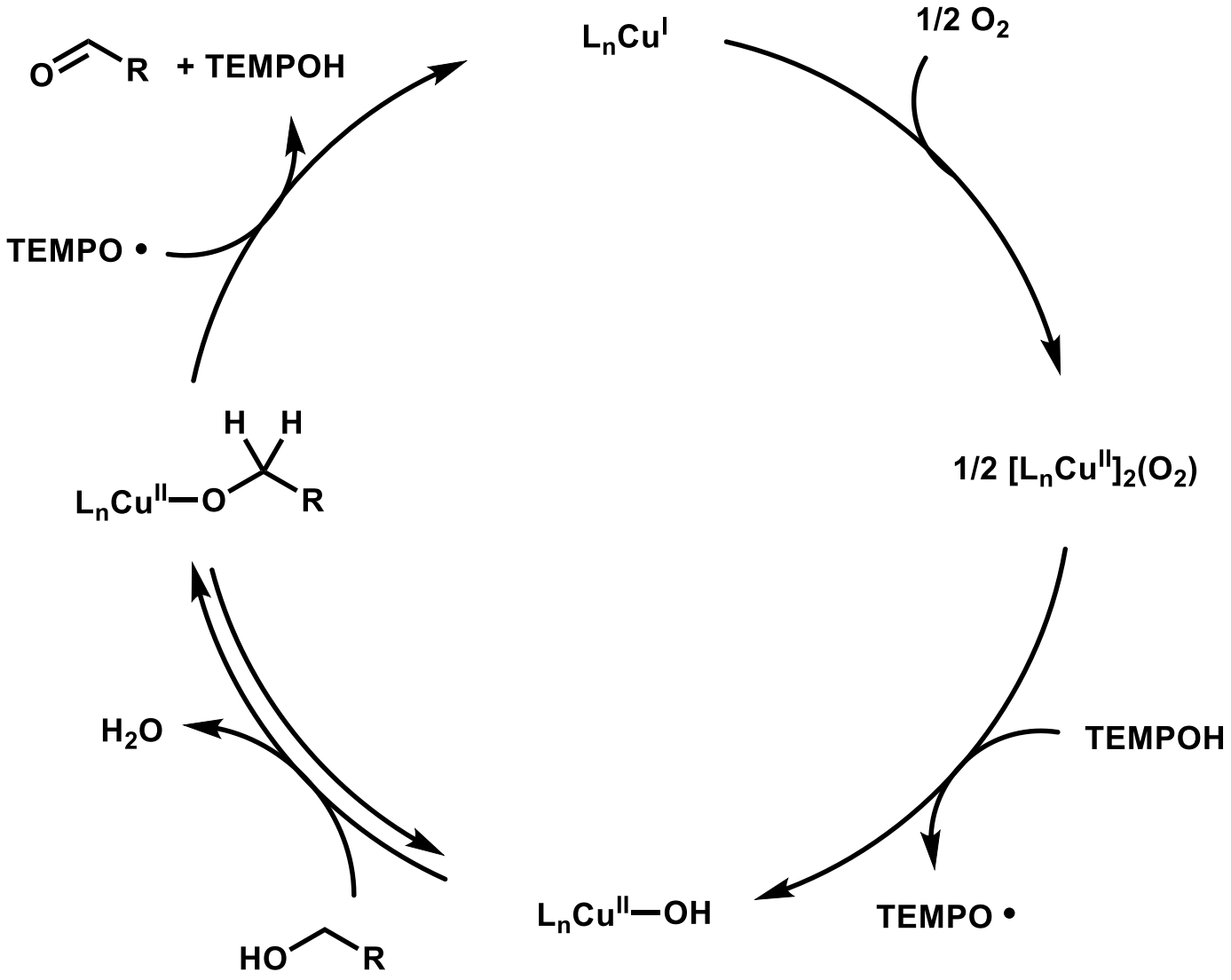
Formation of aldehyde in the oxidation of (A) $PhCH_2OH$ and (B) $CyCH_2OH$ by 5 mol% (bpy)Cu^{I}/TEMPO (blue) and $TEMPO^{+}OTf^{-}$ (red)

Active site of galactose oxidase



1) Stahl, S. S. *et al. J. Am. Chem. Soc.* **2013**, *135*, 2357. 2) Stahl, S. S. *et al. J. Am. Chem. Soc.* **2013**, *135*, 12166.
3) Sheldon, R. A. *et al. Org. Biomol. Chem.* **2003**, *1*, 3232.

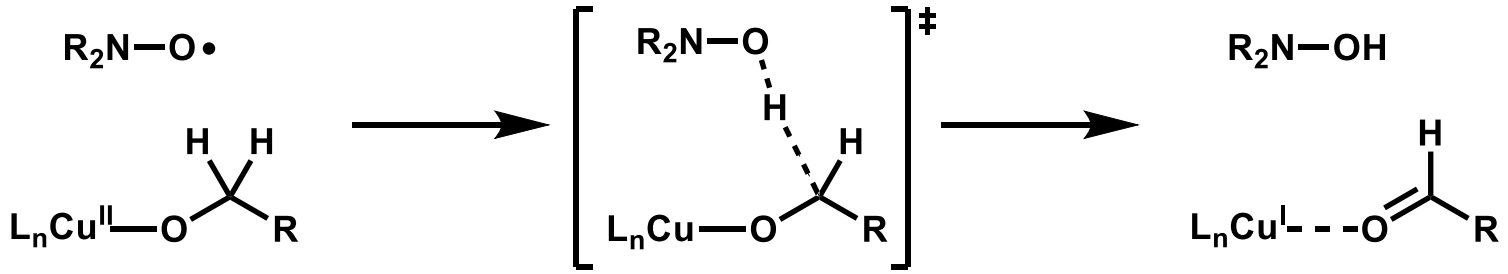
Proposed Mechanism of Cu/TEMPO Catalyzed Alcohol Oxidation



