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Dihydroxybenzoic Acids as Free Radical Scavengers: Mechanisms, Kinetics, and Trends in Activity

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Table 1S. Gibbs free energies of reaction (kcal/mol), at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA**Error! Bookmark not defined.**	35-DHBA
Pentyl Ethanoate						
SET	79.50	87.16	75.84	79.63	84.40	84.41
HT-2a	3.85	13.98	6.59	9.73		
HT-3a	1.60				-1.86	4.89
HT-4a		7.68			-1.57	
HT-5a			-0.93			4.89
HT-6a				9.73		
p1	24.63	25.07	22.07	23.64	20.37	21.69
p2	11.78	20.26	9.73	15.01	14.35	10.73
p3	12.80	15.05	14.56	15.60	13.91	17.64
p4	13.04	18.94	13.80	19.54	12.97	10.95
p5	17.46	15.69	13.84	15.98	17.70	17.82
p6	10.55	16.18	9.25	13.15	16.46	11.72
Water						
SPLET	17.03	24.75	16.73	24.94	29.68	32.19
SdPLET	-2.20	8.27	-5.13	3.00	3.26	5.06
HT-2a	1.91	8.52	1.29	5.09		
HT-3a	-5.29				-5.16	0.79
HT-4a		1.96			-5.12	
HT-5a			-6.93			0.79
HT-6a				5.09		
p1	19.36	19.01	16.74	22.17	14.09	16.06
p2	10.39	16.16	10.10	13.80	12.09	10.89
p3	9.05	11.93	10.79	12.53	11.02	14.10
p4	12.38	15.03	10.90	16.26	9.44	10.03
p5	12.78	13.46	10.13	12.53	15.21	14.10
p6	9.17	13.89	8.52	13.80	10.39	10.89

Table 2S. Gibbs free energies of activation (kcal/mol), at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA**Error! Bookmark not defined.**	35-DHBA
Pentyl Ethanoate						
HT-2a	19.04			23.23		
HT-3a	17.25				14.99	18.72
HT-4a		20.34			16.22	
HT-5a			14.53			18.72
HT-6a				23.23		
Water						
SPLET	17.94	24.76	17.23	25.40	31.60	35
HT-2a				24.35		
HT-3a	14.49				14.63	17.78
HT-4a		18.97			14.45	
HT-5a			13.08			17.78
HT-6a				24.35		
SdPLET	3.17	8.97	4.31	5.60	5.89	6.66

Table 3S. Branching ratios (%), at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
Pentyl Ethanoate						
HT-2a	100.0			50.0		
HT-3a						50.0
HT-4a		100.0				
HT-5a			100.0			50.0
HT-6a				50.0		
Water						
SPLET						
HT-2a				9.3		
HT-3a	0.1				0.1	0.05
HT-4a		0.3			0.2	
HT-5a			2.1			0.05
HT-6a				9.3		
SdPLET	99.9	99.7	97.9	81.4	99.7	99.9

Table 4S. SPLET rate coefficients (k^{SPLET}, M^{-1} s^{-1}) for the electron transfer reactions, in aqueous solution, at 298.15 and *p*H=7.4.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	7.38E+09	7.07E+09	7.40E+09	7.36E+09	6.83E+09	5.67E+09
R2	2.44E+04	1.15E-01	8.22E+04	4.53E-03	1.46E-09	7.24E-15
R3	2.16E+05	2.48E+00	8.43E+05	2.31E-01	2.19E-07	2.91E-12
R4	1.77E+03	6.71E-03	5.53E+03	3.27E-04	2.29E-10	3.72E-15
R5	1.80E+05	1.25E+00	6.62E+05	5.67E-02	1.52E-08	4.49E-14
R6	6.01E+00	1.61E-05	1.64E+01	1.10E-06	2.44E-12	1.99E-16
R7	2.77E+01	8.93E-05	7.97E+01	6.39E-06	1.32E-11	9.21E-16
R8	4.69E+03	3.10E-02	1.61E+04	2.74E-03	4.42E-09	1.64E-13
R9	2.14E-02	1.17E-08	4.01E-02	2.00E-10	1.02E-16	2.52E-21
R10	2.86E-02	1.67E-07	8.53E-02	3.94E-08	7.53E-13	5.70E-16
R11	2.26E+04	5.45E+00	1.14E+05	1.22E+01	6.41E-03	5.70E-05
R12	5.51E+06	6.40E+03	2.91E+07	2.67E+04	5.51E+01	1.27E+00
R13	5.10E+08	2.67E+06	1.98E+09	1.58E+07	1.16E+05	6.15E+03
R14	7.38E-02	6.77E-07	2.39E-01	2.30E-07	7.27E-12	8.33E-15
R15	9.77E+02	6.38E-02	4.36E+03	6.76E-02	9.04E-06	2.77E-08
R16	6.52E-02	4.77E-07	2.03E-01	1.34E-07	3.16E-12	2.82E-15
R17	7.55E+09	7.56E+09	7.50E+09	7.57E+09	7.57E+09	7.57E+09
R18	2.69E+07	4.97E+04	1.39E+08	2.37E+05	7.28E+02	2.18E+01
R19	4.86E+06	2.66E+04	2.43E+07	1.67E+05	2.21E+03	2.07E+02
R20	7.22E+09	3.33E+08	7.58E+09	1.04E+09	2.19E+05	9.15E+01
R21	1.60E+02	2.31E-02	7.61E+02	4.51E-02	2.13E-05	1.98E-07

