

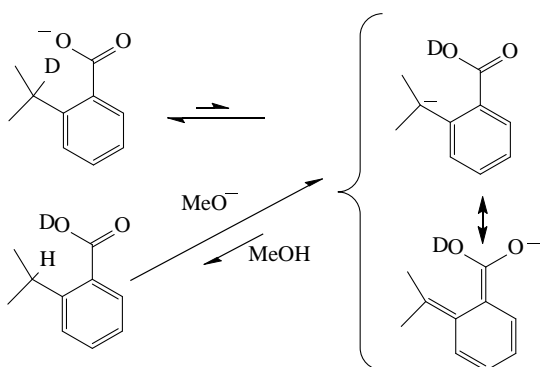
## Supporting Information

# Hydrogen and Proton Exchange at Carbon. Imbalanced Transition State and Mechanism Crossover

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Does the lack of H/D exchange in solutions of 1-*d*<sub>1</sub> with excess CH<sub>3</sub>OH rule out any contribution of the PTET pathway to the global reaction?



MeOH is an immeasurably weak acid in acetonitrile and the basicity of the deuterated carbanion (upper right) is decreased by the  $\pi$ -conjugation represented by the lower right structure. In total, methanol is likely not to be able to protonate the delocalized right-hand species. The reported methanol test therefore does not exclude that the PTET pathway may contribute to the global reaction.

### Kinetics of the PTET reaction pathway

With the same notations as in the main text, the kinetics of disappearance of  $\text{ox}^+$  as measured in the stopped-flow experiments may be expressed as:

$$\frac{d[\text{ox}^+]}{dt} = -k_2^e [{}^-\text{AH}] [\text{ox}^+]$$

The steady-state approximation applied to  ${}^-\text{AH}$  leads to

$$[{}^-\text{AH}] = \frac{k_1^H}{k_{-1}^H + k_2^e [\text{ox}^+]} [\text{HA}^-]$$

And therefore to:

$$\frac{d[\text{ox}^+]}{dt} = -k_2^e \frac{k_1^H [\text{ox}^+]}{k_{-1}^H + k_2^e [\text{ox}^+]} [\text{HA}^-]$$

In all experiments  $\text{HA}^-$  is in excess over  $\text{ox}^+$ . It may thus be considered that  $[\text{HA}^-] \approx [\text{HA}^-]_{t=0}$

The kinetics of the forward and backward PT steps may be obtained from:

$$k_1^H = \chi Z_1^H \exp \left[ -\frac{\lambda_H F}{4RT} \left( 1 + \frac{\Delta G_{PT}^0}{\lambda_H} \right)^2 \right], k_{-1}^H = \frac{k_1^H}{K_1^H}$$

noting that the pre-exponential factor  $Z_1^H$  concerns a first order reaction and may therefore be approximated by  $k_B T / h$  ( $k_B, h$ : Boltzmann and Planck constants respectively)  $\approx 6 \times 10^{12} \text{ s}^{-1}$ . Using the same  $\chi$  factor as before, the global pre-exponential factor for the PT step is thus estimated as  $\chi Z_1^H \approx 6 \times 10^7 \text{ s}^{-1}$ . The ensuing rate constants are thus  $k_1^H = 4.3 \times 10^4 \text{ s}^{-1}$  and  $k_{-1}^H = 2.8 \times 10^9 \text{ s}^{-1}$

The follow-up ET step has standard free energy  $\Delta G_{ET}^0 = \Delta G_{rxn}^0 - \Delta G_{PT}^0$ , whose values are listed in the last column of Table 1. The same standard application of the Marcus model leads to:

$$k_2^e = Z_2^e \exp \left[ -\frac{\lambda_e F}{4RT} \left( 1 + \frac{\Delta G_{ET}^0}{\lambda_e} \right)^2 \right],$$

and therefore to an effective rate constant:

$$\frac{1}{k_2^{e,eff}} = \frac{1}{k_{dif}} + \frac{1}{Z_2^e \exp \left[ -\frac{\lambda_e F}{4RT} \left( 1 + \frac{\Delta G_{ET}^0}{\lambda_e} \right)^2 \right]}$$

The competition between the back proton transfer and the follow-up electron transfer is governed by the factor  $k_{-1}^H / \left( k_2^{e,eff} [\text{ox}^+] \right)$ , which is large in all cases, meaning that the PT step then acts as a pre-equilibrium the electron transfer step and thus that:

$$k^{PTET} = K_1^H k_2^{e,eff}$$