Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The electronic temperature and the effective chemical potential parameters of an atom in a molecule. A Fermi-Dirac semi-local variational approach.

ELECTRONIC SUPPLEMENTARY INFORMATION

INDEX

Table S1. Atom-condensed Fukui functions (f^+, f^- and f^0) and dual descriptor (Δf) values for atoms belonging to several molecular species. Atomic charges were obtained from the Hirshfeld partition scheme using molecular densities calculated at the ω-B97XD/6-311++G(d,p) level of theory.

	f^-	f^+	f^0	Δf		f^-	f^+	f^0	Δf
HCl					**LiH**				
Cl	0.87	0.31	0.59	-0.56	Li	0.44	0.84	0.64	0.40
H	0.13	0.67	0.40	0.54	H	0.56	0.04	0.30	-0.52
H_2O					**H_2S**				
O	0.65	0.10	0.37	-0.55	S	0.78	0.63	0.71	-0.15
H	0.17	0.45	0.31	0.28	H	0.11	0.18	0.15	0.07
C_2H_6					**AlH_3**				
C	0.14	0.05	0.10	-0.09	Al	0.38	0.80	0.59	0.42
H	0.07	0.15	0.22	0.08	H	0.08	0.07	0.07	-0.01
H	0.14	0.15	0.15	0.01	H	0.27	0.07	0.17	-0.20
NH_3					**C_2H_4**				
N	0.54	0.12	0.33	-0.42	C	0.31	0.24	0.28	-0.07
H	0.15	0.29	0.22	0.14	H	0.09	0.13	0.11	0.04
CH_2					**CO**				
C	0.40	0.12	0.26	-0.28	C	0.70	0.79	0.75	0.09
H	0.10	0.36	0.23	0.26	O	0.30	0.21	0.26	-0.09

Table S2. Computed values for the chemical potential (μ_Ω) and electronic temperature (θ_Ω) for the most acidic proton in acids (protonates species) and the most susceptible atomic donor in the corresponding conjugated bases. The absolute value of the logarithm of the Orbital Accepting Descriptor $\left(\mathrm{Log}\left[\left|\mathrm{OAD}_{\mathrm{B,LUMO}}\right|\right]\right)$ was obtained for the LUMO of acids at the highest acidity condition $(\mu_\mathrm{H},\ \theta_\mathrm{H})$ while the logarithm of the Orbital Donating Descriptor $\left(\mathrm{Log}\left[\mathrm{ODD}_{\mathrm{B,HOMO}}\right]\right)$ was calculated for the HOMO of conjugated bases at the highest basicity condition $(\mu_\mathrm{B},\ \theta_\mathrm{B})$.

	Protonated species			Conjugated base			
	μ_H	$\mathrm{Log}\left[\left\|\mathrm{OAD}_{\mathrm{H,LUMO}}\right\|\right]$	θ_H	μ_B	$\mathrm{Log}\left[\mathrm{ODD}_{\mathrm{B,HOMO}}\right]$	θ_B	***p*K$_a$**
INORGANIC							
Perchloric acid	-1032.11	3.012	0.006	-259.94	1.352	0.012	-8.00
Hydrochloric acid	-1693.50	3.219	0.003	-216.42	1.269	0.015	-6.30
Sulfuric acid	-873.58	2.940	0.007	-264.89	1.455	0.011	-3.00
Chloric acid	-1126.87	3.050	0.006	-41.34	0.629	0.074	-1.00
Sulfurous acid	-949.49	2.976	0.007	-219.08	1.362	0.014	1.81
Phosphoric acid	-714.56	2.853	0.009	-178.30	1.167	0.018	2.12
Nitrous acid	-189.31	2.274	0.031	-33.70	0.680	0.081	3.39
Hydrazoic acid	-132.58	2.118	0.041	-28.22	0.503	0.104	4.72
Boric acid	-178.62	2.250	0.035	-38.33	0.594	0.080	6.23
Hydrocyanic acid	-96.43	1.976	0.050	-14.72	0.519	0.152	9.21
ORGANIC							
p-Toluensulfonic acid	-625.40	2.796	0.012	-197.56	0.838	0.021	-2.80
Citric acid	-190.11	2.278	0.039	-53.22	0.161	0.082	2.79
Formic acid	-168.01	2.223	0.035	-30.62	0.630	0.089	3.76
Lactic acid	-159.02	2.200	0.043	-39.69	0.354	0.092	3.75
Ascorbic acid	-181.94	2.259	0.040	-50.80	0.172	0.085	4.20
Benzoic acid	-135.21	2.130	0.052	-35.73	0.140	0.112	4.19
Acetic acid	-149.35	2.172	0.042	-32.41	0.463	0.098	4.80
Propionic acid	-138.97	2.142	0.047	-33.37	0.344	0.104	4.87
Carbonic acid	-188.85	2.274	0.330	-39.09	0.613	0.077	6.32
Phenol acid	-114.06	2.056	0.059	-28.29	0.125	0.135	9.80

