

Supporting Information
Proton-Coupled Electron Transfer in Soybean Lipoxygenase

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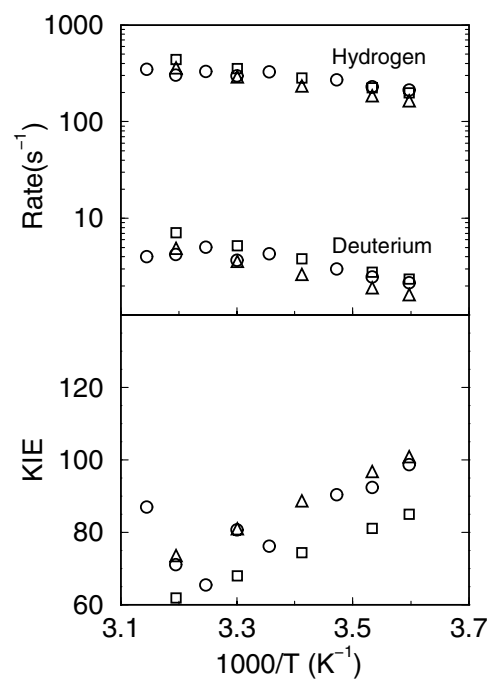


Figure S1: Temperature dependence of the rates and KIEs for multistate continuum theory calculations with a quantum treatment of the proton donor-acceptor vibrational motion. The experimental data are denoted with circles. The theoretical results were generated with two different parameter sets: the original parameter set used to generate Figure 5 (squares) and the same parameters except that the couplings were slightly modified so that these quantum results reproduced the experimental rate and KIE at 303 K (triangles).

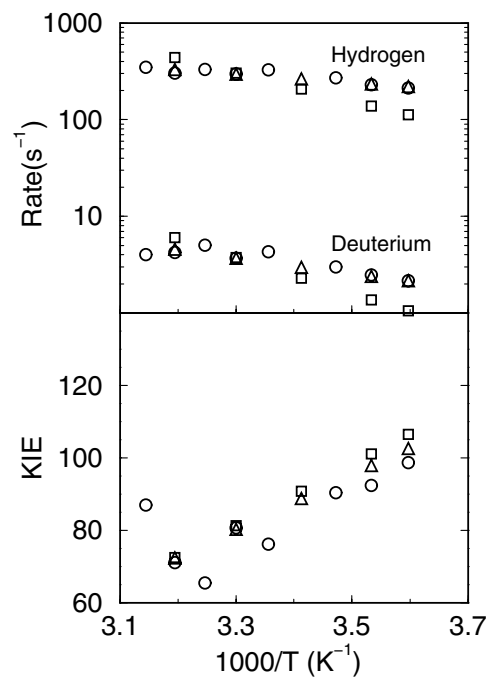


Figure S2: Temperature dependence of the rates and KIEs for multistate continuum theory calculations with a classical treatment of the proton donor-acceptor vibrational motion. The experimental data are denoted with circles. The theoretical calculations use the original parameter set with the inner-sphere reorganization energy modified to be $\lambda_{\text{in}} = 10$ kcal/mol (triangles) and $\lambda_{\text{in}} = 30$ kcal/mol (squares). The equilibrium C--O distance and frequency are $R_1^0 = 2.88$ Å and $\omega_1^0 = 511$ cm⁻¹ and the dominant C--O distance is $R_{\text{dom}} = 2.69$ Å.

