

Supporting Information

Water-catalysis in the Gas Phase Reaction of Dithioformic acid with Hydroxyl Radical: Global Reaction Route Mapping of Oxidative Pathways for Hydrogen abstraction

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Path 1

B1

Energy = -911.3994 a.u.

ZPE= 0.0382 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.505240303100	0.013534252595	-0.024723387913
H	-0.832286958138	0.009206910146	1.007742658549
S	1.072809181518	0.050081165188	-0.387812321079
O	1.053017744048	0.061290707159	2.948698094864
H	1.417056447721	0.066666112665	2.049768234204
S	-1.854702813098	-0.022328908728	-1.091803759706
H	-1.160579554740	-0.009574625020	-2.236632807078

TS1

Energy = -911.3857 a.u.

ZPE= 0.0333 a.u.

One imaginary frequency = -1364.2611

Cartesian coordinates

C	-0.027638138637	0.060766043327	-0.017798036302
H	0.068790094562	0.158189842430	1.161172121551
S	1.267875625728	0.052290545415	-0.948627021185
O	0.024716616115	0.089546214918	2.521407913819
H	0.702038793455	-0.574497859205	2.668879703269
S	-1.706543484176	-0.037730842130	-0.361238852098
H	-1.602117507052	-0.112108944759	-1.695256829059

P1

Energy = -911.4312 a.u.

ZPE= 0.0384 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.133442629317	0.020296877599	-0.259450128038
H	0.241819747098	0.052254200194	2.068937438159
S	1.272066005477	0.055939220968	-0.954279655978
O	0.207439088717	0.060680074315	3.022321768303
H	1.112362050568	0.104624462099	3.309341426001
S	-1.775430380982	-0.032030498644	-0.557062978032
H	-1.784442085615	-0.045292254994	-1.908760563462

Path II

B2

Energy = -911.4032 a.u.

ZPE= 0.0395 a.u.

No imaginary frequency

Cartesian coordinates

C	0.019030246655	-0.064741507883	0.029682068663
H	-0.102391769780	-0.195992535931	1.096311973514
S	1.661101356224	0.022108650010	-0.427615611279
H	-0.576760398065	0.609064336302	-3.399727374985
O	-0.028085746630	-0.054844340042	-2.980839002809
H	1.405716998026	0.137572191786	-1.750388314157
S	-1.311991375401	0.013764029929	-0.901510992024

TS2

Energy = -911.3920 a.u.

ZPE= 0.0345 a.u.

One imaginary frequency = -1206.5692

Cartesian coordinates

C	-0.001092861638	-0.000157345762	0.061648664324
H	0.078462405515	-0.000781311882	1.142459251252

S	1.567226706965	0.000023072828	-0.629936090244
H	-0.432902540315	0.001045550187	-2.854684112174
O	0.482951996519	0.001036125276	-3.173410827372
H	1.193190151561	0.000936929358	-2.023385596385
S	-1.469856858607	0.000420979992	-0.625109289401

P2

Energy = -911.4462 a.u.

ZPE= 0.0419 a.u.

No imaginary frequency

Cartesian coordinates

C	0.001470130482	-0.004037850983	0.100411542358
H	0.057653260072	-0.012216740659	1.185501346541
S	1.555192852306	-0.017780161641	-0.584614565745
H	-0.355726164863	-0.026853343134	-2.808793482604
O	0.519798094144	-0.027988688077	-3.199490579097
H	0.569903219733	0.753230607901	-3.740202273754
S	-1.459233379080	0.012139836790	-0.620523969810

Path III

B3

Energy = -912.08455 a.u.

ZPE= 0.0517 a.u.

No imaginary frequency

Cartesian coordinates

C	1.273978621019	-0.089421769584	-0.106840284690
H	1.942014555667	-0.163945433431	0.742330737978
S	2.128814560741	-0.292473660713	-1.588865763469
H	1.078395116406	-0.153284563620	-2.407185793361
H	1.220170852066	-0.164362888905	3.878812311881
O	1.385225374938	0.136154484946	2.992846072622
H	0.530227792007	0.231432444626	2.576650562089
S	-0.306924797848	0.181008399679	0.116820689952

C1

Energy = -987.8294 a.u.