Table S3. Chemical potential (μ_Ω) and inverse of electronic temperature (θ_Ω^{-1}) values for heteroatoms constituting a set of selected ethenes involved in a Markovniko*v* addition.

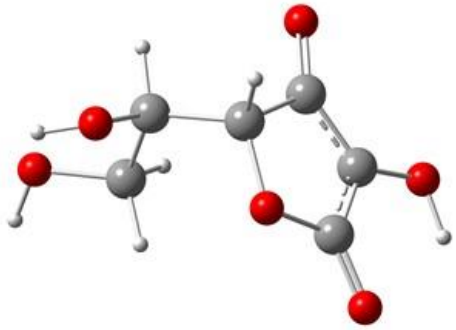
Substituent (R_1)	**atom**	θ_Ω^{-1}	μ_Ω	**Substituent (R_1)**	**atom**	θ_Ω^{-1}	μ_Ω
H	C_1	4.42	-14.42	F	C_1	13.40	-45.04
	C_2	4.42	-14.42		C_2	13.15	-45.40
					F_3	7.07	-20.84
CH_2CH_3	C_1	5.18	-20.72	NHOH	C_1	9.70	-36.34
	C_2	5.16	-20.71		C_2	9.49	-36.39
	C_3	5.14	-20.73		N_3	8.67	-30.71
	C_4	5.15	-20.73		O_4	7.52	-25.94
$CHCH_2$	C_1	5.35	-20.92	OCH_3	C_1	8.67	-33.01
	C_2	5.34	-20.92		C_2	8.46	-33.16
	C_3	5.35	-20.92		O_3	6.52	-22.52
	C_4	5.34	-20.92		C_4	8.46	-33.18
CCH	C_1	5.56	-21.18	$NHNH_2$	C_1	7.56	-29.00
	C_2	5.54	-21.18		C_2	7.38	-29.03
	C_3	5.61	-21.14		N_3	6.83	-24.67
	C_4	5.59	-21.17		N_4	6.81	-24.72
CH_3	C_1	4.95	-18.31	OH	C_1	9.20	-31.86
	C_2	4.94	-18.32		C_2	8.99	-32.19
	C_3	4.93	-18.33		O_3	6.47	-19.99
CHO	C_1	9.04	-33.42	NH_2	C_1	6.49	-23.24
	C_2	9.04	-33.41		C_2	6.34	-23.37
	C_3	8.56	-33.71		N_3	5.72	-18.84
	O_4	6.77	-22.67				
COOH	C_1	11.15	-43.11	$NHCH_3$	C_1	6.43	-25.07
	C_2	11.14	-43.09		C_2	6.26	-25.12
	C_3	10.10	-42.91		N_3	5.83	-21.13
	O_4	9.08	-31.73		C_4	6.27	-25.13
	O_5	9.07	-31.75				
$COCH_3$	C_1	8.60	-34.20				
	C_2	8.60	-34.18				
	C_3	8.13	-34.32				
	C_4	8.60	-34.20				
	O_5	6.69	-24.33				
COF	C_1	14.05	-53.30				
	C_2	14.04	-53.28				
	C_3	12.79	-53.17				
	O_4	11.41	-38.90				
	F_5	9.75	-33.35				

Table S4. Logarithm of the Orbital Donating Descriptor of the Carbon atom involved in the Markovniko*v* addition reaction $\left(\mathrm{Log}\left[\mathrm{ODD}_{\mathrm{C1,HOMO}}\right]\right)$ and their corresponding activation energies E_{act}.

