SUPPLEMENTARY MATERIAL

**The role of guaiacyl moiety in free radical scavenging by**

**3,5-dihydroxy-4-methoxybenzyl alcohol: Thermodynamics of 3H+/3e− mechanisms**

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**Table S1** Reaction enthalpies and reaction free energies related to tHAT, tSPLET and tET-PT mechanism

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*Reaction enthalpies*

The tHAT mechanism (Eqs. 1-3) can be characterized by the bond dissociation enthalpy (BDE). Related BDEs are calculated according to Eqs. (1’-3’), respectively.

BDE1 = *H*((HO)Ar(OCH3)(O•)) + *H*(H•) − *H*((HO)Ar(OCH3)(OH)) (1’)

BDE2 = *H*((HO)Ar(OCH2O)) + *H*(H•) − *H*((HO)Ar(OCH3)(O•)) (2’)

BDE3 = *H*((•O)Ar(OCH2O)) + *H*(H•) − *H*((HO)Ar(OCH2O)) (3’)

where *H*((HO)Ar(OCH3)(OH)), *H*((HO)Ar(OCH3)(O•)), *H*((HO)Ar(OCH2O)), *H*((•O)Ar(OCH2O)) and *H*(H•) are enthalpies of DHMBA, phenoxyl radical, HMBD, phenoxyl radical of HMBD and H-atom, respectively.

The tSPLET mechanism (Eqs. 4-9) can be characterized by the proton affinitiy (IP) and electron transfer energy (ETE). Related PAs and ETEs are calculated according to Eqs. (4’-9’), respectively.

PA1 = *H*((HO)Ar(OCH3)(O−)) + *H*(H+) − *H*((HO)Ar(OCH3)(OH)) (4’)

PA2 = *H*((−O)Ar(OCH3)(O−)) + *H*(H+) − *H*((HO)Ar(OCH3)(O−)) (5’)

ETE1 = *H*((−O)Ar(OCH3)(O•)) + *H*(e−) − *H*((−O)Ar(OCH3)(O−)) (6’)

PA3 = *H*((−O)Ar(OCH2−)(O•)) + *H*(H+) − *H*((−O)Ar(OCH3)(O•)) (7’)

ETE2 = *H*((−O)Ar(OCH2O)) + *H*(e−) − *H*((−O)Ar(OCH2−)(O•)) (8’)

ETE3 = *H*((•O)Ar(OCH2O)) + *H*(e−) − *H*((−O)Ar(OCH2O)) (9’)

*H*((HO)Ar(OCH3)(O−)), *H*((−O)Ar(OCH3)(O−)), *H*((−O)Ar(OCH3)(O•)), *H*((−O)Ar(OCH2−)(O•)), *H*((−O)Ar(OCH2O)), *H*(H+) and *H*(e−) are enthalpies of phenoxide anion, dianion, radical anion, radical dianion, HMBD anion, proton and electron, respectively.

The tET-PT mechanism (Eqs. 10-15) can be characterized by the ionization potential (IP) and proton dissociation enthalpy (PDE). Related IPs and PDEs are calculated according to Eqs. (10’-15’), respectively.

IP1 = *H*((HO)Ar(OCH3)(OH)•+) + *H*(e−) − *H*((HO)Ar(OCH3)(OH)) (10’)

PDE1 = *H*((HO)Ar(OCH3)(O•)) + *H*(H+) − *H*((HO)Ar(OCH3)(OH)•+) (11’)

IP2 = *H*((HO)Ar(OCH3)(O)+) + *H*(e−) − *H*((HO)Ar(OCH3)(O•)) (12’)

PDE2 = *H*((HO)Ar(OCH2O)) + *H*(H+) − *H*((HO)Ar(OCH3)(O)+) (13’)

IP3 = *H*((HO)Ar(OCH2O)•+) + *H*(e−) − *H*((HO)Ar(OCH2O)) (14’)

PDE3 = *H*((•O)Ar(OCH2O)) + *H*(H+) − *H*((HO)Ar(OCH2O)•+) (15’)

*H*((HO)Ar(OCH3)(OH)•+), *H*((HO)Ar(OCH3)(O)+) and *H*((HO)Ar(OCH2O)•+) are enthalpies of radical cation, cationic intermediate and HMBD radical cation, respectively.