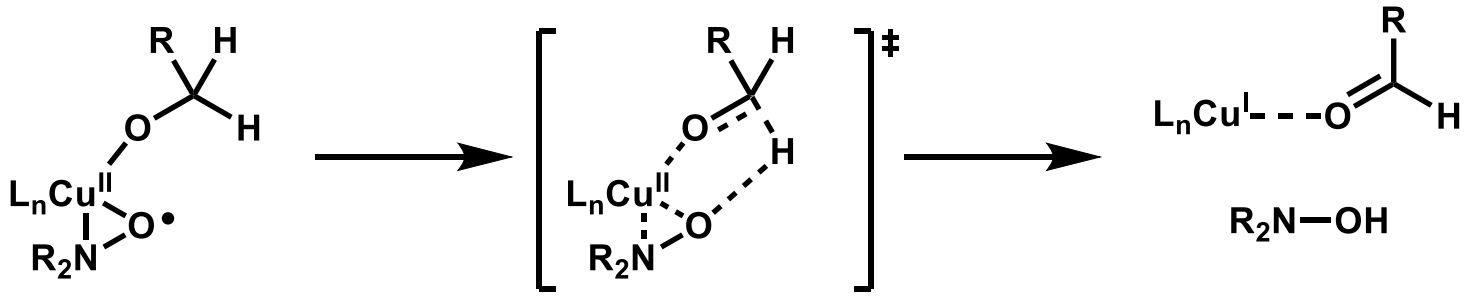
Ryland, R. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 2357.

Mechanistic Proposals for Cu/Nitroxyl Oxidation

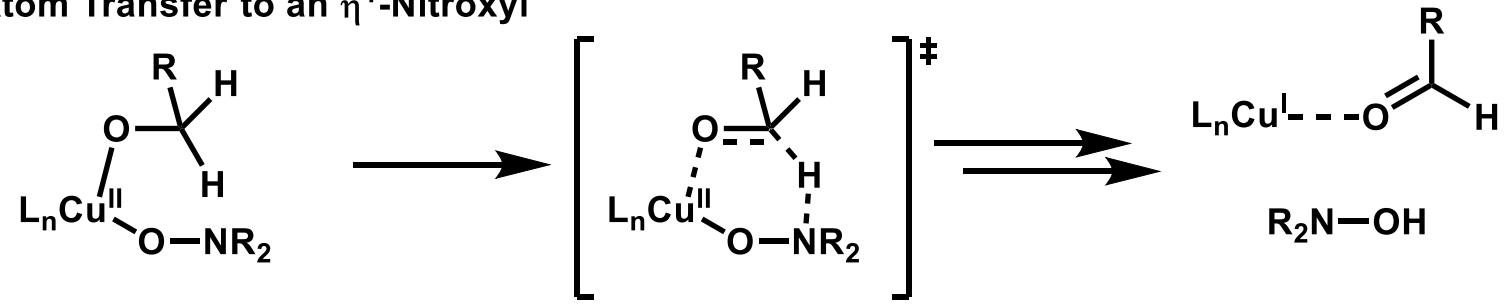
A. Bimolecular Hydrogen-Atom Transfer



B. H-Atom Transfer to an η^2-Nitroxyl



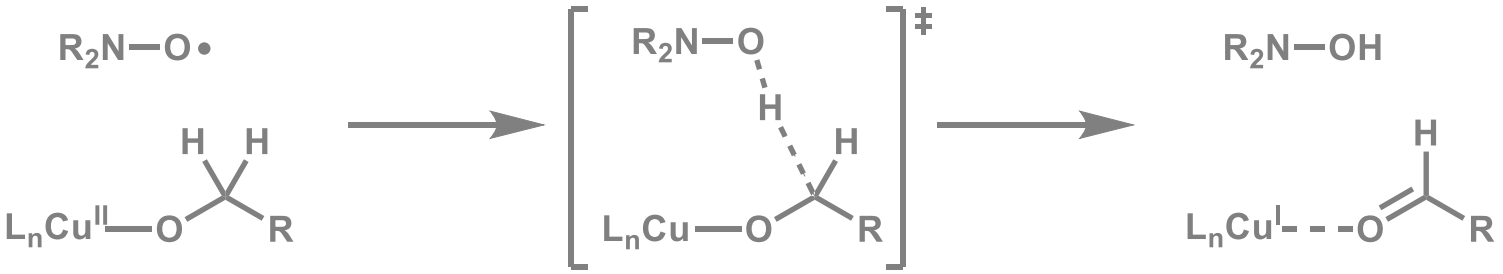
C. H-Atom Transfer to an η^1-Nitroxyl



Ryland, B. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *et al. J. Am. Chem. Soc.* **2014**, *136*, 12166.

