

Supporting Information

Unimolecular Decomposition of Acetyl Peroxy Radical: A Potential Source for Tropospheric Ketene

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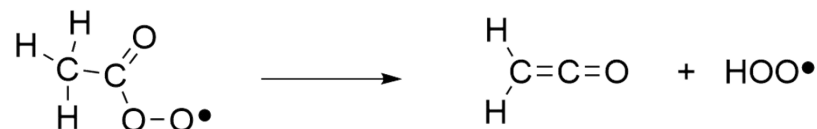
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Computational Details:

The geometries of the stationary points on the ground state potential energy surface of the reactions studied were optimized at UM06-2X/aug-cc-pVQZ level of theory. Harmonic vibrational frequency calculations were performed at the same level to verify the nature of the stationary points. The single point calculations on the UM06-2X/aug-cc-pVQZ optimized structures were carried out at UCCSD(T)/aug-cc-pVTZ and UCCSD(T)-F12/cc-pVTZ levels. The energetic calculated at UM06-2X/aug-cc-pVQZ level are in closer agreement with the UCCSD(T)/aug-cc-pVTZ//UM06-2X/aug-cc-pVQZ results. Hence, the results obtained at UCCSD(T)/aug-cc-pVTZ//UM06-2X/aug-cc-pVQZ level are discussed in the manuscript. The excited state properties of the minima along the PES of the reactions studied were calculated at EOM-CCSD/aug-cc-pVTZ level of theory. The calculations at UCCSD(T)-F12/cc-pVTZ level are performed using MOLPRO program package and all the other calculations are performed using GAUSSIAN 09 program package.

Table S1a: Energetics [in Hartrees] of the stationary points involved in the unimolecular dissociation of acetyl peroxy radical.

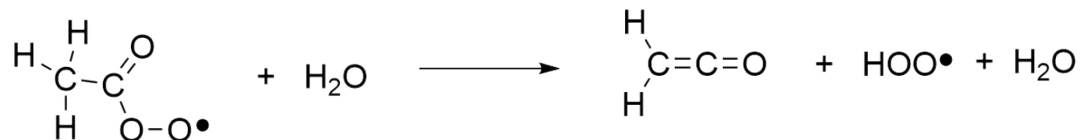


Stationary points	UM06-2X/aug-cc-pVQZ			UCCSD(T)-F12/cc-pVTZ			UCCSD(T)/aug-cc-pVTZ		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
R (R2 ts14 ircr)	-303.573281	-303.513978	-303.549083	-303.240495	-303.181191	-303.216296	-303.146801	-303.087498	-303.122603
TS1 (R2 ts14)	-303.51109	-303.458268	-303.494435	-303.17619	-303.123368	-303.159535	-303.084244	-303.031423	-303.06759
PC1 (R2 ts14 ircp)	-303.531613	-303.474623	-303.514365	-303.194875	-303.137884	-303.177626	-303.103444	-303.046453	-303.086195
ketene	-152.6070284	-152.570697	-152.598696	-152.416574	-152.3802428	-152.4082418	-152.3685192	-152.3321878	-152.3601868
HO ₂	-150.9155949	-150.897150	-150.923082	-150.769160	-150.7507156	-150.7766476	-150.7258743	-150.7074294	-150.7333614

Table S1b: Relative energies [in kcal/mol] of the stationary points involved in the unimolecular dissociation of acetyl peroxy radical.

Stationary points	UM06-2X/aug-cc-pVQZ			UCCSD(T)-F12/cc-pVTZ			UCCSD(T)/aug-cc-pVTZ		
	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}
R (R2 ts14 ircr)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TS1 (R2 ts14)	+39.0	+34.9	+34.3	+40.3	+36.3	+35.6	+39.2	+35.2	+34.5
PC1 (R2 ts14 ircp)	+26.2	+24.7	+21.8	+28.6	+27.2	+24.3	+27.2	+25.7	+22.8
Ketene + HO ₂	+31.8	+28.9	+17.2	+34.4	+31.5	+19.7	+32.9	+30.0	+18.2

Table S2a: Energetics [in Hartrees] of the stationary points involved in the dissociation of acetyl peroxy radical in the presence of a water monomer.

