Supplementary Materials

Mechanism of Methylphosphonic acid photo-degradation: Based on Phosphate Oxygen Isotopes and Density Function Theory

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The supplemental material is 29 pages including 3 tables, cartesian coordinates and energies of the optimized structures and intrinsic reaction coordinate for reaction pathways.

Table S1. Density function theory (DFT) method was used to simulate the reaction process and potential barriers between reactive oxygen specie ($O_2^{\cdot -}$) and methylphosphonic acid, $\Delta G^{\ddagger}$ is free energy barrier and ΔG is the free energy of the reaction.

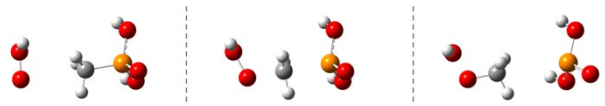
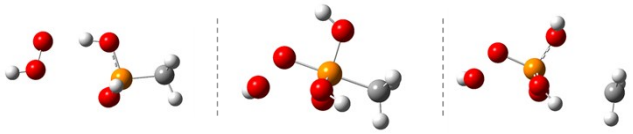
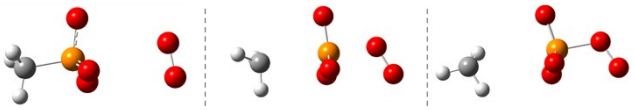
Conditions	Site	Reaction process simulated by density function theory (DFT)	Free energy (kcal/mol)
Acidic	methyl		$\Delta G^{\ddagger}$=53.6 ΔG=23.1
	phosphoryl		$\Delta G^{\ddagger}$=45.1 ΔG=16.1
Alkaline	methyl		$\Delta G^{\ddagger}$=65.4 ΔG=32.5
	phosphoryl		$\Delta G^{\ddagger}$=58.0 ΔG=49.0

Table S2. Density function theory (DFT) method was used to simulate the reaction process and potential barriers between reactive oxygen specie ($^1O_2$) and methylphosphonic acid, $\Delta G^{\ddagger}$ is free energy barrier and ΔG is the free energy of the reaction.

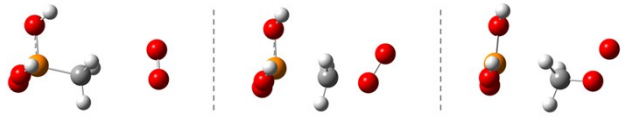
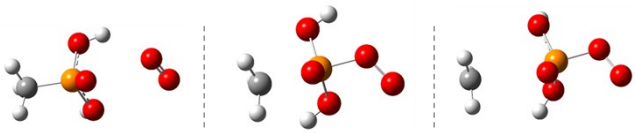
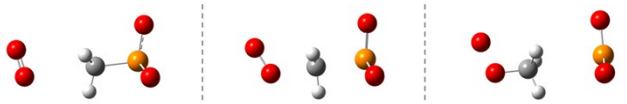
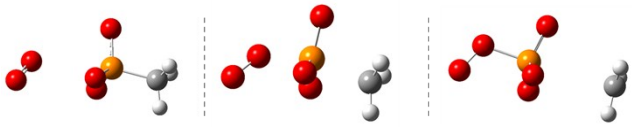
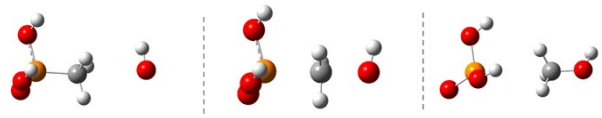
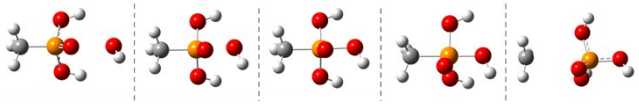
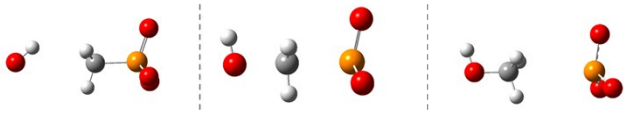
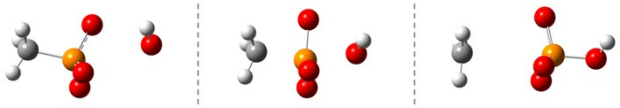
Conditions	Site	Reaction process simulated by density function theory (DFT)	Free energy (kcal/mol)
Acidic	methyl		$\Delta G^{\ddagger}$=61.4 ΔG=19.4
	phosphoryl		$\Delta G^{\ddagger}$=85.4 ΔG=20.5
Alkaline	methyl		$\Delta G^{\ddagger}$=27.5 ΔG=8.9
	phosphoryl		$\Delta G^{\ddagger}$=64.2 ΔG=-4.9

Table S3. Density function theory (DFT) method was used to simulate the reaction process and potential barriers between reactive oxygen specie (•OH) and methylphosphonic acid, $\Delta G^{\ddagger}$ is free energy barrier and ΔG is the free energy of the reaction.

Conditions	Site	Reaction process simulated by density function theory (DFT)	Free energy (kcal/mol)
Acidic	methyl		$\Delta G^{\ddagger}$=37.4 ΔG=0.6
	phosphoryl		**$\Delta G^{\ddagger}$=16.8** ΔG=-18.9
Alkaline	methyl		**$\Delta G^{\ddagger}$=12.5** ΔG=-18.4
	phosphoryl		$\Delta G^{\ddagger}$=27.5 ΔG=-21.6

Cartesian Coordinates and Energies of the Optimized Structures and Intrinsic Reaction Coordinate for Reaction Pathways

1. Reaction of $O2^{\cdot-}$ radical and methylphosphonic acid under acidic condition

R (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -759.074989 Hartree

Charge = 0, Multiplicity = 2

P	1.26417200	0.00312400	0.09813700
O	1.81880100	-0.80423000	-1.17286600
H	1.30528500	-0.70477700	-1.98830400
O	2.05907100	-0.36125900	1.29991600
C	-0.49209600	-0.28676200	0.17945500
H	-0.95856700	0.01406100	-0.76027200
H	-0.66684400	-1.34878800	0.35558500
H	-0.90723000	0.29709500	1.00257700
O	1.47676500	1.56148700	-0.22181600
H	0.97289700	1.91224900	-0.97132400
O	-3.74470000	0.52049100	-0.15151200
H	-3.18126000	0.88593200	0.55977200
O	-3.68085000	-0.77612600	-0.06499300

TS (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -758.9896 Hartree

Charge = 0, Multiplicity = 2

P	1.15573700	-0.00432500	0.10092200
O	1.75193100	-0.81196300	-1.15084100
H	1.28564300	-0.69267500	-1.99311000
O	1.87062000	-0.37912500	1.34762400
C	-1.03371700	-0.36171900	0.07159900
H	-1.03157100	0.05514600	-0.93184600

H	-0.81551800	-1.41667800	0.21535500
H	-1.08652100	0.29716400	0.93311900
O	1.34266800	1.56096200	-0.19772100
H	0.88884000	1.90194700	-0.98462200
O	-3.41456000	0.53568500	-0.15732100
H	-3.51745700	0.91265900	0.73013600
O	-2.76194900	-0.67406600	0.05486300

