Peroxidizable Organic Chemical Handout

Classes of peroxidizable organic chemical			
Class A: Form explosive levels of peroxide without concentration			
Butadiene[a]	Divinylacetylene	**Tetrafluoroethylene**[a]	
Vinylidene chloride[a]	Chloroprene	**Isopropyl ether**	
Class B: Form explosive levels of peroxide upon concentration			
Acetal	Diacetylene	2-Hexanol	2-Phenylethanol
Acetaldehyde	Dicyclopentadiene	Methylacetylene	**2-Propanol**
Benzyl alcohol	**Diethyl ether**	3-Methyl-1-butanol	**Tetrahydrofuran**
2-Butanol	Diethylene glycol dimethyl ether (diglyme)	Methylcyclopentane	Tetrahydronapthalene
Cumene		Methyl isobutyl ketone	Vinyl ethers
Cyclohexanol	**Dioxanes**	4-Methyl-2-pentanol	Other secondary alcohols
2-Cyclohexen-1-ol	Ethylene glycol dimethyl ether (glyme)	2-Penten-1-ol	
Cyclohexene		4-Penten-1-ol	
Decahydronapthalene	4-Heptanol	1-Phenylethanol	
Class C: May autopolymerize due to peroxide accumulation			
Acrylic acid[b]	Chlorotrifluoroethylene	Vinyl acetate	Vinylidiene chloride
Acrylonitrile[b]	**Methyl methacrylate**[b]	Vinylacetylene	
Butadiene[c]	**Styrene**	Vinyl chloride	
Chloroprene[c]	**Tetrafluoroethylene**[c]	Vinylpyridine	
Class D: Forms peroxides; insufficient information to classify			
Acrolein	***tert*-Butyl methyl ether**	Di(1-propynyl) ether[f]	4-Methyl-2-pentanone
Allyl ether[d]	*n*-Butyl phenyl ether	Di(2-propynyl) ether	*n*-Methylphenatole
Allyl ethyl ether	*n*-Butyl vinyl ether	Di-*n*-propoxymethane[d]	2-Methyltetrahydrofuran
Allyl phenyl ether	Chloroacetaldehyde diethylacetal[d]	1,2-Epoxy-3-isopropoxypropane[d]	3-Methoxy-1-butyl acetate

p-(*n*-Amyloxy)benxoyl chloride	2-Chlorobutadiene	1,2-Epoxy-3-phenoxypropane	**2-Methoxyethanol (methyl Cellosolve)**
n-Amyl ether	1-(2-Chloroethoxy)-2-phenoxyethane	Ethoxyacetophenone	3-Methoxyethyl acetate
Benzyl *n*-butyl ether[d]		1-(2-Ethoxyethoxy)ethyl acetate	2-Methoxyethyl vinyl ether
Benzyl ether[d]	Chloroethylene	2-Ethoxyethyl acetate	Methoxy-1,3,5,7-cyclooctatetraene
Benzyl ethyl ether[d]	Chloromethyl methyl ether[e]	(2-Ethoxyethyl)-*o*-benzoyl benzoate	
Benzyl methyl ether	*ß*-Chlorophenatole		*ß*-Methoxypropionitrile
Benzyl 1-napthyl ether[d]	*o*-Chlorophenatole	1-Ethoxynapthalene	*m*-Nitrophenatole
1,2-Bis(chloroethoxy)ethane	*p*-Chlorophenatole	*o,p*-Ethoxyphenyl isocyanate	1-Octene
Bis(2-ethoxyethyl) ether	Cyclooctene[d]	1-Ethoxy-2-propyne	Oxybis(2-ethyl acetate)
Bis(2-methoxyethoxy)ethyl) ether	Cyclopropyl methyl ether	3-Ethoxyopropionitrile	Oxybis(2-ethyl benzoate)
	Diallyl ether[d]	2-Ethylacrylaldehyde oxime	*ß,ß*-Oxydipropionitrile
Bis(2-chloroethyl) ether	*p*-Di-*n*-butoxybenzene	2-Ethylbutanol	1-Pentene
Bis(2-ethoxyethyl) adipate	1,2-Dibenzyloxyethane[d]	Ethyl *ß*-ethoxypropionate	Phenoxyacetyl chloride
Bis(ethoxyethyl) phthalate	*p*-Dibenzyloxybenzene[d]	2-Ethylhexanal	Phenoxypropionyl chloride
Bis(methoxyethyl) carbonate	1,2-Dichloroethyl ethyl ether	Ethyl vinyl ether	Phenyl *o*-propyl ether
Bis(methoxyethyl) ether	2,4-Dichlorophenatole	**Furan**	*p*-Phenylphenetone
Bis(methoxyethyl) phthalate	Diethoxymethane[d]	2,5-Hexadiyn-1-ol	***n*-Propyl ether**
Bis(2-methoxymethyl) adipate	2,2-Diethoxypropane	4,5-Hexadien-2-yn-1-ol	*n*-Propyl isopropyl ether
Bis(2-*n*-butoxyethyl) phthalate	Diethyl ethoxymethylenemalonate	*n*-Hexyl ether	Sodium 8,11,14-eicosatetraenoate
Bis(2-phenoxyethyl) ether	Diethyl fumarate[d]	*o,p*-Iodophenatole	
Bis(4-chlorobutyl) ether	Diethyl acetal[d]	Isoamyl benzyl ether[d]	Sodium ethoxyacetylide[f]

