Proton-Electron Sequential Transfers Mechanism: Theoretical Evidence about Its Biological Relevance.

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Electronic Supplementary Information

Calculation methodology

Geometry optimizations and frequency calculations have been carried out using the M05-2X functional[1] and the 6-31+G(d,p) basis set, in conjunction with the SMD continuum model,[2] using water and methyl butanoate as solvents. The M05-2X functional has been recommended for thermodynamic and kinetic calculations by their developers,[3] and it has been also successfully used by independent authors to that purposes.[4–8] Local minima and transition states were identified by the number of imaginary frequencies (NIMAG = 0 or 1, respectively). In addition, intrinsic reaction coordinate (IRC) calculations have been performed to confirm that the transition state properly connects reactants and products, see figure S3. All of the electronic calculations were performed with the Gaussian 09 package of programs.[9] Thermodynamic corrections at 298.15 K were included in the calculation of relative energies.

The rate constants (k) were calculated using conventional transition state theory (TST)[10–12] and 1 M standard state as

$$k = \sigma\kappa \frac{k_B T}{h} e^{-(\Delta G^{\neq})/RT}$$

where k_B and h are the Boltzmann and Planck constants, $\Delta G^{\ddagger}$ is the Gibbs free energy of activation, σ represents the reaction path degeneracy, accounting for the number of equivalent reaction paths, and κ accounts for tunneling corrections which were calculated using the zero curvature tunneling approach (ZCT).[13] For the electron transfer reactions $\Delta G^{\ddagger}$ was calculated using the Marcus theory[14,15] as

$$\Delta G^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G}{\lambda}\right)^2$$

where ΔG is the free energy of reaction and λ is a reorganization term. Some of the calculated rate constants (k) are close to the diffusion-limit. Accordingly, the apparent rate constant (k_{app}) cannot be directly obtained from TST calculations. In the present work the Collins–Kimball theory is used to that purpose[16]

$$k_{app} = \frac{k_D k_{act}}{k_D + k_{act}}$$

where k_{act} is the thermal rate constant, obtained from TST calculations (equation 1), and k_D is the steady-state Smoluchowski[17] rate constant for an irreversible bimolecular diffusion-controlled reaction

$$k_D = 4\pi R D_{AB} N_A$$

where R denotes the reaction distance, N_A is the Avogadro number, and D_{AB} is the mutual diffusion coefficient of the reactants A (damaged species) and B (repairing species). D_{AB} has been calculated from D_A and D_B according to reference [18], and D_A and D_B have been estimated from the Stokes–Einstein approach[19,20]

$$D = \frac{k_B T}{6\pi\eta a}$$

The methodology used to calculate the highest- and singly-occupied molecular orbitals, HOMO and SOMO, respectively, was the same used by DiLabio and Johnson.[21] The orbitals were obtained for the optimized TS structures using restricted open-shell M05-2X with 6-31+G(d,p) basis set. Quantitative measures of the selected lone pair-π and π - π interactions in these orbitals were calculated using the overlap expressions from Mulliken.[22] A normalized molecular orbital (MO), ϕ, can be expressed as a linear combination of atomic orbitals, $\phi_i = \sum_{s=1}^{b} c_{si}\chi_s$, where the MO is denoted by the index *i* and the basis functions χ by the index *s*, *b* is some finite number of basis functions, and *c* is the basis function coefficient. To determine the overlap between functional groups A (damaged specie) and B (repairer specie) that form a subset of the molecular system, values of $S_{AB} = \sum_{s\in A}\sum_{r\in B} c_{si}c_{ri}\langle \chi_s | \chi_r \rangle$ were calculated.[23]

The data for the analysis of the atomic charges of the H-donor, H-acceptor, and transferring H atoms, as a function of the reaction coordinate, were obtained using the points on the ground state reaction path (generated from intrinsic reaction coordinate calculations, IRC) and the Hirshfeld partition scheme.

Calculating rate constants at pH 7.4

In aqueous solution it is possible to find more than one acid-base form of free radical scavengers to a significant extent at physiological pH. This, of course, would depend on their pK_a values, see figure S5. At pH 7.4, 0.06% of the ascorbic acid is present as H_2Asc, 99.93 as $HAsc^-$ and 0.01% as Asc^{2-}; 2.45% of uric acid is present as H_3Ur, 97.52% as H_2Ur^- and 0.03% as HUr^{2-}. The fraction of damaged species are 99.80% for Trp· and 0.20% for $Trp^{\bullet+}$. Therefore, the rate constants can be calculated as:

$$k_{PT}(H_3Ur) = mF(H_3Ur) * mF(TrpN^{\bullet}) * k_{PT}$$

$$k_{PT}(H_2Asc) = mF(H_2Asc) * mF(TrpN^{\bullet}) * k_{PT}$$

$$k_{SP_{SA}ET}(H_2Ur^-) = mF(H_2Ur^-) * mF(Trp^{\bullet+}) * k_{SET}$$

$$k_{SP_{SA}ET}(HAsc^-) = mF(HAsc^-) * mF(Trp^{\bullet+}) * k_{SET}$$

Where k_{PT} and k_{SET} correspond to rate constants presented in table 1 and molar fractions correspond to those in figure S4.[24]

