Supporting Information

A Surprisingly Complex Aqueous Chemistry of the Simplest Amino Acid: A Pulse Radiolysis and Theoretical Study on H/D Kinetic Isotope Effects in the Reaction of Glycine Anions with Hydroxyl Radicals

by Igor Štefanić, Ivan Ljubić,* Marija Bonifačić,* Aleksandar Sabljić, Klaus-Dieter Asmus, and David A. Armstrong

*E-mails: iljubic@irb.hr, bonifacic@irb.hr

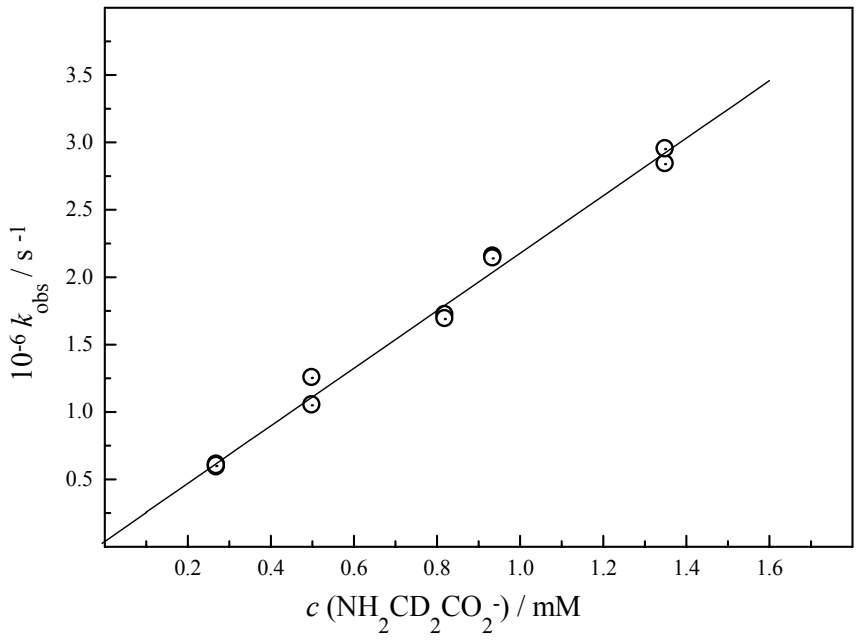

Figure 1S. Plot of k_{obs} (pseudo-first order formation rate constant) from the optical absorption at 260 nm vs. concentration of C-deuterated glycine anion as measured in pulse-irradiated N_2O-saturated aqueous (H_2O) solution containing different concentrations of glycine-d_5 at pH 10.9. From the slope of the obtained straight line the second-order rate constant k = (2.11 ± 0.07) x 10^9 $M^{-1}s^{-1}$ has been calculated for the overall reaction of $^{\bullet}OH$ radicals with NH_2-CD_2-CO_2^-.

Coordinates (Å) of optimized stationary structures in standard orientation, unscaled vibrational frequencies (cm^{-1}), gas-phase energies (a.u.), and total free energies in aqueous solution (a.u.). The levels of theory are UBB1K/6-311+G(3df,2p) and UCCSD(T)/6-311+G(2df,2p).

G^- in H_2O

N	-1.888512	0.016261	-0.002596
C	-0.654548	-0.732309	0.004304
C	0.648524	0.060038	0.000284
O	1.696055	-0.621130	-0.003171
O	0.594292	1.301566	0.001605
H	-1.906009	0.637360	0.794549
H	-1.905817	0.623091	-0.810696
H	-0.626688	-1.399077	-0.865742
H	-0.628537	-1.385067	0.885070

78.4622	189.1700	285.7961
521.2190	587.1484	685.2909
903.2025	927.5393	980.9681
1156.0787	1176.9176	1337.5863
1382.5357	1427.1578	1482.0847
1606.3487	1652.3711	2893.3202
2934.2462	3504.9139	3571.7446

