Supplementary Material (ESI) for *PCCP*

Electronic Supplementary Information

Gas phase fragmentation of protonated betaine and its clusters

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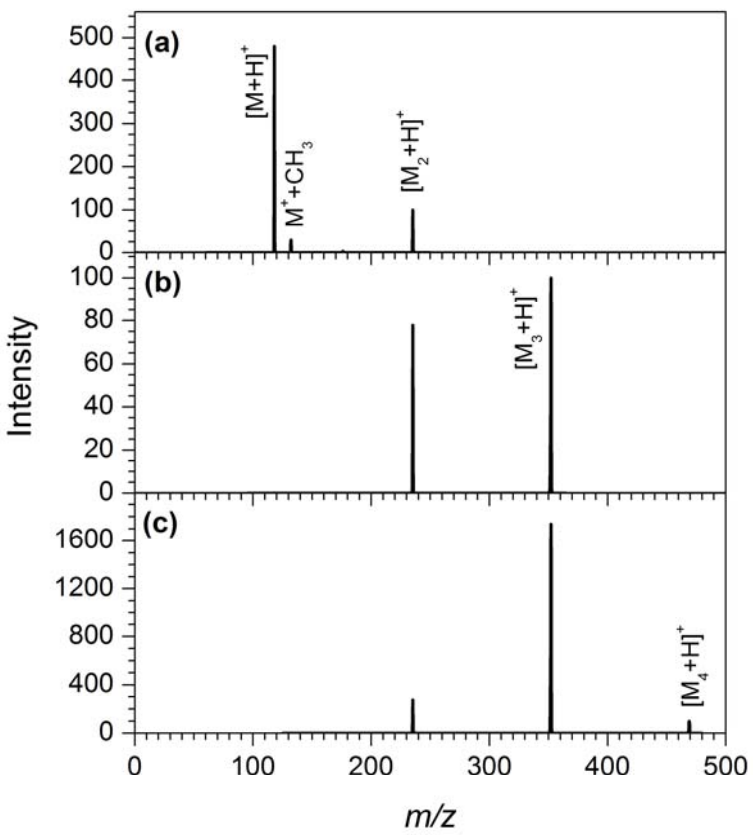


Fig. S1: CID spectra resulting from low energy collisions of $[M_n + H]^+$ with He, where M is $(CH_3)_3N^+CH_2COO^-$ and *n* is (a) 2, (b) 3, and (c) 4. The intensities of the parent peaks are set to 100.

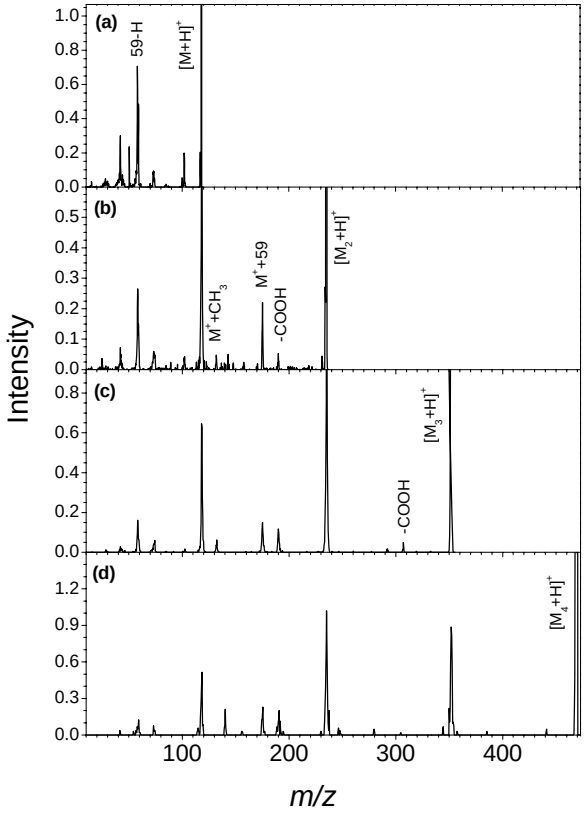


Fig. S2: CID spectra resulting from high energy collisions of $[M_n + H]^+$ with O_2, where M is $(CH_3)_3N^+CH_2COO^-$ and *n* is (a) 1, (b) 2, (c) 3 and (d) 4. The intensities of the parent peaks are set to 100. In (b) and (c) the intensities of the peaks corresponding to evaporation of one neutral betaine molecule are 2.05 and 1.83, respectively. See main text for assignment of peak at *m/z* 59.

