Supporting Information

Probing Nonadiabaticity in the Proton-Coupled Electron Transfer Reaction Catalyzed by Soybean Lipoxygenase

Alexander V. Soudackov and Sharon Hammes-Schiffer*

Department of Chemistry, 600 South Mathews Ave, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801; shs3@illinois.edu

Phenoxyl-Phenol system

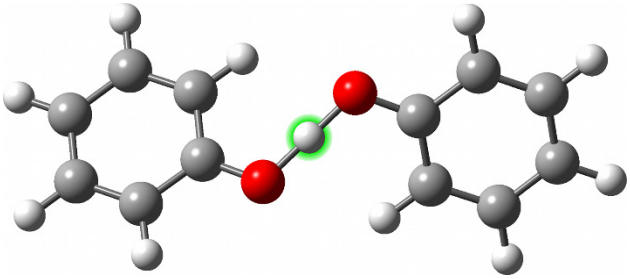

Figure S1: ”Open” transition state geometry for the phenoxyl/phenol system optimized at the ROHF/6-31G* level in Ref. [1]. The transferring hydrogen atom is highlighted. Note that a “stacked” transition state geometry that is lower in energy at certain levels of theory has also been identified.[2]

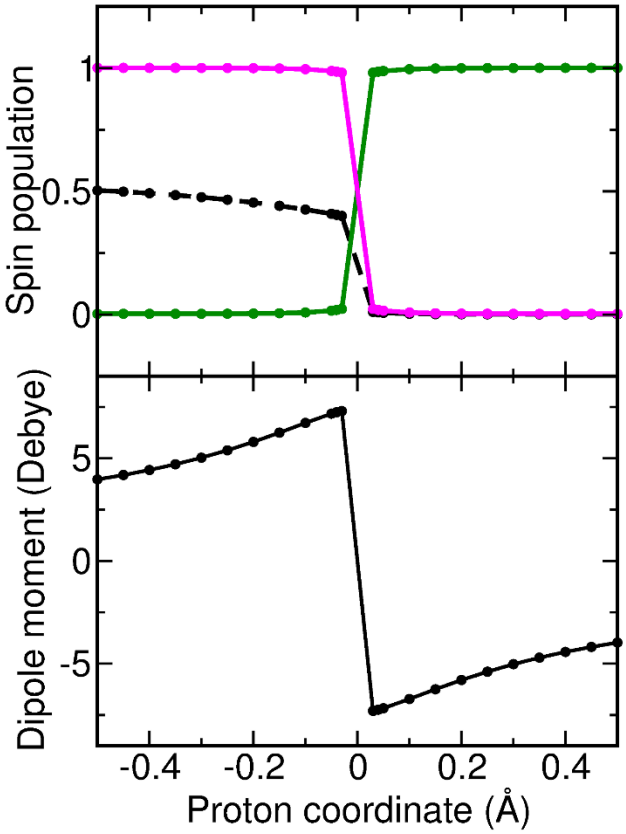

Figure S2: Spin populations of the donor molecule, acceptor molecule, and transferring hydrogen (green, magenta, and black lines, respectively, in top panel) and projection of the dipole moment onto the proton donor-acceptor axis (bottom panel) along the proton coordinate calculated with ground state DFT/ωB97X/6-31G* for the phenoxyl/phenol system at the “open” TS geometry.