E = -283.965263

G^- gas-phase

N	-1.860248	0.033767	0.004026
C	-0.640727	-0.754675	0.108616
C	0.662545	0.067122	0.000135
O	1.701364	-0.598478	-0.079775
O	0.520647	1.300336	0.032780
H	-1.550409	0.971227	0.237168
H	-2.105097	0.102324	-0.970127
H	-0.619263	-1.537360	-0.643958
H	-0.610487	-1.262105	1.072185

93.2811	197.7514	308.4878
503.6118	593.3793	695.8248
903.2296	965.5250	1024.4812
1133.6303	1181.9699	1320.5509
1384.1322	1446.5083	1498.6178
1693.5074	1756.1509	3069.4810
3127.9829	3514.4712	3625.6249

E = -283.848345338
E(CCSD(T)) = -283.44140692

$^{\bullet}$OH in H_2O

O	0.000000	0.000000	0.108669
H	0.000000	0.000000	-0.869351

3542.7331

E = -75.737687

$^{\bullet}$OH gas-phase

O	0.000000	0.000000	0.107032
H	0.000000	0.000000	-0.856253

3863.0110

E = -75.7300244238
E(CCSD(T)) = -75.63324782

3eBH in H_2O

N	1.105378	1.034740	0.307920
C	-0.245640	1.092857	-0.178637
C	-1.025115	-0.198399	0.024109
O	-2.240670	-0.142764	-0.225164
O	-0.406445	-1.209709	0.411742
H	1.168147	0.922777	1.312314
H	1.677063	1.813315	0.005905
H	-0.226777	1.291712	-1.264488
H	-0.832499	1.908093	0.286611
O	2.240941	-0.829967	-0.372254
H	1.350345	-1.086303	-0.083203

-5.2371	73.0359	143.0931
205.6676	285.3539	358.5203
526.8273	598.9112	673.8280
679.9577	766.5836	855.0678
916.9008	980.4685	1100.4737
1161.2355	1274.4176	1357.8045
1411.0253	1484.0979	1607.1537
1638.8247	2699.7298	2754.5605
3423.6981	3513.5305	3607.3790

E = -359.711228

3eB in H_2O

N	1.077763	0.510590	0.099550
C	0.078812	-0.514639	0.040818
C	-1.371084	-0.028390	-0.012287
O	-2.232564	-0.927386	-0.032064
O	-1.582246	1.194581	-0.037026
H	1.064883	1.138029	-0.693940
H	1.074223	1.041499	0.962127
H	0.182358	-1.175478	0.916483
H	0.252073	-1.137022	-0.852962
O	3.154738	-0.182006	-0.142881
H	2.916326	-0.864493	0.496018

6.1944	32.7561	75.3200
115.4875	208.1731	341.7645
353.2759	520.1593	595.6191
654.2842	685.1387	808.6572
907.4484	931.9915	1134.4946
1146.1534	1325.9323	1349.6496
1406.2313	1456.6101	1614.4951
1638.9933	2747.1102	2793.4224
3424.4766	3515.8303	3705.6559

E = -359.710491

3eB gas-phase

N	-1.049391	0.166220	0.526823
C	0.044970	-0.732471	0.260484
C	1.341234	0.048587	-0.069415
O	2.328175	-0.654910	-0.286771
O	1.225954	1.284075	-0.079714
H	-1.503649	0.042731	1.407772
H	-0.688262	1.107083	0.413497
H	-0.176089	-1.377678	-0.586882
H	0.245396	-1.385456	1.105314
O	-3.087671	-0.077936	-0.384860
H	-2.580556	0.143252	-1.163122

29.6690	67.0270	117.8481
170.9361	224.7130	335.7362
411.1806	515.4501	579.9350
598.9917	683.7588	845.5722
899.8965	1012.3924	1106.2128
1187.8979	1256.6985	1348.3013
1430.3862	1504.6357	1620.8635
1781.4503	3085.0368	3125.5638
3508.0026	3744.6555	3960.8061