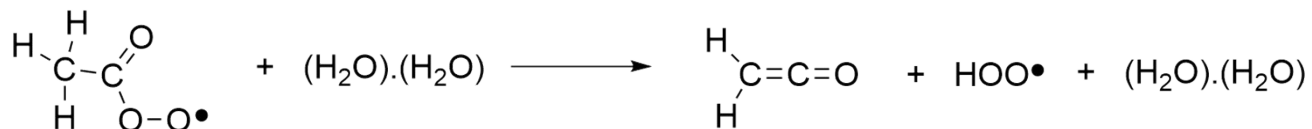


Stationary points	UM06-2X/aug-cc-pVQZ			UCCSD(T)-F12/cc-pVTZ			UCCSD(T)/aug-cc-pVTZ		
	E _{Tot}	H ₂₉₈	G ₂₉₈	E _{Tot}	H ₂₉₈	G ₂₉₈	E _{Tot}	H ₂₉₈	G ₂₉₈
R	-303.573281	-303.513978	-303.549083	-303.240495	-303.181191	-303.216296	-303.146801	-303.087498	-303.122603
H ₂ O	-76.4340463	-76.408679	-76.430745	-76.3635701	-76.3382028	-76.3602688	-76.3422881	-76.3169208	-76.3389868
RC1 (R3 ts2 ircr)	-380.015145	-379.928102	-379.972364	-379.613045	-379.526002	-379.570264	-379.4967858	-379.409743	-379.454005
TS2 (R3 ts2)	-379.948188	-379.869381	-379.908982	-379.541543	-379.462737	-379.502338	-379.425126	-379.34632	-379.385921
PC1 (R3 ts2 ircp)	-379.980463	-379.895617	-379.942949	-379.575559	-379.490713	-379.538045	-379.4604053	-379.375559	-379.422891
Ketene	-152.6070284	-152.570697	-152.598696	-152.4165742	-152.3802428	-152.4082418	-152.3685192	-152.3321878	-152.3601868
HO ₂	-150.9155949	-150.897150	-150.923082	-150.7691605	-150.7507156	-150.7766476	-150.7258743	-150.7074294	-150.7333614
H ₂ O	-76.4340463	-76.408679	-76.430745	-76.3635701	-76.3382028	-76.3602688	-76.3422881	-76.3169208	-76.3389868
Stepwise mechanism									
RC1a	-380.0151128	-379.928074	-379.972293						
TS2a	-379.9600387	-379.878853	-379.919914						
INT2a	-379.9677872	-379.881908	-379.926633						
TS2b	-379.9556736	-379.875313	-379.915847						
INT2b	-380.0068822	-379.920455	-379.965035						
TS2c	-379.9421574	-379.859023	-379.904181						
PC2a	-379.9778812	-379.893099	-379.941015						

Table S2b: Relative Energies [in kcal/mol] of the stationary points involved in the dissociation of acetyl peroxy radical in the presence of a water monomer.

Stationary points	UM06-2X/aug-cc-pVQZ			UCCSD(T)-F12/cc-pVTZ			UCCSD(T)/aug-cc-pVTZ		
	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}
R+H ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
RC1 (R3 ts2 ircr)	-4.9	-3.4	+4.7	-5.6	-4.1	+3.9	-4.8	-3.3	+4.7
TS2 (R3 ts2)	+37.1	+33.4	+44.4	+39.2	+35.5	+46.6	+40.1	+36.4	+47.5
PC1 (R3 ts2 ircp)	+16.8	+16.9	+23.1	+17.8	+17.9	+24.2	+17.9	+18.1	+24.3
Ketene+HO ₂ +H ₂ O	+31.8	+28.9	+17.1	+34.4	+31.5	+19.7	+32.8	+30.0	+18.2
Stepwise mechanism									
RC1a	-4.9	-3.4	+4.7						
TS2a	+29.7	+27.5	+37.6						
INT2a	+24.8	+25.6	+33.4						
TS2b	+32.4	+29.7	+40.2						
INT2b	+0.3	+1.4	+9.3						
TS2c	+40.9	+39.9	+47.5						
PC2a	+18.4	+18.5	+24.3						

Table S3a: Energetics [in Hartrees] of the stationary points involved in the dissociation of acetyl peroxy radical in the presence of a water dimer.