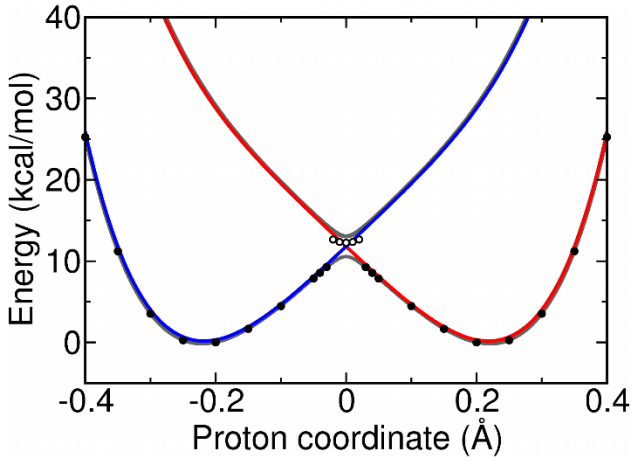

Figure S3: The diabatic (blue and red lines) and adiabatic (gray lines) potential energy profiles along the proton coordinate calculated with CDFT-CI/ωB97X/6-31G* for the phenoxyl/phenol system at the "open" TS geometry. The ground state adiabatic curve calculated with ground state DFT/ωB97X/6-31G* calculations (black dots) coincides with the CDFT-CI ground state curve for most of the grid points except for the small region in the vicinity of the avoided crossing, where the DFT calculation converges to the excited state density (open black dots). The converged densities for the DFT calculations were found to depend strongly on the initial densities used in the calculations, particularly in the crossing region.

Table S1: Nonadiabaticity Parameters for Phenoxyl/Phenol System at the "Open" Transition State Geometry[a]

DFT functional[b]	V^{el}, cm^{-1}	τ_p, fs	τ_e, fs	$p = \tau_p/\tau_e$	V_{00}, cm^{-1}
B3P86	4014	1.19	1.32	9.0×10^{-1}	311.1
B3LYP	4068	1.16	1.31	8.9×10^{-1}	284.5
M06-L	6067	1.72	0.88	2.0	336.4
CAM-B3LYP	1137	0.31	4.67	6.5×10^{-2}	79.1
ωB97X	436	0.11	12.17	8.9×10^{-3}	24.5
ωB97X-D	966	0.25	5.50	4.6×10^{-2}	60.2
SA2-CASSCF(3,6)[c]	700	0.098	7.60	1.3×10^{-2}	7.2

[a] V^{el} is the electronic coupling at the crossing point calculated with CDFT-CI; τ_p and τ_e are the effective proton tunneling and electronic transition times; p is the adiabaticity parameter defined in Eq. (3); V_{00} is the vibronic coupling between the ground reactant and product vibronic states defined in Eq.(2).
[b] Functional used in CDFT-CI calculations with 6-31G* basis set.
[c] Results of the state averaged CASSCF calculations with 3 electrons in 6 orbitals and 6-31G* basis set (obtained from Ref. 3).

SLO Model

Table S2: Nonadiabaticity Parameters for the SLO Model System[a]

CDFT functional[b]//geometry	V^{el}, cm^{-1}	τ_p, fs	τ_e, fs	$p = \tau_p/\tau_e$	V_{00}, cm^{-1}
ωB97X//ωB97X/TS, R=2.58 Å[c]	1559	0.26	3.41	7.5×10^{-2}	16.3
ωB97X//ωB97X/R=2.7 Å[d]	1429	0.20	3.72	5.4×10^{-2}	1.8
ωB97X//ωB97X/R=2.8 Å[d]	1371	0.18	3.87	4.6×10^{-2}	0.3
ωB97X-D//ωB97X/TS, R=2.58 Å[c]	1898	0.36	2.80	1.3×10^{-1}	33.6
ωB97X-D//ωB97X/R=2.7 Å[d]	1735	0.28	3.06	9.1×10^{-2}	4.2
ωB97X-D//ωB97X/R=2.8 Å[d]	1652	0.24	3.21	7.5×10^{-2}	0.6
ωB97X//B3LYP/TS, R=2.61 Å[c]	1637	0.25	3.24	7.8×10^{-2}	13.5
ωB97X//B3LYP/R=2.7 Å[d]	1607	0.22	3.30	6.6×10^{-2}	1.8
ωB97X//B3LYP/R=2.8 Å[d]	1575	0.20	3.37	5.9×10^{-2}	0.2

[a] V^{el} is the electronic coupling at the crossing point calculated with CDFT-CI/ωB97X/6-31G**; τ_p and τ_e are the effective proton tunneling and electronic transition times; p is the adiabaticity parameter defined in Eq. (3); V_{00} is the vibronic coupling between the ground reactant and product vibronic states defined in Eq. (2).

[b] Functional used in CDFT-CI calculations with 6-31G** basis set.

[c] Transition state (TS) geometries were optimized at the DFT/631G** level with the functional indicated.

