

Supporting Information

For

Conversion and Origin of Normal and Abnormal Temperature Dependences of Kinetic Isotope Effect in Hydride Transfer Reactions

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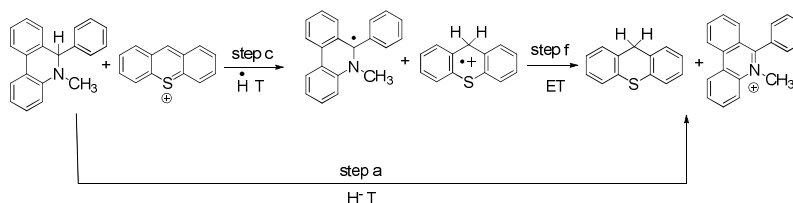
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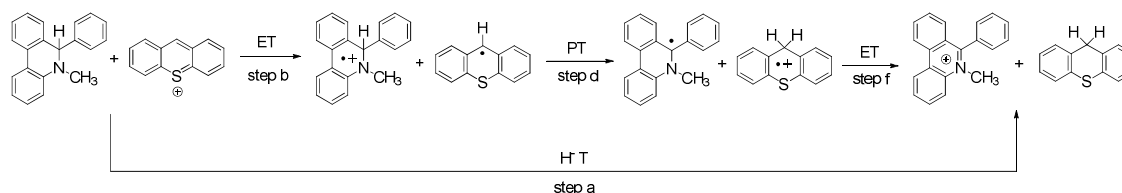
SI-1. Three Thermodynamic Cycles Were Constructed as Shown in Schemes S1-S3 According to the Reaction of G-PDH with TX⁺^{S1}

Scheme S1.



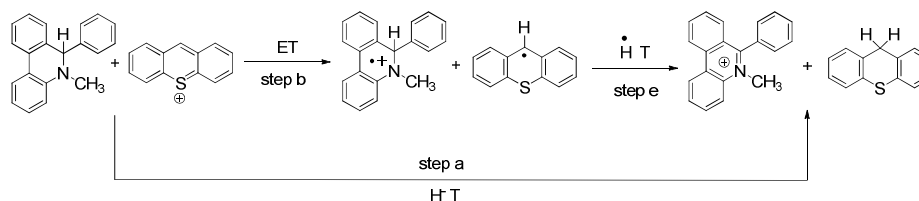
$$\Delta H (\text{step } c) = \Delta H_{\text{rxn}} - F[E_{\text{red}}(\text{G-PD}^+) - E_{\text{ox}}(\text{TXH})]$$

Scheme S2.



$$\Delta H (\text{step } d) = \Delta H_{\text{rxn}} - F[E_{\text{red}}(\text{G-PD}^+) - E_{\text{ox}}(\text{TXH})] + F[E_{\text{red}}(\text{TX}^+) - E_{\text{ox}}(\text{G-PDH})]$$

Scheme S3.



$$\Delta H (\text{step } e) = \Delta H_{\text{rxn}} + F[E_{\text{red}}(\text{TX}^+) - E_{\text{ox}}(\text{G-PDH})]$$

Ref:

^{S1} It should be pointed out herein that we used the term free energy change ΔG_{eT} to replace the enthalpy change ΔH_{eT} for the electron transfer processes. The validation of using free energy change ΔG_{eT} instead of enthalpy change ΔH_{eT} for electron transfer processes is that entropies associated with electron transfer are negligible, and ΔG_{eT} can be combined directly with ΔH_{eT} , which has been verified by Arnett's work. Ref: Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344-355.

SI-2. Representative ^1H NMR Graphs of G-PDH and G-PDD