Table 5S. SdPLET rate coefficients (k^{SdPLET}, M^{-1} s^{-1}) for the electron transfer reactions, in aqueous solution, at 298.15 and *p*H=7.4.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	6.11E+08	7.19E+09	7.50E+07	5.22E+09	6.23E+09	5.80E+09
R2	7.58E+09	6.94E+09	7.55E+09	7.59E+09	7.58E+09	7.58E+09
R3	7.43E+09	7.32E+09	7.40E+09	7.44E+09	7.44E+09	7.44E+09
R4	7.42E+09	3.51E+09	7.41E+09	7.36E+09	7.32E+09	7.19E+09
R5	7.39E+09	7.29E+09	7.37E+09	7.40E+09	7.40E+09	7.40E+09
R6	7.29E+09	2.40E+07	7.38E+09	4.31E+09	3.42E+09	1.34E+09
R7	7.38E+09	1.09E+08	7.41E+09	6.08E+09	5.48E+09	3.39E+09
R8	7.42E+09	5.02E+09	7.41E+09	7.39E+09	7.36E+09	7.29E+09
R9	5.82E+09	6.17E+04	7.16E+09	1.48E+08	9.02E+07	1.14E+07
R10	3.31E+09	1.14E+05	6.44E+09	5.78E+07	3.54E+07	7.72E+06
R11	7.47E+09	5.03E+09	7.46E+09	7.34E+09	7.27E+09	7.14E+09
R12	7.42E+09	7.33E+09	7.41E+09	7.42E+09	7.42E+09	7.41E+09
R13	7.41E+09	7.41E+09	7.39E+09	7.42E+09	7.42E+09	7.42E+09
R14	3.94E+09	2.84E+05	6.58E+09	1.03E+08	6.32E+07	1.56E+07
R15	7.36E+09	1.36E+09	7.39E+09	6.81E+09	6.54E+09	5.86E+09
R16	4.10E+09	2.56E+05	6.65E+09	1.05E+08	6.48E+07	1.53E+07
R17	9.72E-06	4.71E+00	1.09E-07	1.21E-02	4.33E-01	3.30E-03
R18	7.49E+09	7.46E+09	7.47E+09	7.51E+09	7.50E+09	7.51E+09
R19	7.75E+09	7.39E+09	7.72E+09	7.73E+09	7.71E+09	7.70E+09
R20	2.79E+01	3.24E+07	1.94E-01	6.33E+04	4.20E+06	3.33E+03
R21	7.28E+09	2.04E+08	7.52E+09	4.41E+09	3.62E+09	2.33E+09

Table 6S. Gibbs free energies of reaction for the electron transfer reactions from H_2X^- (kcal/mol), i.e. SPLET mechanism, in aqueous solution, at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	-17.38	-9.66	-17.68	-9.47	-4.73	-2.22
R2	10.78	18.49	10.47	18.69	23.43	25.94
R3	9.12	16.84	8.82	17.03	21.77	24.28
R4	12.44	20.15	12.13	20.35	25.09	27.60
R5	9.43	17.14	9.12	17.34	22.07	24.59
R6	15.98	23.69	15.67	23.89	28.62	31.14
R7	15.00	22.72	14.70	22.91	27.65	30.16
R8	11.66	19.38	11.35	19.57	24.31	26.82
R9	19.66	27.37	19.35	27.57	32.30	34.82
R10	18.92	26.64	18.62	26.83	31.57	34.08
R11	7.78	15.50	7.48	15.69	20.43	22.94
R12	2.13	9.84	1.82	10.04	14.78	17.29
R13	-3.55	4.16	-3.86	4.35	9.09	11.61
R14	18.14	25.86	17.84	26.05	30.79	33.30
R15	11.14	18.85	10.83	19.05	23.78	26.30
R16	18.33	26.04	18.02	26.24	30.97	33.49
R17	-24.37	-16.65	-24.68	-16.46	-11.72	-9.21
R18	0.35	8.06	0.04	8.25	12.99	15.51
R19	-4.04	3.67	-4.35	3.87	8.60	11.12
R20	-3.02	4.70	-3.32	4.89	9.63	12.14
R21	11.16	18.87	10.85	19.07	23.81	26.32

