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Study of the peroxidation mechanism of diethyl ether (DEE)

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1. Introduction

A great number of organic compounds spontaneously form unstable peroxides by reaction of the carbon chain with molecular oxygen in a process of auto-oxidation, the so-called "peroxidation".
This is a free-radical and self-propagating reaction that may generate a wide variety of peroxide molecules (above all hydroperoxides and dialkyl peroxides) for each initiating event. In figure 1 are presented some of the involved prototypical reactions)

Initiation	$R + \dot{O}H \rightarrow R^{\cdot} + H_2O$
Oxygen addition	$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$
Hydroperoxide formation	$ROO^{\cdot} + H^{\cdot} \rightarrow ROOH$
Dialkyl peroxide formation	$ROO^{\cdot} + R'^{\cdot} \rightarrow ROOR'$
	$RO^{\cdot} + R'O^{\cdot} \rightarrow ROOR'$

Fig 1. Prototypical reactions of auto-oxidation process

Peroxidation is promoted by a prolonged exposure to air, heat and light during storage and the accumulation of produced peroxides can lead to unexpected explosions. Whereas reactive hazards of organic peroxides are often well-known (usually they are characterized by shock, heat or friction sensitivity), no data are available about the concentration at which these molecules or a mixing pose a potentially explosive hazard[1, 2].
The reaction of peroxidation is most likely to occur in compounds with activated hydrogen atom in which the intermediate free radical can be stabilized through electronic resonance structures. For instance activated hydrogen atoms occur on carbon linked by oxygen as ethers, on tertiary carbon atoms, on carbon atoms in vinyl structures and in allylic and benzylic structures. In figure 2[3] are presented peroxidizable moieties in order of decreasing hazard.