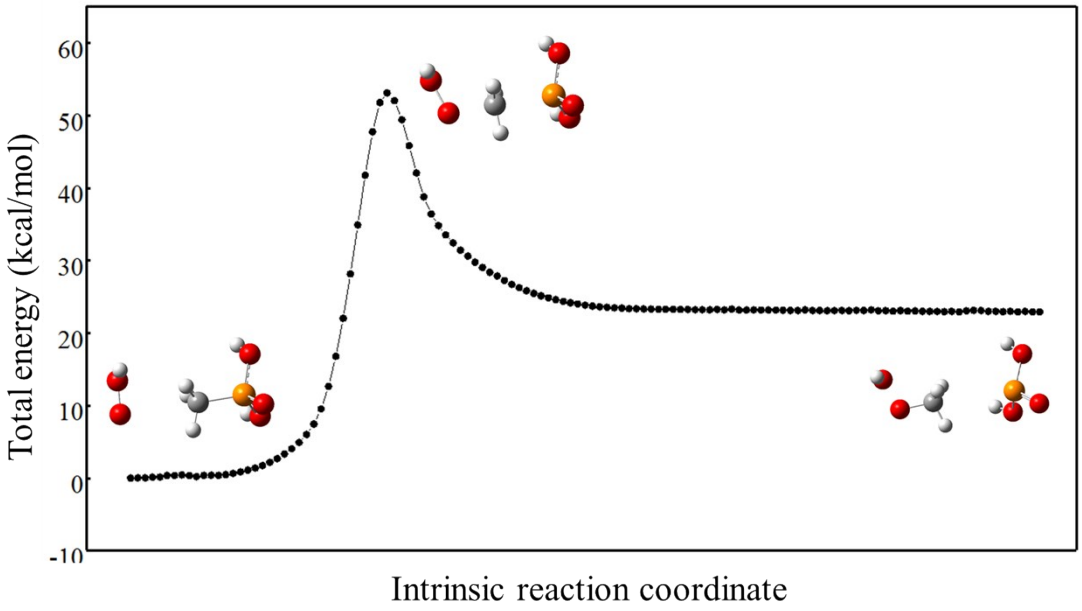
P (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -759.038101 Hartree

Charge = 0, Multiplicity = 2

P	1.54033700	0.06266400	0.27634600
O	1.48033200	-0.79686700	-1.08071400
H	0.74398200	-0.59018700	-1.67894600
O	2.59807300	-0.45727500	1.18166700
C	-1.82328100	-0.42155000	-0.04614500
H	-1.45758100	0.25848300	-0.82084600
H	-1.33683100	-1.39418100	-0.13837500
H	-1.64163300	-0.00444200	0.94820600
O	1.84642200	1.58741600	-0.12913100
H	1.20354600	2.00567800	-0.72442600
O	-3.89827000	0.55252900	-0.16479700
H	-4.13202700	0.62515000	0.77345000
O	-3.20649000	-0.68534500	-0.22941500

Intrinsic Reaction Coordinate (methyl side):



R (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -759.079575 Hartree

Charge = 0, Multiplicity = 2

P	0.86954300	-0.28710200	-0.04320500
O	0.32074600	-1.05105400	-1.19968400
O	-2.38329400	1.26017000	-0.38314500
C	2.63835100	-0.11357700	0.02751400
H	2.97880100	0.42451800	-0.85782000
H	2.92435700	0.43556100	0.92557100
H	3.08709100	-1.10713300	0.04670900
O	0.35600800	1.22199100	0.05566100
H	-0.60564000	1.33701400	-0.11226100
O	0.39269700	-1.01695600	1.30944500
H	0.65352500	-0.57247700	2.12978800
O	-2.68685600	0.09216000	0.09592900
H	-3.64926200	-0.03016900	-0.03409500

TS (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -759.007685 Hartree

Charge = 0, Multiplicity = 2

P	0.33512000	0.04894300	0.00201900
O	0.08323100	-0.85837100	-1.28942900

O	-1.30106200	0.62833700	-0.08461900
C	2.10704200	-0.56609100	-0.13040800
H	2.57026100	-0.23694800	-1.05797300
H	2.62134200	-0.09753200	0.71465300
H	2.16872200	-1.64922600	-0.03950100
O	0.80756200	1.58754200	-0.08770200
H	0.09156200	2.23915900	-0.03778200
O	0.04154500	-0.53185700	1.47942700
H	0.78189000	-1.02036200	1.86513300
O	-2.24232000	-0.42793000	0.05257100
H	-2.53899100	-0.56094400	-0.86001000

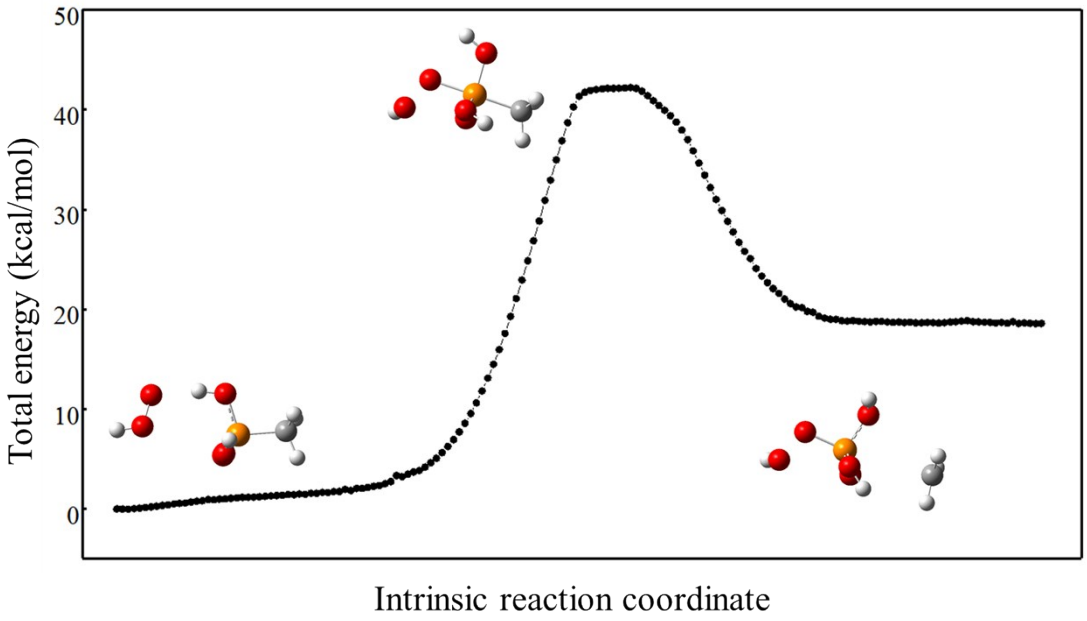
P (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -759.053974 Hartree

