Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Reactivity of α-amino-Peroxyl Radicals and Consequences for Amine Oxidation Chemistry

**Martin T. Schümperli,[a] Ceri Hammond,[a] Ive Hermans*[a]**

[a] *ETH Zurich, Department of Chemistry and Applied Bio-Sciences, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland. Fax: 41 44 6331514; Tel: 41 44 6334258; E-mail: hermans@chem.ethz.ch*

# Supporting Information

## Solvent effect (PCM-DFT//DFT level)

| Solvent | ε | E(HOO) | E(H-abstr) | (e-1)/(2e+1) | ΔE(HOO) | ΔE(H-abs) |
|---|---|---|---|---|---|---|
| 1-Propanol | 20.524 | 9.4 | 11.2 | 0.46432 | -2.9 | 4 |
| 2-Pentanone | 15.2 | 9.6 | 11.2 | 0.45223 | -2.7 | 4 |
| Acetonitrile | 35.688 | 9.3 | 11.2 | 0.47927 | -3 | 4 |
| DiChloroEthane | 10.125 | 9.8 | 11.1 | 0.42941 | -2.5 | 3.9 |
| DiMethylSulfoxide | 46.826 | 9.2 | 11.2 | 0.48415 | -3.1 | 4 |
| Vacuum | 1 | 12.3 | 7.2 | 0.00000 | 0 | 0 |
| Ar | 1.43 | 11.9 | 10.9 | 0.11140 | -0.4 | 3.7 |
| Krypton | 1.519 | 11.8 | 10.9 | 0.12853 | -0.5 | 3.7 |
| Xenon | 1.706 | 11.7 | 10.9 | 0.16002 | -0.6 | 3.7 |
| MethylPentane | 1.89 | 11.5 | 10.9 | 0.18619 | -0.8 | 3.7 |
| 1-Hexene | 2.0717 | 11.4 | 10.9 | 0.20836 | -0.9 | 3.7 |
| 1,4-Dioxane | 2.2099 | 11.3 | 10.9 | 0.22323 | -1 | 3.7 |
| CarbonDiSulfide | 2.6105 | 11.1 | 11 | 0.25888 | -1.2 | 3.8 |
| DibutylEther | 3.0473 | 10.9 | 11 | 0.28857 | -1.4 | 3.8 |
| diethylamine | 3.5766 | 10.7 | 11.2 | 0.31602 | -1.6 | 4 |

## Date from Figures 1-5

**Figure 1** Correlation between the computed H-abstraction barrier (DFT//DFT level) and the αC-H bond strength (B3LYP/6-311++G(d,p) level) for various amines and alcohols.

| *C-H Bond Strength* | *H-abstraction barrier* |
|---|---|
| 93.2 | 14.0 |
| 91.1 | 11.8 |
| 89.5 | 10.3 |
| 89.2 | 9.9 |
| 87.6 | 8.5 |
| 86 | 7.7 |
| 88.5 | 9.2 |

**Figure 2** Computed H-$CH_2X$ bond strength (B3LYP/6-311++G(d,p) level) *vs*. the Mulliken spin density on the C-atom in the $^{\bullet}CH_2X$ radical (see text).

| *spin density on C* | *HCH2-X BDE* |
|---|---|
| 1.145 | 102.9 |
| 1.05 | 98.6 |
| 0.982 | 93.2 |
| 0.926 | 89.2 |
| 1.093 | 98.0 |
| 1.07 | 98.9 |
| 0.908 | 88.5 |

**Figure 3** Computed barriers for $HO_2^{\bullet}$-elimination (average of high levels of theory in Tables 3-6) and H-abstraction (DFT//DFT level) by α-amino-peroxyl radicals *vs*. αC-H bond strength (B3LYP/6-311++G(d,p)-level) for various amines.

| *CH BDE* | *H-abstr barrier* | *$HO_2^{\bullet}$-elimination* |
|---|---|---|
| 89.2 | 12 | 18.1 |
| 87.6 | 10.6 | 17.1 |
| 86 | 7.2 | 16.65 |
| 88.5 | 11.1 | 17.45 |