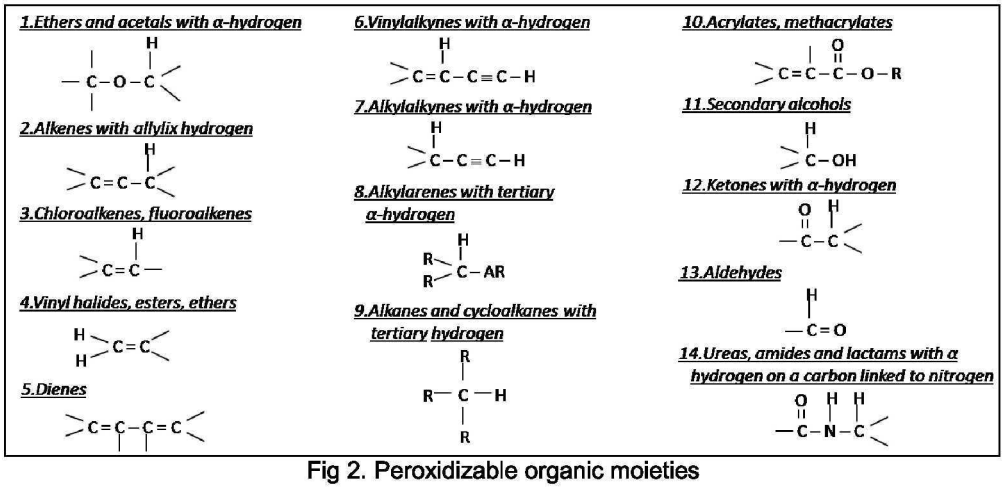


Fig 2. Peroxidizable organic moieties

Among the chemicals widely used in a lot of laboratories and industries as solvent or reactive, ethers are, as shown in figure 2, the most notorious peroxide formers. However, few works propose mechanistic study of their oxidation reactions.
The dimethyl ether (DME) is the most investigated ether both experimentally[4-6] and theoretically[7-9], since it has a relevant role, due to its good ignition properties, in the domain of biofuel. In particular, Andersen and coworkers propose a mechanism for the reaction of low temperature oxidation of DME. They suggest that, analogously to the alkane systems, the reaction occurs when reactive species (the hydroxyl radical for instance) abstract a hydrogen atom from the ether. This initiation step is followed by the reaction of the radical ($R^{\cdot}$) with molecular oxygen. The new adduct ($ROO^{\cdot}$) can decompose, to form two formaldehyde molecules and a $HO^{\cdot}$ radical. Alternatively it can isomerize by intra-molecular hydrogen transfer and then decompose to form various neutral molecules and two $HO^{\cdot}$ radicals instead of one: this leads to a branched chain reaction which causes an increase in the rate of DME oxidation. Experimental study also exist on the oxidation of the other ethers often used as additives in fuel and biofuel like the diethyl ether (DEE)[10, 11], the diisopropyl ether (DIPE)[7] or the methyl tert-butyl ether (MTBE)[12], but, in general, they do not suggest any mechanism.
However, since DEE and DIPE are known to be responsible of a great numbers of laboratory accidents[13-16] for their ability to form explosive peroxides, mechanistic study on the ethers oxidation reaction is fundamental to better understand and to control their accidental risks. The diethyl ether is particularly studied because it is largely used, above all as a very common laboratory solvent. Due to its use as additive in biofuel[17], it is also present in gas phase in the terrestrial atmosphere and it is studied as a contributor to the formation of photochemical smog[8]. From the experimental characterization of final products of decomposition pathways (ethyl formate, ethyl acetate, formaldehyde, methanol, formic acid), Orlando suggests a mechanism for the atmospheric oxidation of DEE. He proposes that the initiation process (via reaction with $HO^{\cdot}$ or $Cl^{\cdot}$ radical) and the reaction of the radical $[CH_3CH_2OCHCH_3]^{\cdot}$ with molecular oxygen, are followed by self-reactions of the 1-ethoxyethylperoxy radical $[CH_3CH_2OCH(OO)CH_3]^{\cdot}$. These self-reactions are a fundamental step for the decomposition of the molecule.
In this scientific context, the present work, carried out in the domain of the INERIS research project named RIPER (for "study of RIsk linked to the PERoxidation of chemical products"), proposes the study of the peroxidation of diethyl ether at both experimental level, through calorimetric tests and analytical methods aiming to detect and measure the amount of produced peroxides, and at theoretical level to identify reaction mechanism, principal products and unstable species. This study will lead to develop a detailed chemical kinetic model of the oxidation process of DEE and, coupled with experimental data, should allow a better understanding of its accidental risks.

2. Materials and methods

2.1 Computational method

All calculations were performed using the Gaussian 03 set of programs[18]. DFT calculations were performed with the hybrid B3LYP functional[19]. The 6-31+G(d,p) basis set was used to optimize geometries and characterize stationary points in the potential energy surface as minima or saddle point (transition state). The intrinsic reaction coordinate (IRC) calculations were also performed to verify that the products and the reactants were correctly connected[20]. Gibbs free energies have been calculated at standard conditions (T=298.15K, P=1atm).

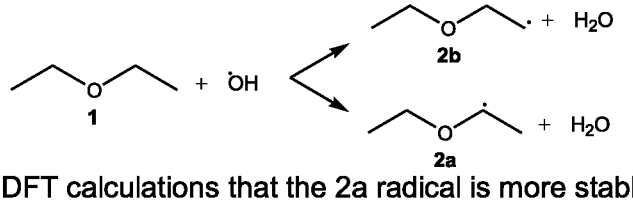
2.2 Experimental method

The work presented in this paper deals with the evolution of the stability of diethyl ether exposed to air and light during 2 months. Samples were investigated by means of a Setaram DSC 131 at 5 K/min heating rate in order to determine the reactivity of the system. Each sample were weighted to a mass of few milligrams and placed into a stainless-steel crucible. Thermal analysis was performed between 20 and 500 °C. It should be noted that iron may slightly influence the decomposition process within the crucible. However, it is not taken into account at the moment.
DEE (99.7%) was obtained from Sigma-Aldrich.

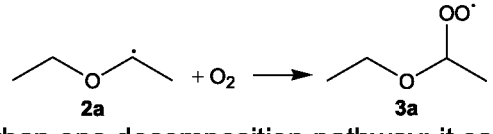
3. Results and discussion

3.1 Theoretical results: the case of one of the possible intramolecular isomerization reaction

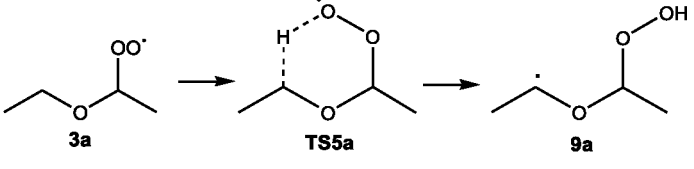
All the chain reactions of DEE (1) decomposition that we have characterized start with the abstraction of a hydrogen atom from the neutral molecule by an initiator (the HO· radical for instance) to form a radical at the carbon atom next to the oxygen (2a) or at the terminal carbon (2b):



It has been verified by DFT calculations that the 2a radical is more stable than the 2b one for 8.2 kcal/mol. The 2a radical (or 2b) can then react with molecular oxygen to form the 3a peroxy radical:



3a radical can follow more than one decomposition pathway: it can react with other radicals (for instance with H· to give a hydroperoxide ROOH) or, as proposed also for DME, it can isomerize by intramolecular hydrogen transfer in a more complex mechanism[5].
In figure 3 is presented the potential energy surface of the isomerization mechanism.
This mechanism starts with the transfer of a hydrogen atom from a carbon atom to the oxygen radical: this first step is endothermic with an energetic barrier of 18.6 kcal/mol.



