

Accidents caused by peroxide-forming substances

In the past, a frequent cause of accidents and occasionally serious injury was the concentration of liquid phases in organic solvents, causing them to detonate. When sealing a seemingly empty 250 ml glass-stoppered flask which had contained diethyl ether, the flask burst. An attempt to unscrew an old diisopropyl ether bottle led to a detonation which cost the life of the chemist. Encrusted residue of potassium and sodium and their amides have also repeatedly resulted in explosion events.

The guidelines for laboratories and the Technical Rules for Hazardous Substances (TRGS) 526, section 5.1.2 stipulates the following: *Liquids that tend to form organic peroxides must be examined for the presence of peroxides prior to distillation and evaporation, and the peroxides must be removed. Such liquids have to be stored protected from the light – in particular UV radiation.*

Organic peroxides are among the most dangerous substances in laboratories.

Organic compounds very often form peroxides and hydroperoxides with atmospheric oxygen when left to stand. Even in freshly purified solvents, appreciable quantities can be verified after just a few days. These oxidation products are particularly sensitive to mechanical influences, for example to shocks or friction, and to heat. They are low-volatile and accumulate in particular in distillations in the still pot, where they can decay and cause detonation. Residue in ether containers from which the solvent has evaporated is particularly dangerous.

Hydroperoxides are formed in accordance with a radical chain mechanism, initiated by photons, sources of radicals or the peroxides themselves. Diagram 1 shows the formation of 1-ethoxyethylhydroperoxide using the example of diethyl ether.

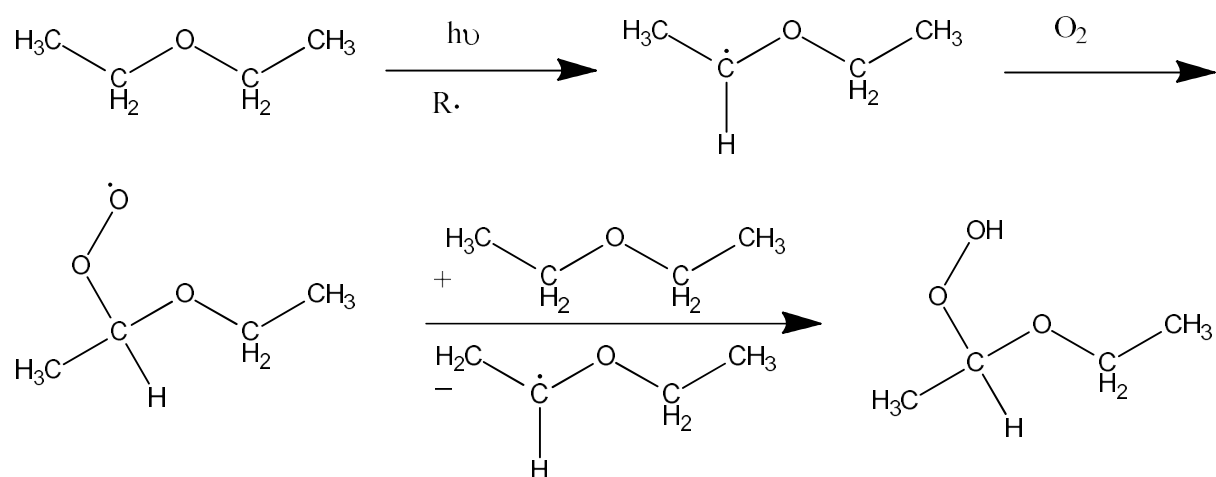


Diagram 1: Formation of 1-ethoxyethylhydroperoxide

According to Diagram 2, the hydroperoxide reacts and forms a potentially explosive polymer when ethanol is eliminated.