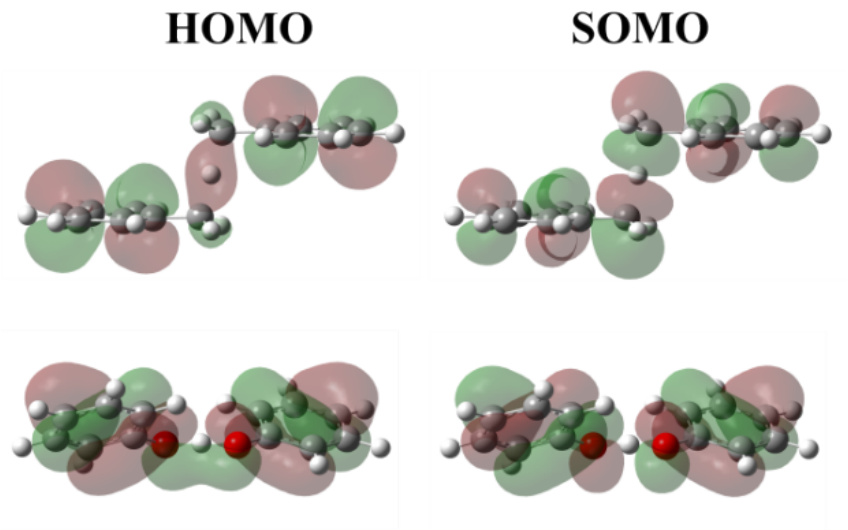

Figure S1. Transition states and their HOMO and SOMO orbitals for the hydrogen atom transfer reaction (HAT) between benzyl radical and toluene, $PhCH_2$-$PhCH_3$ (top) and the proton couple electron transfer reaction (PCET) between phenoxyl radical and phenol, PhO-PhOH (bottom).

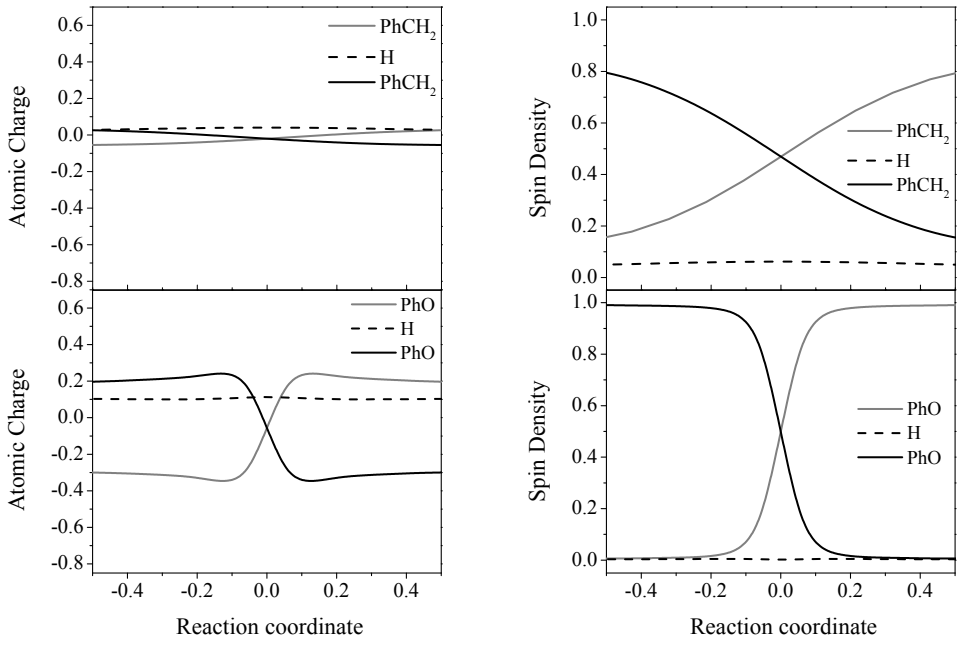

Figure S2. Hirshfeld atomic charges and spin density variation as a function of the reaction coordinate for the hydrogen atom transfer reaction (HAT) between benzyl radical and toluene, $PhCH_2$-$PhCH_3$ (top) and the proton coupled electron transfer reaction (PCET) between phenoxyl radical and phenol, PhO-PhOH (bottom).

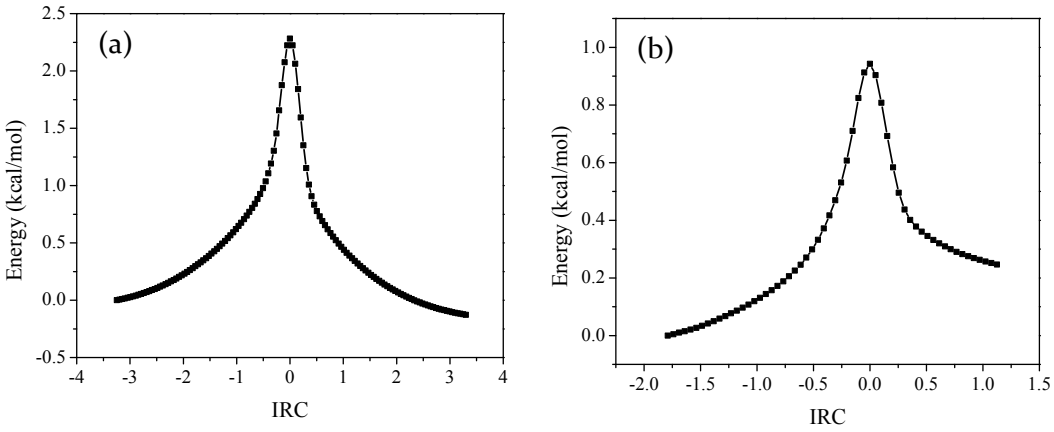

Figure S3. The intrinsic reaction coordinates (IRC) for PEST transitions states. (a) TrpN-H_3Ur and (b) TrpN-H_2Asc in water.

