# Supporting Information

# Reactions of Simple and Peptidic alpha-Carboxylate Radical Anions with Dioxygen in the Gas Phase

*Tony Ly[1†], Benjamin B. Kirk[1], Pramesh I. Hettiarachchi[1], Berwyck L. J. Poad[1‡], Adam J. Trevitt[1], Gabriel da Silva*[2], Stephen J. Blanksby*[1]*

[1]School of Chemistry, University of Wollongong NSW 2522 Australia

[2]Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010 Australia

**Current Address:**

[†]College of Life Sciences, University of Dundee, Dow St, Dundee DD1 5EH UK

[‡]Department of Chemistry and Biochemistry, University of California, San Diego USA

***Correspondence to:**

Stephen J. Blanksby, School of Chemistry University of Wollongong, NSW 2522, AUSTRALIA.

Email: blanksby@uow.edu.au

Gabriel da Silva, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, AUSTRALIA.

Email: gdasilva@unimelb.edu.au

**TABLE OF CONTENTS**

**Figure S1**

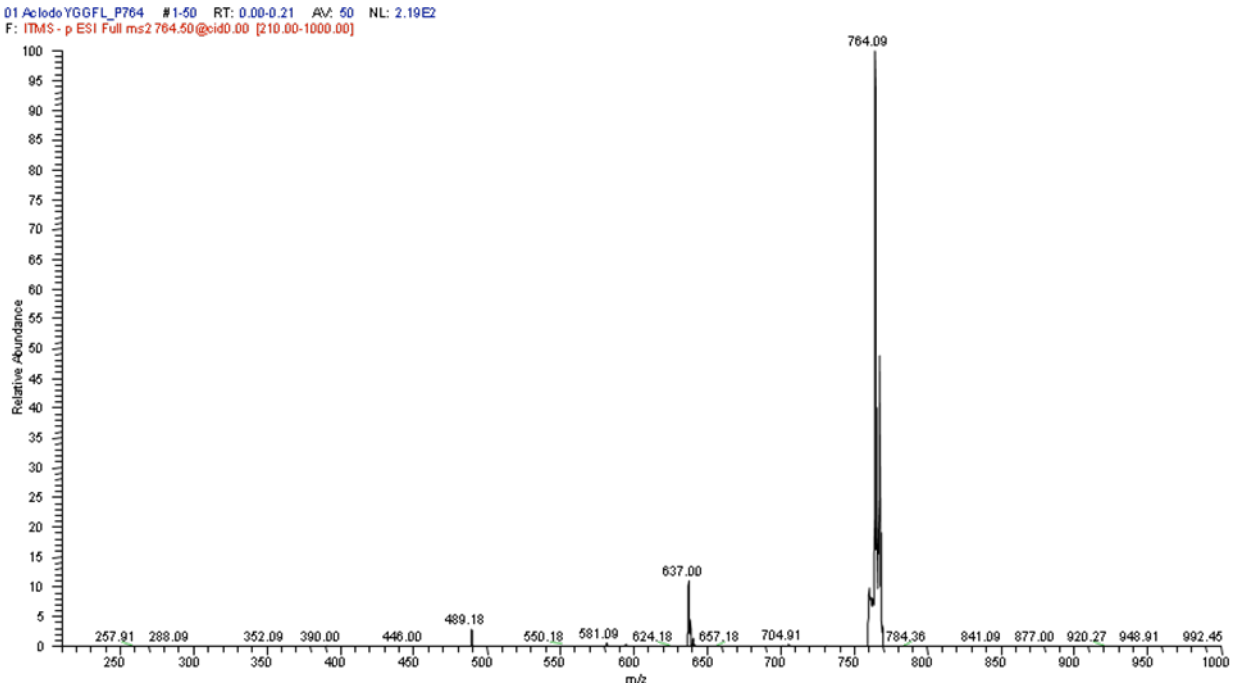

**Figure S2**

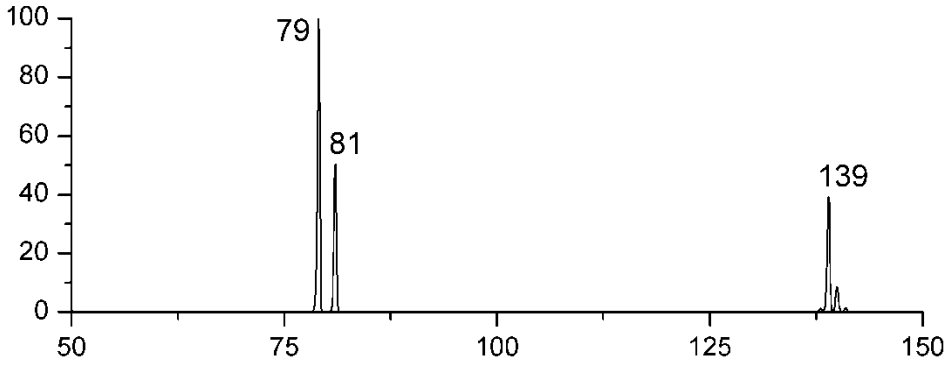

**Figure S3**

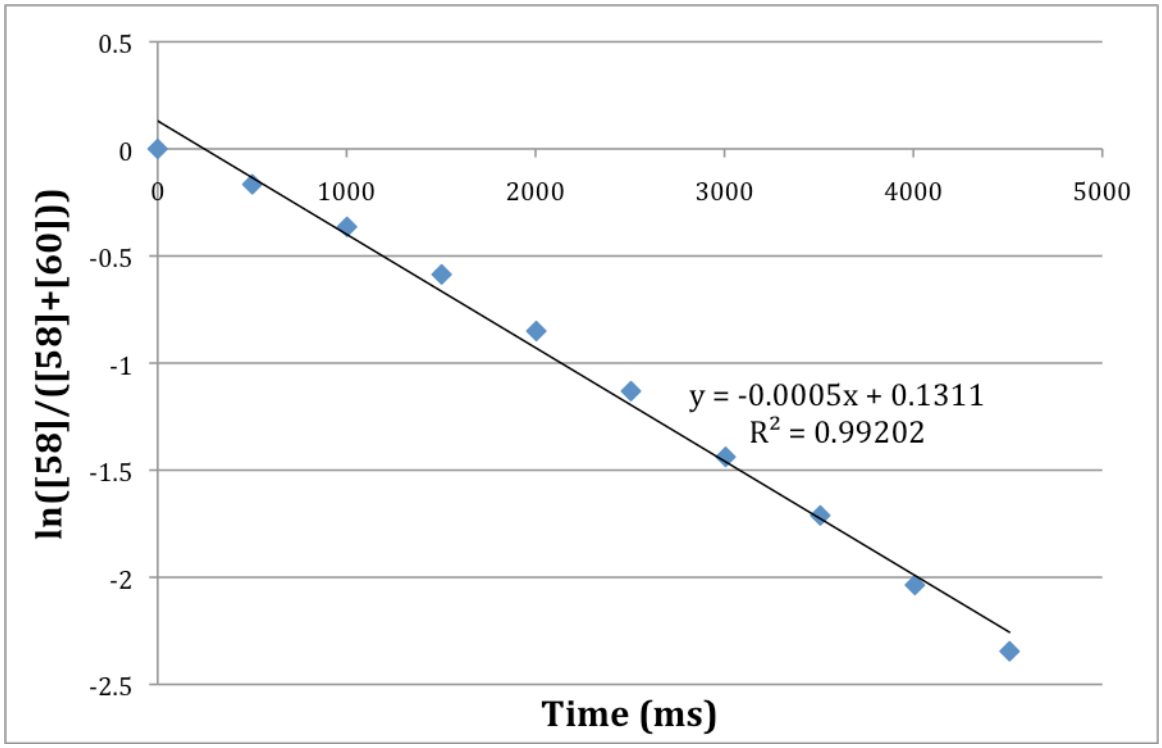

**Figure S4**

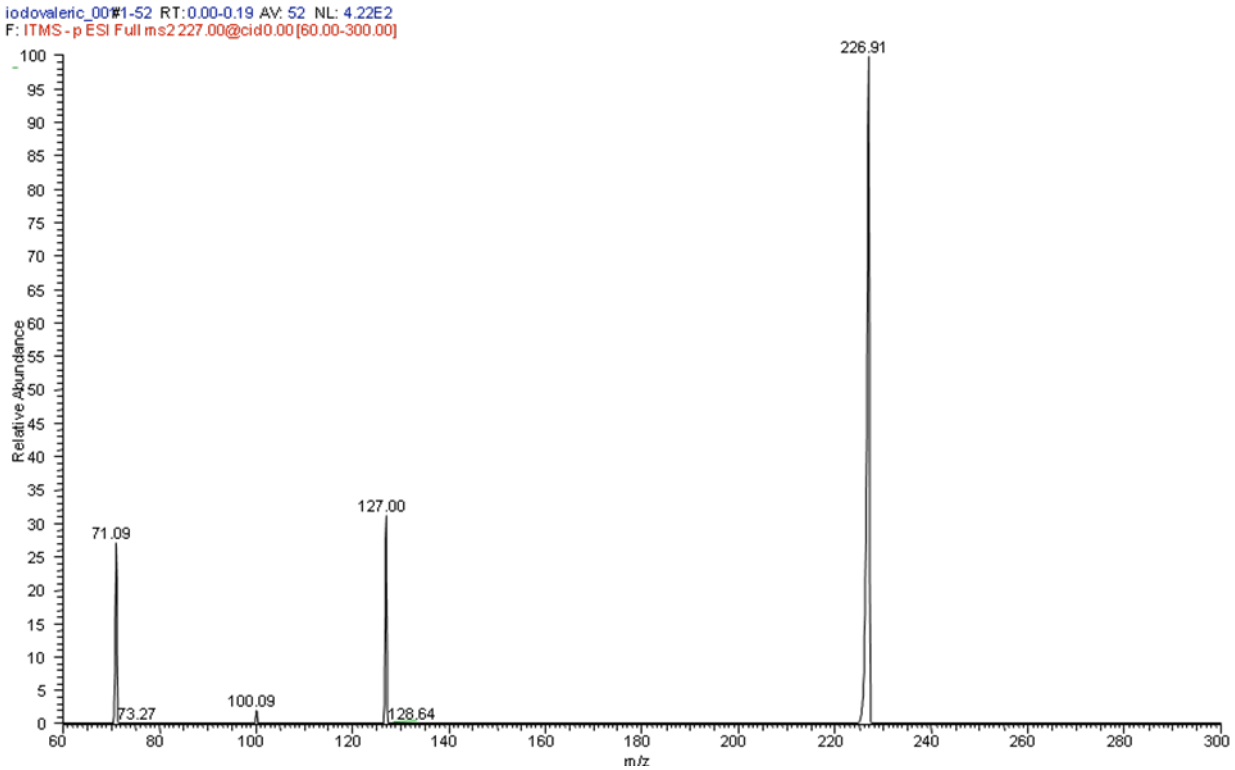
iodovaleric_001#1-52 RT:0.00-0.19 AV: 52 NL: 4.22E2
F: ITMS - p ESI Full ms2 227.00@cid0.00 [60.00-300.00]
Relative Abundance
m/z
226.91
127.00
71.09
100.09
73.27
128.64