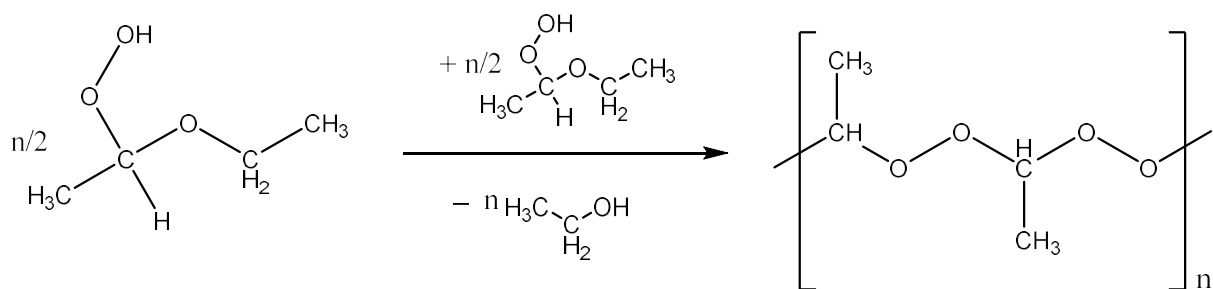
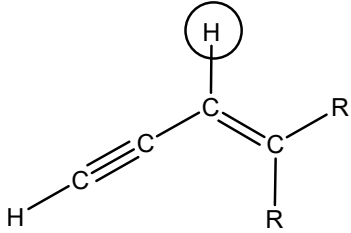
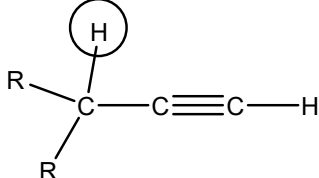
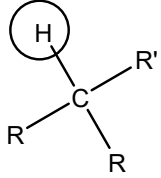
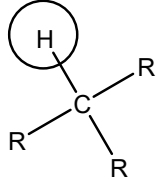
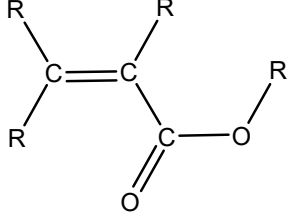
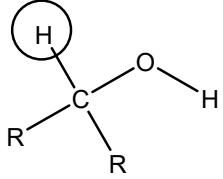
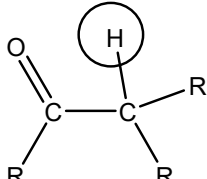
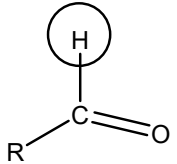


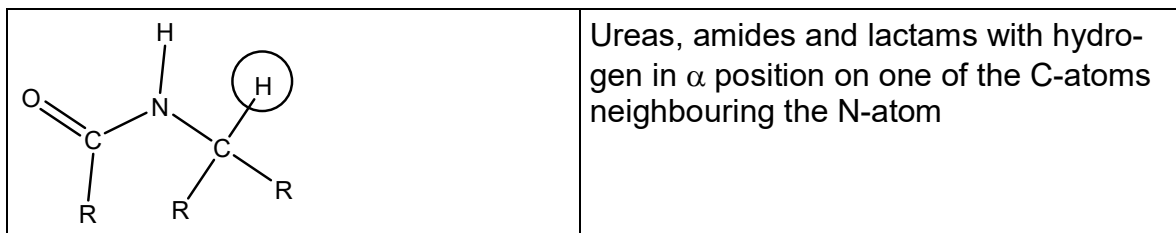
Diagram 2: Polymerisation of 1-ethoxyethylhydroperoxide

Here it is visible that although the absence of oxygen, for instance through storage under argon in leak-tight containers, impedes the formation of peroxides, the exclusion of light as a sole measure does not always prevent peroxide formation. Refrigerated storage is also not a secure measure against oxidation.

Table 1: Potential organic peroxide formers

	Ether and acetals with hydrogen in α position
	Alkenes with allylic hydrogen
	Chloroalkenes and fluoroalkenes
	Vinyl halides, esters and ethers
	Dienes

	Vinyl alkynes with hydrogen in α position
	Alkylalkynes with hydrogen in α position
	Alkylalkynes with tertiary hydrogen in α position
	Alkanes and cycloalkanes with tertiary hydrogen, molecules with benzylic hydrogen
	Acrylates, methacrylates
	Secondary alcohols
	Ketones with hydrogen in α position
	Aldehydes



Unsaturated compounds, in particular those with a lower molar mass, can under certain circumstances, initiated by the peroxides formed, fiercely and explosively auto-polymerise. Small quantities of formed peroxides are sufficient to start the reaction. Examples are: acrylic acids, acrylonitrile, 1,3-butadiene, chlorobutadiene, chlorotrifluoroethylene, methyl methacrylate, styrol, tetrafluoroethylene, vinyl acetate, vinylacetylene, vinyl chloride, vinyl pyridine, 1,2-dichloroethene.