Stationary points	UM06-2X/aug-cc-pVQZ			UCCSD(T)-F12/cc-pVTZ			UCCSD(T)/aug-cc-pVTZ		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
R	-303.573281	-303.513978	-303.549083	-303.240495	-303.181191	-303.216296	-303.146801	-303.087498	-303.122603
H ₂ O	-76.4340463	-76.408679	-76.430745	-76.3635701	-76.3382028	-76.3602688	-76.3422881	-76.3169208	-76.3389868
RC2 (R4 ts21 ircr)	-456.439855	-456.324943	-456.375647	-455.992413	-455.877501	-455.928205	-455.8527165	-455.737804	-455.788508
TS3	-456.39089	-456.284824	-456.329594	-455.913803	-455.807737	-455.852507	-455.7736704	-455.667605	-455.712375
PC3 (R4 ts21 ircp)	-456.406574	-456.293846	-456.348365	-455.956566	-455.843838	-455.898357	-455.8168593	-455.704132	-455.758651
ketene	-152.6070284	-152.570697	-152.598696	-152.4165742	-152.3802428	-152.4082418	-152.3685192	-152.3321878	-152.3601868
HO ₂	-150.9155949	-150.897150	-150.923082	-150.7691605	-150.7507156	-150.7766476	-150.7258743	-150.7074294	-150.7333614

Table S3b: Relative Energies [in kcal/mol] of the stationary points involved in the dissociation of acetyl peroxy radical in the presence of a water dimer.

Stationary points	UM06-2X/aug-cc-pVQZ			UCCSD(T)-F12/cc-pVTZ			UCCSD(T)/aug-cc-pVTZ		
	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}
R+H ₂ O+H ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
RC2 (R4 ts21 ircr)	0.9	+4.0	+21.9	-15.5	-12.5	+5.4	-13.4	-10.3	+7.6
TS3	+31.7	+29.2	+50.8	+33.8	+31.3	+52.9	+36.2	+33.7	+55.3
PC3 (R4 ts21 ircp)	+21.8	+23.5	+39.0	+6.9	+8.6	+24.2	+9.1	+10.8	+26.3
Ketene+HO ₂ +H ₂ O+H ₂ O	+31.8	+28.9	+17.2	+34.4	+31.5	+19.7	+32.9	+30.0	+18.2

Table S4: Excited state properties of the minima involved in the present study

Stationary points	EOM-CCSD/aug-cc-pVTZ Electronic excitation (1 st excited state energy) Excitation energy [eV]
R	0.8727
PC1	1.1113
RC1	0.8690
PC2	1.0840
RC2	*
PC3	1.0427

* SCF not converged

Structures of the stationary points optimized at UM06-2X/aug-cc-pVQZ level

R

6	1.683592000	-0.538368000	-0.000016000
1	2.512488000	0.158833000	-0.000327000
1	1.724753000	-1.179015000	0.878562000
1	1.724465000	-1.179525000	-0.878234000
6	0.401170000	0.224450000	0.000000000
8	0.213365000	1.385290000	0.000006000
8	-0.674020000	-0.716845000	0.000027000
8	-1.848130000	-0.158043000	-0.000020000

TS1

6	0.859190000	1.303163000	-0.011973000
1	1.269189000	1.788023000	-0.889912000
1	-0.512929000	1.252277000	-0.054413000
1	1.133226000	1.763070000	0.930965000
6	1.100933000	-0.055658000	-0.010248000
8	1.583989000	-1.088003000	-0.039713000
8	-0.983146000	-0.556487000	0.080139000
8	-1.544225000	0.582978000	-0.004889000

PC1

6	0.910830000	1.252613000	0.185303000
1	1.365238000	2.026378000	-0.409829000
1	-1.011083000	0.710429000	-0.631466000
1	0.318736000	1.477593000	1.057482000
6	1.307434000	0.009760000	0.010864000
8	1.643607000	-1.071030000	-0.173216000
8	-1.561997000	-0.584211000	0.521611000

8	-1.829419000	0.181662000	-0.497543000
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RC1

6	0.604473000	0.808010000	1.255935000
1	0.289480000	1.803020000	1.550367000
1	0.052605000	0.051651000	1.809243000
1	1.665270000	0.661588000	1.446714000
6	0.310127000	0.653793000	-0.193953000
8	-0.207021000	1.416365000	-0.936738000
8	0.717383000	-0.578590000	-0.790081000
8	1.231295000	-1.431364000	0.048605000
1	-2.334514000	-0.073665000	-0.430129000
8	-2.107001000	-0.617564000	0.329408000
1	-2.237692000	-1.524192000	0.042365000

