Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Oxidation mechanism of diethyl ether: a complex process for a simple molecule

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Contents

S1. Comments on the initiation step

Different mechanisms have been proposed in literature for the autoxidation process of DEE. In particular the initiation step has been the object of a lot of experimental and theoretical studies. Clover[1], for instance, in his experimental work, has assumed that the initiator of the process is the molecular oxygen which gets into a C-H bond of one methylene group to produce the $CH_3CH_2OCH(OOH)CH_3$ hydroperoxide (**a**).

$$CH_3CH_2OCH_2CH_3 + O_2 \rightarrow CH_3CH\left(OOH\right)OCH_2CH_3 \qquad (\mathbf{a})$$

In the same years, Wieland and Wingler[2] have postulated that the DEE autoxidation process begins with dehydration (**b**) of the ether to vinyl ethers with formation of hydrogen peroxide. Some others studies in literature have also proposed that, in a different way, the molecular oxygen is the initiator of the process[3, 4] (**c**). It has also been suggested that O_2 abstracts an hydrogen atom from a methylene group of solvent to produce the radicals $CH_3CH_2O\dot{C}HCH_3$ and $^{\cdot}HO_2$. Lemay[3] in particular has suggested that the radical $^{\cdot}HO_2$ can also act as initiator (**d**). More recently, as already done in numerous experimental works concerning the kinetics of ethers decomposition in atmosphere[5, 6], Galano and co.[7] have investigated, at DFT theoretical level, the initiation of the decomposition process of a series of aliphatic ethers. They have proposed like Andersen[8] for dimethyl ether, that the initiator of the atmospherical ethers autoxidation process is the hydroxyl radical (**e**).

$$CH_3CH_2OCH_2CH_3 + O_2 \rightarrow CH_3CH_2OCH = CH_2 + H_2O_2 \qquad (\mathbf{b})$$

$$CH_3CH_2OCH_2CH_3 + O_2 \rightarrow CH_3CH_2O\dot{C}HCH_3 + \dot{H}O_2 \qquad (\mathbf{c})$$

$$CH_3CH_2OCH_2CH_3 + \dot{H}O_2 \rightarrow CH_3CH_2O\dot{C}HCH_3 + H_2O_2 \qquad (\mathbf{d})$$

$$CH_3CH_2OCH_2CH_3 + {}^{\cdot}OH \rightarrow CH_3\dot{C}HOCH_2CH_3 + H_2O \qquad (\mathbf{e})$$

DFT calculations on the four reactions (**b-e**) described above, have given the results depicted in figure S3. It seems evident that OH radical is the most efficient among the initiators of the chain process explored (**e** reaction is exothermic and barrier less). The three other reactions are in fact all endothermic (from 4.5 kcal/mol (**b**) to 43.0 kcal/mol (**c**)) or present prohibitive activation energies (48.5 kcal/mol for reaction **c** and 43.6 kcal/mol for reaction **b**) or both.

References

1 A. M. Clover, *J. Am. Chem. Soc.*, 1922, **44**, 1107-1118.

2 H. Wieland and A. Wingler, *Liebing Ann. Chem.*, 1923, **431**, 317.

3 A. Lemay and C. Ouellet, *Can. J. Chem.*, 1955, **33**, 1316-1327.

4 D. J. Waddington, *Proc. R. Soc. London, Ser. A*, 1959, **252**, 260-272.

5 F. P. Tully and A. T. Droege, *Int. J. of Chem. Kinet.*, 1987, **19**, 251-259.

6 A. Mellouki, S. Teton and G. Lebras, *Int. J. Chem. Kinet.*, 1995, **27**, 791-805.

7 C. Zavala-Oseguera, J. R. Alvarez-Idaboy, G. Merino and A. Galano, *J. Phys. Chem. A*, 2009, **113**, 13913-13920.

8 A. Andersen and E. A. Carter, *J. Phys. Chem. A*, 2003, **107**, 9463-9478.

Figure S1. Comparison between gas phase and solvent energetic profiles for the first step of one of the dimerization pathways. For each stationary point is noted the calculated $\Delta\Delta E = \Delta E_{gas\ phase} - \Delta E_{solvent}$.

