



react

PEROXIDE FORMING CHEMICALS

Many chemicals can form peroxides when exposed to air over a period of time. Opening a container can introduce enough air for peroxide formation to occur. Structural characteristics of organic compounds that form peroxides are listed below in approximate order of decreasing peroxide forming potential :

- | | | | |
|--|--|---|---|
| 1. $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{O}- \\ \end{array}$ | Ethers and acetals with α hydrogen atoms, e.g. diisopropylether | 8. $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{Ar} \\ \end{array}$ | Alkylarenes that contain tertiary hydrogen atoms, e.g. cumene |
| 2. $\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C}-\text{C} \\ \quad \end{array}$ | Olefins with allylic hydrogen atoms, e.g. 4-vinylcyclohexene | 9. $\begin{array}{c} -\text{H}_2\text{C} \quad \text{H} \\ \quad \\ \text{C}- \\ \end{array}$ | Alkanes and cycloalkanes that contain tertiary hydrogen atoms, e.g. decahydronaphthalene |
| 3. $\begin{array}{c} \text{X} \\ \\ \text{C}=\text{C}- \\ \end{array}$ | Chloroolefins and fluoroolefins, e.g. vinylidenechloride | 10. $\begin{array}{c} \\ \text{C}=\text{C}-\text{CO}_2\text{R} \\ \end{array}$ | Acrylates and methacrylates, e.g. methylmethacrylate |
| 4. $\begin{array}{c} \text{C}=\text{C} \\ \quad \\ \text{H} \end{array}$ | Vinyl halides, esters, and ethers, e.g. vinyl chloride | 11. $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{OH} \\ \end{array}$ | Secondary alcohols, e.g. 2-propanol |
| 5. $\begin{array}{c} \text{C}=\text{C}-\text{C}=\text{C} \\ \quad \quad \quad \end{array}$ | Dienes, e.g. 1,3-butadiene | 12. $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}=\text{O} \\ \end{array}$ | Ketones that contain α hydrogen atoms, e.g. methylisobutylketone |
| 6. $\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C}-\text{C}=\text{CH} \\ \end{array}$ | Vinylacetylenes with α hydrogen atoms, e.g. divinylacetylene | 13. $\begin{array}{c} \text{H} \\ \\ -\text{C}=\text{O} \end{array}$ | Aldehydes, e.g. acetaldehyde |
| 7. $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}=\text{CH} \\ \end{array}$ | Alkylacetylenes with α hydrogen atoms, e.g. propyne | 14. $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}-\text{N}-\text{C}=\text{O} \\ \end{array}$ | Ureas, amides, and lactams that have a hydrogen atom on a carbon attached to nitrogen, e.g. caprolactam |

Ref.: J. Chem. Educ. 47 (1970) 175; J. Chem. Educ. 65 (1988) 226; Reactive Chemical News # 184 (1986)

Scope - Applications

The list above indicates that a lot of chemicals are susceptible to peroxide formation. Presence of peroxides can be verified by the use of peroxide test paper. Extreme care should be taken in such processes where the peroxide can concentrate due to distillation, precipitation, evaporation of solvent, etc.

Significant incidents

Total number of Dow incidents in 1981-1990 : 15

1984 Vinylidene plant: A small explosion occurred in the top part of a filter element. A deposit of shock sensitive vinylidene chloride peroxide had apparently built up in the filter.

1986 Research: During the removal of methylene chloride solvent under vacuum from an organic solution at 25-30°C an explosion took place most probably due to concentrating trace amounts of hydrogen peroxide left from the previous synthesis step.

Outside Dow: A serious explosion occurred during measurement of the oxidation stability (ASTM D525) of a sample rich in conjugated C5 dienes (45-60 %), probably caused by autoignition of polyperoxides formed during the reflux step. The test was developed for gasoline containing low amounts of polymerizable components.

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