The product of this reaction can follow, as showed in figures 3 and 5, two possible paths: it can directly decompose in two acetaldehyde molecules (12) and a HO· radical or react with another O_2 molecule to give 10a. This radical can then isomerize to form the neutral molecule hydroperoxyethyl acetate (11a) and, also in this case, a HO· radical.

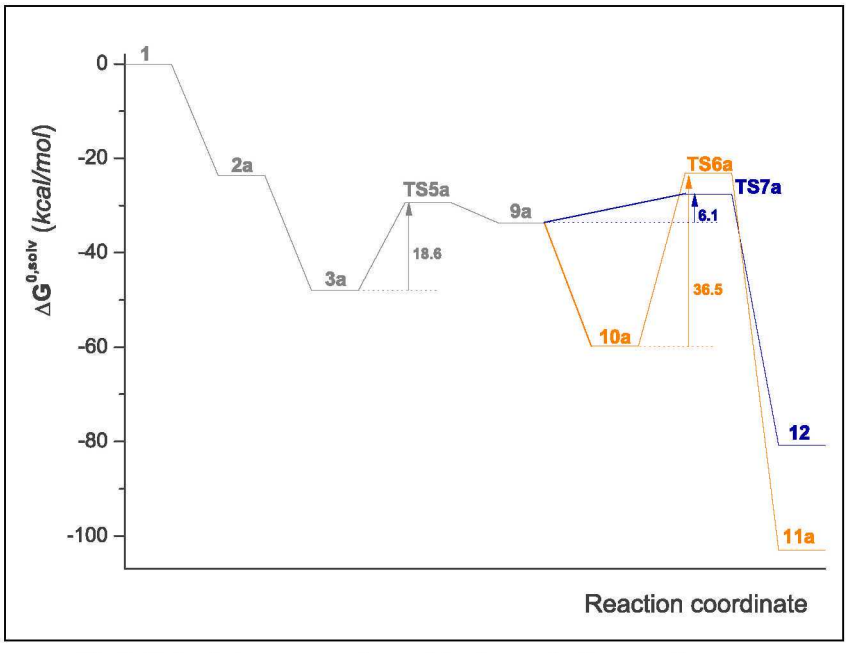


Fig 3. Potential energy surface of the isomerization reaction

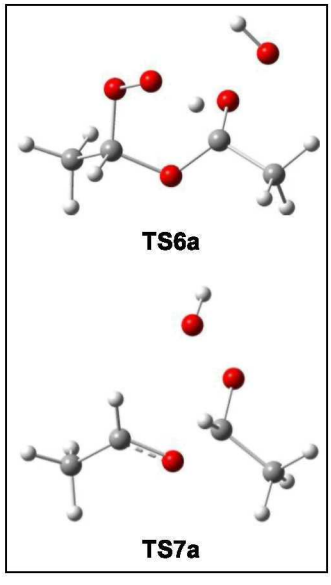


Fig 4. Structures of two transition states

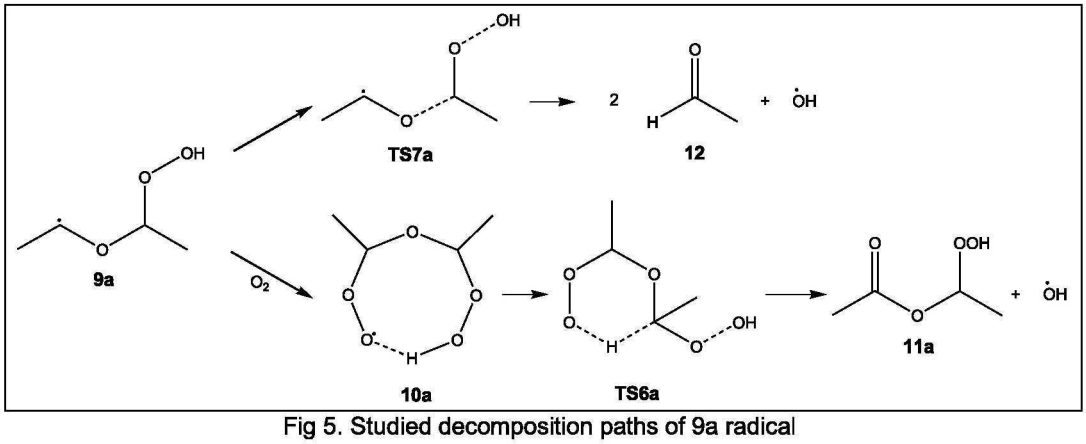


Fig 5. Studied decomposition paths of 9a radical

These processes are both exothermic, but the energetic barriers are very different: 6.1 kcal/mol for the decomposition and 36.5 for the isomerization path. It is verified, as also shown in table 1, that 11a is the more stabilized product for about 25 kcal/mol.