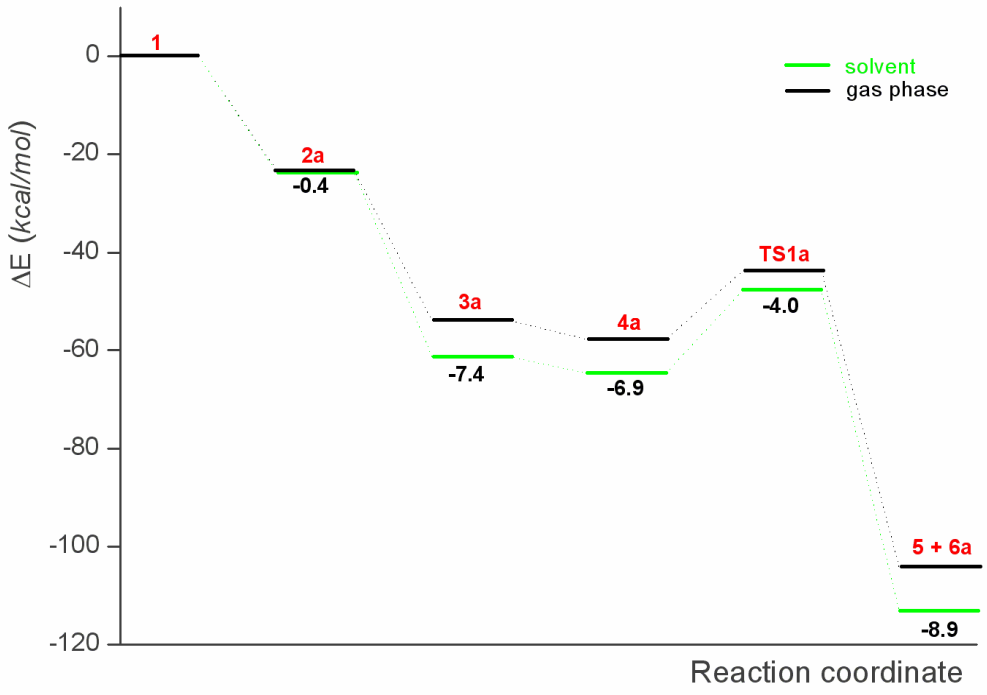


Figure S2. Sketch of oxidation mechanism concerning DEE radical at terminal carbon (path b) with energies (ΔH in kcal/mol) relative to the initiation step.

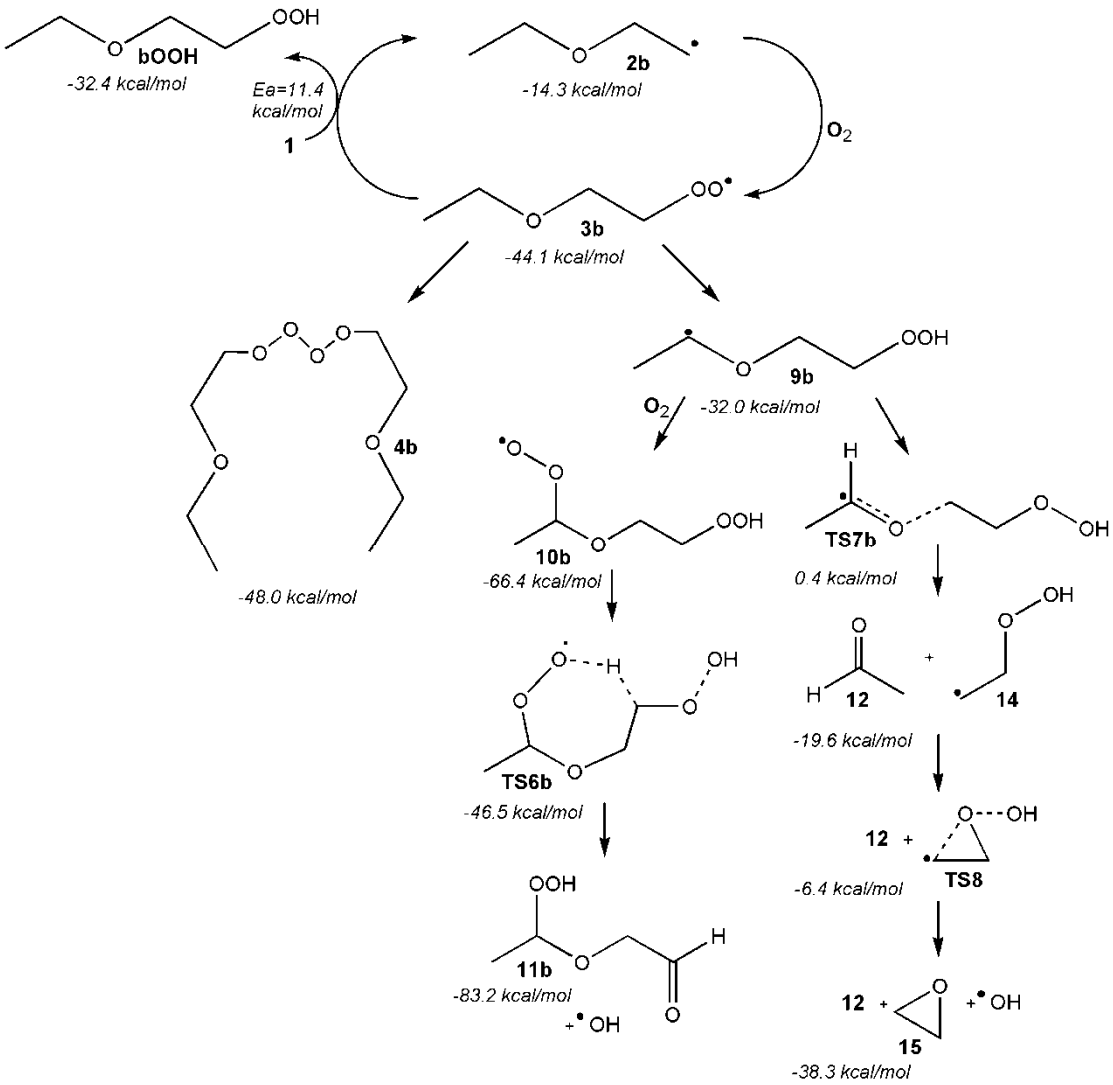


Figure S3. Comparison between the different initiation reactions (see paragraph S1 for labelling).