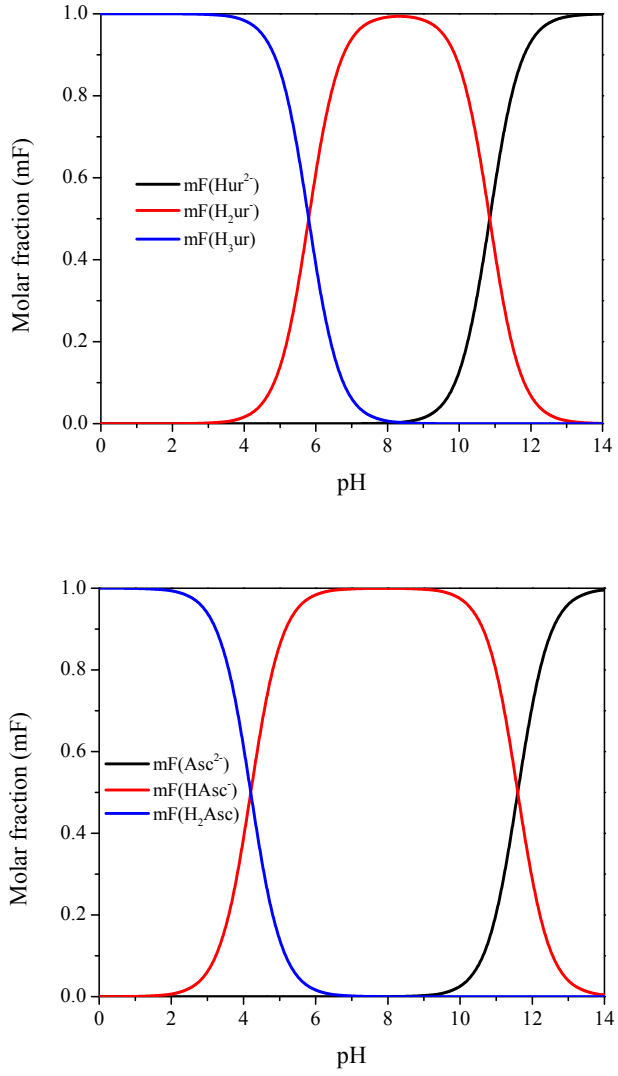

Figure S4. Distribution diagrams at pH=7.4. (a) Ascorbic acid and (b) uric acid.

Table S1. Single electron transfer (SET) thermodynamics data calculated from Marcus theory. Reaction free energies (ΔG_{rx}, kcal/mol), nonadiabatic energy difference between reactants and vertical products (ΔE, kcal/mol), nuclear reorganization energy (λ, kcal/mol), activation free energies ($\Delta G^{\ddagger}$, kcal/mol) and rate constants (k, $M^{-1} s^{-1}$).[24]

Marcus parameters	TrpN·				$Trp^{\cdot+}$	
	H_3Ur	H_2Asc	H_2Ur^-	$HAsc^-$	H_2Ur^-	$HAsc^-$
ΔG_{rx}	34.55	41.28	17.86	13.05	-6.18	-10.98
ΔE	45.63	53.35	29.05	24.70	7.23	2.88
λ	11.08	12.07	11.19	11.65	13.41	13.86
$\Delta G^{\ddagger}$	46.97	58.96	18.85	13.09	0.97	0.15
k [a]	< 1	< 1	< 1	$1.57x10^3$	$7.43x10^9$	$7.42x10^9$

[a] The k values have not been corrected for molar fractions of reagents at pH 7.4.

Transition states and complexes structures.

1. TrpN-H_3Ur reactant complexes transition state for proton transfer in water.

G = -1416.614105
H = -1416.528416
0 2

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.09156276
H	1.03229488	0.00000000	-0.35677838
C	-0.70392062	1.19524915	-0.52335644
C	-1.75297352	1.94707958	0.12506177
C	-0.55073962	1.80947642	-1.80358323
H	-2.13733646	1.75496099	1.11897715
N	-2.22029608	2.91829546	-0.62221413
C	-1.49980009	2.85963446	-1.83864498
C	0.27484757	1.55936401	-2.90284063
C	-1.64499748	3.66779025	-2.94747641
C	0.13241857	2.37581534	-4.02791314
H	1.00298540	0.75694857	-2.88480138
H	-2.37361748	4.46951134	-2.97044191
C	-0.80942701	3.40902644	-4.04869511
H	0.75709988	2.20703816	-4.89577566
H	-0.89884989	4.02649195	-4.93378577
C	-0.67642853	-1.31057324	-0.49144748
N	-2.01849137	-1.46552200	0.02548064
C	0.16031188	-2.48665235	-0.00307306
H	-0.71706342	-1.30825606	-1.58063350
C	-3.10964241	-1.05138435	-0.62497040
H	-2.12602485	-1.93272163	0.91642993
N	1.21771746	-2.79329874	-0.75335511
O	-0.12680751	-3.07468307	1.04922085
O	-3.09788362	-0.48128919	-1.72524356
H	-4.04433844	-1.26499606	-0.09625663
H	1.41003709	-2.29887248	-1.61122219
H	1.84860416	-3.52010846	-0.44896511
H	-3.83577092	3.65224179	-0.58876659
N	-4.85680044	3.88503528	-0.61169495
C	-5.79124556	2.96435352	-0.27284360
C	-5.26191533	5.12146732	-1.03362770
C	-7.13852666	3.18843329	-0.30929465
N	-5.58177010	1.69093990	0.15859140
O	-4.46226202	5.99865364	-1.36965030
N	-6.62314761	5.33429270	-1.06008912
C	-7.64645061	4.44647918	-0.71812132
N	-7.75347320	2.01304041	0.12089297
C	-6.80757142	1.07917502	0.40808283
H	-4.68895595	1.23666018	0.30053326
H	-6.91192100	6.25449837	-1.37283052
O	-8.83208965	4.79253085	-0.79104923
H	-8.74626529	1.84163814	0.18564170
O	-6.96859033	-0.07888400	0.80805593

