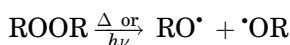


PEROXIDES AND PEROXIDE COMPOUNDS, ORGANIC PEROXIDES

1. Introduction

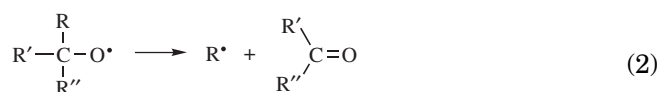
Organic peroxides are compounds possessing one or more oxygen–oxygen bonds. They are derivatives of hydrogen peroxide, HOOH , in which one or both hydrogens are replaced by a group containing carbon (R , R'), ie, ROOH or ROO' . The ultimate source of the oxygen–oxygen linkage in organic peroxides is oxygen; either from direct air oxidation or from reactions of organic compounds with peroxidic materials derived from oxygen, eg, hydrogen peroxide, alkali metal peroxides, ozone (qv), or other organic peroxides (1–6). Organic peroxides are intermediates or products in air oxidation of many synthetic and natural organic compounds. They are involved in many biological processes including development of rancidity in fats, loss of activity of vitamin products, and firefly bioluminescence. Some biological products contain a peroxide group, eg, the natural product, qinghaosu [63968-64-9], is a 1,2,4-trioxane that possesses antimalarial properties (7) and ascaridole [512-85-6], is an endoperoxide that possesses sedative, analgesic, antirheumatic, and anthelmintic properties (8). Organic peroxides are also involved in gum formation in lubricating oils, prepolymerization of some vinyl monomers, and degradation of olefin polymers. Air oxidation of certain solvents, especially ethers, results in formation of organic peroxides which, upon concentration, can form highly explosive peroxidic residues. Oxidation inhibitors are often used to prevent formation of undesirable peroxides in products.

Almost all organic peroxides are thermally and photolytically sensitive owing to the facile cleavage of the weak oxygen–oxygen bond, ie, the range of ΔH is about -84 to -184 kJ/mol (-20 to -44 kcal/mol) (9–11):

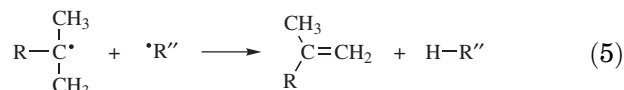


This cleavage is a unimolecular (first-order) reaction. The thermal decomposition rates are affected by the structure of the organic peroxide and the decomposition conditions. For comparison purposes, the thermal activity of a peroxide can be expressed in terms of its 10-hour half-life temperature (10-h HLT, ie, the temperature required for 50% decomposition of a peroxide in a period of 10 hours). This temperature can vary from well below 20°C to well above 200°C . In comparing two peroxides, the one with the lower 10-h HLT is more thermally labile. Another comparison of thermal activity is by active oxygen content, which refers to the quantity of peroxide groups available for thermal decomposition. The concept of active oxygen content is based on the existence of one active oxygen in each oxygen–oxygen bond pair. It is usually expressed as a percentage, ie, $(100)(16\text{ }p/m)$, where p represents the number of peroxide groups present and m represents the molecular weight (pure compound) and is adjusted for assay in diluted formulations. The phrase appears frequently in discussions of peroxide analysis and safety. Peroxide compounds or formulations having low active oxygen content are generally safer to handle than those with high active oxygen content.

Thermal decomposition of peroxides initially forms oxygen-centered free radicals from the oxygen–oxygen bond homolysis. These radicals are reactive intermediates generally having very short lifetimes, ie, half-life times less than 10^{-3} s (12). Once formed, radicals undergo two basic types of reactions: propagating reactions and terminating reactions. In a propagating reaction, a radical reacts to form a covalent bond and to generate a new radical. The three most common propagating reactions are hydrogen abstraction (eq. 1), β -scission (eq. 2), and addition to carbon–carbon double bonds or aromatic rings (eq. 3).



Generally, the higher stability of the generated alkyl radical compared to that of the starting radical provides the driving force and determines the course of a propagating reaction. The radical, $\text{R}\cdot$, formed in the β -scission reaction is the most stable alkyl radical among the three possible radicals, $\text{R}\cdot$, $\text{R}'\cdot$, and $\text{R}''\cdot$. Propagating reactions are also affected by temperature, pressure, steric, and electronic effects. In a termination reaction, two radicals interact in a mutually destructive reaction in which both radicals form covalent bonds and reaction ceases. The two most common termination reactions are coupling (eq. 4) and disproportionation (eq. 5).



Because many organic peroxides undergo thermolysis to form useful free radicals, they are used commercially as initiators for free-radical reactions. Many organic peroxides also undergo reactions in which free radicals are not involved, eg, heterolyses, hydrolyses, reductions, and rearrangements. Numerous reviews of the chemistry and applications of organic peroxides have been published (11,13–41).

The first synthesis of an organic peroxide was that of dibenzoyl peroxide [94-36-0] (BPO) in 1858 (42). In the early 1900s, BPO was employed as a bleaching agent for edible oils and, subsequently, for grain flours. The use of organic peroxides as free-radical initiators for vinyl monomer polymerization became important during World War II due to increased demand for plastics and synthetic rubber for military tires. Approximately 100 different organic peroxides in well over 300 formulations are commercially produced throughout the world as free-radical initiators for polymerizing vinyl monomers, grafting of monomers onto polymers, curing agents for unsaturated resins, rubber, and elastomers, cross-linking of thermoplastics (eg, polyethylene), modification/degradation of

polypropylene, halogenations, anti-Markovnikov additions to terminal olefins (eg, formation of primary mercaptans), and telomerizations. Some are used as bleaching agents (qv) (ie, for grain flours and fabrics), olefin epoxidizing agents, and active species in a variety of other applications, eg, the use of BPO as the active antibacterial component in acne medications.

Organic peroxides can be classified according to peroxide structure. There are seven principal classes: hydroperoxides; dialkyl peroxides; α -oxygen substituted alkyl hydroperoxides and dialkyl peroxides; primary and secondary ozonides; peroxyacids; diacyl peroxides (acyl and organosulfonyl peroxides); and alkyl peroxyesters (peroxycarboxylates, peroxysulfonates, and peroxyphosphates).

2. Hydroperoxides

There are two main subclasses of hydroperoxides: organic (alkyl) hydroperoxides, ie, ROOH, and organomineral hydroperoxides, ie, $R_m Q(OOH)_n$, where Q is silicon (43), germanium, tin, or antimony. The alkyl group in ROOH can be primary, secondary, or tertiary. Except for ethylbenzene hydroperoxide, only *tert*-alkyl hydroperoxides are commercially important.

2.1. Physical Properties. Some physical properties of alkyl hydroperoxides (in order of increasing carbon content) are listed in Table 1 (44). Descriptions of hydroperoxides are given in the chemical literature (1,4–6,10,28,43,45).

Alkyl hydroperoxides can be liquids or solids. Those having low molecular weight are soluble in water and are explosive in the pure state. As the molecular weight increases, ie, as the active oxygen content is reduced, water solubility and the violence of decomposition decrease. Alkyl hydroperoxides are stronger acids than the corresponding alcohols and have acidities similar to those of phenols. *tert*-Alkyl hydroperoxides can be purified through their alkali metal salts (28).

Bond dissociation energies (BDEs) for the oxygen–oxygen and oxygen–hydrogen bonds are 167–184 kJ/mol (40.0–44.0 kcal/mol) and 375 kJ/mol (89.6 kcal/mol), respectively (10,45). Heats of formation, entropies, and heat capacities of hydroperoxides have been summarized (9). Hydroperoxides exist as hydrogen-bonded dimers in nonpolar solvents and readily form hydrogen-bonded associations with ethers, alcohols, amines, ketones, sulfoxides, and carboxylic acids (46). Other physical properties of hydroperoxides have been reported (46).

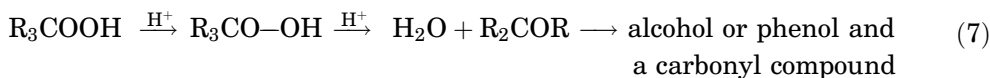
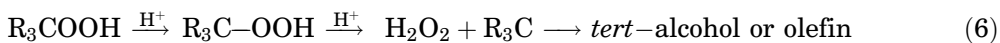
2.2. Chemical Properties. Hydroperoxides can react with or without cleavage of the oxygen–oxygen bond. Reactions resulting in scission of the oxygen–oxygen bond involve heterolytic, homolytic, or metal-promoted oxidation–reduction reactions. Alkyl hydroperoxides also react with a variety of compounds, eg, acyl chlorides, anhydrides, alcohols, alkyl halides, sulfates or sulfonates, epoxides, ethers, olefins, acetals, aldehydes, ketones, ketenes, phenols, amines, aralkanes, nitrites, isocyanates, chloroformates, phosgene, carbamyl chlorides, sulfonyl chlorides, and organomineral halides, amines, hydroxides, and ethers to form other organic peroxides in which the oxygen–oxygen bond is retained (47).

Alkyl hydroperoxides are reduced readily to the corresponding alcohols; many such reductions are quantitative and useful for analytical methods. Alkyl hydroperoxides have been used as oxidizing or hydroxylating reagents in organic syntheses, eg, to produce unsaturated acids and esters from unsaturated aldehydes; hydroxylamines, imines, and nitrones from amines; carboxylic acids from ketones; phosphates from phosphites; phosphine oxides from phosphines; sulfoxides from sulfides; alcohols and phenols from Grignard reagents; epoxides from olefins; phenols from aromatic compounds; ketones from secondary alcohols; stilbenequinones from *p*-methylphenols; and unsaturated ethers and hydroxyethers from dienes (1,4–6,10,28,32,48). A method has been developed for the asymmetric synthesis of optically active epoxy alcohols from unsaturated alcohols using hydroperoxides and tetraalkyl titanates as the epoxidizing system, and optically active tartrate as the asymmetric template (49).

Bases, such as potassium or sodium hydroxide, piperidine, and pyridine, react with primary and secondary hydroperoxides to form aldehydes or ketones (28). In some cases, this reaction is slow or fails unless heating is employed.

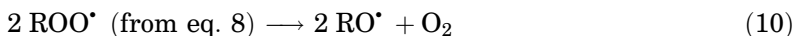
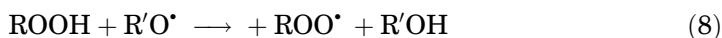
tert-Alkyl hydroperoxides form stable alkali metal salts with caustic; however, when equimolar amounts of the hydroperoxide and its sodium salt are present in aqueous solution, rapid decomposition to *tert*-alcohol and oxygen occurs (28).

Acids react with alkyl hydroperoxides in two different ways, depending on the hydroperoxide structure and the acid strength (45).



Carbon–oxygen cleavage occurs when protonation takes place on the oxygen atom adjacent to the carbon (eq. 6). Thus hydrogen peroxide is the leaving group and the resulting carbonium ion produces *tert*-alcohol or olefin. The more likely oxygen–oxygen bond cleavage occurs when protonation takes place on the second oxygen (eq. 7). In this case the oxygen atom adjacent to the carbon possesses a partial positive charge and one alkyl (or aryl) group migrates from the carbon to the adjacent positive oxygen via a 1,2-shift. Reaction 7 is especially rapid with aralkyl hydroperoxides. The commercial process for production of phenol (qv) and acetone (qv) involves the acid-catalyzed decomposition of α -cumyl hydroperoxide according to this reaction. Strong acids can also decompose hydroperoxides at ca 20°C by oxygen–oxygen bond homolysis. This homolysis accounts for about 30% of the decomposed hydroperoxide and can be used to initiate free-radical polymerization (50). Addition of strong acids, eg, concentrated sulfuric acid, to pure or concentrated solutions of alkyl hydroperoxides is dangerous and, unless carefully controlled, results in explosive decompositions and fire.

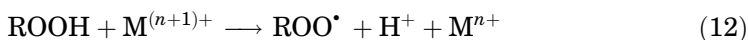
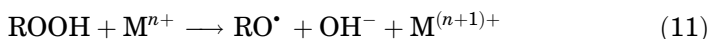
Hydroperoxides are photo- and thermally sensitive and undergo initial oxygen–oxygen bond homolysis, and they are readily attacked by free radicals undergoing induced decompositions (eqs. 8–10).



Therefore, first-order, decomposition rates for alkyl hydroperoxides, ie, from oxygen–oxygen bond homolysis, are valid only if induced decomposition reactions are suppressed completely. This is accomplished only if the decomposition occurs in very dilute solutions and efficient free-radical scavengers are present. Radical-induced decompositions of *tert*-alkyl hydroperoxides are chain reactions (51,52). The alkoxy radicals from equations 9 or 10 react with undecomposed hydroperoxide to generate more alkoxy radicals according to equations 8 and 10. For example, thermal decomposition of *tert*-butyl hydroperoxide, which is either undiluted or in chlorobenzene solution at 140°C, or photolytic decomposition at lower temperatures, yields *tert*-butyl alcohol and oxygen in nearly quantitative amounts (52).

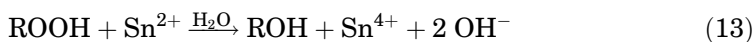
Although primary and secondary alkyl hydroperoxides are attacked by free radicals, as in equations 8 and 9, such reactions are not chain scission reactions since the alkylperoxy radicals terminate by disproportionation without forming the new radicals needed to continue the chain (53). Overall decomposition rates are faster than the true first-order rates if radical-induced decompositions are not suppressed.

Hydroperoxides are decomposed readily by multivalent metal ions, ie, Cu, Co, Fe, V, Mn, Sn, Pb, etc, by an oxidation-reduction or electron-transfer process. Depending on the metal and its valence state, metallic cations either donate or accept electrons when reacting with hydroperoxides (45). Either one or two electrons may be transferred depending on the metal:



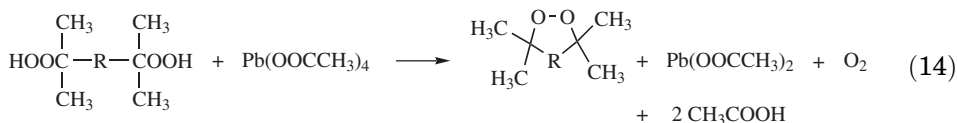
With most transition metals, eg, Cu, Co, and Mn, both valence states react with hydroperoxides via one electron transfer (eqs. 11 and 12). Thus, a small amount of transition-metal ion can decompose a large amount of hydroperoxide and, consequently, inadvertent contamination of hydroperoxides with traces of transition-metal impurities should be avoided.

An example of a reaction involving transfer of two electrons from the metal is the reduction of alkyl hydroperoxides with stannous chloride (10) (eq. 13).



In the reaction of lead tetraacetate with 1,3- or 1,4-dihydroperoxides (10) to produce cyclic monoperoxides there are two electron transfers to the metal

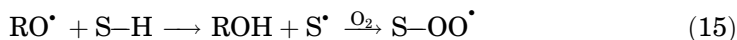
(eq. 14).



The reactions of *tert*-alkyl hydroperoxides with ferrous ion (eq. 11) generate alkoxy radicals. These free-radical initiator systems are used industrially for the emulsion polymerization and copolymerization of vinyl monomers, eg, butadiene–styrene. The use of hydroperoxides in the presence of transition-metal ions to synthesize a large variety of products has been reviewed (48,51).

The ultimate fate of the oxygen-centered radicals generated from alkyl hydroperoxides depends on the decomposition environment. In vinyl monomers, hydroperoxides can be used as efficient sources of free radicals because vinyl monomers generally are efficient radical scavengers which effectively suppress induced decomposition. When induced decomposition occurs, the hydroperoxide is decomposed with no net increase of radicals in the system (see eqs. 8, 9, and 10). Hydroperoxides usually are not effective free-radical initiators since radical-induced decompositions significantly decrease the efficiency of radical generation. Thermal decomposition-rate studies in dilute solutions show that alkyl hydroperoxides have 10-h HLTs of 133–172°C. Alkyl hydroperoxides are among the most thermally stable organic peroxides. However, hydroperoxides are sensitive to chain decomposition reactions initiated by radicals and/or transition-metal ions. Such decompositions, if not controlled, can be autoaccelerating and sometimes can lead to violent decompositions when neat hydroperoxides or concentrated solutions of hydroperoxides are involved.

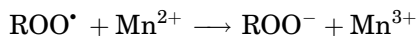
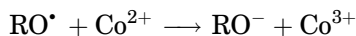
Most solvents for hydroperoxides are not completely inert to radical attack and, consequently, react with radicals from the hydroperoxide to form solvent-derived radicals, either by addition to unsaturated sites or by hydrogen- or chlorine-atom abstraction. In equation 15, S–H represents solvent and $\dot{\text{S}}$ is a solvent radical.



Such solvent-derived radicals can induce the decomposition of the hydroperoxide or react with oxygen in the system to form peroxidic solvent molecules. They may also react with other radicals either by coupling or disproportionation.

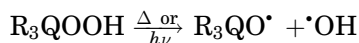
tert-Alkoxy radicals from hydroperoxides can undergo a β -scission reaction (eq. 2) to yield an alkyl radical and a ketone. The higher stability of the generated alkyl radical compared to that of the parent *tert*-alkoxy radical provides the driving force for this reaction, and the R group involved is the one that forms the most stable alkyl radical.

Transition-metal ions also interact with hydroperoxide-generated radicals by converting them into ions, eg:



The radicals are destroyed and are not available to take part in the desired radical reactions, eg, polymerizations. Thus, transition-metal ion concentrations of metal–hydroperoxide initiating systems are optimized to maximize radical generation.

Organomineral hydroperoxides undergo thermal and photolytic homolyses:



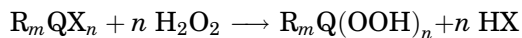
The decomposition products show that the initially formed radicals react by several mechanisms. These hydroperoxides are decomposed by bases, apparently by an ionic pathway, and are surprisingly stable in acids (33).

2.3. Synthesis. Hydroperoxides have been prepared from several types of peroxygen compounds including hydrogen peroxide or sodium peroxide, ozone, oxygen, and other organic peroxides (45). Hydrogen peroxide (H_2O_2) and its anions are powerful nucleophiles and react with reagents RX to form ROOH and HX , where X can be sulfate, acid sulfate, alkane- and arenesulfonate, chloride, bromide, hydroxyl, alkoxide, perchlorate, etc. RX can also be an alkyl orthoformate or *tert*-alkyl carboxylate.

Electron-rich olefins react with hydrogen peroxide under acidic conditions to form hydroperoxides, presumably by means of a carbonium ion intermediate, eg, *tert*-butyl hydroperoxide from isobutylene. *tert*-Butyl hydroperoxide has been produced commercially by mixing either *tert*-butyl alcohol or isobutylene with sulfuric acid followed by reaction with hydrogen peroxide. It also can be prepared by adding *tert*-butyl alcohol to peroxysulfuric acid [7722-86-3], but this method can be dangerous because an explosive composition is formed during addition (54). Other hydroperoxides produced commercially from hydrogen peroxide are *tert*-amyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, 3-hydroxy-1,1-dimethylbutyl hydroperoxide, 2,5-dimethyl-2,5-dihydroperoxy-3-hexyne, and 2,5-dimethyl-2,5-dihydroperoxyhexane.

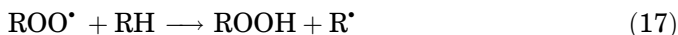
In the preparation of hydroperoxides from hydrogen peroxide, dialkyl peroxides usually form as by-products from the alkylation of the hydroperoxide in the reaction mixture. The reactivity of the substrate (olefin or RX) with hydrogen peroxide is the principal restriction in the process. If elevated temperatures or strongly acidic or strongly basic conditions are required, extensive decomposition of the hydrogen peroxide and the hydroperoxide can occur.

Organomineral hydroperoxides have been prepared from hydrogen peroxide and organomineral halides, hydroxides, oxides, peroxides, and amines (10,33). If HX is an acid, ammonia is used to prevent acidic decomposition.



Many hydroperoxides have been prepared by autoxidation of suitable substrates with molecular oxygen (45,52,55). These reactions can be free-radical chain or nonchain processes, depending on whether triplet or singlet oxygen is

involved. The free-radical process consists of three stages: initiation, propagation, and termination. The reaction can be initiated by free-radical initiators, eg, peroxides, aliphatic azo compounds, multivalent metal ions, uv radiation, etc (see INITIATORS). However, with many organic substrates, this is not required because oxygen serves as an initiator, probably by means of hydrogen abstraction at elevated temperatures: $\text{RH} + \text{O}_2 \longrightarrow \text{R}^\bullet + \text{HOO}^\bullet$. Such autoxidations usually are characterized by induction periods. In the propagation reactions (eqs. **16** and **17**), the rate of cleavage of the carbon–hydrogen bonds is ca 10^6 – 10^8 times slower than the reaction of propagating radical, R^\bullet , with oxygen.

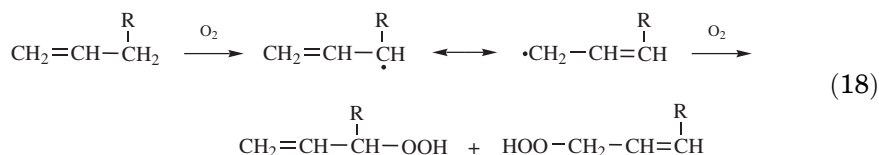


Therefore, steric factors and carbon–hydrogen bond energies significantly affect the autoxidation rate. The point of autoxidative hydrogen abstraction generally is that which forms the most stable alkyl radical. For example, a hydrogen on a tertiary carbon atom is abstracted more readily than a hydrogen on a primary carbon atom since the carbon–hydrogen BDEs are 381 and 406 kJ/mol (91 and 97 kcal/mol), respectively. The type and extent of termination reactions are influenced by substrate structure, oxygen pressure, and the presence of foreign substances, especially those with antioxidant properties.