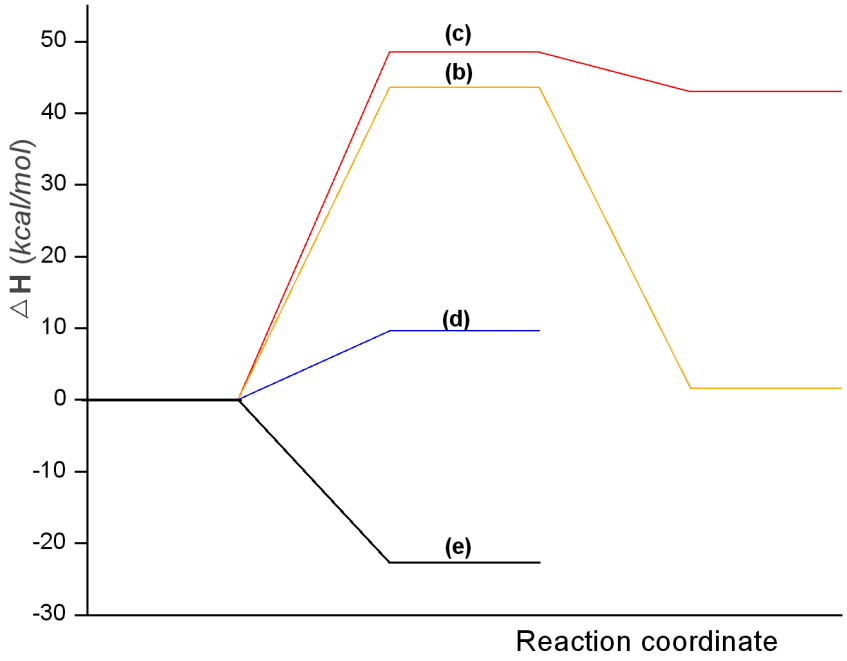
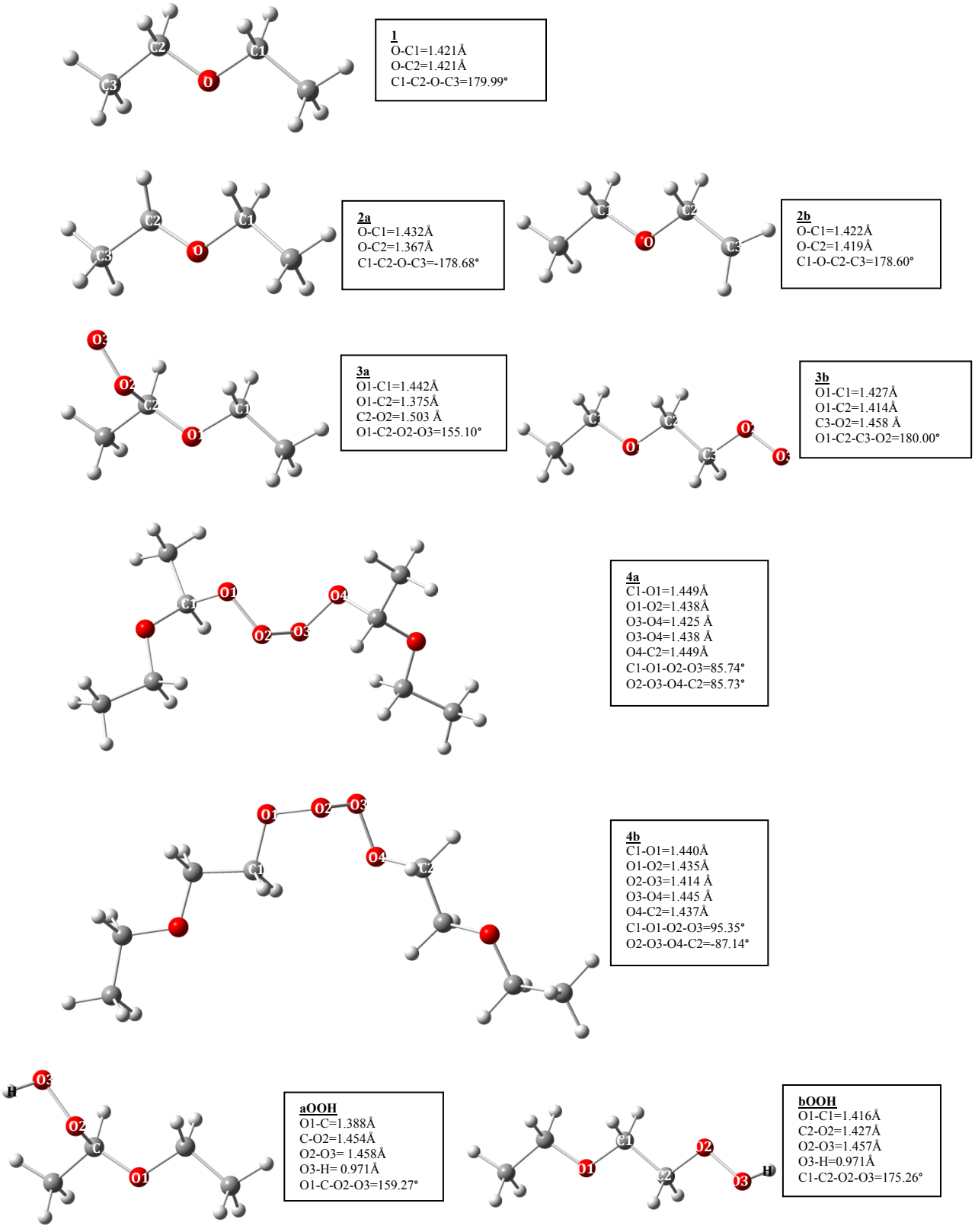
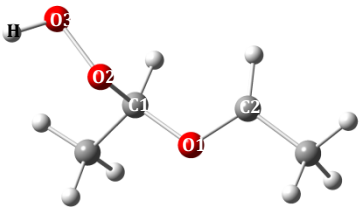
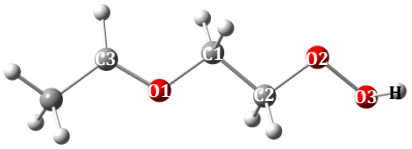


Figure S4. View of optimized structures of the most important minima involved in autoxidation of DEE.