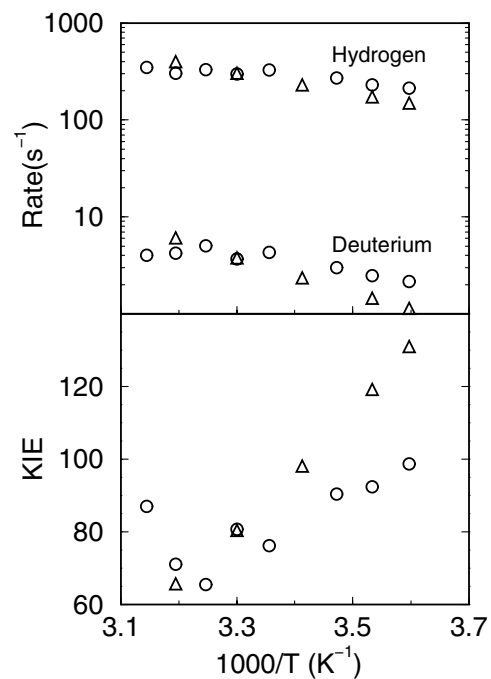


Figure S3: Temperature dependence of the rates and KIEs for multistate continuum theory calculations with a classical treatment of the proton donor-acceptor vibrational motion. The experimental data are denoted with circles. The theoretical calculations use the original parameter set with the C--O Morse parameter R_{CO}° modified to be $R_{\text{CO}}^{\circ} = 3.0$ Å (triangles). In all cases, the couplings V^{ET} and V^{PT} were fit to the experimental rate and KIE at $T=303$ K. The equilibrium C--O distance and frequency are $R_{\text{I}}^{\circ} = 3.02$ Å and $\omega_{\text{I}}^{\circ} = 519$ cm⁻¹ and the dominant C--O distance is $R_{\text{dom}} = 2.79$ Å.

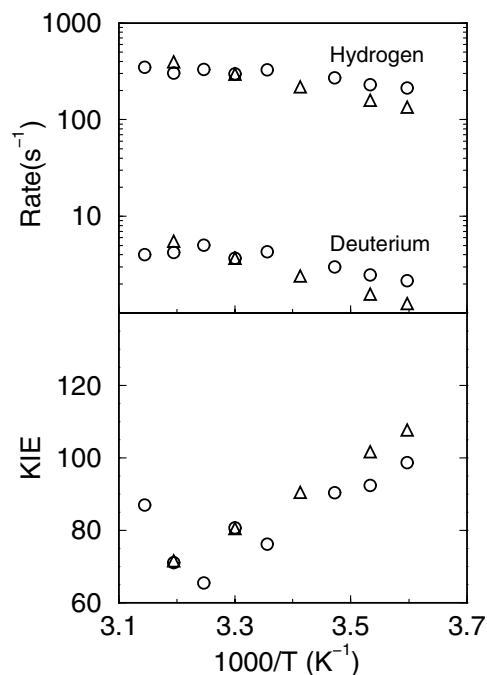


Figure S4: Temperature dependence of the rates and KIEs for multistate continuum theory calculations with a classical treatment of the proton donor-acceptor vibrational motion. The experimental data are denoted with circles, and the theoretical results are denoted with triangles. The calculations use the original parameter set with the following modifications: the solvent reorganization energies are calculated for a conformation with a C--O distance of 3.0 Å, $R_{\text{CO}}^0 = 3.0$ Å, $\beta_{\text{CO}} = 1.8$ Å⁻¹ corresponding to a C--O Morse frequency of 299 cm⁻¹, Fe--O force constant of 25 kcal mol⁻¹ Å⁻², π -C force constant of 100 kcal mol⁻¹ Å⁻², and the couplings V^{ET} and V^{PT} were fit to the experimental rate and KIE at T=303 K. The equilibrium C--O distance and frequency are $R_1^0 = 3.05$ Å and $\omega_1^0 = 284$ cm⁻¹ and the dominant C--O distance is $R_{\text{dom}} = 2.69$ Å.

	$E_{\text{act}}^{\text{H}}$	$E_{\text{act}}^{\text{D}}$
Experiment	2.1	3.0
Original parameters	4.1	5.9
Fixed R , $R = 2.7 \text{ \AA}$	2.6	3.9
Fixed R , $R = 2.8 \text{ \AA}$	3.0	6.0
Quantum R w/ original parameters	3.9	5.4
Quantum R w/ adjusted couplings	3.9	5.4
Original parameters w/ $\lambda_{\text{in}} = 10 \text{ kcal/mol}$	2.0	3.7
Original parameters w/ $\lambda_{\text{in}} = 30 \text{ kcal/mol}$	6.7	8.6
Original parameters w/ $R_{\text{CO}}^{\circ} = 3.0 \text{ \AA}$	4.8	8.2
Alternative model	5.3	7.3

Table S1: The slope of the plots in the figures illustrating the temperature dependence of the rates, where the slope is the activation energy E_{act} defined from the empirical Arrhenius equation $k = A \exp^{-E_{\text{act}}/RT}$. The activation energies are given in units of kcal/mol. The experimental data is from Ref. 12. The data for the original parameters are given in Figure 5, and the data for the fixed proton donor-acceptor distances R are given in Figure 8. The data with the quantum mechanical treatment of R are given in Figure S1, the data with the different inner-sphere reorganization energies are given in Figure S2, the data with the different value of R_{CO}° are given in Figure S3, and the data for the alternative model are given in Figure S4.