Table 7S. Gibbs free energies of reaction for the electron transfer reactions from HX^{2-} (kcal/mol), i.e. SdPLET mechanism, in aqueous solution, at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	-36.61	-26.14	-39.54	-31.41	-31.15	-29.35
R2	-8.45	2.01	-11.39	-3.25	-3.00	-1.19
R3	-10.11	0.36	-13.04	-4.91	-4.65	-2.85
R4	-6.79	3.67	-9.72	-1.59	-1.33	0.47
R5	-9.80	0.66	-12.74	-4.60	-4.35	-2.54
R6	-3.25	7.21	-6.19	1.95	2.20	4.01
R7	-4.23	6.24	-7.16	0.97	1.23	3.03
R8	-7.57	2.90	-10.50	-2.37	-2.11	-0.31
R9	0.43	10.89	-2.51	5.63	5.88	7.69
R10	-0.31	10.16	-3.24	4.89	5.15	6.95
R11	-11.45	-0.98	-14.38	-6.25	-5.99	-4.19
R12	-17.10	-6.64	-20.03	-11.90	-11.64	-9.84
R13	-22.78	-12.32	-25.72	-17.59	-17.33	-15.52
R14	-1.09	9.38	-4.02	4.11	4.37	6.17
R15	-8.09	2.37	-11.03	-2.89	-2.64	-0.83
R16	-0.90	9.56	-3.84	4.30	4.55	6.36
R17	-43.60	-33.13	-46.53	-38.40	-38.14	-36.34
R18	-18.88	-8.42	-21.82	-13.69	-13.43	-11.63
R19	-23.27	-12.81	-26.21	-18.07	-17.82	-16.01
R20	-22.25	-11.78	-25.18	-17.05	-16.79	-14.99
R21	-8.07	2.39	-11.00	-2.87	-2.61	-0.81

Table 8S. Reorganization energies of reaction (λ) for the electron transfer reactions from H_2X^- (kcal/mol), i.e. SPLET mechanism, in aqueous solution, at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	27.40	24.35	24.09	19.51	18.43	17.33
R2	17.77	14.72	14.46	9.88	8.80	7.70
R3	17.78	14.73	14.47	9.89	8.81	7.71
R4	19.10	16.06	15.79	11.22	10.13	9.04
R5	17.06	14.02	13.75	9.17	8.09	6.99
R6	22.00	18.95	18.69	14.11	13.03	11.93
R7	21.42	18.37	18.10	13.53	12.45	11.35
R8	19.47	16.42	16.16	11.58	10.50	9.40
R9	22.13	19.09	18.82	14.25	13.16	12.06
R10	27.24	24.19	23.93	19.35	18.27	17.17
R11	28.34	25.30	25.03	20.46	19.37	18.27
R12	28.60	25.56	25.29	20.72	19.63	18.54
R13	28.79	25.75	25.48	20.91	19.82	18.73
R14	27.90	24.86	24.59	20.02	18.93	17.83
R15	26.55	23.50	23.23	18.66	17.58	16.48
R16	27.33	24.29	24.02	19.45	18.36	17.26
R17	21.09	18.05	17.78	13.21	12.12	11.02
R18	28.56	25.51	25.25	20.67	19.59	18.49
R19	41.01	37.96	37.69	33.12	32.03	30.94
R20	15.00	11.96	11.69	7.12	6.03	4.94
R21	31.51	28.47	28.20	23.63	22.54	21.45

Table 9S. Reorganization energies of reaction (λ) for the electron transfer reactions from HX^{2-} (kcal/mol), i.e. SdPLET mechanism, in aqueous solution, at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	17.27	15.19	17.74	16.33	16.89	15.29
R2	7.64	5.56	8.11	6.70	7.26	5.66
R3	7.65	5.57	8.12	6.71	7.27	5.67
R4	8.97	6.90	9.44	8.04	8.59	6.99
R5	6.93	4.86	7.40	6.00	6.55	4.95
R6	11.87	9.79	12.34	10.93	11.49	9.89
R7	11.29	9.21	11.75	10.35	10.91	9.30
R8	9.34	7.26	9.81	8.41	8.96	7.36
R9	12.00	9.93	12.47	11.07	11.62	10.02
R10	17.11	15.03	17.58	16.17	16.73	15.13
R11	18.21	16.14	18.68	17.28	17.83	16.23
R12	18.47	16.40	18.94	17.54	18.09	16.49
R13	18.66	16.59	19.13	17.73	18.28	16.68
R14	17.77	15.70	18.24	16.84	17.39	15.79
R15	16.42	14.34	16.88	15.48	16.03	14.43
R16	17.20	15.13	17.67	16.27	16.82	15.22
R17	10.96	8.89	11.43	10.03	10.58	8.98
R18	18.43	16.35	18.90	17.49	18.05	16.45
R19	30.88	28.80	31.34	29.94	30.49	28.89
R20	4.87	2.80	5.34	3.94	4.49	2.89
R21	21.38	19.31	21.85	20.45	21.00	19.40