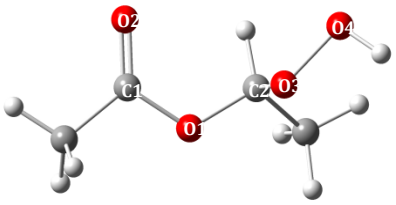




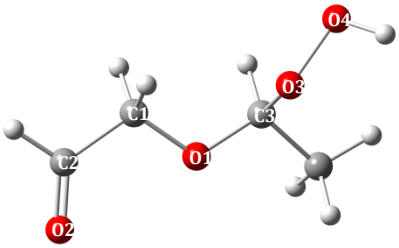
9a
O1-C2=1.381Å
O1-C1=1.399Å
C1-O2=1.445Å
O2-O3=1.460Å
O3-H=0.971Å
O1-C1-O2-O3=162.72°



9b
O1-C3=1.371Å
O1-C1=1.425Å
C2-O2=1.426Å
O2-O3=1.457Å
O3-H=0.971Å
C1-C2-O2-O3=-175.39°



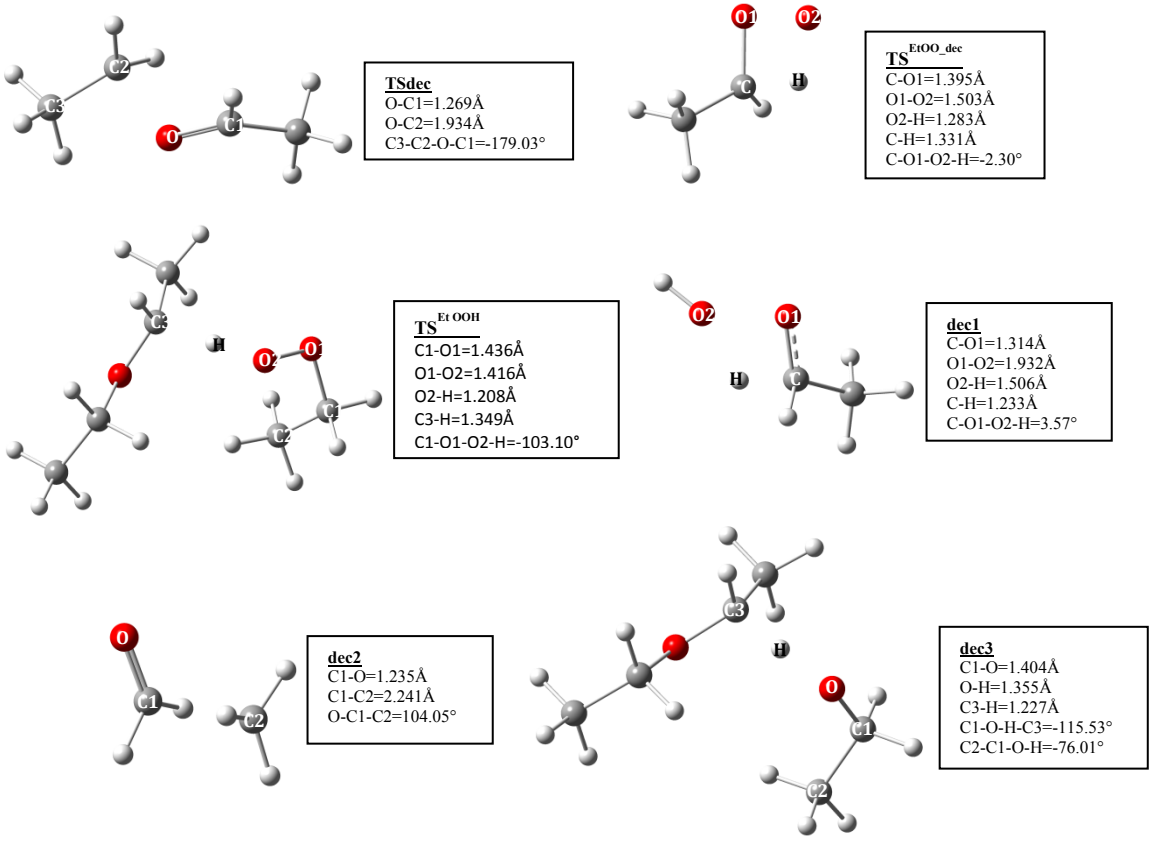
11a
O1-C1=1.374Å
C1-O2=1.208Å
C2-O3=1.439Å
O3-O4=1.457Å
C1-O1-C2-O3=90.01°



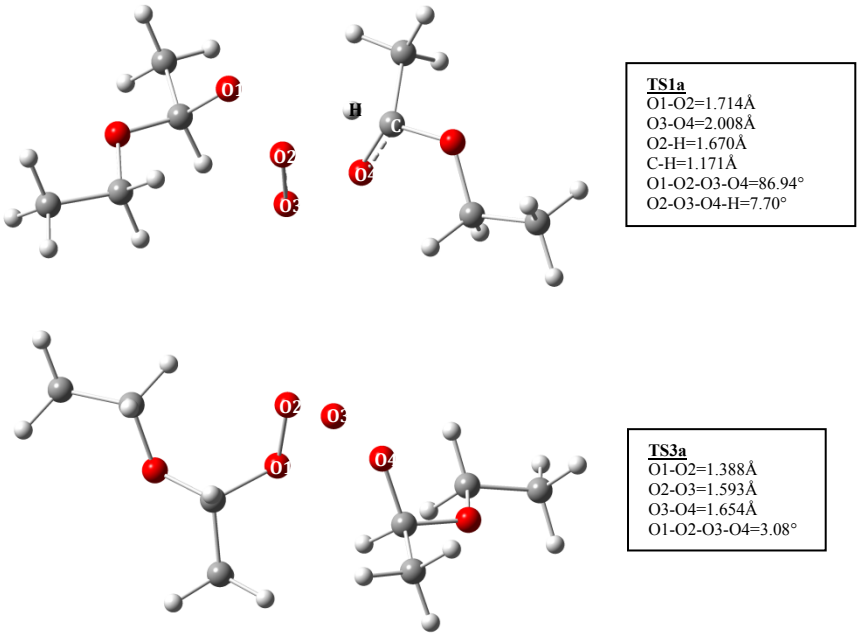
11b
O1-C1=1.412Å
C2-O2=1.209Å
C3-O3=1.451Å
O3-O4=1.457Å
C1-O1-C2-O3=68.61°