Bis(chloromethyl) ether[e]	Diethylketene[f]	Isoamyl ether[d]	Tetrahydropyran
2-Bromomethyl ethyl ether	*m,o,p*-Diethoxybenzene	Isobutyl vinyl ether	Tetraethylene glycol diacetate
ß-Bromophenetole	1,2-Diethoxyethane	Isophorone[d]	Triethylene glycol dipropionate
o-Bromophenetole	Dimethoxymethane[d]	*p*-Isopropoxypropionitrile[d]	1,3,3-Trimethoxypropene[d]
p-Bromophenetole	1,1-Dimethoxyethane[d]	Isopropyl 2,4,5-trichlorophenoxyacetate	1,1,2,3-Tetrachloro-1,3,-butadiene
3-Bromopropyl phenyl ether	Dimethylketene[f]		
1,3-Butadiyne	3,3-Dimethoxypropene	**Limonene**	4-Vinyl cyclohexene
Buten-3-yne	2,4-Dinitrophenatole	1,5-*p*-Methadiene	Vinylene carbonate
tert-Butyl ethyl ether	1,3-Dioxepane[d]	Methyl *p*-(*n*-amyloxy)benzoate	Vinylidene chloride[d]

Notes on Peroxidizable Organic Compounds

Risk factors for peroxidization

- Heat
- Light
- Air/oxygen
- Volatility/ability to be concentrated
- Low molecular weight
- Long storage time
- Catalyzing contaminants (e.g. heavy metals, alkali)

Peroxidizable organic compound classes

1. Form explosive levels without concentration
2. Form explosive levels with concentration
3. Autopolymerize explosively
4. Unknown/uncharacterized hazard

Detection
Kelly, R.J., A critical review of peroxide determination methods, Chem. Health & Safety, 1996, 3(5), 28.

Managing peroxidizable organic compounds

- Purchase limited quantities/small containers/no stockpiling
- Use in receipt order
- Label as peroxide former
- Periodically test (3 mo or more frequently if necessary)
- Test inhibitor levels if used
- Treat or dispose if >100ppm

Storing peroxidizable organic compounds

- Inert blanket (except where inhibitors require oxygen to work)
- Tight-fitting cap (no ground-glass stoppers)
- No plastic (metal preferred)
- Store away from heat and light
- Advisable storage times: (JHU rules: 1 yr after receipt, 6 mo after opening)
    - Unopened containers: 18 months
    - Opened:
        - Class A: 3 months
        - Class B or D: 24 months (with testing every three or fewer months)
        - Class C
            - Uninhibited: 24 hours
            - Inhibited: 12 months (testing both peroxide and inhibitor every three or fewer months)