TS2

6	-0.554348000	1.197392000	-0.780595000
1	-1.151240000	2.099627000	-0.774867000
1	0.740418000	1.297966000	0.021243000
1	-0.148159000	0.886133000	-1.731926000
6	-1.103475000	0.181729000	-0.016957000
8	-1.843713000	-0.140827000	0.811595000
8	-0.096194000	-1.289894000	-0.418396000
8	1.154556000	-1.288960000	-0.104710000
1	2.468985000	1.332669000	0.168369000
8	1.674368000	0.968822000	0.569881000
1	1.527345000	-0.134026000	0.292964000

PC2

6	1.557807000	0.599610000	0.990446000
1	2.345513000	1.315754000	1.152090000
1	-0.161663000	1.543498000	-0.049775000

1	0.835816000	0.352411000	1.750201000
6	1.628314000	-0.178727000	-0.068402000
8	1.697230000	-0.820600000	-1.016894000
8	-0.995615000	-1.159051000	0.581076000
8	-2.056519000	-0.739801000	-0.046861000
1	-1.365457000	2.506537000	-0.208769000
8	-1.011576000	1.664933000	-0.501181000
1	-1.839093000	0.192666000	-0.305127000

RC1a

6	0.596001000	0.809625000	1.256863000
1	0.046819000	0.051855000	1.808811000
1	1.655719000	0.669010000	1.452267000
1	0.275451000	1.802148000	1.549864000
6	0.308412000	0.653230000	-0.194629000
8	-0.207818000	1.413132000	-0.938347000
8	0.723318000	-0.576890000	-0.786965000
8	1.237270000	-1.425716000	0.050972000
1	-2.238805000	-1.527096000	0.036271000
8	-2.106355000	-0.622509000	0.325602000
1	-2.336982000	-0.077177000	-0.430717000

TS2a

6	0.838706000	1.379366000	0.271613000
1	-0.050351000	1.729310000	-0.248929000
1	0.657118000	1.477043000	1.338562000
1	1.703530000	1.960538000	-0.024823000
6	1.106751000	-0.047812000	-0.087952000
8	2.077943000	-0.479758000	-0.615381000
8	0.120176000	-0.970431000	0.212579000
8	-0.947601000	-0.422500000	0.901577000
1	-1.732913000	-0.474012000	0.212055000
8	-2.427663000	0.169817000	-0.755071000

1	-2.832959000	0.940762000	-0.328464000
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INT2a

6	0.391160000	1.327419000	0.345267000
1	-0.467003000	1.453171000	-0.311877000
1	0.015264000	1.221141000	1.359973000
1	1.051857000	2.182904000	0.273147000
6	1.177897000	0.114790000	-0.046105000
8	2.317011000	0.092524000	-0.385261000
8	0.534957000	-1.099839000	-0.010805000
8	-0.799378000	-0.997552000	0.441507000
1	-1.297584000	-1.254547000	-0.345873000
8	-2.776170000	0.410528000	-0.454397000
1	-2.928233000	0.498785000	0.501310000

TS2b

6	0.067028000	-0.974306000	0.841754000
1	1.074548000	-1.065507000	0.197709000
1	0.364008000	-0.461854000	1.749073000
1	-0.275824000	-1.988465000	1.004452000
6	-0.922559000	-0.229521000	0.020025000
8	-1.942084000	-0.661400000	-0.412790000
8	-0.632740000	1.075779000	-0.302253000
8	0.608528000	1.494291000	0.240266000
1	0.378526000	2.379568000	0.544210000
8	2.154026000	-0.865146000	-0.549166000
1	2.116729000	0.105300000	-0.568625000

INT2b

6	-1.718994000	0.920212000	0.582270000
1	2.031366000	-1.109967000	0.148585000
1	-1.264877000	1.891524000	0.535351000

1	-2.653884000	0.759876000	1.090382000
6	-1.140944000	-0.240021000	-0.044004000
8	-1.642478000	-1.334234000	-0.055246000
8	0.057174000	-0.118869000	-0.701994000
8	0.622692000	1.173306000	-0.583036000
1	1.474943000	0.931943000	-0.173074000
8	2.575177000	-0.393512000	0.491052000
1	3.478358000	-0.598498000	0.243783000