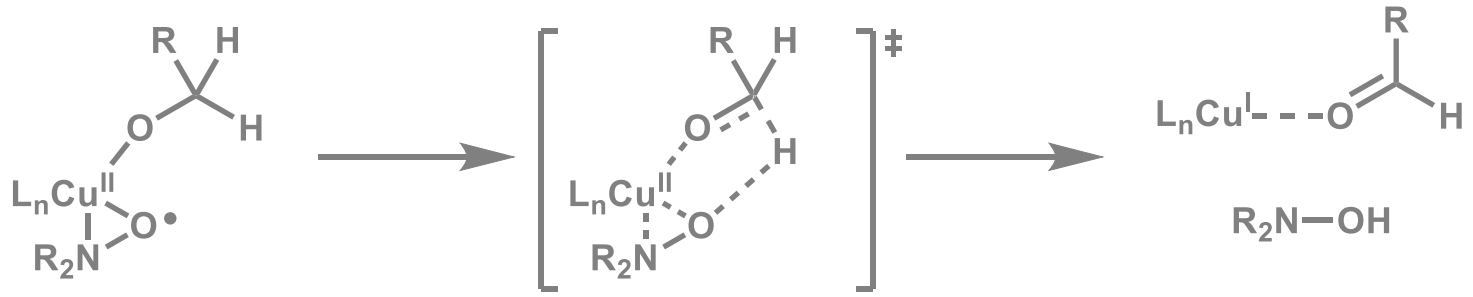
Mechanistic Proposals for Cu/Nitroxyl Oxidation

A. Bimolecular Hydrogen-Atom Transfer



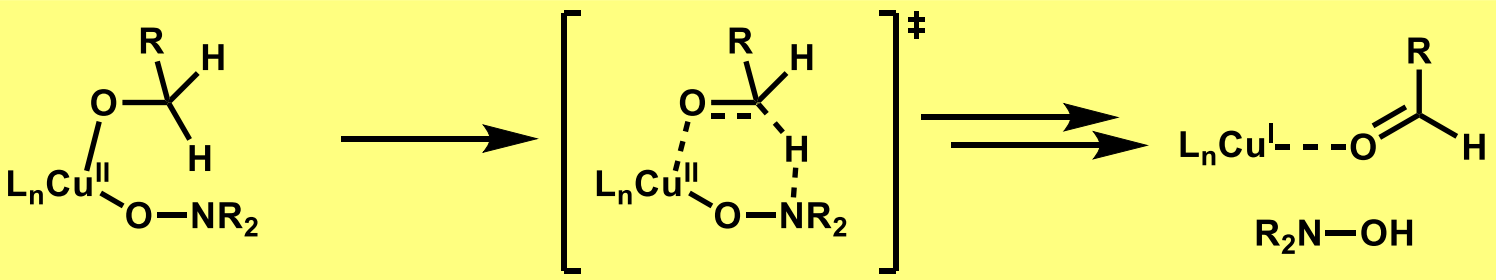
ΔG = 20.6 kcal/mol (R = *n*-Pr)

B. H-Atom Transfer to an η^2-Nitroxyl



ΔG > 25.0 kcal/mol (R = *n*-Pr)

C. H-Atom Transfer to an η^1-Nitroxyl



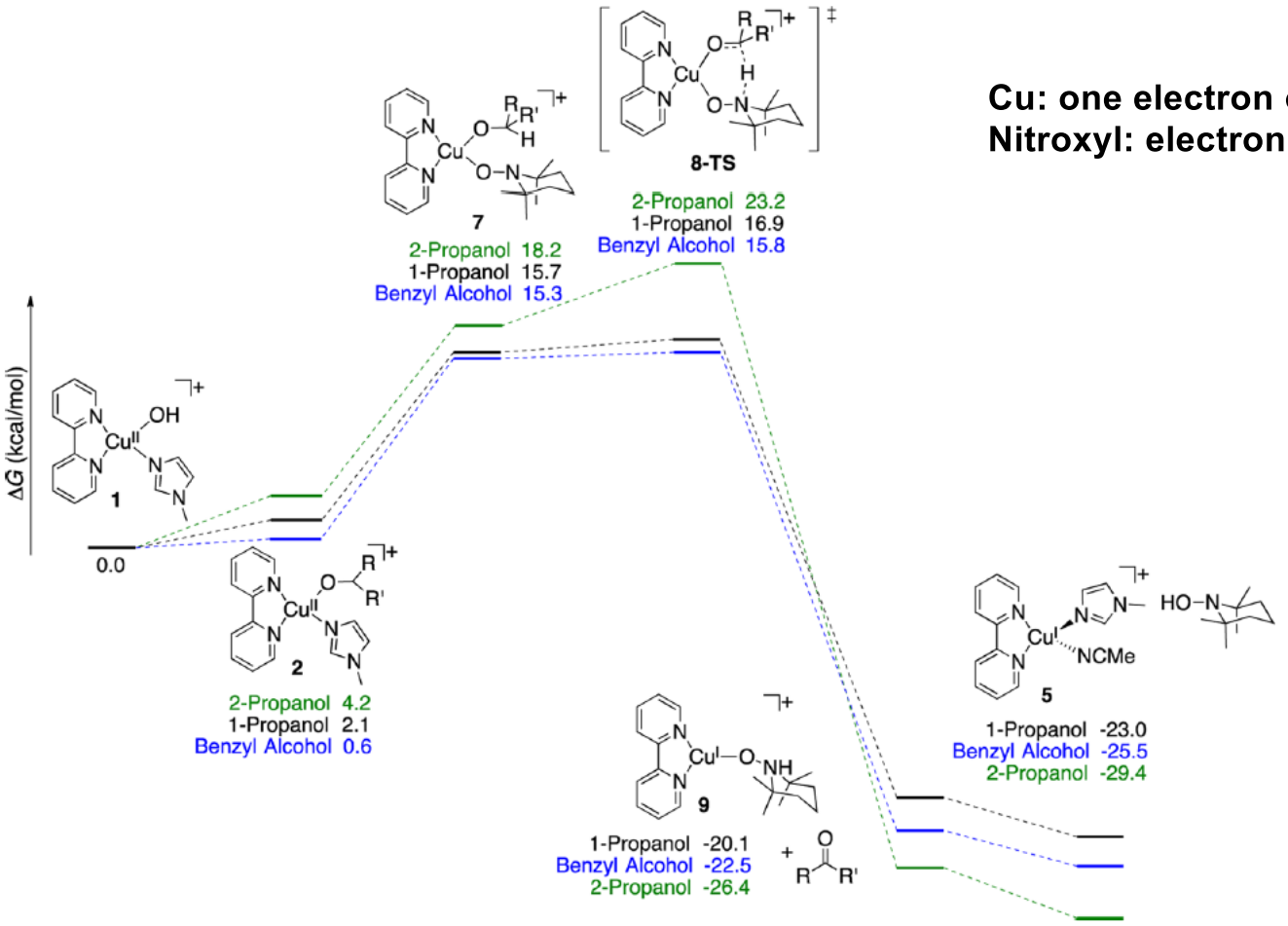
ΔG = 16.9 kcal/mol (R = *n*-Pr)