Autoxidations are usually carried out neat (with substrate as solvent), in a nonoxidizable solvent, or in an aqueous emulsion of the substrate. Because very high conversions generally are not obtained or desired, the hydroperoxide is removed from the oxidation stream by extraction with aqueous alkali.

Other compounds, eg, azoalkanes, acetone, etc, that yield alkyl radicals either thermally or by uv irradiation have been used with molecular oxygen to prepare alkyl hydroperoxides (r56).

In the autoxidation of alkenes, different hydroperoxides are formed, depending on whether ground-state triplet oxygen or singlet oxygen is the oxidizing species. In the triplet state, oxygen abstracts an allylic hydrogen atom and the resulting allylic radical reacts with oxygen to form an allylic peroxy radical, which in turn propagates the oxidation chain by abstracting an allylic hydrogen atom from another olefin molecule (45) (eq. **18**).

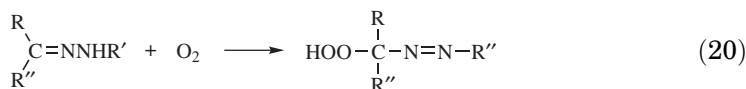


Singlet oxygen reacts with olefins presumably by the “ene” reaction to form allylic hydroperoxides (45,57), eg, 1-methyl-2-propenyl hydroperoxide [20733-08-8] is produced from 2-butene (eq. **19**). The regioselectivity of this reaction has

been investigated (58).



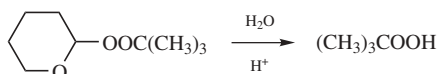
Hydroperoxides have been obtained from the autoxidation of alkanes, aralkanes, alkenes, ketones, enols, hydrazones, aromatic amines, amides, ethers, acetals, alcohols, and organomineral compounds, eg, Grignard reagents (10,45). In autoxidations involving hydrazones, double-bond migration occurs with the formation of hydroperoxy-azo compounds via free-radical chain processes (10,59) (eq. 20).



Commercially, autoxidation is used in the production of α -cumyl hydroperoxide, *tert*-butyl hydroperoxide, *p*-diisopropylbenzene monohydroperoxide, *p*-diisopropylbenzene dihydroperoxide, *p*-menthane hydroperoxide, pinane hydroperoxide, and ethylbenzene hydroperoxide.

Many organic peroxides of metals have been hydrolyzed to alkyl hydroperoxides. The alkylperoxy derivatives of aluminum, antimony, arsenic, boron, cadmium, germanium, lead, magnesium, phosphorus, silicon, tin, and zinc yield alkyl hydroperoxides upon hydrolysis (10,33,60,61).

Saponification of *tert*-alkyl peroxyesters yields alkyl hydroperoxides and carboxylic acids or their alkali metal salts. α -Ether-substituted peroxides can be hydrolyzed to the unsubstituted alkyl hydroperoxides, eg, *tert*-butyl hydroperoxide from *tert*-butyl 2-oxacyclohexyl peroxide [28627-46-5] (62):

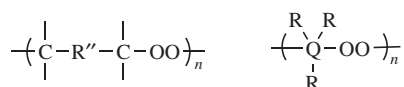


2.4. Other Hydroperoxides. Several hydrotrioxides including alkyl hydrotrioxides, $\text{R}-\text{OOOH}$, have been reported (63,64). There is strong spectroscopic evidence that α -cumyl hydrotrioxide [82951-48-2] is produced in the low temperature ozonization of cumene. Homolytic decomposition of α -cumyl hydrotrioxide in cumene/acetone- d_6 in the presence of a hindered phenol resulted in cumyl alcohol as the only organic product (65). Based on the activation parameters obtained, α -cumyl hydrotrioxide has a 10-h HLT of -26°C and a one-minute half-life temperature of 12°C , therefore α -cumyl hydrotrioxide and other alkyl hydrotrioxides, unlike alkyl hydroperoxides, are very unstable peroxides.

Little is known about the existence of alkyl hydrotetraoxides, $\text{R}-\text{OOOOH}$. There is some kinetic evidence supporting methyl hydrotetraoxide [23594-84-5] as a very labile intermediate in the reaction of methylperoxy radical, ${}_3\text{-OO}^\bullet$, and hydroperoxy radical, $^\bullet\text{OOH}$ (63).

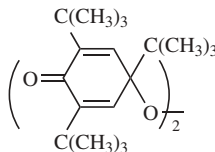
3. Dialkyl Peroxides

Dialkyl peroxides have the structural formula $R-OO-R'$, where R and R' are the same or different primary, secondary, or tertiary alkyl, cycloalkyl, and aralkyl hydrocarbon or hetero-substituted hydrocarbon radicals. Organomineral peroxides have the formulas $R_mQ(OOR)_n$ and R_mQOOQR_m , where at least one of the peroxygens is bonded directly to the organo-substituted metal or metalloid, Q . Dialkyl peroxides include cyclic and bicyclic peroxides where the R and R' groups are linked, eg, endoperoxides and derivatives of 1,2-dioxane. Also included are polymeric peroxides, which usually are called poly(alkylene peroxides) or alkylene-oxygen copolymers, and poly(organomineral peroxides) (44), where $Q = As$ or Sb .



Symmetrical dialkyl peroxides are commonly named as such, eg, dimethyl peroxide. For unsymmetrical dialkyl peroxides, the two radicals usually are listed in alphabetical order, eg, ethyl methyl peroxide. For organomineral peroxides or complex structures, ie, where R and R' are difficult to name as radicals, the peroxide is named as an alkylodioxy derivative, although alkylperoxy is still used by many authors. Cyclic peroxides are normally named as heterocyclic compounds, eg, 1,2-dioxane, or by substitutive oxa nomenclature, eg, 1,2-dioxacyclohexane; however, when the two oxygens form a bridge between two carbon atoms of a ring, the terms epidioxy or epiperoxy are frequently used. The resulting polycyclic structure has been called an endoperoxide, epiperoxide, or transannular peroxide.

3.1. Physical Properties. The structures and the boiling and melting points of several dialkyl peroxides are listed in Table 2; a comprehensive list is given in the literature (66). The melting point of 4,4'-dioxybis[2,4,6-tris(*tert*-butyl)-2,5-cyclohexadien-1-one] [1975-14-0] is 148–149°C.



Infrared, uv, nmr spectra (66), and photoelectron spectra have been reviewed (67). Physical properties of silicon peroxides are summarized in Reference 43. Other physical properties, eg, dipole moments, dihedral angles, and heats of combustion are listed in Reference 68. The oxygen-oxygen bond strengths of various dialkyl peroxides have been reported (69).

Di-*tert*-alkyl peroxides are thermally stable organic peroxides, having 10-h HLTs of 110–135°C for acyclic peroxides and 10-h HLTs approaching 200°C for five- to six-membered cyclic peroxides, eg, 129°C for di-*tert*-butyl peroxide (in decane) (22), 200°C for 3,3,5,5-tetramethyl-1,2-dioxolane [22431-90-9] (in ben-

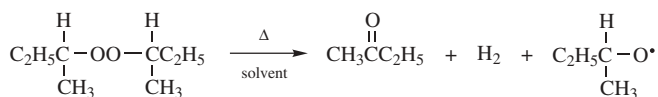
zene) (70), and 197°C for 3,3,6,6-tetramethyl-1,2-dioxane (in carbon tetrachloride) (71).

Metalloid peroxides behave as covalent organic compounds and most are insensitive to friction and impact but can decompose violently if heated rapidly. Most solid metalloid peroxides have well-defined melting points and the more stable liquid members can be distilled (Table 3). Some organomineral peroxides are unstable at ca 20°C, whereas others, eg, those of silicon, are among the most thermally stable organic peroxides known. The 10-h HLTs for *tert*-butylperoxytrimethylsilane, di(*tert*-butylperoxy)dimethylsilane [10196-44-8], and di(*tert*-butylperoxy)diphenylsilane [15188-08-6] are 180, 167, and 136°C, respectively (72).

3.2. Chemical Properties. Acyclic di-*tert*-alkyl peroxides efficiently generate alkoxy free radicals by thermal or photolytic homolysis.

Primary and secondary dialkyl peroxides undergo thermal decompositions more rapidly than expected owing to radical-induced decompositions (73). Such radical-induced peroxide decompositions result in inefficient generation of free radicals.

The low molecular weight primary dialkyl peroxides are shock-sensitive and explosive, with sensitivity decreasing with increasing molecular weight. Low molecular weight primary and secondary dialkyl peroxides should only be distilled at low temperatures and pressures. Primary and secondary dialkyl peroxides undergo thermal decompositions to concurrently generate hydrogen and carbonyl compounds via cyclic transition states, and alkoxy radicals via classical thermolysis (66,74). For example, di-*sec*-butyl peroxide [4715-28-0] yields ~30% 2-butanone and hydrogen and ~70% *sec*-butoxy radical.

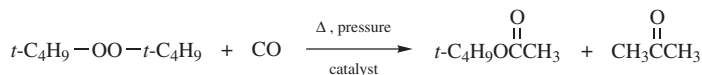


Decomposition products from primary and secondary dialkyl peroxides include aldehydes, ketones, alcohols, hydrogen, hydrocarbons, carbon monoxide, and carbon dioxide (44).

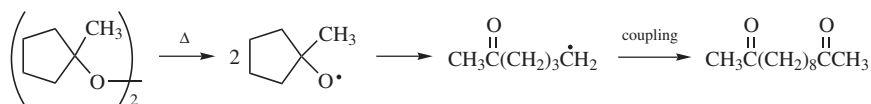
Because di-*tert*-alkyl peroxides are less susceptible to radical-induced decompositions, they are safer and more efficient radical generators than primary or secondary dialkyl peroxides. They are the preferred dialkyl peroxides for generating free radicals for commercial applications. Without reactive substrates present, di-*tert*-alkyl peroxides decompose to generate *tert*-alcohols, ketones, hydrocarbons, and minor amounts of ethers, epoxides, and carbon monoxide. Photolysis of di-*tert*-butyl peroxide generates *tert*-butoxy radicals at low temperatures (75), whereas thermolysis at high temperatures generates methyl radicals by β -scission (44).

Thermal or photo-induced decompositions of dialkyl peroxides in the presence of suitable substrates yield various products. For example, with nitric oxides, alkyl nitrites or nitrates are formed and, with carbon monoxide, *tert*-alkyl

esters are obtained (44):

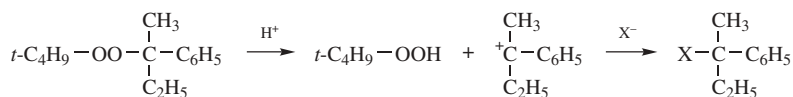


Thermal decompositions of di-*tert*-cycloalkyl peroxides produce *tert*-cycloalkoxy radicals which undergo ring β -scission to give acyclic ketones, diketones, and other products (44):

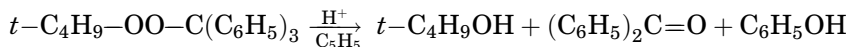


Dialkyl peroxides can be reduced to the corresponding alcohols and/or ethers using a variety of reducing agents, some of which, eg, hydriodic acid, have been used for analysis.

The susceptibility of dialkyl peroxides to acids and bases depends on peroxide structure and the type and strength of the acid or base. In dilute aqueous sulfuric acid (<50%) di-*tert*-butyl peroxide is resistant to reaction whereas in concentrated sulfuric acid this peroxide gradually forms polyisobutylene. In 50 wt% methanolic sulfuric acid, *tert*-butyl methyl ether is produced in high yield (66). In acidic environments, unsymmetrical acyclic alkyl aralkyl peroxides undergo carbon-oxygen fission, forming acyclic alkyl hydroperoxides and aralkyl carbonium ions. The latter react with nucleophiles, X⁻ (44,66):

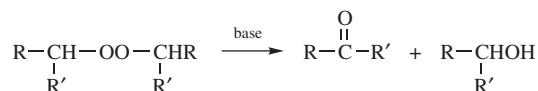


In media that destabilizes carbonium ions, eg, hydrocarbon solvents, Criegee-type rearrangements occur (66,69), eg, for *tert*-butyl trityl peroxide [7664-86-0]:



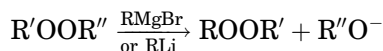
In Lewis acids, carbon-oxygen fission and Criegee-type rearrangements occur. For example, di-*tert*-butyl peroxide undergoes carbon-oxygen fission with BF₃ and Criegee-type rearrangement with AlCl₃ (66).

In the presence of base, di-*tert*-alkyl peroxides are stable, however primary and secondary dialkyl peroxides undergo oxygen-oxygen bond cleavage, forming alcohols, aldehydes, and ketones (44,66):



Dialkyl peroxides also undergo nucleophilic displacements by organometallic

compounds:

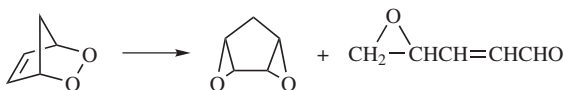


Primary and secondary dialkyl peroxides react much more readily than di-*tert*-alkyl peroxides (66,76). Products derived from the free radical are also produced in these reactions.

Substitution reactions on dialkyl peroxides without concurrent peroxide cleavage have been reported, eg, the nitration of dicumyl peroxide (44), and the chlorination of di-*tert*-butyl peroxide (77). Bromination by nucleophilic displacement on α -chloro- or α -hydroxyalkyl peroxides with hydrogen bromide produces α -bromoalkyl peroxides (78).

The polymeric peroxides, $-(\text{OOCH}_2\text{CXH})_n-$, where $\text{X} = \text{H}, \text{C}_6\text{H}_5, \text{CH}=\text{CH}_2$, etc, are viscous liquids or amorphous solids having as many as 10 repeating units. These compounds usually explode when heated. The products obtained from the thermal or photodecomposition show that cleavage of both oxygen-oxygen and carbon-carbon bonds occurs. The type and amounts of products formed depend on the decomposition conditions and the structure of the peroxide. When $\text{X} = \text{phenyl}$, benzaldehyde and formaldehyde are the principal thermal decomposition products (79). Acids and bases also decompose polymeric peroxides. Oxygen-oxygen bond cleavage occurs under basic conditions, but the initially formed carbonyl compounds also are base-sensitive and are converted to other products. Reduction of polymeric peroxides, which proceeds more readily than that of dialkyl peroxides, has been carried out with a variety of reducing agents, eg, lithium aluminum hydride (44).

Unsaturated aliphatic endoperoxides form bis(epoxides) and/or epoxy aldehydes upon thermolysis (80,81). Thus 3,5-epidioxycyclopentene [6573-26-8] reacts as follows.

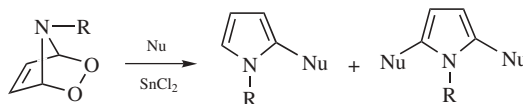


With certain transition metals, eg, Ru(II)-tertiary phosphine complexes, the principal products are bis(epoxides) (82).

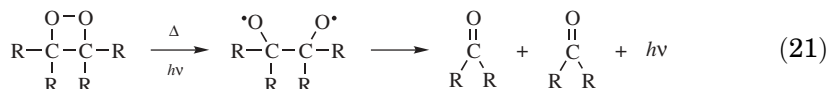
The endoperoxides of polynuclear aromatic compounds are crystalline solids that extrude singlet oxygen when heated, thus forming the parent aromatic hydrocarbon (44,66,80,81). Thus 9,10-diphenyl-9,10-epidioxyanthrancene [15257-17-7] yields singlet oxygen and 9,10-diphenylanthracene.

Endoperoxides undergo carbon-oxygen cleavage in acids and oxygen-oxygen bond cleavage in bases, and they are more easily reduced than dialkyl peroxides. Reduction products depend on the structure and reducing agent. Aliphatic endoperoxides have been reduced, with and without involvement of an adjacent double bond that is present in most aliphatic endoperoxides, to glycols, epoxides, and hydrocarbons (44). Endoperoxides undergo hydrolysis or methanolysis to hydroperoxides (81). In the presence of stannous chloride, endoperoxides of N-substituted 1,2-dihydropyridines and N-substituted pyrroles react with

carbon-centered nucleophiles (Nu) to give substituted products (81,83,84):



1,2-Dioxetanes have very low activation enthalpies (ca 109 kJ/mol), therefore, they are unstable at low temperatures and generally cleave thermally or photochemically at the oxygen–oxygen and carbon–carbon bonds. There is evidence that this fragmentation occurs through a labile 1,4-dioxy–diradical intermediate. Upon further fragmentation, chemiluminescence occurs and two carbonyl compounds are produced in the absence of trapping agents (66,80,85) (see LUMINESCENT MATERIALS, CHEMILUMINESCENCE). In equation 21, the **R** groups can be identical or dissimilar.



Based on reported activation parameters, tetramethyl-1,2-dioxetane [35856-82-7], where $\text{R} = \text{CH}_3$, has a 10-h HLT of about 15°C (85).

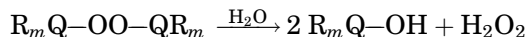
1,2-Dioxetanes are reduced to diols, epoxides, or allylic alcohols; the dioxetane structure and the reducing system determine which product forms or predominates (80). Although alkyl and aryl dioxetanes generally are inert to nucleophilic attack at the carbons, reactions with azides and caustic soda and rearrangements with Lewis acids have been reported (80). A variety of reactions involving 1,2-dioxetanes and heteroatoms have been observed, eg, rearrangements to α -hydroxyketones, nucleophilic additions, and rearrangements of 3,4-unsaturated-1,2-dioxetanes, ie, 1,2-dioxetenes (80). Reaction of 1,2-dioxetanes with diazoalkanes produces 1,3-dioxolanes and carbonyl compounds (86).

Dioxiranes are three-membered cyclic ring peroxides that are expected to



be very unstable owing to ring strain. Dimethyldioxirane [74087-85-7] where R^1 and $\text{R}^2 = 2 \text{CH}_3$ has a 10-h HLT of about 44°C in acetone (87). Dioxiranes are effective oxygenating agents for epoxidations of olefins, allenes, polycyclic aromatic hydrocarbons, enols, and α,β -unsaturated ketones; for insertions of oxygen into X-H bonds of alkanes, primary and secondary alcohols, aldehydes, and silanes; and for oxidations of sulfides (to sulfoxides and sulfones), imines (to nitrones), and primary amines (to nitro compounds) (88–91). In these reactions, the dioxirane transfers oxygen to the substrate and generates the ketone from which the dioxirane was derived. Because of the weak oxygen–oxygen bond in dioxiranes, the mechanisms of these oxygen-transfer reactions are expected to have some diradical character. The autodecomposition of dimethyldioxirane reportedly involves radical intermediates such as methyl radical (92).

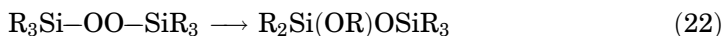
Most organomineral peroxides are hydrolytically unstable and readily hydrolyze to alkyl hydroperoxides or hydrogen peroxide (33,34,44,60,61):



Consequently, most organomineral peroxides must be prepared and stored under anhydrous conditions. In addition, anhydrous hydrogen chloride converts alkyl-substituted organomineral peroxides to alkyl hydroperoxides (33).

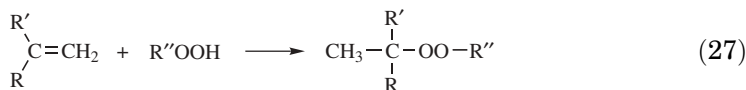
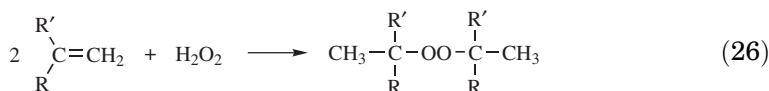
Basic hydrolysis of secondary alkyl-substituted silicon and germanium peroxides results in oxygen-oxygen bond cleavage.

The reduction of alkyl-substituted silicon and tin peroxides with sodium sulfite and triphenylphosphine has been reported (33,93). Alkyl-substituted aluminum, boron, cadmium, germanium, silicon, and tin peroxides undergo oxygen-to-metal rearrangements (33,43,94), eg, equations **22** and **23**.



Organomineral peroxides also undergo thermal and photo-induced homolysis, yielding free radicals that are effective for initiating polymerization of vinyl monomers (44). Baeyer-Villiger oxidations of ketones to esters have been carried out using bis(trialkylsilyl)peroxides (95). Silane peroxides react with carbanions to generate products derived from attack either on silicon or on the oxygen-oxygen bond (96).

3.3. Synthesis. Dialkyl peroxides are prepared by the reaction of various substrates with hydrogen peroxide, hydroperoxides, or oxygen (69). They also have been obtained from reactions with other organic peroxides. For example, dialkyl peroxides have been prepared by the reaction of hydrogen peroxide and alkyl hydroperoxides with alkylating agents, eg, RX and olefins (33,66,97) (eqs. **24-27**).

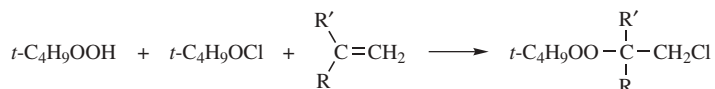


Reaction conditions depend on the reactants and usually involve acid or base catalysis. Examples of X include sulfate, acid sulfate, alkane- or arenesulfonate, chloride, bromide, hydroxyl, alkoxide, perchlorate, etc. RX can also be an alkyl orthoformate or *tert*-alkyl carboxylate. The reaction of cyclic alkylating

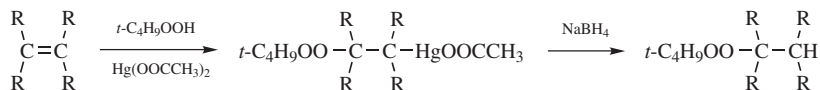
agents, eg, epoxides and aziridines, with sodium or potassium salts of alkyl hydroperoxides also promotes formation of dialkyl peroxides (44,66). Olefinic alkylating agents include acyclic and cyclic olefinic hydrocarbons, vinyl and isopropenyl ethers, enamines, *N*-vinylamides, vinyl sulfonates, divinyl sulfone, and α , β -unsaturated compounds, eg, methyl acrylate, mesityl oxide, acrylamide, and acrylonitrile (44,66).

