Electronic Supplementary Information

Comparing the Performance of Various Density Functionals for Modelling Mechanisms and Kinetics of Bimolecular Free Radical Reactions in Aqueous Solution†

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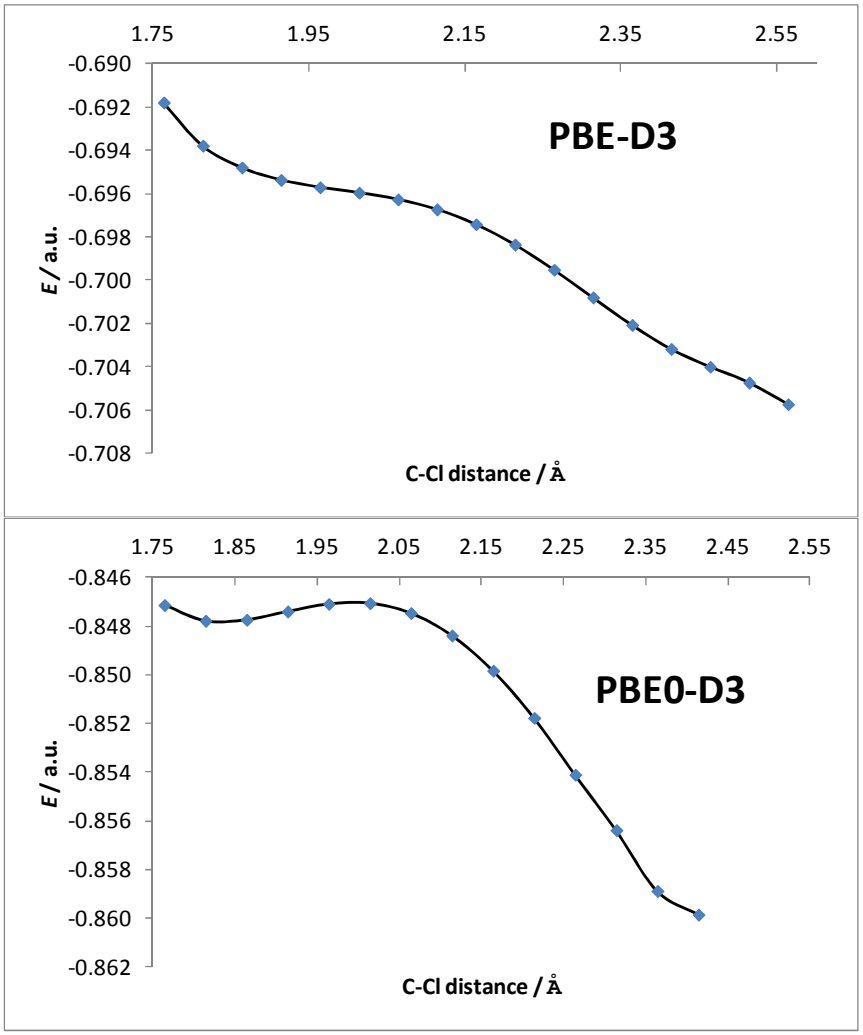

Figure S1: 1-D scans along the C-Cl reaction coordinate of the Cl abstraction in CCl_4 for the PBE-D3 and PBE0-D3 density functionals.