Charge = 0, Multiplicity = 2

P	-0.04567300	0.09866000	-0.12546500
O	0.13473900	-0.78934500	-1.28642800
O	-1.52556100	0.76036100	0.02299400
C	3.19452900	-0.83161100	0.13993600
H	3.34197400	-0.47468600	-0.86919800
H	3.37717300	-0.16803800	0.97339700
H	3.05812900	-1.88960800	0.31691600
O	0.82393500	1.41010300	-0.20840600
H	0.88952300	1.93718500	0.60317600
O	0.14225700	-0.55740500	1.30187700
H	0.79212600	-1.27775100	1.33731700
O	-2.49150800	-0.28088800	0.14318500
H	-2.90124000	-0.27780900	-0.73774800

Intrinsic Reaction Coordinate (phosphoryl side):



2. Reaction of $O2^{\cdot-}$ radical and methylphosphonic acid under alkaline condition

R (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.738508 Hartree

Charge = -3, Multiplicity = 2

P	-1.37394600	0.03798000	0.00454800
O	-1.85616400	-0.63122100	1.31366500
O	-1.96527300	-0.64488000	-1.25216600
C	0.43529800	-0.20164800	-0.06673000
H	0.91113800	0.26634800	0.79796400
H	0.67670800	-1.26658600	-0.06539000
H	0.84232000	0.24868200	-0.97487700
O	-1.61873000	1.56645400	0.00583700
O	3.84898900	0.59283100	0.03325500
O	3.78260100	-0.71167100	0.20448400

TS (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.634303 Hartree

Charge = -3, Multiplicity = 2

P	-1.23060100	0.03089900	-0.00115600
O	-1.72457000	-0.64728200	1.29283900
O	-1.72109200	-0.66409700	-1.28745000
C	1.04312500	-0.30648800	0.00371500
H	1.06450500	0.24889600	0.93308800
H	0.80080500	-1.36349100	0.01310400
H	1.06614400	0.23207000	-0.93545000
O	-1.42599200	1.56037600	-0.01106500
O	3.49751000	0.59614900	-0.01009100
O	2.78936300	-0.63973000	0.00778700

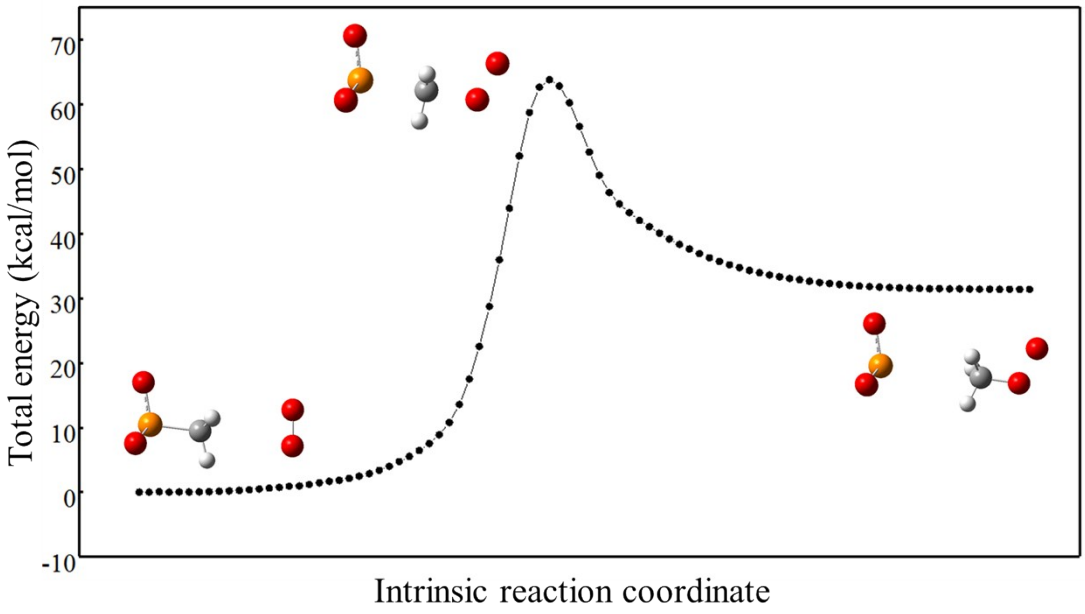
P (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.6867 Hartree

Charge = -3, Multiplicity = 2

P	-1.60559700	0.05336200	-0.10256800
O	-1.83305200	-0.63620500	1.26666500
O	-2.35813500	-0.64625500	-1.26214300
C	1.99404300	-0.42013200	0.08624000
H	1.63857700	0.31494200	0.81852300
H	1.51707000	-1.38472200	0.28184700
H	1.72369200	-0.08076700	-0.92060200
O	-1.85147100	1.58261300	-0.05722600
O	4.03635100	0.65223500	-0.07955800
O	3.38462200	-0.61373800	0.19681200

Intrinsic Reaction Coordinate (methyl side):



R (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.736328 Hartree

Charge = -3, Multiplicity = 2

P	-0.88074500	0.02638700	0.02391200
O	-0.28922700	-0.40724600	1.38609600
O	-0.72155100	1.54538400	-0.22718600
O	2.68685700	0.63128700	-0.17169100
O	-0.34148400	-0.82323800	-1.15051700
C	-2.67812700	-0.29910300	0.11310800
H	-3.12558700	0.26814300	0.93234600
H	-3.16268500	-0.00486300	-0.82064900
H	-2.86196500	-1.36232000	0.28342600
O	2.95264200	-0.64430900	0.02202400

TS (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.643871 Hartree

Charge = -3, Multiplicity = 2

P	-0.21496700	0.15718500	0.02592500
O	-0.17450600	-0.48924200	1.40096100
O	-0.43920500	1.65492100	-0.09708100
O	1.72578400	0.40995400	-0.09214700
O	-0.29955900	-0.72600400	-1.20462300
C	-3.01649300	-0.24054200	0.00972300
H	-3.91161300	0.10299500	0.55732800
H	-3.20842400	-0.05170900	-1.05852700
H	-2.96760100	-1.33313800	0.14015000
O	2.41202900	-0.69315400	-0.05712900

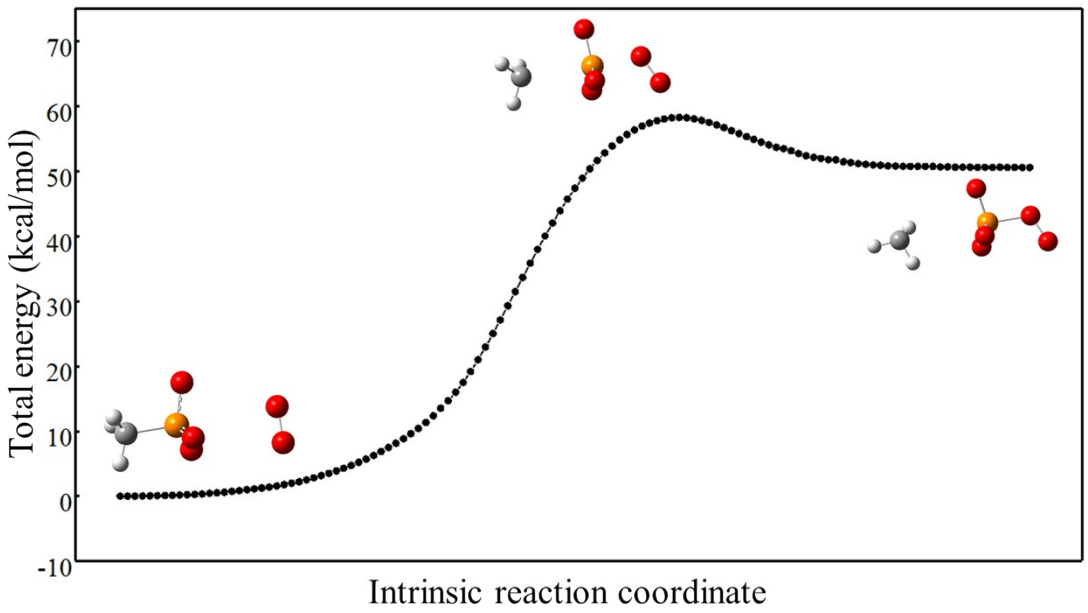
P (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.658318 Hartree

