

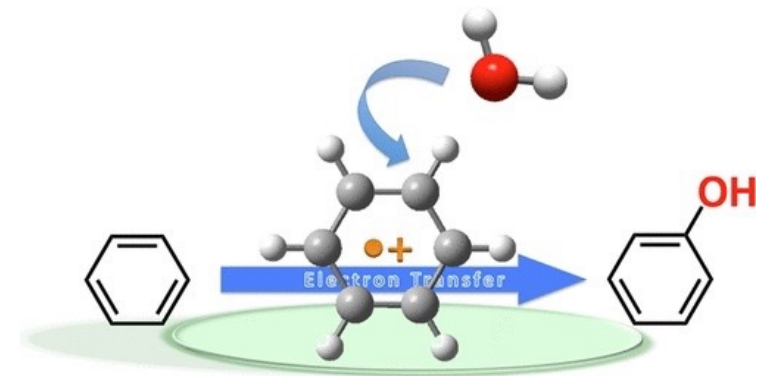
Marcus theory and its application to chemical reactions

Literature seminar

M1, Takeshi Inoue, 2023/7/20

Contents

- Introduction
 - Theory and experiment
- Application to chemical reaction
 - Catalytic oxidation of benzene to phenol
- Summary

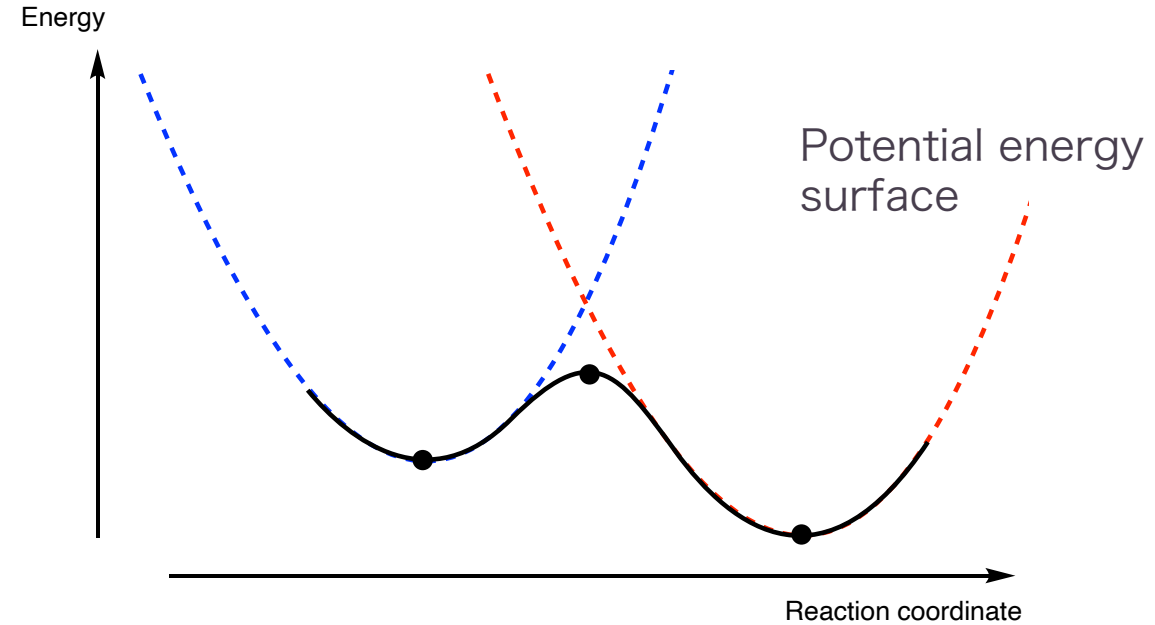
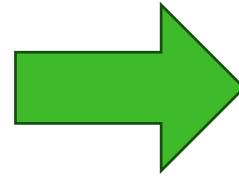
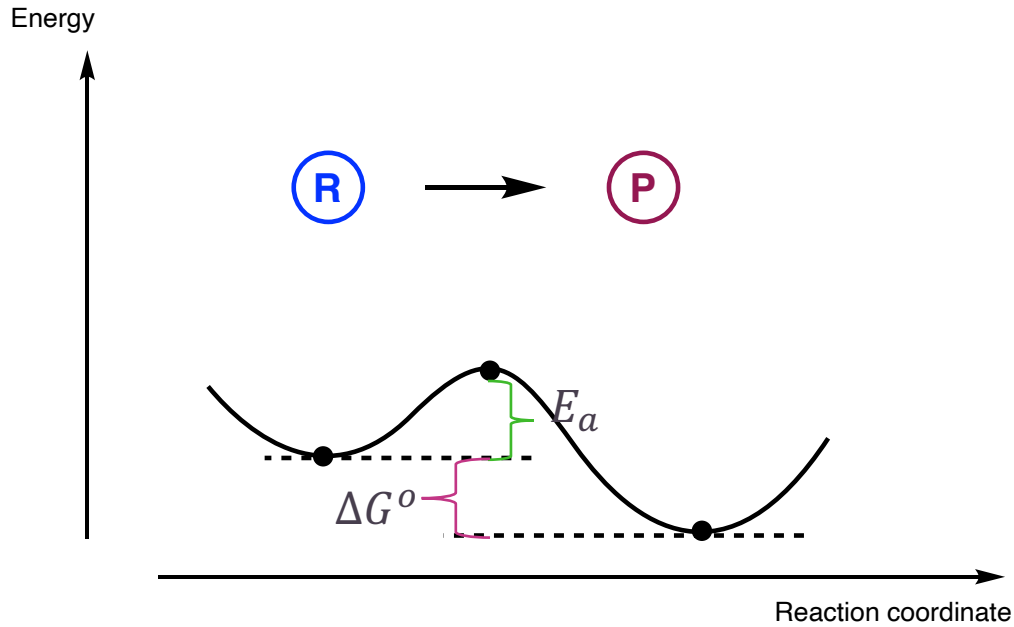


Contents

- Introduction
 - Theory and experiment
- Application to chemical reaction
 - Catalytic oxidation of benzene to phenol
- Summary

Kinetics of thermal chemical reactions

[Reaction coordinate diagram]



(Arrhenius equation)

$$k = A \cdot \exp\left(-\frac{E_a}{k_B T}\right)$$

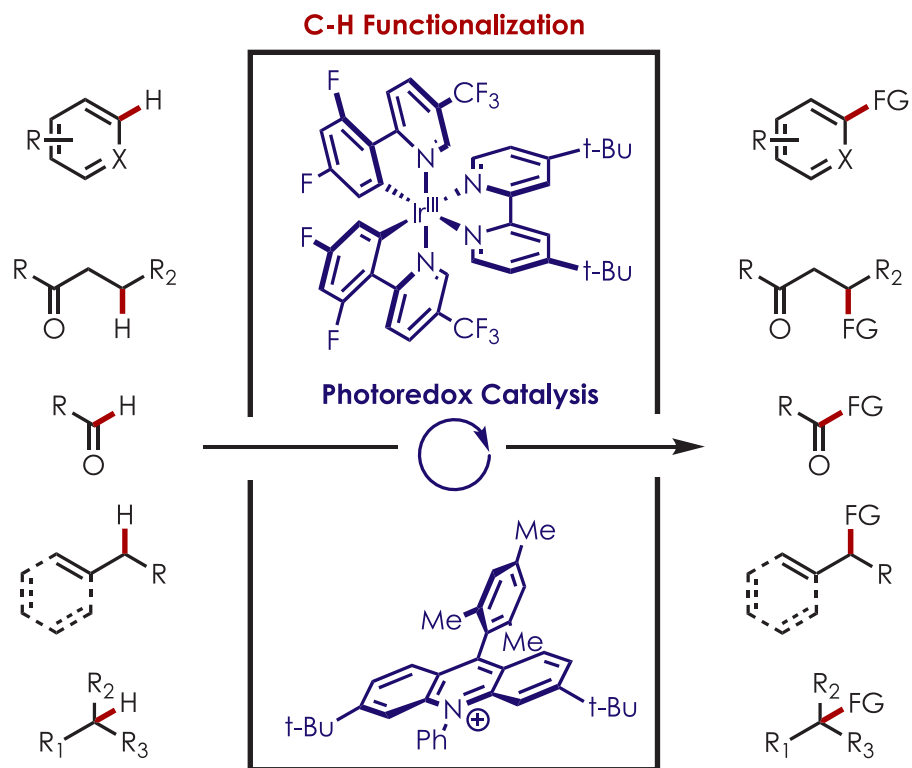
- Intuitive speculation

More exergonic \Rightarrow Reaction proceeds faster

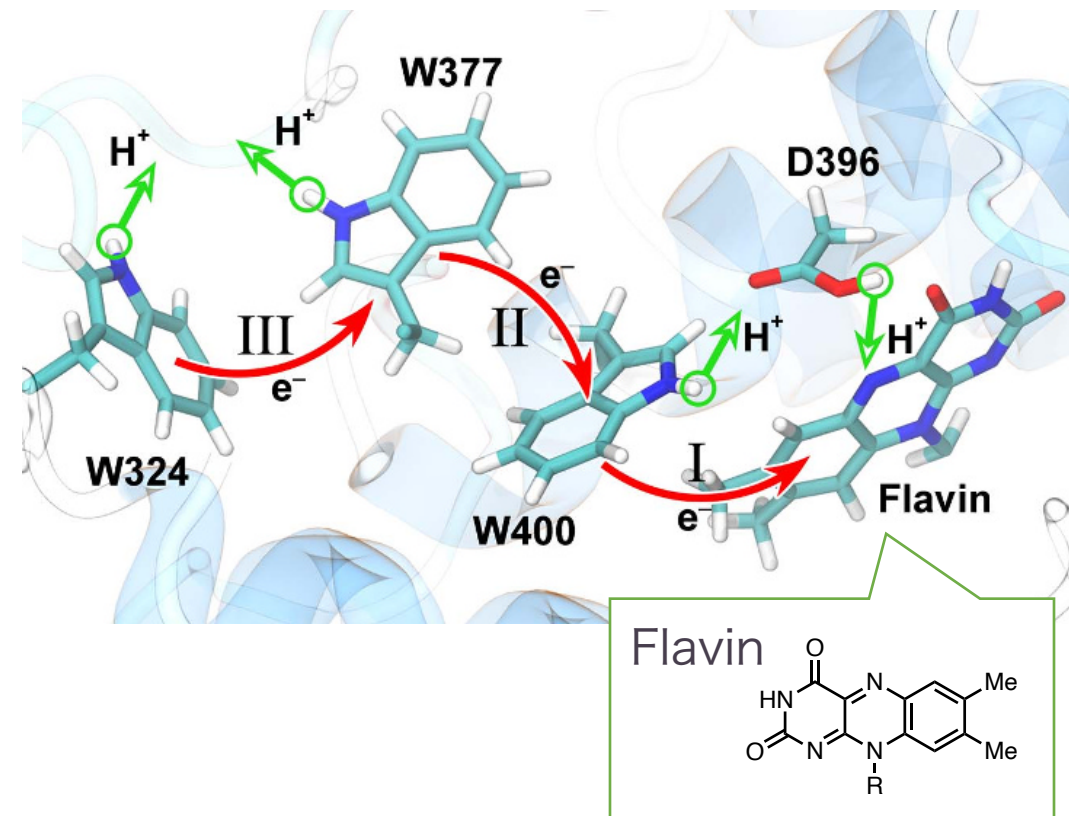
More endergonic \Rightarrow Reaction proceeds slower (?)