The following commercially available dialkyl peroxides are produced according to equations 24–27: di-*tert*-butyl peroxide from hydrogen peroxide and sulfated *tert*-butyl alcohol or isobutylene; dicumyl peroxide from α -cumyl hydroperoxide and cumyl alcohol, cumyl chloride, and/or α -methylstyrene; *m*- and *p*-di(2-*tert*-butylperoxyisopropyl)benzene [2781-00-2] from *tert*-butyl hydroperoxide [75-91-2] and *m*- and *p*-di(2-hydroxyisopropyl)benzene; 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane; and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-3-hexyne from sulfated *tert*-butyl alcohol and 2,5-dimethyl-2,5-dihydroperoxyhexane and 2,5-dimethyl-2,5-dihydroperoxy-3-hexyne, respectively (97–99).

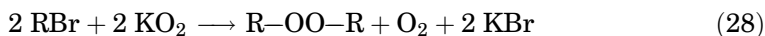
Olefins react with *tert*-butyl hydroperoxide in the presence of *tert*-butyl hypochlorite, forming *tert*-butyl β -chloroalkyl peroxides (66):



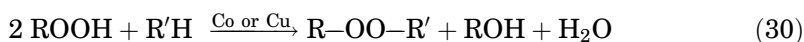
With mercuric acetate ($\text{Hg}(\text{OOCCH}_3)_2$), olefins and *tert*-butyl hydroperoxide form organomercury-containing peroxides (66,100). The organomercury compound can be treated with bromine or a mild reducing agent, such as sodium borohydride, to remove the mercury.



Primary and secondary alkyl halides and sulfonates react with potassium superoxide to form dialkyl peroxides (101,102) (eq. 28). Diazoalkanes, eg, diazomethane, have been used to alkylate hydroperoxides (66) (eq. 29).

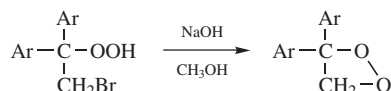


Unsymmetrical dialkyl peroxides are obtained by the reaction of alkyl hydroperoxides with a substrate, ie, $\text{R}'\text{H}$, from which a hydrogen can be abstracted readily in the presence of certain cobalt, copper, or manganese salts (eq. 30). However, this process is not efficient since two moles of the hydroperoxide are consumed per mole of dialkyl peroxide produced. In addition, side reactions involving free radicals produce undesired by-products (44,66).

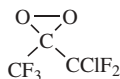


Symmetrical dialkyl peroxides have been prepared from alkyl hydroperoxides and lead tetraacetate. If tertiary dihydroperoxides are used, then cyclic peroxides are obtained in high yields (44,66). Di-*tert*-butyl peroxide is obtained from the mild decomposition of di-*tert*-butyl diperoxyoxalate [1876-22-8] (44). Trifluoromethyl peroxide [927-84-4], CF_3OOCF_3 , is obtained from the photolysis of fluoroformyl peroxide and from the reaction of CF_3OF with COF_2 (66).

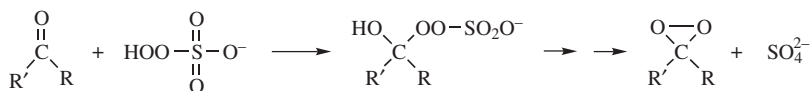
Olefins that are sufficiently electron-donating react with singlet oxygen by 1,2-addition to form 1,2-dioxetanes (80). Such electron-donating olefins are nitrogen heterocycles, *cis*- and *trans*-diethoxyethylene, tetramethoxyethylene, *p*-dioxene, 1,3-dioxole, and 2-methoxynorbornenes (66,85,93,103). 1,2-Dioxetanes are also obtained by the base-catalyzed rearrangement of 4-bromo-3-hydroxy-1,2-dioxolane derivatives and the ring closure of 1-bromo-2-hydroperoxyethane derivatives with methanolic caustic (Kopecky method) (85,104):



Two unstable and explosive dioxiranes, hexafluorodimethyldioxirane [35357-46-1] and chloropentafluorodimethyldioxirane [35357-48-3] have been synthesized (105).

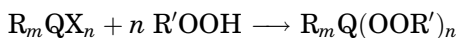
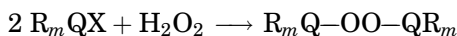


In the late 1970s, evidence showed that dialkyl dioxiranes were generated in ketone-carbate, $2\text{KHSO}_5\text{:KHSO}_4\text{:K}_2\text{SO}_4$, systems (106) and the mechanism of the reaction was determined (88,90):



In the mid-1980s a convenient and relatively safe procedure was developed for vacuum codistillation of dimethyldioxirane and acetone from acetone-carbate systems (107). The resulting acetone solution of dimethyldioxirane could be used in subsequent oxygenation reactions (92).

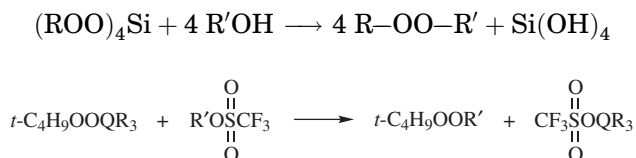
Organomineral peroxides can be prepared by the reaction of certain organometallic or organometalloid compounds, R_mQX_n , with hydrogen peroxide or alkyl hydroperoxides:



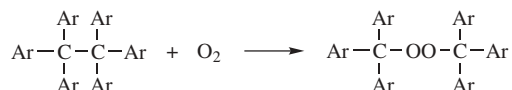
Organometallics and organometalloids that yield peroxides in this manner include those in which Q is aluminum, antimony, arsenic, boron, cadmium, germanium, lead, phosphorus, silicon, and tin and in which X is chlorine, bromine,

alkoxy, acetoxy, cyano, oxide, hydride, hydroxyl, amino, alkyl, and boron tetrafluoride (28,33,44,60) (see Table 3).

Dialkyl peroxides may be prepared by reaction of alcohols or alkyl trifluoromethanesulfonates with organomineral peroxides of silicon, tin, and germanium (44,108), where Q = Sn and Ge:



Diaralkyl peroxides have been prepared by autoxidation. Those compounds which autoxidize to symmetrical diaralkyl peroxides form highly stabilized radical intermediates, eg, triphenylmethane, 9-phenylanthrone, and 2,4,6-tri(*t*-butyl)phenol (44,66). Compounds that form stable radicals by cleavage of carbon-carbon bonds can be autoxidized to diaralkyl peroxides (69).



Starting compounds include hexa- and pentarylethanes; the latter require higher temperatures (ca 100°C) than the former to break the carbon-carbon bond. In the presence of oxygen, stable radicals that are generated by other methods, eg, reduction of arylmethyl ethers and halides, also have been converted to diaralkyl peroxides (66).

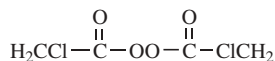
Autoxidation of alkanes generally promotes the formation of alkyl hydroperoxides, but di-*tert*-butyl peroxide has been obtained in >30% yield by the bromine-catalyzed oxidation of isobutane (66). In the presence of iodine, styrene also has been oxidized to the corresponding peroxide (44).

Olefins that polymerize readily in the presence of free radicals form peroxypolymers with oxygen: $\text{CH}_2=\text{CHX} + \text{O}_2 \longrightarrow \text{-(OOCH}_2\text{CHX)-}_n$. Such copolymers of oxygen have been prepared from styrene, α -methylstyrene, indene, ketenes, butadiene, isoprene, 1,1-diphenylethylene, methyl methacrylate, methyl acrylate, acrylonitrile, and vinyl chloride (44, 66, 109). 1,3-Dienes, such as butadiene, yield randomly distributed 1,2- and 1,4-copolymers. Oxygen pressure and olefin structure are important factors in these reactions; for example, other products, eg, carbonyl compounds, epoxides, etc, can form at low oxygen pressures. Polymers possessing dialkyl peroxide moieties in the polymer backbone have also been prepared by base-catalyzed condensations of di(hydroxy-*tert*-alkyl) peroxides with dibasic acid chlorides or bis(chloroformates) (110).

Singlet oxygen adds 1,4- to 1,3-dienes, 1,3-endocyclic dienes, and polynuclear aromatics, forming cyclic peroxides (81). Compounds that yield these peroxides are rubrene, anthracene, substituted anthracenes, nitrogen heterocycles, ergosterol, α -terpinene, cyclopentadiene, 1,3-cycloheptadienes, *N*-phenyllophine, butadiene, and prostaglandin analogues (66,103,111-113).

Unsaturated transannular peroxides from cyclic dienes have been selectively reduced to the saturated peroxide analogues (114). For example, 1,3-cyclohexadiene is converted to 3,6-epidioxycyclohexene [6671-70-1] by singlet oxygen; then reduction leads to 1,4-epidioxycyclohexane [280-53-5].

Organomineral peroxides of antimony, arsenic, boron, magnesium, tin, cadmium, lead, silicon, and zinc have been prepared by autoxidation and some are listed in Table 3 (33,44,60,93,115). For example, dimethyl cadmium reacts with oxygen to form methylperoxy methyl cadmium [69331-62-0] and bis(methylperoxy) cadmium.



Thermally unstable cyclic trioxides, 1,2,3-trioxolanes or primary ozonides are prepared by reaction of olefins with ozone (64) (see OZONE). Dialkyl trioxides, ROOOR, have been obtained by coupling of alkoxy radicals, RO $\dot{\text{O}}$, with alkylperoxy radicals, RO $\dot{\text{O}}$, at low temperatures. Dialkyl trioxides are unstable above -30°C (63). Dialkyl tetraoxides, ROOOOR, have been similarly produced by coupling of two alkylperoxy radicals, RO $\dot{\text{O}}$, at low temperatures. Dialkyl tetraoxides are unstable above -80°C (63).

4. α -Oxygen-Substituted Hydroperoxides and Dialkyl Peroxides

Dialkyl peroxides and hydroperoxides which have either a hydroxy, hydroperoxy, alkoxy, or alkylperoxy group on the carbon adjacent to the parent peroxide group are considered separately from the parent compounds due to their unique reactions and properties, but mainly because of their unique syntheses. Many of these compounds can be prepared by methods previously discussed for hydroperoxides and dialkyl peroxides, eg, autoxidation. However their primary preparation from aldehydes and ketones via reaction with hydrogen peroxide, alkyl hydroperoxides and peroxyacids is unique and makes it almost impossible to discuss them without referring to the parent carbonyl compound(s). These peroxides are often in equilibrium with other α -oxygen-substituted peroxides; they may be generated and used as chemical intermediates without being isolated (isolation may be either dangerous, impossible, or both). Unfortunately this means that the existence of some members of this group is speculative, based on products obtained from reactions of the peroxides rather than on isolation of the peroxides themselves.

The α -oxygen-substituted hydroperoxides and dialkyl peroxides comprise a great variety as shown in Figure 1. When discussing peroxides derived from ketones and hydrogen peroxide, (1) is often referred to as a ketone peroxide monomer and (2) as a ketone peroxide dimer.

4.1. Syntheses, Physical and Chemical Properties. An example of the complex equilibrium that exists for mixtures of carbonyl compounds and hydrogen peroxide is that from aldehydes and hydrogen peroxide. Hydroxyalkyl hydroperoxides (1, X = OH, R³ = H) and di(hydroxyalkyl) peroxides (2, X = Y =

OH) are formed; cyclic diperoxides (4) are formed in some cases, eg, from benzaldehyde with concentrated sulfuric acid (116). Hydroxyalkyl hydroperoxides are the principal products when equimolar amounts of aldehyde and hydrogen peroxide are used at low temperatures. Di(hydroxyalkyl) peroxides are obtained by using excess aldehyde or higher temperatures. These reactions occur without catalysts but occur at much faster rates in the presence of acids. The peroxides (1) and (2) from most straight-chain aldehydes, ie, C_1 – C_{11} , have been characterized, and a few of these and some from other aldehydes are listed in Table 4 (4–6, 10, 44).

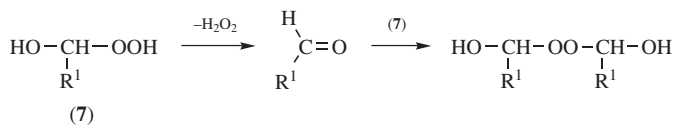
Starting with ketones and hydrogen peroxide in the presence of a catalytic amount of acid, mixtures of up to eight components have been identified, ie, (1, $X = OH$, $R^3 = H$), (1, $X = OOH$, $R^3 = H$), (2, $X = Y = OH$), (2, $X = Y = OOH$), (2, $Y = OH$, $Y = OOH$), (3), (4), and (5). The ketone structure and reaction conditions, ie, acid strength, reactant molar ratios, temperature, and time, determine which compounds form and predominate. Mixtures of several peroxide structures usually are present (4–6, 10, 44, 117–121). Individual peroxides have been isolated from several ketones under different conditions (Table 5). The pure peroxides should be handled with extreme caution since most, especially those derived from the low molecular weight ketones, are shock- and friction-sensitive and can explode violently. Methyl ethyl ketone peroxide [1338-23-4] (MEKP) mixtures are produced commercially only as solutions containing <40 wt% MEKPs in solvents, commonly dialkyl phthalates.

Hydroxyalkyl Hydroperoxides. These compounds, represented by (1, $X = OH$, $R^3 = H$), may be isolated as discreet compounds only with certain structural restrictions, eg, that one or both of R^1 and R^2 are hydrogen, ie, they are derived from aldehydes, or that R^1 or R^2 contain electron-withdrawing substituents, ie, they are derived from ketones bearing α -halogen substituents. Other hydroxyalkyl hydroperoxides may exist in equilibrium mixtures of ketone and hydrogen peroxide.

Hydroxyalkyl hydroperoxides which have been isolated are moderately stable and many are unaffected by distillation. However, the low molecular weight members, eg, hydroxymethyl hydroperoxide (1, $X = OH$, $R^1 = R^2 = R^3 = H$), can decompose violently. 1,1,1,3,3,3-Hexafluoro-2-hydroxy-2-propyl hydroperoxide [32751-01-2] (1), where $X = OH$, $R^3 = H$, and $R^1 = R^2 = CF_3$, is a viscous liquid that decomposes slowly at 25°C (123). The melting points of some hydroxyalkyl hydroperoxides are listed in Tables 4 and 5. Thermal decomposition yields mixtures of carbonyl compounds, carboxylic acids, and alcohols. These hydroxyhydroperoxides have been reduced to the corresponding carbonyl compounds or alcohols with a variety of reducing agents including hydriodic acid, phosphines, zinc and acetic acid, and by catalytic hydrogenation. Upon reaction with lead tetraacetate, hydroxyalkyl hydroperoxides, like other hydroperoxides, liberate oxygen.

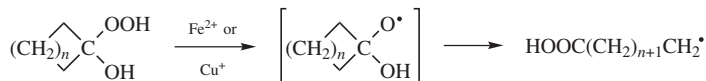
Hydroxyalkyl hydroperoxides from cyclic ketones (1), where $X = OH$, $R^3 =$, H and R^1 , R^2 = alkylene, apparently exist in solution as equilibrium mixtures of the cyclic ketone, hydrogen peroxide, and other peroxides, eg, the dihydroperoxide (1) in which $X = OOH$, and dialkyl peroxides (2) where $X = OH$ and $Y = OH$ or OOH . Due to the existence of this equilibrium, the latter two dialkyl peroxides react as mixtures of monomeric hydroperoxides in solution.

Hydroxyalkyl hydroperoxides having at least one α -hydrogen ie, (7, X = OH, R = alkyl, $R^2 = R^3 = H$), ie, those derived from aldehydes, lose hydrogen peroxide and form dialkyl peroxides (2, X = Y = OH), especially in the presence of water:



Acidic hydrolysis of these hydroxyalkyl hydroperoxides yields carboxylic acids, whereas basic hydrolysis regenerates the parent aldehyde, hydrogen peroxide, and often other products. When derived from either aldehydes or cyclic ketones, peroxides (1, X = OH, $R^3 = H$, $R^1, R^2 = \text{alkylene}$ or $R^1 = \text{alkyl}$, $R^2 = H$) can be condensed, using acid, dehydrating agents (eg, phosphorus pentoxide), or vacuum to form polymeric peroxides (3). Most such polymeric peroxides decompose explosively.

As with other hydroperoxides, hydroxyalkyl hydroperoxides are decomposed by transition-metal ions in an electron-transfer process. This is true even for those hydroxyalkyl hydroperoxides that only exist in equilibrium. For example, those hydroperoxides from cyclic ketones ($R^1, R^2 = \text{alkylene}$) form an oxygen-centered radical initially which then undergoes ring-opening β -scission forming an intermediate carboxyalkyl radical (124):



Without other alternatives, the carboxyalkyl radicals couple to form dibasic acids; $\text{HOOC}(\text{CH}_2)_{2n+4} \text{COOH}$. In addition, the carboxyalkyl radical can be used for other desired radical reactions, eg, hydrogen abstraction, vinyl monomer polymerization, addition of carbon monoxide, etc. The reactions of this radical with chloride and cyanide ions are used to produce amino acids and lactams employed in the manufacture of polyamides, eg, nylon.

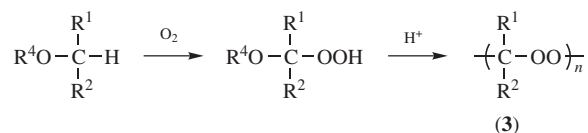
Secondary alcohols, such as isopropyl alcohol, *sec*-butyl alcohol, 2-pentanol, 3-pentanol, cyclopentanol, and cyclohexanol, have been autoxidized to hydroxyalkyl hydroperoxides (1, X = OH; $R^3 = H$) (10,44). These autoxidations usually are carried out at ca 20°C with uv radiation in the presence of a photosensitizer, eg, benzophenone. α -Oxygen-substituted dialkyl peroxides (2, X = Y = OH and X = Y = OOH), also are formed and sometimes they are the exclusive products (10).

Alkoxyalkyl Hydroperoxides. These compounds (1, X = OR⁴, $R^3 = H$) have been prepared by the ozonization of certain unsaturated compounds in alcohol solvents (10,125,126). 2-Methoxy-2-hydroperoxypropane [10027-74-4] (1, X = OR⁴, R⁴ = methyl), has been generated in methanol solution and spectral data obtained (127). A rapid exothermic decomposition upon concentration of this peroxide in a methylene chloride-methanol solution at 0°C has been reported (128). 2-Bromo-1-methoxy-1-methylethyl hydroperoxide [98821-14-8] has been distilled

(bp 60°C (bath temp.), 0.013 kPa) (129). Two cyclic alkoxyalkyl hydroperoxides from cyclodecanone have been reported (**1**, where X = OR⁴; R¹, R² = 5-oxo-1,9-nonanediy) with mp 94–95°C (R⁴ = methyl) and mp 66–68°C (R⁴ = ethyl) (130). Like other hydroperoxides, alkoxyalkyl hydroperoxides can be acylated or alkylated (130,131).

α -Trialkylsiloxyhydroperoxides (**1**, X = OSiR₃, R³ = H) have been prepared by the reaction of appropriate silyl enol ethers with hydrogen peroxide in the presence of acid (132).

Alkoxyalkyl hydroperoxides are more commonly called ether hydroperoxides. They form readily by the autoxidation of most ethers containing α -hydrogens, eg, dioxane, tetrahydrofuran, diethyl ether, diisopropyl ether, di-*n*-butyl ether, and diisooamyl ether (10, 44). From certain ethers, eg, diethyl ether (in the following, R¹ = H; R² = CH₃; R⁴ = CH₂CH₃), the initially formed ether hydroperoxide can yield alcohol on standing, or with acid treatment form dangerously shock-sensitive and explosive polymeric peroxides (**3**).

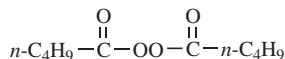


Low molecular weight ether hydroperoxides are similarly dangerous and therefore ethers should be tested for peroxides and any peroxidic products removed from them before ethers are distilled or evaporated to dryness. Many ethers autoxidize so readily that peroxidic compounds form at dangerous levels when stored in containers that are not airtight (133). Used ether containers should be handled cautiously and if they are found to contain hazardous solid ether peroxides, bomb-squad assisted disposal may be required (134). Zeolites have been used for removal of peroxide impurities from ethers (135).

Hydroxyalkyl Alkyl Peroxides and Hydroxyalkyl Peroxyesters. The same structural restrictions discussed for the hydroxyhydroperoxides apply for the hydroxyalkyl alkyl peroxides, and those that exist are derived from aldehydes and certain ketones having electron-withdrawing groups, eg, polyfluorinated α,β -unsaturated ketones (136).

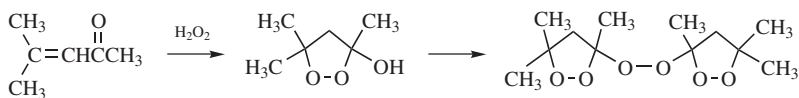
Hydroxyalkyl alkyl peroxides (**1**, X = OH, R³ = alkyl) are reasonably stable and usually can be distilled under a vacuum; the boiling points and structures of representative compounds are listed in Table 6. Low molecular weight compounds, eg, hydroxymethyl methyl peroxide, are unstable and explosive. Reactions with hydriodic acid or titanium trichloride generally are not quantitative but reductions to carbonyl- and hydroxy-containing compounds have been reported (44). Hydrolysis of hydroxyalkyl alkyl peroxides with α -hydrogen (ie, those derived from aldehydes) usually generate a carbonyl compound and the corresponding alkyl hydroperoxide. In alkali, hydrolysis of hydroxymethyl alkyl peroxides liberates hydrogen, formic acid, formaldehyde, and alcohol from R³. Thermal decompositions of hydroxyalkyl alkyl peroxides appear to involve both homolytic and heterolytic processes. Ferrous salts can be used to generate free radicals (4,5,44).