DFT calculations were performed at OPBE/6-31g(d)

Ryland, B. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *et al. J. Am. Chem. Soc.* **2014**, *136*, 12166.

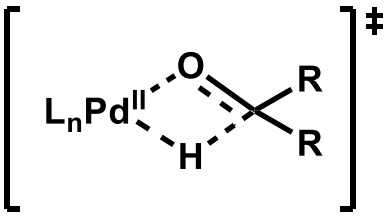
Free Energy Surface for Cu/TEMPO-Mediated Oxidation

C. H-Atom Transfer to an η^1-Nitroxyl



Cu: one electron oxidant
Nitroxyl: electron-proton acceptor

DFT calculations were performed at OPBE/6-31g(d)



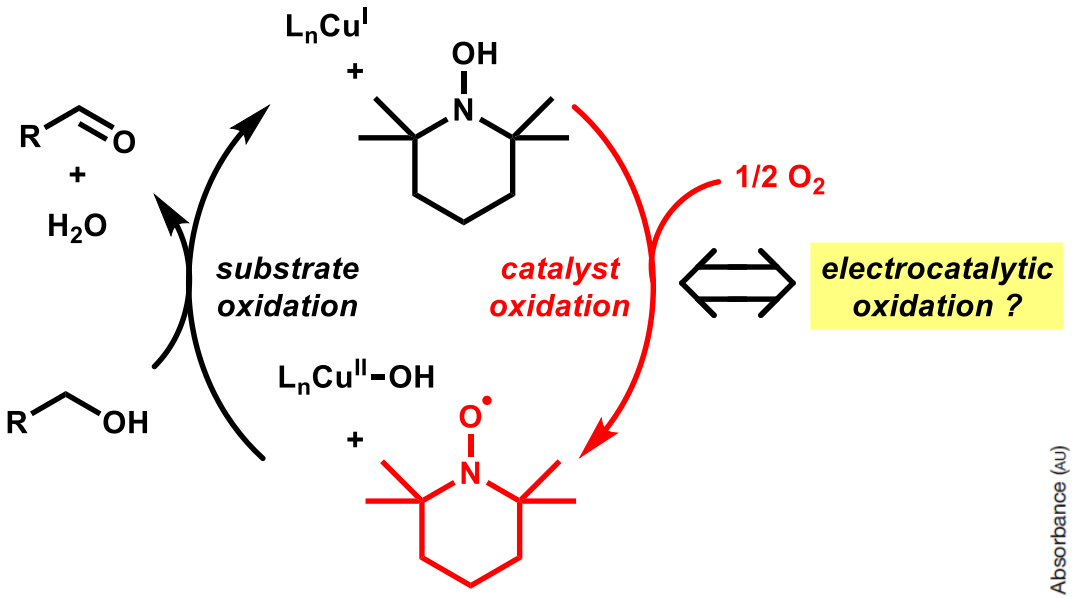
more strained 4-membered TS for β-hydride elimination

Ryland, B. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *et al. J. Am. Chem. Soc.* **2014**, *136*, 12166.

