

The Mechanism of Nitration of Tyrosine by Peroxynitrous Acid

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(1)

C	-1.260	-0.698	0.000
C	-0.061	-1.416	0.000
C	1.149	-0.737	0.000
C	1.208	0.664	0.000
C	0.000	1.360	0.000
C	-1.226	0.694	0.000
H	-0.100	-2.498	0.000
H	2.072	-1.309	0.000
C	2.536	1.384	0.000
H	0.008	2.446	0.000
H	-2.152	1.262	0.000
H	2.399	2.467	0.000
H	3.132	1.125	0.881
H	3.132	1.125	-0.881
O	-2.426	-1.415	0.000
H	-3.170	-0.805	0.000

(2)

H	1.162	-0.581	0.000
O	1.330	0.387	0.000
O	0.000	0.908	0.000
N	-1.000	-0.058	0.000
O	-0.601	-1.172	0.000

(3)

C	-0.516	1.347	-0.299
C	-0.595	-0.147	-0.674
C	0.669	-0.942	-0.548
C	1.800	-0.405	-0.067

C 1.818 1.003 0.353
C 0.754 1.821 0.256
N -1.649 -0.832 0.227
H 0.622 -1.980 -0.860
C 3.078 -1.188 0.065
H 2.750 1.386 0.756
H 0.790 2.860 0.561
H 3.415 -1.204 1.107
H 2.954 -2.218 -0.269
H 3.879 -0.729 -0.524
O -1.473 2.065 -0.496
O -2.243 -1.771 -0.269
O -1.769 -0.419 1.364
H -1.024 -0.228 -1.673

(4)

C 0.830 1.836 -0.000
C -0.432 1.220 -0.000
C -0.458 -0.192 -0.000
C 0.726 -0.944 0.000
C 1.963 -0.326 0.000
C 1.987 1.084 0.000
O -1.515 2.003 -0.000
N -1.721 -0.909 0.000
O -2.773 -0.240 0.000
C 3.246 -1.120 0.000
O -1.716 -2.128 -0.000
H 0.636 -2.022 0.000
H 2.944 1.596 0.000
H 0.858 2.919 -0.000
H 3.853 -0.892 0.882
H 3.048 -2.193 -0.000
H 3.854 -0.891 -0.881
H -2.295 1.406 -0.000

(5)

C 1.311 0.008 -0.000
C 0.592 -1.213 0.000
C -0.778 -1.234 0.000
C -1.548 -0.002 -0.001
C -0.786 1.233 0.000
C 0.588 1.221 -0.000
O -2.798 -0.006 0.000
C 2.814 -0.001 -0.000
H -1.351 2.158 0.000
H 1.137 2.157 0.000

H 1.148 -2.146 0.000
H -1.338 -2.161 0.000
H 3.203 -0.526 -0.879
H 3.223 1.010 -0.001
H 3.203 -0.524 0.880

(6)

C -0.604 1.803 -0.416
C 0.519 1.232 0.136
C 0.479 -0.152 0.687
C -0.843 -0.806 0.641
C -1.933 -0.208 0.080
C -1.816 1.108 -0.460
O 1.672 1.928 0.226
N 1.592 -1.037 -0.138
O 2.732 -0.573 -0.123
C -3.271 -0.903 0.034
O 1.256 -2.059 -0.680
H -0.917 -1.796 1.073
H -2.683 1.577 -0.911
H -0.521 2.811 -0.807
H -4.037 -0.315 0.548
H -3.603 -1.035 -1.000
H -3.226 -1.888 0.502
H 0.960 -0.196 1.672
H 2.405 1.291 0.290

(7)

C 1.722 -1.198 -0.096
C 0.363 -1.197 -0.380
C -0.306 0.018 -0.503
C 0.367 1.222 -0.339
C 1.730 1.206 -0.056
C 2.428 0.001 0.072
O -1.646 0.027 -0.876
N -2.602 -0.009 0.273
O -2.129 -0.044 1.372
C 3.905 -0.017 0.381
O -3.732 0.003 -0.104
H -0.174 2.154 -0.444
H 2.258 2.145 0.067
H 2.245 -2.143 -0.004
H -0.184 -2.122 -0.516
H 4.107 -0.558 1.310
H 4.468 -0.517 -0.413
H 4.303 0.994 0.488

Hydroxyl Radical

O 0.000 0.000 0.108
H 0.000 0.000 -0.867

Carbonate radical

C 0.000 0.000 0.000
O 0.000 1.272 0.000
O 1.101 -0.636 0.000
O -1.101 -0.636 0.000

Nitrogen Dioxide Radical

N 0.000 0.000 0.323
O 0.000 1.101 -0.141
O 0.000 -1.101 -0.141

Water

O 0.000 0.000 0.119
H 0.000 0.757 -0.475
H 0.000 -0.757 -0.475

TS [HOONO \rightarrow HO + NO₂]

