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

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**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\(_3\)CH\(_2\)OCH(OOH)CH\(_3\) hydroperoxide \((\text{a})\).

\[
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{OOH})\text{OCH}_2\text{CH}_3 \quad (\text{a})
\]

In the same years, Wieland and Wingler\(^2\) have postulated that the DEE autoxidation process begins with dehydration \((\text{b})\) 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\(^3\),\(^4\) \((\text{c})\). It has also been suggested that O\(_2\) abstracts an hydrogen atom from a methylene group of solvent to produce the radicals CH\(_3\)\(_2\)OCHCH\(_3\) and \(\cdot\text{HO}_2\). Lemay\(^3\) in particular has suggested that the radical \(\cdot\text{HO}_2\) can also act as initiator \((\text{d})\). 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 atmospheric ethers autoxidation process is the hydroxyl radical \((\text{e})\).

\[
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OCH} = \text{CH}_2 + \text{H}_2\text{O}_2 \quad (\text{b})
\]

\[
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OCHCH}_3 + \cdot\text{HO}_2 \quad (\text{c})
\]

\[
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \cdot\text{HO}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OCHCH}_3 + \text{H}_2\text{O}_2 \quad (\text{d})
\]

\[
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \cdot\text{OH} \rightarrow \text{CH}_3\cdot\text{CHOCH}_2\text{CH}_3 + \text{H}_2\text{O} \quad (\text{e})
\]

DFT calculations on the four reactions \((\text{b-e})\) 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 \((\text{e})\) reaction is exothermic and barrier less). The three other reactions are in fact all endothermic (from 4.5 kcal/mol \((\text{b})\) to 43.0 kcal/mol \((\text{c})\)) or present prohibitive activation energies (48.5 kcal/mol for reaction \(\text{c}\) and 43.6 kcal/mol for reaction \(\text{b}\)) or both.
References

**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 \( \Delta \Delta E = \Delta E_{\text{gas phase}} - \Delta E_{\text{solvent}} \).
**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.
**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 2a decomposition.

**TSdec**

O-C1=1.269 Å
O-C2=1.934 Å
C3-C2-O-C1=179.03°

**POO dec**

C-O1=1.795 Å
O1-O2=1.503 Å
O2-H=1.283 Å
C-H=1.331 Å
C-O1-O2-H=2.30°

**TSdec**

C1-O1=1.436 Å
O1-O2=1.416 Å
O2-H=1.208 Å
C3-H=1.349 Å
C1-O1-O2-H=103.10°

**TS dec**

C1-O1=1.235 Å
C1-C2=2.241 Å
O-C1-O2=104.05°

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

Transition states involved in 3a dimerization reactions.

**TS1a**

O1-O2=1.714 Å
O1-O4=2.008 Å
O2-H=1.670 Å
C-H=1.171 Å
O1-O2-O4=96.94°
O2-O3-O4=7.70°

**TS3a**

O1-O2=1.388 Å
O2-O3=1.593 Å
O3-O4=1.654 Å
O1-O2-O3-O4=3.08°
Transition states and minima involved in 3a isomerization

TS2\(a\)

\[
\begin{align*}
O1-O2 &= 2.029\text{ Å} \\
O2-H &= 1.008\text{ Å} \\
O1-H &= 1.608\text{ Å} \\
\end{align*}
\]

\(E_a = 17.2\text{ kcal/mol}\)

TS5\(a\)

\[
\begin{align*}
O1-O2 &= 1.424\text{ Å} \\
O2-H &= 1.188\text{ Å} \\
C2-H &= 1.392\text{ Å} \\
C1-O1-O2-H &= 31.47° \\
E_a &= 36.1\text{ kcal/mol} \\
\end{align*}
\]

TS6\(a\)

\[
\begin{align*}
C1-H &= 1.345\text{ Å} \\
O4-H &= 1.212\text{ Å} \\
O1-C1-C2-O3 &= -62.50° \\
C2-O3-O4-H &= 60.13° \\
\end{align*}
\]

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Transition states and minima involved in 11a decomposition reactions

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

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

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

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

TS14a
O1-O2=1.445 Å
C1-H= 1.452 Å
C3-H2= 1.147 Å
H1-H2= 0.951 Å
O-C2= 2.325 Å
C1-H1-H2-C3= 15.93°
Transition states and minima involved in aOOH decomposition reactions

TS\textsuperscript{a}OHH
\begin{align*}
C1-O1 & = 1.457\text{Å} \\
O1-O2 & = 1.414\text{Å} \\
O2-H & = 1.206\text{Å} \\
C2-H & = 1.351\text{Å} \\
C1-O1-O2-H & = -102.34^\circ \\
O1-O2-H-C2 & = -136.54^\circ
\end{align*}

TS\textsuperscript{b}OHH
\begin{align*}
C1-O1 & = 1.301\text{Å} \\
O1-O2 & = 1.975\text{Å} \\
O2-H & = 1.638\text{Å} \\
C-H & = 1.195\text{Å} \\
C-O1-O2-H & = 8.83^\circ
\end{align*}

TS\textsuperscript{c}OHH
\begin{align*}
C1-O1 & = 1.330\text{Å} \\
O1-O2 & = 2.023\text{Å} \\
O2-H & = 1.317\text{Å} \\
C2-H & = 1.315\text{Å} \\
C1-O1-O2-H & = -26.71^\circ
\end{align*}

TS\textsuperscript{d}OHH
\begin{align*}
C1-O1 & = 1.325\text{Å} \\
O1-O2 & = 2.086\text{Å} \\
O2-H & = 1.455\text{Å} \\
C1-O1-O2-H & = -51.69^\circ
\end{align*}

TS\textsuperscript{e}OHH
\begin{align*}
C1-O1 & = 1.361\text{Å} \\
C-O2 & = 1.318\text{Å} \\
O2-O3 & = 1.903\text{Å} \\
C-O3 & = 1.918\text{Å} \\
C1-O1-O2-O3 & = 178.22^\circ
\end{align*}
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**

![Transition states involved in 3b dimerizations](image)

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

![Transition states and minima involved in 3b isomerization](image)
Transition state involved in bOOH production

Transition state involved in bOOH production

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