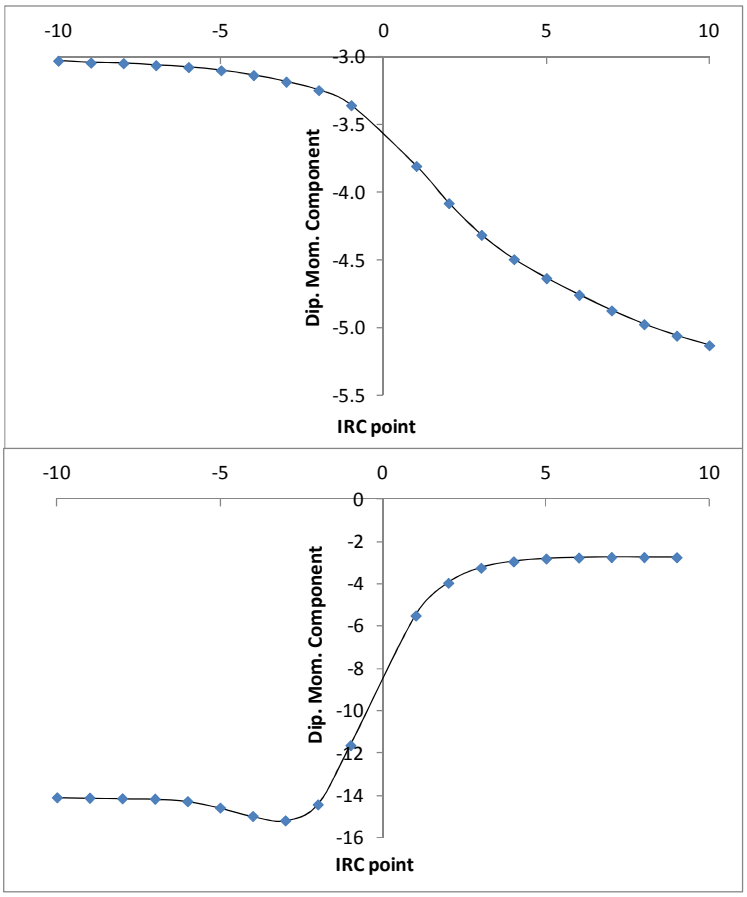

Figure S2: Projection of the dipole moment on the donor-acceptor axis for the two variants of the PCET TS in NO_2U^- calculated at the M06-D3/6-31G(d) level. The point on the IRC that corresponds to the TS is set to 0.

Table S1. Free energies of activation for BrU ortho-addition (o-Ad), ortho-addition with one explicit molecule of H_2O (o-AD-H_2O), PCET from the N3-deprotonated BrU (BrU^--PCET-N3) and the BrU iminol tautomer (o-Ad-taut).

DFs	$\Delta G^{\ddagger}$(o-Ad)	$\Delta G^{\ddagger}$(o-Ad-H_2O)	$\Delta G^{\ddagger}$(BrU^--PCET-N3)	$\Delta G^{\ddagger}$(o-Ad-taut)
B97-D3	7.451	5.818	4.792	7.847
PBE-D3	6.778	3.581	0.435	6.403
TPSS-D3	7.451	4.730	3.117	7.922
MN12-L	10.571	8.073	11.981	10.704
B3LYP-D3	10.203	7.529	7.116	10.796
PBE0-D3	8.485	5.994	7.941	9.117
PW6B95-D3	10.815	8.083	11.686	10.877
M05-2X-D3	9.035	6.301	14.189	9.348
M06-HF-D3	8.213	4.411	13.665	7.928
M06-D3	7.780	4.913	9.118	8.433
M06-2X-D3	9.763	6.835	13.310	9.890
M08-HX	9.748	6.826	13.793	9.724
MN12-SX	11.536	9.303	12.995	11.815
MN15	10.535	7.567	11.777	10.534
ωB97X-D	11.495	8.788	14.696	11.450
B2PLYP-D3	11.025	8.442	13.306	10.857
DSD-PBEP86	11.195	8.534	14.464	10.592
PBEQIDH	12.760	10.423	17.354	12.311

Table S2. Scaling of the harmonic frequencies by the factors of 0.97 and 0.95 at the M05-2X-D3/6-311+G(2d,p) level.

	Scaling factors; $\Delta G^{\ddagger}$			$\Delta G^{\ddagger}$ differences	
Substrate (mech.)	**1.00**	**0.97**	**0.95**	$\Delta_{0.97}$	$\Delta_{0.95}$
CCl_4 (ClA)	6.997	6.897	6.830	-0.100	-0.167
$CHCl_3$ (ClA)	12.295	12.205	12.142	-0.090	-0.152
Cl_3Ac^- (ClA)	11.337	11.238	11.170	-0.099	-0.167
IAc^- (PCET)	7.929	7.867	7.824	-0.062	-0.105
IAm (PCET/H2O)	8.407	8.316	8.254	-0.092	-0.154

Table S3. Effects on $\Delta E^{\ddagger}$ of extending the basis set from 6-311+G(2d,p) to aug-cc-pVTZ for the B2PLYP-D3 and DSD-PBEP86 double-hybrid DFs.