Single electron transfer

[Photoredox catalysts]

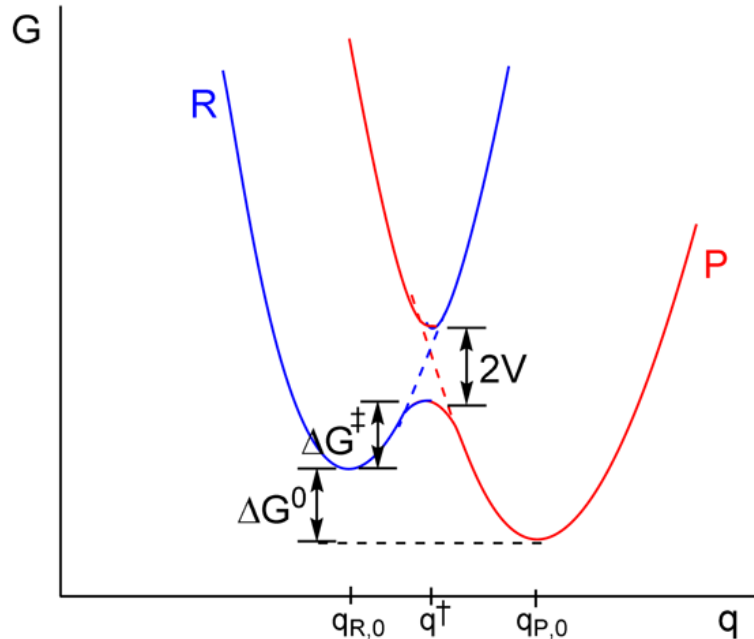
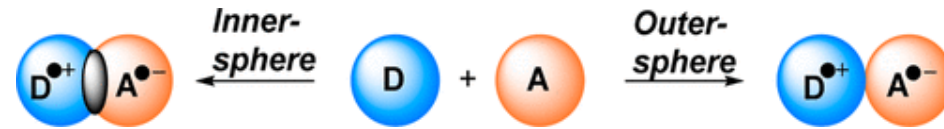


[Electron transfer in the cell]



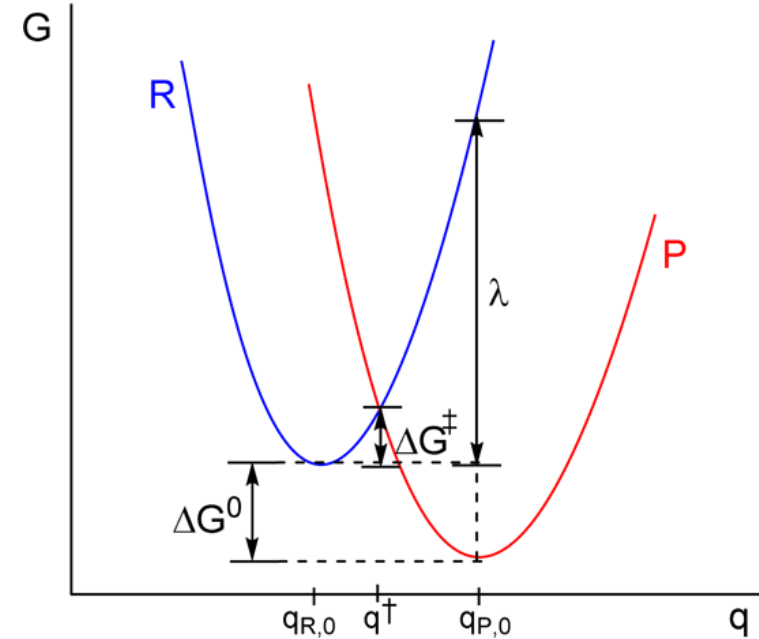
SET is also the important process in photosynthesis, solar cells, chemoluminescence . . .
→ Marcus theory describes kinetics of these electron transfer.

Inner-sphere and outer-sphere mechanism



[Inner-sphere mechanism]

- Adiabatic process
- $H_{DA} > 0$



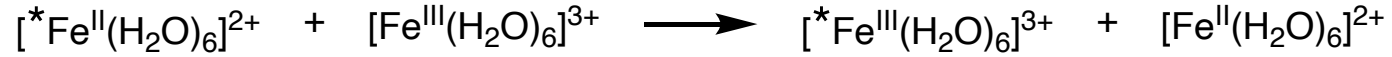
[Outer-sphere mechanism]

- Non-adiabatic process
- $H_{AD} = 0$

Marcus theory was originally developed to explain the outer-sphere (non-adiabatic) electron transfer.

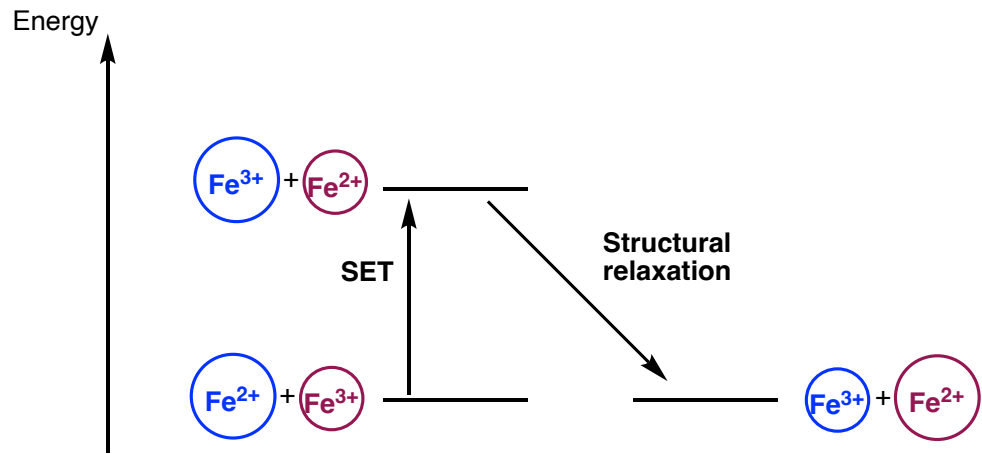
Reorganization energy

[Self-exchange reactions (with isotopic labelling)]

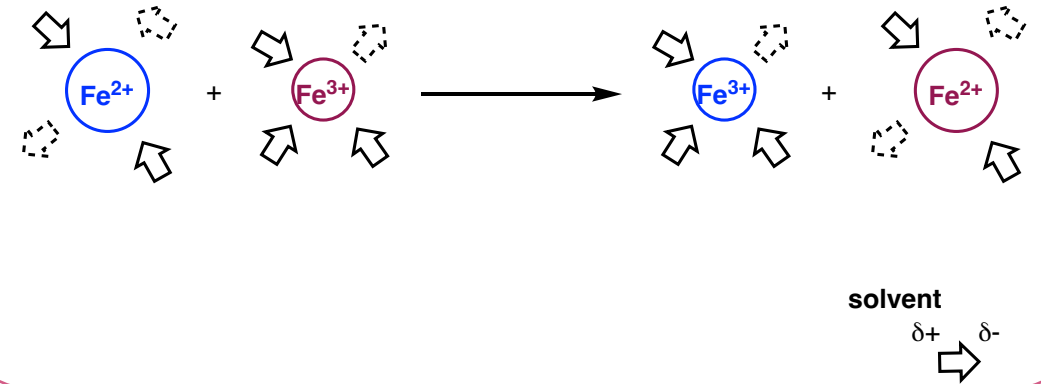


*; Isotopic labelling

[Reorganization of structure]



[Reorganization of solvents]

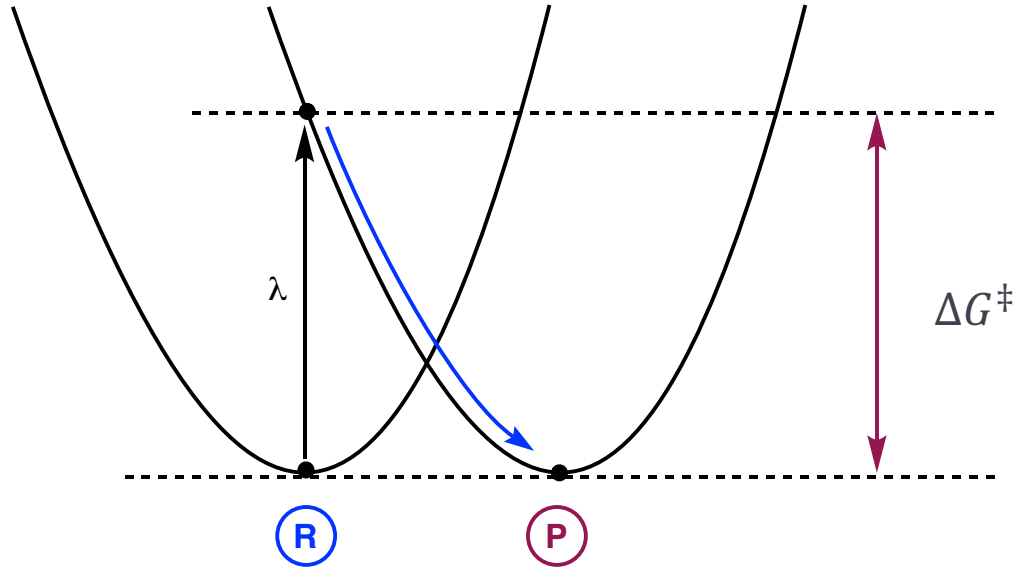


Reorganization energy (λ); Energy needed for a vertical electron transition without changes in the nuclear configuration.