Hydroxyalkyl peroxyesters (**1**, $X = OH$, $R^1, R^2 = \text{hydrogen, alkyl}$; $R^3 = \text{acyl}$) are proposed as intermediates in the Baeyer-Villiger oxidation of aldehydes and ketones to esters by peroxycarboxylic acids. Such a peroxyester has been isolated from the reaction of peroxyacetic acid and acetaldehyde (137):



Hydroxyalkyl peroxyesters also have been isolated from the autoxidation products of aldehydes and by esterification of hydroxyhydroperoxides (44).

Mesityl oxide and hydrogen peroxide react initially to form the cyclic hydroxyalkyl alkyl peroxide, a 1,2-dioxolane. Prolonged equilibration results in formation of the cyclic di(alkylperoxyalkyl) peroxide, 3,3'-dioxybis(3,5,5-trimethyl-1,2-dioxolane) [4507-98-6] (122,138):



In the presence of strong acid catalysts such as sulfuric acid, aliphatic ($R^1\text{CHO}$) aldehydes react with alkyl hydroperoxides, eg, *tert*-alkyl hydroperoxides, to form hydroxyalkyl alkyl peroxides (**1**), where $X = OH$; $R^1, R^2 = \text{hydrogen, alkyl}$; and $R^3 = \text{tert-alkyl}$.

Alkoxyalkyl Alkyl Peroxides. *tert*-Butyl tetrahydropyran-2-yl peroxide [28627-46-5] (**1**), where $R^3 = \text{tert-butyl}$, $X = \text{OR}^4$, $R^1 = \text{H}$, R^2 and $R^4 = 1,4\text{-butanediyl}$, has been isolated. This is one of many examples of alkoxyalkyl alkyl peroxides which may be prepared by reaction of hydroperoxides with vinyl ethers (139):

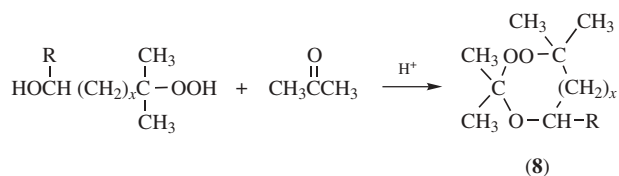


2-Methoxy-1-methylethyl alkyl peroxides (**1**, $X = \text{OR}^4$, $R^1 = R^2 = R^4 =$, methyl $R^3 = \text{decyl, undecyl, pentadecyl, 2-octyl}$) are liquids that have been isolated using flash chromatography (131). Peroxyester derivatives ($R^3 = \text{acyl}$) have also been prepared (131).

1,2,4-Trioxacycloalkanes. 1,2,4-Trioxanes (**1**, $X = \text{OR}_4$; R^3 and $R^4 = \text{alkylene}$) are generally prepared by the interaction of aldehydes with zwitterionic intermediates made from reaction of singlet oxygen with olefins. They can also be prepared by catalyzed reaction of ketones or aldehydes with 1,2-dioxetanes or endoperoxides, and they can be prepared directly from certain hydroperoxides. Their preparation, molecular structure, and reactivity have been reviewed (140). 1,2,4-Trioxan-5-ones ($R^3, R^4 = \text{oxoethylene}$) are prepared by reaction of ketones or aldehydes with trimethylsilyl α -trimethylsilylperoxycarboxylates (141).

1,2,4-Trioxacycloheptanes ($x = 1$) and 1,2,4-trioxacyclooctanes ($x = 2$) are synthesized by the reaction of suitable hydroxyhydroperoxides with aldehydes

and ketones in the presence of acid catalysts (17). Cyclic peroxides are significantly more stable than the analogous acyclic peroxides; eg, 3,3,5,7,7-pentamethyl-1,2,4-trioxacycloheptane (8), where $x = 1$ and $R = \text{CH}_3$, is characterized by a 10-h HLT of 173°C in benzene (142).

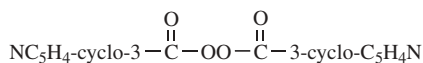


Geminal Dihydroperoxides. These dihydroperoxides (1, $X = \text{OOH}$, $R^3 = \text{H}$) can be made from many different carbonyl compounds. The structural restrictions discussed for hydroxyalkyl hydroperoxides generally do not apply. These peroxides can also be synthesized by perhydrolysis of ketals (143).

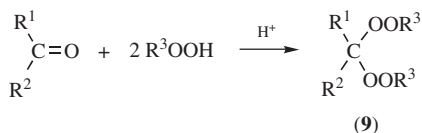
Low molecular weight dihydroperoxides (1, $X = \text{OOH}$; $R^3 = \text{H}$, R^1 and $R^2 = \text{short-chain alkyl}$) are soluble in water and are explosive when pure. They have been reduced to the corresponding ketones with hydriodic acid or zinc and acetic acid. Hydrolysis also gives the corresponding ketones. In the presence of catalytic amounts of acids or on prolonged storage, solutions of dihydroperoxides form equilibrium amounts of hydrogen peroxide and di(hydroperoxyalkyl) peroxides (2, $X = Y = \text{OOH}$) and ultimately equilibrium amounts of cyclic triperoxides (5). Oxygen evolution and formation of polymeric peroxides (3) also are observed from dihydroperoxides, especially in the presence of impurities, eg, trace transition metals, bases, etc. In the presence of sulfuric acid, dihydroperoxides can form cyclic diperoxides (4) via the first-formed cyclic triperoxide (5) (118). With cold formic acid, dihydroperoxides are converted to esters, apparently by a Baeyer-Villiger-like reaction (44). Dihydroperoxides have been characterized by esterification to solid diperoxyester derivatives (144) and by hydriodic acid titration.

Thermal decomposition of dihydroperoxides results in initial homolysis of an oxygen-oxygen bond followed by carbon-oxygen and carbon-carbon bond cleavages to yield mixtures of carbonyl compounds (ketones, aldehydes), esters, carboxylic acids, hydrocarbons, and hydrogen peroxide. Commercially available MEKP formulations are mixtures of the dihydroperoxide (1), where $X = \text{OOH}$; $R^3 = \text{H}$, $R^1 = \text{methyl}$, and $R^2 = \text{ethyl}$ (2,2-dihydroperoxybutane [2625-67-4]), and dialkyl peroxide (2), where $X = \text{OOH}$, $Y = \text{OOH}$, $R^1 = \text{methyl}$, and $R^2 = \text{ethyl}$ (di(2-hydroperoxy-2-butyl) peroxide [126-76-1]). These formulations are widely used as free-radical initiators in the metal-promoted cure of unsaturated polyester resins at about 20°C.

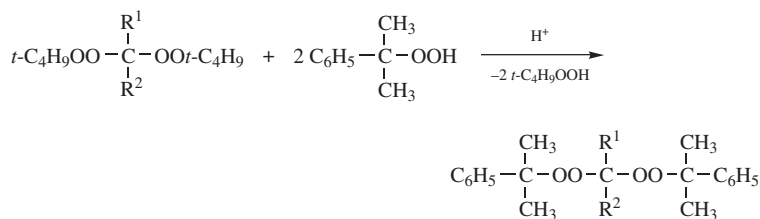
When derived from cyclic ketones, dihydroperoxides (1, $X = \text{OOH}$; $R^3 = \text{H}$, R^1 and $R^2 = \text{alkylene}$) react with vinyl monomers in the presence of Cr, V, or Ti salts to form difunctional compounds (145):



Diperoxyketals and Diperoxyacetals. Aromatic aldehydes react with alkyl hydroperoxides in the presence of strong acid catalysts such as sulfuric acid to form diperoxyacetals (**1**, $X = \text{OOR}^5$; $R^1 = \text{H}$, $R^2 = \text{Ar}$, $R^3 = R^5 = \text{alkyl}$). Diperoxyketals (**1**, $X = \text{OOR}^5$; $R^1, R^2, R^3, R^5 = \text{alkyl}$) are generally prepared by acid-catalyzed reaction of a ketone with two equivalents of an alkyl hydroperoxide. There are few structural limitations on the R^1 and R^2 groups. Aromatic ketones react with alkyl hydroperoxides only under extremely strong acid-dehydrating conditions to generate the diperoxyketal (**9**, $R^1 = \text{Ar}$, $R^2 = \text{Ar}$ or alkyl).



Diperoxyketals are solids or colorless liquids and are soluble in common organic solvents and insoluble in water. The physical properties and structures of some diperoxyketals are listed in Table 7. In the pure state, the low molecular weight compounds can decompose violently when heated, and addition of concentrated sulfuric acid can result in flaming decompositions. There are many commercial diperoxyketals, and they are usually diluted with solvents for improved safety. Diperoxyketals can be analyzed using hydriodic acid or stannous chloride even in the presence of less reactive dialkyl peroxides. Diperoxyketals have been reduced to alcohols with hydrogen and Raney nickel (44). Acid hydrolysis yields a ketone and alkyl hydroperoxide. Diperoxyketals undergo exchange reactions with hydroperoxides; such reactions are used to synthesize cumylperoxy derivatives (44):



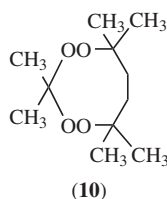
In the presence of strong acid catalysts many commonly used commercial *tert*-alkyl hydroperoxides decompose to acetone to some extent. Consequently, the diperoxyketals derived from other ketones and *tert*-alkyl hydroperoxides are often contaminated with small amounts of diperoxyketals derived from acetone (**1**, $X = \text{OOR}^5$, $R^1 = R^2 = \text{methyl}$, $R^3 = R^5 = \text{tert-alkyl}$).

Tertiary diperoxyketals (**1**, $X = \text{OOR}^5$, $R^1, R^2 = \text{alkyl}$, $R^3, R^5 = \text{tertiary alkyl}$) are excellent free-radical initiators. Such diperoxyketals are stable, and those with $R^3 = R^5 = \text{tert-butyl}$ have 10-h HLTs in the 93–114°C range. Less thermally stable diperoxyketals are those derived from cyclic ketones and those with bulkier *tert*-alkyl groups, eg, *tert*-amyl, *tert*-octyl, *tert*-cumyl. Commercial

members of this group all have $R^3 = R^5$, and thermally decompose to free radicals by cleavage of only one oxygen–oxygen bond initially, usually followed by β -scission of the resulting alkoxy radicals (146). For acyclic diperoxyketals, β -scission produces an alkyl radical and a peroxyester. Owing to similarity of thermal stability, the peroxyester decomposes almost simultaneously. With cyclic diperoxyketals, such as 1,1-di(*tert*-butylperoxy)cyclohexane, β -scission cleaves the cycloalkyl ring to give an alkyl radical with an attached peroxyester group. The effect, after peroxyester decomposition, is the production of two monoradicals, a diradical, and carbon dioxide (147). In the presence of polymerizable monomers, certain cyclic diperoxyketals partially decompose and the peroxyester moiety becomes a polymeric end group, thus forming a peroxy polymer (148).

Diperoxyketals, and many other organic peroxides, are acid-sensitive, therefore removal of all traces of the acid catalysts must be accomplished before attempting distillations or kinetic decomposition studies. The low molecular weight diperoxyketals can decompose with explosive force and commercial formulations are available only as mineral spirits or phthalate ester solutions.

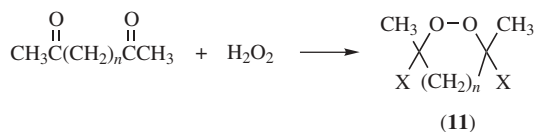
Diperoxyketals in which the peroxide groups are in a ring are among the most thermally stable organic peroxides, eg, 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetraoxacyclononane [22397-33-7] (**10**) which has 10-h HLT = 141°C in benzene.



Di(hydroxyalkyl) Peroxides. The lowest molecular weight member of this group (**2**, $X = Y = OH$), di(hydroxymethyl) peroxide ($R^1 = R^2 = OH$) is a dangerously explosive solid. With increasing molecular weight, di(hydroxyalkyl) peroxides become liquids and eventually solids of decreasing explosive nature and water solubility. In solution, these dialkyl peroxides exist in equilibrium with other α -oxygen-substituted peroxides, carbonyl compounds, and hydrogen peroxide (44). The existence of several equilibrium components explains some chemical properties of these mixtures, eg, formation of dibasic acids with ferrous salts or by thermal decomposition of cyclic peroxides, and the quantitative liberation of iodine from acidified iodides. Di(hydroxyalkyl) peroxides have been reduced to carbonyl- and hydroxy-containing derivatives with zinc and acetic acid, lithium aluminum hydride, sodium, sulfur dioxide, and ferrous salts. Hydrolysis can occur in neutral, acidic, or basic solutions and yields the corresponding carbonyl compounds, hydrogen peroxide, carboxylic acids, and hydrogen (44).

Formaldehyde reacts with di(hydroxymethyl) peroxide and phosphorus pentoxide to form di(hydroxymethoxymethyl) peroxide (**2**), where $X = Y = OCH_2OH$, $R^1 = R^2 = H$ (122).

Reaction of 1,3- and 1,4-diketones ($n = 1$ or 2) with hydrogen peroxide yields cyclic di(hydroxyalkyl) ($X = OH$) or di(hydroperoxyalkyl) ($X = OOH$) peroxides (**11**) (122).



The di(hydroxyalkyl) peroxide (**2**) from cyclohexanone is a solid which is produced commercially. The di(hydroxyalkyl) peroxide (**2**) from 2,4-pentanedione (**11**, $n = 1$; $\text{X} = \text{OH}$) is a water-soluble solid which is also produced commercially (see Table 5). Both these peroxides are used for curing cobalt-promoted unsaturated polyester resins. Because these peroxides are susceptible to promoted decomposition with cobalt, they must exist in solution as equilibrium mixtures with hydroperoxide structures (122,149).

Hydroxyalkyl Hydroperoxyalkyl Peroxides. There is evidence that hydroxyalkyl hydroperoxyalkyl peroxides (**2**, $\text{X} = \text{OH}$, $\text{Y} = \text{OOH}$) exist in equilibrium with their corresponding carbonyl compounds and other α -oxygen-substituted peroxides. For example, reaction with acyl halides yields diperoxyesters. Dilute acid hydrolysis yields the corresponding ketone (44). Reduction with phosphines yields di(hydroxyalkyl) peroxides and dehydration results in formation of cyclic diperoxides (**4**).

Thermal decomposition of hydroxyalkyl hydroperoxyalkyl peroxides produces mixtures of starting carbonyl compounds, mono- and dicarboxylic acids, cyclic diperoxides, carbon dioxide, and water. One specific hydroxyalkyl hydroperoxyalkyl peroxide from cyclohexanone (**2**, $\text{X} = \text{OH}$, $\text{Y} = \text{OOH}$) is a solid that is produced commercially as a free-radical initiator and bleaching agent (see Table 5). On controlled decomposition, it forms 1,12-dodecanedioic acid (150).

Di(hydroperoxyalkyl) Peroxides. Low molecular weight di(hydroperoxyalkyl) peroxides (**2**, $\text{X} = \text{Y} = \text{OOH}$) are dangerously prone to explosive decomposition when they are pure. Some have been characterized by acylation to the corresponding diperoxyesters (**2**, $\text{X} = \text{Y} = \text{OOR}^5$, $\text{R}^5 = \text{acyl}$), eg, with *p*-nitrobenzoyl chloride. Upon reaction with lead tetraacetate, di(hydroperoxyalkyl) peroxides can also be converted to cyclic diperoxides (**4**). They are also converted to symmetrical or unsymmetrical cyclic triperoxides (**5**) in the presence of a second ketone and a catalyst, eg, $\text{CuSO}_4\text{--HCl}$ (44,119).

Cyclic Peroxides. Cyclic diperoxides (**4**) and triperoxides (**5**) are solids and the low molecular weight compounds are shock-sensitive and explosive (151). The melting points of some characteristic compounds of this type are given in Table 5. They can be reduced to carbonyl compounds and alcohols with zinc and alkali, zinc and acetic acid, aluminum amalgam, Grignard reagents, and warm acidified iodides (44,122). They are more difficult to analyze by titration with acidified iodides than the acyclic peroxides and have been successfully analyzed by gas chromatography (112).

Acid hydrolysis of peroxides (**4**) and (**5**) generates carbonyl compounds (parent ketones or aldehydes) and hydrogen peroxide. Basic hydrolysis of cyclic diperoxides with α -hydrogen (those from aldehydes) yields carboxylic acids (44):



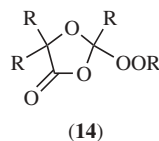
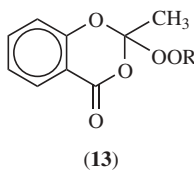
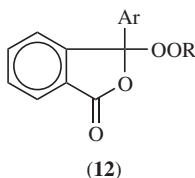
Thermal and photochemical decomposition of peroxides (4) and (5) lacking α -hydrogens (those derived from ketones) produces macrocyclic hydrocarbons and lactones (119,152,153). For example, 7,8,15,16,23,24-hexaoxatrispiro [5.2.5.2.5.2] tetracosane (see Table 5) yields cyclopentadecane and oxacycloheptadecan-2-one.

Stereoisomers of peroxides (4) and (5) are known to exist and their conformations have been studied using photoelectron, nmr, and other spectroscopic methods, and their crystalline structures have been determined (122,154,155).

Polymeric α -Oxygen-Substituted Peroxides. Polymeric peroxides (3) are formed from the following reactions: ketone and aldehydes with hydrogen peroxide, ozonization of unsaturated compounds, and dehydration of α -hydroxyalkyl hydroperoxides; consequently, a variety of polymeric peroxides of this type exist. Polymeric peroxides are generally viscous liquids or amorphous solids, are difficult to characterize, and are prone to explosive decomposition.

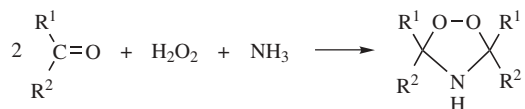
Polymeric *gem*-peroxides (3) from hydrogen peroxide and lower carbon ketones have been separated by paper or column chromatography and have been characterized by conversion to the bis(*p*-(nitro)peroxybenzoates). Oligomeric peroxides (3, $\text{R}^1 = \text{methyl}$, $\text{R}^2 = \text{ethyl}$, $n = 1 - 4$) from methyl ethyl ketone have been separated and interconverted by suitable treatment with ketone and hydrogen peroxide (44).

Miscellaneous α -Substituted Peroxides. 3-Aryl-3-(*tert*-alkylperoxy)-phthalides (12) are prepared from the corresponding 3-chlorophthalides and *tert*-alkyl hydroperoxide (156). 2-Methyl-2-(*tert*-alkylperoxy)-1,3-benzodioxan-4-ones (13) are obtained from *o*-acetylsalicyloyl chloride and *tert*-alkyl hydroperoxides (157). Trisubstituted 2-(*tert*-alkylperoxy)-1,3-dioxolan-4-ones (14) are synthesized from sterically favored α -acyloxy acid chlorides and *tert*-alkyl hydroperoxides (158).

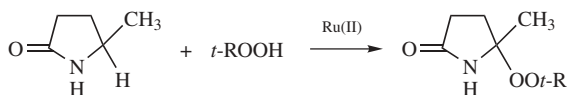


1-(*tert*-Butyldimethylsiloxy)-1-methoxyhexyl hydroperoxide [87258-13-7] has been synthesized from the corresponding ester-derived silyl ketene acetal and anhydrous hydrogen peroxide (132).

Certain ketones, eg, cyclohexanone, react with hydrogen peroxide in the presence of ammonia, yielding 1,2,4-dioxazolidines (159):

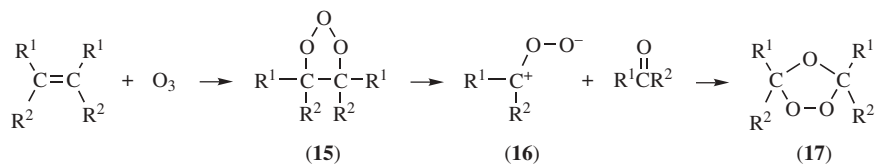


α -Amido-dialkyl peroxides have been prepared by ruthenium-catalyzed oxidation of amides with *t*-alkyl hydroperoxides (160):

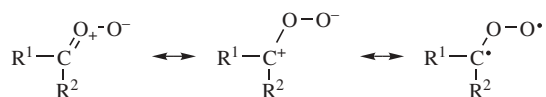


5. Ozonides and Ozonization

Unsaturated compounds undergo ozonization to initially produce highly unstable primary ozonides (**15**), ie, 1,2,3-trioxolanes, also known as molozonides, which rapidly split into carbonyl compounds (aldehydes and ketones) and 1,3-zwitterion (**16**) intermediates. The carbonyl compound-zwitterion pair then recombines to produce a thermally stable secondary ozonide (**17**), also known as a 1,2,4-trioxolane (44,64,125,161,162).

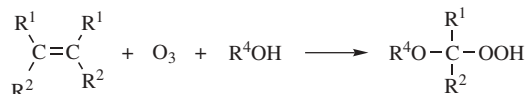


The 1,3-zwitterion appears to have some diradical as well as 1,2-zwitterionic (carbonyl oxide) character:



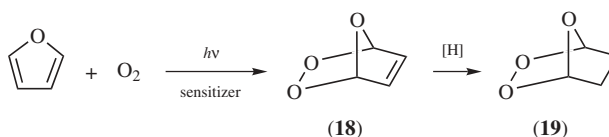
Most ozonolysis reaction products are postulated to form by the reaction of the 1,3-zwitterion with the extruded carbonyl compound in a 1,3-dipolar cycloaddition reaction to produce stable 1,2,4-trioxanes (ozonides) (**17**) as shown; with itself (dimerization) to form cyclic diperoxides (**4**); or with protic solvents, such as alcohols, carboxylic acids, etc, to form α -substituted alkyl hydroperoxides. The latter can form other peroxidic products, depending on reactants, reaction conditions, and solvent.

