

A Combined Experimental and DFT Approach on Free Radical Induced Oxidations of Kynurenic Acid

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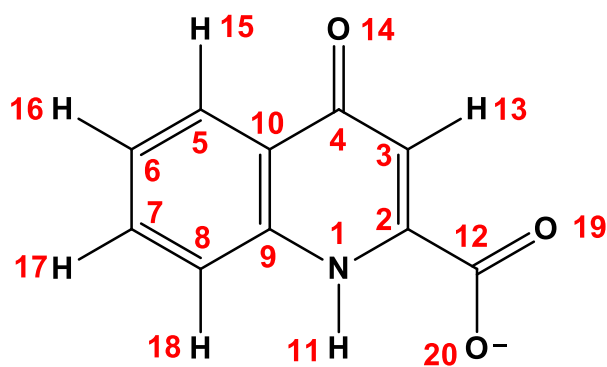
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1. Table S1, condensed Fukui functions for radical attack ($f_k^\bullet$) calculated on all atoms of kynurenic acid



Kynurenic acid

Atom	$f_k^\bullet$	Atom	$f_k^\bullet$
N ₁	0.102	H ₁₁	0.025
C ₂	0.062	C ₁₂	0.016
C ₃	0.106	H ₁₃	0.024
C ₄	0.061	O ₁₄	0.164
C ₅	0.073	H ₁₅	0.017
C ₆	0.075	H ₁₆	0.016
C ₇	0.030	H ₁₇	0.016
C ₈	0.083	H ₁₈	0.018
C ₉	0.003	O ₁₉	0.046
C ₁₀	0.017	O ₂₀	0.040

2. Table S2, Cartesian coordinates and energy values of kynurenic acid and various radical species considered in the study

Species	Geometry obtained at B3LYP/6-311+G(d,p)/SMD(water)			
KA	6	-1.504423000	0.012509000	0.000025000
	6	0.761169000	-0.759035000	-0.000043000
	6	1.233751000	0.573048000	-0.000067000
	6	0.278775000	1.689728000	-0.000220000
	6	-1.108246000	1.323959000	0.000012000
	1	1.278289000	-2.853520000	0.000007000
	6	1.663976000	-1.840236000	-0.000007000
	6	2.626205000	0.791018000	-0.000021000
	1	-1.857222000	2.103891000	0.000123000
	6	3.509490000	-0.270314000	0.000022000
	6	3.021311000	-1.591881000	0.000025000
	1	2.989522000	1.811265000	-0.000054000
	1	4.578058000	-0.090670000	0.000037000
	1	3.716595000	-2.423456000	0.000057000
	8	0.662581000	2.890504000	0.000199000
	7	-0.594351000	-0.988374000	-0.000072000
	6	-2.967438000	-0.436929000	0.000048000
	8	-3.154580000	-1.683118000	0.000157000
	8	-3.842353000	0.462250000	-0.000139000
	1	-0.957398000	-1.937173000	-0.000058000
	Sum of electronic and thermal Energies = -665.350146			
	Sum of electronic and thermal Enthalpies = -665.349202			
	Sum of electronic and thermal Free Energies = -665.397460			
KA ^{•+}	6	1.515069000	0.027964000	-0.000123000
	6	-0.766117000	-0.739438000	0.000123000
	6	-1.252013000	0.595769000	0.000133000
	6	-0.283460000	1.709594000	0.000009000
	6	1.126431000	1.345024000	-0.000448000
	1	-1.241992000	-2.848210000	-0.000103000
	6	-1.648471000	-1.843896000	-0.000039000
	6	-2.625293000	0.797388000	0.000089000
	1	1.869488000	2.130734000	-0.001073000
	6	-3.499841000	-0.296846000	-0.000063000
	6	-3.010231000	-1.610184000	-0.000109000
	1	-3.014677000	1.807448000	0.000134000
	1	-4.568602000	-0.122030000	-0.000146000
	1	-3.699772000	-2.444713000	-0.000281000
	8	-0.635373000	2.897864000	0.000254000
	7	0.577127000	-0.947401000	0.000008000
	6	2.968080000	-0.462280000	0.000100000
	8	3.100088000	-1.710765000	0.000174000
	8	3.850282000	0.422020000	-0.000033000