Species	$\mathrm{Log}\left[\mathrm{ODD}_{\mathrm{C1,HOMO}}\right]$	E_{act} (kcal/mol)	Species	$\mathrm{Log}\left[\mathrm{ODD}_{\mathrm{C1,HOMO}}\right]$	E_{act} (kcal/mol)
CH3	0.043	30.1	F	0.56	32.4
COF	0.443	44.8	NHOH	0.30	10.8
CH2CH3	-0.037	28.6	NHNH2	0.17	1.0
CHCH2	0.005	29.0	OCH3	0.23	13.6
H	0.138	36.1	OH	0.37	18.3
CCH	0.053	33.5	NH2	0.19	6.0
CHO	0.289	38.4	NHCH3	0.08	0.6
COOH	0.322	41.6			
COCH3	0.176	37.7			

Cartesian coordinates of ascorbic acid conjugated bases

Ascorbic anion H1



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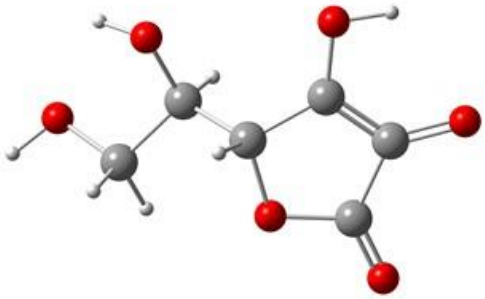
C, -0.779136, 1.162551, -0.333151
C, 0.201865, 0.175982, -1.004377
O, -2.179065, -2.004303, 0.169799
O, -2.909143, 0.703019, 0.871291
O, -0.565028, 2.386911, -0.307319
C, 1.595898, 0.299697, -0.416113
C, 1.642886, -0.162444, 1.029507
H, 0.262522, 0.378511, -2.078061
H, -3.366681, -0.127913, 1.035588
H, 1.282741, -1.194306, 1.089625
O, 2.520338, -0.441337, -1.201503
H, 3.315824, -0.510988, -0.66744
H, 1.846258, 1.368609, -0.450609
O, 3.012, -0.084786, 1.453337
H, 3.106238, -0.599375, 2.253111
H, 1.009809, 0.486664, 1.641879

Ascorbic anion H2



O, 0.284949, -1.186005, 0.531885
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C, 2.068339, 0.171893, -0.180262
C, 1.002636, 0.951821, 0.155253
C, -0.16627, 0.169898, 0.622924
O, 2.133203, -2.291311, -0.074766
O, 3.214759, 0.534518, -0.593705
O, 1.0326, 2.317426, 0.11548
C, -1.458111, 0.289762, -0.195869
C, -2.402494, -0.869073, 0.083824
H, -0.428406, 0.372406, 1.672726
H, 1.932187, 2.49782, -0.194029
H, -2.586857, -0.932162, 1.164528
O, -2.083985, 1.510723, 0.15386
H, -2.961715, 1.478406, -0.233919
H, -1.196791, 0.28487, -1.263221
O, -3.623789, -0.586103, -0.610392
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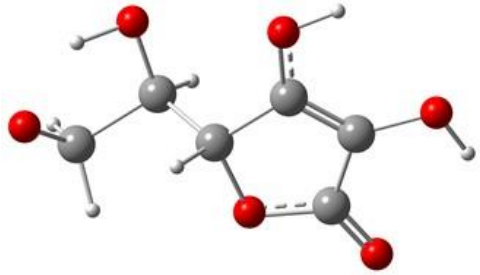
H, -1.958481, -1.804014, -0.264252