In the presence of alcohols, the ozonization products are alkoxyalkyl hydroperoxides (**1**, X = OR⁴, R³ = H):



By-products include ozonides (**17**). Other peroxidic products including polymeric peroxides and polymeric ozonides can form, depending on reaction conditions, solvent, and olefin used. A variety of cyclic diperoxides (**4**) have been obtained by ozonolysis of olefins. Both *cis*- and *trans*-1,2,4-trioxanes (**17**) are formed when asymmetrical internal olefins are ozonized. Boiling point data for several 1,2,4-trioxanes are listed in Table 8. Ozonolysis of asymmetrical olefins produces asymmetrical and symmetrical 1,2,4-trioxanes, ie, cross ozonides form. This is due to generation of two different 1,3-zwitterion intermediates and two different carbonyl compounds from the asymmetrical primary ozonide. 1,2,4-Trioxanes also have been synthesized by dehydration of di(hydroxyalkyl) peroxides (**2**), where X = Y = OH, with phosphorus pentoxide (44,122).

Cyclic 1,2,4-trioxanes (**18** and **19**) have been obtained from the photosensitized oxidation of furans (10,44,163). These compounds are 2,3,7-trioxabicyclo [2.2.1] hept-5-ene [6824-18-6] (**18**) and 2,3,7-trioxabicyclo [2.2.1] heptane [279-56-1] (**19**).



There is evidence that dioxirane is an intermediate product in the low temperature ozonization of ethylene and is probably formed from the diradical resonance isomer of the 1,3-zwitterion (164).

6. Peroxyacids

There are two broad classes of organic peroxyacids: peroxycarboxylic acids, R[C(O)OOH]_n, where R is an alkyl, aralkyl, cycloalkyl, aryl, or heterocyclic group and *n* = 1 or 2, and organoperoxysulfonic acids, RSO₂-OOH. Peroxycarboxylic acids are commonly named by adding the prefix peroxy to the parent acid as in peroxypropionic acid. The prefix per- is accepted only for the well-established products, ie, performic, peracetic, and perbenzoic acids. This article uses the former nomenclature. Organoperoxysulfonic acids are named by inserting peroxy in the sulfonic acid name, eg, cyclohexaneperoxysulfonic acid [74232-61-4]. For diacids, the prefixes monoperoxy- or diperoxy- are used, eg, monoperoxysuccinic acid and diperoxyisophthalic acid [1786-87-4].

Three peroxyacids are produced commercially for the merchant market: peroxyacetic acid as a 40 wt% solution in acetic acid, *m*-chloroperoxybenzoic acid, and magnesium monoperoxyphthalate hexahydrate. Other peroxyacids are produced for captive use, eg, peroxyformic acid generated *in situ*, as an epoxidizing agent.

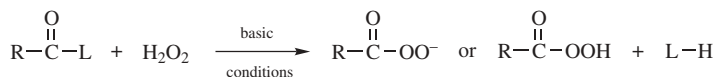
6.1. Physical Properties. Physical properties of peroxyacids have been extensively reviewed in the literature (4–6,34,44,115,165–168). The melting points of some peroxycarboxylic acids are listed in order of increasing number of carbon atoms in Table 9. The aliphatic peroxycarboxylic acids of low carbon number are liquids, whereas the aromatic and diperoxy aliphatic members are

solids. Results of ir and x-ray studies show that peroxycarboxylic acids are dimeric in the solid state owing to hydrogen-bonding interactions, whereas they are monomeric in the vapor, pure liquid and solution states owing to lack of intermolecular hydrogen bonding. Because of their monomeric structure, peroxycarboxylic acids have higher vapor pressures and lower extrapolated boiling points than the corresponding parent acids. Also, peroxycarboxylic acids are more water soluble and are much weaker acids than the parent carboxylic acids, eg, the pK_a value for peroxy-pivalic acid [14909-78-5] is 8.23 and that for pivalic acid [75-98-9] is 5.03 (169,170). Long-chain, aliphatic peroxycarboxylic acids are insoluble in water but are soluble in ethers and alcohols. The C_6 – C_{16} peroxycarboxylic acids are soluble in hydrocarbon solvents. The C_5 – C_7 aliphatic diperoxycarboxylic acids are water soluble; the higher carbon diperoxycarboxylic acids are soluble in ethanol, acetone, ether, and dioxane but insoluble in hydrocarbons. Aliphatic peroxyacids are characterized by sharp unpleasant odors, the intensity of which decreases with increasing chain length. They also are irritating to the skin and mucous membranes.

6.2. Chemical Properties. Organic peroxyacids are not noted for their stability and many lose active oxygen during storage at room temperature. Those that are water soluble hydrolyze slowly to the parent acid and hydrogen peroxide; however, peroxyformic acid hydrolyzes more rapidly. The longer-chain aliphatic members decompose rapidly in methanol. Stabilizers are commonly used for peroxycarboxylic acid solutions, eg, dipicolinic acid, phytic acid, and pyro- and metaphosphates (34,44). Stability of peroxycarboxylic acids increases with increasing molecular weight. The stabilities of peroxybenzoic acids are enhanced when ring substituents are present (34,44).

Hydrolysis is accelerated in the presence of strong acids. However, in the presence of aqueous bases such as sodium hydroxide, the rate of decomposition increases with increasing pH and reaches a maximum at the pK_a of the peroxycarboxylic acid (ca 8.25), then decreases at higher pH (169,170). The basic decomposition products include the parent carboxylic acid and singlet oxygen (171,172). Because the maximum rate of decomposition occurs at the pK_a , the peroxycarboxylic acid and its anion are involved in the transition state (169).

Peroxycarboxylic acids and precursors to peroxycarboxylic acids are used as bleaches for removal of stains and soils from textiles (173). Precursors to peroxycarboxylic acids are nonperoxidic compounds possessing a reactive acyl group and a good leaving group, L. These precursors react under basic conditions with hydrogen peroxide, inorganic perborates, and inorganic percarbonates to generate peroxycarboxylic acids or salts:



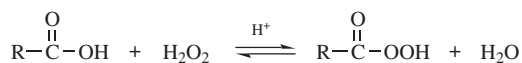
The bleaching activity of peroxycarboxylic acids is less damaging to colors and fibers than hypochlorite bleaches and bleaching can be carried out at temperatures much lower than those required for peroxygen bleaches, such as perborates. Under the basic laundering conditions, oxygen is generated which causes the bleaching action.

Thermal decompositions of peroxycarboxylic acids and their salts can proceed by free-radical and nonradical paths. Often the decomposition products and the rate are affected by the nature of the solvent (44,165,174,175). Peroxycarboxylic acids undergo photodecomposition and radical-induced decomposition (176). They also are decomposed by a variety of metals, metal ions, and complexes (176–180). One-electron transfers occur with transition metals in the same manner as with hydroperoxides. Peroxycarboxylic acids generally are not shock-sensitive but can explode upon heating; relatively pure peroxyformic and peroxyacetic acids are particularly dangerous in this respect (34,44,165). Peroxycarboxylic acids usually are not used as free-radical initiators, although there are many references regarding this application (34).

Peroxycarboxylic acids are among the most powerful organic peroxide oxidizing agents. Typical reactions include epoxidation and hydroxylation of olefins (165) and oxidation of sulfides to sulfoxides or sulfones; disulfides to thiosulfonates; *S*-alkyl thioacetates to alkanesulfonic acids; nitroso compounds or oximes to nitro compounds; nitrosoamines to nitramines; imines to oxaziranes or nitrosoalkane dimers; azo compounds, hydrazones, or amines to azoxy compounds; amines to amine oxides, nitroso compounds, or nitro compounds; azines to azine monoxides or ketones; unsymmetrical dialkylhydrazines to tetraalkyl tetrazenes; aromatic hydrazones to diazo compounds; diazo compounds to ketones; tertiary amines to amine oxides; phenols to muconic acids or quinones; aromatic hydrocarbons to phenols; aromatic ethers to quinones; aldehydes to carboxylic acids; β -diketones to alcohols and α -ketoacids; α -diketones to carboxylic acids; and ketones to esters or lactones, eg, the Baeyer-Villiger reaction (44). Generally, polar solvents accelerate oxidation rates. Reviews on oxidations with magnesium monoperoxyphthalate hexahydrate have been published (181).

The main industrial uses of peroxycarboxylic acids are in the manufacture of epoxides, synthetic glycerol (qv), and epoxy resins (qv) (165,167,168). They also have been used as disinfectants (177), fungicides, and bleaching agents and for shrink-proofing wool (34).

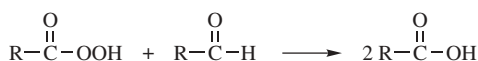
6.3. Synthesis. Many different methods for the preparation of peroxyacids have been described (165). The most widely used method is the direct, acid-catalyzed equilibrium reaction of 30–98 wt% hydrogen peroxide with carboxylic acids (168):



The proportion and concentration of hydrogen peroxide determine the extent of the equilibrium shift. Best results are obtained by using 70–95 wt% hydrogen peroxide. The equilibrium also can be shifted to the right by removing water azeotropically and/or under a vacuum. Chelating agents may be added during processing to reduce metal-catalyzed decompositions. When high concentrations of water-soluble peroxycarboxylic acids are not required for an application, the equilibrium mixture can be used. Pure peroxycarboxylic acids can be obtained by careful distillation followed by fractional freezing. Sulfuric acid, methanesul-

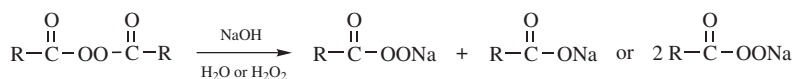
fonic acid, and sulfonic acid ion-exchange resins are the most commonly used acid catalysts. Continuous processes for manufacturing dry solutions of peroxy-carboxylic acids free of hydrogen peroxide have been reported (182). Concentrated sulfuric acid has been used with water-insoluble C₂–C₁₆ aliphatic acids. Methanesulfonic acid is used for the higher aliphatic acids and for the aromatic acids.

Another method for producing peroxy-carboxylic acids is by autoxidation of aldehydes (168). The reaction is a free-radical chain process, initiated by organic peroxides, uv irradiation, ozone, and various metal salts. It is terminated by free-radical inhibitors (181,183). In certain cases, the peroxy-carboxylic acid forms an adduct with the aldehyde from which the peroxy-carboxylic acid can be liberated by heating or by acid hydrolysis. If the peroxy-carboxylic acid remains in contact with excess aldehyde, a redox disproportionation reaction occurs that forms a carboxylic acid:



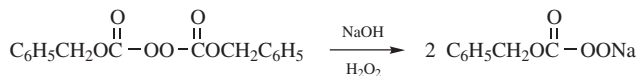
Peroxy-carboxylic acids also have been prepared by the reaction of acid chlorides, anhydrides, or boric-carboxylic anhydrides with hydrogen or sodium peroxide. These reactions are carried out at low temperature and with excess peroxide to avoid the formation of diacyl peroxides (44,168,181,184).

Also, basic hydrolysis or perhydrolysis of diacyl peroxides has been used to produce peroxy-carboxylic acids (44,181). Perhydrolysis produces two moles of the peroxy-carboxylic acid salt:



Peroxy-carboxylic acids have been obtained from the hydrolysis of stable ozonides with carboxylic acids, perhydrolysis of acylimidazolides, reaction of ketenes with hydrogen peroxide, electrochemical oxidation of alcohols and carboxylic acids, and oxidation of carboxylic acids with oxygen in the presence of ozone (181).

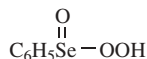
An example of an alkyl monoperoxy-carbonic acid, *O*-benzyl monoperoxy-carbonic acid [52123-51-0], was prepared in aqueous methanol solution by basic perhydrolysis of dibenzyl peroxydicarbonate [2144-45-8] and subsequently isolated in 97% purity. It has been used as an epoxidizing agent (185):



Organoperoxy-sulfonic acids and their salts have been prepared by the reaction of arenesulfonyl chlorides with calcium, silver, or sodium peroxide; treatment of metal salts of organosulfonic acids with hydrogen peroxide; hydrolysis of di(organosulfonyl) peroxides, RS(O)₂–OO–S(O)₂R, with hydrogen peroxide;

and sulfoxidation of saturated, nonaromatic hydrocarbons, eg, cyclohexane (44,181).

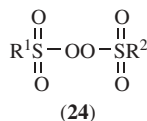
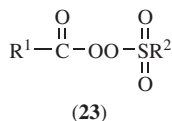
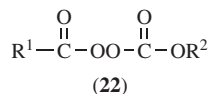
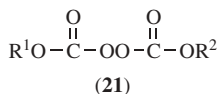
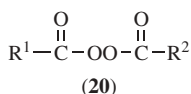
6.4. Other Peroxyacids. Benzeneperoxyseleninic acid [62885-97-6], has been



prepared *in situ* from benzeneseleninic acid and hydrogen peroxide and is used to epoxidize terpenic olefins (186) and Baeyer-Villiger oxidation of cyclic ketones.

7. Acyl Peroxides

The acyl peroxide class is characterized by the following structures:



Acyl peroxides of structure (20) are known as diacyl peroxides. In this structure R^1 and R^2 are the same or different and can be alkyl, aryl, heterocyclic, imino, amino, or fluoro. Acyl peroxides of structures (21), (22), (23), and (24) are known as dialkyl peroxydicarbonates, *OO*-acyl *O*-alkyl monoperoxycarbonates, acyl organosulfonyl peroxides, and di(organosulfonyl) peroxides, respectively. R^1 and R^2 in these structures are the same or different and generally are alkyl and aryl (4-6,44,166,187,188). Many diacyl peroxides (20) and dialkyl peroxydicarbonates (21) are produced commercially and used in large volumes.

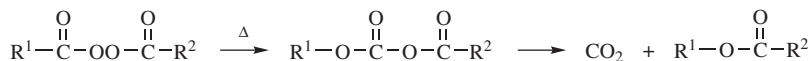
7.1. Physical Properties. Almost all liquid diacyl peroxides (20) and concentrated solutions of the solid compounds are unstable to normal ambient temperature storage; many must be stored well below 0°C. Most of the solid compounds are stable at ca 20°C but many are shock-sensitive (187). Other physical constants and properties have been reviewed (187,188). The melting points and refractive indexes of some acyl peroxides are listed in Tables 10-12.

7.2. Chemical Properties. Diacyl peroxides (20) decompose when heated or photolyzed (<300 nm). Although photolytic decompositions generally produce free radicals (198), thermal decompositions can produce nonradical and radical intermediates, depending on diacyl peroxide structure. Symmetrical aliphatic diacyl peroxides of certain structures, ie, diacyl peroxides (20, $\text{R}^1 = \text{R}^2 = \text{alkyl}$) without α -branches or with a mono- α -methyl substituent, and

diaroyl peroxides (**20**, $R^1 = R^2 = \text{aryl}$) thermally decompose almost exclusively by homolysis:



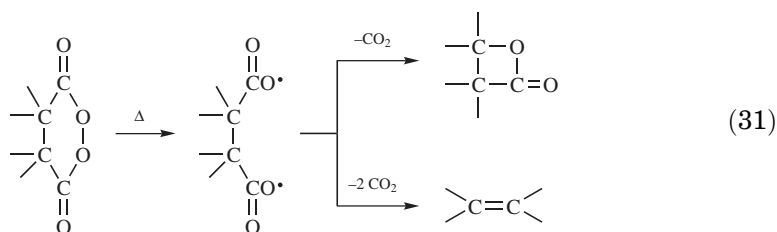
Of these diacyl peroxides the ones that generate the most stable radicals ($R^{1\bullet}$) are the most unstable diacyl peroxides. Most other diacyl peroxides decompose by competing free-radical and polar decomposition, ie, carboxy inversion (188). Carboxy inversion occurs to a much greater extent with certain diacyl peroxides having unsymmetrical diacyl peroxide structures (52,187,188,199):



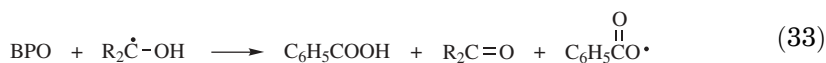
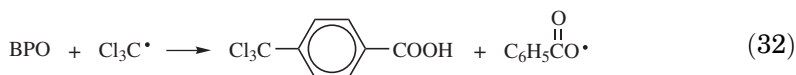
The inversion reaction is more pronounced in polar than in nonpolar solvents and is catalyzed by Lewis acids. For example, under normal conditions, BPO undergoes thermolysis to produce free radicals, whereas in the presence of AlCl_3 , BF_3 , or SbCl_5 , it undergoes carboxy inversion (44). Generally, the diacyl peroxides with electron-donating substituents on one side and electron-withdrawing substituents on the other side of the oxygen–oxygen bond are most susceptible to carboxy inversion.

Diaroyl peroxides and diacyl peroxides without α -branches are significantly more thermally stable than those with mono- or di- α -substituents (188). For example, in 0.2M benzene, dibenzoyl, diacetyl, dilauroyl, and diisobutyryl peroxides have 10-h HLTs of 73, 69, 62, and 21°C, respectively (72). Based on published rate data in carbon tetrachloride (200), dipivaloyl peroxide has an estimated 10-h HLT of about –5°C. Fluorinated diacyl peroxides are much less stable than nonfluorinated diacyl peroxides, eg, the 10-h HLTs for di(perfluorooctanoyl) peroxide [34434-27-0] and dioctanoyl peroxide are 18 and 51°C, respectively (201). The primary use of most commercial diacyl peroxides (**20**, $R^1 = R^2 = \text{alkyl or aryl}$) is initiation of free-radical reactions. In some cases, thermally unstable peroxides, eg, diisobutyryl peroxide, have been prepared *in situ* to initiate vinyl monomer polymerizations (202). Unsymmetrical compositions containing two diacyl peroxide moieties of different thermal stabilities decompose sequentially and can be used as free-radical polymerization initiators for generating peroxy polymers with diacyl peroxide end groups and block copolymers (203,204).

Cyclic diacyl peroxides decompose thermally and photolytically to yield products derived from diradical intermediates (188,198,205) (eq. 31).

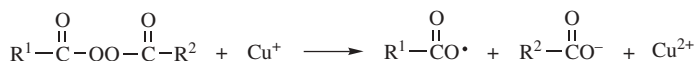


Diacyl peroxides (**20**, $\text{R}^1 = \text{R}^2 = \text{alkyl or aryl}$) also undergo three types of radical induced decomposition (187) all of which produce the radical $\text{C}_6\text{H}_5\text{COO}\cdot$ from BPO. The first type involves direct radical displacement on the oxygen–oxygen bond and is the preferred mode for nucleophilic radicals, eg, $\cdot\text{CH}(\text{R})\text{OR}'$. The second type involves radical addition to, or abstraction from, the hydrocarbyl group adjacent to the peroxide; this is the preferred mode for electrophilic radicals, eg, $\text{Cl}_3\dot{\text{C}}$ (eq. **32**). In the last type (eq. **33**), there is hydrogen donation from certain hydrogen-donating radicals, eg, ketyls (52,187,188,199).



As a consequence of their susceptibility to radical-induced decomposition, neat and concentrated solutions of diacyl peroxides undergo self-accelerating decompositions (205). Kinetics studies can be significantly affected if high dilution and free-radical scavengers are not employed. Decomposition rates of diacyl peroxides are faster in more polar solvents.

Diacyl peroxide decompositions also are catalyzed by the metal ions of copper, iron, cobalt, and manganese:



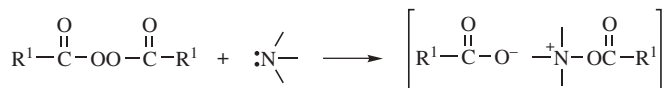
This radical-generating reaction has been used in synthetic applications, eg, aryloxylation of olefins and aromatics, oxidation of alcohols to aldehydes, etc (52,187). Only alkyl radicals, $\text{R}\cdot$, are produced from aliphatic diacyl peroxides, since decarboxylation occurs during or very shortly after oxygen–oxygen bond scission in the transition state (187,188,199). For example, diacetyl peroxide is well known as a source of methyl radicals (206).

Hydrolysis and perhydrolysis of diacyl peroxides yields peroxydicarboxylic acids. Carbanions react by displacement on oxygen:



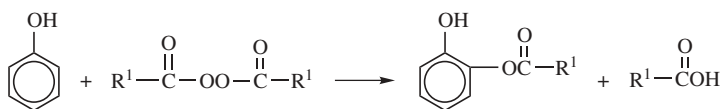
Diacyl peroxides have been reduced with a variety of reducing agents, eg, lithium aluminum hydride, sulfides, phosphites, phosphines, and halide ions (187). Halides yield carboxylic acid salts; $(\text{RO})_3\text{P}$ gives acid anhydrides. With iodide ion and certain trivalent phosphorus compounds, the reductions are sufficiently quantitative for analytical purposes.

Amines also react with diacyl peroxides by nucleophilic displacement on the oxygen–oxygen bond forming an ion pair intermediate (187):



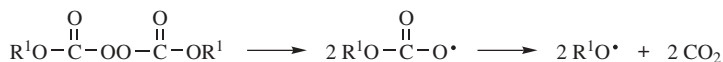
The fate of the ion pair intermediate depends on the structure of the amine and the reaction conditions. Certain tertiary amines, eg, dimethylaniline (DMA), react with specific diacyl peroxides such as dibenzoyl peroxide (BPO) to generate free radicals at ca 20°C. Some reactions, eg, DMA–BPO, are explosive when neat reactants are mixed. Primary and secondary amines do not yield free radicals.