	1	0.950768000	-1.902953000	0.000229000
	Sum of electronic and thermal Energies = -665.135882 Sum of electronic and thermal Enthalpies = -665.134938 Sum of electronic and thermal Free Energies = -665.183822			
KA(C ₃ OH)•	6	-1.339432000	-0.367151000	0.057693000
	6	1.037996000	-0.833652000	0.041907000
	6	1.369981000	0.543988000	0.015256000
	6	0.311439000	1.547532000	0.011465000
	6	-1.090414000	1.073925000	0.408459000
	1	1.795211000	-2.852829000	0.042313000
	6	2.060781000	-1.801596000	0.030604000
	6	2.727516000	0.918275000	-0.027001000
	6	3.726999000	-0.035576000	-0.029184000
	6	3.383118000	-1.401694000	-0.001960000
	1	2.971702000	1.973700000	-0.046320000
	1	4.768291000	0.261787000	-0.049479000
	1	4.164811000	-2.152827000	-0.007911000
	8	0.504728000	2.738776000	-0.235211000
	7	-0.279588000	-1.220329000	0.031963000
	6	-2.686968000	-0.947768000	-0.042412000
	8	-2.785700000	-2.199392000	-0.218387000
	8	-3.678863000	-0.140786000	0.057444000
	1	-0.504000000	-2.205331000	-0.077348000
	1	-1.105691000	1.169708000	1.513856000
	8	-2.069810000	1.945548000	-0.140380000
	1	-2.902150000	1.417220000	-0.095549000
	Sum of electronic and thermal Energies = -741.139728 Sum of electronic and thermal Enthalpies = -741.138784 Sum of electronic and thermal Free Energies = -741.190593			
KA(C ₈ OH)•	6	1.663341000	0.069079000	-0.045202000
	6	-0.669267000	-0.421371000	-0.154098000
	6	-0.999594000	0.927572000	-0.033241000
	6	0.069246000	1.920510000	0.108719000
	6	1.410587000	1.405415000	0.092256000
	6	-1.706423000	-1.515900000	-0.252104000
	6	-2.369253000	1.314551000	-0.060470000
	1	2.236111000	2.097326000	0.190008000
	6	-3.384490000	0.352775000	-0.228977000
	6	-3.098848000	-0.980512000	-0.349260000
	1	-2.615905000	2.362939000	0.040029000
	1	-4.417047000	0.682642000	-0.269672000
	1	-3.885786000	-1.713101000	-0.486694000
	8	-0.177023000	3.151828000	0.237129000
	7	0.627763000	-0.806644000	-0.166204000
	6	3.054489000	-0.554387000	-0.077529000
	8	3.088479000	-1.805326000	-0.233076000

	8	4.033097000	0.221074000	0.052066000
	1	0.875392000	-1.790317000	-0.246877000
	1	-1.477089000	-2.145017000	-1.119453000
	8	-1.578276000	-2.440362000	0.867440000
	1	-1.858957000	-1.972060000	1.667048000
	Sum of electronic and thermal Energies = -741.138791			
	Sum of electronic and thermal Enthalpies = -741.137847			
	Sum of electronic and thermal Free Energies = -741.190761			
KA(N ₁)•	6	1.484070000	-0.082260000	-0.001263000
	6	-0.750205000	-0.764747000	0.017742000
	6	-1.241376000	0.571541000	-0.012086000
	6	-0.259998000	1.662273000	-0.043159000
	6	1.127989000	1.260791000	-0.024907000
	1	-1.292746000	-2.848135000	0.071696000
	6	-1.675148000	-1.834828000	0.049173000
	6	-2.616674000	0.803721000	-0.012680000
	1	1.884221000	2.034075000	-0.032959000
	6	-3.510426000	-0.265374000	0.019068000
	6	-3.036948000	-1.583903000	0.050417000
	1	-2.983994000	1.822446000	-0.037690000
	1	-4.576960000	-0.074227000	0.019353000
	1	-3.738465000	-2.409300000	0.074816000
	8	-0.587245000	2.868843000	-0.076564000
	7	0.580408000	-1.073935000	0.009913000
	6	2.971126000	-0.472660000	0.006318000
	8	3.262302000	-1.669952000	-0.244406000
	8	3.786272000	0.454278000	0.263927000
	Sum of electronic and thermal Energies = -664.699119			
	Sum of electronic and thermal Enthalpies = -664.698175			
	Sum of electronic and thermal Free Energies = -664.747705			
RC	6	1.249690000	-0.531586000	0.002850000
	6	-0.824819000	0.641905000	0.011877000
	6	-1.541485000	-0.577012000	-0.002326000
	6	-0.813782000	-1.850736000	-0.014687000
	6	0.615780000	-1.748233000	-0.010081000
	1	-0.945757000	2.796585000	0.034598000
	6	-1.512636000	1.872954000	0.023743000
	6	-2.950606000	-0.530988000	-0.004338000
	1	1.205747000	-2.653910000	-0.017392000
	6	-3.619577000	0.676228000	0.007083000
	6	-2.891883000	1.883101000	0.021117000
	1	-3.497838000	-1.465567000	-0.015120000
	1	-4.702891000	0.700286000	0.005311000
	1	-3.419603000	2.829827000	0.029956000
	8	-1.411058000	-2.961752000	-0.028149000
	7	0.549947000	0.624591000	0.014280000