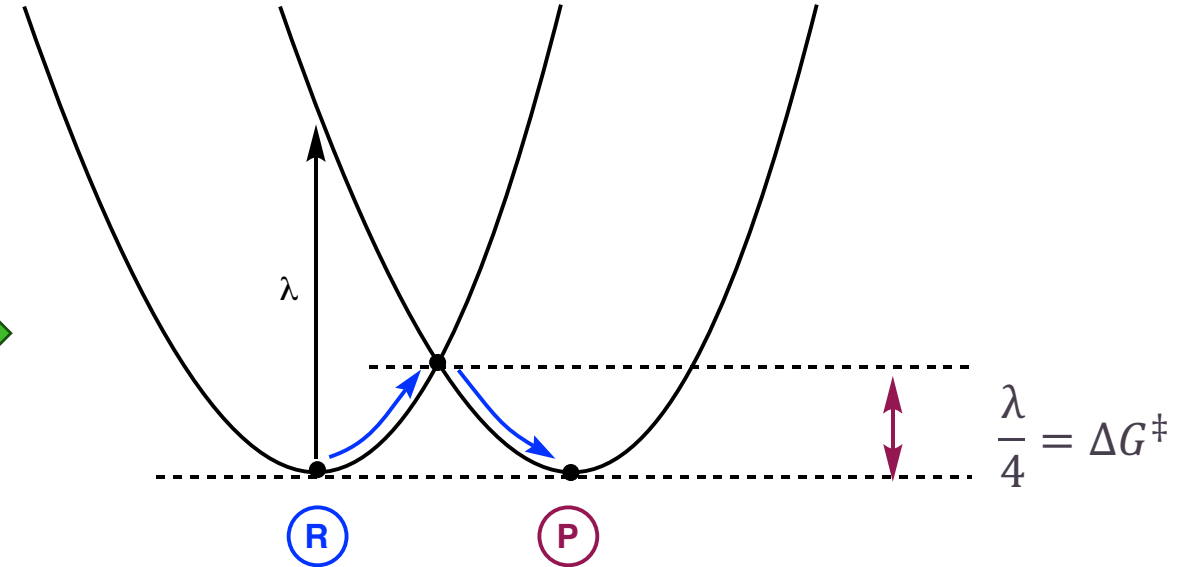
$$\lambda = \lambda_{inner}(\text{structure}) + \lambda_{outer}(\text{solvent})$$

Marcus theory

[Libby's model]



[Marcus's model]

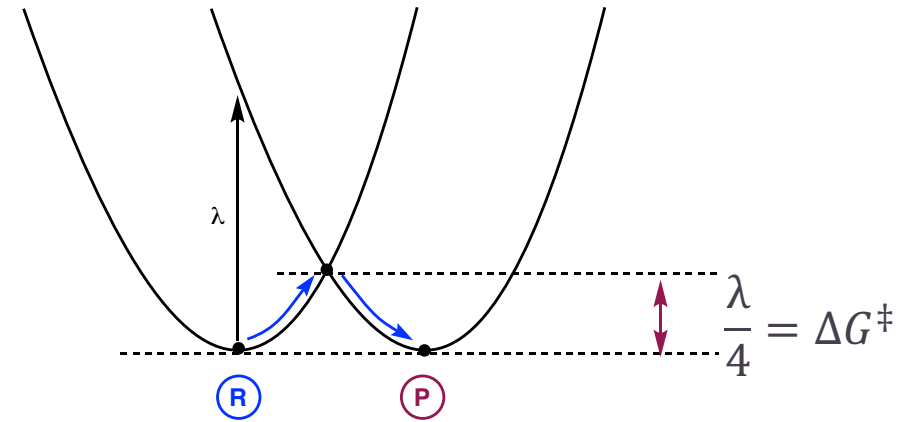
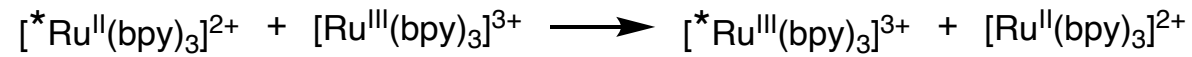
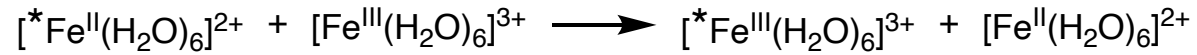


- Requires a great deal of energy.
→ Contradictory to the fact that this reaction proceeds even in the dark.

- Electron transfer occurs at the intersection of the two potential energy surface.

Effects of reorganization energy

[Self exchange reactions]



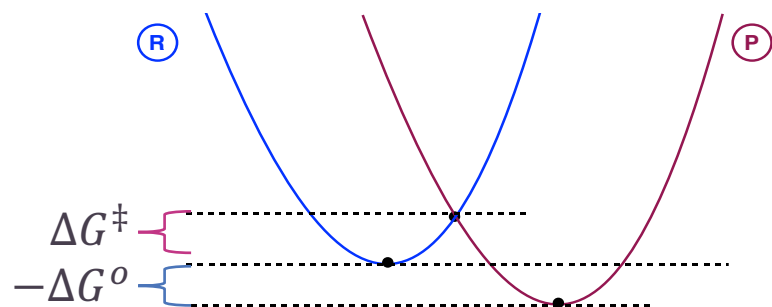
Parameters	$[\text{Fe}^{\text{III/II}}(\text{OH}_2)_6]^{3+/2+}$	$[\text{Ru}^{\text{III/II}}(\text{bpy})_3]^{3+/2+}$
radii (+2), Å	3.52	5.9
radii (+3), Å	3.39	5.9
λ_{inner} (eV)	1.25	0
λ_{outer} (eV)	1.16	0.67
ΔG^0 (eV)	0	0
ΔG^\ddagger (eV)	0.60	0.27
k_{ET} (s^{-1})	50	4.9×10^8

The reorganization energy has a significant effect on these electron transfers.

Marcus inverted region

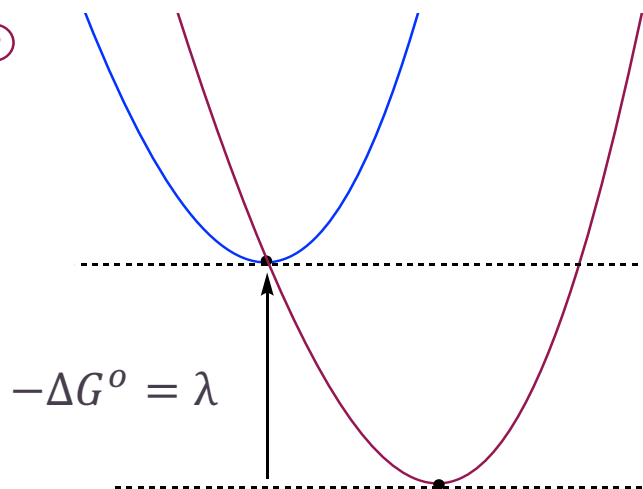
(i) Normal region

$$-\Delta G^o < \lambda, \quad \Delta G^\ddagger > 0$$



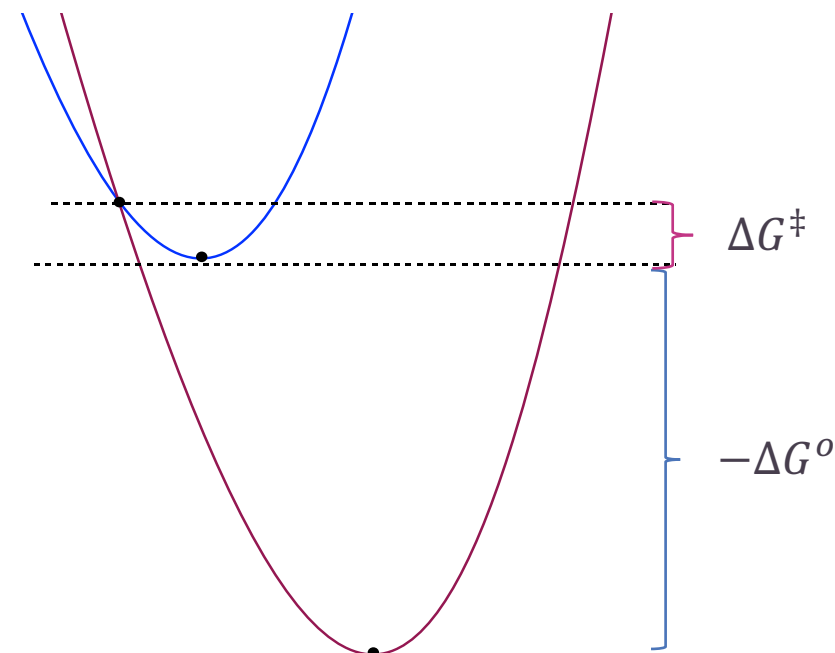
(ii) Barrierless (Top region)

$$-\Delta G^o = \lambda, \quad \Delta G^\ddagger = 0$$



(iii) Inverted region

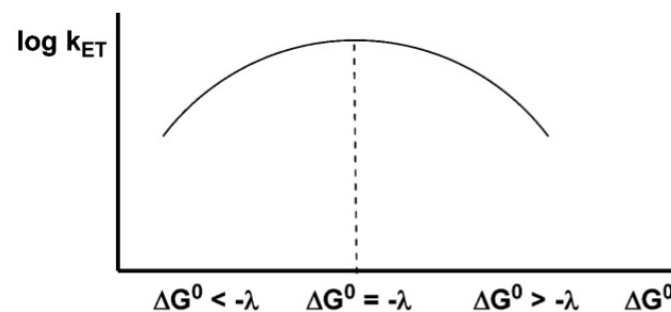
$$-\Delta G^o > \lambda, \quad \Delta G^\ddagger > 0$$