2. TrpN-H_3Ur transition state for proton transfer in water.

G = -1416.614313
H = -1416.529393
If = -1385.3770
0 2

C	-3.50891800	0.04228700	-1.16689500
H	-3.43377600	-0.44336900	-2.14153600
H	-4.33290100	0.75794200	-1.18519700
C	-2.24888400	0.74785700	-0.83492000
C	-0.91231400	0.34735600	-1.19998300
C	-2.08279300	1.90121800	-0.01650000
H	-0.63641700	-0.49946700	-1.81394200
N	-0.01105600	1.14833300	-0.68306000
C	-0.68924200	2.13119300	0.06839000
C	-2.97841100	2.74608100	0.65027800
C	-0.15786000	3.17771900	0.78996100
C	-2.45078700	3.80676000	1.38668100
H	-4.04739500	2.57989300	0.59414100
H	0.91022600	3.34902500	0.84291400
C	-1.06924500	4.01792200	1.45348700
H	-3.11667700	4.47824400	1.91301500
H	-0.68911300	4.85184500	2.02990400
C	-3.83237400	-1.04270600	-0.09985000
N	-2.86874900	-2.12184800	-0.09721200
C	-5.19808800	-1.63141400	-0.43307800
H	-3.85212200	-0.58169700	0.88770100

C -1.78589000 -2.14996800 0.68509000
H -3.05962700 -2.91692700 -0.69374300
N -6.24748400 -0.96427800 0.04402100
O -5.29110300 -2.64693200 -1.13679400
O -1.45912700 -1.24588500 1.46720400
H -1.19266200 -3.06361600 0.57679900
H -6.12497400 -0.14275000 0.61621200
H -7.18014400 -1.25918200 -0.20595300
H 1.25105400 0.90953000 -0.65790800
N 2.48157700 0.58612700 -0.56035400
C 2.88957200 -0.60352100 -0.07583700
C 3.44835700 1.48279000 -0.88623000
C 4.19293200 -0.99911200 0.09307800
N 2.09149200 -1.63631900 0.33382700
O 3.18660000 2.61777400 -1.32317800
N 4.76728100 1.09525600 -0.72132400
C 5.24665600 -0.11769700 -0.23275200
N 4.16580000 -2.29218600 0.61907000
C 2.87689500 -2.69398100 0.77311600
H 1.08048200 -1.64949700 0.35789600
H 5.46417000 1.78553100 -0.97588000
O 6.46849600 -0.32227200 -0.12631500
H 4.96295400 -2.86423700 0.85576900
O 2.45854500 -3.77437900 1.21043500

3. TrpN-H_3ur product metastable complex for proton transfer in water.

G = -1416.615396
H = -1416.530382
0 2
C 0.00000000 0.00000000 0.00000000
H 0.00000000 0.00000000 1.09054839
H 1.02991597 0.00000000 -0.36117711
C -0.69589213 1.19413406 -0.53150771
C -1.79141930 1.89149799 0.08323916
C -0.51197929 1.80810919 -1.79912119
H -2.24727871 1.69541195 1.04328497
N -2.22849190 2.84128795 -0.71580758
C -1.48496671 2.82691334 -1.91112192
C 0.36881148 1.56205141 -2.86289660
C -1.62015976 3.61065813 -3.03375051
C 0.24515422 2.34644656 -4.00663137
H 1.11728110 0.78213657 -2.79302307
H -2.37209154 4.38553166 -3.10573615
C -0.72938464 3.34842563 -4.08915001
H 0.90868544 2.18137909 -4.84515858
H -0.80143834 3.94209444 -4.99130009
C -0.69003645 -1.30375868 -0.50035517
N -1.98002803 -1.52667866 0.11729467
C 0.20758403 -2.48251299 -0.13868302
H -0.81417550 -1.25026189 -1.58263309
C -3.11674858 -0.98838734 -0.32163855
H -2.00368713 -2.11896424 0.93843288
N 1.20601571 -2.72459032 -0.98589513
O 0.01016793 -3.13132174 0.89735554
O -3.19830744 -0.23213911 -1.30426503
H -3.99663738 -1.26675004 0.26642681
H 1.32790137 -2.16933875 -1.81949440
H 1.87985065 -3.44377282 -0.76707655
H -3.12462238 3.36565555 -0.56382608
N -4.83803779 3.76934386 -0.37215591
C -5.75557971 2.79141998 -0.34588404
C -5.29785100 4.99667198 -0.05133063
C -7.09410986 2.90829499 -0.03210556
N -5.52693778 1.46612319 -0.62883300
O -4.56328122 6.01311117 -0.02887995
N -6.64333386 5.15326380 0.26513155
C -7.62115745 4.16678118 0.30840867
N -7.65766386 1.63261703 -0.12457799
C -6.69834853 0.74269528 -0.49170544
H -4.64868647 1.02618877 -0.90288718
H -6.93903412 6.09308265 0.49896902
O -8.79886806 4.44635052 0.62193381
H -8.62146989 1.38217298 0.03740716
O -6.82279862 -0.47979246 -0.67338497