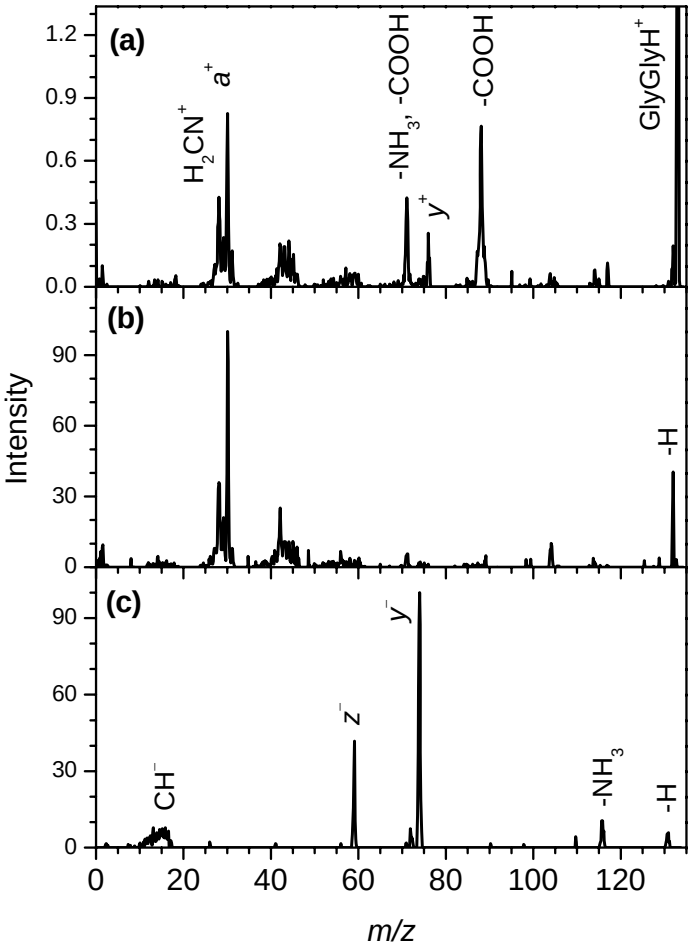


Fig. S3: Spectra resulting from high energy collisions of $GlyGlyH^+$ with Cs and O_2. The graphs show spectra from experiments investigating (a) CID (O_2), (b) neutral reionisation and (c) charge reversal. The largest peaks in the spectra are set to 100.

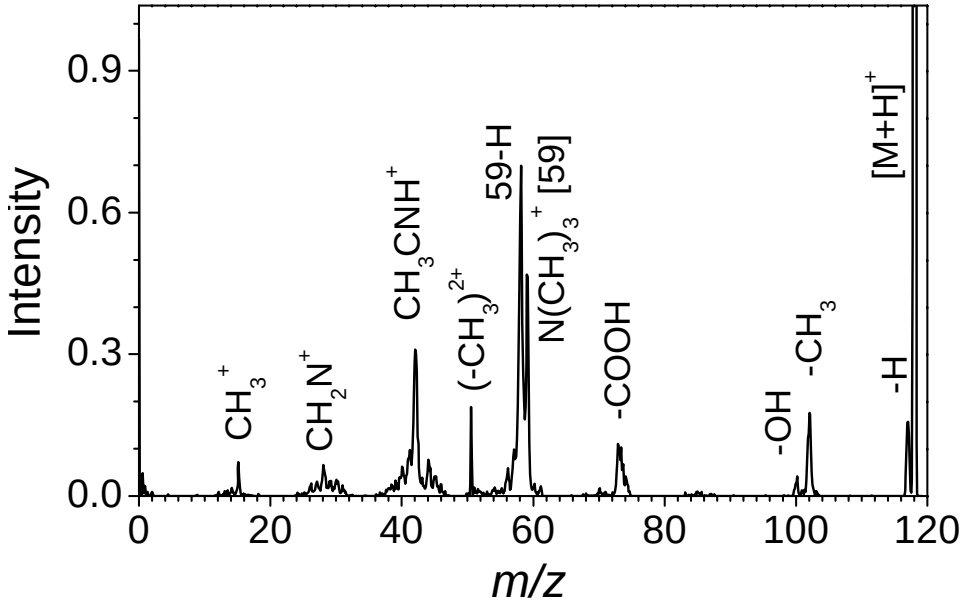


Fig. S4: CID spectrum resulting from high energy collisions of $^+(CH_3)_3NCH_2COOH$ with Cs and O_2. The intensity of the parent peak is set to 100.

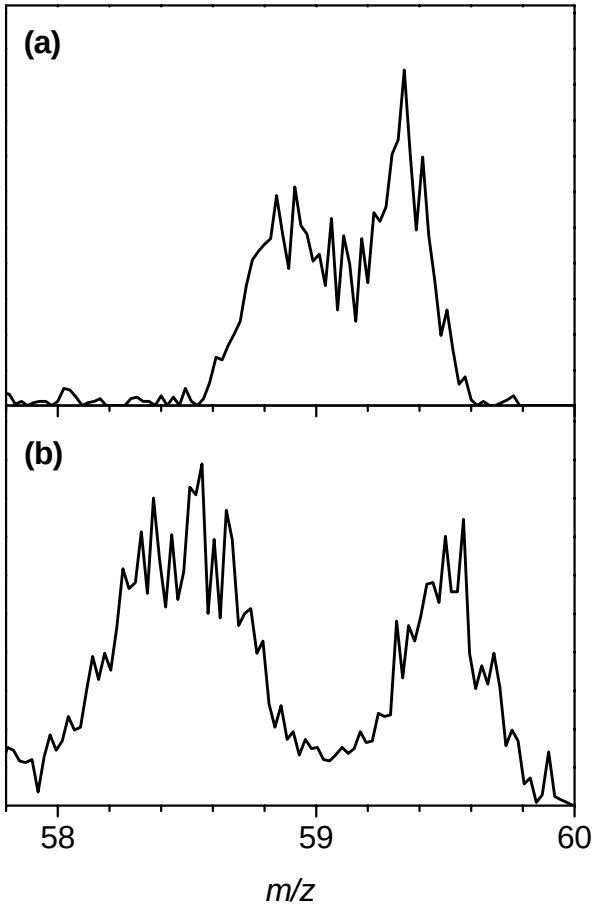
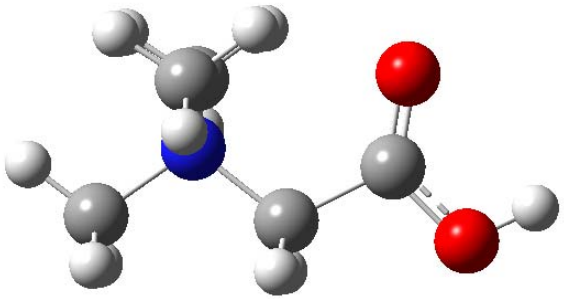
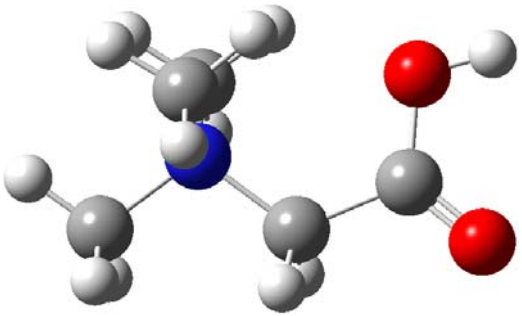


Fig. S5: Charge reversal spectra resulting from high energy collisions of $^{+}(CH_3)_3NCH_2COOH$ with Cs. The energy of the projectile beam is (a) 50 keV and (b) 25 keV.