Nonhindered phenols are acyloxyated by diacyl peroxides in nonradical reactions (187):



Phenols with bulky ortho- and para-substituents, eg, phenolic antioxidants, do not undergo this reaction; however, they scavenge radicals generated by thermolysis of diacyl peroxides and other peroxides. Diacyl peroxides react with potassium superoxide, KO_2 , forming singlet oxygen (207).

Dialkyl peroxydicarbonates (**21**) undergo thermolysis to form two alkoxy-carbonyloxy radicals that subsequently undergo β -scission to form CO_2 and alkoxy radicals:

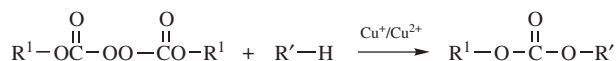


These low temperature peroxides are susceptible to radical-induced decompositions. This susceptibility largely accounts for the hazards associated with their production and storage. In contrast to diacyl peroxides (**20**), the true first-order decomposition rates for dialkyl peroxydicarbonates (**21**) are not affected by the nature of the R group. In free-radical scavenging solvents, eg, trichloroethylene, the decomposition rates of di-*n*-propyl, diisopropyl, di-*sec*-butyl, dicyclohexyl, di-2-ethylhexyl, and dehexadecyl peroxydicarbonates are all essentially the same, ie, 10-h HLT = 49 – 50°C, whether the R groups are primary, secondary, or cycloalkyl (208). In nonradical-scavenging solvents or environments, decomposition rates are much faster due to competing radical-induced decompositions; such reactions are second-order decompositions (18). Homolysis and

induced decomposition reactions of peroxydicarbonates generally proceed at faster rates in solvents of increased polarity.

All liquid dialkyl peroxydicarbonates are unstable at ca 20°C and therefore require temperature controlled storage. Many undergo extremely rapid decomposition on warming to ca 20°C, which can be dangerous if the peroxide is confined. Decomposition characteristics, but not necessarily stability, are moderated by dilution. Most solid peroxydicarbonates are stable at 20°C with stability increasing with increasing melting point. Di(2-phenoxyethyl) peroxydicarbonate has a melting point of 97–100°C and is stable in the solid state at 50°C, its 10-h HLT, for at least four weeks (190). However, solid peroxydicarbonates lose their thermal stability when they melt or are dissolved in solvents.

Dialkyl peroxydicarbonates are used primarily as free-radical initiators for vinyl monomer polymerizations (18,208). Dialkyl peroxydicarbonate decompositions are accelerated by certain metals, concentrated sulfuric acid, and amines (44). Violent decompositions can occur with neat or highly concentrated peroxides. As with most peroxides, they liberate iodine from acidified iodides. In the presence of copper ions and suitable substrates, dialkyl peroxydicarbonates have been used to synthesize alkyl carbonates (44):



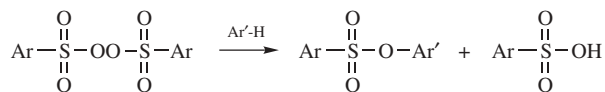
Thermal decomposition of *OO*-acyl *O*-alkyl monoperoxycarbonates (**22**, R¹, R² = alkyl or aryl) yield first-order decomposition rates between those of dialkyl peroxydicarbonates (**21**) and that of the symmetrical diacyl peroxide (**20**) having the same acyl moiety. These peroxides are also sensitive to radical-induced decompositions (187).

Acyl organosulfonyl peroxides (**23**) such as acetyl cyclohexanesulfonyl peroxide are efficient radical initiators for vinyl chloride polymerization (24,209). However, in the presence of Lewis acids or strong protic acids most acyl organosulfonyl peroxides decompose in organic solvents by ionic rearrangement with the formation of mixed anhydrides (33):



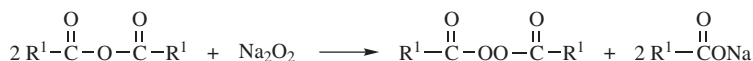
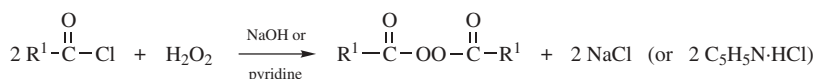
The rearrangement is self-catalyzed by the organosulfonic acid that is already present or acid from hydrolysis of the mixed anhydride product. If the organosulfonic acid is removed, eg, with dry potassium carbonate, the acyl organosulfonyl peroxides decompose predominantly by homolysis to free radicals (33). These peroxides also rapidly decompose in the presence of amines (44).

Di(arenesulfonyl) peroxides (**24**, R¹ = R² = aryl) react with aromatic solvents to form aryl arenesulfonates (33):

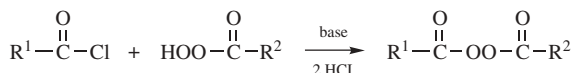


These peroxides also form 1:1 adducts with styrene and form hydrobenzoin diarenesulfonates with stilbenes. Di(benzenesulfonyl) peroxide decomposes in water to phenol and sulfuric acid (33).

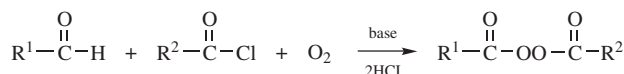
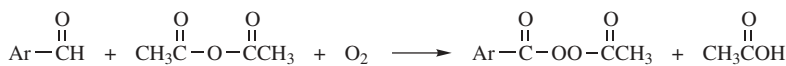
7.3. Synthesis. Symmetrical diacyl peroxides (**20**, $\text{R}^1 = \text{R}^2 = \text{alkyl or aryl}$) are prepared by the reaction of an acyl chloride or anhydride with sodium peroxide or hydrogen peroxide and a base:



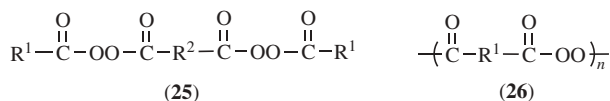
Unsymmetrical diacyl peroxides (**20**, $\text{R}^1 \neq \text{R}^2 = \text{alkyl or aryl}$) are prepared by the reaction of acid chlorides or anhydrides with peroxycarboxylic acids in the presence of a base:



The peroxycarboxylic acid can be generated *in situ* by autoxidation of aldehydes, either in the presence of anhydrides or an acyl chloride and a base, eg, sodium carbonate, or basic ion-exchange resins (44,187,188,210):



Use of diacid chlorides for acyl chlorides in the latter reaction results in generation of di(diacyl peroxides) (**25**).

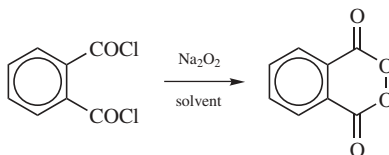


Other unsymmetrical peroxides can be prepared by this reaction by employing other acylating agents, eg, alkyl chloroformates, organosulfonyl chlorides, and carbamoyl chlorides (210). Unsymmetrical and symmetrical di(diacyl peroxides) also are obtained by the reaction of dibasic acid chlorides directly with per-

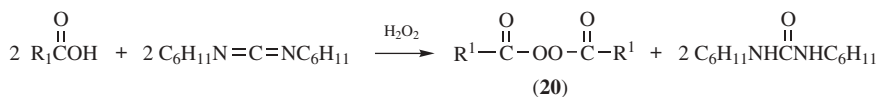
oxycarboxylic acids or monoacid chlorides directly with diperoxydicarboxylic acids in the presence of a base (44,187,203).

Polymeric diacyl peroxides (**26**) can be prepared from the reaction of dibasic acid chlorides, eg, succinoyl, fumaryl, sebacoyl, and terephthaloyl chlorides, with sodium or hydrogen peroxide (187).

Cyclic diacyl peroxides can be generated from suitable dibasic acid chlorides and sodium or hydrogen peroxide, especially in dilute solutions (187,205), eg, 2,3-benzodioxin-1,4-dione [4733-52-2] from phthaloyl chloride:



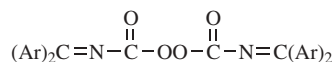
Symmetrical or unsymmetrical diacyl peroxides (**20**, R¹, R² = alkyl or aryl) can be synthesized directly from carboxylic acids and hydrogen peroxide or from peroxydicarboxylic acids with dicyclohexylcarbodiimide or *N,N*-dicarbonyldiimidazole as condensing agents (187):



Diacyl peroxides (**20**, R¹ = R² = alkyl or aryl) have been obtained from the oxidation of carboxylic acid potassium salts by Kolbe electrolysis or by elemental fluorine (187).

Fluoroformyl peroxide [692-74-0] (**20**, R¹ = R² = F), has been prepared by the reaction of carbon monoxide, fluorine, and oxygen or by the photolytic reaction of oxalyl fluoride with oxygen (187).

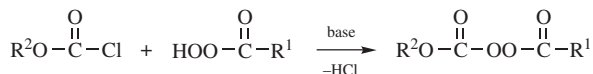
Bis(carbamoyl) peroxides of the following structure were prepared by reaction of the corresponding carbamoyl chlorides and hydrogen peroxide-urea complex in the presence of pyridine (211).



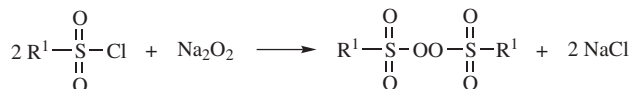
Dialkyl peroxydicarbonates (**21**) are produced by reaction of alkyl chloroformates with sodium peroxide (44,187):



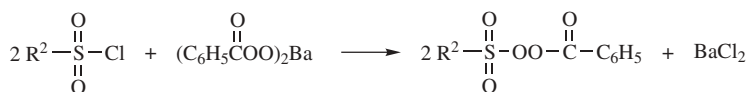
OO-Acyl *O*-alkyl monoperoxydicarbonates (**22**) are obtained from the reaction of alkyl chloroformates with peroxydicarboxylic acids in the presence of a base (44,212):



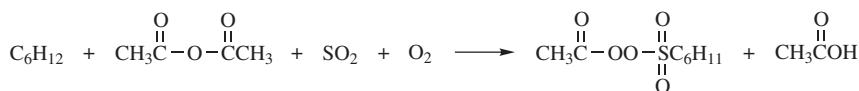
Symmetrical di(organosulfonyl) peroxides (**24**, $\text{R}^1 = \text{R}^2$) have been prepared by the reaction of organosulfonyl chlorides with sodium peroxide or hydrogen peroxide in the presence of a base (44):



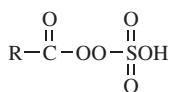
Acyl organosulfonyl peroxides (**23**) are prepared from the organosulfonyl chlorides and a metal salt of a peroxydicarboxylic acid (44):



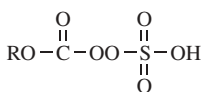
Acetyl cyclohexanesulfonyl peroxide has been produced commercially by the sulfoxidation of cyclohexane, C_6H_{12} , in the presence of acetic anhydride (44):



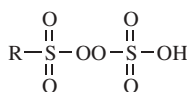
Potassium salts of the peroxides (**27–29**) are prepared from the reaction of Caro's acid [7722-86-3], H_2SO_5 , with acyl chlorides, chloroformates, or organosulfonyl chlorides in the presence of potassium hydroxide (44).



(27)



(28)



(29)

8. Alkyl Peroxyesters

Peroxyesters include the alkyl esters of peroxydicarboxylic acids; monoperoxydicarboxylic acids; diperoxydicarboxylic acids; monoperoxy- (**30**) and diperoxydicarboxylic (**31**) acids; monoperoxy- (**32**) and diperoxyoxalic (**33**) acids; peroxydicarbamic acids (**34**); peroxydicarboxylic acids (**35**); and peroxyphosphoric acids (**36**).

Alkyl peroxyesters are commonly named like their nonperoxidic counterparts, except for incorporation of the peroxy- prefix. Trivial names are also commonly used, eg, *tert*-butyl peracetate. Alkyl peroxyesters derived from di- and polybasic peroxyacids use *OO*- or *O*- when required to locate groups, eg, *OO-tert*-butyl *O*-isopropyl monoperoxydicarbonate and *OO-tert*-butyl *O*-hydrogen

monoperoxymaleate. Descriptions of alkyl peroxyesters have been given in the chemical literature (1,4-6,19,20,44,168,213).

8.1. Synthesis. Peroxyesters are prepared by the reaction of alkyl hydroperoxides $R'OOH$, with acylating agents, eg, acid chlorides, anhydrides, ketenes, organosulfonyl chlorides, phosgene (qv), alkyl chloroformates, oxalyl chloride, alkyl chlorooxalates, isocyanates, carbamoyl chlorides, carboxylic acids, and esters, under appropriate reaction conditions, according to Figure 2. Reactions with acylating agents that generate hydrogen chloride are carried out in the presence of a base, eg, pyridine or sodium hydroxide, or by using the sodium or potassium salt of the hydroperoxide.

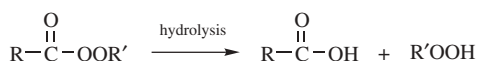
Because primary and secondary alkyl hydroperoxides are base-sensitive they are converted to peroxyesters by reaction with a ketene or by the reaction of their barium salts with acid chlorides (44).

Peroxyesters may also be prepared by condensation of hydroperoxides with carboxylic acids using condensing agents, eg, dicyclohexylcarbodiimide (214), imidazolides (213), and *p*-toluenesulfonyl chloride with pyridine (213). Suitable esters, eg, monoesters of ethylene glycol, have been used to prepare peroxyesters by ester interchange with alkyl hydroperoxides (215). Generally, reactions of isocyanates to form peroxycarbamates are catalyzed by dibutyltin dilaurate (213,216).

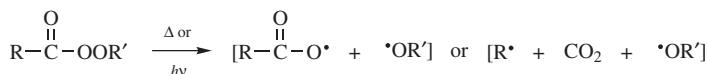
Oligomeric and polymeric peroxides possessing peroxyester moieties have been prepared. Those with peroxyester end groups have been prepared by reaction of the bis(chloroformates) of hydroxy-terminated polymers and oligomers, eg, polycaprolactones, with *tert*-alkyl hydroperoxides in the presence of base (217). Those with pendent peroxyester functions have been synthesized by free-radical copolymerization of *OO-tert*-alkyl *O*-allyl monoperoxycarbonates with vinyl monomers (218). Those possessing peroxyester functions in the polymer backbone have been prepared by base-catalyzed condensation of dihydroperoxides, eg, 2,5-dimethyl-2,5-dihydroperoxyhexane, with dibasic acid chlorides (219) or bis(chloroformates) (220) and by base-catalyzed condensations of hydroxy-hydroperoxides, eg, 3-hydroxy-1,1-dimethylbutyl hydroperoxide, with dibasic acid chlorides or bis(chloroformates) (110). Polymers having peroxycarbamate end groups have been prepared by reaction of isophorone diisocyanate [4098-71-9] with dihydroxy-terminated polyethers and *tert*-butyl hydroperoxide (221).

8.2. Physical Properties. Properties of some *tert*-alkyl peroxyesters are listed in Table 13 and the properties of some *tert*-alkyl areneperoxysulfonates are given in Table 14. Mass spectra (226), total energies, and dipole moments (227); oxygen-oxygen bond-dissociation energies (44,228); and boiling points, melting points, densities, and refractive indexes (44,168,213) have been reported for a variety of *tert*-butyl peroxycarboxylates.

8.3. Chemical Properties. Alkyl peroxyesters are hydrolyzed more readily than the analogous nonperoxidic esters and yield the original acids and hydroperoxides from which they were prepared rather than alcohols and peroxyacids:



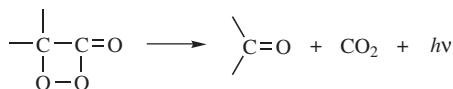
The *tert*-alkyl peroxyesters undergo homolysis, thermally and photochemically, to generate free radicals (168,213,229–232):



Simultaneous cleavage of two bonds occurs when R· is relatively stable (168) or when R is bulky. Thermal first-order decomposition rates of *tert*-alkyl peroxyesters are influenced strongly by structure. Variation of both R and R' groups of peroxyesters provides a convenient means of altering the relative thermal activity of peroxyesters. For example, increasing the steric bulk of either or both of R and R' generally lowers the thermal stability of a peroxyester. These trends are illustrated in Table 15. *tert*-Butyl peroxyacetate is significantly more thermally stable and less active than 3-hydroxy-1,1-dimethylbutyl peroxyneodecanoate. Although other factors affect thermal stability, the concept of steric bulk of R and R' can be used to qualitatively predict peroxyester reactivity trends.

Table 15 shows that peroxyester stability decreases for the *tert*-alkyl groups in the following order: *tert* – butyl > *tert* – amyl > *tert* – octyl > *tert* – cumyl > 3 – hydroxy – 1, 1 – dimethylbutyl. The order of activity of the R' group in peroxyesters is also observed in other *tert*-alkyl peroxides. Peroxyesters derived from benzoic acids and non- α -branched carboxylic acids are more stable than those derived from mono- α -branched acids which are more stable than those derived from di- α -branched acids (19,21,168). The size of the α -branch also is important, since steric acceleration of homolysis occurs with increasing branch size (236). Suitably substituted peroxyesters show rate enhancements because of anchimeric assistance (168,213,237).

β -Peroxylactones undergo thermal decarboxylation to carbonyl compounds by the initial formation of a 1,5-diradical (238). α -Peroxylactones undergo similar decarboxylation, emitting light since the ketone is generated in the triplet excited state (85,239,240):

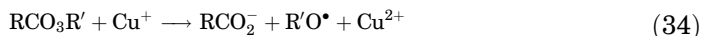


Primary and secondary alkyl peroxyesters thermally decompose by a non-radical process, giving almost quantitative yields of carboxylic acids and carbonyl compounds (213,241):



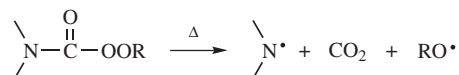
tert-Alkyl peroxyesters are much less sensitive to radical-induced decompositions than diacyl peroxides. Induced decomposition is only significant in peroxyesters containing nonhindered α -hydrogens or α , β -unsaturation (213,242).

Peroxyesters decompose by an electron-transfer process catalyzed by transition metals (44,168,213) (eq. 34). This reaction has been used synthetically to bond an acyloxy group to appropriate coreactive substrates (eq. 35).



Apparently the alkoxy radical, $\text{R}'\text{O}^\bullet$, abstracts a hydrogen from the substrate, $\text{R}''\text{H}$, and the resulting radical, R''^\bullet , is oxidized by Cu^{2+} (one-electron transfer) to form a carbonium ion that reacts with the carboxylate ion, RCO_2^- . The overall process is a chain reaction in which copper ion cycles between +1 and +2 oxidation states. Suitable substrates include olefins, alcohols, mercaptans, ethers, dienes, sulfides, amines, amides, and various active methylene compounds (44). This reaction can also be used with *tert*-butyl peroxy-carbamates to introduce carbamoyloxy groups to these substrates (243).

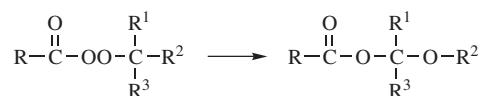
Normally, *tert*-alkyl peroxy-carbamates undergo thermolysis to yield free radicals and carbon dioxide (20).



The first-order decomposition rates of *tert*-alkyl peroxy-carbamates are strongly influenced by structure, eg, electron-donating substituents on nitrogen increase the rate of decomposition, and some substituents increase sensitivity to induced decomposition (20). *tert*-Alkyl peroxy-carbamates have been used to initiate vinyl monomer polymerizations and to cure rubbers (244). They liberate iodine quantitatively from hydriodic acid solutions. Decomposition products include carbon dioxide, hydrazo and azo compounds, amines, imines, and *O*-alkylhydroxylamines. Many peroxy-carbamates are stable at ca 20°C but decompose rapidly and sometimes violently above 80°C (20,44).

Acid-catalyzed, ionic decompositions have been reported for peroxyesters, $\text{RC(O)-OOR}'$, in which the R group can form a particularly stable carbonium ion, eg, tropylium ion (213).

Criegee rearrangement competes with homolysis in *tert*-alkyl peroxyesters, $\text{RC(O)-OOCR}^1\text{R}^2\text{R}^3$, in which R is strongly electron-withdrawing and the *tert*-alkyl group, ie, $\text{CR}^1\text{R}^2\text{R}^3$, contains a group with high migratory aptitude and ability to stabilize adjacent carbonium ions (213). The rearrangement converts the peroxyester to a nonperoxidic ester:



Some peroxyesters are difficult to prepare because of this facile rearrangement, eg, attempts to prepare triphenylmethyl peroxyesters yield only rearrangement products (44).

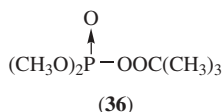
tert-Butyl peroxybenzoate and probably other *tert*-alkyl peroxyesters react with carbanions, eg, Grignard reagents or phenyllithium, at low temperatures to form ethers, via nucleophilic displacement at the oxygen adjacent to the *tert*-alkyl group (44):



Lithium amides of primary *tert*-alkylamines yield *N*-(*tert*-alkyl)-*O*-(*tert*-butyl)hydroxylamines, whereas lithium amides of primary alkylamines yield *N*-alkylbenzamides and $\text{LiOO}-t\text{-C}_4\text{H}_9$ due to nucleophilic attack on the carbonyl group (245).

The instability of *tert*-butyl areneperoxyulfonates is increased by the presence of electron-withdrawing substituents on the aromatic ring and decreased by electron-donating substituents. However, even the most stable members decompose violently on warming, as indicated in Table 14. These peroxyesters appear to decompose heterolytically without the formation of free radicals (44).

OO-tert-Alkyl dialkyl monoperoxyphosphates such as *OO-tert*-butyl dimethyl monoperoxyphosphate [18963-64-9] (mp, 23–25°C) (**36**) have been prepared and appear to decompose heterolytically at the oxygen–oxygen bond (33).