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*Reaction free energies*

Δr*G*BDE1, Δr*G*BDE2 and Δr*G*BDE3 represent the free energies of tHAT mechanism, and are given by Eqs. (16’-18’), respectively:

Δr*G*BDE1 = [*G*((HO)Ar(OCH3)(O•)) + *G*(ROH)] – [*G*((HO)Ar(OCH3)(OH)) + *G*(RO•)] (16’)

Δr*G*BDE2 = [*G*((HO)Ar(OCH2O)) + *G*(ROH)] – [*G*((HO)Ar(OCH3)(O•)) + *G*(RO•)] (17’)

Δr*G*BDE3 = [*G*((•O)Ar(OCH2O)) + *G*(ROH)] – [*G*((HO)Ar(OCH2O)) + *G*(RO•)] (18’)

In the tSPLET mechanism, Δr*G*PA1, Δr*G*PA2, Δr*G*ETE1, Δr*G*PA3, Δr*G*ETE2 and Δr*G*ETE3 are related to the involved processes, and are calculated by Eqs. (19’-24’), respectively:

Δr*G*PA1 = [*G*((HO)Ar(OCH3)(O−)) + *G*(ROH)] – [*G*((HO)Ar(OCH3)(OH)) + *G*(RO–)] (19’)

Δr*G*PA2 = [*G*((−O)Ar(OCH3)(O−)) + *G*(ROH)] – [*G*((HO)Ar(OCH3)(O−)) + *G*(RO–)] (20’)

Δr*G*ETE1 = [*G*((−O)Ar(OCH3)(O•)) + *G*(RO–)] – [*G*((−O)Ar(OCH3)(O−)) + *G*(RO•)] (21’)

Δr*G*PA3 = [*G*((−O)Ar(OCH2−)(O•)) + *G*(ROH)] – [*G*((−O)Ar(OCH3)(O•)) + *G*(RO–)] (22’)

Δr*G*ETE2 = [*G*((−O)Ar(OCH2O)) + *G*(RO–)] – [*G*((−O)Ar(OCH2−)(O•)) + *G*(RO•)] (23’)

Δr*G*ETE3 = [*G*((•O)Ar(OCH2O)) + *G*(RO–)] – [*G*((−O)Ar(OCH2O)) + *G*(RO•)] (24’)

The tET-PT mechanism, is characterized by Δr*G*IP1, Δr*G*PDE1, Δr*G*IP2, Δr*G*PDE2, Δr*G*IP3 and Δr*G*PDE3, which are calculated by Eqs. (25’-30’), respectively:

Δr*G*IP1 = [*G*((HO)Ar(OCH3)(OH)•+) + *G*(RO–)] – [*G*((HO)Ar(OCH3)(OH)) + *G*(RO•)] (25’)

Δr*G*PDE1 = [*G*((HO)Ar(OCH3)(O•)) + *G*(ROH)] – [*G*((HO)Ar(OCH3)(OH)•+) + *G*(RO–)] (26’)

Δr*G*IP2 = [*G*((HO)Ar(OCH3)(O)+) + *G*(RO–)] – [*G*((HO)Ar(OCH3)(O•)) + *G*(RO•)] (27’)

Δr*G*PDE2 = [*G*((HO)Ar(OCH2O)) + *G*(ROH)] – [*G*((HO)Ar(OCH3)(O)+) + *G*(RO–)] (28’)

Δr*G*IP3 = [*G*((HO)Ar(OCH2O)•+) + *G*(RO–)] – [*G*((HO)Ar(OCH2O)) + *G*(RO•)] (29’)

Δr*G*PDE3 = [*G*((•O)Ar(OCH2O)) + *G*(ROH)] – [*G*((HO)Ar(OCH2O)•+) + *G*(RO–)] (30’)

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**Table S2** The optimized geometries of DHMBA, DHMBA phenoxyl radical, DHMBA diradical in triplet state and HMBD in water and pentyl ethanoate