Charge = -3, Multiplicity = 2

P	-0.01175900	0.14471100	0.00561100
O	-0.12483400	-0.39821500	1.41518400
O	-0.50251700	1.55811100	-0.22422000
O	1.76173500	0.47411700	-0.13210300
O	-0.23775200	-0.84909600	-1.11514600
C	-3.64246300	-0.54299000	0.08730100
H	-4.68483700	-0.81356500	-0.14236500
H	-3.25466000	-0.00248600	-0.78935600
H	-3.07610100	-1.48384700	0.15611800
O	2.50556300	-0.58448100	0.00552200

Intrinsic Reaction Coordinate (methyl side):



3. Reaction of •OH radical and methylphosphonic acid under acidic condition

R (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.913538 Hartree

Charge = 0, Multiplicity = 2

P	-0.71648800	-0.04951700	-0.07737200
O	-1.30810800	-0.46648000	1.35471800
H	-0.91888000	-0.01578400	2.11876600
O	-1.37502800	-0.85903600	-1.13520400
C	1.05930000	-0.16158100	0.02883800
H	1.42097700	0.47866300	0.83584300
H	1.33700100	-1.19769300	0.22583400
H	1.48464300	0.16177000	-0.92252500

O	-1.08098200	1.49908200	-0.28868100
H	-0.65298800	2.11857200	0.32083200
O	4.01540000	0.00272000	0.00905300
H	3.83894200	0.92330000	-0.26014100

TS (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.853976 Hartree

Charge = 0, Multiplicity = 2

P	-0.65629100	-0.04546400	-0.08369400
O	-1.17194100	-0.50250300	1.36156500
H	-0.83488100	0.00429400	2.11718500
O	-1.26576800	-0.88370000	-1.14457600
C	1.47251500	-0.07570100	0.00335400
H	1.41323400	0.63748400	0.82260800
H	1.44429900	-1.13969100	0.21352300
H	1.47220400	0.27019000	-1.02703400
O	-1.05173300	1.49367400	-0.27823700
H	-0.64805100	2.11909800	0.34391800
O	3.26904100	-0.08345200	0.07115900
H	3.45958600	0.83384700	-0.17080500

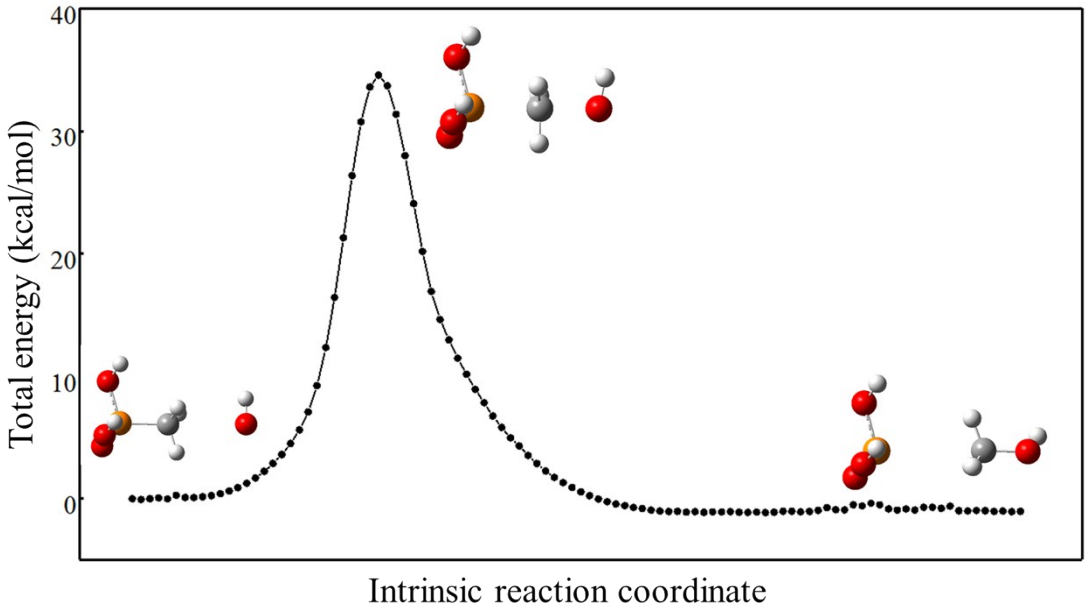
P (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.912524 Hartree

Charge = 0, Multiplicity = 2

P	-1.07285300	-0.12630600	-0.20285500
O	-0.93889400	-0.42055900	1.37206000
H	-0.16373700	-0.03419600	1.81106500
O	-2.21849500	-0.87805200	-0.77857500
C	2.30208000	-0.07487700	0.06037700
H	1.81145400	0.84597900	0.39464700
H	1.91966300	-0.91496700	0.64090900
H	2.07179300	-0.24170400	-0.99605300
O	-1.29033000	1.45607500	-0.38381600
H	-0.56026000	2.01998100	-0.08159700
O	3.70755300	-0.01426800	0.27988300
H	4.06113300	0.71331500	-0.24224400

Intrinsic Reaction Coordinate (methyl side):



R (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.915142 Hartree

Charge = 0, Multiplicity = 2

P	-0.41917700	0.03297800	0.07960900
O	0.37201100	0.06585500	1.34826500
O	-0.17632400	1.33380800	-0.83014500
H	0.73278600	1.66934300	-0.81775200
O	2.52006100	-0.21887400	-0.09513200
H	2.81031200	-0.57913800	0.76308100
O	-0.06667200	-1.23549300	-0.83707200
H	0.89084300	-1.39589100	-0.89173800
C	-2.18640000	-0.03917100	0.21161500
H	-2.53356400	0.83483500	0.76293400
H	-2.62657900	-0.04541900	-0.78596100