The use of monomers that do not homopolymerize, eg, maleic anhydride and dialkyl maleates, reduces the shock sensitivity of *tert*-butyl peroxyesters and other organic peroxides, presumably by acting as radical scavengers, that prevent self-accelerating, induced decomposition (246).

The main industrial use of *tert*-alkyl peroxyesters is in the initiation of free-radical chain reactions, primarily for vinyl monomer polymerizations. Decomposition of unsymmetrical diperoxyesters, in which the two peroxyester functions decompose at different rates, results in the formation of polymers of enhanced molecular weights, presumably due to chain extension by sequential initiation (204).

9. Manufacture and Processing

The general chemical approaches for syntheses of commercial organic peroxides have been described in earlier sections of this article. Owing to the inherent hazards of organic peroxides, they are almost never distilled or confined during manufacture. Generally, open reactors are employed that can be easily vented and deluged with water if an unanticipated exotherm occurs. The preferred materials of reactor construction are 316 stainless steel, plastic, and glass. Brass and copper should be avoided owing to the sensitivity of many organic

peroxides to copper salts. Significant cooling capacity is required to handle reaction exotherms and to maintain temperature. Because over 100 different organic peroxides are produced commercially, organic peroxide producers manufacture many organic peroxides in the same equipment. Batch processing is generally employed when relatively small production volumes are required, whereas semi-continuous and continuous processing are employed when larger production volumes are required and when safety is a primary issue (247). In batch processing, a reactor is charged with all of the reactants, optional solvents, and catalysts early in the process and the reaction is allowed to proceed. The reaction is completed under controlled conditions and the entire batch of product is purified with various aqueous washes and extractions and dried using a desiccant, dry gas blowing, or stripping under a vacuum. In continuous processing, the raw materials in relatively small amounts are continuously added to a mixing zone and held in the mixing zone for the required reaction time. Centrifuges are often used for purification. Drying is accomplished as previously described. Semi-continuous processing employs some continuous processing steps, usually the reaction step, and some batch processing steps. Continuous processes are significantly safer to operate than batch processes as smaller amounts of organic peroxides are continuously in process. Besides safer continuous processing, another trend has been the use of reactants of higher purity. These process improvements have resulted in reduced environmental impact as unplanned process decompositions have been decreased and waste streams have been reduced.

10. Economic Aspects

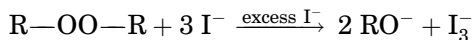
Prices of commercial organic peroxides range from ca \$2.50 to >\$35/kg, depending on peroxide type, production volume, assay, nature of formulation, cost of raw materials, and degree of special processing and handling requirements. For example, >98 wt% BPO is sold only in 0.45-kg paper-lined bags for >\$13/kg, whereas the more stable 78 wt% assay, wetted product is sold in 11.3-kg quantities for ca \$8/kg, 100 wt% basis. Prices of low temperature peroxides, eg, the liquid peroxydicarbonates and low temperature peroxyesters, are high, ie, >11/kg, 100 wt% basis, because they must be refrigerated during storage and shipment.

11. Analytical and Test Methods

Analytical methods for organic peroxides have been reviewed (248). The most general chemical analytical methods for organic peroxides involve the reduction of the peroxide group followed by the determination of the excess reducing agent or of the oxidized form of the reducing agent (249–252). The approximate order of organic peroxides in terms of decreasing ease of reduction, based on polarographic studies and reduction with iodide ion, is peroxyacids > diacyl peroxides > hydroperoxides > peroxydicarbonates > diperoxyketals > ozonides > peroxyesters > dialkylperoxides. There is no one general method of analysis

for all peroxides because of the various reactivity differences between classes and within each class.

The most commonly used reducing agent is iodide ion:



The liberated iodine, as the complex triiodide ion, may be titrated with standard thiosulfate solution. A general iodometric assay method for organic peroxides has been published (253). Some peroxyesters may be determined by ferric ion-catalyzed iodometric analysis or by cupric ion catalysis. The latter has become an ASTM Standard procedure (254). Other reducing agents are ferrous, titanous, chromous, stannous, and arsenite ions; triphenylphosphine; diphenyl sulfide; and triphenylarsine (255,256).

Polarography is a useful instrumental technique for analysis of peroxides that are irreversibly reduced at the mercury electrode, eg, hydroperoxides, peroxyesters, diacyl peroxides, and peroxydicarbonates (257–259). Examination of ir absorption bands in the carbonyl region and at $800 - 900 \text{ cm}^{-1}$ is useful for analysis of diacyl peroxides, peroxyesters, and peroxydicarbonates (260). Gas chromatography (gc) may be used to analyze thermally stable hydroperoxides, peroxyesters, diacyl peroxides, dialkyl peroxides, and their mixtures (261–263). Mass spectrometry, gc-mass spectrometry, nmr, and infrared and uv-absorption techniques are useful for structural characterization and analysis. Thin-layer, paper, and column chromatography are useful for identification and separation of peroxides in complex mixtures (264–267). High pressure liquid chromatography is excellent for the separation and analysis of peroxide mixtures, especially those containing components with low volatility or temperature sensitivity. A liquid chromatographic method for assaying dicumyl peroxide has been published (268).

There are many colorimetric methods used for trace analysis of peroxides using reagents such as ferrous ion, leuco base of methylene blue, *sym*-diphenylcarbohydrazide, titanium(IV), iodide ion, and *N,N*-dimethyl-*p*-phenylenediamine. The latter two are the most commonly used reagents (269,270).

12. Health and Safety Factors

12.1. Toxicology. In general, organic peroxides are characterized by a low order of acute toxicity. Most organic peroxides have some oxidizing properties and are irritants. Hydroperoxides, peroxyacids, ketone peroxides, and other peroxides with hydroperoxy groups generally are more irritating to the skin and eyes than peroxyesters, peroxydicarbonates, diacyl peroxides, or dialkyl peroxides. Hydroperoxides, MEKPs, and some other ketone peroxides are particularly injurious to eyes and can cause blindness (271,272). In contrast, most peroxyesters seem to be more irritating to the skin than the eye. Of the organic peroxides that have been evaluated for skin sensitization, only BPO has produced positive effects under specific conditions. Most of the available toxicity data on commercial organic peroxides are summarized in the literature (273,274).

Two studies conducted by the National Toxicology Program have suggested that effects after repeated administration are primarily due to the irritant nature of these materials. *tert*-Butyl peroxybenzoate, administered by gavage to rats and mice for up to 90 days, produced damage in the stomach with no systemic toxicity (275). A 45% formulation of MEKP in dimethyl phthalate applied to the skin of rats and mice for 13 weeks produced skin corrosion which was limited to the application site. Changes in the spleen and bone marrow were considered secondary responses to the ulcerative skin lesions (276). Occupational exposure to dicumyl peroxide in the atmosphere has been reported to produce nasal irritation and crusting with the appearance of visible blood vessels in the nose. These effects have also been reproduced in rabbits exposed by inhalation or by direct installation of this peroxide in the nose. Rats exposed to α -cumyl hydroperoxide by inhalation for 90 days had signs of irritation of the respiratory tract and mucous membranes (including eyes and noses) at 124 mg/m³. Exposures were terminated after five days due to excessive toxicity. No adverse effects were reported at 31 mg/m³ (277).

There is limited evidence to suggest that organic peroxides are carcinogenic. Generally, most studies have focused on the skin tumor promoting potential of these materials. For example, BPO does not seem to be a complete carcinogen, but can act as a promoter of skin tumors in mice treated with known initiating carcinogens. Similar findings have been reported for lauroyl peroxide and peroxybenzoic acid (278).

Several organic peroxides have been tested for mutagenicity in bacterial and animal cells, and in animals. In general, a variety of short-term screening studies have indicated that many organic peroxides are mutagenic when tested in bacterial and animal cells, but are not mutagenic when tested in whole animal studies. For example, *tert*-butyl hydroperoxide was mutagenic in the Ames test in mouse lymphoma assay, and produced chromosomal damage in Chinese hamster ovary cells, but did not demonstrate mutagenic activity in rat bone marrow after inhalation exposure for five days, and in a mouse dominant lethal study (274). Similar findings have been reported with MEKPs and *tert*-butyl peroxybenzoate (277,278).

12.2. Decomposition Hazards. The main causes of unintended decompositions of organic peroxides are heat energy from heating sources and mechanical shock, eg, impact or friction. In addition, certain contaminants, ie, metal salts, amines, acids, and bases, initiate or accelerate organic peroxide decompositions at temperatures at which the peroxide is normally stable. These reactions also liberate heat, thus further accelerating the decomposition. Commercial products often contain diluents that desensitize neat peroxides to these hazards. Commercial organic peroxide decompositions are low order deflagrations rather than detonations (279).

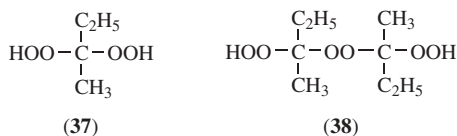
Methyl and ethyl hydroperoxides explode violently with heating or jarring, and their barium salts are extremely explosive in the dry state. The alkylidene peroxides that are derived from hydrogen peroxide and low molecular weight aldehydes or ketones are sensitive and explode violently. Polymeric peroxides are often sensitive, eg, the polymeric peroxide of dimethylketene [67772-28-5] explodes in the dry state when rubbed at -80°C. Owing to sensitivity and high energy potential, pure low molecular weight peroxyacids, ether peroxides, and

diacetyl, dimethyl, and dipropionyl peroxides should be handled only in small quantities and with extreme care.

Within each organic peroxide class, sensitivity to shock increases with increasing active oxygen content. Besides active oxygen content, sensitivity is also dependent on the heat of decomposition, the activation energy, and the decomposition kinetics. Some peroxides that usually are regarded as relatively nonhazardous under certain conditions may be highly hazardous under other conditions. For instance, α -cumyl hydroperoxide is quite thermally stable at room temperature. However, α -cumyl hydroperoxide decomposes violently when inadvertently contaminated with strong acids. In addition, many mixtures of organic compounds and aqueous hydrogen peroxide detonate upon initiation (280).

The organic peroxides and peroxide compositions produced commercially are those that can be manufactured, shipped, stored, and used safely. Organic peroxides can be thermally and mechanically desensitized by wetting or by dilution with suitable solvents, inert solid fillers, or insoluble liquids (suspension of solid peroxides in liquid plasticizers or water, and emulsions of liquid peroxides in water).

Dry BPO is hazardous. Desensitized BPO is commercially available in several solid forms, eg, wetted solid BPO compositions, wetted BPO pastes, and aqueous BPO dispersions. Because of the heat-absorbing capacity of interstitial water, wetted formulations are much more difficult to decompose or burn than comparable dry compositions having the same BPO concentration. The presence of small amounts of water in BPO significantly reduces its burning hazards. Commercial MEKP compositions contain two principal MEKP structures, (37) and (38), small amounts of free hydrogen peroxide, plasticizer solvents (commonly phthalates), and other solvents. Shipping of ketone peroxide solutions having more than 9 wt% active oxygen is unlawful.



Recommendations for safe handling and storage of commercial organic peroxides are available from organic peroxide manufacturers (25,26,281). Test methods have been developed for evaluating the hazards associated with the handling, storage, and transportation of organic peroxides, particularly commercial organic peroxide compositions. Many test methods are used to determine the labeling requirements for commercial organic peroxide compositions. Table 16 lists the important hazard tests used with commercial organic peroxides, references that describe the test methodologies and interpretation of results, and the relevance of the hazard testing with respect to requirements for handling, storage, shipping, and labeling.

In thermal stability tests, small samples of the peroxide composition are tested for various periods at several temperatures. The loss of activity is a guide in setting the maximum allowable storage and shipping temperature for

the commercial organic peroxide composition. The self-accelerating decomposition temperature (SADT) test is a refinement of the thermal stability test and is used to determine the maximum allowable storage and transportation temperature for an organic peroxide composition in a particular package size. The SADT is the lowest ambient (storage) temperature at which the product undergoes self-accelerating decomposition within seven days. Generally, the SADT decreases as the package size increases. Thus, the SADT is usually determined for a peroxide formulation in its largest commercial package. Because large-scale testing can destroy the test ovens, attempts have been made to develop smaller scale tests that would be less destructive and consume less product. The results of such small-scale tests have been used to reliably determine the SADT of a product in any type and size of package. Examples of small-scale tests include the adiabatic storage test (AST) (286), the isothermal storage test (IST) (287), and the Wärmestau Verfahren test (287,288). An attempt was made to use an accelerating rate calorimeter (ARC) for determining SADTs of peroxides (289).

A hazard classification system has been developed for organic peroxides, particularly commercial organic peroxide compositions. A numeric rating is assigned based on results of several tests including the pressure vessel test, the rapid heat test, the SADT test, the impact sensitivity test, the modified trauz block test, and the burning test (282).

To meet customer needs, organic peroxide producers have developed highly diluted solutions of organic peroxides that can be shipped in large bulk containers or tank trucks. The need for safe bulk shipping led to development of large-scale vent tests that determine the size and rating of venting devices for bulk containers. Vent testing of organic peroxide compositions was initially done on small-volume vessels (ca 20 mL) (72) and subsequently on larger volume vessels (121 and 10,000 L) (284,285).

In 1984 the United Nations (UN) Committee on the Transportation of Dangerous Goods, made up of experts from Prins Maurits Laboratory (TNO), Bundesanstalt für Materialprüfung (BAM), and the organic peroxide producers, developed a test procedure for the classification of organic peroxide compositions for transport purposes. The test procedure was accepted by most of the industrial countries of the world. The Department of Transportation (DOT) mandated that the United States peroxide industry would comply with the UN classification system by October 1993. The test scheme is used to assign each organic peroxide composition to one of seven hazard categories, A through G, with A being the most hazardous and G being exempt from regulations. The flow chart classification scheme for organic peroxides has been published (290).

Material Safety Data Sheets (MSDS) and the organic peroxides producers' recommendations should be followed carefully for handling and storage of organic peroxide compositions.

13. Uses

There are more than 100 commercially available organic peroxides in well over 300 formulations, eg, neat liquids and solids, and pastes, powders, solutions, dispersions, and emulsions, that have utility in many commercial applications

(13,14,14,21,22,24–26,44,98,99,208,209,291,292,292–305). Many of the commercially available peroxides are listed in Table 17 along with 10-h HLTs.

Excluding the peroxyacids, which are used primarily as epoxidizing and bleaching agents, approximately 90% of the commercial organic peroxides are consumed by the polymer industry. The 1993 consumption of organic peroxides in the United States and in the world according to peroxide type is given in Table 18. In 1993, more than 103,000 metric tons of organic peroxides were consumed in the world, more than 33,000 metric tons in the United States. The three primary producers of organic peroxides in the United States are Elf Atochem North America, Inc., AKZO, and Laporte Industries. In the world the leading producers are AKZO, Elf Atochem North America, Inc., and Laporte Industries. Other producers include Witco Chemical Corp., Hercules, Inc., Norac Co., Reichhold Chemicals, Inc., Freeman Resins, ARCO Chemical Co., Nippon Oil & Fats Co., and Sanken Kako.

Organic peroxides are used in the polymer industry as thermal sources of free radicals. They are used primarily to initiate the polymerization and copolymerization of vinyl and diene monomers, eg, ethylene, vinyl chloride, styrene, acrylic acid and esters, methacrylic acid and esters, vinyl acetate, acrylonitrile, and butadiene (see INITIATORS). They are also used to cure or cross-link resins, eg, unsaturated polyester–styrene blends, thermoplastics such as polyethylene, elastomers such as ethylene–propylene copolymers and terpolymers and ethylene–vinyl acetate copolymer, and rubbers such as silicone rubber and styrene–butadiene rubber.

The decomposition kinetics of an organic peroxide, as judged by 10-h HLT, largely determines the suitability of a particular peroxide initiator in an end use application (22). Other important factors are melting point, solubility, cost, safety, efficiency, necessity for refrigerated storage and shipment, compatibility with production systems, effects on the finished product, and potential for activation.

Free-radical reactions are accomplished using a variety of processes with different temperature requirements, eg, vinyl monomer polymerization and polymer modifications such as curing, cross-linking, and vis-breaking. Thus, the polymer industries are offered many different, commercial, organic peroxides representing a broad range of decomposition temperatures, as shown in Table 17 (19,22,31).

Organic peroxides also are used as flame-retardant synergists for polystyrene (306), for preparing block and graft copolymers, for reactive processing, for reducing the molecular weight of polypropylene (ie, controlled rheology or vis-breaking), for curing adhesives, for drying alkyd resin films, and for initiating cationic polymerization with cyclic ethers and maleic anhydride (44). Di- and triperoxides, which contain at least two peroxide moieties having different 10-h HLTs, decompose sequentially in the presence of vinyl monomers, yielding peroxy polymers and block copolymers (307,308). Organic peroxide initiators containing attached uv light absorbers, hindered amine light stabilizers (HALS), and antioxidants yield polymers to which uv-light stabilizer, HALS, and antioxidant groups are bound (309–311). Organic peroxides containing allyl groups have been used as molecular weight regulators in vinyl monomer polymerizations (312) and for attachment of epoxide groups to polymers and copolymers (313–315).

BPO is the preferred bleaching agent for flour and has been used to bleach gums, waxes, fats, and oils. It is the active ingredient in many acne medications. Diacyl peroxides have been used as burnout agents for acetate yarn, drying agents for Chinawood oils, and as free-radical sources in many organic syntheses (44). Di-*tert*-butyl peroxide is used as an ignition accelerator for diesel fuels and has been used in many organic syntheses either as a source of *tert*-butoxy (photo) or methyl (thermal) radicals.

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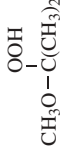


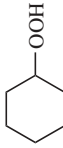
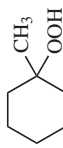
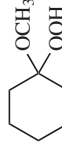


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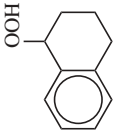
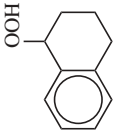
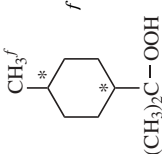
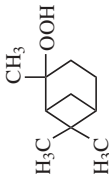
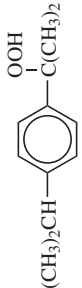
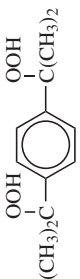
JOSE SANCHEZ

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Table 1. Properties of Some Alkyl Hydroperoxides^a

Hydro-peroxide	CAS Registry Number	Structure	Bp, °C (kPa) ^b	Mp, °C	<i>n</i> _D ²⁰
methyl	[3031-73-0]	CH ₃ -OOH	45.5–46.5 (24.53)		1.3654 ^c
ethyl	[3031-74-1]	C ₂ H ₅ -OOH	43–44 (6.67)		
isopropyl	[3031-75-2]	(CH ₃) ₂ CH-OOH	38–38.5 (2.67)		
<i>n</i> -butyl	[4813-50-7]	<i>n</i> -C ₄ H ₉ -OOH	40–42 (1.07)		1.4057
<i>sec</i> -butyl	[13020-06-9]	<i>sec</i> -C ₄ H ₉ -OOH	41–42 (1.47)		1.4050
<i>tert</i> -butyl	[75-91-2]	<i>t</i> -C ₄ H ₉ -OOH	33–42 (2.27)	4.0–4.5	1.3983 ^d
2-methoxy-2-propyl	[10027-74-4]		61–63 (2.40)		
<i>tert</i> -amyl	[3425-61-4]	<i>t</i> -C ₅ H ₁₁ -OOH	34–35 (0.93)		1.4120 ^d
1,1-di-methylpropynyl	[36566-81-1]		42 (2.27)		1.4418 ^e
3-hydroxy-1,1-di-methylbutyl	[66734-30-3]				
cyclohexyl	[766-07-4]		57 (0.16)	–20	1.4622
<i>n</i> -heptyl	[764-81-8]	<i>n</i> -C ₇ H ₁₅ -OOH	42–43 (0.008)	35.5	1.4269
3-ethyl-3-pentyl	[18428-34-7]	(C ₂ H ₅) ₃ C-OOH	71–73 (2.27)	2–3	1.4379
1-methyl-cyclo-hexyl	[4952-03-8]		38 (0.004)		1.4652
1-methoxy-cyclo-hexyl	[16580-35-1]		54.5–55 (0.027)		
ethylbenzene	[3071-32-7]		48.2 (0.027)		1.5265
1,1,3,3-tetra-methyl-butyl	[5809-08-5]		44–45 (0.12)		

2,5-di-methyl-2,5-di-hydro-peroxy-hexane	[3025-88-5]		105	
2,5-di-methyl-2,5-dihydro-droper-oxy-3-hex- yne	[3491-36-9]		107–109	1.5242
α -cumyl	[80-15-9]		60 (0.027)	
1,2,3,4-tetra-hydro-naph-thalene	[26447-24-5]		120–125 (0.027)	56
<i>p</i> -men-thane	[26762-92-5]			1.4558 ^g
pinane	[28324-52-9]			
<i>p</i> -diisopro-pylben-zene mono-hydro-perox- ide	[98-49-7]		57 (0.013)	33–34
<i>p</i> -diisopro-pylben-zene dihydro-peroxide	[3159-98-6]			140–141.5
stearyl	[56537-19-0]			49–50

^a Refs. 10 and 44.

^b To convert kPa to mm Hg, multiply by 7.5.

^c At 21°C.

^d At 25°C.

^e 94% assay material. Courtesy of Elf Atochem North America, Inc.

^f The OOH group may alternatively be at the positions marked by an asterisk.

^g At 25°C for 54% *p*-menthane in *p*-menthane.