**Figure 4** Kirkwood plot for the correlation of the changes in activation barrier for $HO_2^{\bullet}$-elimination and bimolecular H-abstraction from $^{i}PrNH_2$ as predicted by PCM-DFT//DFT for $^{\bullet}OOC(CH_3)_2NH_2$.

| *(ε-1)/(2ε+1)* | *Delta barrier HO2-elim* | *Delta barrier H-abstr* |
|---|---|---|
| 0.46433 | -2.9 | 4.0 |
| 0.45223 | -2.7 | 4.0 |
| 0.47927 | -3.0 | 4.0 |
| 0.42941 | -2.5 | 3.9 |
| 0.48415 | -3.1 | 4.0 |
| 0.1114 | -0.4 | 3.7 |
| 0.12853 | -0.5 | 3.7 |
| 0.16002 | -0.6 | 3.7 |
| 0.18619 | -0.8 | 3.7 |
| 0.20836 | -0.9 | 3.7 |
| 0.22324 | -1.0 | 3.7 |
| 0.25888 | -1.2 | 3.8 |
| 0.28857 | -1.4 | 3.8 |
| 0.31602 | -1.6 | 3.9 |

**Figure 5** Imine/α-amino-hydroperoxide selectivity for the case of isopropylamine at 353 K as a function of (ε-1)/(2ε+1) (amine concentration is assumed to be 1 M).

| *(ε-1)/(2ε+1)* | *imine/hydroperoxide* |
|---|---|
| 0.1114 | 5 |
| 0.12853 | 6 |
| 0.16002 | 6 |
| 0.18619 | 9 |
| 0.20836 | 10 |
| 0.22324 | 11 |
| 0.25888 | 17 |
| 0.28857 | 23 |
| 0.31602 | 41 |
| 0.42941 | 129 |
| 0.45223 | 198 |
| 0.46433 | 264 |
| 0.47927 | 304 |
| 0.48415 | 351 |

# Cartesian coordinates of the involved Transition States.

## HOO• elimination from methylamino-peroxyl radical

Transition state (dublet)

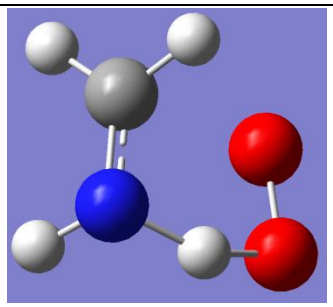
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | -1.17932400 | 0.60448300 | 0.09519300 |
| H | -0.95439600 | 1.09497500 | 1.03736800 |
| H | -1.59297100 | 1.22426000 | -0.69994400 |
| N | -1.13514700 | -0.69993300 | 0.03568500 |
| H | -1.41949000 | -1.05024600 | -0.87944200 |
| H | 0.08161500 | -0.94083000 | 0.21219700 |
| O | 1.10063000 | 0.69061500 | -0.14394200 |
| O | 1.26277200 | -0.57255700 | 0.08255000 |

Energy (Hartree): -245.6423092

ZPE (Hartree): 0.0574439

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**HOO$^{\bullet}$ elimination from ethylamino-peroxyl radical**

Transition state (dublet)

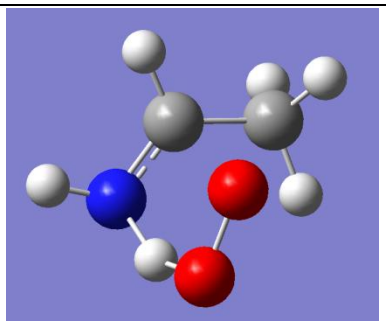
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | 0.90764000 | 0.33300500 | 0.44366100 |
| N | 0.30453500 | 1.32220700 | -0.17315900 |
| O | -1.12403800 | -0.78939100 | 0.49380500 |
| O | -1.66616600 | -0.03631100 | -0.41034400 |
| H | -0.73765700 | 0.80464900 | -0.59029000 |
| H | 1.16203700 | 0.41140000 | 1.50274800 |
| C | 1.52894800 | -0.78819900 | -0.32468800 |
| H | 2.59881500 | -0.57800900 | -0.46242500 |
| H | 1.43906700 | -1.73344400 | 0.21548300 |
| H | 1.07126500 | -0.88456600 | -1.31165700 |
| H | 0.03683200 | 2.06129300 | 0.47672900 |