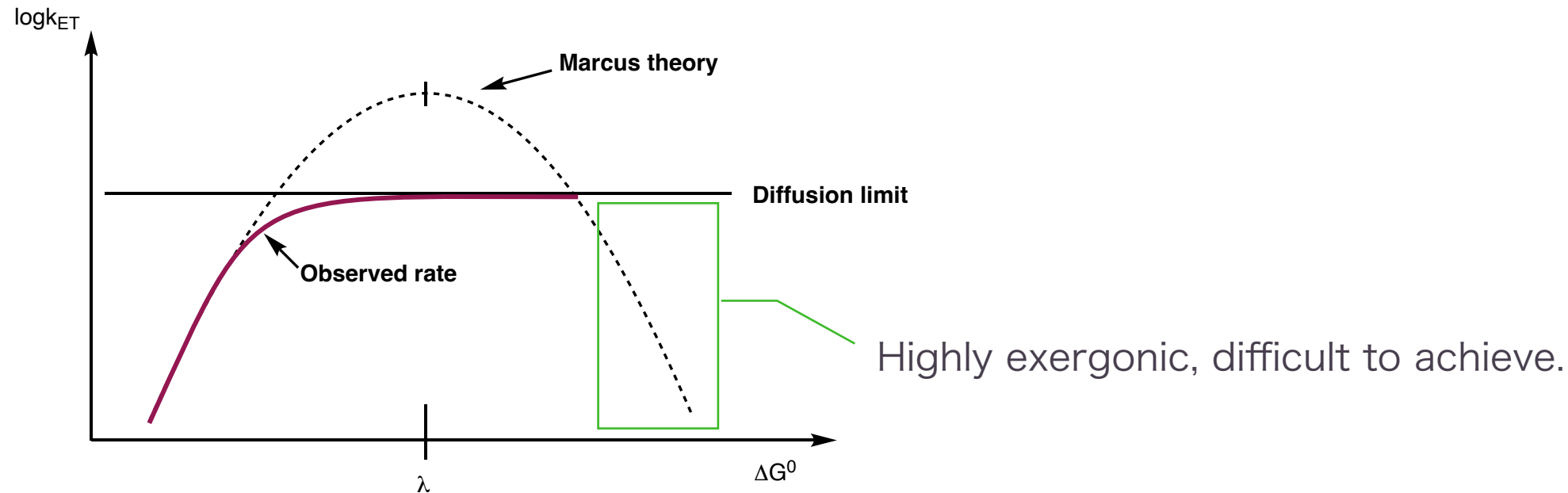
$$\Delta G^\ddagger = \frac{(\Delta G^o + \lambda)^2}{4\lambda}$$

$$k_{ET} = \frac{2\pi}{\hbar} \cdot \frac{H_{DA}^2}{\sqrt{4\pi\lambda k_B T}} \cdot \exp\left[-\frac{(\Delta G^o + \lambda)^2}{4\lambda k_B T}\right]$$

Bell-shaped $v - \Delta G^o$ graph



Experimental observation of inverted region



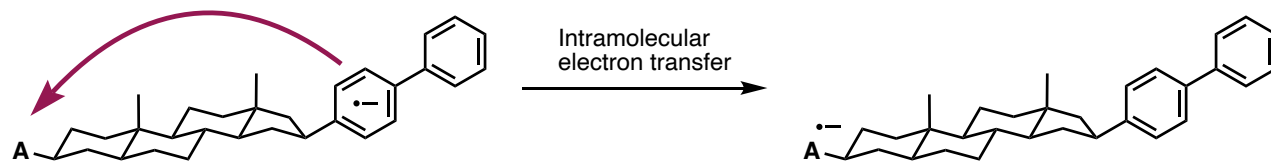
- Inverted region can't be observed to the extent that k_{ET} is bigger than k_{dif} .



- Observation of intramolecular single electron transfer.
- Observation of back electron transfer in radical ion pair.
- Suppress the diffusion with highly viscous solvent.

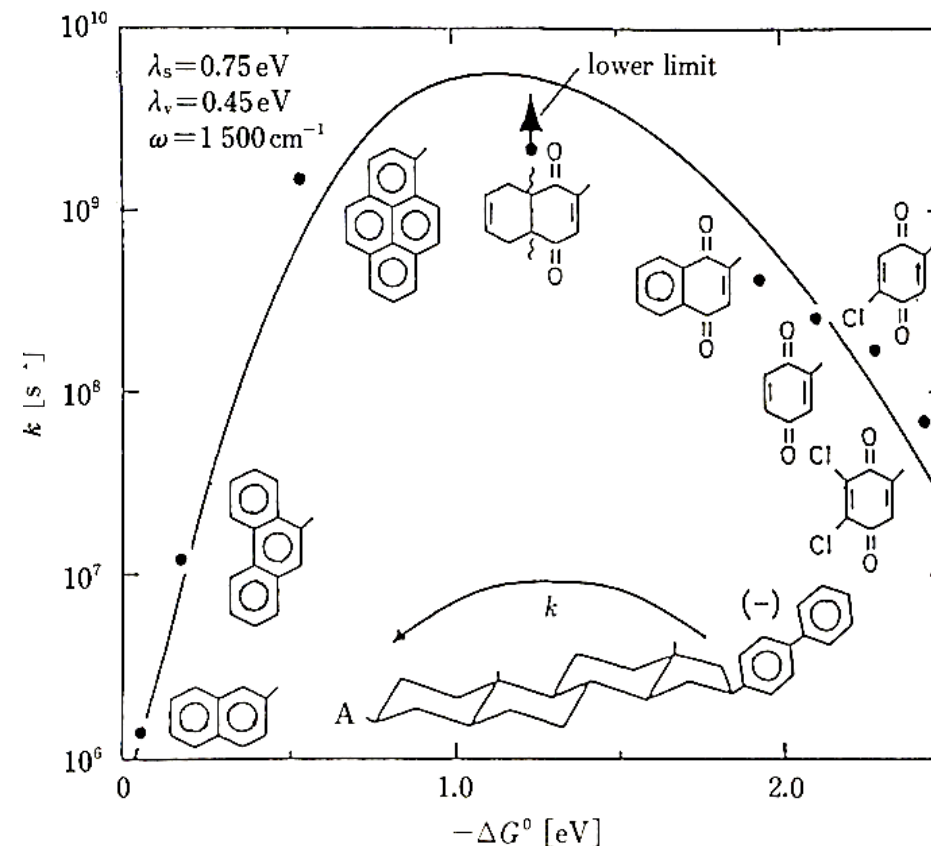
First observation of Marcus inverted region

- Intramolecular electron transfer



Acceptor group (A)	$-\Delta G^0$ (eV)	k_{intra} (s^{-1})
4-biphenyl	0	5.6×10^5
2-naphthyl	0.05	$(1.5 \pm 0.5) \times 10^6$
9-phenanthryl	0.16	$(1.25 \pm 0.2) \times 10^7$
1-pyrenyl	0.52	$(1.5 \pm 0.5) \times 10^9$
Hexahydronaphthoquinon-2-yl	1.23	$> 2 \times 10^9$
2-naphthoquinonyl	1.93	$(3.8 \pm 1) \times 10^8$
2-benzoquinonyl	2.10	$(2.5 \pm 0.3) \times 10^8$
5-chlorobenzoquinon-5-yl	2.29	$(1.7 \pm 0.2) \times 10^8$
5,6-dichlorobenzoquinon-2-yl	2.40	$(7 \pm 3) \times 10^7$

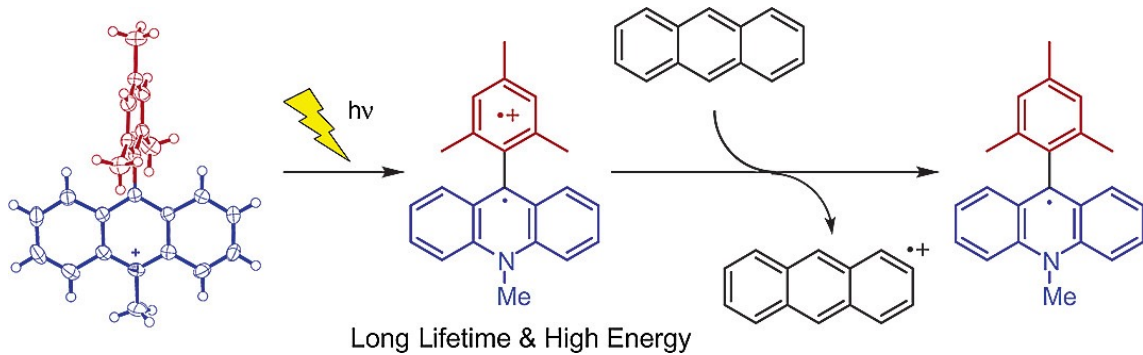
Solvent ; 2-Me-THF



Millar *et al.* *J. Am. Chem. Soc.* 1984, 106, 3047.

Photocatalyst with long-lived charge-separated state

[Fukuzumi's catalyst]



$$k_{ET} = 2.4 \times 10^{-11} \text{ s}^{-1}$$

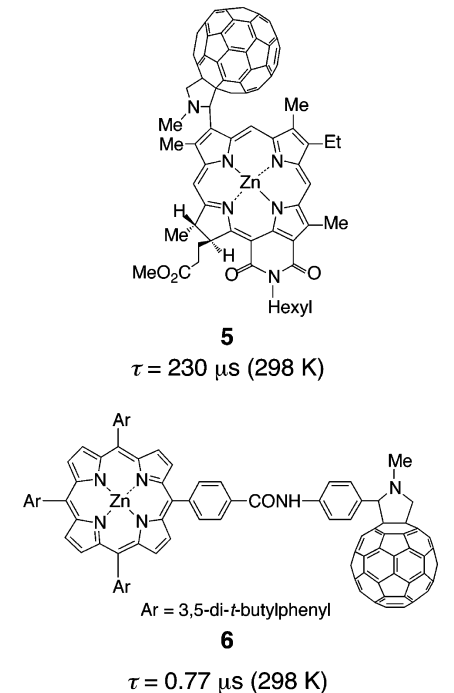
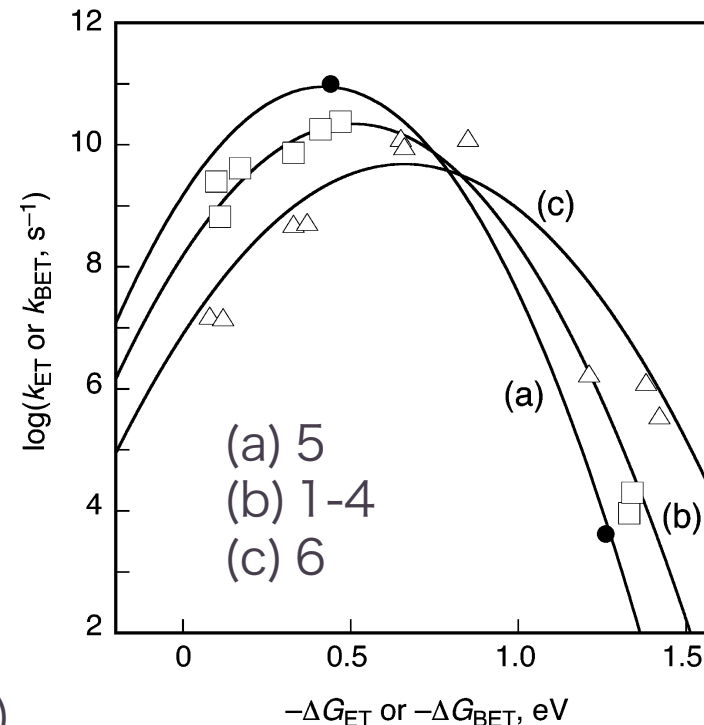
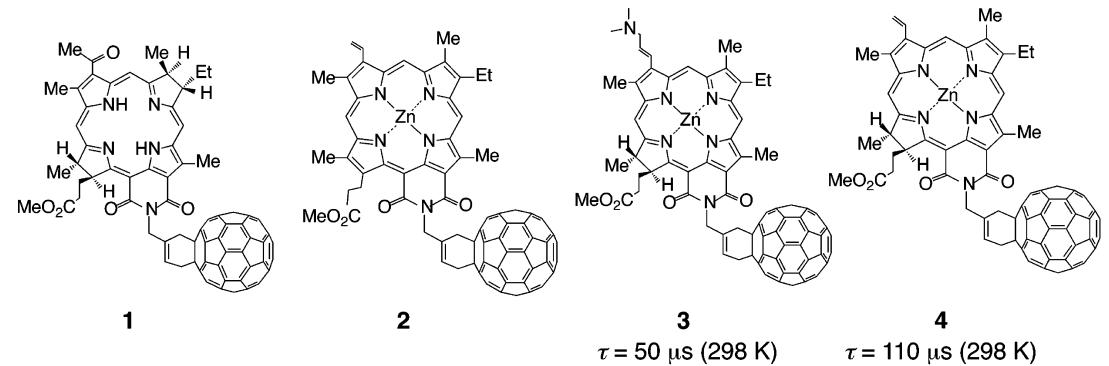
$$k_{BET} = 98 \text{ s}^{-1}$$

PhCN, 298K (intramolecular ET)

Lemmetyinen *et al.* *J. Am. Chem. Soc.* 2004, 126, 1600.