	CCl_4	$CHCl_3$	Cl_3Ac^-	ClH	BrU	NO_2U	Cys^+	IAc^-	IAm	MAE
B2PLYP-D3										
6-311+G(2d,p)										
$\Delta E^{\ddagger}$	-3.579	2.587	0.673	1.489	-0.866	-6.852	-0.484	-1.628	-4.538	
aug-cc-pVTZ										
$\Delta E^{\ddagger}$	-2.352	3.691	1.759	2.727	-1.179	-5.394	-0.961	-1.844	-5.050	
$\Delta\Delta E^{\ddagger}$	1.227	1.104	1.086	1.238	-0.313	1.459	-0.478	-0.216	-0.512	0.85
DSD-PBEP86										
6-311+G(2d,p)										
$\Delta E^{\ddagger}$	-1.629	4.514	2.652	3.514	-0.648	-5.983	-0.170	-0.171	-2.245	
aug-cc-pVTZ										
$\Delta E^{\ddagger}$	-0.405	5.555	3.708	4.715	-1.361	-6.052	-0.934	-0.697	-2.857	
$\Delta\Delta E^{\ddagger}$	1.224	1.041	1.057	1.201	-0.713	-0.069	-0.763	-0.526	-0.612	0.80

Table S4. Imaginary frequencies and Wigner transmission coefficients (WTC)