E = -359.596839489
E(CCSD(T)) = -359.09108719

MCH in H_2O

N	1.929743	-1.257048	0.000611
C	0.549867	-0.837073	0.008464
C	0.279430	0.660719	0.003223
O	-0.934307	0.995015	0.024052
O	1.229284	1.449437	-0.019976
H	2.394295	-0.868472	-0.813279
H	2.407941	-0.854198	0.799231
H	0.040739	-1.253182	0.894043
H	0.030461	-1.259592	-0.868265
O	-2.945265	-0.675553	-0.014478
H	-2.155117	-0.058283	-0.002905

4.9359	61.9023	107.0727
213.0042	235.0064	294.9980
521.1942	578.9753	690.4360
759.5241	899.9779	913.1583
929.0848	985.0393	1157.9910
1169.4869	1322.0802	1377.4820
1421.2006	1472.6297	1630.6634
1641.9785	2758.6176	2795.8495
3039.1887	3418.8974	3482.6601

E = -359.709091

MCH gas-phase

N	-1.918482	-1.228910	-0.055657
C	-0.557140	-0.828899	0.252586
C	-0.271975	0.665007	0.040678
O	0.932984	0.998757	0.096166
O	-1.246212	1.397659	-0.127527
H	-2.461701	-0.382760	0.062788
H	-1.975470	-1.415259	-1.043199
H	0.157631	-1.411143	-0.320350
H	-0.340984	-1.038951	1.299507
O	2.922841	-0.663761	-0.135092
H	2.147674	-0.027403	-0.037110

41.7047	65.1564	105.1777
191.5962	255.2821	312.9405
508.0329	593.8252	699.5497
710.8257	917.5497	962.2011

1001.2015	1023.4532	1147.5327
1193.4453	1335.1793	1393.8932
1456.8532	1500.6959	1695.5508
1747.9637	2993.9429	3073.1211
3140.4031	3542.0517	3634.6598

E = -359.608789376
E(CCSD(T)) = -359.10558168

MNH in H_2O

N	-0.664370	1.601580	-0.007981
C	0.698836	1.135876	0.006908
C	0.954694	-0.366404	-0.000656
O	2.143734	-0.718753	0.002226
O	-0.023269	-1.148748	-0.008016
H	-1.152981	1.271322	-0.830812
H	-1.168350	1.277624	0.807838
H	1.211745	1.535424	0.898261
H	1.236232	1.548977	-0.863479
O	-2.594441	-0.709135	0.006596
H	-1.605431	-0.848159	0.000099

13.4768	87.7858	100.9358
236.8858	310.4780	385.2615
523.3688	584.1734	664.9273
773.8201	870.0174	877.1488
919.7593	958.6783	1146.3261
1162.4437	1327.9033	1364.8575
1410.1105	1477.3750	1626.1203
1647.2539	2744.4818	2783.0928
3111.5109	3449.0937	3528.1020

E = -359.709209

MNH gas-phase

N	-0.709206	1.570404	-0.000070
C	0.672061	1.139874	0.000425
C	0.970728	-0.370845	0.000066
O	2.162300	-0.668526	-0.000737
O	-0.011987	-1.145739	0.000808
H	-1.179076	1.167281	-0.795423
H	-1.179862	1.165920	0.794112
H	1.176403	1.560197	0.866747
H	1.176998	1.560765	-0.865259
O	-2.563902	-0.705256	-0.000403
H	-1.578045	-0.904994	0.000025

```
   20.6653                92.4812                96.6964
  250.3181               309.1974               322.3817
  513.7039               586.2102               685.0698
  833.7259               910.8715               932.2037
  961.6263               997.0692              1157.9985
 1173.8665              1338.6845              1395.7604
 1447.9716              1486.8987              1691.7991
 1753.0884              3018.1748              3093.5215
 3133.9075              3580.5927              3647.1750

E =  -359.608038603
E(CCSD(T)) = -359.10477455
```