Energy (Hartree): -284.979953

ZPE (Hartree): 0.0847653

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**$HOO^{\bullet}$ elimination from iso-propylamino-peroxyl radical**

Transition state (dublet)

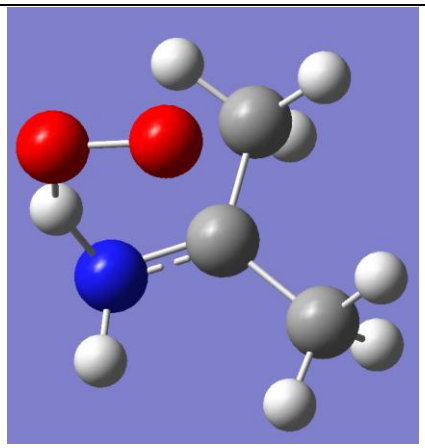
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | -0.72618700 | -0.02227600 | 0.23606200 |
| C | -1.68819000 | -0.77777800 | -0.63619600 |
| H | -1.55549000 | -0.48724300 | -1.68238300 |
| H | -1.55115300 | -1.85906000 | -0.55256500 |
| H | -2.72239900 | -0.53431300 | -0.36043900 |
| C | -0.77867700 | 1.47940900 | 0.19141800 |
| H | -1.69249000 | 1.81982200 | 0.69811000 |
| H | 0.07800900 | 1.91433900 | 0.70839200 |
| H | -0.80673600 | 1.84612000 | -0.83699400 |
| N | -0.04021800 | -0.59145000 | 1.20407800 |
| H | -0.14590300 | -1.60629900 | 1.19621200 |
| H | 1.12275200 | -0.33200800 | 0.95019600 |
| O | 1.29923400 | 0.05824700 | -0.97984100 |
| O | 2.03992300 | -0.14541500 | 0.06774300 |

Energy (Hartree): -324.3169968

ZPE (Hartree): 0.111093

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**$HOO^{\bullet}$ elimination from sec-methylamino-peroxyl radical**

Transition state (dublet)

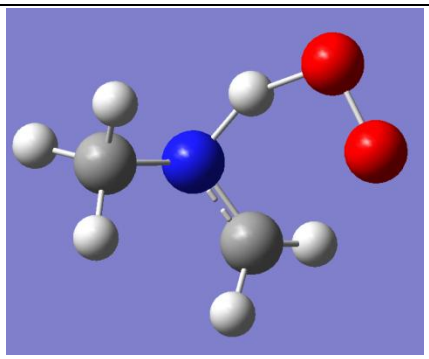
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | 0.34647800 | 1.25664800 | -0.09844300 |
| H | -0.34749400 | 1.81690500 | -0.71424200 |
| H | 0.76954600 | 1.74947400 | 0.77762000 |
| N | 0.78614800 | 0.10502900 | -0.51814900 |
| H | -0.20428900 | -0.53574100 | -0.69605700 |
| O | -1.66764400 | 0.19407600 | 0.46908400 |
| O | -1.40513200 | -0.84517500 | -0.25753000 |
| C | 1.77902100 | -0.61171800 | 0.28401000 |
| H | 2.09438400 | -0.03478200 | 1.16106000 |
| H | 1.35608100 | -1.56204000 | 0.62305100 |
| H | 2.65795000 | -0.82980500 | -0.33022700 |

Energy (Hartree): -284.9640075

ZPE (Hartree): 0.083018

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular methylamine α-hydrogen abstraction by methylamino-peroxyl radical**

Transition state (dublet)