Table 10S. Gibbs free energies of activation for the electron transfer reactions from H_2X^- (kcal/mol), i.e. SPLET mechanism, in aqueous solution, at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	0.92	2.22	0.43	1.29	2.54	3.29
R2	11.47	18.74	10.75	20.65	29.51	36.74
R3	10.18	16.91	9.37	18.32	26.54	33.19
R4	13.02	20.42	12.35	22.21	30.60	37.13
R5	10.28	17.32	9.51	19.15	28.12	35.66
R6	16.39	23.99	15.79	25.58	33.29	38.87
R7	15.48	22.98	14.86	24.54	32.29	37.96
R8	12.44	19.51	11.71	20.95	28.85	34.89
R9	19.73	28.27	19.36	30.68	39.27	45.55
R10	19.56	26.70	18.91	27.55	33.99	38.25
R11	11.51	16.45	10.55	15.97	20.44	23.24
R12	8.25	12.26	7.27	11.41	15.08	17.31
R13	5.53	8.69	4.59	7.63	10.54	12.28
R14	19.00	25.87	18.30	26.51	32.65	36.66
R15	13.37	19.08	12.49	19.05	24.33	27.76
R16	19.07	26.07	18.40	26.83	33.14	37.30
R17	0.13	0.03	0.67	0.20	0.00	0.07
R18	7.31	11.04	6.33	10.12	13.55	15.63
R19	8.33	11.42	7.37	10.33	12.89	14.29
R20	2.39	5.80	1.50	5.07	10.17	14.78
R21	14.45	19.68	13.52	19.29	23.82	26.60

Table 11S. Gibbs free energies of activation for the electron transfer reactions from HX^{2-} (kcal/mol), i.e. SdPLET mechanism, in aqueous solution, at 298.15 K.

	23-DHBA	24-DHBA	25-DHBA	26-DHBA	34-DHBA	35-DHBA
R1	5.41	1.97	6.70	3.48	3.01	3.23
R2	0.02	2.58	0.33	0.44	0.63	0.88
R3	0.20	1.58	0.75	0.12	0.24	0.35
R4	0.13	4.05	0.00	1.29	1.53	1.99
R5	0.30	1.57	0.96	0.08	0.19	0.29
R6	1.56	7.38	0.77	3.79	4.08	4.88
R7	1.10	6.48	0.45	3.10	3.38	4.09
R8	0.08	3.55	0.01	1.08	1.31	1.69
R9	3.22	10.92	1.99	6.30	6.59	7.82
R10	4.12	10.55	2.92	6.86	7.15	8.06
R11	0.63	3.56	0.25	1.76	1.97	2.23
R12	0.03	1.45	0.02	0.45	0.57	0.67
R13	0.23	0.27	0.57	0.00	0.01	0.02
R14	3.92	10.01	2.77	6.52	6.81	7.64
R15	1.06	4.87	0.51	2.56	2.80	3.20
R16	3.86	10.07	2.71	6.50	6.79	7.65
R17	24.29	16.53	26.95	20.07	17.95	20.84
R18	0.00	0.96	0.11	0.21	0.30	0.35
R19	0.47	2.22	0.21	1.18	1.32	1.44
R20	15.48	7.20	18.42	10.90	8.42	12.65
R21	2.07	6.10	1.35	3.78	4.02	4.45

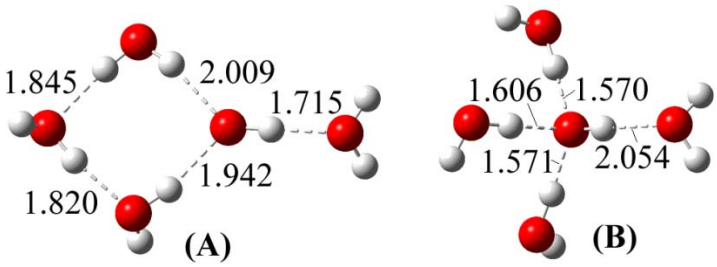

Figure 1S. Optimized geometries of the OH radical (A) and the OH anion (B) with 4 explicit water molecules.