**DHMBA in water**

*H*(RM06-2X)= -611.515964 Ha

Charge = 0; Multiplicity =1

 C 1.59749600 0.26199100 0.20353300

 C 1.05022800 -1.01846900 0.11787700

 C -0.31239100 -1.16591400 -0.10514500

 C -1.13245100 -0.04357900 -0.22638900

 C -0.57551600 1.23035500 -0.15425000

 C 0.79034600 1.38712100 0.06096200

 H 1.67122800 -1.90110800 0.21539500

 H 1.20816600 2.38631300 0.10563800

 C 3.06935400 0.42815700 0.47614800

 H 3.27927500 0.17821000 1.52162200

 H 3.35888900 1.46916100 0.30827700

 O -1.36197400 2.33686100 -0.30374900

 H -2.25511900 2.05785900 -0.55190100

 O -2.48187000 -0.19932700 -0.46724500

 O -0.84613200 -2.41919800 -0.19969200

 H -1.78479900 -2.34649900 -0.42462400

 O 3.80761500 -0.44074300 -0.38166700

 H 4.72623200 -0.43134500 -0.09119400

 C -3.27243100 -0.23146000 0.73709100

 H -2.96966400 -1.07388100 1.36344200

 H -3.15567200 0.70406400 1.28901400

 H -4.30747600 -0.35272500 0.42419500

 1 2 1.5 6 1.5 9 1.0

 2 3 1.5 7 1.0

 3 4 1.5 15 1.0

 4 5 1.5 14 1.0

 5 6 1.5 12 1.0

 6 8 1.0

 7

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 9 10 1.0 11 1.0 17 1.0

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 12 13 1.0

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 14 19 1.0

 15 16 1.0

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 17 18 1.0

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 19 20 1.0 21 1.0 22 1.0

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 22

**DHMBA in water**

*H*(RM06-2X)= -611.515957 Ha

Charge = 0; Multiplicity =1

 C -1.59749200 0.26236300 0.20301300

 C -0.79005900 1.38734700 0.06064300

 C 0.57577700 1.23028900 -0.15434500

 C 1.13249200 -0.04377200 -0.22636500

 C 0.31217600 -1.16591600 -0.10527800

 C -1.05048700 -1.01818600 0.11742200

 H -1.20765900 2.38663400 0.10524800

 H -1.67174800 -1.90066800 0.21466200

 C -3.06931500 0.42900900 0.47556100

 H -3.35884300 1.46971900 0.30578900

 H -3.27894400 0.18111500 1.52158300

 O 0.84564600 -2.41932700 -0.19973100

 H 1.78445000 -2.34682100 -0.42416600

 O 2.48191400 -0.19981100 -0.46698000

 O 1.36249600 2.33662500 -0.30379300

 H 2.25553600 2.05746000 -0.55212600

 O -3.80779000 -0.44148900 -0.38035100

 H -4.72650300 -0.43078100 -0.09023700

 C 3.27239400 -0.23150900 0.73741400

 H 3.15554900 0.70416500 1.28906100

 H 2.96964700 -1.07375700 1.36401000

 H 4.30746700 -0.35280500 0.42462400

 1 2 1.5 6 1.5 9 1.0

 2 3 1.5 7 1.0

 3 4 1.5 15 1.0

 4 5 1.5 14 1.0

 5 6 1.5 12 1.0

 6 8 1.0

 7

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 9 10 1.0 11 1.0 17 1.0

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 12 13 1.0

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 14 19 1.0

 15 16 1.0

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 17 18 1.0

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 19 20 1.0 21 1.0 22 1.0

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**DHMBA in pentyl ethanoate**