Ascorbic anion H3



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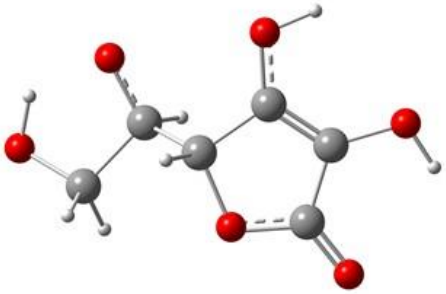
C, -1.862317, 0.325213, 0.009133
C, -0.708398, 0.949499, -0.256663
C, 0.370859, -0.0755, -0.421481
O, -2.473016, -1.969887, 0.128033
O, -3.090359, 0.865044, 0.247392
O, -0.478012, 2.259348, -0.386536
C, 1.488809, -0.05084, 0.642679
C, 2.64717, -1.021307, 0.209178
H, 0.847395, -0.02651, -1.405617
H, -3.686402, 0.118783, 0.376217
H, -1.292832, 2.727833, -0.187199
H, 2.190609, -1.934815, -0.230005
O, 2.066416, 1.215556, 0.676314
H, 2.866851, 1.001163, 0.083397
H, 1.037239, -0.310908, 1.610969
O, 3.463522, -0.331935, -0.619022
H, 3.13703, -1.35301, 1.159778

Ascorbic anion H4



O, 0.317635, -1.237567, 0.54869
C, 1.56552, -1.156809, 0.071478
C, 1.906003, 0.23866, -0.112478
C, 0.859409, 0.989829, 0.253993
C, -0.27516, 0.090446, 0.626603
O, 2.288555, -2.10878, -0.145905
O, 3.130759, 0.639059, -0.558952
O, 0.762264, 2.320988, 0.296713
C, -1.518509, 0.20199, -0.305968
C, -2.499384, -0.973289, 0.029789
H, -0.607345, 0.246551, 1.656197
H, 3.625847, -0.170309, -0.727497
H, 1.567347, 2.690624, -0.07537
H, -2.486801, -1.164746, 1.118684
O, -2.142457, 1.372437, -0.159561
H, -1.118152, 0.012708, -1.338873
O, -3.775955, -0.547327, -0.376925
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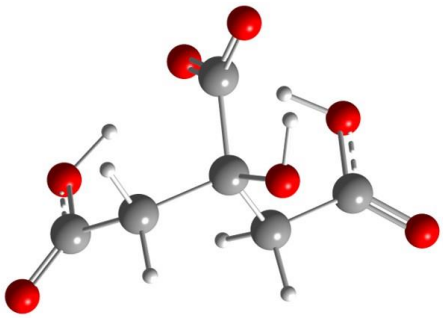
Cartesian coordinates of citric acid conjugated bases

Citric anion H1



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O, 3.589555, -0.192864, -0.835535
O, -3.052941, 0.671773, 0.093228
O, 2.574298, -0.935021, 1.031429
O, -3.292564, -1.519214, 0.197847
C, 0.001377, -0.222792, -0.065797
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H, 1.109192, -1.635709, -1.240413
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H, -1.324731, -0.234969, -1.777652
H, 1.033509, -0.926857, 1.379425
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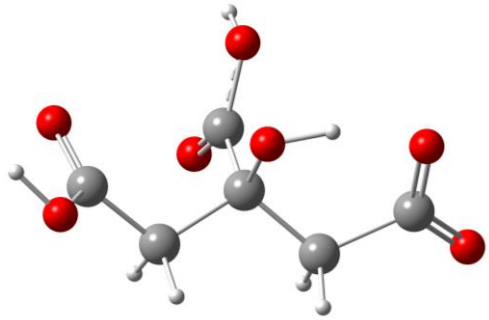
Citric anion H2, H3



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O, 3.665805, -0.451446, -0.677039
O, -3.22563, -1.484726, 0.085775
O, 2.487744, -0.606846, 1.232694
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