$[M+H]^+$

C	1.53931600	0.00701200	-0.00017800
C	0.26625700	-0.83481700	-0.00119900
O	1.59099600	1.20649100	0.00017800
O	2.58543700	-0.81714800	-0.00009300
N	-1.02630100	-0.05489200	-0.00006600
H	0.27084700	-1.47718900	-0.88230600
H	0.27083400	-1.47909700	0.87851300
H	3.40748100	-0.29593200	0.00011900
C	-1.14510100	0.80428400	1.23874500
C	-2.15562600	-1.05588900	-0.00194100
C	-1.14489600	0.80901800	-1.23561400
H	-0.35430700	1.54652800	1.22752200
H	-1.06103600	0.16360300	2.11441900
H	-2.12102500	1.28369800	1.22324600
H	-3.09734000	-0.51226400	-0.00083000
H	-2.08345700	-1.67604600	0.88896400
H	-2.08355400	-1.67254000	-0.89527600
H	-2.12060500	1.28880300	-1.21816100
H	-1.06126500	0.17157700	-2.11369100
H	-0.35363500	1.55071700	-1.22162100

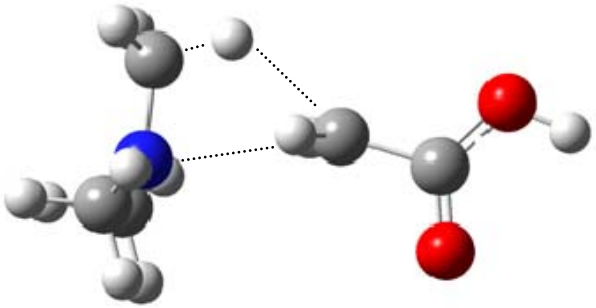
Filename: betH+
Sum of electronic and
zero-point energies = -402.67793 Hartrees

$[M+H]^+$ isomer

C	1.62084200	-0.19982100	-0.03748500
C	0.24508800	-0.85104500	-0.18492100
O	1.62666200	1.14453500	-0.01067700
O	2.59034400	-0.89287600	0.01728500
N	-1.02277800	-0.03783500	0.00277200
H	0.20457200	-1.28520000	-1.18481000
H	0.21486700	-1.66936200	0.53278300
C	-1.05447300	0.61568300	1.36314800
C	-2.18255400	-1.00149200	-0.09320700
C	-1.18058600	1.00525400	-1.07790000
H	-0.25532800	1.34671500	1.42499800
H	-0.92831600	-0.15364200	2.12243300
H	-2.01995900	1.10117000	1.48535400
H	-3.10731600	-0.44052600	0.01895600
H	-2.09667900	-1.74062800	0.70009900
H	-2.15897200	-1.48957000	-1.06506900
H	-2.13174600	1.51000200	-0.92499900
H	-1.17777000	0.50606400	-2.04474100
H	-0.36149300	1.71261500	-1.01342400
H	2.55164600	1.44245700	0.05833900

Filename: Bet_TS-6ringB_high_OPT_REV
Sum of electronic and
zero-point energies = -402.67148 Hartrees

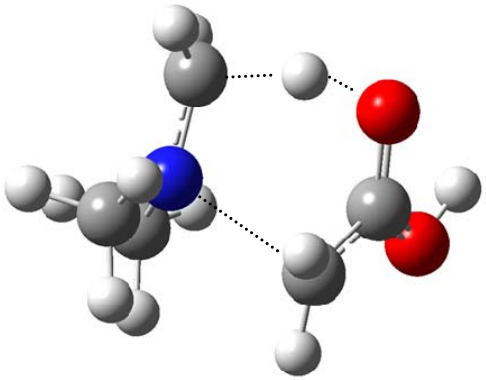
Figure S6: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for species relevant to the $[M+H]^+$.



TS1

N	-1.86393000	0.03353400	0.00000900
C	-1.69095400	1.43965900	-0.00017300
H	-0.58422900	1.71685700	-0.00034800
H	-2.09403100	1.90957700	-0.89776400
H	-2.09381900	1.90977700	0.89740600
C	-2.29746000	-0.61303400	1.23577100
H	-2.04346400	-1.67187900	1.20896600
H	-1.81652900	-0.14789600	2.09578000
H	-3.38425000	-0.51855300	1.35697000
C	-2.29741500	-0.61332400	-1.23561600
H	-1.81636600	-0.14846500	-2.09571200
H	-2.04352500	-1.67218700	-1.20850900
H	-3.38418500	-0.51876800	-1.35693700
C	2.32909600	-0.12259700	-0.00000300
O	2.39306400	-1.32905300	0.00004800
O	3.29581000	0.75907100	0.00001000
H	4.16722200	0.31922100	0.00006000
C	0.92833600	0.32453700	-0.00004700
H	0.40008400	0.32824600	0.93803000
H	0.39998800	0.32774100	-0.93806800

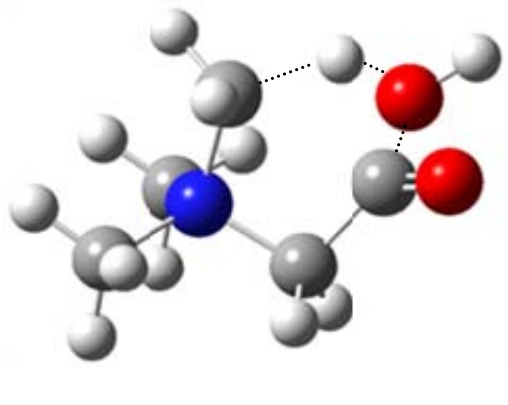
Filename: Bet_TS-4ring_A7_1_high
Sum of electronic and
zero-point energies = -402.55982 Hartrees