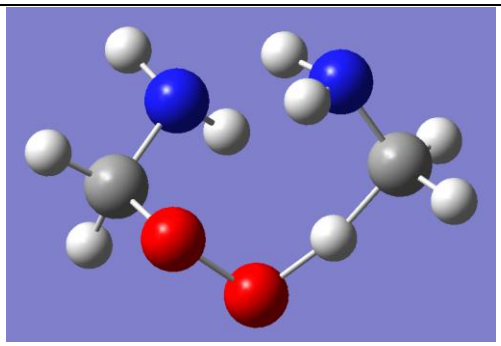
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | -2.00070100 | 0.12705700 | -0.40878000 |
| H | -2.11011400 | -0.31854500 | -1.40154900 |
| H | -0.93637000 | 0.89028700 | -0.50956400 |
| N | -1.73958900 | -0.83018200 | 0.58724000 |
| H | -0.88913700 | -1.36258800 | 0.38588900 |
| H | -1.68506800 | -0.43473400 | 1.51970600 |
| O | 0.19011300 | 1.44773400 | -0.44991300 |
| O | 0.75286200 | 0.80442200 | 0.68676100 |
| C | 1.70919600 | -0.12609800 | 0.21506000 |
| N | 1.08455900 | -1.24451000 | -0.48754400 |
| H | 0.86875600 | -0.95528700 | -1.43847700 |
| H | 1.73227200 | -2.02584900 | -0.54773000 |
| H | 2.44483900 | 0.41652900 | -0.39637400 |
| H | 2.19589300 | -0.50337300 | 1.12119700 |
| H | -2.83063700 | 0.79339600 | -0.16343000 |

Energy (Hartree): -341.5552478

ZPE (Hartree): 0.122782

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular ethylamine α-hydrogen abstraction by ethylamino-peroxyl radical**

Transition state (dublet)

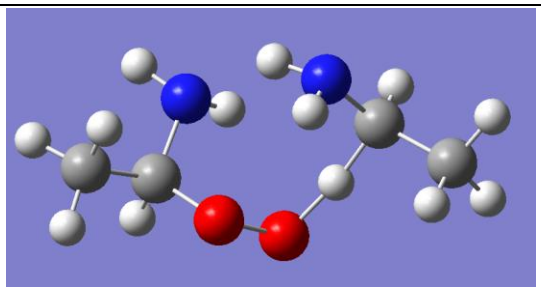
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | 1.96182200 | -0.32297200 | 0.33294400 |
| H | 2.11864500 | -0.64031000 | 1.37091500 |
| H | 1.10449400 | 0.64679600 | 0.45389500 |
| N | 1.31632400 | -1.33528800 | -0.40915700 |
| H | 0.42049500 | -1.59633500 | 0.01064200 |
| H | 1.16789900 | -1.07268700 | -1.37934900 |
| C | 3.20032900 | 0.26365200 | -0.31443000 |
| H | 3.60367900 | 1.07881500 | 0.29276900 |
| H | 3.98423500 | -0.49435400 | -0.43711500 |
| H | 2.96669300 | 0.67148800 | -1.30468900 |
| O | 0.13361700 | 1.47264800 | 0.44211300 |
| O | -0.73154000 | 0.86499100 | -0.50521800 |
| C | -1.81518800 | 0.26684300 | 0.20111900 |
| C | -2.75327100 | -0.28709900 | -0.86045200 |
| H | -2.25530900 | -1.07880300 | -1.42693100 |
| H | -3.65432500 | -0.70127100 | -0.39703200 |
| H | -3.05239500 | 0.50797500 | -1.54739500 |
| N | -1.31349600 | -0.80097200 | 1.06947500 |
| H | -0.79689400 | -0.36130300 | 1.82874900 |
| H | -2.09567500 | -1.29774000 | 1.48975800 |
| H | -2.31010200 | 1.06789300 | 0.77330800 |

Energy (Hartree): -420.2210396

ZPE (Hartree): 0.1789019

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular iso-propylamine α-hydrogen abstraction by iso-propylamino-peroxyl radical**

Transition state (dublet)