ZPE= 0.0641 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.182441529811	-0.016411167381	-0.062284723385
H	-0.226556995558	-0.045052145259	1.020548259125
S	1.239877656654	0.002255359402	-0.844669815404
H	2.608162219178	-0.114163213186	1.159093280611
O	2.816203556978	-0.176235895940	2.094987953010
H	3.694049797934	0.166815615769	2.216333987194
H	1.267644937738	-0.099263194231	3.034721372552
O	0.317395791039	-0.051273122531	3.246042119496
S	-1.763451290643	0.003802560065	-0.737039802946
H	-1.395748771240	0.037407238154	-2.024337893382

TS3

Energy = -987.8124 a.u.

ZPE= 0.0589 a.u.

One imaginary frequency = -1982.8690

Cartesian coordinates

C	-0.044600823720	-0.005210904469	0.009545900904
H	-0.008006435231	-0.011376619011	1.234433169161
S	1.286540351342	-0.003840501504	-0.880962458650
H	2.810396070377	-0.140270803312	1.205991349115
O	2.823544383646	-0.184486573719	2.161368426695
H	3.499564003250	0.417818038994	2.451839704597
H	0.968326876431	-0.109151754423	2.625450264201
O	0.009217077257	-0.043190932972	2.508294465014
S	-1.704213554232	-0.000493768419	-0.403652844193
H	-1.551056949120	0.006959818830	-1.735960976847

P3

Energy = -987.8537 a.u.

ZPE= 0.0635 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.178903042864	0.036492207722	-0.306304562456
H	-0.102576966690	0.133024455294	2.348918455572
S	1.262242256681	0.078589517499	-0.928134204128
H	2.844233324990	-0.191222792783	1.322878648220
O	2.963671888008	-0.321375747059	2.259812701028
H	3.682526547675	0.244894137213	2.518727036943
H	1.174854495081	-0.141444234206	3.096764784818
O	0.243534896929	0.036286836817	3.229319068369
S	-1.801124775547	-0.046620131721	-0.682377488334
H	-1.742510177022	-0.089209562359	-2.032420101471

Path IV

B4

Energy = -912.0876 a.u.

ZPE= 0.0524 a.u.

No imaginary frequency

Cartesian coordinates

C	0.631268191163	-0.068464801679	0.156895104212
H	1.045356638677	-0.116766275169	1.155630829667
S	1.895919354883	-0.081620772136	-1.006780877335
H	1.138347605411	-0.021726275163	-2.119213056088
H	-0.906214164855	-0.351425619001	-3.991045301104
O	-0.472984203009	0.153510489082	-3.311851108562
H	-1.035483459967	0.121437154765	-2.536588447124
S	-0.979932763303	0.004451572303	-0.029852567668

C2

Energy = -987.8234 a.u.

ZPE= 0.0632 a.u.

No imaginary frequency

Cartesian coordinates

C	0.651174350257	-0.068542814983	0.170595927869
H	1.050215215445	-0.106952744345	1.174565631626
S	1.895174126239	-0.084431653583	-1.004899269911
H	1.126148283112	-0.030504546354	-2.109903239707

H	-0.891345251990	-0.333693425493	-4.023935756504
O	-0.474321637071	0.141655221028	-3.313852795728
H	-1.076519215466	0.120405998449	-2.570364156745
H	-1.690069489290	-0.160410072545	2.778233282363
O	-0.820531637627	0.227646325229	2.658928884560
S	-0.964248670938	0.001459438066	-0.005011764448

TS4

Energy = -987.8097 a.u.

ZPE= 0.0580 a.u.

One imaginary frequency = -1440.8972

Cartesian coordinates

C	-0.208533042146	-0.123361450843	0.088382307931
H	-0.124564384758	-0.211578463705	1.273404946070
S	1.384189927812	-0.001224009948	-0.512207608859
H	1.080770257599	0.055021725315	-1.825115679186
H	0.000150038146	-0.282808501506	-4.375472500610
O	0.029368493924	0.158349280801	-3.533516318654
H	-0.832553372651	0.055911989940	-3.134806485742
H	-0.609951305162	0.502823087241	2.827280659423
O	0.075459903054	-0.131616355578	2.605771616599
S	-1.659556515822	-0.146654301716	-0.596028936977

P4

Energy = -987.8543 a.u.

ZPE= 0.0627 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.025358010454	0.009272496203	-0.139372387886
H	-0.066807377473	-0.040978660141	2.241788048431
S	1.527566820901	0.012837597868	-0.746319188923
H	1.249226145159	0.040773278487	-2.072345544566
H	0.005275297376	-0.128735896631	-4.612346988494
O	0.016881730829	0.123647958659	-3.695488249719
H	-0.886743530703	0.107990726779	-3.392901087122
H	-0.939875241460	-0.005379645910	3.477838354147
O	-0.034140979868	-0.059438833159	3.195038402145
S	-1.549184409181	0.027634593935	-0.534734936451

Path V

B5

Energy = -912.08455 a.u.