MC in H_2O

```
N       -0.999807    0.631938    0.049071
C       -0.043464   -0.456578    0.021590
C        1.429478   -0.067443   -0.006720
O        2.237862   -1.017361   -0.001318
O        1.721114    1.139948   -0.037641
H       -0.844648    1.196403    0.879411
H       -0.823336    1.253557   -0.734956
H       -0.236645   -1.085284   -0.864259
H       -0.204458   -1.101784    0.901020
O       -3.535846   -0.320611   -0.037414
H       -2.593392    0.041861   -0.002941

    8.6209                42.0371                67.2019
  192.3886               338.1252               344.3936
  526.0473               597.4854               682.0358
  767.5371               914.9641               928.9409
 1002.3865              1035.4972              1141.9629
 1169.5576              1343.6816              1372.8588
 1414.8531              1476.0232              1620.9862
 1632.1719              2741.4525              2782.3027
 2879.6603              3396.2805              3454.6752

E = -359.709570
```

MC gas-phase

```
N       -0.976507    0.371548    0.456238
C        0.053854   -0.630306    0.194230
C        1.440349   -0.004162   -0.076576
O        2.376811   -0.803320   -0.137581
O        1.437468    1.229154   -0.222725
H       -0.997472    0.553565    1.446337
H       -0.564140    1.215443    0.063212
H       -0.215310   -1.212607   -0.684025
```

```
H         0.135464   -1.330107    1.018863
O        -3.549876   -0.179750   -0.348437
H        -2.603436    0.011011   -0.074033

   41.9640                57.4184               115.6882
  208.9809               329.6298               350.0080
  516.4853               594.4953               696.7357
  783.7373               909.8102               946.0130
 1010.2434              1079.1003              1141.4100
 1180.0560              1325.5759              1381.6845
 1441.2195              1502.7814              1687.9980
 1772.5737              3054.9477              3096.2982
 3149.5196              3464.6669              3625.9460

E =  -359.603251567
E(CCSD(T)) = -359.10045555
```

TSCH in H_2O

```
N         1.430623    1.434976   -0.008512
C         0.280685    0.712504    0.397853
C         0.304816   -0.775874    0.076453
O        -0.767666   -1.380725    0.312057
O         1.335459   -1.275644   -0.384738
H         1.642280    1.301125   -0.990364
H         1.348800    2.426295    0.185417
H        -0.682675    1.083549   -0.069768
H         0.108374    0.833496    1.482778
O        -2.309307    0.759823   -0.340888
H        -2.012033   -0.136710   -0.085766

 -285.1547                92.3425               141.7559
  228.7066               240.7433               330.2904
  519.1182               613.3672               632.1067
  661.3558               695.5404               827.0841
  919.5089               999.2817              1113.8164
 1223.5065              1274.0909              1361.4981
 1376.9123              1461.5171              1613.3525
 1658.5970              2317.0395              2726.7707
 3414.1518              3496.9745              3498.7725

E = -359.702510
```

TSCH gas-phase

```
N         1.322417    1.469035    0.083393
C         0.187854    0.704360    0.460619
C         0.315794   -0.779746    0.082020
```

```
O       -0.668280   -1.471716    0.394116
O        1.345410   -1.103083   -0.514909
H        1.807151    0.949218   -0.633986
H        1.109096    2.402740   -0.213029
H       -0.797250    1.017784   -0.077320
H       -0.075529    0.816309    1.509182
O       -2.217451    0.721339   -0.414323
H       -1.999707   -0.189300   -0.143520

  -554.4332              87.8942             196.4601
   215.3489             284.5261             329.2597
   502.3725             605.9620             642.6470
   680.8551             734.7605             853.4375
   907.8823            1018.4676            1140.1512
  1210.6343            1244.6751            1350.7386
  1381.2756            1441.5698            1604.5390
  1761.1162            1916.3042            3109.4267
  3559.6958            3596.3761            3697.4225

E =  -359.596168288
E(CCSD(T)) = -359.09103925
```

