PCET Concepts: HAT vs. EPT and Nonadiabaticity

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References on HAT vs. EPT and nonadiabaticity:


PCET web site: [http://webpcet.scs.uiuc.edu/](http://webpcet.scs.uiuc.edu/)

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Definitions Relevant to PCET


- PCET can occur by sequential or concerted mechanism (not rigorously defined but clearly sequential if a stable intermediate can be isolated and clearly concerted if products of single ET and PT are much less thermodynamically favorable than product of concerted PCET)
- Concerted PCET includes HAT (hydrogen atom transfer) and EPT (electron-proton transfer)
  - HAT: electron and proton transfer from the same donor and acceptor* (not rigorous definition but used in the field); negligible amount of electronic charge redistribution as H transfers; electronically adiabatic†
  - EPT: electron and proton transfer between different donors and acceptors* (not rigorous); significant amount of electronic charge redistribution as H transfers; electronically nonadiabatic‡

*donor/acceptor can be molecular orbitals, chemical bonds, or atoms
‡Distinguishing HAT and EPT by electron-proton nonadiabaticity introduced in Skone, Soudackov, SHS, JACS 2006
Nonadiabaticity


• Electron-proton subsystem wrt other nuclei

\[ V_{\mu\nu} \ll k_B T \quad \quad k_{\text{PCET}} \propto V_{\mu\nu}^2 \]

\[ V_{\mu\nu} = \langle \Phi_{\mu}^{\mu} (r_e, r_p) | \hat{H} | \Phi_{\nu}^{\mu} (r_e, r_p) \rangle \]

• Electron-proton nonadiabaticity:

determines form of vibronic coupling

nonadiabatic

\[ V_{\mu\nu}^{(na)} = V^{\text{el}} \langle \phi_{\mu} | \phi_{\nu} \rangle \]

adiabatic

\[ V_{\mu\nu}^{(ad)} = \Delta / 2 \]

\[ \Delta \]

quantum ← classical

vib nad

ep nad

e: electrons
p: proton(s)
n: other nuclei
Electron-Proton Nonadiabaticity

- Relative timescales of electronic transition and proton tunneling
  - determine timescales with semiclassical formulation
  - nonadiabatic when proton tunneling faster than electronic transition
  \[ \tau_p < \tau_e \]

- Nonadiabatic coupling with respect to transferring proton coordinate
  - determine from electronic wavefunctions
  - nonadiabatic when character of electronic wavefunction changes significantly with respect to proton motion
  \[ d_{12}^{(ep)}(r_p) = \left\langle \Psi_1^e \left| \frac{\partial \Psi_2^e}{\partial r_p} \right. \right\rangle \]

- Change in electronic charge distribution as proton transfers
  - determine from dipole moment, electrostatic potential, partial charges
  - nonadiabatic when significant change
  - hydrogen atom transfer (HAT) vs electron-proton transfer (EPT)
Representative Chemical Examples

Mayer, Hrovat, Thomas, Borden, JACS 2002; Skone, Soudackov, SHS, JACS 2006

benzyl/toluene
C---H---C

SOMO

DOMO

HAT
same donor/acceptor
electronically adiabatic

EPT
different donors/acceptors
electronically nonadiabatic

phenoxyl/phenol
O---H---O

HAT: hydrogen atom transfer
EPT: concerted PCET
Semiclassical Treatment: Timescales

Georgievskii and Stuchebrukhov, JCP 2000; Skone, Soudackov, SHS, JACS 2006

Electronically nonadiabatic PT: \( p << 1, \; \tau_p < \tau_e \)

\[
V_{DA}^{(na)} = V^e \left( \phi_D | \phi_A \right)
\]

adiabaticity parameter: \( p = \frac{\tau_p}{\tau_e} \)

\[
\tau_e \approx \frac{\hbar}{V^e} \quad \tau_p \approx \frac{|V^e|}{|\Delta F| v_i}
\]

vibronic coupling: \( V_{DA}^{(sc)} = \kappa(p)V_{DA}^{(ad)} \)

\[
v_i = \sqrt{2(V_c - E)/m_p} : \text{tunneling velocity}
\]