- Rigid frameworks such as Mes-Acr⁺ and fullerene minimize the reorganization energy.

[Artificial photosynthesis]



(a)

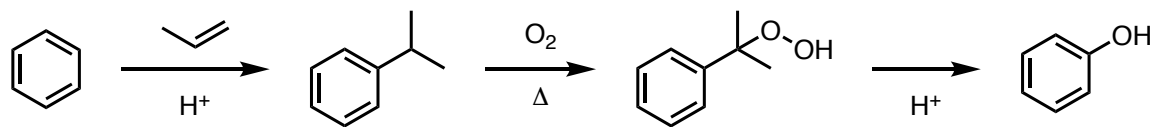
Suenobu *et al.* *Acc. Chem. Res.* 2014, 47, 1455.

Contents

- Introduction
 - Theory and experiment
- Application to chemical reaction
 - Catalytic oxidation of benzene to phenol
- Summary

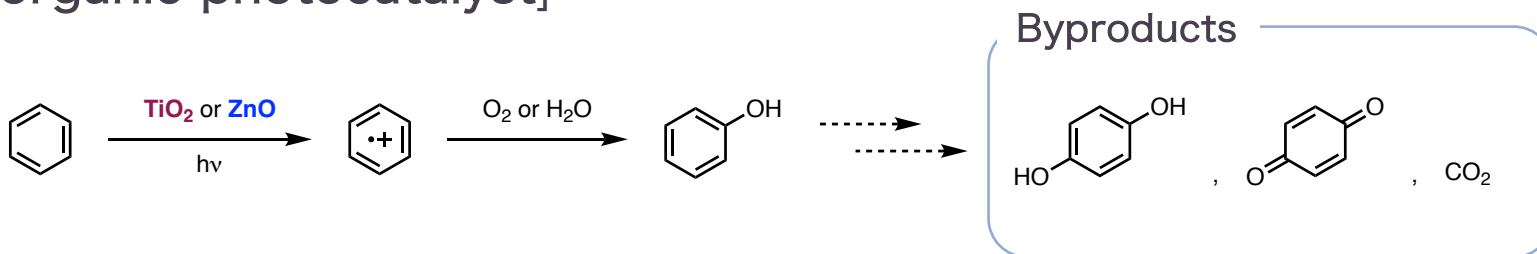
Synthesis of phenol from benzene

[Conventional method (Cumene process)]



- × Low yield. (~5%)
- × High energy is required.

[Inorganic photocatalyst]



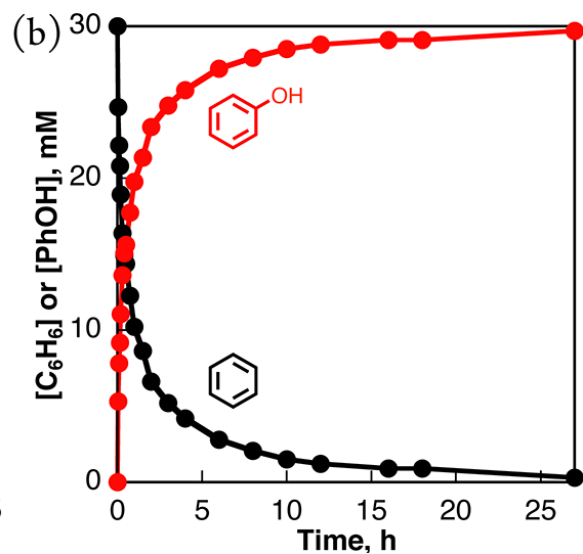
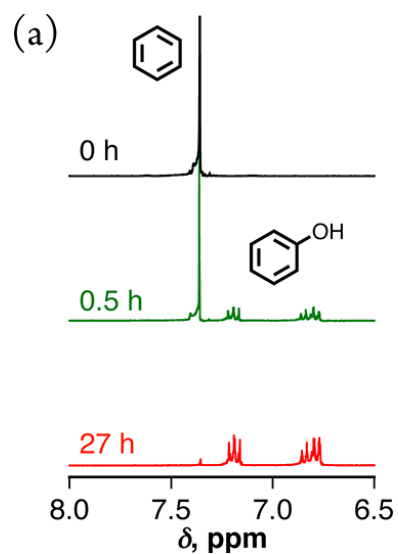
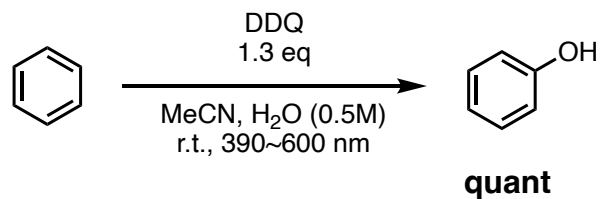
- × Low yield by overoxidation of phenol.



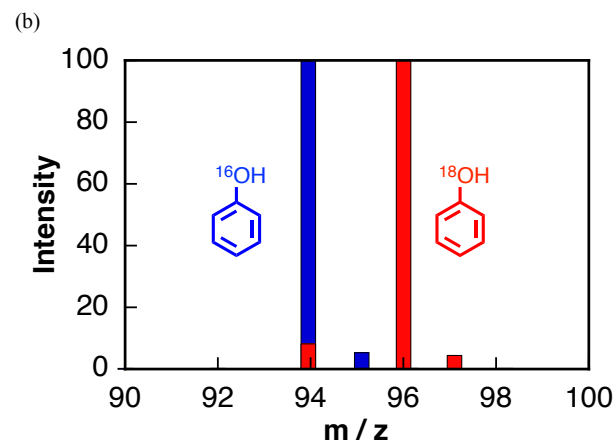
Selective photocatalytic synthesis of phenol from benzene is highly valuable.

Single electron oxidation by excited DDQ

[Photooxygenation by DDQ]

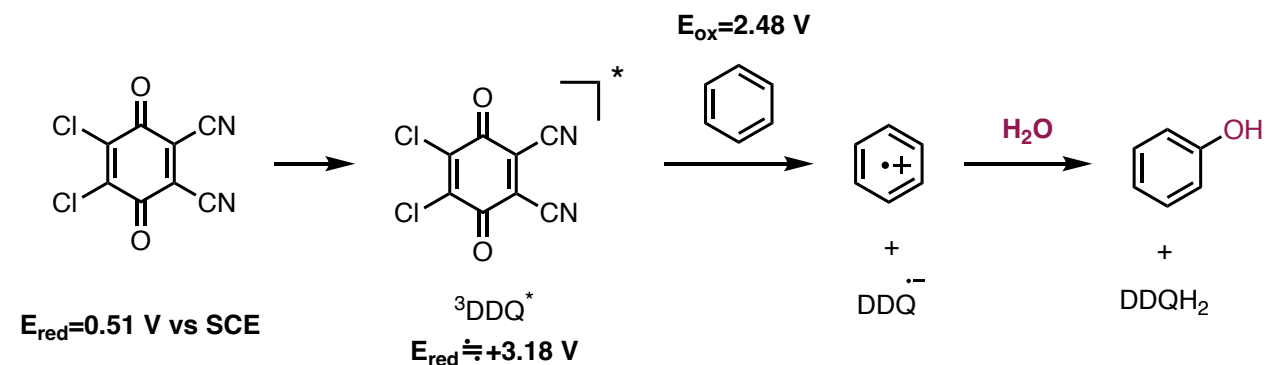


[GC-MS]



Blue; Reaction w/ H_2^{16}O
Red; Reaction w/ H_2^{18}O

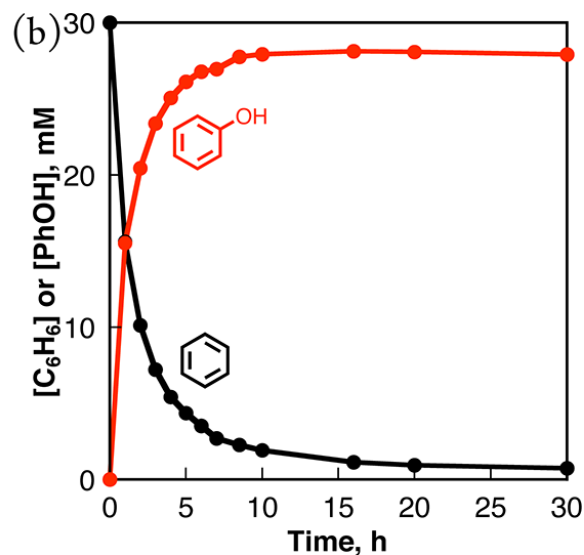
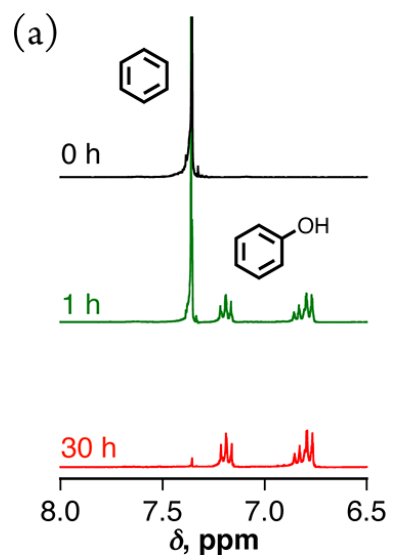
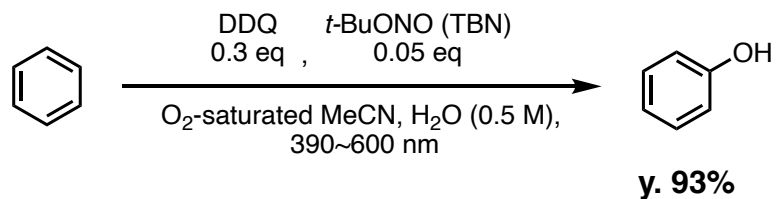
The source of oxygen atom is H_2O .