TSNH in H_2O

```
N       -1.147462    1.141801    0.343204
C        0.196129    1.116351   -0.144442
C        1.001767   -0.174698    0.050943
O        2.160411   -0.148552   -0.393161
O        0.456445   -1.133719    0.626993
H       -1.814600    0.488724   -0.204573
H       -1.179000    0.852957    1.315568
H        0.763272    1.905014    0.375282
H        0.208025    1.361966   -1.211994
O       -2.096765   -0.845132   -0.484774
H       -1.293563   -1.231964   -0.108186

  -911.2749              90.1776             110.6147
   181.4666             286.3446             393.0627
   512.9551             579.0425             595.4580
   670.5417             787.0018             883.0873
   930.1404             965.1280            1127.6101
  1163.0409            1295.9320            1356.0148
  1397.0769            1448.7421            1520.2471
  1631.4437            2035.8074            2831.7430
  2925.9091            3493.0633            3682.6509

E = -359.702533
```

TSNH gas-phase

```
N       -1.145425    1.142467    0.360869
C        0.195726    1.118955   -0.145992
C        1.009614   -0.194248    0.048442
O        2.155023   -0.150858   -0.392264
O        0.417844   -1.118159    0.634039
H       -1.797815    0.445008   -0.203517
H       -1.120678    0.728952    1.284116
H        0.770256    1.890602    0.366430
H        0.198136    1.372367   -1.200633
O       -2.073451   -0.827487   -0.499523
H       -1.259283   -1.210405   -0.125192

 -1223.9814              61.2825             127.0434
   193.9486             282.1687             422.8174
   499.2476             591.6859             674.5026
   730.1265             833.9692             903.5682
   939.1484            1039.7509            1117.7332
  1170.7346            1269.7060            1364.0389
  1395.8210            1472.5106            1488.3890
  1766.6140            1858.4989            3071.7874
  3151.5419            3564.2163            3581.0133

E =  -359.599393729
E(CCSD(T)) = -359.09542110
```

TSC in H_2O

```
N        0.886109    1.355040    0.266786
C        0.278863    0.115556    0.608714
C       -1.089978   -0.156127   -0.013682
O       -1.640592   -1.214853    0.333522
O       -1.528424    0.683493   -0.814861
H        0.343130    1.829221   -0.443120
H        1.000510    1.968600    1.063361
H        0.242243   -0.045571    1.698973
H        0.918163   -0.742163    0.228297
O        2.388568   -0.996738   -0.461986
H        2.403468   -0.027155   -0.438605

  -382.7304              66.2186              87.2093
   149.6329             195.7830             294.2453
   422.3354             509.9055             611.1183
   655.4585             687.9287             737.9340
   906.2655             984.4996            1098.4510
  1179.5105            1264.6543            1335.6804
  1392.7790            1468.4149            1606.8968
  1658.5176            2286.5856            2758.3669
```

```
  3445.7703              3534.0211              3678.7945

E = -359.698660
```

TSC gas-phase

```
N        0.833167    1.339124    0.333272
C        0.310931    0.031049    0.552960
C       -1.110963   -0.179627   -0.041856
O       -1.684427   -1.202051    0.326914
O       -1.481243    0.726007   -0.800990
H        0.193253    1.771166   -0.324214
H        0.858590    1.886398    1.173478
H        0.358341   -0.277088    1.591086
H        0.984566   -0.737341    0.005723
O        2.432262   -0.919859   -0.454788
H        2.440526    0.041694   -0.414683

  -453.1184               72.9421              144.8190
   193.8616              276.0252              325.1638
   485.3378              494.8204              561.5570
   692.3349              745.3259              881.2728
   910.2692              982.4048             1112.2539
  1171.3953             1219.1396             1372.0085
  1388.9014             1458.3692             1646.2242
  1786.2120             2047.2358             3153.3940
  3507.9853             3680.7714             3819.8150

E =  -359.590922824
E(CCSD(T)) = -359.08547286
```