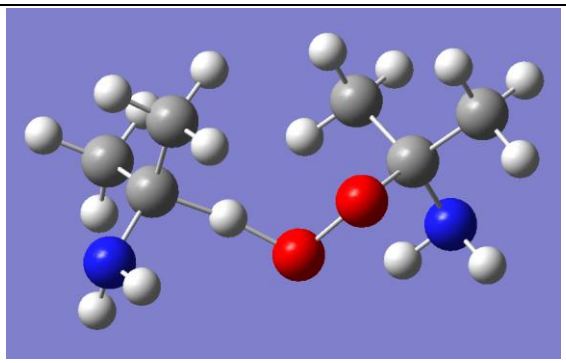
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | 2.21574000 | 0.04062400 | -0.02907500 |
| C | 2.54381300 | 0.56522900 | 1.35924100 |
| C | 2.03337000 | 1.10856300 | -1.09613400 |
| H | 1.78668400 | 1.27965200 | 1.69256500 |
| H | 2.58629400 | -0.24707500 | 2.09384500 |
| H | 1.27765400 | 1.83616700 | -0.79035800 |
| H | 1.70462000 | 0.66857800 | -2.04342200 |
| C | -2.01454600 | 0.05258400 | 0.06059300 |
| C | -2.95991200 | 0.68771100 | -0.95848000 |
| C | -1.45532200 | 1.07210700 | 1.05330200 |
| H | -3.82028900 | 1.12140300 | -0.44369000 |
| H | -3.31731900 | -0.06622600 | -1.66688300 |
| H | -2.26347900 | 1.48340000 | 1.66295000 |
| H | -0.73026200 | 0.59142800 | 1.71492000 |
| N | -2.68705200 | -1.00007000 | 0.78029600 |
| H | -3.04081000 | -1.68541300 | 0.11564100 |
| H | -1.99661100 | -1.48464300 | 1.34999900 |
| O | -0.92991500 | -0.45864100 | -0.79378100 |
| O | -0.01694200 | -1.19576900 | -0.00935800 |
| N | 3.11554300 | -0.98216000 | -0.44342700 |
| H | 3.23256700 | -1.71719000 | 0.24671900 |
| H | 2.85909600 | -1.39471600 | -1.33480200 |
| H | 1.02864500 | -0.50864600 | 0.04408100 |
| H | 2.97703900 | 1.64146600 | -1.27310600 |
| H | -2.44755000 | 1.47043600 | -1.52368900 |
| H | 3.51838900 | 1.07154800 | 1.36171900 |
| H | -0.95811600 | 1.88981500 | 0.52385300 |

Energy (Hartree): -498.8825504

ZPE (Hartree): 0.233219

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular sec-methylamine α-hydrogen abstraction by sec-methylamino-peroxyl radical**

Transition state (dublet)

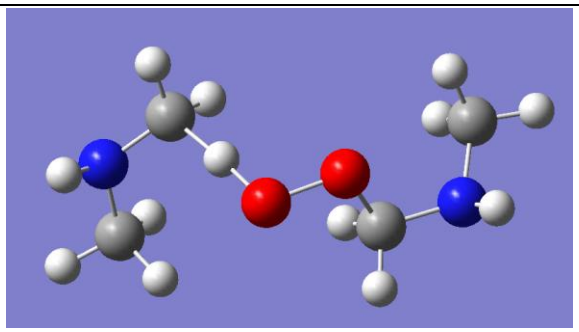
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | -1.49193500 | 0.16958000 | -0.80888300 |
| N | -2.82305200 | -0.25443200 | -0.53351000 |
| C | -2.99352500 | -1.07076100 | 0.66841600 |
| H | -4.03898300 | -1.38451700 | 0.74407000 |
| H | -2.38389000 | -1.97626900 | 0.57205300 |
| H | -2.70917700 | -0.56880000 | 1.60378100 |
| H | -3.44823700 | 0.54583300 | -0.51766400 |
| O | -1.01169700 | 1.03569200 | 0.24538100 |
| O | 0.28717000 | 1.47058800 | -0.10721100 |
| H | -1.45563200 | 0.72335400 | -1.75400000 |
| H | -0.82698200 | -0.70290300 | -0.87890000 |
| C | 1.91537500 | -0.06946600 | 1.12710900 |
| H | 1.34412600 | -0.99703300 | 1.23173800 |
| H | 2.11855900 | 0.40203100 | 2.09073500 |
| H | 1.04215700 | 0.74417700 | 0.52268800 |
| N | 3.07456300 | -0.23866600 | 0.34997300 |
| H | 3.67061800 | 0.58118600 | 0.33556500 |
| C | 2.91761600 | -0.84681000 | -0.96332900 |
| H | 2.24050900 | -0.27283600 | -1.61372500 |
| H | 3.89288600 | -0.93352000 | -1.44900600 |
| H | 2.50450200 | -1.85452200 | -0.84781600 |