\(|\Delta F| : \text{difference of slopes of potential energy curves at crossing point}
\]

\( V^e : \text{electronic coupling} \)

Electronically adiabatic PT: \( p >> 1, \; \tau_e < \tau_p \)

\[
V_{DA}^{(ad)} = \Delta / 2
\]
Nonadiabaticity: Relative Timescales

Skone, Soudackov, SHS, JACS 2006: CASSCF calculations

Phenoxyl-phenol: O---H---O, electronically nonadiabatic, EPT

\[ \tau_e \approx 80 \tau_p \]
\[ V^{\text{el}} = 700 \text{ cm}^{-1} \]
\[ V^{(\text{na})}_{DA} = V^{\text{el}} \langle \varphi_D | \varphi_A \rangle \]

Benzyl-toluene: C---H---C, electronically adiabatic, HAT

\[ \tau_e \approx 0.25 \tau_p \]
\[ V^{\text{el}} = 14,000 \text{ cm}^{-1} \]
\[ V^{(\text{ad})}_{DA} = \Delta/2 \]
Nonadiabatic Coupling

Solid lines: phenoxy/phenol, electronically nonadiabatic, EPT

Dotted lines: benzyl/toluene, electronically adiabatic, HAT

Electron-proton nonadiabatic coupling from CASSCF states

\[
\langle \Psi_1^{\text{el}} | \frac{\partial \Psi_2^{\text{el}}}{\partial r_p} \rangle
\]

- Nonadiabatic coupling much greater for EPT than for HAT
- EPT has greater molecular charge redistribution along \( r_p \)

Sirjoosig and SHS, JPC A 2011, JCTC 2011
Electrostatic Potential Maps

phenoxyl/phenol: electronically nonadiabatic, EPT

benzyl/toluene: electronically adiabatic, HAT

reactant  transition state  product

Red: negative charge  Blue: positive charge

Sirjoosinhg and SHS, JPC A 2011, JCTC 2011
Molecular Charge Redistribution

phenoxyl/phenol: PCET electronically nonadiabatic

benzyl/toluene: HAT electronically adiabatic

Sirjoosingh and SHS, JPC A 2011, JCTC 2011
Vibronic Couplings

Phenoxy1-phenol: electronically nonadiabatic, EPT

\[ \tau_e \approx 80 \tau_p \]
\[ V^{\text{el}} = 700 \text{ cm}^{-1} \]
\[ V_{DA}^{(\text{na})} = V^{\text{el}} \langle \varphi_D | \varphi_A \rangle \]

Benzyl-toluene: electronically adiabatic, HAT

\[ \tau_p \approx 0.25 \tau_e \]
\[ V^{\text{el}} = 14,000 \text{ cm}^{-1} \]
\[ V_{DA}^{(\text{ad})} = \Delta / 2 \]

Vibronically nonadiabatic

Sirjoosingh and SHS, JPC A 2011, JCTC 2011
Nonadiabaticity in Lipoxygenase

Soudackov and Hammes-Schiffer, JPCL 2014

- Model system
- C–O distance 2.7 Å
- Constrained DFT/ωB97X/6-31G**

\[ \tau_e \approx 85 \tau_p \]
\[ V^{\text{el}} = 4.6 \text{ kcal/mol} \]
\[ V^{(\text{na})}_{DA} \approx V^{\text{el}} \left\langle \phi_D | \phi_A \right\rangle = 0.0051 \text{ kcal/mol} \]

Electronically nonadiabatic PT and vibronically nonadiabatic PCET
Spin Densities and Charge Distribution

$d_{12}^{(ep)}(r_p) = \langle \Psi_1^\text{el} | \partial \Psi_2^\text{el} / \partial r_p \rangle$

Soudackov and Hammes-Schiffer, JPCL 2014