

Electron Transfer in Electrophilic Aromatic Nitration and Nitrosation

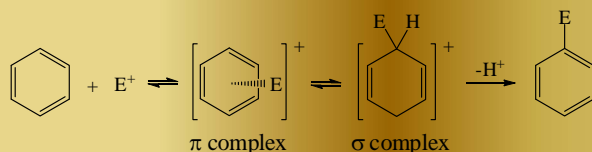
Zhenhua Chen and Yirong Mo*

Department of Chemistry, College of Arts and Sciences
Western Michigan University, Kalamazoo MI 49008



Introduction

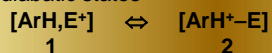
Electron transfer (ET) is ubiquitous in chemical and biological processes. A synthetically and industrially important ET reaction is the electrophilic aromatic substitution, which is typically elucidated with three steps as



Interestingly, nitronium (NO^+) and nitronium (NO_2^+) have similar inherent physical properties, but NO_2^+ is 10^{14} times more reactive than NO^+ . This will be the focus of this work.

Methods

Two-State Model: An ET process is interpreted with two electron-localized diabatic states



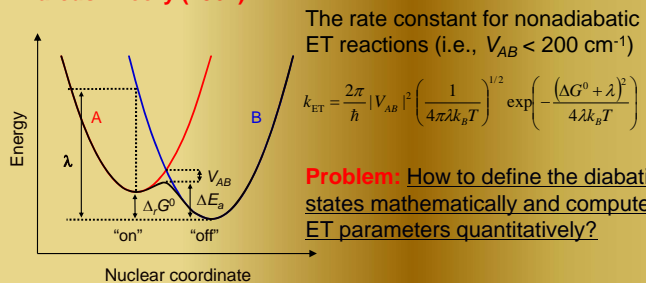
Mulliken proposed (1952):

$$\Psi_{GS} = c_a \Psi_{D,A} + c_b \Psi_{D^+A^-}$$

$$\Psi_{ES} = c_b \Psi_{D,A} - c_a \Psi_{D^+A^-}$$

$$H_{DA} = \langle \Psi_{D,A} | \hat{H} | \Psi_{D^+A^-} \rangle$$

Marcus Theory (1961):



Our Solution: Block-localized Wavefunction (BLW) Method

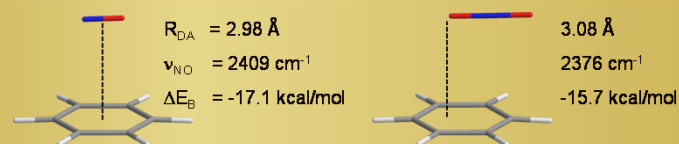
$$[\text{ArH}, \text{E}^+] \quad \Psi_{D,A} = \hat{A}(\Phi_{\text{C}_6\text{H}_6}^{42} \Phi_{\text{E}^+}^{14/22})$$

$$[\text{ArH}^+ - \text{E}] \quad \Psi_{D^+A^-} = \hat{A}(\Phi_{\text{C}_6\text{H}_6}^{40} \Phi_{\text{E}^+}^{14/22} \varphi^2)$$

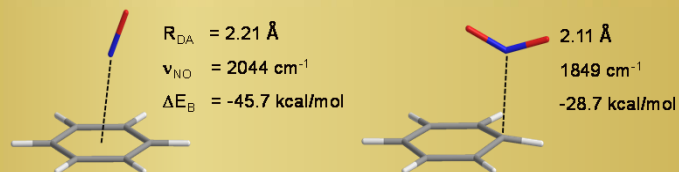
$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - E \end{vmatrix} = 0 \quad \rightarrow \quad H_{DA} = H_{11/22} - E_1$$

Results

BLW Geometry Optimizations:

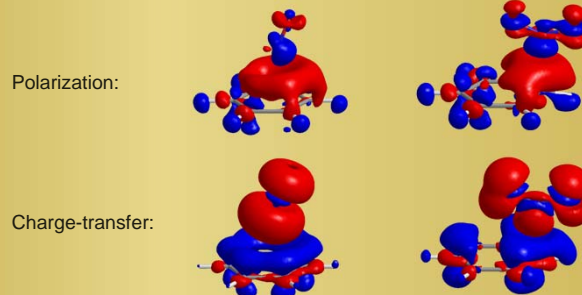


DFT Geometry Optimizations:



BLW Energy Decomposition:

Deformation	= 3.2	35.2
Heitler-London	= 15.0	29.2
Polarization	= -13.8	-17.3
Charge-Transfer	= -50.1	-75.8



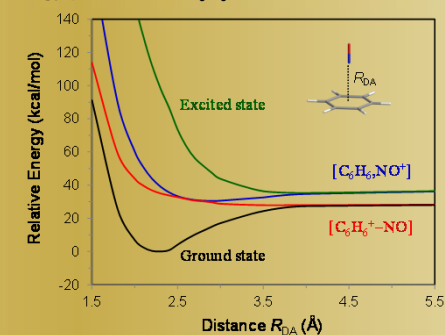
Two-State Interactions:

State	E=NO		E=NO ₂	
	[C ₆ H ₆ , E ⁺]	[C ₆ H ₆ ⁺ -E]	[C ₆ H ₆ , E ⁺]	[C ₆ H ₆ ⁺ -E]
Structural E	-359.60495	-359.63720	-434.29026	-434.41445
Coefficients c	0.5414	0.6982	-0.3321	0.8533
Structural w	40.3%	59.7%	19.1%	80.9%
E _i (Cl)	-359.68584		-434.43662	
H _{DA}	1.32		0.60	

Findings:

- The charge transfer state is more stable;
- Explains why [C₆H₆, NO]⁺ has a tilted NO rather than takes a C_{6v} geometry;
- Coupling energy is significant.

Full energy profiles for [C₆H₆, NO]⁺:



Findings:

- Outer-sphere ET at ~2.6 Å;
- $H_{DA} = 1.06 \text{ eV}$, compared with the experimental $1.4 \pm 0.5 \text{ eV}$;
- The C₆H₆ + NO⁺ ET reaction falls in the "inverted region" in Marcus theory.

Acknowledgment

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