ZPE= 0.0517 a.u.

No imaginary frequency

Cartesian coordinates

C	1.273978621019	-0.089421769584	-0.106840284690
H	1.942014555667	-0.163945433431	0.742330737978
S	2.128814560741	-0.292473660713	-1.588865763469
H	1.078395116406	-0.153284563620	-2.407185793361
H	1.220170852066	-0.164362888905	3.878812311881
O	1.385225374938	0.136154484946	2.992846072622
H	0.530227792007	0.231432444626	2.576650562089
S	-0.306924797848	0.181008399679	0.116820689952

C3

Energy =-987.8227 a.u.

ZPE= 0.0629 a.u.

No imaginary frequency

Cartesian coordinates

C	1.248517352416	-0.085441170836	-0.118716694471
H	1.885420212270	-0.161154675471	0.753523901733
S	2.145615500755	-0.299223685787	-1.563571713531
H	1.136539658426	-0.160660055172	-2.439470237987
H	1.311643354122	-0.156443459484	3.868938835590
O	1.379110235657	0.117423883858	2.961676990184
H	0.485720050078	0.231170430634	2.645474660598
H	-1.106919520519	0.236259382346	-2.232414235986
O	-0.942612596996	0.162621402603	-3.187301816321
S	-0.340664288276	0.199435744171	0.096712790049

TS5

Energy = -987.8139 a.u.

ZPE= 0.0589 a.u.

One imaginary frequency= -1194.2058

Cartesian coordinates

C	1.136464687431	-0.070273108975	-0.155878955748
H	1.825899145551	-0.158682705482	0.676580326491
S	1.951169143923	-0.271867934906	-1.643740773864
H	0.832326471880	-0.110775178952	-2.538107734433
H	1.515128546433	-0.200263024948	3.803479153753
O	1.497832075078	0.095113013272	2.900595181427
H	0.579426914213	0.219319589213	2.672980751237
H	-0.945365460804	0.213941919066	-2.254408781638
O	-0.408263484618	0.084478405588	-3.050847375936
S	-0.433619039085	0.218178026112	0.160722208699

P5

Energy = -987.8686 a.u.

ZPE= 0.0664 a.u.

No imaginary frequency

Cartesian coordinates

C	1.186235478589	-0.086316372069	-0.132944780179
H	1.867600329599	-0.176740636672	0.710037829903
S	1.978137424028	-0.293726254954	-1.611670743650
H	-0.563124414360	0.863505517217	-3.572114384416
H	1.379408924466	-0.272417734132	3.796961637010
O	1.456902609978	0.120981274742	2.935600273131
H	0.565900839317	0.235202192859	2.610025446645
H	-0.873914755456	0.171739380755	-2.247252946987
O	-0.415436812446	0.061950580385	-3.081424465521
S	-0.393162586534	0.212340320673	0.171952795311

ENERGY = -987.868640275639

Path VI

B6

Energy = -912.0876 a.u.

ZPE= 0.0524 a.u.

No imaginary frequency

Cartesian coordinates

C	0.631268191163	-0.068464801679	0.156895104212
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H	1.045356638677	-0.116766275169	1.155630829667
S	1.895919354883	-0.081620772136	-1.006780877335
H	1.138347605411	-0.021726275163	-2.119213056088
H	-0.906214164855	-0.351425619001	-3.991045301104
O	-0.472984203009	0.153510489082	-3.311851108562
H	-1.035483459967	0.121437154765	-2.536588447124
S	-0.979932763303	0.004451572303	-0.029852567668

C4

Energy = -987.8302 a.u.

ZPE= 0.0642 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.123282462881	-0.084756988032	0.304295799439
H	-0.307539539955	-0.129714407571	1.369915304915
H	2.257966093443	-0.842965215612	-4.003322237122
O	1.401761767517	-0.638989292142	-3.645275032841
H	1.440046115523	-0.775739690626	-2.695131009812
H	0.064569207828	0.487404716255	-3.980260936765
O	-0.701741587265	1.069448823630	-3.817770480451
S	-1.315455972747	0.888965063085	-0.448244218946
H	-0.906599278546	0.812983054874	-1.728808438134
S	1.150328061477	-0.893581429129	-0.298089068465

TS6

Energy = -987.8176 a.u.