4. TrpN-H_3ur product complex for electron transfer in water.

G = -1416.618314
H = -1416.531773
0 2
C -3.57872800 0.22164300 -1.26264200
H -3.57635900 -0.25286700 -2.24648600
H -4.40200400 0.94014300 -1.23469000
C -2.27903200 0.90916700 -1.00261800
C -1.07385100 0.68431300 -1.61695000
C -2.02871600 1.87478300 0.03576500
H -0.83594600 0.02285600 -2.43664500
N -0.09511600 1.46181000 -1.03982900
C -0.64896900 2.19016000 -0.01509200
C -2.83963400 2.48830400 1.00631300
C -0.05873200 3.10180700 0.86825800
C -2.25962600 3.39089600 1.88474300
H -3.89802300 2.25812300 1.06533500
H 0.99836700 3.33245800 0.81181800
C -0.88160700 3.69295900 1.81515600
H -2.86866300 3.87385400 2.63928900
H -0.45912400 4.40235800 2.51647300
C -3.85790000 -0.87033000 -0.19987900
N -2.90341600 -1.95525400 -0.28749800
C -5.25200400 -1.42775900 -0.43664500
H -3.79545900 -0.43521500 0.79702600
C -1.80433200 -2.05275200 0.46438800
H -3.05079200 -2.64655900 -1.01104400
N -6.24630900 -0.76268600 0.15361700
O -5.43095300 -2.40811800 -1.17542400
O -1.48488800 -1.26845000 1.37032500
H -1.18915700 -2.92462600 0.21923400
H -6.05713100 0.03545900 0.74076700
H -7.20330700 -1.02180400 -0.03682300
H 0.88885100 1.42998900 -1.27340100
N 2.93487600 0.56399900 -1.04143100
C 2.89501200 -0.49802800 -0.29100600
C 4.18889900 1.11748400 -1.22012400
C 4.00492700 -1.13482300 0.34136800
N 1.79812300 -1.23227400 0.05410800
O 4.35335600 2.12757100 -1.89869800
N 5.30533900 0.52771500 -0.62241100
C 5.33156800 -0.59307700 0.17398100
N 3.54711400 -2.19155100 1.02771000
C 2.15746100 -2.28669700 0.87523000
H 0.83797300 -1.03399800 -0.20229900
H 6.19246300 0.98894600 -0.79510400
O 6.35756700 -1.05355500 0.66577200
H 4.09398300 -2.84406200 1.58019400
O 1.43637000 -3.12940600 1.36740100

5. TrpN-H_3Ur transition state for proton transfer in methyl butanoate.

G = -1416.595316

H = -1416.513265

If = -118.1714 cm^{-1}

0 2

C	-3.49993500	0.09214200	-1.14647800
H	-3.48636000	-0.28608400	-2.17087400
H	-4.36761000	0.74286000	-1.02338900
C	-2.26317400	0.85213700	-0.84565800
C	-0.92858900	0.52328200	-1.28389600
C	-2.10650800	1.95487900	0.03877700
H	-0.64145400	-0.27251400	-1.95767600
N	-0.04230900	1.30797100	-0.72418800
C	-0.71699800	2.21663100	0.11224800
C	-3.00446200	2.73303600	0.78383400
C	-0.19075700	3.21526300	0.90115800
C	-2.48456900	3.74703900	1.58446500
H	-4.07191100	2.55435900	0.73632400
H	0.87446400	3.40307200	0.94668000
C	-1.10544700	3.98163400	1.64255700
H	-3.15258600	4.36520800	2.17011700
H	-0.73101000	4.77754000	2.27379400
C	-3.65400800	-1.12592000	-0.18595900
N	-2.68252300	-2.16533700	-0.44562000
C	-5.03863100	-1.73718400	-0.41735800
H	-3.55066700	-0.78858700	0.84663400
C	-1.47936700	-2.22214500	0.13820000
H	-2.99577100	-2.94022900	-1.01817400
N	-6.04989100	-1.12772500	0.21917800
O	-5.18117000	-2.68723800	-1.18060100
O	-1.02842200	-1.34222200	0.87756100
H	-0.90843900	-3.12369000	-0.11156000
H	-5.88807500	-0.41063300	0.90790300
H	-6.99047300	-1.46669900	0.08380100
H	1.11383500	1.09021700	-0.70374300
N	2.44041200	0.65953900	-0.54942300
C	2.77513400	-0.48861800	0.07226500
C	3.46068300	1.38702900	-1.08746500
C	4.04294500	-0.99998400	0.21160100
N	1.91027500	-1.37112900	0.67416800
O	3.28616300	2.45803500	-1.67669900
N	4.75065800	0.87456600	-0.95448700
C	5.15672600	-0.31061200	-0.33214700
N	3.92810600	-2.20871800	0.90505600
C	2.61660600	-2.45173000	1.20393500
H	0.90322600	-1.27049700	0.79914100
H	5.48443200	1.43380600	-1.36835200
O	6.34527300	-0.64116600	-0.30020600
H	4.68325000	-2.81805600	1.17500700
O	2.13617600	-3.40935000	1.80508100