[d] Geometries obtained from the TS geometry by rigid translation of the substrate and Fe cofactor along the C-O axis to the C-O distance R.

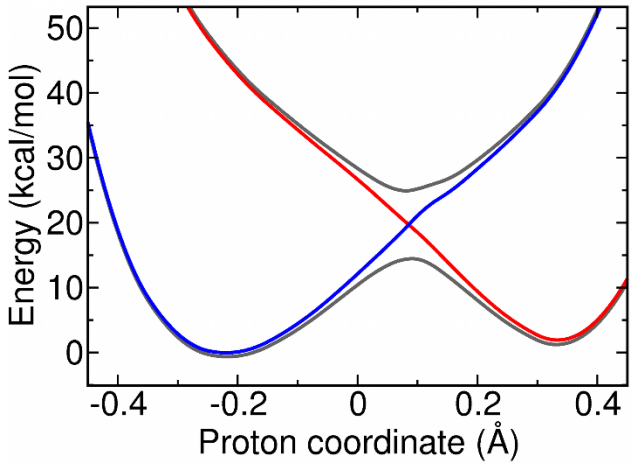

Figure S4: Diabatic potentials (solid blue and red lines) calculated with CDFT-CI/ωB97X/6-31G** and adiabatic potentials (solid gray lines) obtained by diagonalization of the [2×2] Hamiltonian matrix in the CDFT diabatic basis using a constant electronic coupling evaluated at the crossing point for the TS geometry used in the main paper. A constant electronic coupling was used because of difficulties with convergence and unstable couplings encountered for certain points with proton coordinates greater than ~0.2 Å. These numerical issues in the product region are not expected to impact the nonadiabaticity analysis in the main paper and in Table S2.

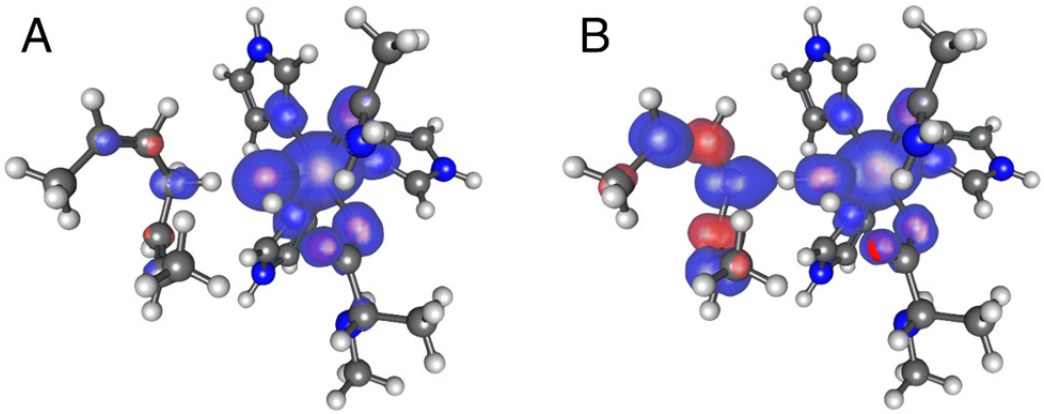

Figure S5: Spin densities for the (A) reactant diabatic state and (B) product diabatic state. The spin densities are calculated at the minimum of each diabatic curve in Figure 2 of the main paper. This figure shows that unpaired spin density is delocalized along the π backbone for the product state and is present near the iron center for both diabatic states.