H	-2.46726000	-0.94731100	0.74544300

TS1 (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.888341 Hartree

Charge = 0, Multiplicity = 2

P	-0.14092600	-0.00581200	0.01352000
O	0.29218500	-0.03029100	1.52580800
O	-0.07599700	1.36870300	-0.81949900
H	0.81902300	1.65339100	-1.05135300
O	1.76078600	0.08433500	0.05561600
H	2.17820400	-0.72473600	0.38658200
O	-0.06039300	-1.34017900	-0.88639100
H	0.82011400	-1.56521700	-1.21624000
C	-1.93253000	-0.03026100	0.22229600
H	-2.24506000	0.84146300	0.79830300
H	-2.42506300	-0.01144000	-0.75069000
H	-2.22860600	-0.93497900	0.75479000

IM (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.890387 Hartree

Charge = 0, Multiplicity = 2

P	-0.03508600	-0.00465000	-0.00259000
O	0.13856000	-0.05579600	1.60912500
O	-0.09019600	1.39261300	-0.81894500
H	0.78150600	1.71293400	-1.09051000
O	1.68344200	0.08060300	-0.03427200
H	2.12147000	-0.68498000	0.35991200
O	-0.07853600	-1.37224500	-0.87830200
H	0.77945300	-1.64914000	-1.22818100
C	-1.86217100	-0.02458300	0.24864800
H	-2.18534300	0.85632500	0.80286400

H	-2.33178200	-0.01599600	-0.73726000
H	-2.17359600	-0.92391300	0.77988500

TS2 (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.891011 Hartree

Charge = 0, Multiplicity = 2

P	0.00776700	-0.00391000	0.00386800
O	-0.21064600	-0.49952300	1.50554600
O	0.04402100	1.55899400	-0.41444300
H	0.93925800	1.92655000	-0.43377500
O	1.68842700	0.01393900	0.22487800
H	2.04582800	-0.81911200	0.55915700
O	0.05376200	-1.07108700	-1.21919400
H	0.95110800	-1.29551500	-1.50210000
C	-1.88631100	-0.00204600	-0.04147200
H	-2.29769000	-0.99378100	0.13280800
H	-2.30426800	0.71462400	0.66199600
H	-2.11389300	0.31130400	-1.06420700

P (phosphoryl side)

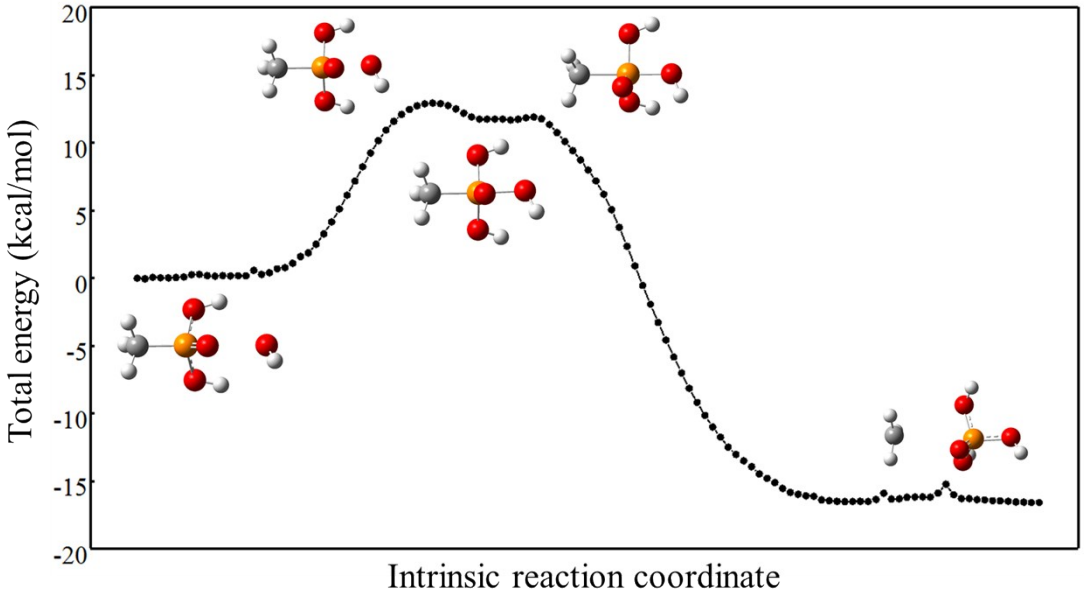
M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.945224 Hartree

Charge = 0, Multiplicity = 2

P	0.40861200	-0.02942700	0.13513400
O	-0.20154000	-0.43794900	1.41779300
O	0.01565100	1.39848600	-0.43146200
H	0.19372600	2.14640200	0.15883300
O	1.99931200	0.04604000	0.14230700
H	2.43803300	-0.67640300	0.61621900
O	-0.02110300	-1.00362500	-1.03805500
H	0.39576100	-0.83884800	-1.89770300
C	-2.99512400	0.11698800	-0.30536100

H	-3.13522200	-0.89063600	0.05854000
H	-3.05162200	0.94766100	0.38320300
H	-2.96185500	0.30307200	-1.36918100

Intrinsic Reaction Coordinate (phosphoryl side):



4. Reaction of O2·- radical and methylphosphonic acid under alkaline condition

R (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.001669 Hartree

Charge = -2, Multiplicity = 2

P	0.79285200	0.03539300	-0.08667600
O	1.33488700	-0.80075400	-1.21800400
O	1.29597400	-0.59357400	1.32525100

C	-1.00275300	-0.02605500	-0.05567600
H	-1.39037700	0.44752000	-0.95953200
H	-1.33696700	-1.06409000	-0.02843400
H	-1.37702900	0.50266600	0.82148800
O	1.29269100	1.45930700	0.09911400
O	-4.42195400	0.00364300	0.05149000
H	-3.69784700	0.63558900	0.03128100

TS (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -682.98168 Hartree

Charge = -2, Multiplicity = 2

P	0.79155700	0.00943000	0.00000400
O	1.15883400	-0.74829100	-1.28116700
O	1.15564800	-0.71378100	1.30170000
C	-1.49656200	-0.02909900	-0.00059200
H	-1.44004400	0.50013500	-0.94213200
H	-1.43286300	-1.10847000	0.00991900
H	-1.43946700	0.51855400	0.93033900
O	1.11901900	1.50658500	-0.01971800
O	-3.33981900	-0.08966500	0.00139700
H	-3.54988200	0.85171400	-0.00415300

P (methyl side)