*H*(RM06-2X)= -611.507797 Ha

Charge = 0; Multiplicity =1

 C 1.59366300 0.33408100 0.03873300

 C 1.08676600 -0.95716100 -0.05627800

 C -0.28625600 -1.14106600 -0.20067100

 C -1.14131800 -0.04395400 -0.23008200

 C -0.62095900 1.24951100 -0.16991400

 C 0.74556600 1.44150300 -0.02846500

 H 1.74364900 -1.81631500 -0.02958900

 H 1.13642100 2.45208800 0.01991600

 C 3.07119200 0.57802600 0.21952500

 H 3.23338300 1.05236100 1.19517600

 H 3.41534300 1.27735300 -0.55185800

 O -1.45363100 2.31811200 -0.24433400

 H -2.33154300 2.00112800 -0.49495500

 O -2.49935200 -0.23145200 -0.37211400

 O -0.78845000 -2.39702200 -0.30392500

 H -1.72170900 -2.33208500 -0.54631200

 O 3.77747700 -0.64653300 0.13818900

 H 4.70734600 -0.46791400 0.30454800

 C -3.18007300 -0.35328700 0.88794800

 H -2.77640300 -1.19107700 1.46311800

 H -3.07619100 0.56576500 1.47125800

 H -4.23014400 -0.53207400 0.66139500

 1 2 1.5 6 1.5 9 1.0

 2 3 1.5 7 1.0

 3 4 1.5 15 1.0

 4 5 1.5 14 1.0

 5 6 1.5 12 1.0

 6 8 1.0

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 9 10 1.0 11 1.0 17 1.0

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 12 13 1.0

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 14 19 1.0

 15 16 1.0

 16

 17 18 1.0

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 19 20 1.0 21 1.0 22 1.0

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 21

 22

**DHMBA in pentyl ethanoate**

*H*(RM06-2X)= -611.507798 Ha

Charge = 0; Multiplicity =1

 C -1.59368800 0.33405000 0.03862400

 C -0.74565000 1.44152300 -0.02841400

 C 0.62089600 1.24963100 -0.16983300

 C 1.14133400 -0.04379700 -0.23005800

 C 0.28633100 -1.14096300 -0.20077600

 C -1.08670500 -0.95715800 -0.05644300

 H -1.13656600 2.45208400 0.02002500

 H -1.74353900 -1.81635400 -0.02989000

 C -3.07126300 0.57792300 0.21913300

 H -3.41549300 1.27640400 -0.55297900

 H -3.23358600 1.05321200 1.19429900

 O 0.78861200 -2.39688900 -0.30409600

 H 1.72176200 -2.33188900 -0.54688500

 O 2.49939200 -0.23115200 -0.37206700

 O 1.45350400 2.31828000 -0.24415100

 H 2.33150800 2.00130700 -0.49447100

 O -3.77734400 -0.64683200 0.13898400

 H -4.70750200 -0.46790700 0.30338900

 C 3.18001300 -0.35370000 0.88798200

 H 3.07622000 0.56508500 1.47172800

 H 2.77619500 -1.19171300 1.46272300

 H 4.23007500 -0.53252200 0.66141200

 1 2 1.5 6 1.5 9 1.0

 2 3 1.5 7 1.0

 3 4 1.5 15 1.0

 4 5 1.5 14 1.0

 5 6 1.5 12 1.0

 6 8 1.0

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 9 10 1.0 11 1.0 17 1.0

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 12 13 1.0

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 14 19 1.0

 15 16 1.0

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 17 18 1.0

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 19 20 1.0 21 1.0 22 1.0

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**DHMBA phenoxyl radical in pentyl ethanoate**

*H*(UM06-2X)= -610.877829 Ha

Charge = 0; Multiplicity =2

 C -1.62543300 0.23010200 0.00377400

 C -0.83906700 1.42114900 -0.00313500

 C 0.53244900 1.35969100 -0.02783900

 C 1.18672100 0.11076600 -0.03715300

 C 0.41328700 -1.12726700 -0.06493700

 C -1.02862900 -0.99158900 -0.02223600

 H -1.31959000 2.39396100 0.01814500

 H -1.60824100 -1.90552000 -0.02581800

 C -3.11900300 0.40030300 0.03705100

 H -3.42633600 0.97134000 -0.84852500

 H -3.38550000 0.99335600 0.92132300

 O 0.97420400 -2.23721400 -0.13705000

 O 2.51638500 0.19594900 -0.05705300

 O 1.26462700 2.49912300 -0.03201700

 H 2.20122200 2.26169900 -0.03055600

 O -3.74651800 -0.86466300 0.06761600

 H -4.69854900 -0.73079300 0.06756300

 C 3.37519500 -0.93062300 0.18539300

 H 3.06839700 -1.45327900 1.09019400

 H 3.36002900 -1.61293000 -0.66155800

 H 4.36586800 -0.49858500 0.31175500

 1 2 1.5 6 2.0 9 1.0

 2 3 2.0 7 1.0

 3 4 1.5 14 1.0

 4 5 1.0 13 1.5

 5 6 1.0 12 2.0

 6 8 1.0

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 9 10 1.0 11 1.0 16 1.0

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 13 18 1.0

 14 15 1.0

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 16 17 1.0

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 18 19 1.0 20 1.0 21 1.0

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**DHMBA diradical in pentyl ethanoate**