TS2

C	1.51879300	0.03097900	0.34539700
C	0.55672800	-0.46272200	1.22552300
O	1.49023500	1.26489200	0.00453800
O	2.32272900	-0.81801100	-0.28537500
N	-1.15858900	0.02027000	-0.16586400
H	0.49791700	-1.52465800	1.42182400
H	0.16572800	0.22150100	1.96084200
H	2.90908700	-0.33402300	-0.89059700
C	-0.90170200	1.19435700	-0.81301800
C	-2.21134500	0.04689700	0.88121700
C	-1.17368500	-1.21116000	-0.99546900
H	0.41913600	1.48179400	-0.41053900
H	-1.40900600	2.07296300	-0.42885800
H	-0.73653000	1.12666900	-1.88297200
H	-3.18291800	0.07902300	0.38340100
H	-2.09256500	0.93503000	1.49699900
H	-2.14421700	-0.84706600	1.49529000
H	-2.07484300	-1.19832500	-1.61213700
H	-1.18319200	-2.08600800	-0.35176100
H	-0.29492300	-1.23394600	-1.63565700

Filename: Bet_TS-59_form_6C_high
Sum of electronic and
zero-point energies = -402.58549 Hartrees

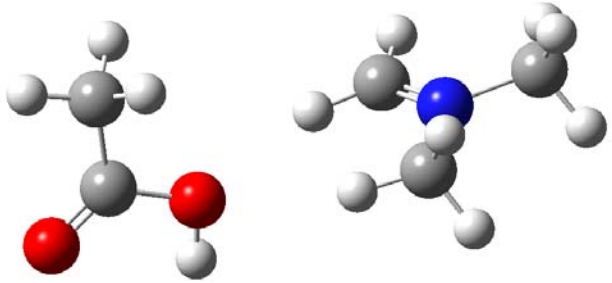


TS3

C	1.34847600	-0.40262300	-0.15951600
C	0.05235900	-0.56721100	-0.91912400
O	1.67431600	1.28247300	-0.03744000
O	2.26207600	-1.10194200	0.01240500
N	-1.00455500	-0.03390600	0.01305600
H	0.06535900	-0.04621600	-1.87635500
H	-0.08967100	-1.63407900	-1.08449400
C	-0.21443400	0.10802300	1.32087600
C	-2.16924400	-0.98229800	0.12086800
C	-1.50942100	1.30494800	-0.45122900
H	1.05588900	1.11772900	0.82143500
H	-0.20478500	-0.86418900	1.80952000
H	-0.72375800	0.82230700	1.97085200
H	-2.86865400	-0.57381400	0.84640000
H	-1.80437500	-1.94704800	0.46551000
H	-2.65343500	-1.08427600	-0.84996400
H	-2.21820800	1.67510700	0.28559800
H	-2.00225400	1.18282000	-1.41421700
H	-0.67453800	1.99415800	-0.54250300
H	2.61276400	1.38556600	0.20585200

Filename: Bet_TS-6ringB_high
Sum of electronic and
zero-point energies = -402.54746 Hartrees

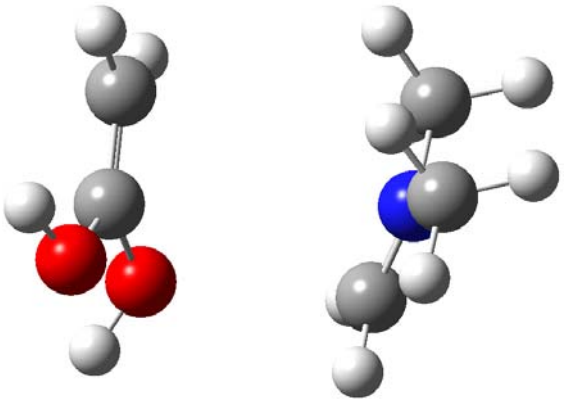
Figure S7: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for transition states relevant to the $[M+H]^+$.



IM_c1

N	2.39416500	0.03826400	-0.06606100
C	1.61640900	0.65476400	-0.86497100
H	-1.93424100	0.98612200	1.66428900
H	2.03433600	1.36146200	-1.57260100
H	0.54669100	0.46121100	-0.82936200
C	1.88249200	-0.93644800	0.91868500
H	2.16489500	-0.59929700	1.91593400
H	0.80173800	-1.00880800	0.83015400
H	2.34920100	-1.90173100	0.72253700
C	3.85451000	0.24683000	-0.06345600
H	4.12517900	0.97652400	-0.82155400
H	4.15288400	0.59870700	0.92397900
H	4.34104500	-0.70716800	-0.26606400
C	-2.66820000	-0.05798800	-0.05413500
O	-3.64619100	-0.66133800	-0.37612300
O	-1.41315300	-0.46479600	-0.49577200
H	-1.58965300	-1.23976200	-1.05612900
C	-2.59806800	1.16075100	0.81532100
H	-3.59495100	1.40192700	1.17357800
H	-2.20438400	2.00458400	0.24415500

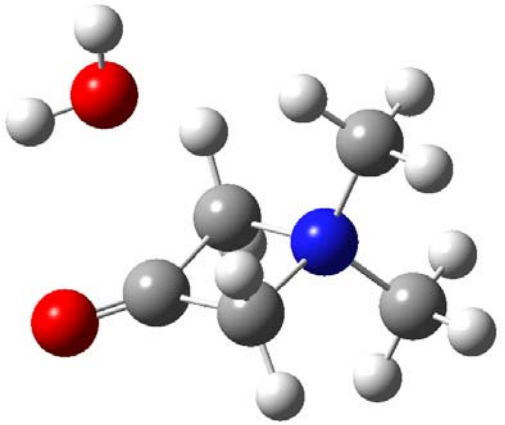
Filename: Bet_TS-4ring_A7_1_high_OPT_REV
Sum of electronic and
zero-point energies -402.67904 Hartrees