TS2c

6	-0.876866000	-0.541462000	1.302225000
1	0.552607000	2.307746000	-0.559598000
1	0.083036000	-0.358863000	1.747025000
1	-1.636139000	-1.137593000	1.781720000
6	-1.115158000	-0.124835000	0.035332000
8	-1.706154000	0.282100000	-0.863912000
8	0.446421000	-0.952988000	-0.722568000
8	1.649002000	-0.786311000	-0.083707000
1	1.943773000	-1.685077000	0.104891000
8	0.806708000	1.912953000	0.276595000
1	1.441054000	1.225537000	0.049360000

PC2a

6	-0.897186000	-0.856275000	1.059927000
1	-0.175092000	2.740813000	-0.013110000
1	-0.536787000	-0.083257000	1.719070000
1	-1.069331000	-1.866270000	1.395282000
6	-1.505377000	-0.469136000	-0.046666000
8	-2.014079000	-0.191293000	-1.034086000
8	2.104514000	0.202542000	-0.392043000
8	1.837099000	-1.047163000	-0.154293000
1	0.913580000	-1.064127000	0.210184000
8	-0.106609000	1.878147000	0.397779000

1	0.715613000	1.487446000	0.070147000
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RC2

6	1.712198000	-0.063249000	1.167675000
1	2.623147000	0.516870000	1.267786000
1	0.903740000	0.389820000	1.736932000
1	1.858137000	-1.081337000	1.521302000
6	1.337396000	-0.059023000	-0.270857000
8	1.841513000	0.490642000	-1.184386000
8	0.199093000	-0.874122000	-0.623499000
8	-0.381272000	-1.442803000	0.388823000
1	-2.327719000	-0.898683000	-0.146405000
1	-3.651928000	-0.231983000	0.267037000
8	-2.845409000	-0.089435000	-0.232396000
1	-1.555811000	1.226617000	0.186155000
8	-0.751496000	1.720678000	0.410434000
1	-0.646563000	2.372652000	-0.285522000

TS3

6	1.157000000	0.894262000	0.974327000
1	1.842031000	1.679629000	1.258026000
1	-0.230078000	1.394860000	0.113868000
1	0.568195000	0.420812000	1.743564000
6	1.615503000	0.089094000	-0.031518000
8	2.346852000	-0.095878000	-0.917309000
8	0.284746000	-1.145904000	-0.223582000
8	-0.529746000	-1.302390000	0.762504000
1	-1.755081000	-1.038581000	0.117360000
1	-3.298141000	-0.425659000	0.082195000
8	-2.463913000	-0.431063000	-0.393315000
1	-1.911719000	0.596388000	-0.379786000
8	-1.152096000	1.585710000	-0.365745000
1	-1.514318000	2.401752000	-0.012600000

PC3

6	1.668762000	0.049977000	1.399979000
1	2.186282000	0.619306000	2.154390000
1	0.094913000	1.689950000	0.309650000
1	0.850741000	-0.610793000	1.637742000
6	2.159983000	0.020047000	0.183522000
8	2.581887000	0.030939000	-0.887925000
8	-0.316949000	-1.127729000	-0.701158000
8	-1.200359000	-1.616322000	0.125765000
1	-1.919024000	-0.914790000	0.191170000
1	-3.415710000	0.703446000	0.844576000
8	-2.806748000	0.428931000	0.157106000
1	-2.131339000	1.130535000	0.046194000
8	-0.543237000	1.778367000	-0.408861000
1	-0.355090000	1.008712000	-0.964141000

Ketene

6	-1.203425000	-0.000005000	-0.000029000
1	-1.727744000	0.939458000	0.000122000
1	-1.727704000	-0.939495000	0.000122000
6	0.103749000	0.000021000	-0.000044000
8	1.256688000	-0.000008000	0.000024000

HO₂

1	-0.879212000	-0.865528000	0.000000000
8	0.054951000	0.706493000	0.000000000
8	0.054951000	-0.598302000	0.000000000

H₂O

1	0.761485000	-0.465688000	0.000000000
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8	0.000000000	0.116422000	0.000000000
1	-0.761485000	-0.465686000	0.000000000