	6	2.767815000	-0.428441000	0.010996000
	8	3.300748000	0.728770000	-0.010997000
	8	3.423823000	-1.489345000	0.043947000
	1	1.076399000	1.512075000	0.012961000
	8	2.281917000	2.795831000	-0.142612000
	1	2.799883000	2.877378000	0.674813000
	Sum of electronic and thermal Energies = -741.114973			
	Sum of electronic and thermal Enthalpies= -741.114029			
	Sum of electronic and thermal Free Energies= -741.169112			
TS	6	-1.244983000	0.463291000	-0.004054000
	6	0.806358000	-0.634740000	0.001821000
	6	1.507528000	0.602421000	0.000224000
	6	0.758156000	1.858983000	-0.003519000
	6	-0.659472000	1.717472000	-0.005305000
	1	0.997218000	-2.785434000	0.007023000
	6	1.540540000	-1.847375000	0.005360000
	6	2.919373000	0.588239000	0.001660000
	1	-1.279248000	2.604243000	-0.009667000
	6	3.617327000	-0.601369000	0.004516000
	6	2.917574000	-1.827432000	0.006470000
	1	3.446009000	1.535005000	0.000056000
	1	4.701213000	-0.599261000	0.005225000
	1	3.469073000	-2.760931000	0.008818000
	8	1.335801000	2.990834000	-0.006119000
	7	-0.560903000	-0.688441000	-0.000582000
	6	-2.747960000	0.367738000	-0.000500000
	8	-3.338760000	-0.787529000	-0.027179000
	8	-3.462421000	1.380169000	0.032161000
	1	-1.295638000	-1.825807000	-0.022581000
	8	-2.062065000	-2.662601000	-0.101515000
	1	-2.379383000	-2.839079000	0.796377000
	Sum of electronic and thermal Energies = -741.108242			
	Sum of electronic and thermal Enthalpies = -741.107298			
	Sum of electronic and thermal Free Energies = -741.160125			
PC	6	1.199458000	-0.613387000	0.063289000
	6	-0.790248000	0.607419000	0.101656000
	6	-1.600015000	-0.557262000	-0.026282000
	6	-0.922577000	-1.856125000	-0.119199000
	6	0.521521000	-1.819464000	-0.063247000
	1	-0.788602000	2.752576000	0.285035000
	6	-1.415685000	1.873681000	0.189984000
	6	-2.988526000	-0.432938000	-0.063342000
	1	1.060774000	-2.755162000	-0.122493000
	6	-3.584326000	0.824195000	0.025967000
	6	-2.795850000	1.976163000	0.151930000
	1	-3.599576000	-1.321976000	-0.162061000

	1	-4.664027000	0.910075000	-0.003740000
	1	-3.268404000	2.948785000	0.219166000
	8	-1.540364000	-2.936878000	-0.236427000
	7	0.573521000	0.569829000	0.139881000
	6	2.732842000	-0.603605000	0.115347000
	8	3.313348000	0.514863000	0.047457000
	8	3.300375000	-1.720109000	0.219840000
	1	1.571681000	3.192809000	-0.352729000
	8	2.531705000	3.109532000	-0.390498000
	1	2.693424000	2.152775000	-0.221944000
	Sum of electronic and thermal Energies = -741.149796			
	Sum of electronic and thermal Enthalpies = -741.148852			
	Sum of electronic and thermal Free Energies = -741.206982			
1	6	-1.928973000	-1.490413000	0.000128000
	6	0.320952000	-0.900191000	-0.000071000
	6	0.021313000	0.493743000	-0.000122000
	6	-1.390815000	0.902999000	-0.000294000
	6	-2.354289000	-0.175010000	0.000130000
	1	1.892115000	-2.372302000	0.000008000
	6	1.674102000	-1.311147000	-0.000029000
	6	1.061804000	1.422106000	-0.000069000
	1	-3.409371000	0.070311000	0.000347000
	6	2.389289000	0.994656000	-0.000025000
	6	2.692795000	-0.372687000	-0.000008000
	1	0.830872000	2.480410000	-0.000102000
	1	3.188887000	1.725903000	-0.000008000
	1	3.726543000	-0.696889000	0.000034000
	8	-1.749073000	2.100391000	0.000192000
	7	-0.641813000	-1.871946000	0.000005000
	1	-2.660839000	-2.291273000	0.000309000
	Sum of electronic and thermal Energies = -476.515373			
	Sum of electronic and thermal Enthalpies = -476.514428			
	Sum of electronic and thermal Free Energies = -476.556230			
KA ²⁻	6	1.467442000	-0.092873000	-0.000161000
	6	-0.729686000	-0.783486000	-0.000172000
	6	-1.215422000	0.558612000	-0.000426000
	6	-0.255629000	1.656032000	-0.001084000
	6	1.099820000	1.257862000	-0.000398000
	1	-1.310169000	-2.861063000	0.000383000
	6	-1.680389000	-1.841549000	0.000197000
	6	-2.609726000	0.792497000	-0.000187000
	1	1.866187000	2.021896000	-0.000126000
	6	-3.508279000	-0.253961000	0.000194000
	6	-3.033358000	-1.584708000	0.000362000
	1	-2.963228000	1.817122000	-0.000372000
	1	-4.575177000	-0.060386000	0.000341000