*H*(UM06-2X)= -610.221221 Ha

Charge = 0; Multiplicity =3

 C -1.56826900 0.27103000 0.01775100

 C -0.72626000 1.40832800 0.01224500

 C 0.66454600 1.28116200 -0.07466500

 C 1.22944400 0.02575500 -0.14867000

 C 0.40486800 -1.17290600 -0.18051300

 C -1.02962200 -0.98229000 -0.06808600

 H -1.14909200 2.40546100 0.08400000

 H -1.65324600 -1.86708700 -0.07362600

 C -3.05236300 0.50416700 0.11939000

 H -3.37122300 1.11705600 -0.73292800

 H -3.25828500 1.07362600 1.03427900

 O 0.92072700 -2.29455200 -0.31072800

 O 2.58237900 -0.05178700 -0.27959700

 O 1.42102500 2.40069900 -0.07514600

 H 2.35001800 2.14713000 -0.16141700

 O -3.72502700 -0.73702700 0.13186000

 H -4.66995900 -0.56903400 0.19145600

 C 3.27178500 -0.75225900 0.68367500

 H 2.70362800 -1.37408000 1.36030600

 H 4.29054500 -0.96966100 0.40005200

 1 2 1.5 6 2.0 9 1.0

 2 3 1.5 7 1.0

 3 4 2.0 14 1.0

 4 5 1.0 13 1.0

 5 6 1.0 12 2.0

 6 8 1.0

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 9 10 1.0 11 1.0 16 1.0

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 13 18 1.0

 14 15 1.0

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 16 17 1.0

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 18 19 1.0 20 1.0

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**HMBD in pentyl ethanoate**

*H*(RM06-2X)= -610.314917 Ha

Charge = 0; Multiplicity =1

 C -1.52884800 0.21548500 0.05661200

 C -0.84308900 1.42836300 0.03403500

 C 0.55355500 1.47223800 -0.01314300

 C 1.21457600 0.26218400 -0.03519600

 C 0.52876600 -0.93866100 -0.02042900

 C -0.84667200 -1.00953400 0.02553000

 H -1.38532200 2.36781400 0.05596700

 H -1.37765300 -1.95103500 0.02995000

 C -3.03339500 0.24314000 0.17113500

 H -3.42933300 1.04415300 -0.46310500

 H -3.30828800 0.47058500 1.20886300

 O 1.44000600 -1.95821900 -0.10721100

 O 2.56421000 0.03449000 -0.14467300

 O 1.19423900 2.66786400 -0.04978300

 H 2.14826800 2.52559600 -0.07019400

 O -3.56343500 -1.01422100 -0.21367400

 H -4.50451200 -1.01710800 -0.01725400

 C 2.69153300 -1.34734400 0.19863500

 H 2.88047600 -1.43352500 1.27472500

 H 3.47764000 -1.80101500 -0.39930100

 1 2 1.5 6 1.5 9 1.0

 2 3 1.5 7 1.0

 3 4 2.0 14 1.0

 4 5 2.0 13 1.0

 5 6 2.0 12 1.0

 6 8 1.0

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 9 10 1.0 11 1.0 16 1.0

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 12 18 1.0

 13 18 1.0

 14 15 1.0

 15

 16 17 1.0

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 18 19 1.0 20 1.0

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**Table S3** Standard Gibbs free energies of reaction (Δr*G*in kJ/mol) for a) tHAT, b) StPLtET and c) tPT-ET mechanism of free radical scavenging by DHMBA in aqueous medium.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| a) | Δr*G*HAT1 | Δr*G*HAT2 | Δr*G*HAT3 | Δr*G*tHAT |
| free radical | Δr*G*BDE1 | Δr*G*BDE2 | Δr*G*BDE3 | Δr*G*tBDE |
| HO• | -137.03 | -321.71 | -147.44 | -606.18 |
| (CH3)3C–O• | -82.97 | -267.65 | -93.39 | -444.01 |
| CH3O• | -74.06 | -258.74 | -84.47 | -417.27 |
| CCl3–O–O• | -35.40 | -220.08 | -45.81 | -301.29 |
| PhO• | -6.23 | -190.92 | -16.65 | -213.80 |
| HOO• | -4.39 | -189.03 | -14.77 | -208.19 |
| CH2=CH–O–O• | -3.26 | -187.95 | -13.64 | -204.85 |
| CH3−O–O• | 2.72 | -181.92 | -7.66 | -186.86 |
| H2C=CH–CH2–O–O•– | 3.01 | -181.67 | -7.41 | -186.07 |
| O–O•– | 65.35 | -119.33 | 54.94 | 0.96 |