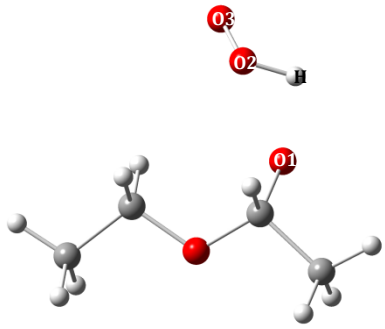
Figure S5. View of optimized structures of the most important transition states involved in autoxidation of DEE: path a.

Transition states *involved in* ***2a*** *decomposition*

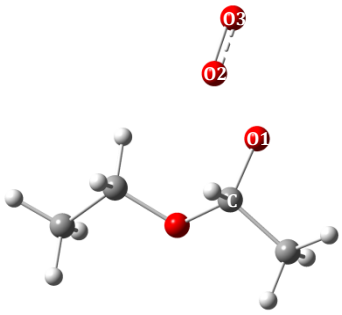


Transition states *involved in* ***3a*** *dimerization reactions*



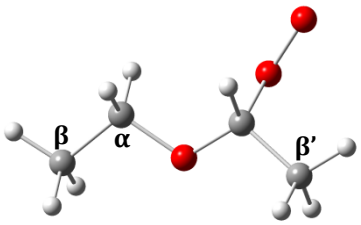


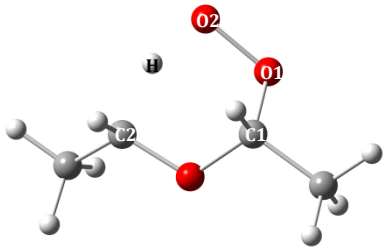
TS2a
O1-O2=2.029Å
O2-H=1.008Å
O1-H=1.608Å



TS4a
O1-O2=1.754Å
O2-O3=1.220Å
C-O1-O2-O3=-177.29°

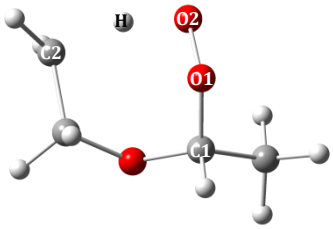
Transition states *and minima involved in* ***3a*** *isomerization*





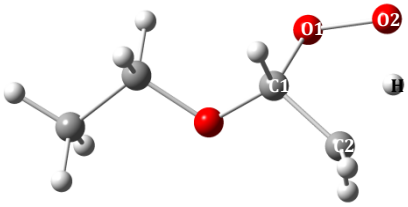
TS5a
O1-O2=1.424Å
O2-H=1.209Å
C2-H=1.364Å
C1-O1-O2-H=-49.12°

Ea= 17.2 kcal/mol



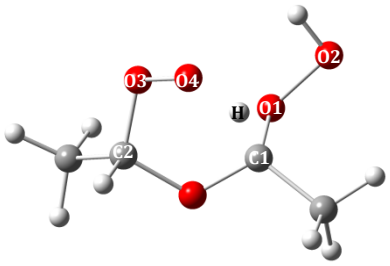
TS5a (7)
O1-O2=1.418Å
O2-H=1.157Å
C2-H=1.393Å
C1-O1-O2-H=79.10°

Ea= 25.1 kcal/mol

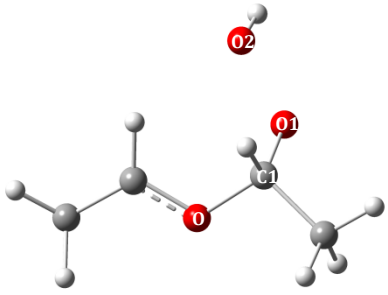


TS5a (5)
O1-O2=1.425Å
O2-H=1.188Å
C2-H=1.392Å
C1-O1-O2-H=31.47°

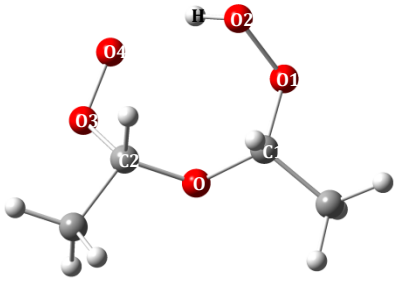
Ea= 36.1 kcal/mol



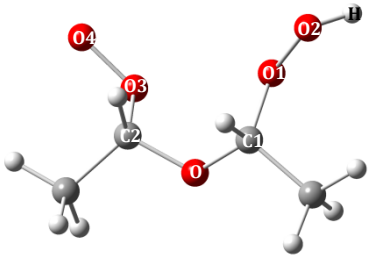
TS6a
C1-H=1.345Å
O4-H=1.212Å
O1-C1-C2-O3=-62.50°
C2-O3-O4-H=60.13°



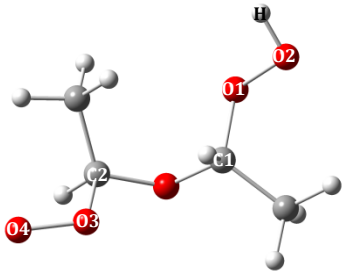
TS7a
O1-O2=1.734Å
O-C1=1.490Å
O-C1-O1-O2=94.52°