ZPE= 0.0605 a.u.

One imaginary frequency = -1519.6412

Cartesian coordinates

C	-0.073668625151	-0.000476522456	0.159761260250
H	-0.154329930769	0.151465121571	1.230369160359
H	2.445212523187	0.235882633079	-3.637155002418
O	1.621307778808	-0.223510502184	-3.517504759251
H	1.647902037329	-0.640678546129	-2.653212093633
H	-0.007041547997	0.402957525070	-3.515592419556
O	-0.944033057583	0.622664761607	-3.335567513963
S	-1.160379122243	1.057319742557	-0.630768568449

H	-1.091939869213	0.612403700938	-2.023281666320
S	0.979099813636	-1.115488914051	-0.380144397016

P6

Energy = -987.8736 a.u.

ZPE= 0.0675 a.u.

No imaginary frequency

Cartesian coordinates

C	-0.117869842159	-0.075911030339	0.270212348796
H	-0.375390127649	-0.061364717870	1.325940748211
H	2.351663035961	-0.029001967119	-3.715582513960
O	1.490453685129	-0.377304575133	-3.513530433769
H	1.501473594120	-0.617823439611	-2.583169187198
H	-0.104497377862	0.514193550814	-3.675993693375
O	-0.968679927635	0.904580500099	-3.508299768953
S	-1.159747663182	0.901174248232	-0.637375256640
H	-1.586718987677	0.405811710095	-4.030578571104
S	1.144376092191	-0.985970396266	-0.222228589371

Path VII

B2

Energy = -911.4032 a.u.

ZPE= 0.0394 a.u.

No imaginary frequency

Cartesian coordinates

C	0.019030246655	-0.064741507883	0.029682068663
H	-0.102391769780	-0.195992535931	1.096311973514
S	1.661101356224	0.022108650010	-0.427615611279
H	-0.576760398065	0.609064336302	-3.399727374985
O	-0.028085746630	-0.054844340042	-2.980839002809
H	1.405716998026	0.137572191786	-1.750388314157
S	-1.311991375401	0.013764029929	-0.901510992024

C5

Energy = -987.8286 a.u.

ZPE= 0.0650 a.u.

No imaginary frequency

Cartesian coordinates

C	1.469253697616	0.316094619676	-0.174990977005
H	2.395130164236	0.265367539424	-0.730883864902
S	0.711382942880	-1.086057703594	0.166503348060
H	-2.218732163830	-0.387348308063	-0.452814757809
O	-2.670373729691	-0.589598996180	-1.277271773997
H	-3.501611174269	-0.132742798532	-1.235728800660
H	-1.264036588502	-0.531370232117	1.817475116262
O	-1.170577788403	0.019576460324	1.041254271250
S	1.009689674039	1.905728754275	0.210830301053
H	-0.133940762149	1.527731914618	0.836537236144

TS7

Energy = -987.8280 a.u.

ZPE= 0.0635 a.u.

One imaginary frequency = -467.4213

Cartesian coordinates

C	1.538387232957	0.328722111834	-0.106594598766
H	2.516078473838	0.246253632251	-0.559781050355
S	0.692245377222	-1.064354670884	0.103918842668
H	-2.279946499324	-0.416380633968	-0.471009692122
O	-2.800171720503	-0.762549762778	-1.202021026005
H	-3.568917827473	-0.208228324046	-1.257793392964
H	-1.252568145486	-0.244412567265	1.729523028034
O	-1.133541746989	0.168801760781	0.875548586002
S	1.051767701389	1.891217446827	0.293652203578
H	-0.185269085630	1.384018492250	0.767064830931

P7

Energy = -987.8736 a.u.

ZPE= 0.0675 a.u.

No imaginary frequency

Cartesian coordinates

C	1.657388814462	0.264722204339	-0.096101897421
H	2.726053008742	0.167817400824	-0.268308794695
S	0.820560136462	-1.122451718507	-0.585333010464
H	-2.278323974015	-0.393556438636	0.022767749440
O	-2.057445979385	-1.145170059841	-0.537252421052
H	-2.552226592880	-1.027121608049	-1.340216878078
H	-2.467308549900	1.270945767926	1.901389510617
O	-2.216553548746	1.163312473347	0.990686810746
S	1.085017074901	1.646851006549	0.556691263664
H	-1.290298304111	1.411837305175	0.928446010870

Path VIII

B2

Energy = -911.4032 a.u.