IM_c2

C	-1.81688200	0.21504100	-0.10469100
C	-1.49945300	1.50653500	-0.15066700
O	-2.56132700	-0.42385200	0.82897000
O	-1.35433600	-0.68067400	-1.02344600
N	1.74746400	-0.22678200	0.03301000
H	-0.99577300	1.90580200	-1.01765100
H	-1.82215000	2.18618300	0.62442300
H	-1.99140700	-1.40869500	-1.08686300
C	1.26253800	-1.19244700	-0.64092100
C	1.77349200	-0.23376800	1.50710300
C	2.30913200	0.97535900	-0.60967300
H	-3.08707400	0.20843200	1.33616700
H	0.87444200	-2.06297900	-0.13016200
H	1.25874300	-1.14967600	-1.72151300
H	2.80629600	-0.12627000	1.83809600
H	1.35421500	-1.16465500	1.87844900
H	1.18535500	0.61085200	1.86346600
H	3.35766500	1.06280300	-0.32476000
H	1.76083800	1.84575100	-0.25272500
H	2.21894500	0.89181400	-1.68909100

Filename: Bet_TS-59_form_6C_high_OPT_FWD
Sum of electronic and
zero-point energies = -402.64303 Hartrees

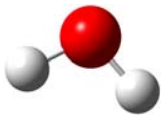


IM_c3

C	-0.70045000	-1.08891100	0.00002500
C	0.13813000	-0.43123800	1.09771400
O	-2.34387000	1.40006200	-0.00008100
O	-1.63685700	-1.81335800	0.00002600
N	1.03595200	0.17652100	0.00000100
H	-0.39112800	0.34163600	1.65215900
H	0.68815800	-1.09436100	1.76341400
C	0.13779100	-0.43082100	-1.09766500
C	2.42186500	-0.38668000	-0.00032100
C	1.06452800	1.67311200	0.00030000
H	-3.08766800	0.78348000	0.00023700
H	0.68761800	-1.09371500	-1.76376000
H	-0.39165800	0.34224300	-1.65166000
H	2.94089300	-0.04007000	-0.89211400
H	2.36849100	-1.47371400	-0.00051400
H	2.94117600	-0.04040100	0.89143500
H	1.58981000	2.01114700	-0.89129100
H	1.59005600	2.01078400	0.89188300
H	0.04046400	2.03670600	0.00051300
H	-2.75323700	2.27421500	-0.00018600

Filename: Bet_TS-6ringB_high_OPT_FWD
Sum of electronic and
zero-point energies = -402.64066 Hartrees

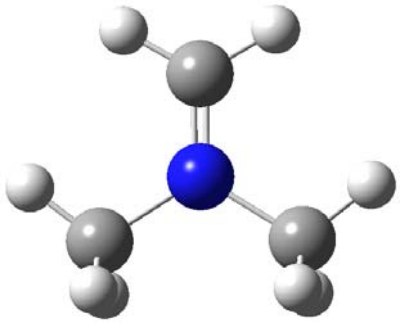
Figure S8: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for ion-molecule complexes IM_c relevant to the $[M+H]^+$.



H_2O

O	0.00000000	0.11696400	0.00000000
H	0.76518100	-0.46784500	0.00000000
H	-0.76518100	-0.46787100	0.00000000

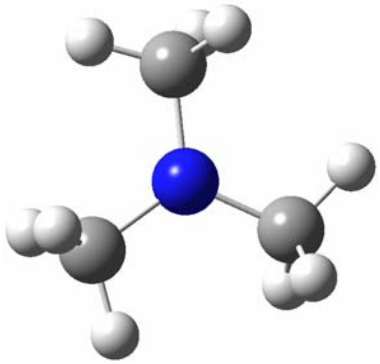
Filename: Bet_TS-6ringB_high_f18
Sum of electronic and
zero-point energies -76.43852 Hartrees



$(CH_3)_2CH_2N^+$

N	0.00000000	0.12348300	-0.00000100
C	-0.00000300	1.39627700	0.00000000
C	1.25009900	-0.66272300	0.00000000
C	-1.25009700	-0.66272700	0.00000000
H	0.93929200	1.93655400	0.00000000
H	-0.93930000	1.93654900	-0.00000100
H	1.26081000	-1.29334200	0.88883400
H	2.10675500	0.00540900	0.00004100
H	1.26084900	-1.29328300	-0.88887600
H	-1.26084300	-1.29328500	0.88887700
H	-1.26080600	-1.29334800	-0.88883300
H	-2.10675500	0.00540200	-0.00004100

Filename: Bet_TS-59_form_6C_high_f58
Sum of electronic and
zero-point energies = -173.56446 Hartrees

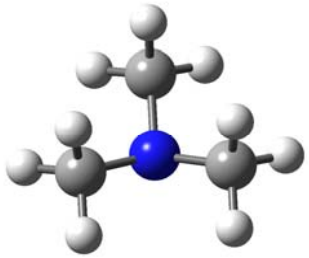


$(CH_3)_3N^+$

N	-0.00018762	-0.00024624	-0.00234866
C	1.27757451	-0.67836878	-0.00023574
C	-1.22665443	-0.76611886	-0.00001961
C	-0.05091794	1.44413182	0.00077597
H	2.09113000	0.04144415	-0.02476903
H	1.32986630	-1.34629788	-0.86705780
H	1.34770736	-1.30092826	0.89948852
H	-1.80603401	-0.50703729	0.89399896
H	-1.01220695	-1.83105712	-0.01572624
H	-1.82579507	-0.48290729	-0.87281899
H	0.49993634	1.82022870	0.87039251
H	-1.08062227	1.78961181	0.02443841
H	0.45731878	1.82080185	-0.89462945

Filename: Bet_TS-59_form_high_f59+
Sum of electronic and
zero-point energies = -174.13201 Hartrees

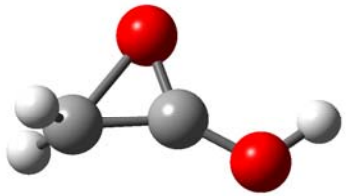
Figure S9: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for products relevant to the dissociation of $[M+H]^+$.