Energy (Hartree): -420.1918144

ZPE (Hartree): 0.1779378

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular methylamine α-hydrogen abstraction by methyl-peroxyl radical**

Transition state (dublet)

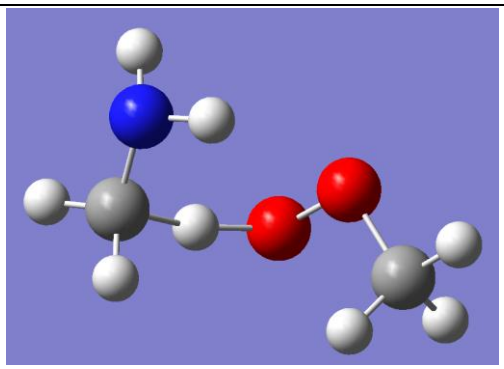
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | 1.68102900 | 0.35881000 | 0.56945100 |
| H | 0.52638400 | 0.89647200 | 0.18341200 |
| H | 2.43199600 | 1.14469200 | 0.46730400 |
| H | 1.51570700 | 0.07595000 | 1.61204600 |
| N | 1.93277800 | -0.75113200 | -0.26309200 |
| H | 2.13713700 | -0.49326700 | -1.22267000 |
| H | 1.17627000 | -1.42841600 | -0.25606300 |
| O | -0.56896000 | 1.13729800 | -0.31612800 |
| O | -1.04841300 | -0.16940800 | -0.57935700 |
| C | -1.97162300 | -0.50307700 | 0.44974700 |
| H | -2.79752900 | 0.21562500 | 0.47991400 |
| H | -2.35330800 | -1.49695800 | 0.19389800 |
| H | -1.48355400 | -0.53369400 | 1.43249600 |

Energy (Hartree): -286.1742461

ZPE (Hartree): 0.103656

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular ethylamine α-hydrogen abstraction by methyl-peroxyl radical**

Transition state (dublet)

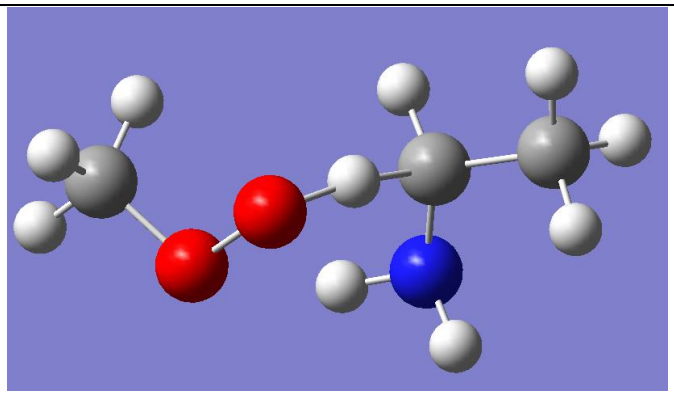
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | 1.26717100 | 0.10546300 | 0.44141500 |
| H | 0.24127400 | -0.58687500 | 0.00406500 |
| H | 1.05392000 | 0.20003800 | 1.51224300 |
| N | 1.19954300 | 1.36705300 | -0.19918500 |
| H | 0.29265700 | 1.81051800 | -0.08401200 |
| H | 1.40849600 | 1.30902900 | -1.19191800 |
| O | -0.80904600 | -1.00718800 | -0.52038600 |
| O | -1.60448400 | 0.16368300 | -0.52851200 |
| C | -2.51165000 | 0.07515500 | 0.56344800 |
| H | -1.98185900 | 0.05692300 | 1.52456700 |
| H | -3.13732400 | 0.97156200 | 0.50178600 |
| H | -3.13601700 | -0.82072500 | 0.47873100 |
| C | 2.51883700 | -0.69129500 | 0.13907200 |
| H | 2.48021800 | -1.66938700 | 0.62635500 |
| H | 2.62587400 | -0.85990900 | -0.93895400 |
| H | 3.41805100 | -0.16843700 | 0.48900900 |