Contents

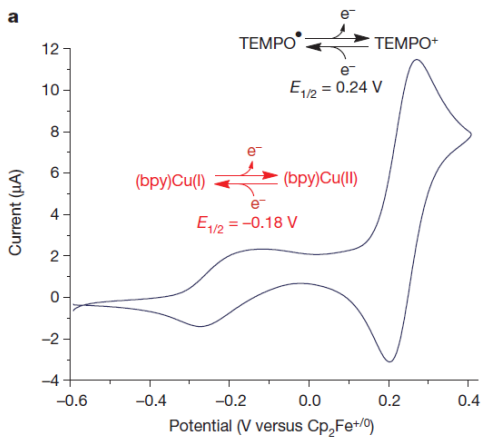
Preliminary Studies of Electrochemical Behavior of Cu/TEMPO System under Anaerobic Conditions

1. Simplified Catalytic Cycle for Aerobic Oxidation by Cu/TEMPO



⟺ ***electrocatalytic oxidation ?***

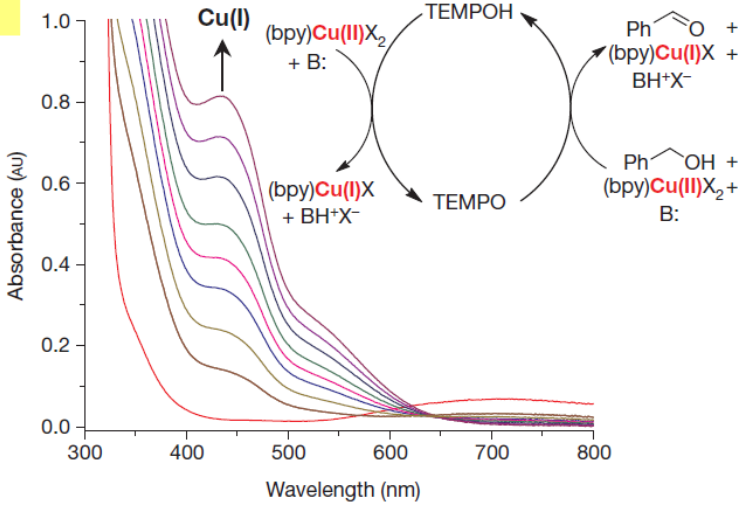
2. Cyclic Voltammogram



Cu^{II} is not capable of oxidizing TEMPO into $TEMPO^+$.

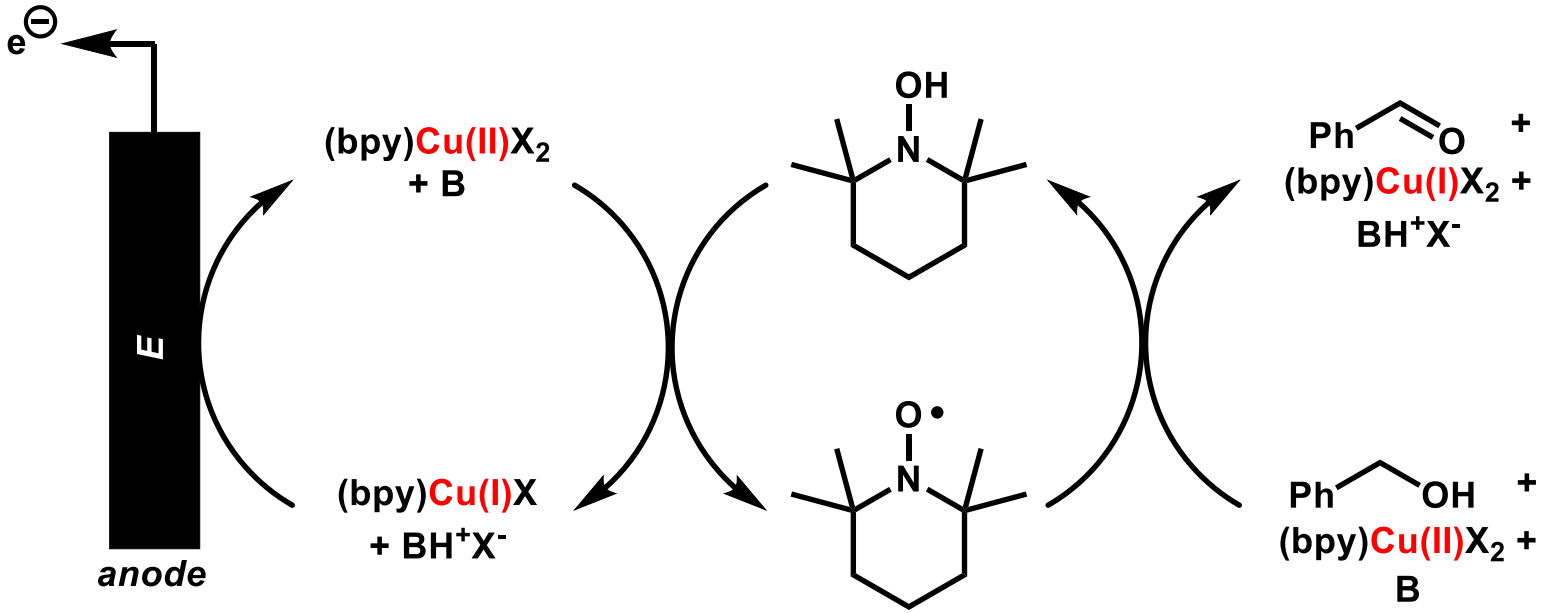
1 mM (bpy)CuOTf, 1 mM TEMPO
0.1 M Bu_4NClO_4/CH_3CN