|  |  |  |  |
| --- | --- | --- | --- |
| b) | Δr*G*SPLET1 | Δr*G*SPLET2 | Δr*G*SPLET3 |
| free radical | Δr*G*PA1 | Δr*G*ETE1 | Δr*G*PA2 | Δr*G*ETE2 | Δr*G*PA3 | Δr*G*ETE3 |
| HO• | -67.45 | -69.62 | -24.18 | -297.52 | -74.98 | -72.47 |
| (CH3)3C–O• | -77.45 | -5.52 | -34.18 | -233.47 | -85.02 | -8.41 |
| CH3O• | -71.80 | -2.26 | -28.58 | -230.16 | -79.37 | -5.10 |
| CCl3–O–O• | 30.38 | -65.81 | 73.64 | -293.72 | 22.84 | -68.66 |
| PhO• | -7.49 | 1.26 | 35.73 | -226.65 | -15.06 | -1.59 |
| HOO• | -26.82 | 22.47 | 16.40 | -205.48 | -34.39 | 19.58 |
| CH2=CH–O–O• | -6.40 | 3.14 | 36.86 | -224.76 | -13.93 | 0.29 |
| CH3−O–O• | -27.07 | 29.79 | 16.19 | -198.11 | -34.60 | 26.94 |
| H2C=CH–CH2–O–O•– | -24.39 | 27.36 | 18.87 | -200.54 | -31.92 | 24.52 |
| O–O•– | -117.36 | 182.72 | -74.10 | -45.23 | -124.89 | 179.83 |

|  |  |  |  |
| --- | --- | --- | --- |
| c) | Δr*G*ET-PT1 | Δr*G*ET-PT2 | Δr*G*ET-PT3 |
| free radical | Δr*G*IP1 | Δr*G*PDE1 | Δr*G*IP2 | Δr*G*PDE2 | Δr*G*IP3 | Δr*G*PDE3 |
| HO• | 48.24 | -185.27 | 11.05 | -332.75 | 19.29 | -166.77 |
| (CH3)3C–O• | 112.26 | -195.27 | 75.10 | -342.75 | 83.39 | -176.77 |
| CH3O• | 115.56 | -189.62 | 78.37 | -337.10 | 86.65 | -171.13 |
| CCl3–O–O• | 52.01 | -87.40 | 14.81 | -234.93 | 23.10 | -68.91 |
| PhO• | 119.08 | -125.31 | 81.88 | -272.80 | 90.17 | -106.82 |
| HOO• | 140.25 | -144.64 | 103.09 | -292.13 | 111.38 | -126.15 |
| CH2=CH–O–O• | 120.96 | -124.22 | 83.76 | -271.71 | 92.05 | -105.73 |
| CH3−O–O• | 147.61 | -144.89 | 110.46 | -292.38 | 118.70 | -126.40 |
| H2C=CH–CH2–O–O•– | 145.18 | -142.17 | 108.03 | -289.70 | 116.27 | -123.68 |
| O–O•– | 300.49 | -235.18 | 263.34 | -382.67 | 271.63 | -216.69 |

**Table S4** Standard Gibbs free energies of reaction (Δr*G*in kJ/mol) for a) tHAT, b) StPLtET and c) tPT-ET mechanism of free radical scavenging by DHMBA in pentyl ethanoate.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| a) | Δr*G*HAT1 | Δr*G*HAT2 | Δr*G*HAT3 | Δr*G*tHAT |
| free radical | Δr*G*BDE1 | Δr*G*BDE2 | Δr*G*BDE3 | Δr*G*tBDE |
| HO• | -141.29 | -302.42 | -144.14 | -587.85 |
| (CH3)3C–O• | -87.45 | -248.57 | -90.29 | -426.31 |
| CH3O• | -77.49 | -238.57 | -80.33 | -396.39 |
| CCl3–O–O• | -33.10 | -194.18 | -35.94 | -263.22 |
| PhO• | -14.43 | -175.56 | -17.28 | -207.27 |
| HOO• | -7.24 | -168.36 | -10.04 | -185.64 |
| CH2=CH–O–O• | -2.64 | -163.76 | -5.48 | -171.88 |
| CH3−O–O• | 2.34 | -158.78 | -0.50 | -156.94 |
| H2C=CH–CH2–O–O•– | 3.35 | -157.78 | 0.50 | -153.93 |
| O–O•– | 87.70 | -73.43 | 84.81 | 99.08 |