**Figure S5**

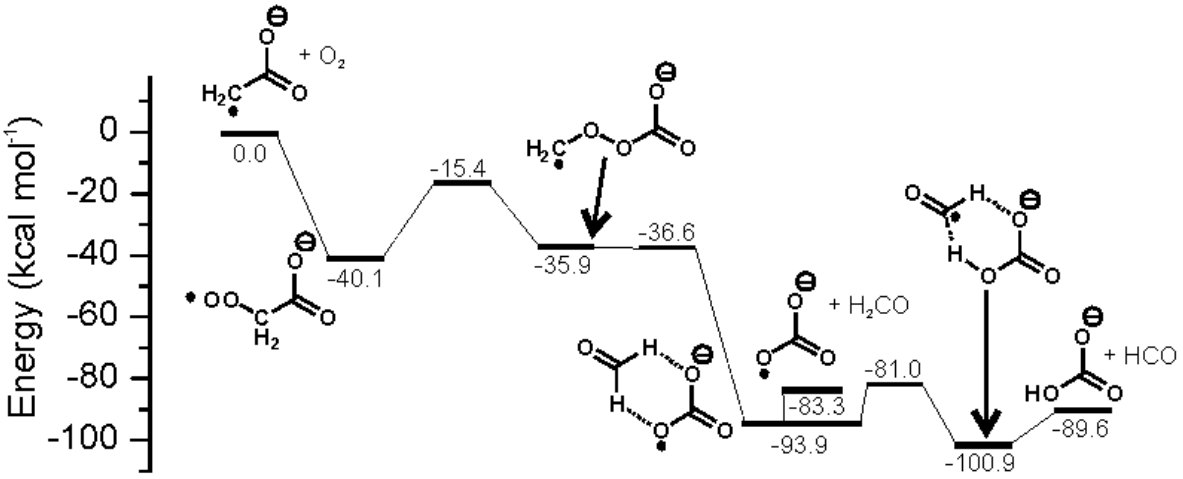

**Figure S6**

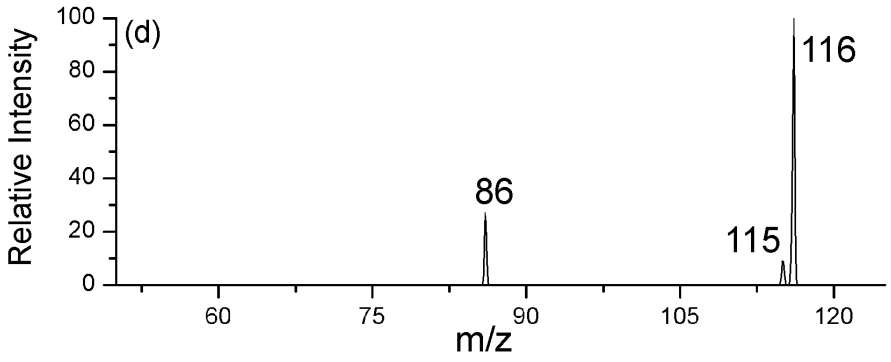

**Figure S7**

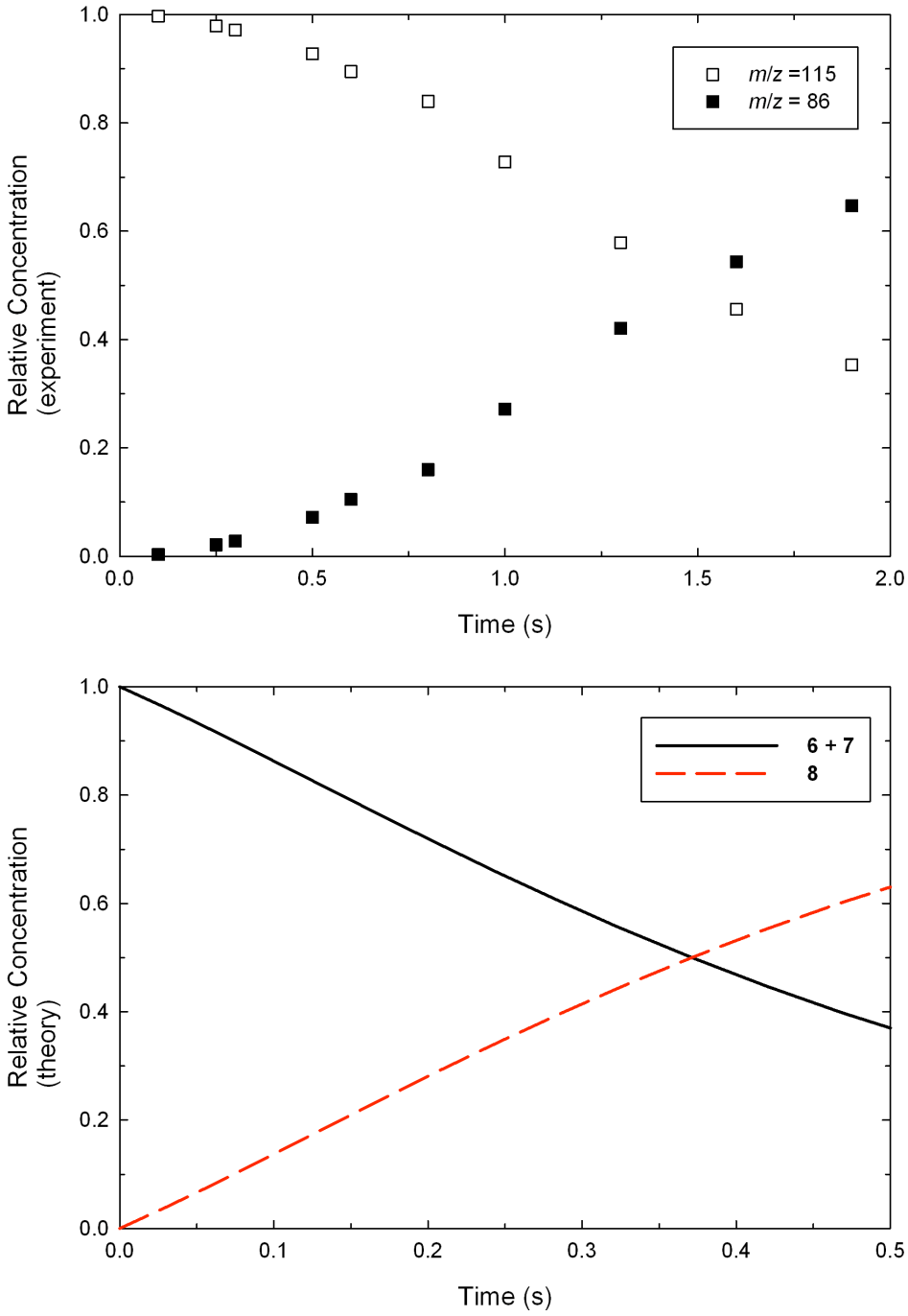
Relative Concentration (experiment)
Time (s)
m/z =115
m/z = 86
Relative Concentration (theory)
Time (s)
6 + 7
8

**Figure S8**. a) PD of iodinated YGGFL produces loss of iodine atom. inset) CID of the radical peptide yields several sidechain losses, including loss of leucine sidechain, which produces YGGFG• as the product. b) Reaction of YGGFG• with $O_2$ produces a 29 Da loss, which was observed for radical acetylglycinate. c) CID of the YGGFG• does not yield the 29 Da loss, indicating that this loss is due to ion-molecule chemistry.