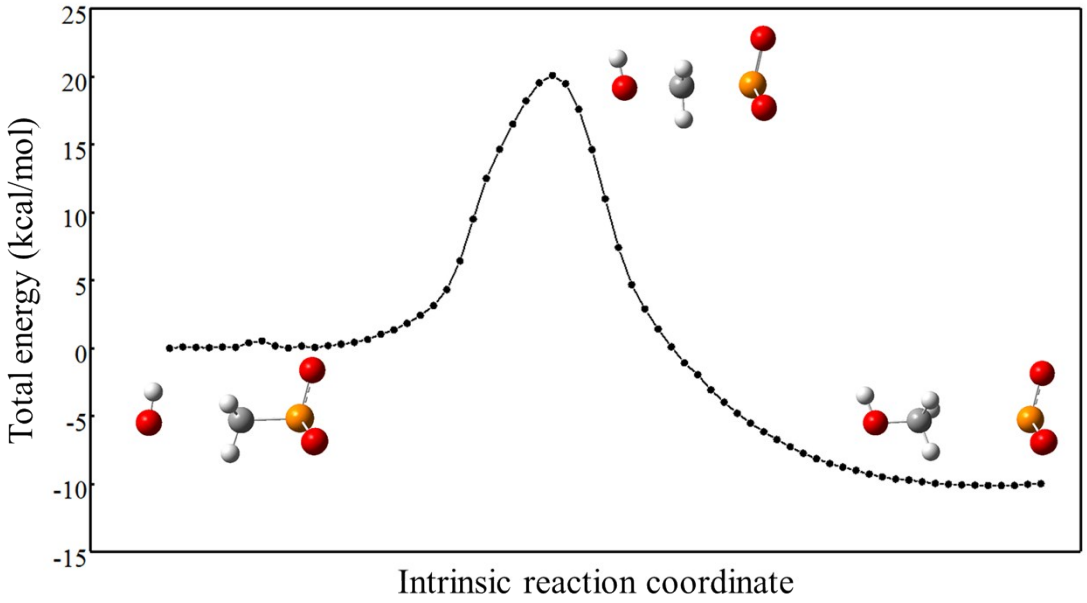
M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.030914 Hartree

Charge = -2, Multiplicity = 2

P	1.04864400	-0.02272100	0.07955300
O	1.28129100	-0.71089000	-1.28947100
O	1.81079100	-0.71206000	1.23875300
C	-2.53253500	-0.03574900	0.01461800
H	-2.08932500	0.38623900	-0.89147000
H	-2.19899800	-1.06779600	0.11986100
H	-2.18989700	0.53575000	0.88127000
O	1.27535400	1.50938600	0.03186800
O	-3.95703900	-0.05549900	-0.06450900

H	-4.26186200	0.85253200	-0.15812000

Intrinsic Reaction Coordinate (methyl side):



R (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.026564 Hartree

Charge = -2, Multiplicity = 2

P	-0.39780800	-0.39415300	-0.13427000
O	0.53253000	0.76562600	-0.62053600
O	-0.55748200	-1.47633900	-1.21792000
O	2.67205100	1.28526700	0.57553300
H	1.77558900	1.04964500	0.09421700
O	0.07312700	-0.95122400	1.22278300
C	-2.03386800	0.36414000	0.11906500
H	-2.39409700	0.80239800	-0.81397200
H	-2.74916800	-0.39171900	0.45016200

H	-1.97561100	1.14822900	0.87669500

TS (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -682.98278 Hartree

Charge = -2, Multiplicity = 2

P	-0.08428400	-0.10692800	0.02507800
O	0.03134100	1.45942800	-0.34805400
O	-0.01535600	-1.14951600	-1.10260300
O	1.89775800	0.15428400	-0.13486300
H	2.17809900	0.65000400	0.64155100
O	0.04970200	-0.52233400	1.50097200
C	-1.98807500	0.22212800	-0.00201900
H	-2.35007600	0.50525200	-0.99148200
H	-2.43135400	-0.73793600	0.27674500
H	-2.29334400	0.97279500	0.72873900

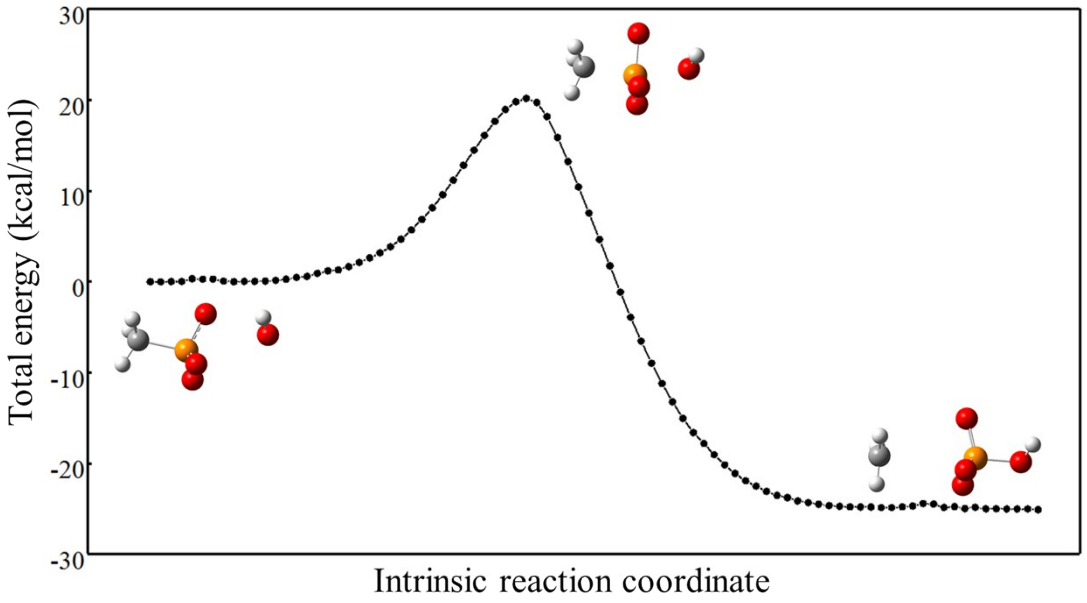
P (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -683.060967 Hartree

Charge = -2, Multiplicity = 2

P	0.36946500	0.00738100	-0.02282000
O	0.04957700	1.48800300	-0.26616400
O	-0.10582100	-0.93046900	-1.13425200
O	2.03432500	-0.12773100	-0.14366000
H	2.48099100	0.42864800	0.50556700
O	0.01215400	-0.46068300	1.39356300
C	-3.15511100	0.08737500	0.07428700
H	-3.18557900	0.39014900	-0.96212200
H	-3.18924000	-0.96112000	0.33117100
H	-3.16156800	0.83494900	0.85386100

Intrinsic Reaction Coordinate (phosphoryl side):



5. Reaction of $^1O_2$ radical and methylphosphonic acid under acidic condition

R (methyl side)

M06-2X/6-311G+(d,p) free energy in water (298.15 K): -758.435223 Hartree

Charge = 0, Multiplicity = 1

P	-1.22501100	-0.05040900	-0.10124800
O	-1.90459800	-0.42169700	1.30481800
H	-1.47499100	-0.04785800	2.08844200
O	-1.97296000	-0.72044700	-1.19697900
C	0.51186100	-0.42310600	0.03252000

H	0.94467300	0.12826300	0.86902700
H	0.63159800	-1.49455300	0.19652400
H	1.00555400	-0.13196900	-0.89542700
O	-1.35281800	1.54197900	-0.26108700
H	-0.80334300	2.06772300	0.33952000
O	3.62934800	0.54479000	-0.03828200
O	3.65195500	-0.62634800	0.14289300