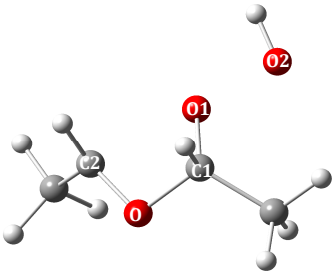
10a(a)
C1-O1=1.404Å
C2-O3=1.499Å
O2-H=0.982Å
O4-H=1.877Å
O1-C1-C2-O3=29.72°



10a(b)
C1-O1=1.438Å
C2-O3=1.487Å
O2-H=0.971Å
O1-C1-C2-O3=21.04°

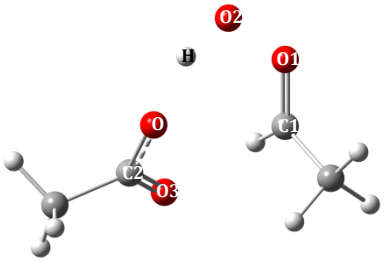


10a(c)
C1-O1=1.445Å
C2-O3=1.494Å
O2-H=0.971Å
O1-C1-C2-O3=-149.95°

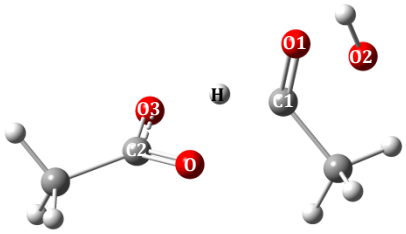


TScyc
O1-O2= 1.701Å
C2-O1=2.096Å
O-C1-O1=99.61°

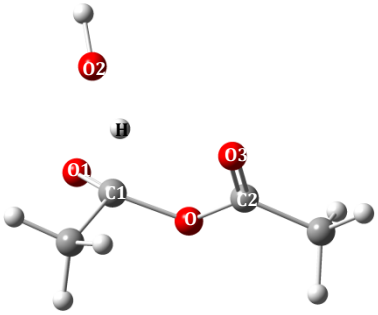
Transition states *and minima involved in* ***11a*** *decomposition reactions*



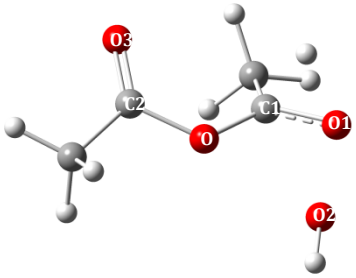
TS9a
O1-O2=1.440Å
O2-H=1.064Å
O-H= 1.457Å
O-C1-O1-O2=-48.79°



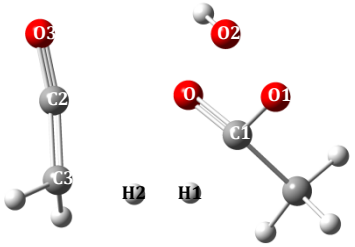
TS10a
O1-O2=1.623Å
C1-O= 2.128Å
O-H= 1.457Å
O3-H= 1.256Å
C1-H= 1.342Å
O1-C1-H-O3=-105.47°



TS11a
O1-O2=1.951Å
C1-H= 1.227Å
O2-H= 1.551Å
O1-C1-H-O2=-6.50°

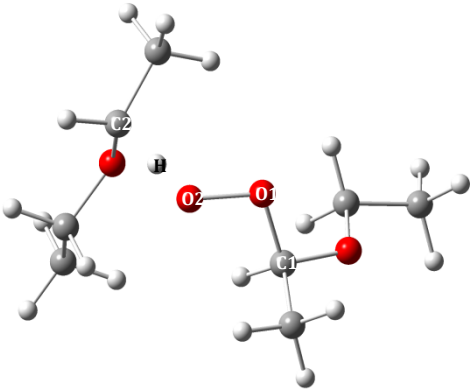


TS13a
O1-O2=1.930Å
C1-O1= 1.324Å
C1-O2= 2.144Å
O-H= 1.457Å
C1-H-O1= 57.35°
O1-C1-O-C2= 153.07°

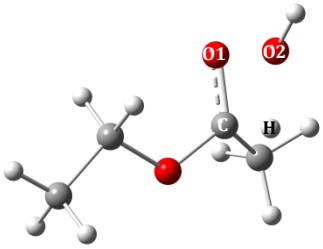


TS14a
O1-O2=1.445Å
C1-H= 1.452Å
C3-H2= 1.147Å
H1-H2= 0.951Å
O-C2= 2.325Å
C1-H1-H2-C3= 15.93°

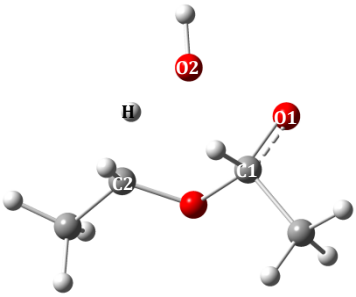
Transition states *and minima involved in* ***aOOH*** *decomposition reactions*



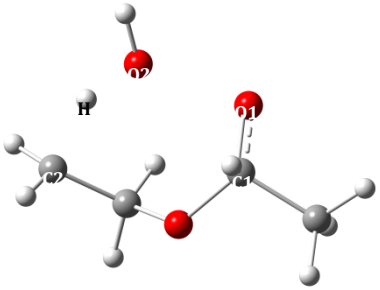
TS$^{a\ OOH}$
C1-O1=1.457Å
O1-O2= 1.414Å
O2-H= 1.206Å
C2-H= 1.351Å
C1-O1-O2-H= -102.34°
O1-O2-H-C2= -136.54°