3. Spectrophotometric evidence for Cu(II)-mediated oxidation of TEMPOH



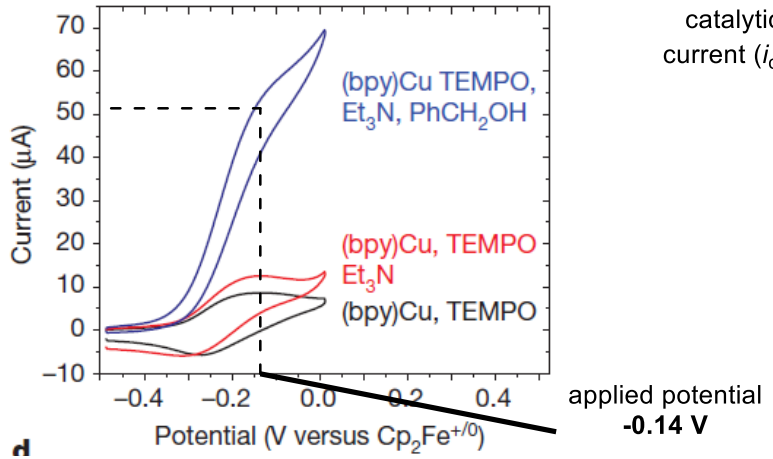
1 mM $Cu(II)(OTf)_2$, 1 mM bpy, 0.1 mM TEMPO
50 mM 2,6-lutidine, 100 mM BnOH
2 mL, 0.1 M Bu_4NClO_4/CH_3CN, 20 min, rt

Electrochemical Oxidation of Benzyl Alcohol

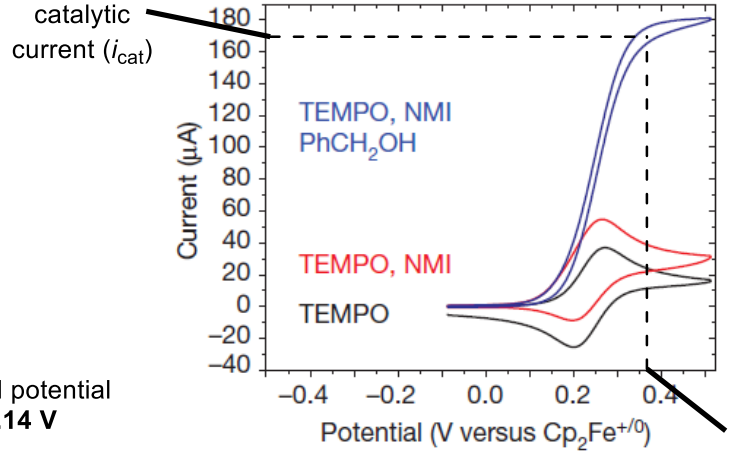


Optimized condition: 1 mM Cu(I)OTf, 1 mM bpy, 5 mM TEMPO, 50 mM Et_3N, 100 mM BnOH
(Et_3N was chosen as Brønsted base(**B**) instead of 2,6-lutidine)

CV with (bpy)Cu/TEMPO catalyst



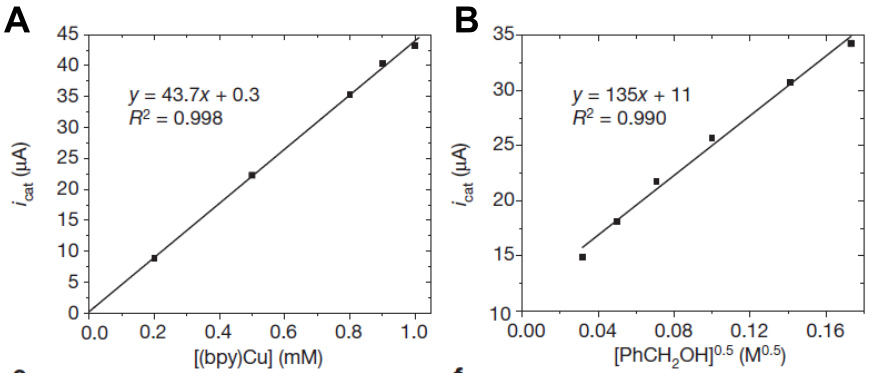
CV with TEMPO only catalyst



	pKa
NMI-H^+	17.1
Et_3N-H^+	18.8

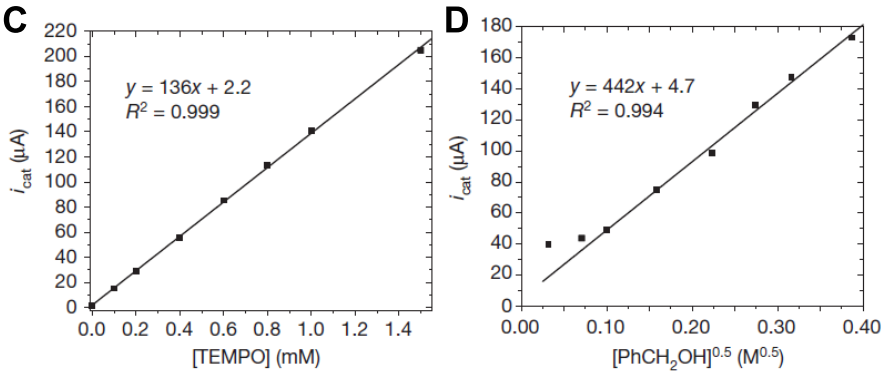
Kinetic Anaysis for the Reaction Mechanism

Plots of i_{cat} vs. [(bpy)Cu] or $[PhCH_2OH]^{0.5}$
(Cu/TEMPO system)