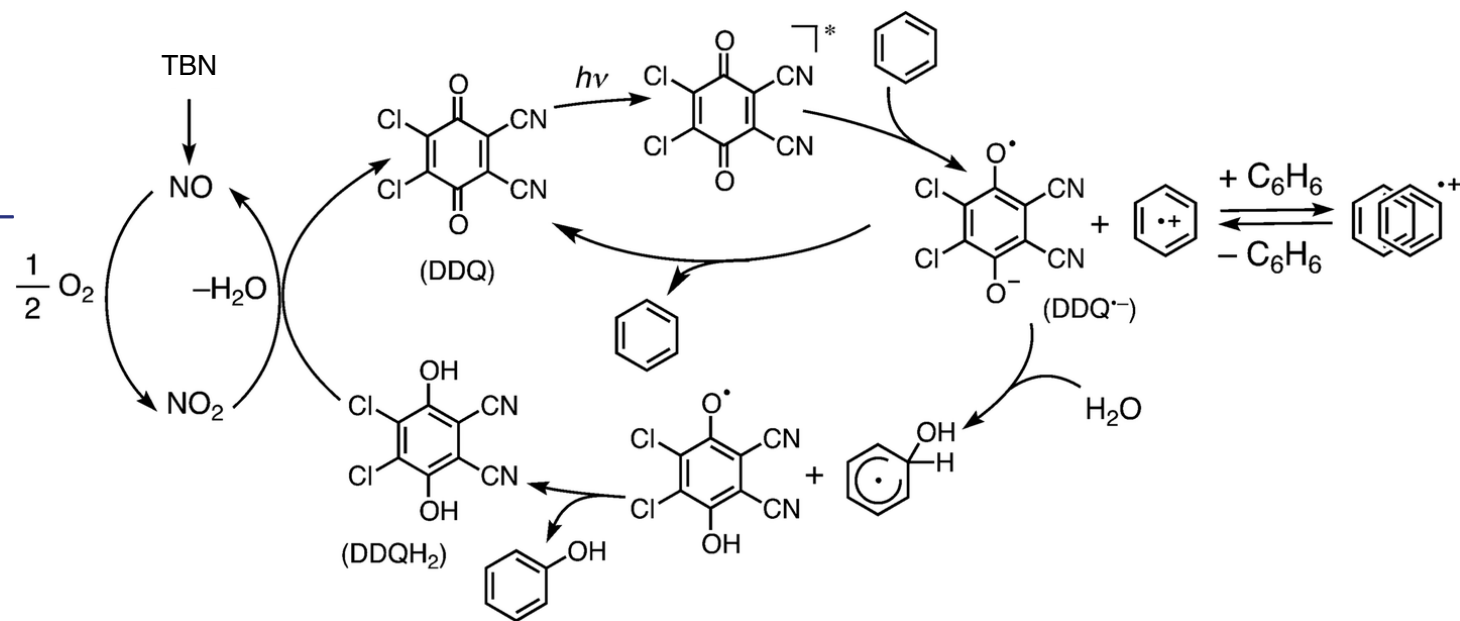
Fukuzumi *et al.* *J. Am. Chem. Soc.* 2013, 135, 5368.
König *et al.* *Chem. Eur. J.* 2017, 23, 18161.

Catalytic cycle

[Reaction with TBN]



[Proposed mechanism]

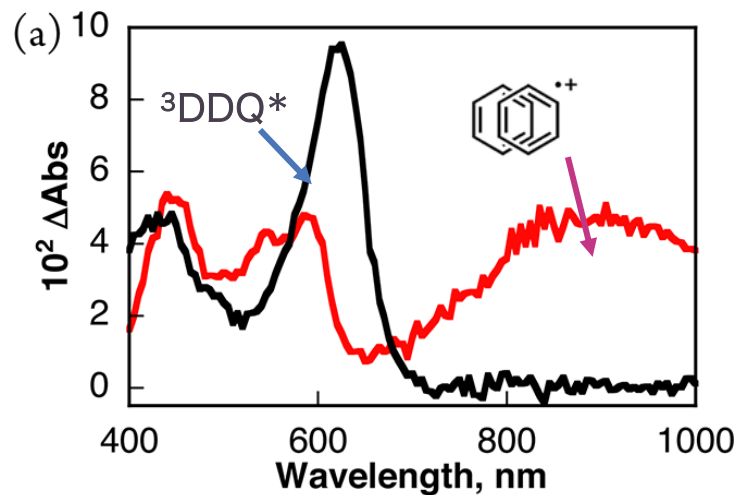


Catalytic cycle with TBN;
 Hu *et al.* *Adv. Synth. Catal.* 2011, 353, 3031.

- Phenol was obtained in 93% yield without overoxidation.

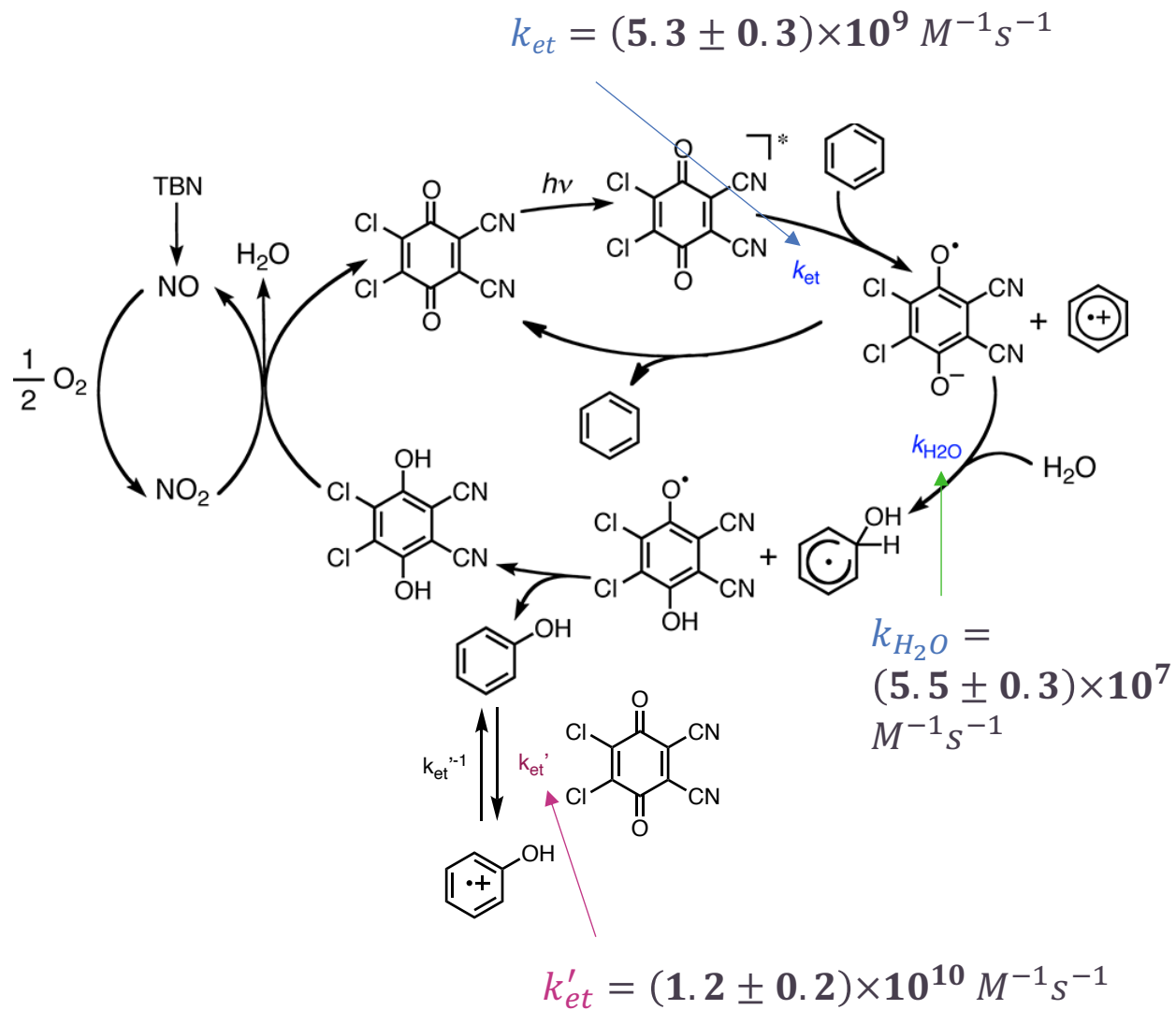
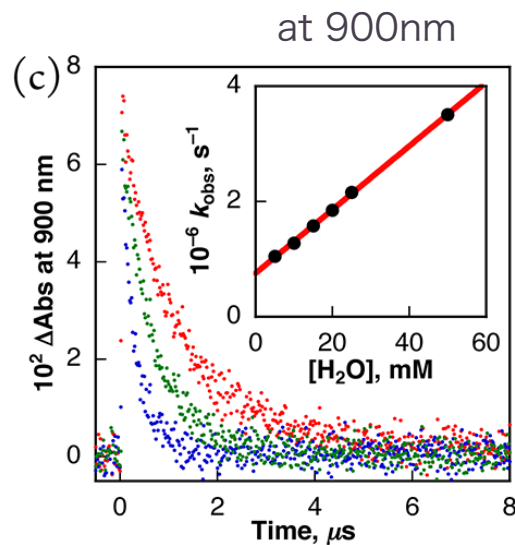
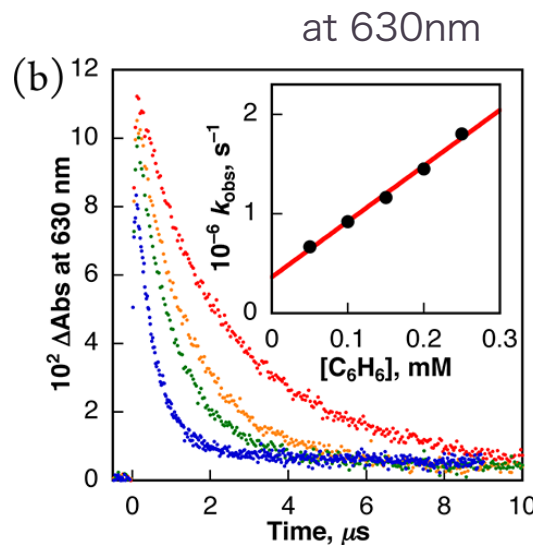
Measurement of rate constants

[Transient absorption]



Black; DDQ
Red; DDQ+benzene

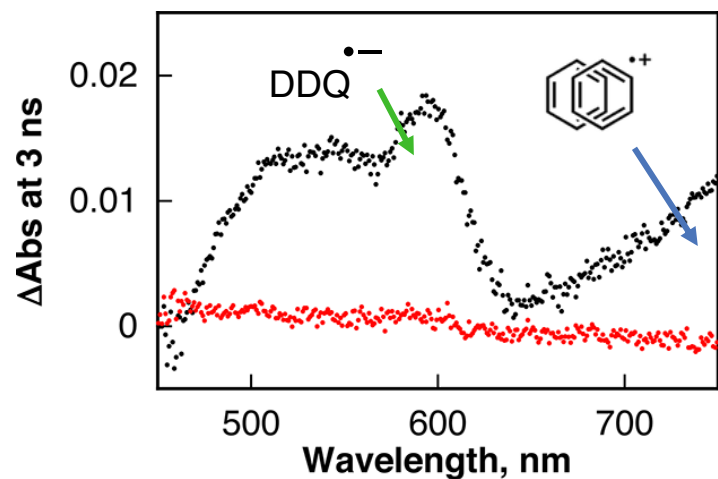
[Decay time profile]



Oxidation of phenol occurs at a rate greater than that of benzene.