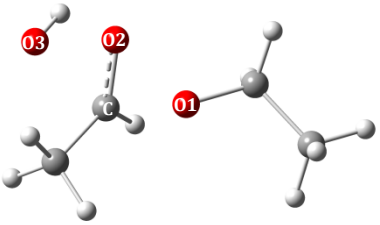
TS1$^{a\ OOH}$
C-O1=1.301Å
O1-O2= 1.975Å
O2-H= 1.638Å
C-H= 1.195Å
C-O1-O2-H= 8.83°



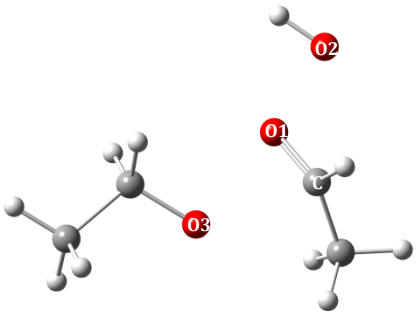
TS2$^{a\ ooh}$
C1-O1=1.330Å
O1-O2= 2.023Å
O2-H= 1.317Å
C2-H= 1.315Å
C1-O1-O2-H= -26.71°



TS3$^{a\ OOH}$
C1-O1=1.325Å
O1-O2= 2.086Å
O2-H= 1.110Å
C2-H= 1.455Å
C1-O1-O2-H= -51.69°



TS4$^{a\ OOH}$
C-O1=1.861Å
C-O2=1.318Å
O2-O3= 1.903Å
C-O3= 1.918Å
O1-C-O2-O3= 178.22°



TS5$^{a\ OOH}$
C1-O1=1.325Å
O1-O2= 2.086Å
O2-H= 1.110Å
C2-H= 1.455Å
C1-O1-O2-H= -51.69°

Figure S6. Relative enthalpies of **3b** dimerization reactions I (purple) and II (orange).

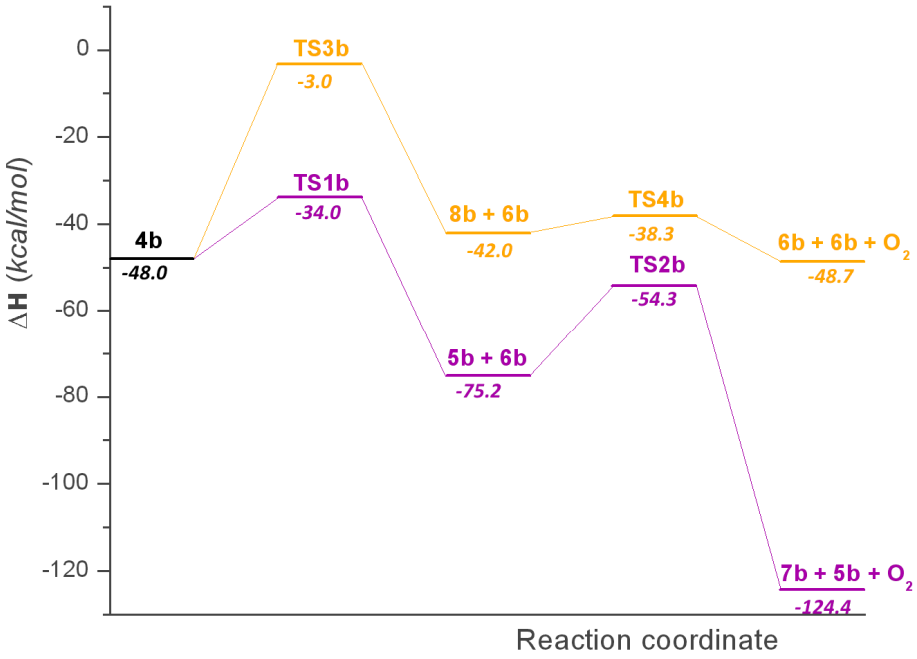
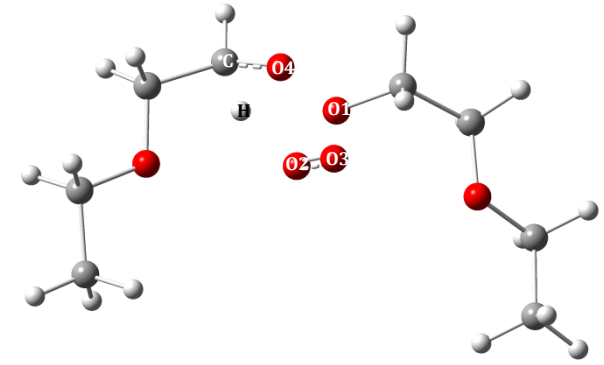
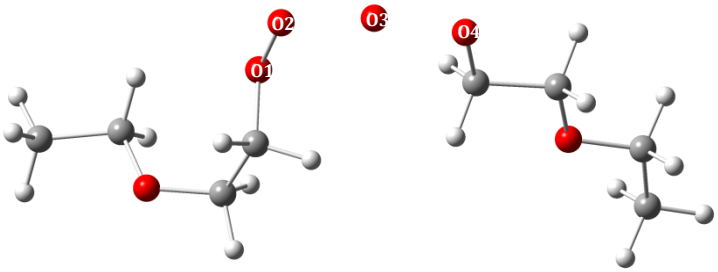


Figure S7. View of optimized structures of the most important transition states involved in autoxidation of DEE: path b.