|  |  |  |  |
| --- | --- | --- | --- |
| b) | Δr*G*SPLET1 | Δr*G*SPLET2 | Δr*G*SPLET3 |
| free radical | Δr*G*PA1 | Δr*G*ETE1 | Δr*G*PA2 | Δr*G*ETE2 | Δr*G*PA3 | Δr*G*ETE3 |
| HO• | -129.16 | -12.13 | -76.36 | -226.06 | -136.23 | -7.87 |
| (CH3)3C–O• | -110.79 | 23.35 | -57.99 | -190.58 | -117.86 | 27.61 |
| CH3O• | -109.45 | 32.01 | -56.65 | -181.92 | -116.57 | 36.23 |
| CCl3–O–O• | 33.72 | -66.82 | 86.53 | -280.75 | 26.65 | -62.55 |
| PhO• | 0.33 | -14.77 | 53.14 | -228.70 | -6.78 | -10.54 |
| HOO• | -76.02 | 68.78 | -23.22 | -145.14 | -83.14 | 73.05 |
| CH2=CH–O–O• | -27.11 | 24.43 | 25.69 | -189.45 | -34.18 | 28.70 |
| CH3−O–O• | -71.17 | 73.51 | -18.37 | -140.37 | -78.28 | 77.78 |
| H2C=CH–CH2–O–O•– | -64.35 | 67.70 | -11.59 | -146.19 | -71.46 | 71.96 |
| O–O•– | -366.18 | 453.88 | -313.38 | 239.95 | -373.30 | 458.15 |

|  |  |  |  |
| --- | --- | --- | --- |
| c) | Δr*G*ET-PT1 | Δr*G*ET-PT2 | Δr*G*ET-PT3 |
| free radical | Δr*G*IP1 | Δr*G*PDE1 | Δr*G*IP2 | Δr*G*PDE2 | Δr*G*IP3 | Δr*G*PDE3 |
| HO• | 208.82 | -350.08 | 218.82 | -521.24 | 211.71 | -355.85 |
| (CH3)3C–O• | 244.30 | -331.71 | 254.30 | -502.87 | 247.19 | -337.48 |
| CH3O• | 252.92 | -330.41 | 262.96 | -501.58 | 255.85 | -336.18 |
| CCl3–O–O• | 154.14 | -187.19 | 164.14 | -358.36 | 157.03 | -192.97 |
| PhO• | 206.19 | -220.62 | 216.19 | -391.75 | 209.07 | -226.35 |
| HOO• | 289.74 | -296.98 | 299.74 | -468.11 | 292.63 | -302.71 |
| CH2=CH–O–O• | 245.39 | -248.03 | 255.43 | -419.19 | 248.32 | -253.80 |
| CH3−O–O• | 294.47 | -292.13 | 304.51 | -463.29 | 297.40 | -297.90 |
| H2C=CH–CH2–O–O•– | 288.65 | -285.31 | 298.70 | -456.47 | 291.58 | -291.08 |
| O–O•– | 674.84 | -587.14 | 684.88 | -758.31 | 677.72 | -592.91 |



|  |
| --- |
| Calculated parameters using M06-2X/6-31G\* level of theory in gas-phase |
|  |
| Sum of electronic and thermal enthalpies of dimer (Hartrees) | -1221.372766 |
| Sum of electronic and thermal enthalpies of monomer (Hartrees) | -610.663193 |
| Bond dissociation enthalpy (BDE) (kJ/mol) | 121.77 |
| Central C−C bond length (Å) | 1.57801 |

**Figure S1.** Dissociation of DHMBA phenoxyl radical dimer to give monomer.



**Figure S2.** Influence of electron donating groups (methylenedioxy group and hydroxymethyl group) on BDE values of sesamol like structures.



**Figure S3.** tET-PT mechanism of DHMBA in water.