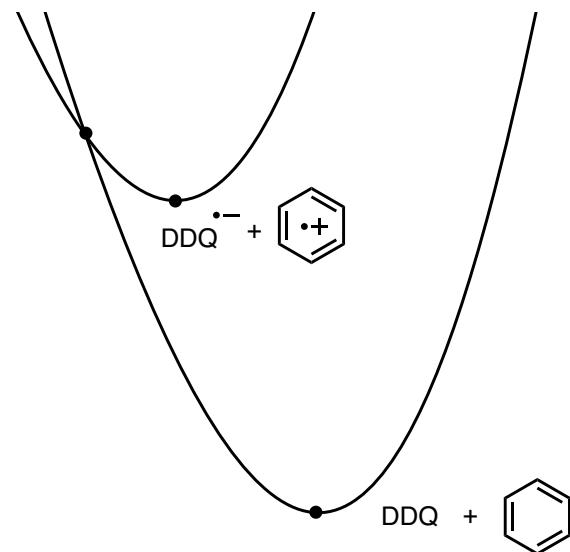
Back electron transfer

[Transient absorption]



Black; DDQ+benzene
Red; DDQ+phenol

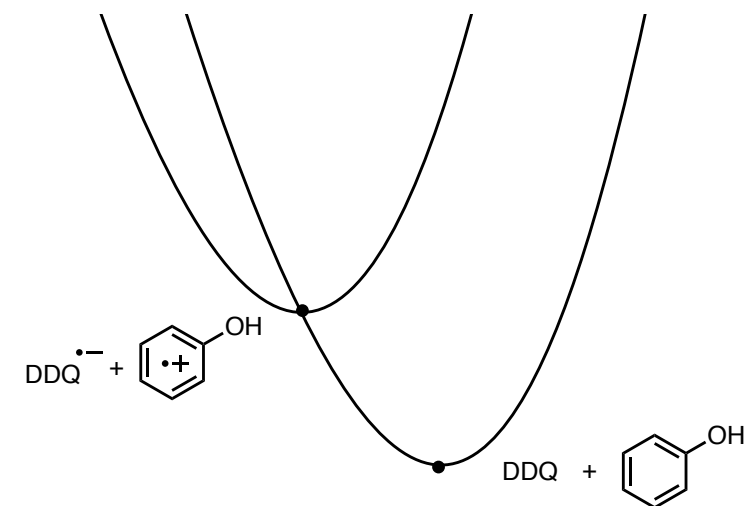
[Oxidation of benzene]



Inverted region

BET < Dissociation of
radical ion pair
(addition of H₂O)

[Oxidation of phenol]



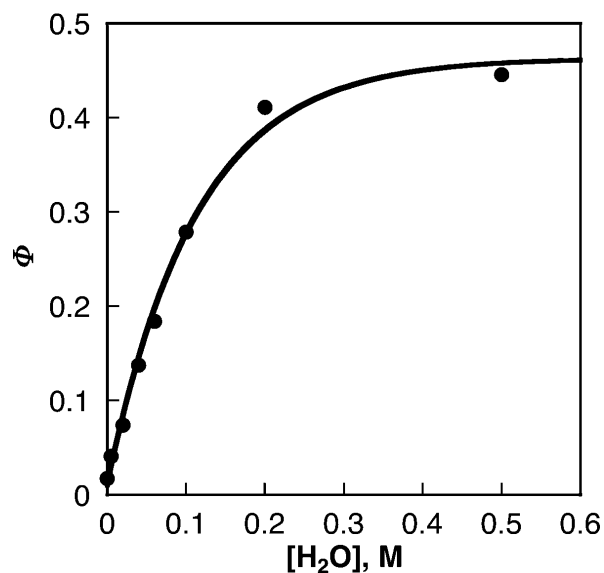
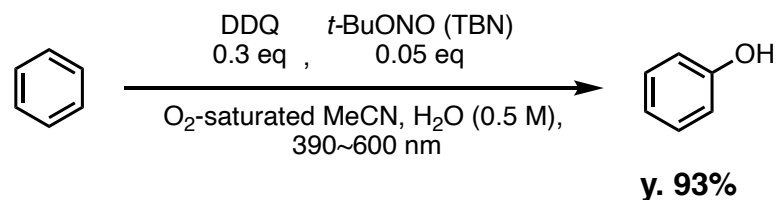
Marcus top region

BET >> Dissociation of
radical ion pair

Overoxidation of phenol doesn't proceed because of very fast BET

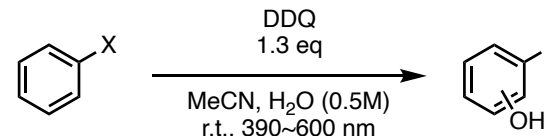
Photooxygenation of halogenated benzene

[Quantum yield]



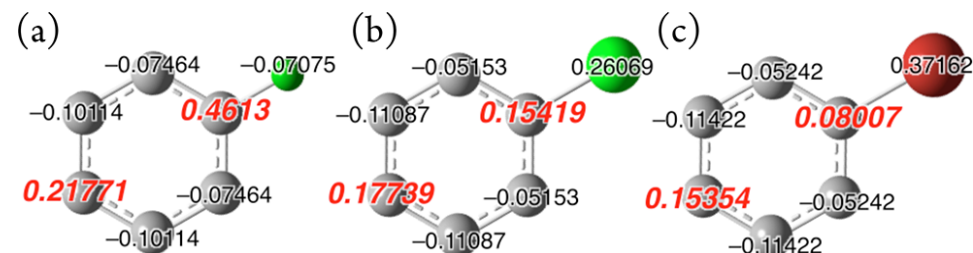
- High quantum yield for the formation of phenol ($\Phi = 0.45$).

[*o*, *p*-selective oxygenation]



substrate (conversion, %)	product: yield, % (selectivity, %)
fluorobenzene (44)	phenol: 14 (32) <i>p</i> -fluorophenol: 24 (55) <i>o</i> -fluorophenol: 5.7 (13)
chlorobenzene (34)	phenol: 0 (0) <i>p</i> -chlorophenol: 28 (82) <i>o</i> -chlorophenol: 6.1 (18)
bromobenzene (14)	phenol: 0 (0) <i>p</i> -bromophenol: 11 (80) <i>o</i> -bromophenol: 2.8 (20)

[Electronic charges of radical cation]

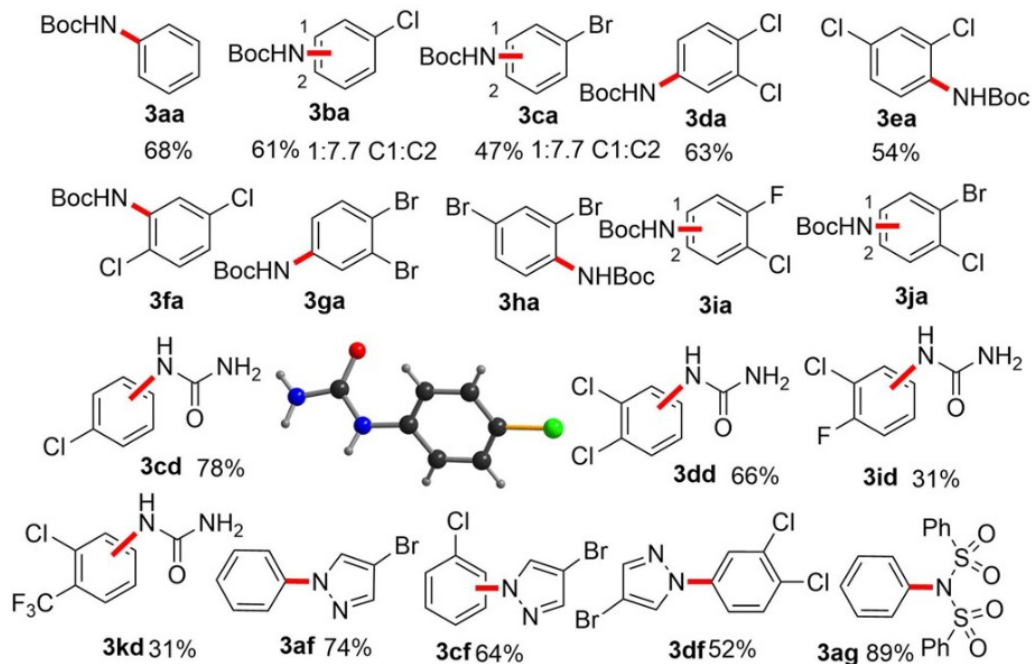


Applications to other reactions

[Synthesis of protected aniline]