ZPE= 0.0394 a.u.

No imaginary frequency

Cartesian coordinates

C	0.019030246655	-0.064741507883	0.029682068663
H	-0.102391769780	-0.195992535931	1.096311973514
S	1.661101356224	0.022108650010	-0.427615611279
H	-0.576760398065	0.609064336302	-3.399727374985
O	-0.028085746630	-0.054844340042	-2.980839002809
H	1.405716998026	0.137572191786	-1.750388314157
S	-1.311991375401	0.013764029929	-0.901510992024

C8

Energy = -987.8286 a.u.

ZPE= 0.0650 a.u.

No imaginary frequency

Cartesian coordinates

C	1.254680723976	0.245528171567	0.633833645722
H	1.970634990884	0.481014764827	1.408928957679
S	0.405108695952	-1.137927056539	0.780205469791
H	-3.835812916908	0.338776898283	0.132473382795
O	-3.134844567008	-0.045663747792	0.644558660516

H	-2.438843104179	-0.260102974981	0.016705031944
H	-0.911736356474	-1.487207068372	-1.473345030186
O	-0.956296686623	-0.623198488235	-1.065437969531
S	1.180627197991	1.425685263722	-0.586291975702
H	0.208030510169	0.783886781227	-1.283006540513

TS8

Energy = -987.8123 a.u.

ZPE= 0.0595 a.u.

One imaginary frequency = -1195.9229

Cartesian coordinates

C	1.499409518897	0.118300109911	0.548513225797
H	2.366087963756	0.557699892420	1.028574022320
S	1.173217640978	-1.452227469295	0.783751945516
H	-4.341980134779	0.777573728388	-0.415463688334
O	-3.579082622675	0.860071222169	0.144488237593
H	-2.894935170347	0.336086461621	-0.266403596607
H	-0.799413274817	-1.239616263765	-0.561390244760
O	-1.251073884517	-0.540085127923	-1.064120149487
S	0.684242598789	1.314019302148	-0.369852225271
H	-0.351062727275	0.487013787313	-0.924156592796

P8

Energy = -987.8736 a.u.

ZPE= 0.0675 a.u.

No imaginary frequency

Cartesian coordinates

C	1.457417033612	0.275332672940	0.527358187957
H	2.440737041679	0.599295089693	0.857920156438
S	1.154893613248	-1.323518973816	0.400371544092
H	-2.993428660361	1.258389172724	0.238817127215
O	-2.322302688300	1.131152383137	-0.422187041944
H	-2.350524823428	0.196327386871	-0.651811158874
H	-1.061230242743	-1.636868976869	-0.509584658753
O	-1.956196732855	-1.582616907878	-0.855527000451
S	0.440715272053	1.592869587774	0.220362314950
H	-1.962453445390	-2.067537668209	-1.673245914949

Input and options applied in GRRM run

Without water

GRRM/BHandHLYP/6-311++G**

0 2

C	-0.505240303100	0.013534252595	-0.024723387913	1
H	-0.832286958138	0.009206910146	1.007742658549	1
S	1.072809181518	0.050081165188	-0.387812321079	1
O	1.053017744048	0.061290707159	2.948698094864	2
H	1.417056447721	0.066666112665	2.049768234204	2
S	-1.854702813098	-0.022328908728	-1.091803759706	1
H	-1.160579554740	-0.009574625020	-2.236632807078	1

Options

LADD=5

NRUN=20

NLowest=20

EQOnly

UpDC=15

DownDC=15

With water

GRRM/BHandHLYP/6-311++G**

0 2

C	0.363371778557	-0.157405036628	0.673496468000	1
H	-0.428170500687	-0.777148748083	0.267700040972	1
S	0.469423247043	1.419448240362	0.302400532773	1
H	-2.775656352298	1.826297940890	-1.870786018699	2
O	-2.194495697730	1.096899893129	-1.688324074792	2
H	-1.448143431417	1.439652247707	-1.189836979358	2
H	-2.431087116561	-0.643677144652	-1.238899033975	3
O	-2.300015033106	-1.517010889889	-0.826456995906	3
S	1.395729848978	-1.077333799941	1.694977887484	1
H	2.231524034154	-0.084748976692	2.026266962679	1

Options

LADD=5

NRUN=20

NLowest=20

EQOnly
UpDC=15
DownDC=15