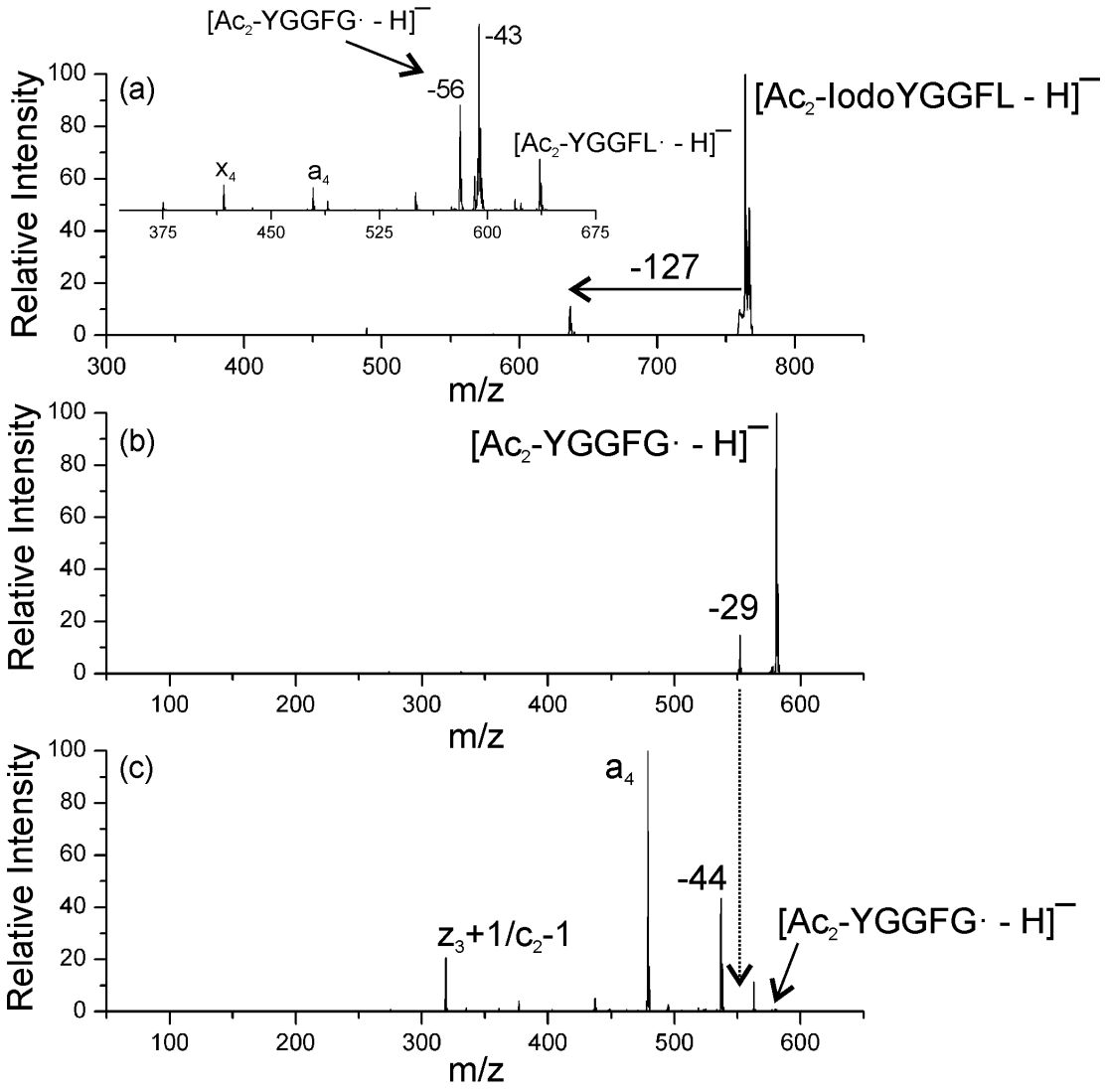

**Table S1**

| $CH_2(OO)COO^-$ | | | |
|---|---|---|---|
| C | -0.584732 | -0.484399 | 1.748618 |
| O | -1.003699 | 0.213376 | 0.804203 |
| C | -1.738195 | -1.478491 | 2.234603 |
| H | -1.938609 | -2.201628 | 1.439768 |
| H | -2.637554 | -0.895711 | 2.455594 |
| O | -0.780079 | -3.318098 | 3.222779 |
| O | -1.467666 | -2.210387 | 3.440537 |
| O | 0.500570 | -0.553497 | 2.333936 |

| TS: $CH_2(OO)COO^- \rightarrow HCHO + CO_3^-$ | | | |
|---|---|---|---|
| C | -0.070585 | -0.428146 | 1.215461 |
| O | -0.543704 | 0.619451 | 0.957518 |
| C | -2.077056 | -1.641427 | 2.145729 |
| H | -1.413905 | -2.477307 | 2.376639 |
| H | -3.049486 | -1.877169 | 1.699371 |
| O | -0.989378 | -0.460201 | 3.753369 |
| O | -2.207242 | -0.727391 | 3.117372 |
| O | 0.714476 | -1.309293 | 1.248143 |

| $CH_3C(O)NHCH(OO)COO^-$ | | | |
|---|---|---|---|
| C | 3.877672 | 0.151728 | 1.146122 |
| O | 2.974611 | 0.773719 | 0.547973 |
| C | 4.796633 | 1.096107 | 2.072937 |
| O | 7.036572 | 0.463704 | 2.152609 |
| O | 6.144498 | 1.155712 | 1.474516 |
| O | 4.204963 | -1.036632 | 1.172407 |
| N | 4.243364 | 2.400211 | 2.080105 |
| H | 3.482591 | 2.463516 | 1.39984 |
| H | 4.954264 | 0.647932 | 3.055219 |
| C | 4.555331 | 3.46248 | 2.870143 |
| C | 5.654118 | 3.226836 | 3.901424 |
| H | 5.313848 | 2.51601 | 4.663347 |
| H | 6.552885 | 2.801889 | 3.448224 |
| H | 5.882604 | 4.17972 | 4.380053 |
| O | 3.984686 | 4.540423 | 2.777837 |

| $CH_3C(O)N^-CH(OO)COOH$ | | | |
|---|---|---|---|
| C | 1.363039 | 2.840275 | 0.094988 |
| O | 2.209007 | 4.777067 | -0.922746 |
| O | 1.724646 | 3.583618 | -1.170652 |
| N | 0.249893 | 3.381372 | 0.755288 |
| H | 1.262117 | 3.725964 | 1.992796 |
| C | -0.951452 | 2.864736 | 0.431449 |
| O | -1.200405 | 2.013848 | -0.432679 |
| C | -2.108982 | 3.425209 | 1.267314 |
| H | -1.776103 | 4.183039 | 1.980084 |
| H | -2.86102 | 3.859374 | 0.599192 |
| H | -2.597917 | 2.60566 | 1.80652 |
| C | 2.585296 | 2.930612 | 1.045222 |
| O | 2.250521 | 3.531445 | 2.181374 |
| O | 3.681493 | 2.486132 | 0.798132 |
| H | 1.227752 | 1.829725 | -0.308307 |