CCl4	**B97 D3**	**PBE D3**	**TPSS D3**	**MN12L**	**B3LYP D3**	**PBE0 D3**	**PW6B95 D3**	**M05-2X D3**	**M06-HF D3**	**M06 D3**	**M06-2X D3**	**M08-HX**	**MN12-SX**	**MN15**	**ωB97X-D**	**B2PLYP D3**	**DSD-PBEP86**	**PBEQIDH**
ClA				-253.6	-113.6	-252.5	-283.4	-338.7	-482.9	-290.6	-383.6	-398.4	-327.0	-404.1	-351.4	-190.4	-351.6	-344.1
WTC	1.0	1.0	1.0	1.1	1.0	1.1	1.1	1.1	1.2	1.1	1.1	1.2	1.1	1.2	1.1	1.0	1.1	1.1
CHCl3																		
ClA	-218.2	-230.1	-209.7	-341.3	-311.5	-364.9	-378.4	-440.2	-535.4	-401.5	-454.8	-460.1	-411.0	-479.2	-446.8	-395.6	-488.2	-474.5
HAT	-1310.4	-809.0	-1189.8	-810.0	-1323.2	-1192.7	-1451.8	-1399.7	-1013.1	-1814.4	-1455.6	-1570.2	-1484.2	-1473.7	-1371.2	-1410.4	-1455.9	-1430.4
WTC(ClA)	1.0	1.1	1.0	1.1	1.1	1.1	1.1	1.2	1.3	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
WTC(HAT)	2.7	1.6	2.4	1.6	2.7	2.4	3.0	2.9	2.0	4.2	3.1	3.4	3.1	3.1	2.8	2.9	3.1	3.0
Cl3Ac																		
PCET	-325.2	-334.3	-358.9	-450.7	-581.4	-760.6	-660.2	-1207.3		-732.5	-1453.7	-787.8	-512.3	-698.4	-2114.3	-1266.5	-1383.1	
ClA	-82.4	-91.2		-359.4	-310.3	-360.9	-372.4	-430.6	-555.5	-397.8	-484.2	-484.5	-419.9	-491.2	-461.3	-364.2	-489.1	-466.5
WTC(PCET)	1.1	1.1	1.1	1.2	1.3	1.6	1.4	2.4	1.0	1.5	3.0	1.6	1.3	1.5	5.3	2.6	2.9	1.0
WTC(ClA)	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.2	1.3	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.2	1.2
IAc																		
PCET		-123.0	-119.1	-134.2	-294.7	-335.7	-300.3	-381.7	-457.0	-928.7	-420.2	-341.2	-264.4	-318.2	-392.9	-383.9	-459.8	-450.1
IA		-91.0	-113.4	-252.5	-206.2	-209.0	-333.8	-278.5	-276.0	-283.7	-299.3	-319.5	-308.2	-351.3	-298.1	-275.1	-328.5	-299.0
WTC(PCET)	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.2	1.8	1.2	1.1	1.1	1.1	1.1	1.1	1.2	1.2
WTC(IA)	1.0	1.0	1.0	1.1	1.0	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
IAm																		
PCET/H2O					-256.2	-291.5	-385.4	-355.3	-685.3	-439.0	-384.8	-275.8	-270.9	-342.4	-484.3	-513.3	-666.8	-593.2
IA	-65.9		-87.7	-229.4	-178.3	-185.7	-187.0	-261.7	-243.5	-258.4	-268.6	-300.6	-253.4	-295.2	-271.9	-248.0	-302.1	-275.7
WTC(PCET/H2O)	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.5	1.2	1.1	1.1	1.1	1.1	1.2	1.3	1.4	1.3
WTC(IA)	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
BrU/BrU-																		
o-Ad (BrU)	-260.0	-223.1	-258.1	-437.2	-312.3	-246.7	-282.1	-276.9	-294.4	-303.6	-368.1	-313.0	-370.5	-390.1	-331.0	-302.1	-325.4	-300.4
PCET-N3 (BrU^-)	-1420.1	-792.0	-717.1	-1455.6	-844.5	-1631.1	-549.4	-902.8	-855.7	-1602.4	-928.1	-838.6	-1379.7	-1337.7	-118.6	-201.5	-166.5	-317.6
o-AD (BrU-taut)	-363.6	-221.4	-262.5	-429.0	-313.1	-241.8	-277.6	-276.9	-274.4	-300.7	-342.4	-288.5	-367.2	-382.4	-312.2	-268.7	-266.2	-260.6
WTC(o-Ad)	1.1	1.0	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
WTC(PCET-N3)	3.0	1.6	1.5	3.1	1.7	3.6	1.3	1.8	1.7	3.5	1.8	1.7	2.8	2.7	1.0	1.0	1.0	1.1
WTC (o-Ad taut)	1.1	1.0	1.1	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
ClH																		
ClA	-193.6	-205.3	-188.9	-318.7	-295.2	-347.3	-351.3	-418.0	-513.4	-373.4	-440.6	-438.1	-387.0	-455.3	-426.6	-367.0	-460.8	-448.4
HAT		-1115.4	-1486.6	-1142.5	-1691.7	-1617.3	-1711.0	-1770.2	-1011.9	-1979.9	-1639.5	-1708.8	-1787.9	-1722.7	-1725.5	-1778.0	-1825.7	-1792.5
WTC(ClA)	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.2	1.3	1.1	1.2	1.2	1.1	1.2	1.2	1.1	1.2	1.2
WTC(HAT)	1.0	2.2	3.1	2.3	3.8	3.5	3.8	4.0	2.0	4.8	3.6	3.8	4.1	3.9	3.9	4.1	4.2	4.1
NO_2U																		
PCET (NO2U-)				-485.5	-1201.1	-2189.4	-2331.5	-1478.5	-2214.2	-1997.0	-1563.9	-1844.2	-1478.3	-1565.8	-1581.0	-1439.5	-1510.3	-1417.5
PCET2 (NO2U-)				-1418.2		-1333.3	-1494.8			-1125.1			-1599.7					
o-Ad (NO2U)	-300.1	-231.1	-256.5	-366.9	-351.5	-283.7	-320.4	-173.3	-211.7	-374.6	-152.2	-38.9	-382.2	-375.0	-290.8	-235.0	-166.3	-88.6
WTC(PCET)	1.0	1.0	1.0	1.2	2.4	5.6	6.3	3.1	5.8	4.9	3.4	4.3	3.1	3.4	3.4	3.0	3.2	2.9
WTC(PCET2)	1.0	1.0	1.0	3.0	1.0	2.7	3.2	1.0	1.0	2.2	1.0	1.0	3.5	1.0	1.0	1.0	1.0	1.0
WTC(o-Ad)	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.0	1.1	1.0	1.0	1.1	1.1	1.1	1.1	1.0	1.0
Cys^+																		
HAT1 H b.	-355.7		-536.7	-638.9	-783.4	-591.0	-735.8	-845.9	-189.8	-859.4	-499.9	-793.9	-1132.2	-1073.8	-857.9	-873.2	-969.1	-887.8
HAT2			-168.1	-566.1	-541.9	-269.3	-455.4	-611.9	-74.6	-741.4	-352.5	-648.9	-1094.7	-1019.9	-644.7	-594.3	-655.9	-608.1
HAT3 st.	-206.1		-349.8	-630.6	-617.7	-408.4	-614.1	-749.9	-175.7	-811.8	-429.0	-801.1	-1146.5	-1087.9	-736.4	-688.3	-792.3	-726.8
WTC(HAT1 H b.)	1.1	1.0	1.3	1.4	1.6	1.3	1.5	1.7	1.0	1.7	1.2	1.6	2.2	2.1	1.7	1.7	1.9	1.8
WTC(HAT2)	1.0	1.0	1.0	1.3	1.3	1.1	1.2	1.4	1.0	1.5	1.1	1.4	2.2	2.0	1.4	1.3	1.4	1.4
WTC(HAT3 st.)	1.0	1.0	1.1	1.4	1.4	1.2	1.4	1.5	1.0	1.6	1.2	1.6	2.3	2.1	1.5	1.5	1.6	1.5