TS (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -758.33736 Hartree

Charge = 0, Multiplicity = 1

P	-1.12896900	-0.01229500	-0.05361900
O	-1.57492300	-0.49571900	1.36178700
H	-1.31405500	0.02773200	2.14052700
O	-1.68691800	-0.76727800	-1.17416800
C	0.96689500	-0.40001200	-0.06669800
H	0.83970400	0.23422700	0.81787200
H	0.71909200	-1.45715900	0.01265200
H	0.97136400	0.03993900	-1.06167400
O	-1.18826500	1.54014400	-0.19814500
H	-0.81243100	2.09592600	0.50752100
O	3.23500900	0.61735400	0.02740800
O	2.58480700	-0.53979800	0.17801500

P (methyl side)

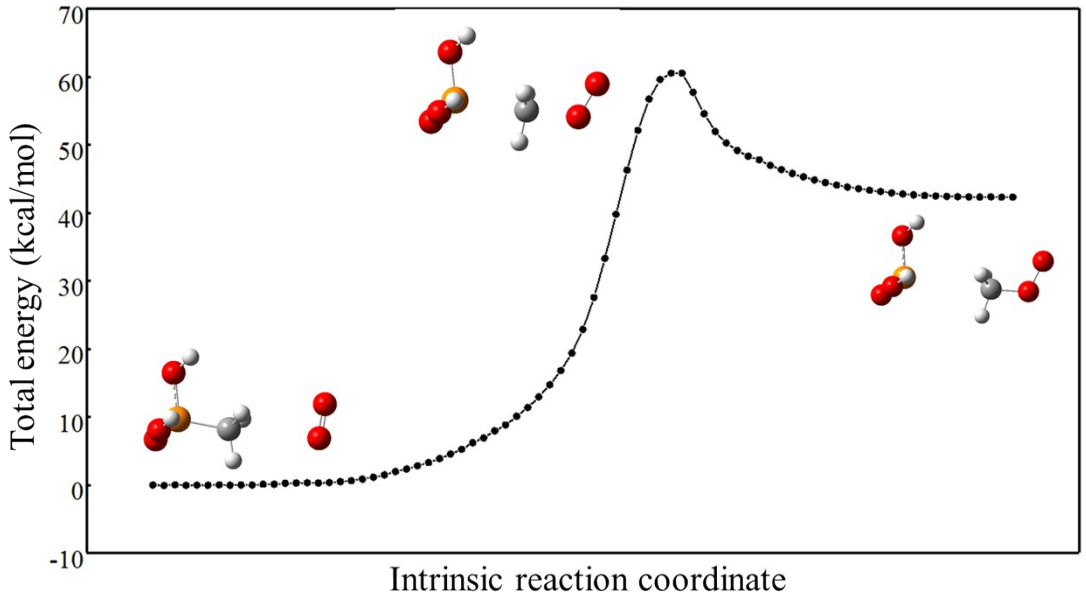
M06-2X/6-311+G(d,p) free energy in water (298.15 K): -758.404342 Hartree

Charge = 0, Multiplicity = 3

P	-1.53982600	-0.14860200	0.63348800
O	-3.05560400	-0.07676900	1.16127800
H	-3.18965500	0.40406600	1.99384400
O	-1.44419100	-0.99656600	-0.58392600
C	1.77925100	-0.42559600	-0.27966800
H	1.59145100	0.19723500	0.59469700
H	1.40364400	-1.43638700	-0.14021700
H	1.38165600	0.02773200	-1.18672900
O	-1.06731800	1.35196300	0.30379600

H	-1.06901400	1.97157900	1.05105100
O	3.80078100	0.56802600	-0.59865900
O	3.20955700	-0.56998600	-0.42882500

Intrinsic Reaction Coordinate (methyl side):



R (phosphoryl side)

M06-2X/6-311G+(d,p) free energy in water (298.15 K): -758.43709 Hartree

Charge = 0, Multiplicity = 1

P	-0.84449000	-0.10462600	0.06759500
O	-0.34168900	-0.13165500	1.46973200
O	2.16982600	0.70703400	0.39788900
C	-2.58600100	-0.37794900	-0.16025600
H	-3.14087300	0.41388000	0.34402000
H	-2.82769000	-0.37913100	-1.22370500
H	-2.84481900	-1.34249600	0.27781900
O	2.84688500	-0.07671400	-0.17930000

O	-0.60725900	1.28551400	-0.69717100
H	0.30363400	1.61463300	-0.63356700
O	-0.04645000	-1.21650800	-0.77374600
H	-0.27117500	-1.26024500	-1.71515700

TS (phosphoryl side)

M06-2X/6-311G+(d,p) free energy in water (298.15 K): -758.301022 Hartree

Charge = 0, Multiplicity = 1

P	-0.24026100	0.06612400	-0.00222400
O	-0.46783400	-0.05677600	1.47412700
O	1.40180400	0.49423100	0.20614800
C	-2.30694600	-0.45169800	0.10647800
H	-2.80542100	0.29838600	0.70711800
H	-2.45928900	-0.33457700	-0.96938500
H	-2.38786100	-1.46728300	0.47642900
O	2.31198100	-0.44975400	0.13014200
O	-0.64518200	1.42717500	-0.73014700
H	0.08702300	1.94345700	-1.10127300
O	0.10163400	-1.12443100	-0.99643500
H	-0.62283900	-1.70908700	-1.26367300

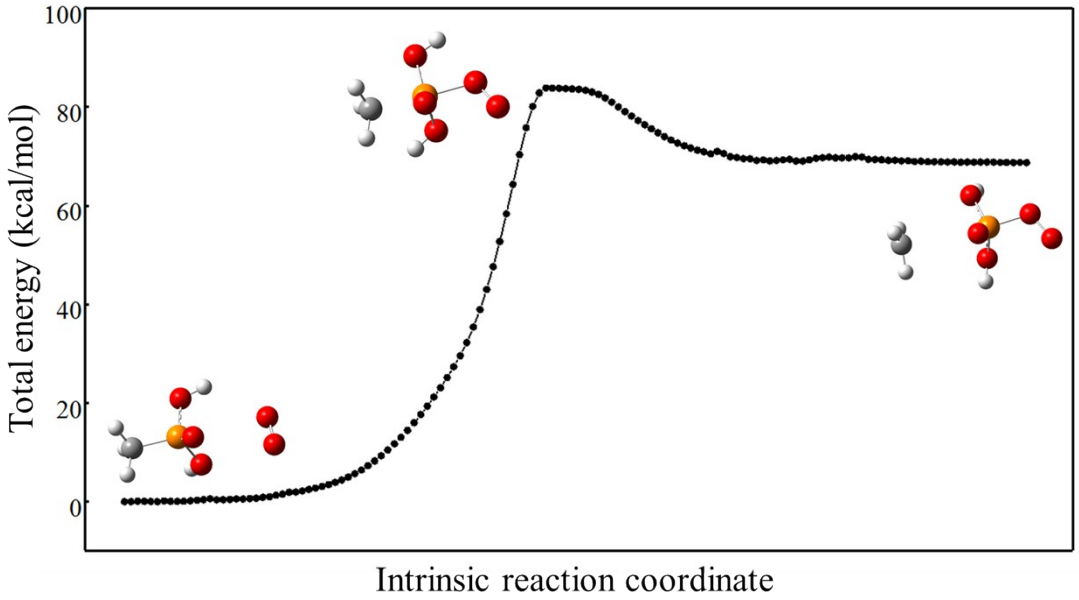
P (phosphoryl side)M06-2X/6-311G+(d,p) free energy in water (298.15 K): -758.404455 Hartree