H 0.846 -1.643 0.000
O -0.113 -1.514 0.000
O 1.058 0.432 0.000
N 0.000 0.977 0.000
O -1.051 0.433 0.000

TS [O₂COONO⁻ \rightarrow CO₃⁻ + NO₂]

C -0.851 -1.077 0.245
C -0.973 -0.040 -0.734
C -2.203 0.545 -1.023
C -3.376 0.167 -0.370
C -3.273 -0.851 0.601
C -2.069 -1.453 0.903
C -4.704 0.816 -0.675
O 0.264 -1.636 0.547
N 0.779 1.551 0.962
O 1.082 2.443 0.219
H -2.247 1.324 -1.781
H -4.171 -1.170 1.127
H -2.003 -2.236 1.651
H -5.466 0.079 -0.958
H -5.101 1.368 0.187
H -4.613 1.527 -1.501
H -0.090 0.240 -1.295

H 1.471 -1.264 -0.187
O 1.476 0.639 1.364
O 3.215 0.501 0.465
C 3.296 -0.383 -0.506
O 4.376 -0.413 -1.092
O 2.297 -1.167 -0.831

HCO₃

C 0.000 0.178 0.000
O 1.226 0.418 0.000
O -0.301 -1.249 0.000
O -0.999 0.901 0.000
H 0.588 -1.620 0.000

O₂COONO⁻

N 1.943 0.185 -0.117
O 1.738 0.207 1.057
O 0.967 -0.389 -0.908
O -0.167 -0.918 -0.194
C -1.302 0.150 0.005
O -2.234 -0.451 0.530
O -1.027 1.276 -0.386

CO₃--NO₂ Complex

C 1.390 0.000 -0.001
O 0.765 1.108 0.055
O 0.765 -1.107 -0.067
O 2.658 -0.000 0.007
O -1.664 -0.063 1.093
N -2.169 0.000 0.003
O -1.669 0.062 -1.089

O₂COONO₂⁻--(1) Complex

C -2.499 -1.514 -0.491
C -1.408 -0.667 -0.243
C -1.667 0.643 0.198
C -2.978 1.070 0.380
C -4.073 0.233 0.140
C -3.802 -1.066 -0.302
O -0.171 -1.148 -0.443
C -5.490 0.705 0.378
O 1.492 0.815 0.175
C 2.529 1.352 -0.233
O 2.935 2.485 -0.368
O 3.617 0.404 -0.692
O 3.226 -0.978 -0.631

N	3.465	-1.589	0.608
O	3.907	-0.899	1.452
H	-3.151	2.089	0.718
H	-4.628	-1.743	-0.505
H	-2.297	-2.521	-0.838
H	-6.207	0.125	-0.210
H	-5.782	0.608	1.432
H	-5.613	1.758	0.107
H	-0.825	1.301	0.384
H	0.519	-0.461	-0.245

ONO--HO Complex

O	-2.217	0.265	0.000
N	-1.042	-0.053	0.000
O	0.000	0.595	0.000
H	1.992	-0.322	0.000
O	2.880	-0.774	0.000

TS1 (ONOOH decomposition TS in the presence of p-methyphenol and one water molecule)

C	-0.192	-1.229	0.515
C	-0.446	-1.051	-0.853
C	-1.629	-0.448	-1.264
C	-2.592	-0.007	-0.346
C	-2.325	-0.198	1.014
C	-1.144	-0.792	1.448
C	-3.858	0.672	-0.809
O	0.932	-1.815	0.985
O	2.863	-1.564	-0.979
O	2.996	1.231	-0.692
O	2.043	1.107	0.838
N	0.923	1.608	0.846
O	0.417	2.258	-0.010
H	-1.812	-0.323	-2.327
H	-3.052	0.126	1.751
H	-0.944	-0.939	2.503
H	-4.658	0.568	-0.072
H	-3.698	1.744	-0.968
H	-4.213	0.252	-1.753
H	0.280	-1.398	-1.580
H	2.380	1.765	-1.223
H	1.612	-1.876	0.280
H	3.032	-0.601	-0.950
H	3.722	-1.995	-0.954

TS2 (Re-aromatization transition state)

C 2.106 -1.101 -0.411
C 0.941 -1.732 -0.725
C -0.340 -1.143 -0.431
C -0.301 0.246 0.113
C 0.982 0.866 0.369
C 2.156 0.205 0.191
O -1.404 -1.806 -0.489
N -1.329 1.191 -0.398
O -0.962 2.312 -0.729
C 3.491 0.809 0.542
O -2.504 0.818 -0.435
O -2.055 -0.815 1.699
H 0.977 1.894 0.711
H 3.046 -1.604 -0.620
H 0.927 -2.721 -1.167
H 4.155 0.834 -0.328
H 3.379 1.831 0.908
H 3.998 0.228 1.320
H -1.106 -0.207 1.259
H -2.097 -1.374 0.825
H -2.797 -0.196 1.629