6. TrpN-H_3ur metastable complex in methyl butanoate.

G = -1416.595543

H = -1416.511866

0 2

C	-3.49030000	0.07054300	-1.15665200
H	-3.46324700	-0.31654400	-2.17749500
H	-4.36315100	0.71727400	-1.04919400
C	-2.26176800	0.83997100	-0.84763900
C	-0.92122000	0.51773300	-1.26984600
C	-2.12332800	1.94894500	0.03060000
H	-0.61858200	-0.27927900	-1.93532200
N	-0.04849300	1.31571100	-0.70651500
C	-0.73772800	2.22504500	0.11712700
C	-3.03722800	2.72436900	0.75932800
C	-0.22937600	3.23660900	0.90156500
C	-2.53620400	3.75140100	1.55498800
H	-4.10222300	2.53445500	0.70170200
H	0.83327700	3.43609000	0.95626200
C	-1.16005400	4.00074100	1.62491000
H	-3.21656800	4.36855500	2.12738700
H	-0.80071600	4.80698800	2.25179000
C	-3.64584100	-1.14075200	-0.18729100
N	-2.67349700	-2.18151000	-0.43910200
C	-5.02981500	-1.75318100	-0.41660200
H	-3.54325200	-0.79635900	0.84325400
C	-1.47129000	-2.23429600	0.14720100
H	-2.98550500	-2.96055000	-1.00645000
N	-6.04027100	-1.14687700	0.22426400
O	-5.17262300	-2.70097600	-1.18244000
O	-1.02133000	-1.34932900	0.88109100
H	-0.90038400	-3.13801400	-0.09469800
H	-5.87714600	-0.43252000	0.91557100
H	-6.98057900	-1.48670800	0.09025600
H	1.08853700	1.11565700	-0.68711400
N	2.44953200	0.67309600	-0.53368900
C	2.78705900	-0.47874800	0.07728600
C	3.46916500	1.40327400	-1.06752100
C	4.05526000	-0.99309000	0.21011600
N	1.92316600	-1.36719400	0.67317900
O	3.29576100	2.48113400	-1.64585200
N	4.75984900	0.88862600	-0.94398700
C	5.16725900	-0.30169600	-0.33231000
N	3.94072800	-2.20775900	0.89361300
C	2.62981400	-2.45239700	1.19290700
H	0.91643700	-1.26801000	0.79998300
H	5.49279800	1.45080700	-1.35492200
O	6.35616200	-0.63382400	-0.30846700
H	4.69586300	-2.81966900	1.15718400
O	2.14964500	-3.41421000	1.78797500

7. TrpN-H_3ur product complex for electron transfer in methyl butanoate.

G = -1416.608253

H = -1416.519375

0 2

C	-4.17436100	-0.31195400	-1.16970300
H	-4.24284500	-1.24589200	-1.73380400
H	-4.61858600	0.47521800	-1.78565600
C	-2.74680000	0.01156000	-0.86715900
C	-1.69647300	-0.86724700	-0.77843500
C	-2.20776600	1.30904200	-0.55190900
H	-1.68302500	-1.93458700	-0.94255600
N	-0.54559600	-0.20391000	-0.43334700
C	-0.82596900	1.13038700	-0.28669100
C	-2.75800200	2.59992300	-0.47480900
C	0.01018800	2.20089600	0.05348300
C	-1.93330100	3.66202300	-0.13916200
H	-3.81117700	2.76523300	-0.67539400
H	1.06195900	2.04079100	0.25667200
C	-0.56103000	3.46190000	0.12350400
H	-2.34388600	4.66264500	-0.07507300
H	0.05653800	4.31268700	0.38632400
C	-5.02830800	-0.47057700	0.11364500
N	-4.59636800	-1.60780300	0.89084800
C	-6.48126800	-0.68143800	-0.30087200
H	-4.92643700	0.41576900	0.73977800
C	-3.98623800	-1.50895400	2.08674300
H	-4.83711800	-2.52567400	0.54481300
N	-7.19818400	0.44449200	-0.46979900
O	-6.92193000	-1.80683000	-0.52202100
O	-3.71793400	-0.46017000	2.66288200

H	-3.74552300	-2.48908100	2.51971400
H	-6.82616700	1.34677300	-0.22185100
H	-8.15061800	0.38367900	-0.79498200
H	0.35948200	-0.64886900	-0.32800000
N	3.08447200	-0.19907000	-0.03014700
C	4.31704300	0.19442100	0.07197700
C	2.90433200	-1.55482400	-0.24662000
C	5.48220800	-0.63085800	-0.01161000
N	4.77915400	1.46329700	0.28036600
O	1.78694900	-2.04094900	-0.36024500
N	4.01479600	-2.39966500	-0.34086900
C	5.34762500	-2.05203600	-0.24127300
N	6.56250500	0.15107900	0.14140700
C	6.16692300	1.48730800	0.33095900
H	4.20717100	2.29054200	0.39056900
H	3.80684000	-3.37816500	-0.50362700
O	6.26982000	-2.84602500	-0.33687500
H	7.53177600	-0.14454800	0.12708400
O	6.89351400	2.43611100	0.50055300