| $CH_3C(O)NCHCOO^-$ --- $HO_2$ | | | |
|---|---|---|---|
| C | 1.538110 | 1.398858 | 3.623587 |
| O | 2.331548 | 3.014640 | 0.590445 |
| O | 3.506683 | 3.604906 | 0.455942 |
| N | 2.555273 | 1.605675 | 2.841515 |
| H | 2.389972 | 2.465388 | 1.468354 |
| C | 3.822286 | 1.167065 | 3.311468 |
| O | 4.040832 | 0.750320 | 4.432075 |
| C | 4.904063 | 1.276445 | 2.259929 |
| H | 4.697200 | 0.557821 | 1.457618 |
| H | 4.878856 | 2.266942 | 1.795318 |
| H | 5.878264 | 1.059342 | 2.700709 |
| C | 0.096925 | 1.637721 | 3.229370 |
| O | -0.376260 | 2.771116 | 3.141029 |
| O | -0.380407 | 0.489074 | 3.056535 |
| H | 1.716710 | 0.906465 | 4.584956 |

| TS: $CH_3C(O)NHCH(OO)COO^-$ → $CH_3C(O)NHCHO + CO_3^-$ | | | |
|---|---|---|---|
| C | 5.856921 | 6.041961 | 2.426469 |
| O | 5.547452 | 5.777996 | 3.532037 |
| C | 8.308933 | 6.007014 | 2.603380 |
| H | 8.393312 | 6.395475 | 1.588513 |
| O | 7.652560 | 8.062474 | 3.278849 |
| O | 8.384768 | 6.896585 | 3.589185 |
| O | 5.754335 | 6.259581 | 1.268334 |
| N | 9.057875 | 4.840371 | 2.910066 |
| H | 9.345498 | 4.754196 | 3.875942 |
| C | 9.303407 | 3.752288 | 2.136911 |
| O | 9.905422 | 2.763532 | 2.558134 |
| C | 8.784203 | 3.852228 | 0.712522 |
| H | 9.328310 | 4.623310 | 0.153288 |
| H | 8.923346 | 2.887610 | 0.223181 |
| H | 7.728112 | 4.143151 | 0.697362 |

| TS: $CH_3C(O)NHCH(OO)COO^-$ → $CH_3C(O)N^-CH(OO)COOH$ | | | |
|---|---|---|---|
| C | 1.378687 | 2.791420 | 0.036770 |
| O | 2.108504 | 4.742795 | -1.008288 |
| O | 1.769356 | 3.492765 | -1.219842 |
| N | 0.247602 | 3.345370 | 0.672185 |
| H | 0.959132 | 3.637422 | 1.752864 |
| C | -0.981335 | 2.879561 | 0.372092 |
| O | -1.267897 | 2.083743 | -0.525396 |
| C | -2.091260 | 3.427871 | 1.274789 |
| H | -1.729876 | 4.193776 | 1.964687 |
| H | -2.889525 | 3.844014 | 0.651775 |
| H | -2.528965 | 2.603205 | 1.848649 |
| C | 2.531474 | 2.934203 | 1.092761 |
| O | 2.059308 | 3.502353 | 2.164596 |
| O | 3.661973 | 2.535385 | 0.889598 |
| H | 1.252538 | 1.768936 | -0.333005 |

| TS: $CH_3C(O)NHCH(OO)COO^-$ → $CH_3C(O)N^-CHO + CO_2 + OH$ | | | |
|---|---|---|---|
| C | 8.891193 | 3.500433 | 3.619458 |
| O | 8.530487 | 3.529437 | 2.480820 |
| C | 10.641121 | 4.744282 | 3.720906 |
| H | 10.434167 | 5.065066 | 4.739271 |
| O | 12.291324 | 3.976646 | 2.335103 |
| O | 11.690394 | 3.870602 | 3.628346 |
| O | 8.759419 | 3.104894 | 4.743138 |
| N | 10.669867 | 5.611158 | 2.666161 |
| H | 11.519863 | 5.036840 | 2.077931 |
| C | 9.849678 | 6.671981 | 2.516101 |
| O | 9.020884 | 7.045650 | 3.345099 |
| C | 10.010205 | 7.403700 | 1.185406 |
| H | 9.928516 | 8.481535 | 1.352146 |
| H | 10.958196 | 7.174268 | 0.691824 |
| H | 9.193750 | 7.110873 | 0.514892 |

| TS: $CH_3C(O)N^-CH(OO)COOH$ → $CH_3C(O)N^-CHO + CO_2 + OH$ | | | |
|---|---|---|---|
| C | 0.963370 | 2.137801 | 0.148416 |
| O | 2.523342 | 0.486159 | -0.669367 |
| O | 1.482937 | 0.767723 | 0.220452 |
| N | -0.123150 | 2.059268 | -0.760459 |
| H | 2.937505 | 1.521814 | -0.793887 |
| C | -1.371020 | 2.169402 | -0.220755 |
| O | -1.675791 | 2.011090 | 0.963222 |
| C | -2.446910 | 2.449773 | -1.267405 |
| H | -2.743463 | 1.508346 | -1.744787 |
| H | -3.324240 | 2.885705 | -0.784111 |
| H | -2.071223 | 3.111616 | -2.051589 |
| C | 1.996705 | 3.240414 | -0.253133 |
| O | 3.087393 | 2.805528 | -0.771563 |
| O | 1.672033 | 4.398886 | -0.038232 |
| H | 0.635661 | 2.315175 | 1.180323 |