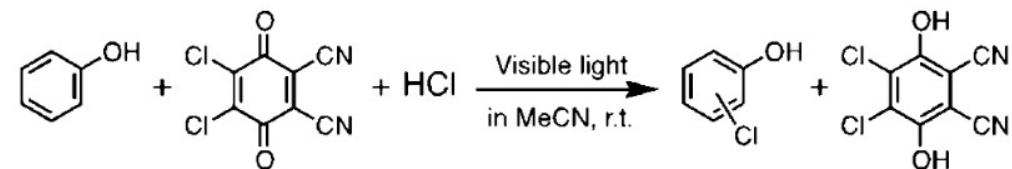


Substrate scope

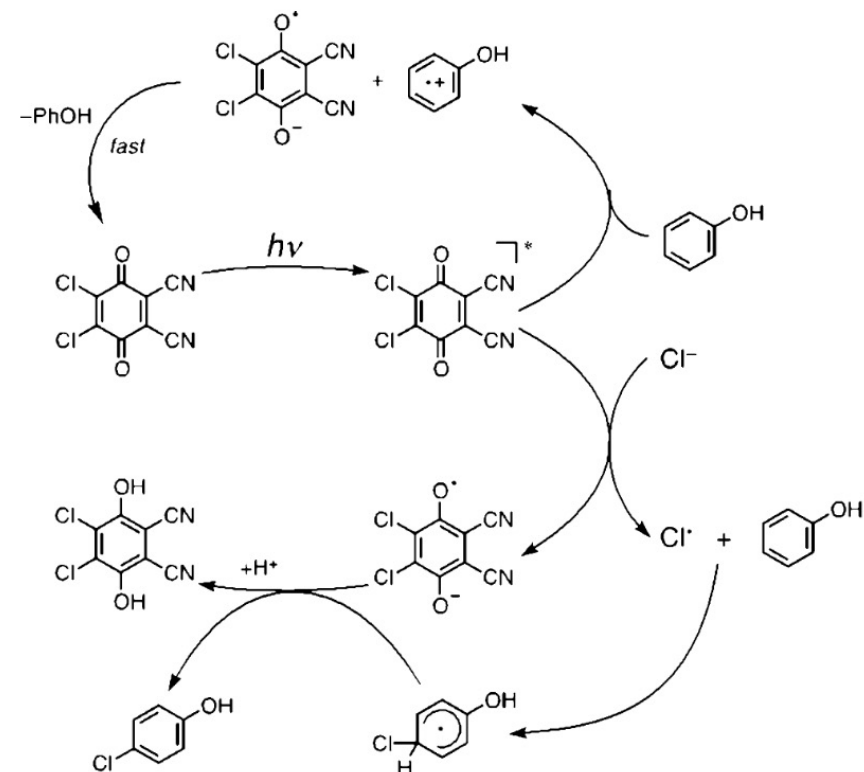


König *et al. Chem. Eur. J.* 2017, 23, 18161.

[Oxidation of chloride ion]



Reaction mechanism



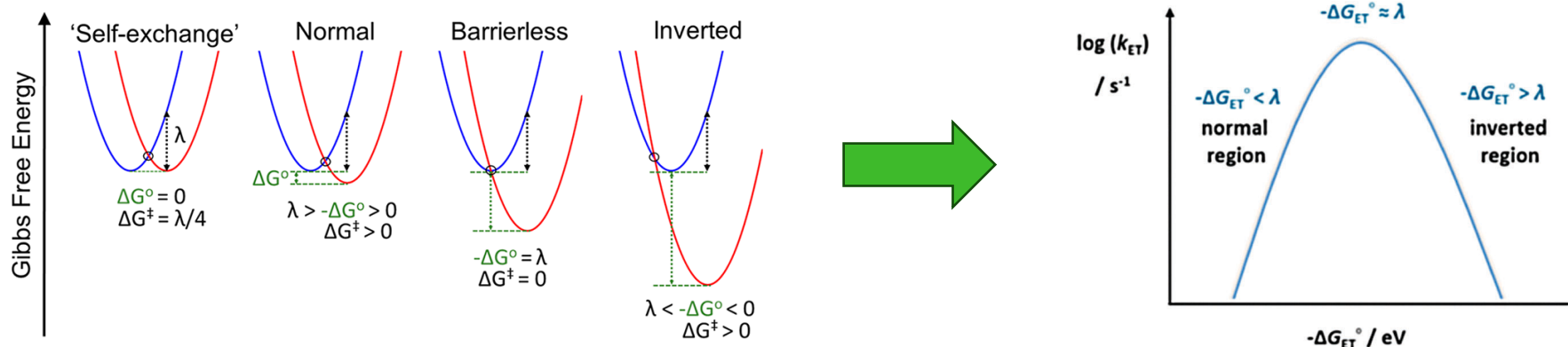
Fukuzumi *et al. Chem. Asian J.* 2016, 11, 996.

Contents

- Introduction
 - Theory and experiment
- Application to chemical reaction
 - Catalytic oxidation of benzene to phenol
- Summary

Summary

[Marcus theory]



- Clarified the relationship between electron transfer rate, Gibbs free energy change, and reorganization energy, and predicted the inverted region.

Guldi *et al.* *Chem. Soc. Rev.* 2018, 47, 702.
Meyer *et al.* *J. Chem. Educ.* 2019, 96, 2450.

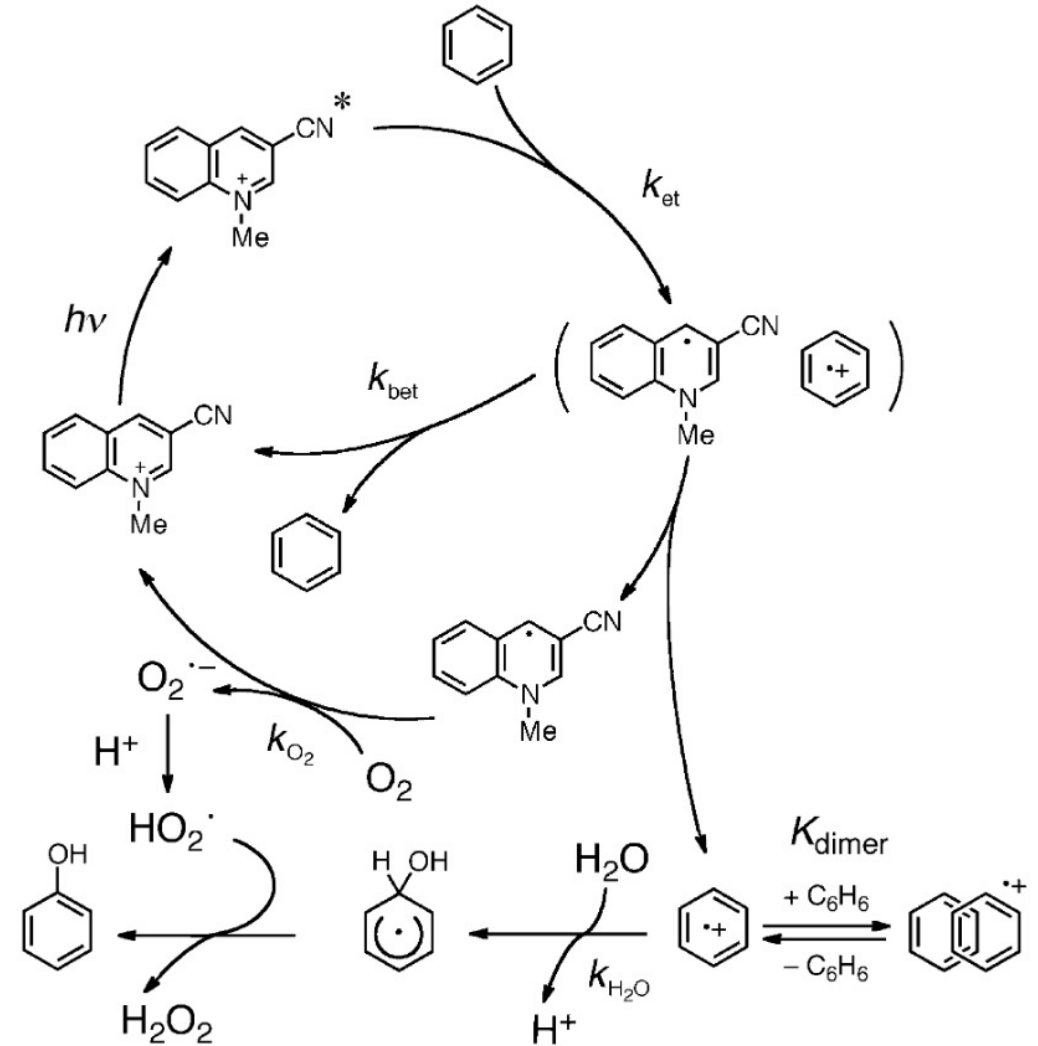
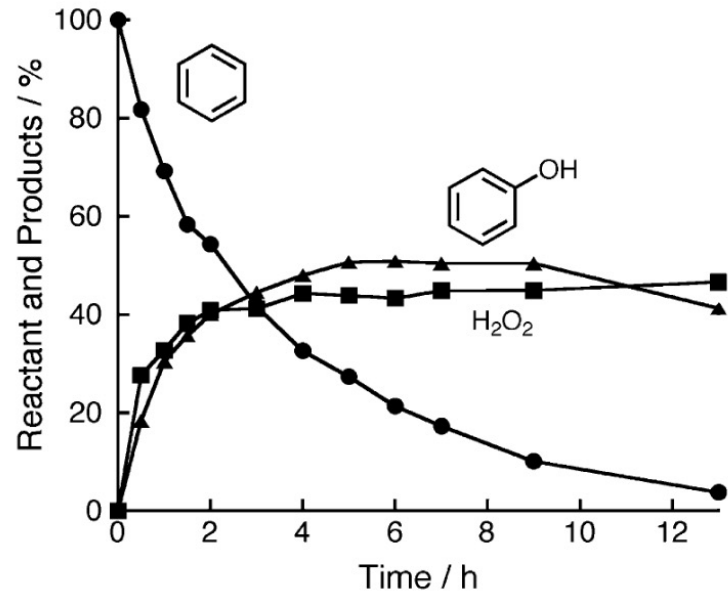
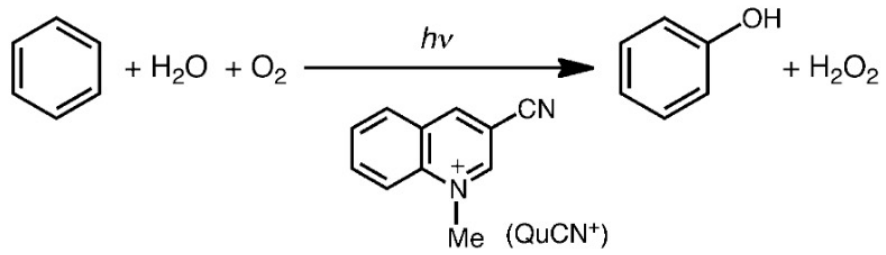
[Selective photocatalytic synthesis of phenol]



- Selective catalytic reaction was achieved using Marcus theory.
- It can also be applied to other useful conversions.

Appendix

[Previous report]



Fukuzumi *et al.* *Angew. Chem. Int. Ed.* 2011, 50, 8652.