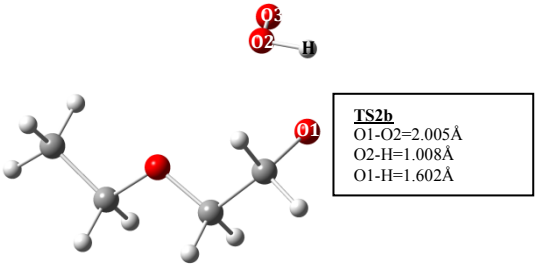
Transition states *involved in* ***3b*** *dimerizations*



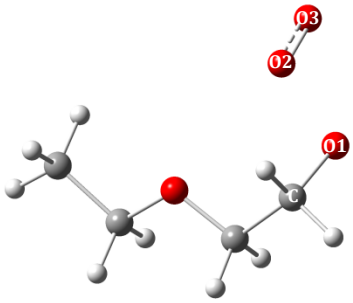
TS1b
O1-O2=1.834Å
O3-O4=2.075Å
O2-H=1.424Å
C-H=1.247Å
O1-O2-O3-O4=89.30°
O2-O3-O4-H=3.90°



TS3b
O1-O2=1.353Å
O2-O3=1.728Å
O3-O4=1.714Å
O1-O2-O3-O4=1.71°

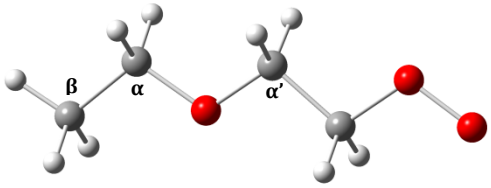


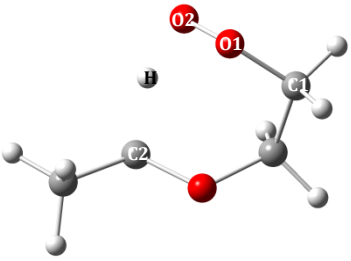
TS2b
O1-O2=2.005Å
O2-H=1.008Å
O1-H=1.602Å



TS4b
O1-O2=1.763Å
O2-O3=1.218Å
C-O1-O2-O3=-168.92°

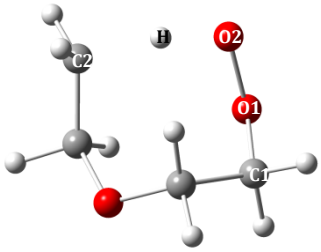
Transition states *and minima involved in* ***3b*** *isomerization*





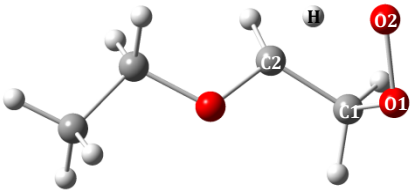
TS5b
O1-O2=1.417Å
O2-H=1.217Å
C2-H=1.345Å
C1-O1-O2-H=81.41°

Ea= 17.7 kcal/mol



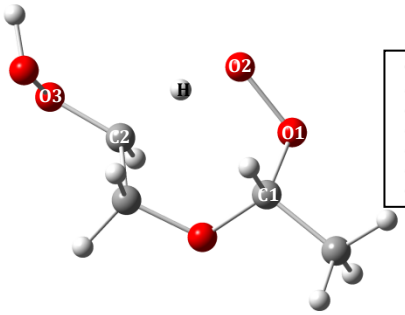
TS5b(8)
O1-O2=1.416Å
O2-H=1.158Å
C2-H=1.434Å
C1-O1-O2-H=-87.19°

Ea= 23.5 kcal/mol

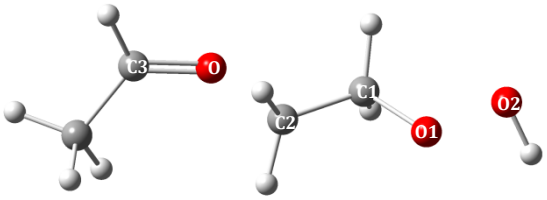


TS5b(5)
O1-O2=1.423Å
O2-H=1.265Å
C2-H=1.344Å
C1-O1-O2-H=35.20°

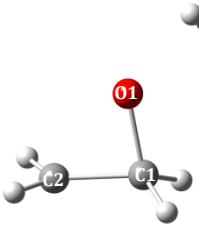
Ea= 26.0 kcal/mol



TS6b
C1-O1=1.429Å
O2-H=1.202Å
C2-H=1.345Å
C2-O3=1.382Å
C1-O1-O2-H=-71.78°
O2-H-C2-O3=139.45°

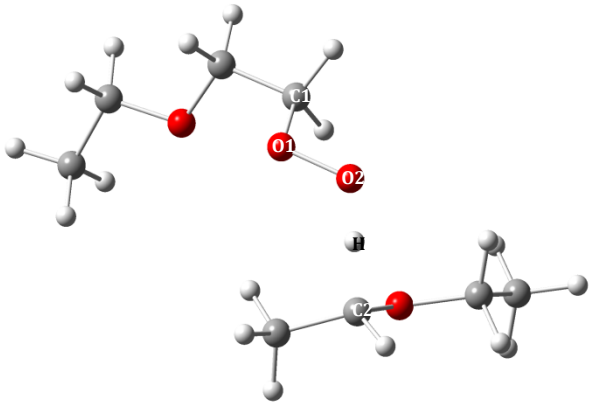


TS7b
C1-O1=1.437Å
O1-O2=1.469Å
C2-O=1.890Å
O-C3=1.272Å
C1-C2-O-C3=-169.38°
C2-C1-O1-O2=-177.78°



TS8
C1-O1=1.404Å
C1-C2=1.477Å
O1-O2=1.753Å
C2-C1-O1=83.81°
C2-C1-O1-O2=171.50°

Transition state *involved in* ***bOOH*** *production*



TS$^{b\,OOH}$
C1-O1=1.432Å
O1-O2= 1.413Å
O2-H= 1.213Å
C2-H= 1.345Å
C1-O1-O2-H= -96.31°
O1-O2-H-C2= -28.08°