Table 1. Gibbs energies of stationary points and transition states of the two competing paths

Isomerization		*Decomposition*	
species	$\Delta G^{0,solv}$ *(kcal/mol)*	**Species**	$\Delta G^{0,solv}$ *(kcal/mol)*
1 + HO·	0		
2a + H_2O	-23.7		
3a	-48.0		
TS5a	-29.4		
9a + O_2	-33.7		
10a	-59.7	**TS7a**	-27.6
TS6a	-23.2	*2x* **12 + HO·**	-80.8
11a + HO·	-103.0		

Hydroperoxyethyl acetate (11a) is not the final product of the reaction of DEE oxidation. We have found a lot of possible competing decomposition paths of the 11a neutral molecule, that are collected in figure 6, in order of increasing activation energies (table 2).

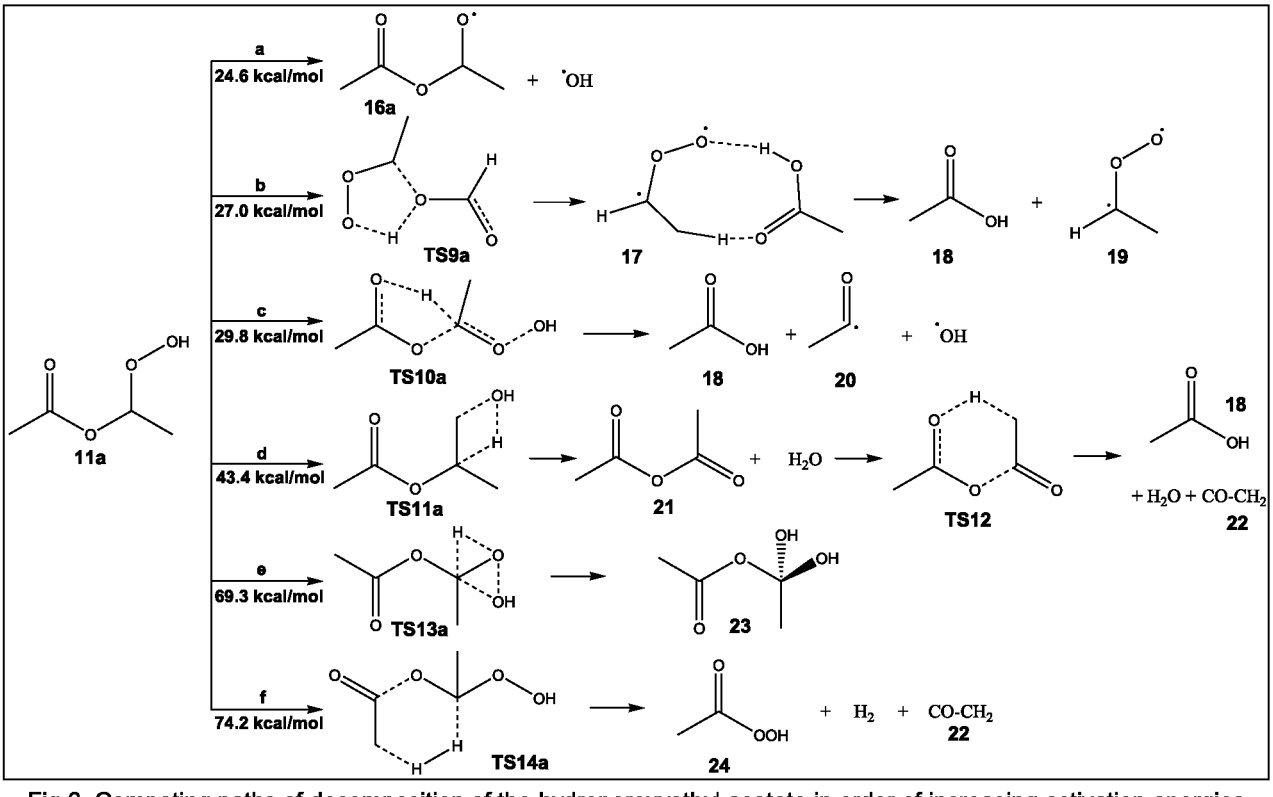


Fig 6. Competing paths of decomposition of the hydroperoxyethyl acetate in order of increasing activation energies