	1	-3.739818000	-2.407920000	0.000659000
	8	-0.630373000	2.887098000	0.000019000
	7	0.598179000	-1.105792000	-0.000193000
	6	2.962072000	-0.455099000	0.000387000
	8	3.283976000	-1.675881000	0.000146000
	8	3.790632000	0.502650000	0.000858000
	Sum of electronic and thermal Energies = -664.880899 Sum of electronic and thermal Enthalpies = -664.879955 Sum of electronic and thermal Free Energies = -664.928561			
2	6	-1.310449000	-0.405424000	0.107714000
	6	0.959153000	-0.866756000	-0.035981000
	6	1.342045000	0.513067000	0.106309000
	6	0.339643000	1.517049000	0.248220000
	6	-1.109713000	1.088978000	0.162111000
	1	1.672220000	-2.878129000	-0.290761000
	6	1.973355000	-1.841354000	-0.183347000
	6	2.729517000	0.836321000	0.111892000
	6	3.690810000	-0.137301000	-0.032789000
	6	3.310138000	-1.495039000	-0.185858000
	1	3.018513000	1.874879000	0.226567000
	1	4.741788000	0.130503000	-0.031616000
	1	4.069719000	-2.260213000	-0.300686000
	8	0.584621000	2.751879000	0.434174000
	7	-0.344530000	-1.288180000	-0.011868000
	6	-2.739679000	-0.878870000	0.146027000
	8	-2.997367000	-2.111112000	0.271422000
	8	-3.632678000	0.031344000	0.045426000
	1	-1.641763000	1.511050000	1.025001000
	8	-1.696042000	1.729366000	-1.028852000
	1	-2.625950000	1.443320000	-0.988580000
	Sum of electronic and thermal Energies = -740.673547 Sum of electronic and thermal Enthalpies = -740.672602 Sum of electronic and thermal Free Energies = -740.724381			
3	6	1.611790000	-0.013934000	-0.058044000
	6	-0.646281000	-0.442659000	-0.162203000
	6	-0.992442000	0.923183000	-0.038530000
	6	0.078951000	1.894593000	0.094975000
	6	1.392409000	1.348402000	0.079822000
	1	-1.538072000	-2.109471000	-1.156864000
	6	-1.725397000	-1.508572000	-0.255739000
	6	-2.357854000	1.316900000	-0.049775000
	1	2.233591000	2.022723000	0.177534000
	6	-3.388035000	0.361475000	-0.183141000
	6	-3.120053000	-0.975491000	-0.288654000
	1	-2.602032000	2.367655000	0.042189000
	1	-4.418329000	0.702526000	-0.205669000
	1	-3.920381000	-1.699962000	-0.394023000

8	-0.145294000	3.153806000	0.221020000
7	0.603969000	-0.910035000	-0.184053000
6	3.041759000	-0.554891000	-0.074685000
8	3.214308000	-1.792916000	-0.261283000
8	3.977832000	0.280670000	0.101575000
8	-1.626459000	-2.423805000	0.882909000
1	-0.714749000	-2.749307000	0.887291000
Sum of electronic and thermal Energies = -740.673904			
Sum of electronic and thermal Enthalpies = -740.672960			
Sum of electronic and thermal Free Energies = -740.726732			