Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


Supplementary Information

# Photo-impulsive reactions in the electronic ground state without electronic excitation: Non-photo, non-thermal chemical reactions

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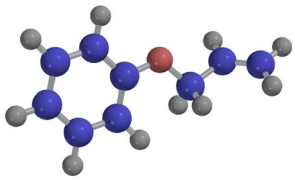
**Content**

## Reactant : Allyl Phenyl Ether (Table2 & 3)

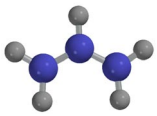


Charge = 0 Multiplicity = 1

H,0,-0.0115962383,0.0504904146,-0.0120996256
C,0,-0.0053473981,0.0322419212,1.072161165
C,0,0.0324172232,-0.0150917067,3.8611591501
C,0,1.2079357381,-0.0081786828,1.7448204395
C,0,-1.2109534951,0.0484884206,1.7792811004
C,0,-1.1810809186,0.0250281687,3.1687767576
C,0,1.2326302681,-0.0330279122,3.1452733897
H,0,2.1500776397,-0.0212572959,1.2100350703
H,0,-2.1563862019,0.079473538,1.2509682734
H,0,-2.1074778013,0.0384818753,3.7324452046
H,0,0.0258871344,-0.0295449703,4.9426461994
O,0,2.4746671482,-0.070518111,3.7143370161
C,0,2.5771876154,-0.1426682186,5.13951694
H,0,2.1402256782,0.7508382523,5.6007827201
H,0,2.023063109,-1.0219208424,5.4964590331
C,0,4.0259676451,-0.2687011454,5.4939444739
H,0,4.5588620352,-1.0781526192,5.001764017
C,0,4.6498582235,0.5174040422,6.3659286589
H,0,5.6927947096,0.3668223905,6.6196906894
H,0,4.1401357309,1.3389688253,6.8602003667

E = -424.282651274 (Hartree/Particle)
Zero-point correction = 0.165310 (Hartree/Particle)
S**2 = 0.0000

## Allyl Radical (Table 2)



Charge = 0 Multiplicity = 2

C,0,0.0351540868,-0.0002347816,-0.0317060708

C,0,-0.0357439849,0.0000156048,1.3505291779

H,0,0.9028193892,-0.0000550517,1.9011809637

C,0,-1.2077392736,0.0003444902,2.0867544331

H,0,-1.1951785294,0.0005342682,3.1691751906

H,0,-2.1761018224,0.0004310031,1.5980206521

H,0,-0.8638974476,-0.0001765269,-0.6385777165

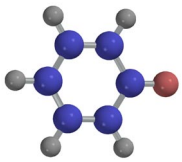
H,0,0.9861510054,-0.0004873934,-0.5488109543

E = -117.298251119 (Hartree/Particle)

Zero-point correction = 0.065843 (Hartree/Particle)

S**2 = 0.7779

## Phenoxy Radical (Table2)



Charge = 0 Multiplicity = 2

H,0,-0.0165553025,-0.0010360995,-0.0151076457

C,0,0.012608514,-0.0004695939,1.0688742863

C,0,1.2186193003,-0.0001857968,1.7299003927

C,0,1.2720295073,0.0005668089,3.1807532019

C,0,0.0048985364,0.0011589228,3.8893007288

C,0,-1.1866950077,0.0007941475,3.2025103645

C,0,-1.194615308,-0.0000363663,1.7941521744

H,0,-2.1395414036,-0.0003692168,1.2630160022

H,0,-2.127880803,0.0012191688,3.741062771

H,0,0.0449973031,0.0021881112,4.9722525277

O,0,2.3644371619,0.0007428421,3.7948744992

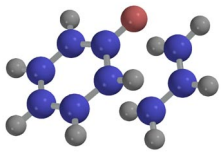
H,0,2.1646335828,-0.0006146775,1.2012778969

E = -306.913377028 (Hartree/Particle)

Zero-point correction = 0.091079 (Hartree/Particle)

S**2 = 0.7863

## Transition State (Table 3)

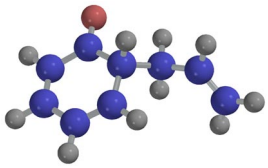


Charge = 0 Multiplicity = 1

C,0,0.0293406448,-0.0439252998,-0.0000049761
C,0,0.0284659559,-0.0183201788,1.423025973
H,0,0.9710813693,-0.0185378678,-0.5324783241
C,0,-1.1524608831,0.3461416281,-0.7349158412
C,0,-2.3544443426,0.5441433543,0.0328570189
O,0,-1.146867269,0.4000705403,-2.0061890847
C,0,-1.2632249173,-1.6774305313,-2.6514280919
H,0,-1.1787622541,-1.5024693705,-3.7156912541
H,0,-2.2657168497,-1.6771767852,-2.2453544453
C,0,-0.1979234363,-2.15227592,-1.9190482698
H,0,0.7710493705,-2.2281158111,-2.4035083903
C,0,-0.2526847168,-2.2202085714,-0.5278850656
H,0,-1.2064708035,-2.2917247147,-0.0191446841
H,0,0.6037215785,-2.5665783804,0.0366753615
C,0,-1.1327812657,0.2229044193,2.1130328017
H,0,0.9537316864,-0.2088440817,1.9568860273
C,0,-2.3328771446,0.502472856,1.4031459763
H,0,-3.2618195883,0.7810977693,-0.5116406064
H,0,-3.2422458802,0.6978283235,1.9624292403
H,0,-1.1391762259,0.2214354064,3.1969294567

E = -424.226337400 (Hartree/Particle)
Zero-point correction = 0.163079 (Hartree/Particle)
S**2 = 0.0000
i = -358.8549