TSN in H_2O

```
N       -1.045011    0.708332    0.713602
C        0.125553    0.967371   -0.061333
C        1.165018   -0.140694    0.004175
O        2.203464    0.073829   -0.651330
O        0.916722   -1.149648    0.680376
H       -1.514703   -0.208343    0.548281
H       -1.711365    1.477015    0.711308
H        0.591559    1.900570    0.310245
H       -0.105502    1.151924   -1.130987
O       -2.448514   -0.707595   -0.575921
H       -3.061706    0.027769   -0.716116

  -575.0432              -29.1503               74.2058
   125.3634              152.7395              282.1757
   337.1182              516.8862              576.9813
```

```
   604.1442              666.4908              712.7169
   916.1714              967.3253             1077.7630
  1168.2782             1214.5316             1347.3076
  1387.5419             1481.0545             1551.5580
  1648.0352             2637.2287             2697.9883
  2793.7915             3408.4866             3643.0771

E = -359.698901
```

Glycyl radical in H_2O

```
N        1.813000    0.028015   -0.052129
C        0.654649   -0.667742    0.004241
C       -0.612967    0.019891    0.001467
O       -1.664853   -0.676945    0.002989
O       -0.595530    1.281286    0.001156
H        1.755070    1.019731    0.109050
H        2.679483   -0.421156    0.188093
H        0.707423   -1.742303    0.000349

   202.2118              271.9505              355.5655
   435.3546              545.0771              635.2115
   692.5311              793.6467              955.5085
  1117.6707             1297.7191             1349.2724
  1534.2011             1554.7890             1635.3783
  3243.2328             3538.6089             3654.6432

E = -283.327218
```

Glycyl radical gas-phase

```
N        1.804026   -0.001307   -0.096899
C        0.633356   -0.720535    0.006912
C       -0.633229    0.035408    0.002636
O       -1.686205   -0.625316   -0.000325
O       -0.493654    1.281760    0.014416
H        1.560808    0.972407    0.035771
H        2.576247   -0.307951    0.465586
H        0.672873   -1.796088    0.006917

   176.2237              297.8939              367.0349
   493.5984              528.1791              693.1453
   784.8081              807.8132              945.4113
  1107.0870             1291.0026             1352.7695
  1478.5202             1583.8200             1707.9399
  3246.7511             3520.3396             3666.7900

E =  -283.202778837
E(CCSD(T)) = -282.79170976
```

Aminyl radical in H_2O

```
N        1.896849    0.053202   -0.210458
C        0.747341   -0.675896    0.152530
C       -0.597781    0.051889    0.009165
O       -1.594556   -0.679689   -0.111897
O       -0.587427    1.291868    0.050007
H        1.761298    1.027938    0.104395
H        0.814014   -0.905106    1.257527
H        0.705246   -1.648631   -0.363765

    46.2298              292.6885              351.4678
   502.1459              580.7274              703.8318
   909.3416              918.7384             1079.2560
  1131.8350             1231.2820             1335.0268
  1373.6218             1435.6965             1649.2910
  2333.8571             2766.0306             3126.9988

E = -283.302588
```

Aminyl radical gas-phase

```
N        1.875342    0.041677   -0.225287
C        0.743612   -0.695005    0.179907
C       -0.614315    0.061777    0.007417
O       -1.599804   -0.662946   -0.134544
O       -0.524828    1.293527    0.071885
H        1.592767    1.003674   -0.027505
H        0.794965   -0.863478    1.265910
H        0.706144   -1.677216   -0.284069

   98.2997               295.8098              439.0360
  483.0544               588.0690              710.4844
  879.6343               935.9866             1085.9058
 1122.4938              1244.1778             1384.3627
 1412.2617              1456.1987             1782.8327
 2957.6366              3111.2930             3443.0174

E =  -283.190783118
E(CCSD(T)) = -282.78142459
```

Water in H_2O

```
O        0.000000    0.000000    0.117183
H        0.000000    0.757883   -0.468731
H        0.000000   -0.757883   -0.468731

 1609.9336             3817.1865             3893.9942
```

```
E = -76.432660
```

Water gas-phase

```
O        0.000000    0.000000    0.115180
H        0.000000    0.756283   -0.460718
H        0.000000   -0.756283   -0.460718

 1654.2090              3966.9811              4074.3926

E =  -76.4231834916
E(CCSD(T)) = -76.32792876
```