| TS: $CH_3C(O)NHCH(OO)COO^-$ → $CH_3C(O)NCHCOO^-$ --- $HO_2$ | | | |
|---|---|---|---|
| C | 6.996894 | 2.926122 | 0.616351 |
| O | 9.627141 | 4.146470 | -0.010473 |
| O | 9.324236 | 3.002309 | -0.556911 |
| N | 7.281838 | 4.228174 | 0.645444 |
| H | 8.434039 | 4.377073 | 0.600981 |
| C | 6.573764 | 5.104156 | -0.180350 |
| O | 5.462168 | 4.881072 | -0.617504 |
| C | 7.320813 | 6.398776 | -0.454342 |
| H | 7.515968 | 6.926326 | 0.485598 |
| H | 8.292799 | 6.177206 | -0.905502 |
| H | 6.724491 | 7.030319 | -1.113506 |
| C | 7.281059 | 2.003158 | 1.784352 |
| O | 8.342103 | 1.495979 | 2.109524 |
| O | 6.115877 | 1.991780 | 2.276124 |
| H | 6.272106 | 2.591999 | -0.122533 |

**Table S2**

| $CH_2(OO)COO^-$ | | | | | |
|---|---|---|---|---|---|
| 54.5018 | 393.7268 | 672.2038 | 992.0499 | 1278.436 | 1791.106 |
| 92.1143 | 514.5036 | 820.2241 | 1129.286 | 1334.546 | 3046.351 |
| 246.9155 | 595.0701 | 900.2668 | 1256.315 | 1426.468 | 3117.081 |

| TS: $CH_2(OO)COO^- \rightarrow HCHO + CO_3^-$ | | | | | |
|---|---|---|---|---|---|
| 117.9032 | 259.8918 | 515.0576 | 919.7203 | 1297.726 | 3005.183 |
| 139.3896 | 460.2529 | 615.9406 | 1155.062 | 1442.52 | 3124.62 |
| 166.6173 | 486.9479 | 715.1706 | 1226.03 | 2269.815 | |

| $CH_3C(O)NHCH(OO)COO^-$ | | | | | | |
|---|---|---|---|---|---|---|
| 36.2584 | 237.5598 | 589.6495 | 854.4227 | 1235.745 | 1470.907 | 3112.216 |
| 56.6862 | 295.9537 | 646.8605 | 899.7196 | 1295.842 | 1486.967 | 3152.149 |
| 77.6105 | 382.1549 | 680.4974 | 1029.674 | 1333.629 | 1761.714 | 3423.991 |
| 87.0261 | 408.5724 | 753.8194 | 1051.216 | 1354.604 | 1804.218 | |
| 128.5216 | 424.5014 | 806.4876 | 1187.042 | 1394.759 | 3041.256 | |
| 150.7792 | 512.2178 | 827.4959 | 1197.976 | 1449.693 | 3098.718 | |

| $CH_3C(O)N^-CH(OO)COOH$ | | | | | | |
|---|---|---|---|---|---|---|
| 51.5005 | 228.1974 | 586.298 | 991.5152 | 1216.49 | 1481.511 | 3046.928 |
| 66.4902 | 286.1673 | 636.5899 | 1007.587 | 1280.362 | 1571.154 | 3086.305 |
| 82.3531 | 367.3953 | 679.6387 | 1019.249 | 1344.589 | 1687.457 | 3122.658 |
| 83.5096 | 384.681 | 744.6869 | 1049.085 | 1351.999 | 1842.027 | |
| 117.564 | 520.5106 | 830.078 | 1136.1 | 1386.518 | 2789.562 | |
| 151.9726 | 557.3293 | 910.7217 | 1186.596 | 1474.842 | 3026.801 | |

| $CH_3C(O)NCHCOO^-$ --- $HO_2$ | | | | | | |
|---|---|---|---|---|---|---|
| 27.6525 | 158.471 | 417.2031 | 917.8881 | 1240.703 | 1557.425 | 3080.526 |
| 34.6236 | 196.7685 | 583.5339 | 978.8292 | 1329.615 | 1680.347 | 3097.3 |
| 50.4844 | 233.3296 | 618.684 | 989.7182 | 1385.955 | 1763.073 | 3146.093 |
| 71.9102 | 269.1618 | 684.1402 | 1022.166 | 1396.685 | 1772.315 | |
| 92.6074 | 310.1742 | 761.1207 | 1070.99 | 1470.252 | 2556.855 | |
| 139.2692 | 341.81 | 895.5422 | 1227.696 | 1477.328 | 3032.262 | |

| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)NHCHO + CO_3^-$ | | | | | | |
|---|---|---|---|---|---|---|
| 40.4375 | 183.9707 | 525.3479 | 861.4544 | 1278.04 | 1480.292 | 3145.275 |
| 60.329 | 207.9924 | 535.1328 | 909.0035 | 1285.299 | 1741.711 | 3592.288 |
| 82.5402 | 278.9617 | 601.7919 | 1029.142 | 1353.153 | 2257.889 | |
| 115.1626 | 353.8188 | 620.9753 | 1044.266 | 1400.613 | 3026.529 | |
| 139.0099 | 396.9248 | 672.9083 | 1160.433 | 1463.652 | 3084.377 | |
| 153.1775 | 490.4829 | 735.6285 | 1232.253 | 1476.11 | 3090.164 | |

| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)N^-CH(OO)COOH$ | | | | | | |
|---|---|---|---|---|---|---|
| 51.454 | 236.3118 | 628.2601 | 994.0321 | 1256.142 | 1482.624 | 3094.226 |
| 61.6842 | 300.2938 | 668.8831 | 1026.387 | 1343.688 | 1710.968 | 3125.366 |
| 79.9102 | 370.4006 | 712.9698 | 1050.023 | 1360.959 | 1804.248 | |
| 100.6666 | 490.2036 | 810.703 | 1137.056 | 1366.513 | 2046.452 | |
| 122.346 | 538.1434 | 874.6179 | 1181.078 | 1417.131 | 3031.787 | |
| 160.154 | 578.3468 | 908.7907 | 1215.031 | 1477.863 | 3069.214 | |

| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)N^-CHO + CO_2 + OH$ | | | | | | |
|---|---|---|---|---|---|---|
| 44.9693 | 169.4822 | 596.6333 | 924.1494 | 1195.87 | 1487.973 | 3122.093 |
| 47.3736 | 210.1597 | 611.9886 | 985.3566 | 1261.026 | 1713.204 | 3132.702 |
| 60.437 | 260.7728 | 646.1008 | 1038.58 | 1345.285 | 2103.719 | |
| 78.9282 | 384.5925 | 663.2684 | 1047.577 | 1380.724 | 2180.371 | |
| 86.4119 | 462.6115 | 771.4767 | 1063.263 | 1463.175 | 3030.888 | |
| 139.6416 | 522.9486 | 843.2304 | 1119.27 | 1475.34 | 3095.795 | |

| TS: $CH_3C(O)N^-CH(OO)COOH \rightarrow CH_3C(O)N^-CHO + CO_2 + OH$ | | | | | | |
|---|---|---|---|---|---|---|
| 36.5203 | 238.8006 | 621.0106 | 945.3916 | 1253.295 | 1475.004 | 3102.829 |
| 53.5202 | 347.6749 | 699.5294 | 981.2895 | 1300.346 | 1634.949 | 3135.932 |
| 58.438 | 389.5804 | 732.5013 | 992.2793 | 1317.612 | 1802.159 | |
| 79.0469 | 439.3504 | 804.1146 | 1043.763 | 1371.364 | 1898.476 | |
| 128.5462 | 542.2094 | 841.35 | 1105.408 | 1424.733 | 3034.414 | |
| 214.5607 | 598.1679 | 901.1679 | 1154.011 | 1470.104 | 3035.098 | |

| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)NCHCOO^-$ --- $HO_2$ | | | | | | |
|---|---|---|---|---|---|---|
| 51.221 | 160.5886 | 565.7832 | 917.3399 | 1320.611 | 1587.277 | 3151.689 |
| 76.1689 | 221.9623 | 596.2938 | 988.6765 | 1352.863 | 1785.741 | 3164.094 |
| 87.932 | 278.4413 | 659.9525 | 1056.266 | 1381.326 | 1788.917 | |
| 91.7978 | 353.7269 | 747.2524 | 1075.489 | 1402.193 | 1814.136 | |
| 123.556 | 423.3192 | 757.8384 | 1234.763 | 1474.272 | 3041.64 | |
| 143.963 | 443.5603 | 887.4312 | 1257.569 | 1477.181 | 3107.624 | |

**Table S3**

| | *1D* | *2D* |
|---|---|---|
| $CH_2(OO)COO^-$ | 59.4531 | 227.8358 |
| TS: $CH_2(OO)COO^- \rightarrow HCHO + CO_3^-$ | 88.7986 | 209.6666 |
| $CH_3C(O)NHCH(OO)COO^-$ | 260.5116 | 612.7246 |
| $CH_3C(O)N^-CH(OO)COOH$ | 235.7866 | 607.1541 |
| $CH_3C(O)NCHCOO^-$ --- $HO_2$ | 846.8681 | 451.2652 |
| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)NHCHO + CO_3^-$ | 269.5926 | 691.6023 |
| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)N^-CH(OO)COOH$ | 239.2606 | 598.4794 |
| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)N^-CHO + CO_2 + OH$ | 317.2466 | 563.1054 |
| TS: $CH_3C(O)N^-CH(OO)COOH \rightarrow CH_3C(O)N^-CHO + CO_2 + OH$ | 240.5580 | 619.2209 |
| TS: $CH_3C(O)NHCH(OO)COO^- \rightarrow CH_3C(O)NCHCOO^-$ --- $HO_2$ | 296.5573 | 612.9434 |