## Keto-Intermediate : 6-Allyl-Cyclohexa-2,4-Dienone (Table3)



Charge = 0 Multiplicity = 1

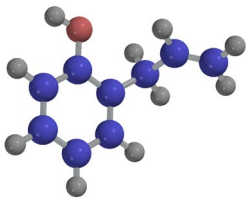
C,0,-0.0095328841,0.012383867,0.0012100784
C,0,-0.0196599597,0.0001925671,2.4564797832
C,0,2.1582520776,0.0240432498,1.3764603066
C,0,1.4335209667,-0.0028191723,2.5056499916
C,0,1.5283039276,0.0697923841,0.0165613353
C,0,-0.7042665059,0.0104873544,1.2920230579
H,0,1.9191800278,-0.032320258,3.4745261148
H,0,-1.7875280719,-0.0053900363,1.2593957522
H,0,-0.5624533129,-0.0166049251,3.3968958716
H,0,3.2428818591,0.0124062725,1.415384639
H,0,1.7669480011,1.0528742939,-0.4208140574
O,0,-0.6146000483,-0.0160979382,-1.0597862566
C,0,2.1218561918,-0.9993507023,-0.9497786178
H,0,1.4954601252,-0.9828691562,-1.8468854839
H,0,2.0225428647,-1.9903403471,-0.496332049
C,0,3.5516391091,-0.7349528981,-1.319053376
C,0,4.5768478617,-1.5458189425,-1.0647156478
H,0,3.7376150939,0.2009777299,-1.8453446522
H,0,4.4399387234,-2.4893649592,-0.5445600569
H,0,5.5860111661,-1.3011946148,-1.3765696599

E = -424.267073307 (Hartree/Particle)

Zero-point correction = 0.164427 (Hartree/Particle)

S**2 = 0.0000

## Phenol Product : *o*-Allyl Phenol (Table3)



Charge = 0 Multiplicity = 1

C,0,0.1167494684,0.1406870168,0.0571845208
C,0,-0.0158199067,0.0148105232,2.4648142677
C,0,2.0918201337,-0.2850742224,1.3433664411
C,0,1.3535359796,-0.2283753719,2.5249231897
C,0,1.4972887218,-0.1056712087,0.0935953283
C,0,-0.6348829821,0.1989489492,1.2305539936
H,0,1.8432712084,-0.3748212118,3.4803093757
H,0,-1.703482609,0.3883055958,1.1771021827
H,0,-0.6063963122,0.0612261354,3.3726350534
H,0,3.1593383404,-0.475784697,1.386675164
O,0,-0.4540438128,0.3189569251,-1.1802112977
C,0,2.3098696576,-0.1607744523,-1.185947205
H,0,1.7357588544,-0.7017562591,-1.9463665787
H,0,3.2280131476,-0.7263614489,-1.0055519815
C,0,2.6569517115,1.2073518279,-1.7208295556
C,0,3.8951785644,1.6489747641,-1.9279396045
H,0,1.8110131523,1.8534820903,-1.9425686849
H,0,4.7639604228,1.0316403608,-1.7178075474
H,0,4.0855714252,2.6428635542,-2.3174178491
H,0,-1.4011529413,0.4608071513,-1.0823364406

E = -424.298309089 (Hartree/Particle)
Zero-point correction = 0.165152 (Hartree/Particle)
S**2 = 0.0000

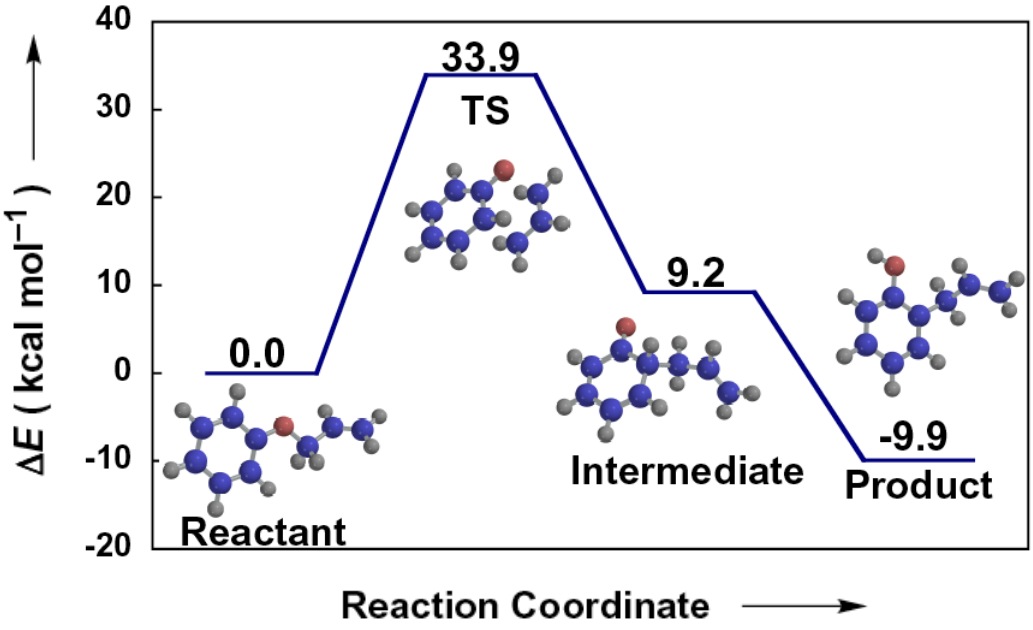



**Fig. S1.** Reaction pathway including ZPE corrections.