Energy (Hartree): -325.5065817

ZPE (Hartree): 0.132348

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular iso-propylamine α-hydrogen abstraction by methyl-peroxyl radical**

Transition state (dublet)

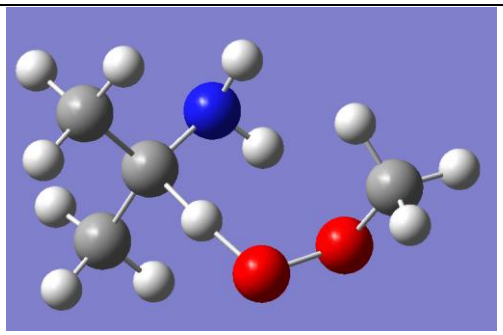
Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | -1.16022500 | -0.08252600 | 0.04067800 |
| H | -0.06617500 | 0.30977400 | -0.55110700 |
| N | -0.75384800 | -0.66509200 | 1.27318800 |
| H | -0.29344500 | -1.56225900 | 1.15838200 |
| H | -0.15473400 | -0.04897900 | 1.81509200 |
| C | -1.90469800 | 1.22933700 | 0.24106700 |
| H | -2.09648200 | 1.71266000 | -0.72090800 |
| H | -2.86582000 | 1.05851100 | 0.74321100 |
| H | -1.31815400 | 1.92356400 | 0.85143700 |
| O | 1.04595000 | 0.79334900 | -0.89206900 |
| O | 1.83205500 | 0.55871100 | 0.25943600 |
| C | 2.65606000 | -0.56913200 | -0.00315700 |
| H | 3.29060700 | -0.39299700 | -0.87841200 |
| H | 2.05812000 | -1.47481800 | -0.16970700 |
| C | -1.84373100 | -1.07674600 | -0.88252800 |
| H | -2.03977600 | -0.62408200 | -1.85836800 |
| H | -1.22277500 | -1.96516700 | -1.04471000 |
| H | -2.80239000 | -1.40722600 | -0.46057000 |
| H | 3.27948200 | -0.69540700 | 0.88804700 |

Energy (Hartree): -364.8382329

ZPE (Hartree): 0.160136

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d



**Bimolecular sec-methylylamine α-hydrogen abstraction by methyl-peroxyl radical**

Transition state (dublet)

Cartesian Coordinates (Å)

| | | | |
|---|---|---|---|
| C | -1.10286600 | -0.96202600 | 0.57612400 |
| H | 0.00266900 | -0.79620800 | -0.15010700 |
| H | -1.24374200 | -2.04341900 | 0.62930500 |
| H | -0.81600800 | -0.53363400 | 1.54147400 |
| N | -2.19994500 | -0.29909600 | -0.00070200 |
| H | -2.54856600 | -0.75225800 | -0.83774200 |
| O | 0.99052900 | -0.57970600 | -0.84681300 |
| O | 2.05875100 | -0.48683100 | 0.07576800 |
| C | 2.32923900 | 0.88876800 | 0.28751600 |
| H | 1.47998000 | 1.39816900 | 0.76376200 |
| H | 3.19542600 | 0.91914900 | 0.95660000 |
| H | 2.57041600 | 1.39479000 | -0.65458600 |
| C | -2.11550100 | 1.14783900 | -0.13240400 |
| H | -1.26063400 | 1.46402200 | -0.74926800 |
| H | -3.03778500 | 1.53312600 | -0.57454600 |
| H | -2.00161300 | 1.59474400 | 0.86096600 |

Energy (Hartree): -325.493649

ZPE (Hartree): 0.131880

Level: UB3LYP/6-311(3df,3pd)//UB3Lyp/631G** 5d