Table 2. Gibbs energies of stationary points and transition states of competing paths of 11a decomposition

	Species	$\Delta G^{0,solv}$ *(kcal/mol)*		species	$\Delta G^{0,solv}$ *(kcal/mol)*
	11a	0			
			d	**TS11a**	43.4
a	**16a + HO˙**	24.6		**21 + H_2O**	-73.1
b	**TS9a**	27.0		**TS12**	-40.7
	17	15.2		**18 + 22**	-60.5
	18 + 19	22.9	***e***	**TS13a**	61.0
c	**TS10a**	29.8		**23**	69.3
	18 + 20 + HO˙	8.0	***f***	**TS14a**	74.2
				24 + H_2 + 22	16.5

All the stationary points and transition states involved in the identified paths are above the energetic zero represented by the sum of Gibbs energies of DEE and of the radical initiator. The reaction paths *a*, *b* and *c* are characterized by the lowest energetic barriers (i.e. kinetically favored). However in all these three cases the final reaction products are less stable than 11a. The reaction of dehydration of hydroperoxyethyl acetate (path *d*) is the thermodynamically favored one. The energetic barrier (see table 2) for this path is not the smallest (43.4 kcal/mol for the rate determining step), but the stabilization of final products (acetic acid, water and CO-CH_2 formed by anhydride decomposition) is the greatest (i.e. thermodynamically controlled).

The two last reaction channels (*e*, *f*) for the 11a decomposition are both unfavourable due to their prohibitive energetic barriers.

3.2 Experimental results

Auto-oxidation process of DEE is mainly characterized by a long induction period (i.e. few months at 298 K and atmospheric pressure)[21]. Relatively slow until 155°C[21], peroxidation leads to the formation of hydroperoxides that decompose to organic compounds such as ethyl formate, ethyl acetate, formaldehyde, methanol, formic acid, acetic acid, ethanol[13, 22] as well as some gases like methane or carbon dioxide[23, 24]. These early results seem to be in accordance with the latest scientific work performed by Orlando[11], who also proposed an atmospheric oxidation mechanism of DEE initiated by HO· or Cl· radical. In fact, they showed by experimental characterization (infrared spectra) that the final products of the decomposition pathways of hydroperoxydes were the same compounds as above mentioned. Hydroperoxides are relatively stable and may not trigger any explosion event. However, hydroperoxides tend sometimes to polymerize to form a highly reactive compound which is likely responsible of the accidental events[13, 23]. Peroxidation process is under the dependence of several parameters, like temperature, pressure, geometry of the storage, exposure to light, air heat, which determine the long term stability of the product. In order to decrease the complexity of the study, it is necessary to consider specific tests allowing to determine globally the evolution of the system. Thus it was decided to perform in a first step a preliminary study enabling to characterize in a simple way the evolution of the reactivity of the system along the time by using calorimetric tools. Here are briefly presented the first results of that experimental work which have just started and will last two years.
In the thermal analysis performed on the samples, a single exothermic peak (22 J/g) was observed around 410°C for each "old" samples (exposed to air and light during two months), but no peak was previously observed in the case of fresh DEE. It was first thought that it would witness peroxide compounds formation, but qualitative tests with Quantofix tests strips were negative, i.e that ether samples do not contain peracetic acid nor peroxides compounds. Further tests with 2,4 DNPH were then carried out, showing a slight yellow precipitate. It means that the exothermic peak may be due to the presence of aldehydes or ketones compounds and not peroxide compounds. At the moment, the risk stability of our samples is still low but the evolution of this parameter needs to be studied in a long-term period to define more accurate and reliable conclusions which is the present work performed at INERIS.

4. Conclusion

The theoretical study of the oxidation reaction of diethyl ether molecule by DFT calculations confirms the great variety of the possible decomposition mechanisms supposed in literature. At present, we have characterized (in structures and energies) more than ten different radical chains.
The objective of the work is now to collect thermodynamical data of all the available reaction paths.
Furthermore this theoretical study has as fundamental aim also the development of a detailed chemical kinetic model of the auto-oxidation process of DEE. These informations, coupled with the data obtained from the experimental work (that is at present just at the beginning), will lead to better understand the accidental risks of diethyl ether.

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