Charge = 0, Multiplicity = 3

P	0.02694700	0.09047800	0.12930100
O	-0.30414500	-0.31841000	1.49807100
O	1.65113600	0.53843200	-0.03024900
C	-3.21421500	-0.57783600	-0.05177700
H	-3.42667900	0.20974100	0.65704400
H	-3.28679600	-0.37663400	-1.11130000
H	-3.13161100	-1.59842000	0.29483500

O	2.47118800	-0.44157100	0.26134100
O	-0.63689800	1.42865700	-0.33760500
H	-0.56385100	1.66112500	-1.27802100
O	-0.07975000	-0.97096100	-1.02403200
H	-0.58780600	-1.77342100	-0.81994500

Intrinsic Reaction Coordinate (phosphoryl side):



6. Reaction of O2·- radical and methylphosphonic acid under alkaline condition

R (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.538856 Hartree

Charge = -2, Multiplicity = 1

P	1.33605300	0.01424600	-0.01706100
O	1.77152600	-0.70195000	-1.31679000
O	1.91143300	-0.66630400	1.24751000
C	-0.48307700	-0.14944100	0.07631200
H	-0.94243700	0.32142900	-0.79558200
H	-0.76482300	-1.20478400	0.09659000
H	-0.86161400	0.33581800	0.97867100
O	1.63889300	1.53096500	-0.05230800
O	-3.95998700	0.41613900	-0.14418400
O	-3.43530600	-0.64513400	-0.07307200

TS (methyl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.495019 Hartree

Charge = -2, Multiplicity = 1

P	1.24980000	0.03743500	-0.00035600
O	1.64687800	-0.67128300	-1.28246800
O	1.64636000	-0.64647400	1.29526500
C	-0.84693000	-0.27067500	0.00266700
H	-0.97727400	0.23155300	-0.94491800
H	-0.73964300	-1.34712900	0.02018900
H	-0.97745200	0.26256500	0.93311500
O	1.33454700	1.55237100	-0.01444700
O	-3.46528500	0.51609600	-0.00976400
O	-2.77767800	-0.56434200	0.00828100

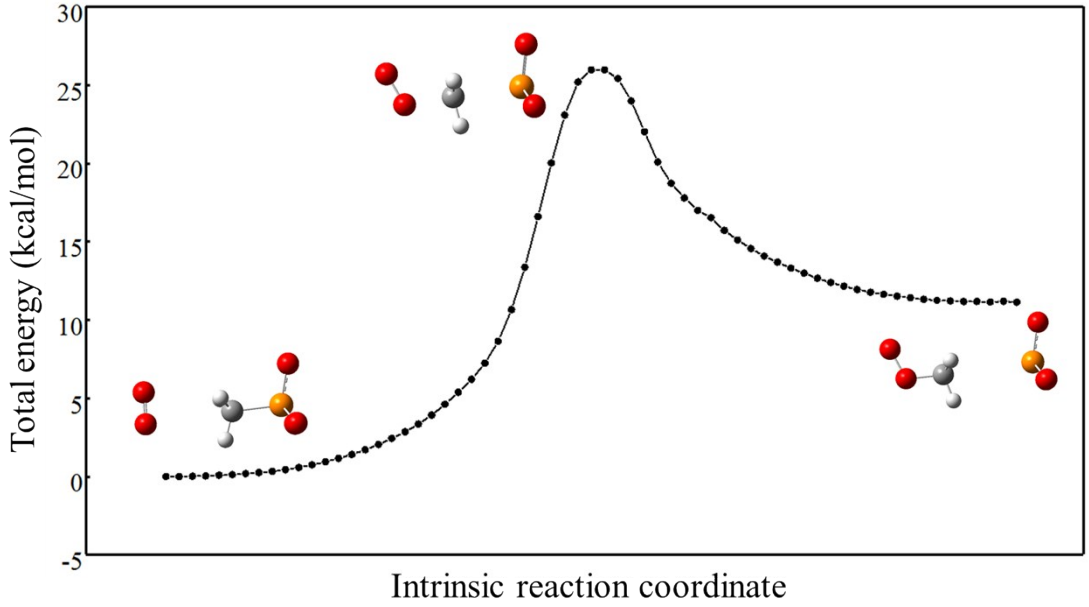
P (methyl side)M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.524641 Hartree

Charge = -2, Multiplicity = 3

P	1.17459500	0.13314100	-0.05035400
O	1.57055200	-1.09392900	-0.90938400
O	1.15693700	-0.17197800	1.46824000
C	-2.23219800	-0.40537100	-0.11593400
H	-2.15499300	0.52802200	-0.67142300

H	-1.71906700	-1.21639400	-0.62701000
H	-1.88009800	-0.29257000	0.90835000
O	1.98218500	1.40738000	-0.40290700
O	-4.36900400	0.08724700	0.49959500
O	-3.62559000	-0.79943700	-0.07858800

Intrinsic Reaction Coordinate (methyl side):



R (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.540167 Hartree

Charge = -2, Multiplicity = 1

P	0.80775800	0.02828100	0.05946600
O	0.21212400	-0.78225900	-1.11714100
O	0.76874100	1.55330500	-0.20081300
O	-2.32359400	0.29510400	-0.56357100
O	0.16313400	-0.35010100	1.41344300

C	2.57224400	-0.43262000	0.16664800
H	3.08518000	-0.17349800	-0.76230700
H	3.05244400	0.10094400	0.99001900
H	2.67769700	-1.50626600	0.33726200
O	-2.92275600	-0.43721400	0.15383900

TS (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.437897 Hartree

Charge = -2, Multiplicity = 1

P	0.32591700	0.15810100	0.08847600
O	0.27233300	-0.81734800	-1.09865400
O	0.67133300	1.60962600	-0.18785900
O	-1.51539200	0.25116800	-0.50610800
O	0.07883800	-0.31284600	1.50454900
C	2.33867900	-0.63877400	-0.05827700
H	2.78159200	-0.41852000	-1.02344500
H	2.71054900	0.00705100	0.73795700
H	2.35431300	-1.69152600	0.20322300
O	-2.40998100	-0.46345700	0.15816600

P (phosphoryl side)

M06-2X/6-311+G(d,p) free energy in water (298.15 K): -757.548023 Hartree

Charge = -2, Multiplicity = 3

P	0.22083900	-0.00383900	-0.05607000
O	0.19860500	-1.06532500	-1.13832600
O	0.90245200	1.30442600	-0.39876800
O	-1.48409500	0.59534200	-0.07427600
O	0.36990700	-0.50107700	1.36688600
C	3.42076400	-0.90797500	-0.01992500
H	3.58616800	-0.59377300	-1.04018200
H	3.63320900	-0.22816100	0.79244900
H	3.18544000	-1.94085400	0.19234400
O	-2.36666100	-0.32131300	0.19684700

Intrinsic Reaction Coordinate (phosphoryl side):