8. TrpN-H_2Asc reactant complexes transition state for proton transfer in water.

G = -1463.664759

H = -1463.572956

0 2

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.09199531
H	1.03092038	0.00000000	-0.35954507
C	-0.70989973	1.19450533	-0.51518682
C	-1.77871742	1.91192074	0.13825334
C	-0.54133520	1.84951389	-1.77135977
H	-2.16462730	1.70349338	1.12799360
N	-2.25186945	2.89039440	-0.59623669
C	-1.50672145	2.88545469	-1.79930188
C	0.31710223	1.64944359	-2.85678362
C	-1.63435143	3.73013732	-2.88225323
C	0.19282990	2.50233851	-3.95569622
H	1.05811974	0.85902426	-2.84417802
H	-2.37338221	4.52184312	-2.89904418
C	-0.76394226	3.52205945	-3.96663281
H	0.84476947	2.37540319	-4.81031551
H	-0.83747310	4.16964448	-4.83126995
C	-0.67955172	-1.31073857	-0.48739299
N	-2.04325674	-1.42948142	-0.01859531
C	0.11933015	-2.47961235	0.07405089
H	-0.67758116	-1.33719907	-1.57704628
C	-3.09867899	-0.99874590	-0.71588698
H	-2.19243594	-1.84343214	0.89242138
N	1.16408098	-2.87246344	-0.65286092
O	-0.18347679	-2.98046025	1.16639975
O	-3.03283095	-0.46789950	-1.83343209
H	-4.05534072	-1.16207781	-0.21059944
H	1.36475139	-2.45172176	-1.54748808
H	1.77202918	-3.59544489	-0.29648951
H	-3.13747793	4.04702952	-0.02812446
O	-3.69334880	4.80833257	0.41185940
C	-3.00980370	5.43816375	1.35526502
C	-3.46173719	6.35009348	2.23709204
C	-1.53354062	5.24487735	1.57508737
C	-2.36046850	6.75461003	3.08074978
O	-4.73141303	6.83429718	2.37206892
O	-1.23165544	6.08542696	2.70964831
C	-0.67843439	5.69227575	0.38497974
H	-1.29850074	4.21487405	1.84832899
O	-2.36214037	7.54863483	4.00791782
H	-4.77288830	7.39052244	3.16388101
O	-0.77568753	7.09488797	0.18682860
C	0.76445511	5.25035058	0.55788040
H	-1.08071132	5.23706939	-0.51989843
H	-0.43204747	7.54405179	0.97210790
O	1.53954751	5.58992139	-0.58802203
H	0.79865996	4.16442119	0.65393260
H	1.19258411	5.70274412	1.45827325
H	1.52930352	6.55109678	-0.68084758

9. TrpN-H_2Asc transition state for proton transfer in water.

G = -1463.668489

H = -1463.575557

If = -1048.3454

0 2

C	-3.18849800	-0.24973500	-1.20358300
H	-2.89210900	-1.00573200	-1.93312500
H	-3.59262400	0.61839200	-1.72814200
C	-2.02493800	0.16401900	-0.38555000
C	-0.87696100	-0.64164000	-0.04954500
C	-1.82060600	1.40451700	0.28429200
H	-0.67443100	-1.64855300	-0.38900600
N	-0.05214200	0.00143500	0.74239200
C	-0.59381300	1.28344100	0.97803000
C	-2.56085200	2.58976000	0.36245100
C	-0.07568900	2.30695200	1.74141100
C	-2.04603700	3.63222500	1.13413800
H	-3.50209900	2.69431200	-0.16326700
H	0.86531600	2.20513500	2.26737100
C	-0.82838400	3.49289800	1.80849300
H	-2.59366300	4.56228700	1.21307700
H	-0.45256300	4.31933400	2.39827500
C	-4.31792700	-0.84335000	-0.31513300
N	-3.91298400	-2.06010800	0.35462900
C	-5.49102500	-1.17225400	-1.22928800
H	-4.61395300	-0.10890200	0.43370500
C	-3.36724600	-2.07830000	1.57460000
H	-4.05123800	-2.93476200	-0.13475000
N	-6.35246500	-0.18062100	-1.44857400
O	-5.58481500	-2.29114000	-1.75358000
O	-3.14267200	-1.06874400	2.25683000
H	-3.13097900	-3.08379900	1.93523200
H	-6.24775500	0.71288600	-0.99258800
H	-7.10852000	-0.31629800	-2.10387400
H	1.08436800	-0.42656700	1.14202600
O	2.12596200	-0.87023800	1.54101100
C	3.04576400	-1.05588400	0.63411100
C	4.19046000	-1.77665300	0.71884500
C	2.99449000	-0.42879200	-0.73962400
C	4.88905800	-1.69538100	-0.53123600
O	4.63941200	-2.49816500	1.79611300
O	4.18243300	-0.91414000	-1.40354300
C	3.02834100	1.09838100	-0.70512800
H	2.12370300	-0.77110600	-1.30308300
O	5.94903700	-2.21466400	-0.85961300
H	5.46846000	-2.93487700	1.55362800
O	4.18793700	1.57471300	-0.03311000
C	2.93180500	1.68577300	-2.10318500
H	2.17566500	1.44171400	-0.11615900
H	4.97095700	1.30117200	-0.53222400
O	2.84326600	3.10794300	-2.04776800
H	2.02328100	1.32982200	-2.58844600
H	3.79822200	1.38254100	-2.69827100
H	3.64098200	3.43767600	-1.61481600

