Ethers: their storage and the detection and removal of peroxides

Introduction

It is generally recognized that ether peroxides are dangerous; diethyl ether, isopropyl ether, dioxin, tetrahydrofuran and many others tend to absorb and react with oxygen from the air to form unstable peroxides. However, the danger is often underestimated when ethers are being distilled, resulting in explosions which could really be avoided. These peroxides may detonate with extreme violence when they become concentrated by evaporation or distillation, or when combined with other compounds that produce an explosive mixture, or when disturbed by unusual heat, shock or friction. Di-isopropyl ether seems to be unusually susceptible to this type of peroxidation. Explosions can also occur when containers of peroxide-containing liquids are merely jolted or the peroxides ignite as a result of friction upon opening.

Peroxides formed in organic compounds by auto-oxidation have caused many laboratory accidents, including unexpected explosions of the residues of solvents after distillation, and have occasioned a number of hazardous disposal operations. Incidents resulting in fatality, sight loss and more minor injuries have been reported.

Case study

There has occurred within this University in the past incident of unexpected laboratory explosion involving an unopened, but fairly full, two litre bottle of diethyl ether inside a solvent storage cupboard. The bottle of ether had been stored under cool and dark conditions for some seven months prior to being issued to the laboratory, and the solvent cupboard concerned in this incident had not been subject to either heat or direct sunlight. The precise cause of the explosion at that particular time remains obscure, but investigation concluded peroxide formation was more than likely the cause of this accident. However, because no drip tray had been provided, ether and broken glass spilled out onto the floor and could well have led to a serious fire had a source of ignition been present; luckily in this event, no fire occurred.

Storage of Ethers

Despite the lack of fire the above incident highlights the value of following good laboratory practice and always storing glass bottles of flammable liquids in properly designed flammable solvent storage cabinets and on shelves fitted with drip trays constructed with a volume capable of containing any foreseeable spillage. In the past, this point has been continuously stressed by the University's Insurance Brokers AON Risk Services during insurance liability surveys.

It can generally be assumed that commercially supplied ethers in full unopened bottles may be stored out of direct light and under cool conditions, in amber glass bottles, for up to one year without the formation of dangerous levels of peroxide. Remember that an “empty” bottle of ether is usually full of vapour unless this has been displaced, for example with water, and a bottle of ether vapour and air represents ideal conditions for the formation of the peroxide, which can be easily detonated by removing a ground glass stopper or a screw cap. Exposure to air, as occurs in opened and partially emptied containers, accelerates the formation of peroxides however the exposure to light does not appear to be fully understood and it is generally accepted that ethers, which have the ability to form peroxides, be kept in amber glass bottles in the dark.

It is strongly recommended that all bottles containing ethers should be clearly labelled with the date when the material is delivered to the School; stores persons should then make arrangements to use stocks in rotation. On receipt by a particular laboratory the bottle should be labelled with the date of opening and thereafter it is in the best interests of the laboratory workers concerned that all samples of ethers in opened bottles should be tested for the presence of peroxides at a minimum of three monthly intervals.

Refrigeration does not appear to inhibit peroxide formation. Indeed, refrigeration of ethers in non-spark-proofed refrigerators can lead to a serious explosion and should never be considered.

Detection of Peroxides

If there is gross evidence of the formation of peroxides, such as either appreciable quantities of crystalline solids, or a quantity of viscous liquid in the bottom of a glass bottle of ether, further testing should not be attempted as opening the suspect bottle for testing purposes can be a very hazardous operation in itself. Unless professional expertise is available to deal with this situation, the material should be stored safely until it can be disposed of to a licensed waste disposal contractor.

Several chemical and physical methods for the detection of peroxides have been described; two such methods are:

a. Peroxide test strips: The Peroxide Test detects inorganic and organic compounds containing a peroxide or a hydroperoxide group. It is well suited to the routine semi quantative checking of simple ethers such as diethyl ether (ethyl ether), tetrahydrofuran and dioxan. The polymeric peroxides sometimes occurring in simple ethers are only detected with reduced sensitivity, if at all. This being so, it is advisable to perform a trial determination in the laboratory to verify that the Peroxide Test strip gives satisfactory results. Principle of the Method Peroxidase (POD) transfers oxygen from peroxide to an organic redox indicator, which is converted to a blue oxidation product. The blue colours developed by the test strip cover the range 0 - 0.5 - 2 - 5 - 10 - 25mg/l (ppm) H2O2 When organic solvents are tested, the moisture required for the

reaction to occur is provided by breathing on the reaction zone several times or by immersing in distilled water.

Volatile Ethers

1. Immerse a test strip for approximately 1 second in the solvent being tested and allow to evaporate.
2. Breathe on the reaction zone 4 times for 3-5 seconds each time. Alternatively, immerse briefly in distilled water.
3. Compare the reaction zone with the colour scale. Merck Peroxide Test Strips - Merckoquant ® Peroxide Test 10011, Test Kit Cat No. 31514 2K (100 determinations). VWR International Literature hotline - 01202 664421

b. Potassium Iodide Test - to check for the presence of peroxides, shake 10ml of the ether with 1ml of fresh 10% (w/v) potassium iodide solution and a few drops of hydrochloric acid. Peroxides liberate iodine and the aqueous phase becomes yellow. If the result is uncertain, add a little starch solution. A blue colour results from a trace of liberated iodine.

References for other methods can be obtained by contacting: occupational.hygiene@ed.ac.uk

Warning on Distillation

On no account should any ether with a peroxide content above 50 ppm be used without purification, an on no account should any ether be distilled or evaporated to dryness, since when using large volumes even low peroxide concentrations, which are not readily detected by the above methods, can concentrate to dangerous levels.

Removal of Peroxides

1. Peroxides may generally be removed form ethers by percolating through a column of activated alumina. Ether purified in this way should be used directly and not stored for a further time, since the alumina will probably have removed any antioxidant present, thus making the material more susceptible to peroxide formation in the presence of air.
2. Shake before use with a freshly prepared solution of iron (II) sulphate (for each litre of ether, use 5 g iron (II) sulphate dissolved in 20ml water). Repeat until no more peroxide is detected with the test strips.

Other methods for the detection and removal of peroxides from ethers have been described; several are to be found in 'Control of Peroxides in Ethers', in the Steere Handbook of Laboratory Safety.