Conditions:
5 mM TEMPO, 50 mM Et_3N
100 mM $PhCH_2OH$ (**A**), 1 mM (bpy)Cu(I)OTf (**B**)

Plots of i_{cat} vs. [TEMPO] or $[PhCH_2OH]^{0.5}$
(TEMPO-only system)



Conditions:
450 mM NMI
100 mM $PhCH_2OH$ (**C**), 1 mM TEMPO (**D**)

Kinetic framework formulated by reference[1)]

$$i_{cat} = nFAC^0_{cat}(D_{cat}2k_{obs})^{0.5}, \quad \text{where } k_{obs} = kC^0_{subst}. \qquad (1)$$

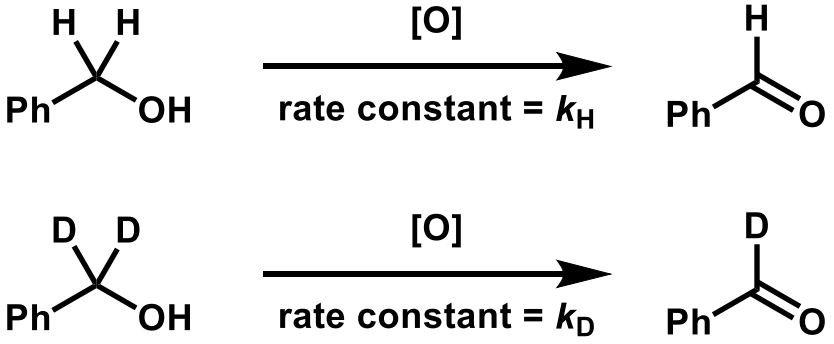
$$i_{cat}/i_p = (RT2k_{obs}/Fnv)/0.4463 \qquad (2)$$

Catalyst system	(bpy)Cu/TEMPO	TEMPO
Kinetic order in catalyst	**1st**	**1st**
Kinetic order in $PhCH_2OH$	**1st**	**1st**
k_{obs} (20 mM $PhCH_2OH$)	**11.6 s^{-1}**	**2.3 s^{-1}**

1) Costentin, C.; Savéant, J.-M. *ChemElectroChem* **2014**, *1*, 1226.

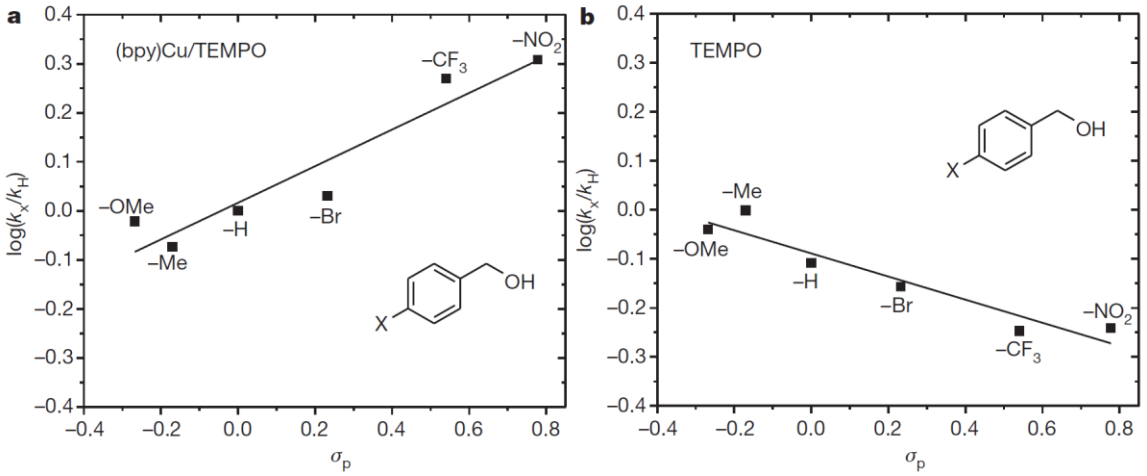
Kinetic Isotope Effect and Hammett Plot

KIE



	(bpy)Cu/TEMPO	TEMPO
KIE = k_H/k_D	1.0	3.2
Kinetic order in catalyst	1st	1st
Kinetic order in BnOH	1st	1st