Transition State Geometries

*ω*B97X/6-31G**/TS

SCF energy: -2863.297872 Hartrees

Fe	0.5646883303	0.8552614628	-0.5590317987
N	-0.9154545385	2.3534597220	-1.1565100714
C	-2.0563854298	2.1876729534	-1.9136455172
H	-2.2374929567	1.2764254549	-2.4659079985
C	-2.8296007693	3.3062657103	-1.8223587590
H	-3.7809914385	3.5672217773	-2.2590206478
N	-2.1404688056	4.1618317712	-0.9932685678
H	-2.4359149622	5.0834278091	-0.7116653614
C	-0.9999732860	3.5521326115	-0.6155646617
H	-0.2584764312	3.9817769766	0.0425336587
N	1.9216028164	1.4633787998	-2.1546844970
C	1.7210005721	2.3748594608	-3.1679976707
H	0.7905194271	2.9169834497	-3.2596174675
C	2.8367182917	2.4459873797	-3.9471014322
H	3.0730783454	3.0334425531	-4.8207435633
N	3.7280279277	1.5583009312	-3.3903781770
H	4.6600674831	1.3657046805	-3.7212742259
C	3.1393468831	0.9904994303	-2.3173429886
H	3.5984136077	0.2444536150	-1.6842541774
N	-0.3567074619	-0.6176807420	-1.8668395475
C	-0.7954984541	-1.7831363766	-1.4330868552
H	-0.9210922137	-2.0691852160	-0.3972917351
N	-1.0633760175	-2.6019872452	-2.4661691308
H	-1.3788868563	-3.5554766196	-2.3865534047
C	-0.7685642176	-1.9329531541	-3.6327127187
H	-0.8946053372	-2.3803858763	-4.6061317108
C	-0.3283857666	-0.7043189849	-3.2436981232
H	0.0111105573	0.1202552411	-3.8550316797
O	1.4816735058	2.4402167802	0.5729530179
C	1.9842337990	2.4884517027	1.7163798739
N	2.1014552263	1.4343685555	2.5161520950
H	1.7673397718	0.5012035671	2.2487542399
H	2.5159693876	1.5394242668	3.4270768904
C	2.5052764938	3.8113136572	2.2165139280
H	1.6960921403	4.5450811528	2.1901389761
H	2.9100248296	3.7653059369	3.2289003707
H	3.2839526998	4.1561902817	1.5321199483
O	1.9892437519	-0.5843462683	-0.1243920286
C	1.9057980731	-1.4673782300	0.7989571507
O	1.3801813516	-1.2756794912	1.9172985131
C	2.5115653860	-2.8272535583	0.4682109470
H	2.1813037626	-3.5260323247	1.2446153993
C	4.0419542428	-2.7260824128	0.4955535719
H	4.3872745685	-2.0285702722	-0.2759769736
H	4.3902220786	-2.3620798028	1.4671359729
H	4.5079886560	-3.6990604555	0.3190733744
N	1.9342284184	-3.2573652624	-0.8033505747
H	2.1670154539	-2.5577651452	-1.5028422256
C	2.3534496099	-4.5787721614	-1.2423723098
H	3.4357121925	-4.6884383510	-1.4123951348
H	2.0593699579	-5.3221966056	-0.4934305376
H	1.8413148366	-4.8281492639	-2.1767137691
O	-0.5292570377	0.4036852666	0.9819910769
H	-0.1381974320	-0.3020885752	1.5356316306
H	-1.7630082513	0.0967145537	0.8616343146
C	-3.0135413773	-0.2140203045	0.7268716311
H	-3.0996902022	-0.1104490059	-0.3618378878
C	-3.6537242747	0.9315861457	1.3956324842
H	-3.4692585738	1.8668501826	0.8618903879
C	-4.3774755918	1.0377407812	2.5252837070

H	-4.6905562147	2.0483556408	2.7892787848
C	-4.8504855537	-0.0218365350	3.4725683383
H	-5.8894743812	0.1716128684	3.7580624594
H	-4.2640815865	-0.0002090385	4.4000892734
H	-4.7878653784	-1.0256728955	3.0541614474
C	-3.1271659725	-1.6402380833	1.1400894713
H	-3.6597064850	-2.2905246106	0.4441740345
C	-2.5737629266	-2.2134071098	2.2171841063
H	-2.7071644806	-3.2883707722	2.3395249082
C	-1.7875003433	-1.5285827108	3.2938839533
H	-1.8046307278	-0.4398324878	3.1942484121
H	-2.1948144661	-1.7861687515	4.2778758691
H	-0.7433268877	-1.8662790526	3.2811909789