$(CH_3)_3N$

N	0	-0.04465	-0.07143	0.02708
C	0	-0.00795	-0.0214	1.48269
H	0	1.03025	0.0341	1.82547
H	0	-0.53108	0.87278	1.83629
H	0	-0.47975	-0.90627	1.95648
C	0	0.70254	-1.21102	-0.48835
H	0	1.74152	-1.15769	-0.14766
H	0	0.28311	-2.18454	-0.16217
H	0	0.70187	-1.19036	-1.58282
C	0	-1.41187	-0.05457	-0.47614
H	0	-1.40375	-0.03162	-1.57056
H	0	-2.00078	-0.93765	-0.15468
H	0	-1.92622	0.84426	-0.12132

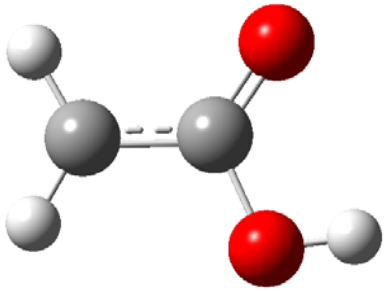
Filename: nme3_sp
Sum of electronic and
zero-point energies -174.4111025 Hartrees



CH_2COOH^+

C	0	0.16839	0.22598	-0.06949
H	0	-0.07916	-0.76079	0.31561
H	0	1.18893	0.45876	-0.36547
C	0	-0.8191	1.25403	-0.06874
O	0	-0.90572	0.71184	-1.20068
O	0	-1.3824	2.1913	0.56221
H	0	-2.09406	2.65496	0.06487

Filename: ch2cooh_cation_sp
Sum of electronic and
zero-point energies -228.121929 Hartrees

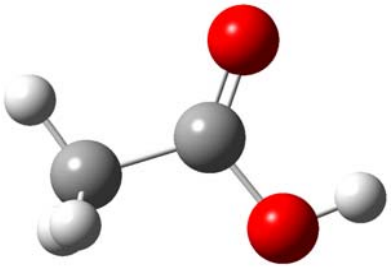


CH_2COOH

H	-2.12505000	0.48203100	0.00094500
C	0.01168500	0.10942800	-0.00032200
O	0.39998300	1.26263200	-0.00003500
O	0.87156400	-0.94755300	0.00013100
H	1.76710600	-0.57656000	0.00038200
C	-1.37230500	-0.29125200	0.00017600
H	-1.65071600	-1.33515800	-0.00121800

Filename: Bet_TS-59_form_high_f59_2
Sum of electronic and
zero-point energies = -228.45665 Hartrees

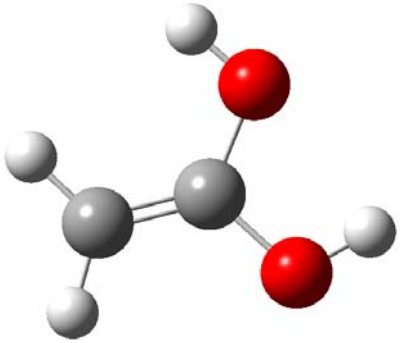
Figure S10: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for products relevant to the dissociation of $[M+H]^+$.



CH_3COOH

H	1.66721400	-0.71133100	0.88059500
C	-0.08855600	0.12694900	-0.00004500
O	-0.62188000	1.20623900	0.00000700
O	-0.79632000	-1.03159800	-0.00001000
H	-1.73488800	-0.78599700	0.00012100
C	1.39219600	-0.12776900	-0.00001800
H	1.92449900	0.81946000	-0.00161500
H	1.66693600	-0.71434300	-0.87869200

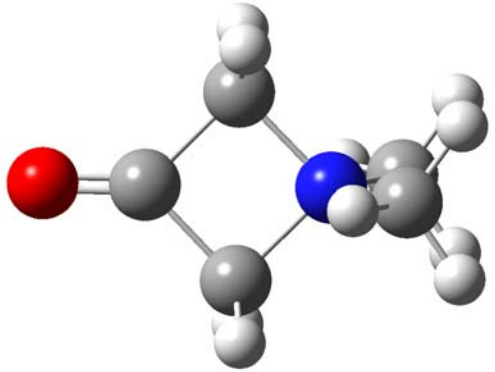
Filename: Bet_TS-4ring_A7_1_high_f60
Sum of electronic and
zero-point energies -229.10932 Hartrees



$CH_2C(OH)_2$

C	0.07745100	-0.03551900	-0.00000100
C	1.39493300	-0.22388500	-0.00012700
O	-0.56905200	1.16663900	0.00004500
O	-0.81581000	-1.04723300	0.00004000
H	1.79589700	-1.22494700	0.00017000
H	2.07472100	0.61527200	0.00040400
H	-1.70467200	-0.66996600	-0.00023700
H	0.07864100	1.88081000	-0.00024400

Filename: Bet_TS-59_form_6C_high_f60
Sum of electronic and
zero-point energies = -229.06571 Hartrees

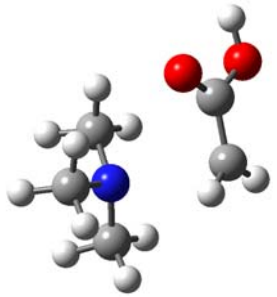


$[(CH_3)_2N(CH_2)_2CO]^+$

C	-1.42081000	-0.00252000	0.00000000
C	-0.35175900	-0.00568500	-1.09915400
O	-2.60250500	0.00140200	0.00000000
N	0.73186600	-0.00010400	0.00000000
H	-0.30691300	-0.90468400	-1.71256800
H	-0.30774400	0.88589600	-1.72325600
C	-0.35175900	-0.00568500	1.09915400
C	1.57300700	1.23899600	0.00000000
C	1.58957300	-1.22762400	0.00000000
H	-0.30774500	0.88589600	1.72325600
H	-0.30691300	-0.90468500	1.71256700
H	2.19678700	1.23887500	0.89204600
H	0.92402600	2.11253400	0.00000000
H	2.19678700	1.23887500	-0.89204500
H	2.21337800	-1.21913900	0.89200000
H	2.21337800	-1.21913800	-0.89200000
H	0.95242000	-2.10980900	0.00000000

Filename: Bet_TS-6ringB_high_f100
Sum of electronic and
zero-point energies -326.18773 Hartrees

Figure S11: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for products relevant to the dissociation of $[M+H]^+$.