10. TrpN-H_2Asc product metastable complex for proton transfer in water.

G = -1463.667716
H = -1463.573317
0 2

C	-3.33938000	-0.20649000	-1.23265700
H	-3.09756400	-0.94723000	-1.99657000
H	-3.73900800	0.69001500	-1.71060500
C	-2.13200600	0.15121700	-0.45270000
C	-0.99172600	-0.69285500	-0.21056500
C	-1.87722400	1.35261700	0.26454400
H	-0.81339700	-1.68543400	-0.59938700
N	-0.13119300	-0.08965700	0.57809300
C	-0.62788400	1.18783300	0.90556600
C	-2.59682800	2.54374900	0.42925000
C	-0.06352600	2.16148700	1.69781600
C	-2.03786300	3.53939800	1.22910000
H	-3.55559200	2.68487700	-0.05416000
H	0.89425600	2.02110500	2.18237000
C	-0.79745300	3.35169600	1.84858100
H	-2.56756800	4.47161100	1.37396900
H	-0.38761400	4.14349400	2.46233800
C	-4.44229800	-0.79452400	-0.30729700
N	-4.05371600	-2.05894000	0.27833200
C	-5.68430600	-1.02728700	-1.15790600
H	-4.65727000	-0.08603500	0.49220800
C	-3.42208400	-2.15951000	1.45250200
H	-4.25217800	-2.90057300	-0.24708600
N	-6.52387100	0.00211000	-1.25196300
O	-5.84988100	-2.10733500	-1.74192900
O	-3.10841400	-1.19386100	2.16223500
H	-3.20164800	-3.18991500	1.74593000
H	-6.35808400	0.85692700	-0.74299900
H	-7.33098800	-0.06785800	-1.85444700
H	0.85008300	-0.48964000	0.88014900
O	2.12080100	-1.05336500	1.33273800
C	3.11164400	-1.14256200	0.51843000
C	4.27723700	-1.84877700	0.62234800
C	3.16728500	-0.39122200	-0.79714500
C	5.07637300	-1.62490400	-0.53445900
O	4.65519000	-2.65721700	1.67349200
O	4.42643100	-0.77109600	-1.39297600
C	3.13147500	1.12183400	-0.61423800
H	2.36184700	-0.70861500	-1.46284100
O	6.18182600	-2.08015900	-0.82464600
H	5.47784000	-3.10854900	1.43761600
O	4.21884300	1.56807800	0.18891200
C	3.11542500	1.84975000	-1.94711300
H	2.22422700	1.37162400	-0.06163900
H	5.04451700	1.34572300	-0.26488900
O	2.96303800	3.25447600	-1.75285000
H	2.26193200	1.51741500	-2.53748200
H	4.03687600	1.64094900	-2.49923400
H	3.70697100	3.56065400	-1.21859900

11. TrpN-H_2Asc product complex for electron transfer in water.

G = -1463.675959
H = -1463.582153
0 2

C	-2.72703500	-0.90154800	-0.98721300
H	-2.42369500	-1.92705300	-1.21126000
H	-2.86038700	-0.37030100	-1.93306000
C	-1.69637900	-0.22311800	-0.14558700
C	-0.76503200	-0.81964700	0.66531200
C	-1.57442000	1.19512900	0.07527500
H	-0.54182000	-1.86816300	0.79487300
N	-0.08282700	0.13343900	1.38716800
C	-0.54572900	1.37821800	1.03147600
C	-2.23828400	2.31974100	-0.44340800
C	-0.15097700	2.64803400	1.46879000
C	-1.85278500	3.58033700	-0.01149700
H	-3.03466500	2.20265500	-1.17021100
H	0.64257100	2.76863900	2.19665100
C	-0.81685500	3.74105100	0.93400100
H	-2.35177400	4.45846700	-0.40300000
H	-0.53694500	4.73904600	1.24888400
C	-4.09916900	-0.95087800	-0.26623200
N	-4.02685200	-1.72095900	0.95677300
C	-5.10552100	-1.61169700	-1.19440200
H	-4.42074100	0.06113600	-0.02067100
C	-3.81253500	-1.19123400	2.16368600
H	-4.04368000	-2.72867800	0.87221800
N	-5.71310500	-0.80200800	-2.06220500
O	-5.29420600	-2.83770500	-1.16109500
O	-3.74226300	0.02197700	2.41003400
H	-3.72254600	-1.94098000	2.95614200
H	-5.53232500	0.19013500	-2.06020200
H	-6.32593200	-1.19195500	-2.76297200
H	0.74469100	-0.04456900	1.94000300
O	2.99918600	-0.57433400	2.08183400
C	3.44527500	-0.84995100	0.97060600
C	4.65629000	-1.53502800	0.63690100
C	2.78813200	-0.50135700	-0.35264300
C	4.76194400	-1.62209000	-0.81958000
O	5.52776900	-2.01223700	1.48841900
O	3.67637100	-1.03959900	-1.37115500
C	2.64392000	1.00444100	-0.54706700
H	1.82650000	-1.00710500	-0.44675700
O	5.65224100	-2.12964200	-1.46772500
H	6.27009300	-2.44737300	1.02914400
O	3.91941800	1.62840400	-0.59660600
C	1.81068900	1.32308800	-1.77724000
H	2.14597600	1.40325300	0.33810600
H	4.39002700	1.32060800	-1.38475600
O	1.58866200	2.72531300	-1.88807400
H	0.83231100	0.85110600	-1.68037900
H	2.30719100	0.94130200	-2.67512300
H	2.44804600	3.15816500	-1.97191200

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