B3LYP/6-31G**/TS

SCF energy: -2863.704930 Hartrees

Fe	0.521401	0.890633	-0.704447
N	-0.887663	2.439781	-1.400214
C	-2.003511	2.290108	-2.204902
H	-2.225165	1.353321	-2.690161
C	-2.697587	3.467674	-2.251470
H	-3.604880	3.752874	-2.759244
N	-1.986694	4.345299	-1.457805
H	-2.229010	5.307046	-1.269411
C	-0.909830	3.690660	-0.964068
H	-0.172920	4.125367	-0.308015
N	1.999849	1.466814	-2.244340
C	1.902048	2.405446	-3.254865
H	1.002014	2.980633	-3.404177
C	3.076909	2.454143	-3.954504
H	3.393891	3.046112	-4.798035
N	3.900202	1.524536	-3.351904
H	4.847977	1.305471	-3.621507
C	3.217128	0.954419	-2.330736
H	3.604688	0.183418	-1.683924
N	-0.381180	-0.562765	-2.063182
C	-0.966219	-1.668178	-1.624626
H	-1.205383	-1.890517	-0.596127
N	-1.237133	-2.497961	-2.655793
H	-1.656681	-3.412332	-2.574511
C	-0.793399	-1.902774	-3.820188
H	-0.896191	-2.372560	-4.785124
C	-0.262525	-0.702982	-3.435042
H	0.195939	0.061303	-4.042774
O	1.423005	2.489702	0.440547
C	1.919265	2.607997	1.587717
N	2.071111	1.591632	2.433704
H	1.762293	0.633498	2.204776
H	2.473528	1.753695	3.343779
C	2.370173	3.977671	2.046113
H	1.492864	4.622038	2.159386
H	2.911501	3.958274	2.994096
H	3.007462	4.418518	1.276209
O	1.908801	-0.582065	-0.223182
C	1.867047	-1.383563	0.779521
O	1.385411	-1.094467	1.903186
C	2.477790	-2.771865	0.567468
H	2.090687	-3.409402	1.369341
C	4.012986	-2.685476	0.706912
H	4.437223	-2.045595	-0.074847
H	4.290322	-2.268009	1.680081
H	4.472778	-3.673987	0.627105
N	1.976674	-3.299089	-0.705380
H	2.274415	-2.672795	-1.448875

C	2.360757	-4.676298	-1.001847
H	3.444866	-4.861004	-1.071136
H	1.962254	-5.339966	-0.226523
H	1.912024	-4.975673	-1.953998
O	-0.607461	0.413532	0.809139
H	-0.159406	-0.188475	1.439880
H	-1.847956	0.186044	0.927581
C	-3.159944	-0.048380	1.056572
H	-3.457805	0.326294	0.068937
C	-3.544466	0.921323	2.096880
H	-3.245562	1.938154	1.837577
C	-4.201516	0.797634	3.273197
H	-4.327367	1.720672	3.839460
C	-4.844716	-0.403719	3.896104
H	-5.875359	-0.164201	4.184407
H	-4.327985	-0.691101	4.821752
H	-4.861148	-1.268711	3.234580
C	-3.294701	-1.520696	1.147621
H	-3.866078	-1.987824	0.343629
C	-2.705128	-2.353595	2.031880
H	-2.881649	-3.421721	1.907008
C	-1.816034	-1.972263	3.177909
H	-1.779104	-0.892151	3.332379
H	-2.166276	-2.435455	4.108135
H	-0.791002	-2.328653	3.014754

References

1. Mayer, J. M.; Hrovat, D. A.; Thomas, J. L.; Borden, W. T. Proton-coupled electron transfer versus hydrogen atom transfer in benzyl/toluene, methoxyl/methanol, and phenoxyl/phenol self-exchange reactions. *J. Am. Chem. Soc.* **2002,** *124*, 11142-11147.
2. DiLabio, G. A.; Johnson, E. R. Lone pair-π and π-π interactions play an important role in proton-coupled electron transfer reactions. *J. Am. Chem. Soc.* **2007,** *129*, 6199-6203.
3. Sirjoosingh, A.; Hammes-Schiffer, S. Proton-coupled electron transfer versus hydrogen atom transfer: Generation of charge-localized diabatic states. *J. Phys. Chem. A* **2011,** *115*, 2367-2377.