[$(CH_3)_3NCH_2COOH$]

C	0	-1.04312	-1.34837	-0.73614
H	0	-0.6461	-1.2597	-1.73686
H	0	-0.85244	-2.23438	-0.14538
C	0	-1.87943	-0.29467	-0.23778
O	0	-2.39853	-0.55844	1.0048
O	0	-2.12748	0.76207	-0.81617
H	0	-2.95105	0.20589	1.23575
N	0	1.2994	0.04252	0.0071
C	0	1.05145	0.74344	1.26093
H	0	0.17265	1.38546	1.15487
H	0	0.85827	0.02071	2.0591
H	0	1.90722	1.37691	1.5635
C	0	1.43782	0.96275	-1.11622
H	0	0.52354	1.55359	-1.21998
H	0	2.29569	1.65028	-0.99118
H	0	1.58717	0.3965	-2.04068
C	0	2.41212	-0.89218	0.1067
H	0	2.51184	-1.45183	-0.82843
H	0	3.37463	-0.38401	0.30828
H	0	2.22684	-1.60443	0.91662

Filename: betaine_neutral_sp
Sum of electronic and
zero-point energies -402.8686103 Hartrees

Figure S12: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for products relevant to the dissociation of [M+H].

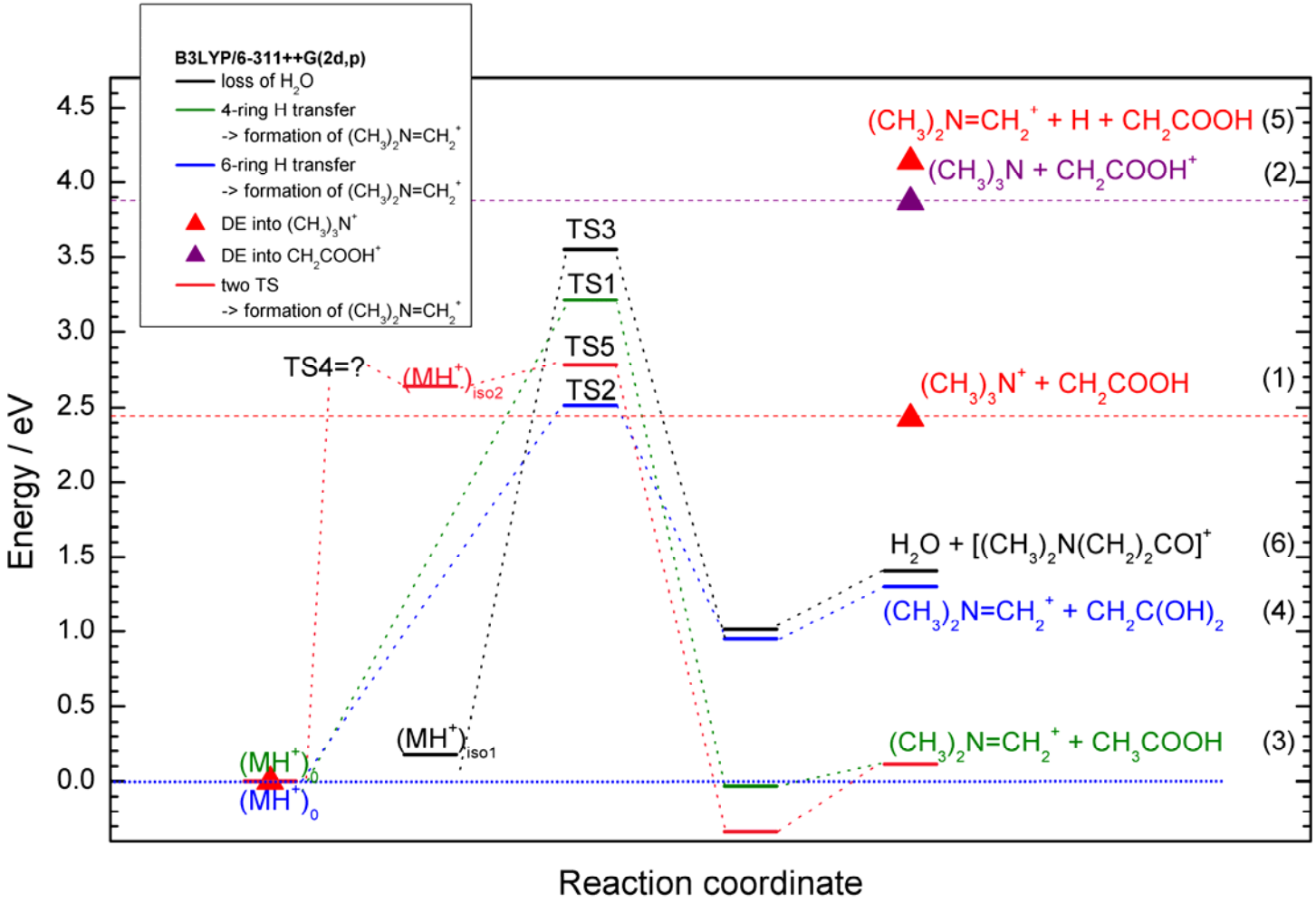
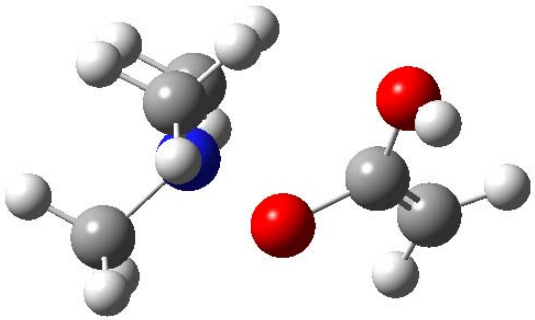