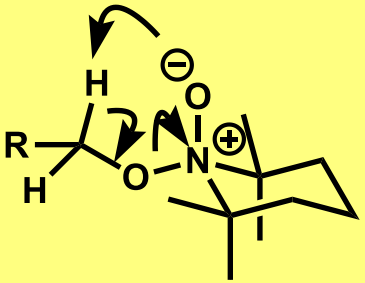
Hammett Plot



ρ = +0.37

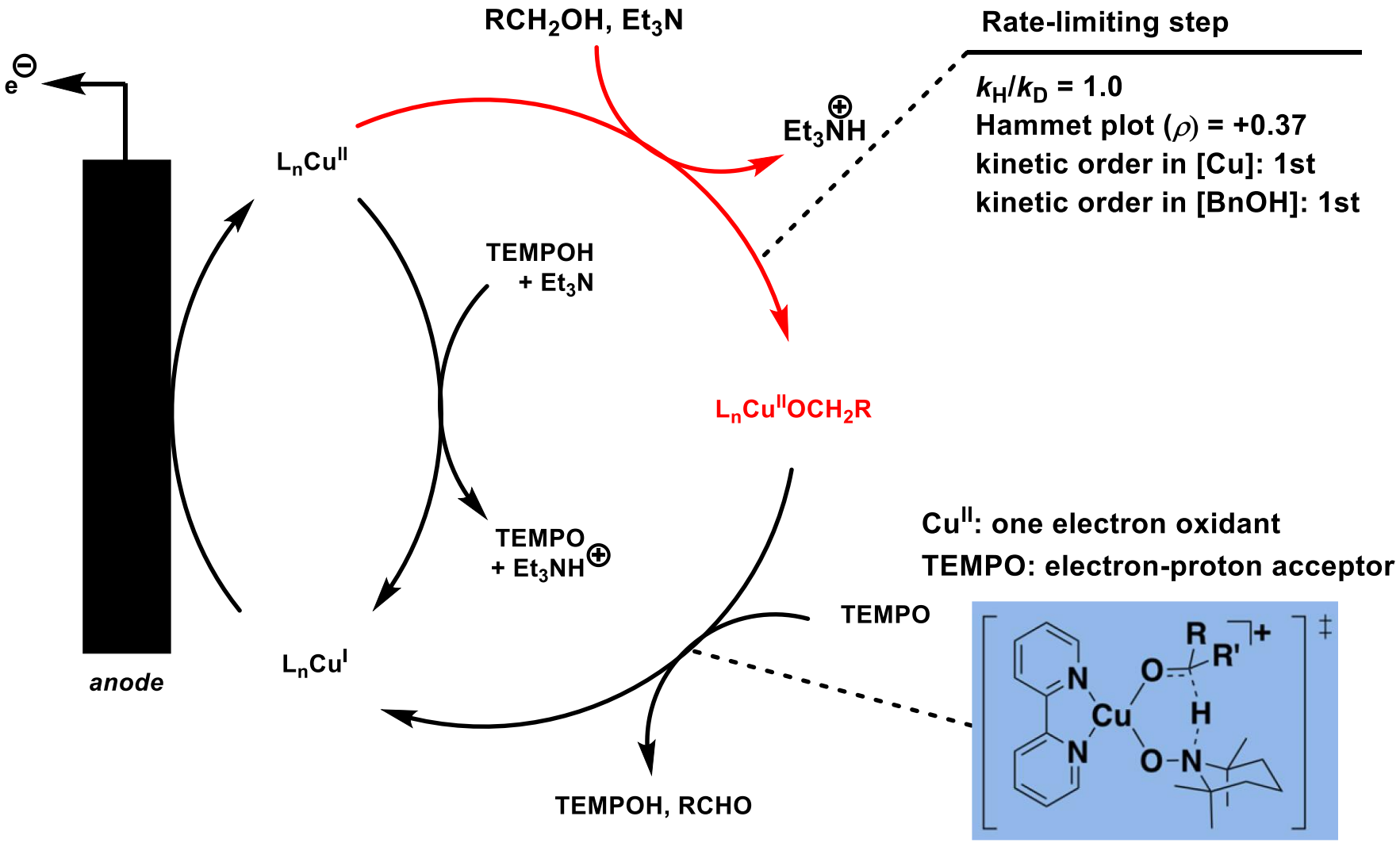
ρ = -0.24

Rate-limiting step for TEMPO

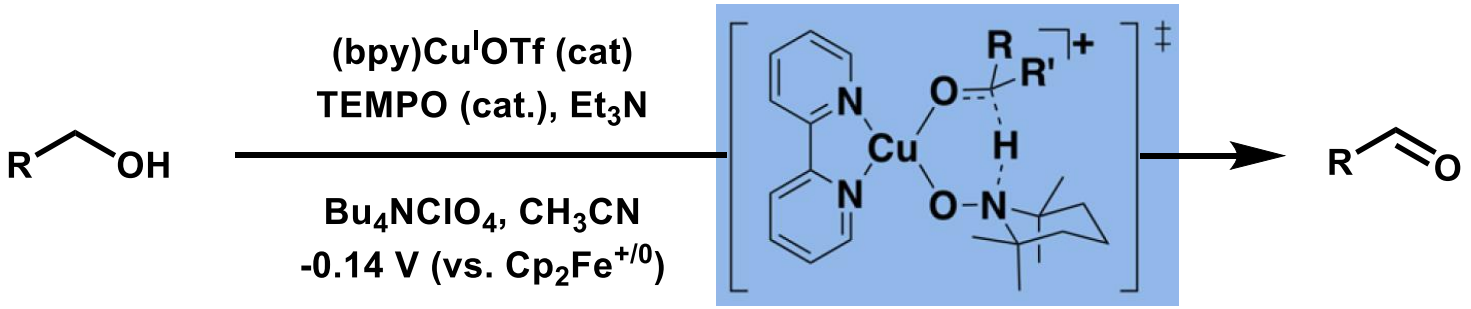


hydrogen transfer

Proposed Mechanism of (bpy)Cu/TEMPO-electrooxidation



Summary



Low electrode potential (0.5 V lower than TEMPO/TEMPO$^+$ system)

Fast reaction rate (k_{obs} = 11.6 s^{-1})

Dirived from cooperative reactivity of Cu/TEMPO catalyst.

Working with transition metals (Cu), electron-proton-transfer mediators (TEMPO) provide the basis for efficient proton-coupled two-electron reactivity.

Development of new cooperative electrocatalyst is expected!