Due to the concentration of formed peroxides, for example through distillation, many organic substances present a danger. Examples of these are: 1,1-diethoxyethane, isopropylbenzene, cyclopentene, cyclohexene, cyclooctene, 1,3-butadiyne, dicyclopentadiene, diglyme, dimethoxyethane, diethyl ether, *p*-dioxane, furan, propyne, methylcyclopentane, *i*-butyl methyl ketone, tetrahydrofuran, tetralin, vinyl ether, cyclohexanol, 4-heptanol, 4-penten-1-ol, 2-phenylethanol, 1-phenylethanol, 2-butanol, cyclohexen-1-ol, decahydronaphthalene, 3-methylbutan-1-ol, 2-pentanol, isopropanol, tetralin and secondary alcohols. High and dangerous concentrations of peroxides can also be caused by very long or unsuitable storage.

For several substances a risk of explosion can be expected even when no concentration processes have taken place, for example divinyl ether, divinylacetylene, diisopropyl ether, 1,3-butadiene, chlorobutadiene, tetrafluoroethylene and 1,2-dichloroethene.

Discolourations, crystallisation or the formation of layers should always be viewed as an indication of a possible risk of explosion.

Inhibitors in goods are consumed with the passage of time, and the formation of peroxides thus commences even in these containers. Some inhibitors require small quantities of oxygen and do not function following inertisation. It is recommended to label such containers with the goods receipt date and the date they were opened for the first time. As a general rule, a time period can be specified within which the container is to be consumed or destroyed. A sensible period can be between one and two years, depending on the speed at which peroxides form. The substance classes listed at the beginning of Table 1 form peroxides most quickly. It is recommended to take this data into account in the chemicals register. When working with substances that form peroxides quickly, such as diethyl ether, it is recommended to test them for peroxide content on a monthly basis. A peroxide content of 1% was found in a 10-year-old original container of "isopropanol for the electronics industry". Peroxide contents of 4.2% for isopropanol and 12% for 2-butanol have been reported. Substances that can present a danger due to the formation of peroxides even without concentration should be procured and consumed when they are as fresh as possible in order to prevent storage periods. Even when substances have been dried or purified, the in-

hibitors that protect from oxidation have generally been removed during this process. These substances should preferably be stored in air-tight containers under inert gas.

Prior to processing, these compounds must always be tested for the presence of peroxides, in particular those which are known to potentially present a danger even without steps that concentrate peroxides or for containers that have been stored unsuitably or for long periods of time. It is beneficial to remove peroxides using standard commercial reagent sets for destroying peroxides, as some peroxides cannot be attacked using various methods but at the same time can be very mechanically sensitive. If the caps of such containers are stuck, these should be disposed of unopened. Glass equipment in which peroxide-forming substances have been processed and in which oily or crystalline residue is visible must not be scratched or rubbed.

Inorganic compounds, too, can form dangerous reaction products with air. Alkali metals and their amides form highly reactive compounds when left to stand with atmospheric oxygen, and also react with the water vapour in the air. This even occurs more or less quickly in air-tight vessels or in protective fluid. For example, potassium forms yellow-orange deposits consisting of a mixture of potassium-hydroxide monohydrate and potassium superoxide. As an extremely strong oxidising agent, the potassium superoxide forms sensitive mixtures which are capable of detonating when in contact with organic protective fluids under mechanical pressure. The potassium-hydroxide monohydrate abruptly releases its water when warmed up, which then comes into contact with the metallic potassium. Under certain circumstances, such old stock can no longer be disposed of safely. A chunk of this is shown in *Fig. 1*. The alkali metal amides also form such potentially explosive mixtures during storage due to air admission.



Fig. 1: Encrusted potassium (image: LMU, Munich)