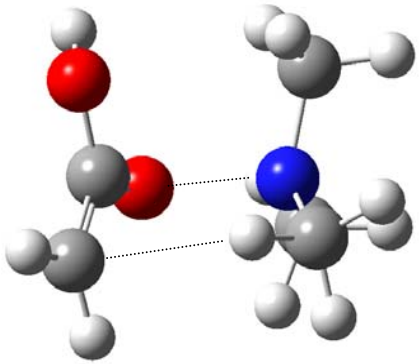
Figure S13: B3LYP/6-311++G(2d,p) DFT calculations on the competing reactions shown in eqns. 1-6. Relative energy diagram in eV. Note that the energy associated with the formation of products in eqn. 5 is calculated by adding the bond dissociation energy (see ref [35]) to the final energy of products shown in eqn. 3. Data includes alternative loss of acetic acid via TS5 (see reference 36).



$[M+H]^+$ isomer2
$[(CH_3)_3N\text{-}O\text{-}C(OH)=CH_2]^+$

C	-1.45153100	-0.06252900	-0.20514600
C	-2.28644100	-1.06861900	-0.00527600
O	-0.21250400	-0.32021000	-0.79797300
O	-1.68851600	1.23819700	0.10256800
N	0.98518600	-0.03542900	0.03409100
H	-1.98333200	-2.08655200	-0.20094100
H	-3.29832900	-0.87154500	0.31967000
H	-1.93102500	1.75031900	-0.68344600
C	1.37930700	1.39730200	-0.16689200
C	2.00364900	-0.95766100	-0.56162400
C	0.74067200	-0.35363700	1.47339100
H	0.61937100	2.03180500	0.27577200
H	1.46002700	1.57451000	-1.23587900
H	2.34212800	1.54903600	0.31901800
H	2.95573900	-0.77631000	-0.06679700
H	2.07403200	-0.74003800	-1.62378400
H	1.67266200	-1.98015900	-0.40549400
H	1.68803300	-0.22807300	1.99484500
H	0.39822900	-1.38164100	1.55149400
H	0.00039000	0.33362600	1.87343000

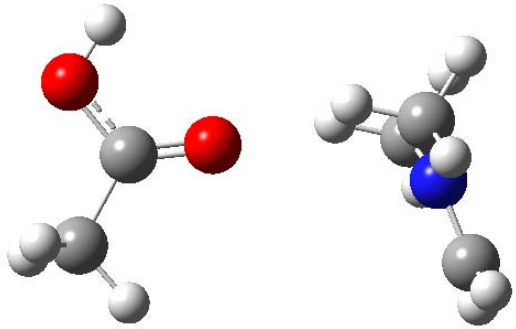
Filename: Bet_TS-4ring_R4
Sum of electronic and
zero-point energies = -402.58096 Hartrees



TS5

C	-1.49343100	-0.00683100	-0.27480900
C	-2.15235800	-1.15353300	0.08817600
O	-0.40343300	-0.06753500	-0.96047200
O	-1.98046600	1.18759600	0.12399700
N	1.16537800	-0.02875900	0.11269500
H	-1.73045300	-2.10911500	-0.18443300
H	-3.12324700	-1.11256300	0.56391800
H	-1.66325700	1.88789900	-0.46459800
C	1.34744200	1.38832600	0.45578000
C	2.07101500	-0.52756100	-0.92723700
C	0.88750000	-0.91326000	1.21785400
H	0.59012800	1.69323400	1.17391900
H	1.28455300	1.98680000	-0.44971000
H	2.33999700	1.51131700	0.90126200
H	3.08550000	-0.55727500	-0.51776200
H	2.03815600	0.14341400	-1.78191900
H	1.76337700	-1.52635600	-1.22460800
H	1.23451500	-1.91981900	1.00121700
H	-0.20770600	-0.94885300	1.39338000
H	1.34096800	-0.53070500	2.13368500

Filename: Bet_TS-4ring_R5
Sum of electronic and
zero-point energies = -402.57562 Hartrees



IM_c5

C	-2.17439200	0.00300600	-0.00007000
C	-2.80690800	1.36064700	-0.00075400
O	-0.97667400	-0.22046900	0.00008400
O	-3.08371900	-0.97776100	0.00035300
N	2.30095700	0.05292800	-0.00004900
H	-3.44766100	1.46688900	0.87670200
H	-3.44716900	1.46619600	-0.87865600
H	-2.62537700	-1.83325900	0.00076800
C	1.95437200	-0.65610900	-1.24634200
C	1.95417500	-0.65245000	1.24826500
C	2.83874500	1.20496400	-0.00169600
H	2.26184800	-0.06326300	-2.10341000
H	0.87551300	-0.80895800	-1.24515800
H	2.46800200	-1.61726600	-1.24726700
H	2.46795400	-1.61351900	1.25217500
H	0.87533600	-0.80546200	1.24728400
H	2.26134800	-0.05700500	2.10363900
H	3.06641500	1.69557300	0.93678600
H	-2.04228900	2.13224500	-0.00086100
H	3.06657400	1.69281500	-0.94157600

Filename: Bet_TS-4ring_R5_IRC_REV_OPT
Sum of electronic and
zero-point energies = -402.69025 Hartrees

Figure S14: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for species relevant to the $[M+H]^+$, transition states relevant to the $[M+H]^+$ and ion-molecule complex IM_c relevant to the $[M+H]^+$.