Table 2. Properties of Some Dialkyl Peroxides^a


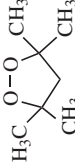
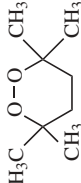

Dialkyl peroxide	CAS Registry number	Structure	Bp, °C (kPa) ^b	Mp, °C
dimethyl peroxide	[690-02-8]	<chem>CH3-OO-CH3</chem>	13.5 (98.66)	
perfluoro dimethyl peroxide	[927-84-4]	<chem>CF3-OO-CF3</chem>	-37 (101.32)	
diethyl peroxide	[628-37-5]	<chem>C2H5-OO-C2H5</chem>	62-63 (101.32)	
1,2-dioxane	[5703-46-8]		61.5 (14.67)	
<i>tert</i> -butyl methyl peroxide	[51392-67-7]	<chem>t-C4H9-OO-CH3</chem>	23 (2.53)	
<i>tert</i> -butyl 2-hydroxyethyl peroxide	[15476-85-4]	<chem>t-C4H9-OO-CH2CH2OH</chem>	37-38 (0.27)	
diisopropyl peroxide	[16642-57-2]	<chem>i-C3H7-OO-i-C3H7</chem>		14
3,3,5,5-tetramethyl-1,2-dioxolane	[22431-90-9]		55-58 (29.73), 46 (3.33)	
di- <i>tert</i> -butyl peroxide	[110-05-4]	<chem>t-C4H9-OO-t-C4H9</chem>	109 (101.32)	-18
perfluoro-di- <i>tert</i> -butyl peroxide	[26842-85-3]	<chem>(CF3)3C-OO-C(CF3)3</chem>	99 (101.32)	
3,3,6,6-tetramethyl-1,2-dioxane	[22431-89-6]		44-45 (1.5) ^c	-26c
di- <i>tert</i> -amyl peroxide	[10508-09-5]	<chem>t-C5H11-OO-t-C5H11</chem>	44 (1.33)	
<i>tert</i> -butyl <i>tert</i> -cumyl peroxide	[3457-61-2] [4741-24-6]	<chem>t-C4H9-OO-C(CH3)2C6H5</chem>	40 (0.027)	13
9,10-dihydro-9,10-epidioxyanthracene				120 ^d

Table 3. Properties of Some Organomineral Peroxides^a

Organomineral peroxide	CAS Registry number	Structure	Bp, °C (kPa) ^b	Mp, °C
diethoxy-aluminum <i>tert</i> -cumyl peroxide	[34914-67-5]	(C ₂ H ₅ O) ₂ Al-OO-C(CH ₃) ₂ -C ₆ H ₅		
tri (<i>tert</i> -butyl-peroxy)-borane	[22632-09-3]	(<i>t</i> -C ₄ H ₉ -OO) ₃ B	60–70 (0.0013)	113 dec 18
<i>tert</i> -butyl triethyl-germanium peroxide	[26452-74-4]	(C ₂ H ₅) ₃ Ge-OO- <i>t</i> -C ₄ H ₉	78 (1.87–2.0)	
dioxybis-[triethyl-germane]	[58468-05-6]	(C ₂ H ₅) ₃ Ge-OO-Ge(C ₂ H ₅) ₃	56–57 (0.0067)	
(<i>tert</i> -butyl-dioxy)triethyl-plumbane	[18594-12-6]	(C ₂ H ₅) ₃ Pb-OO- <i>t</i> -C ₄ H ₉		34–36 35–40
tetra(<i>tert</i> -butylperoxy)-silane	[10196-46-0]	(<i>t</i> -C ₄ H ₉ OO) ₄ Si	78 (0.067)	
dioxybis-[trimethyl-silane]	[5796-98-5]	(CH ₃) ₃ Si-OO-Si(CH ₃) ₃	36–38 (4.0)	
<i>tert</i> -butyl-peroxy-trimethyl-silane	[3965-63-7]	(CH ₃) ₃ Si-OO- <i>t</i> -C ₄ H ₉	78 (28.66)	
dioxybis-[triethyl-stannane]	[4403-63-8]	(C ₂ H ₅) ₃ Sn-OO-Sn(C ₂ H ₅) ₃	^c	60 ^c
<i>tert</i> -butyl-peroxy-trimethyl-stannane	[20121-56-6]	(CH ₃) ₃ Sn-OO- <i>t</i> -C ₄ H ₉	56 (1.60)	

^a Ref. 33.

^b To convert kPa to mm Hg, multiply by 7.5.

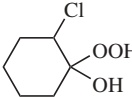
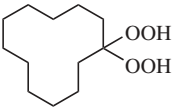
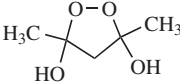
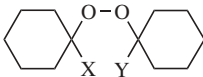
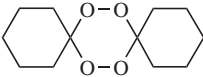
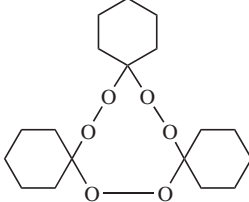
^c Explodes at 60°C.

Table 4. **Melting Points of Some Peroxy Compounds from Aldehydes and Hydrogen Peroxide^a**

Peroxy compound	CAS Registry number	R ¹	Mp, °C
<i>Structure (1)^b</i>			
hydroxymethyl hydroperoxide	[15932-89-5]	H	oil
1-hydroxyethyl hydroperoxide	[19393-68-1]	CH ₃	oil
2,2,2-trichloro-1-hydroxyethyl hydroperoxide	[77573-54-7]	CCl ₃	122
1-hydroxypentyl hydroperoxide	[77573-55-8]	<i>n</i> -C ₄ H ₉	oil
1-hydroxyoctyl hydroperoxide	[38279-15-1]	<i>n</i> -C ₇ H ₁₅	46
1-hydroxynonyl hydroperoxide	[34040-68-1]	<i>n</i> -C ₈ H ₁₇	50–54
<i>Structure (2)^b</i>			
di(hydroxymethyl) peroxide	[17088-73-2]	H	63–64
di(1-hydroxyethyl) peroxide	[77573-56-9]	CH ₃	
di(2,2,2-trichloro-1-hydroxyethyl) peroxide	[20614-22-6]	CCl ₃	
di(1-hydroxypentyl) peroxide	[35079-48-2]	<i>n</i> -C ₄ H ₉	72
di(1-hydroxyoctyl) peroxide	[57335-83-8]	<i>n</i> -C ₇ H ₁₅	
di(1-hydroxynonyl) peroxide	[57702-06-4]	<i>n</i> -C ₈ H ₁₇	

^a Refs. 4 and 44.^b See Fig. 1; R² = R³ = H and X = Y = OH.

Table 5. **Melting Points of Some Peroxy Compounds from Ketones and Hydrogen Peroxide^a**

Peroxy compound	CAS Registry number	Structure	Mp, °C
2-chloro-1-hydroperoxy-cyclohexanol ^b	[15250-08-5]		76
1,1-dihydroperoxycyclo-dodecane ^c	[16623-96-4]		140
3,5-dihydroxy-3,5-dimethyl-1,2-dioxolane ^d	[37187-22-7]		90–91
di(1-hydroxycyclohexyl) peroxide ^e	[2407-94-5]	 (6) X = Y = OH	69–71
1-hydroxycyclohexyl 1-hydroperoxycyclohexyl peroxide	[78-18-2]	(6) X = OH Y = OOH	76–77
di(1-hydroperoxycyclohexyl) peroxide	[2699-12-9]	(6) X = Y = OOH	82–83
di(2-hydroperoxy-2-butyl) peroxide	[126-76-1]	(2) R ¹ = CH ₃ R ² = C ₂ H ₅ X = Y = OOH	39–42
3,3,6,6-tetramethyl-1,2,4,5-tetroxane	[1073-91-2]	(4) R ¹ = R ² = CH ₃	131–133
3,6-diethyl-3,6-dimethyl-1,2,4,5-tetroxane	^f	(4) R ¹ = CH ₃ R ² = C ₂ H ₅	^f
7,8,15,16-tetraoxadispiro-[5.2.5.2]-hexadecane ^g	[183-84-6]		127–128
3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxononane	[17088-37-8]	(5) R ¹ = R ² = CH ₃	96–97
3,6,9-triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexoxononane	[24748-23-0]	(5) R ¹ = CH ₃ R ² = C ₂ H ₅	30–32
7,8,15,16,23,24-hexaoxatrispiro-[5.2.5.2.5.2] tetracosane ^h	[182-01-4]		93

^a Refs. (10,44), and 122.

^b Type (1) R¹ and R² are the ring; R³ = H; X = OH.

^c Type (1) R¹ and R² are the ring; R³ = H; X = OOH.

^d Type (2) R¹ = CH₃; R² is -CH₂-; X = Y = OH.

^e Structure (6) is type (2) wherein R¹ and R² are the ring and X and Y are specified.

^f The cis compound CAS Registry Number is [33817-91-3] with an mp of 12–14°C; the CAS Registry Number for the trans compound is [33817-92-4], mp 23–25°C.

^g Type (4) R¹ and R² are the ring.

^h Type (5) R¹ and R² are the ring.

Table 6. Boiling Points of Some Hydroxyalkyl Alkyl Peroxides^a


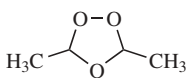
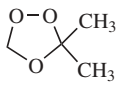
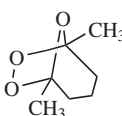
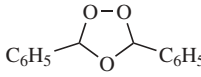
Hydroxyalkyl alkyl peroxide	CAS Registry number	R ³	R ¹	Bp, °C (kPa) ^b
hydroxymethyl methyl peroxide	[40116-50-5]	CH ₃	H	45 (2.27)
<i>tert</i> -butyl hydroxy-methyl peroxide	[17742-78-8]	<i>t</i> -C ₄ H ₉	H	52–53 (1.07)
1-hydroxyethyl methyl peroxide	[28567-26-2]	CH ₃	CH ₃	25–27 (2.27)
1-hydroxyethyl ethyl peroxide	[28567-28-4]	C ₂ H ₅	CH ₃	48–50 (8.67)
<i>tert</i> -butyl 1-hydroxy-ethyl peroxide	[4202-06-6]	<i>t</i> -C ₄ H ₉	CH ₃	30–31.5 (0.13)
<i>tert</i> -butyl 1-hydroxy-butyl peroxide	[13258-56-5]	<i>t</i> -C ₄ H ₉	<i>n</i> -C ₃ H ₇	34–37 (0.13)

^a Figure 1, structure (1), R² = H; X = OH; R¹ and R³ are specified.^b To convert kPa to mm Hg, multiply by 7.5.Table 7. Boiling Points of Some Diperoxyketals^a

Diperoxyketal	CAS Registry number		Bp, °C (kPa) ^b
2,2-di(<i>t</i> -butyl-peroxy) propane	[4262-61-7]	$t\text{-C}_4\text{H}_9\text{-OO}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-OO-}t\text{-C}_4\text{H}_9$	69–70 (2.0)
2,2-di(<i>t</i> -amyl-peroxy) propane	[3052-70-8]	$t\text{-C}_5\text{H}_{11}\text{-OO}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-OO-}t\text{-C}_5\text{H}_{11}$	68 (0.17)
2,2-di(<i>t</i> -butyl-peroxy) butane	[2167-23-9]	$t\text{-C}_4\text{H}_9\text{-OO}-\overset{\text{CH}_3}{\underset{\text{C}_2\text{H}_5}{\text{C}}}\text{-OO-}t\text{-C}_4\text{H}_9$	50 (0.27)
1,1-di(<i>t</i> -butyl-peroxy)cyclo-hexane	[3006-86-8]	$t\text{-C}_4\text{H}_9\text{-OO}-\overset{(\text{CH}_2)_5}{\underset{\text{R}^2}{\text{C}}}\text{-OO-}t\text{-C}_4\text{H}_9$	52–54 (0.02)
2,2-bis[4,4-di(<i>t</i> -butyl-peroxy)cyclo-hexyl]-propane	[1705-60-8]	$\left[\begin{array}{c} (\text{CH}_3)_3\text{COO} \\ (\text{CH}_3)_3\text{COO} \end{array} \right] \text{Cyclohexyl} \text{C(CH}_3)_2$	117–120 ^c

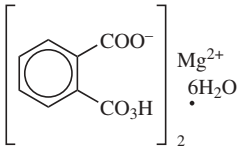
^a Refs. 4 and 44.^b To convert kPa to mm Hg, multiply by 7.5.^c Mp, °C; Ref. 72.

Table 8. **Boiling Points of Some 1,2,4-Trioxolanes**^a

1,2,4-Trioxolanes	CAS Registry number	Structure	Bp, °C (kPa) ^b
1,2,4-trioxolane	[289-14-5]		18 (2.13)
3,5-dimethyl-1,2,4-trioxolane	[765-57-1]		15 (2.67)
3,3-dimethyl-1,2,4-trioxolane	[22409-33-2]		42–42.5 (18.67)
1,5-dimethyl-6,7,8-trioxabicyclo [3.2.1] octane	[19987-14-5]		58.8 (2.0)
3,5-diphenyl-1,2,4-trioxolane	[23888-15-5]		

^a Secondary ozonides (4,44).^b To convert kPa to mm Hg, multiply by 7.5.

Table 9. Properties of Some Organic Peroxyacids^a

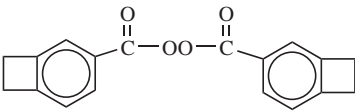
Peroxyacid	CAS Registry number	Structure	Mp, °C
peroxyformic acid	[107-32-4]	HCO ₃ H	−18 ^{b,c,d}
peroxyacetic acid	[79-21-0]	CH ₃ CO ₃ H	0
peroxypropionic acid	[4212-43-5]	C ₂ H ₅ CO ₃ H	−13 ^e
peroxybutyric acid	[13122-71-9]	<i>n</i> -C ₃ H ₇ CO ₃ H	−10 ^f
monoperoxy succinic acid	[3504-13-0]	HO ₂ C(CH ₂) ₂ CO ₃ H	107, dec
peroxyhexanoic acid	[5106-46-7]	<i>n</i> -C ₅ H ₁₁ CO ₃ H	15 ^g
peroxybenzoic acid	[93-59-4]	C ₆ H ₅ CO ₃ H	41–42
<i>m</i> -chloroperoxybenzoic acid	[937-14-4]	<i>m</i> -Cl-C ₆ H ₄ CO ₃ H	88
diperoxyhexanedioic acid	[5824-51-1]	HO ₃ C(CH ₂) ₄ CO ₃ H	116–117, dec
peroxyoctanoic acid	[33734-57-5]	<i>n</i> -C ₇ H ₁₅ CO ₃ H	31
4-methylperoxybenzoic acid	[937-21-3]	4-CH ₃ C ₆ H ₄ CO ₃ H	95–96
monoperoxyphthalic acid	[2311-91-3]	2-HO ₂ CC ₆ H ₄ CO ₃ H	110 ^c
peroxynonanoic acid	[3058-35-3]	<i>n</i> -C ₈ H ₁₇ CO ₃ H	35
peroxycinnamic acid	[16667-07-5]	C ₆ H ₅ CH=CHCO ₃ H	67–68, dec
diperoxy nonanedioic acid	[1941-79-3]	HO ₃ C(CH ₂) ₇ CO ₃ H	90
peroxydecanoic acid	[14156-10-6]	<i>n</i> -C ₉ H ₁₉ CO ₃ H	41
diperoxydecanedioic acid	[5796-85-0]	HO ₃ C(CH ₂) ₈ CO ₃ H	98
peroxydodecanoic acid	[2388-12-7]	<i>n</i> -C ₁₁ H ₂₃ CO ₃ H	50
peroxytetradecanoic acid	[19816-73-0]	<i>n</i> -C ₁₃ H ₂₇ CO ₃ H	56
peroxyhexadecanoic acid	[7311-29-7]	<i>n</i> -C ₁₅ H ₃₁ CO ₃ H	61
peroxyoctadecanoic acid	[5796-86-1]	<i>n</i> -C ₁₇ H ₃₅ CO ₃ H	65
magnesium monoperoxyphthalate hexahydrate	[84665-66-7]		93

^a Refs. 44 and 165.^b 90 wt % melts at the given temperature.^c Bp = 50° C at 13.33 kPa^d^d To convert kPa to mm Hg, multiply by 7.5.^e Bp = 25° C at 1.6 kPa^d for peroxyacetic acid, and 2.67 kPa^d for peroxypropionic acid.^f Bp = 26 – 29° C at 1.6 kPa^d.^g Bp = 41 – 43° C at 0.067 kPa^d.

Table 10. Properties of Some Diacyl Peroxides^a

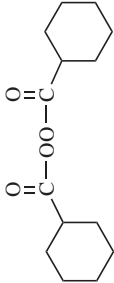
Diacyl peroxide	CAS Registry number	R group	Mp, °C ^b
<i>Symmetrical, R¹ = R²</i>			
diacetyl peroxide	[110-22-5]	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	30
di(chloroacetyl) peroxide	[14295-66-0]	$\text{H}_2\text{CCl}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{ClCH}_2$	85
dipropionyl peroxide	[3248-28-0]	$\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$	oil
diisobutyryl peroxide	[3437-84-1]	$i\text{-C}_3\text{H}_7-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-i\text{-C}_3\text{H}_7$	80–80.5
di(3-carboxypropio- nyl) peroxide	[123-23-9]	$(\text{H}_2\text{C})_2\text{CO}_2\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{HO}_2\text{C}(\text{CH}_2)_2$	132–133
dipentanoyl peroxide	[925-19-9]	$n\text{-C}_4\text{H}_9-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-n\text{-C}_4\text{H}_9$	oil
di(4-carboxybutyryl) peroxide	[10195-54-7]	$(\text{H}_2\text{C})_3\text{CO}_2\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{HO}_2\text{C}(\text{CH}_2)_3$	104
di(2-furanylcarbo- nyl) peroxide	[22023-27-4]		86–87
di(2-thienylcarbo- nyl) peroxide	[30930-49-5]		92–93
dinicotinoyl peroxide	[13689-05-9]	$\text{NC}_5\text{H}_4\text{-cyclo-3}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}\text{-3-cyclo-C}_5\text{H}_4\text{N}$	88–89
diheptanoyl peroxide	[869-90-9]	$n\text{-C}_6\text{H}_{13}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-n\text{-C}_6\text{H}_{13}$	
di(cyclohexylcarbo- nyl) peroxide	[4904-55-6]	$\text{C}_6\text{H}_{11}\text{-cyclo}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}\text{-cyclo-C}_6\text{H}_{11}$	oil
dibenzoyl peroxide	[94-36-0]	$\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$	106–107
di(4-chlorobenzoyl) peroxide	[94-17-7]	$\text{C}_6\text{H}_4\text{Cl-4}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}\text{-4-ClC}_6\text{H}_4$	137–138
di(4-nitrobenzoyl) peroxide	[1712-84-1]	$\text{C}_6\text{H}_4\text{O}_2\text{N-4}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}\text{-4-NO}_2\text{C}_6\text{H}_4$	157–158
di(2-methylbenzoyl) peroxide	[3034-79-5]	$\text{C}_6\text{H}_4\text{H}_3\text{C-2}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}\text{-2-CH}_3\text{C}_6\text{H}_4$	54
di(2-carboxybenzoyl) peroxide	[37051-42-6]	$\text{C}_6\text{H}_4\text{CO}_2\text{H-2}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}\text{-2-HO}_2\text{CC}_6\text{H}_4$	156
dioctanoyl peroxide	[762-16-3]	$n\text{-C}_7\text{H}_{15}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-n\text{-C}_7\text{H}_{15}$	29

Table 10. (Continued)

Diacyl peroxide	CAS Registry number	R group	Mp, °C ^b
di(phenylacetyl) peroxide	[14666-76-3]	$\text{H}_2\text{CC}_6\text{H}_5-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5\text{CH}_2$	41
dinonanoyl peroxide	[762-13-0]	$n\text{-C}_8\text{H}_{17}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-n\text{-C}_8\text{H}_{17}$	13.0–13.5
di(3,5,5- trimethylhexa- nonyl) peroxide	[3851-87-4]	$\text{H}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CC}(\text{H}_3\text{C})_3-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$	
dicinnamoyl peroxide	[15036-31-4]	$\text{HC}=\text{HCC}_6\text{H}_5-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5\text{CH}=\text{CH}$	133–134
di(benzocyclobu- tene-4- carbonyl) peroxide	[153213-06-0]		130–132 ^e
didecanoyl peroxide	[762-12-9]	$n\text{-C}_9\text{H}_{19}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-n\text{-C}_9\text{H}_{19}$	44–45
di(2-naphthaleny carbonyl) peroxide	[38512-20-8]	$\text{C}_{10}\text{H}_7-2-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-2-\text{C}_{10}\text{H}_7$	138–140
didodecanoyl perox- ide	[105-74-8]	$n\text{-C}_{11}\text{H}_{23}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-n\text{-C}_{11}\text{H}_{23}$	54.7–55
dihexadecanoyl per- oxide	[2697-96-3]	$n\text{-C}_{15}\text{H}_{31}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-n\text{-C}_{15}\text{H}_{31}$	71.4–71.9
dioctadecanoyl per- oxide	[3273-75-4]	$n\text{-C}_{17}\text{H}_{35}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-n\text{-C}_{17}\text{H}_{35}$	76.5–76.9
<i>Unsymmetrical, R¹ = CH₃; R² as given</i>			
acetyl propionyl peroxide	[13043-82-8]	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_2\text{H}_5$	
acetyl cyclohexyl carbonyl peroxide	[3901-10-8]	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{cyclo-C}_6\text{H}_{11}$	42
acetyl benzoyl per- oxide	[644-31-5]	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5$	37–39
adipoyl bis(acetyl peroxide)	[6039-32-3]	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2\text{COOC}(\text{CH}_2)_4$	61–62

^a Refs. 44 and 187.^b Most of these peroxides decompose on melting, some violently.^c $n_{\text{D}}^{25} = 1.4340$.^d $n_{\text{D}}^{20} = 1.4382$ ^e Ref. 189.^f $n_{\text{D}}^{20} = 1.4069$

Table 11. Properties of Some Dialkyl Peroxydicarbonates^a

	CAS Registry number	R ¹	n _D ²⁰	Mp, °C ^b
diethyl peroxydicarbonate	[14666-78-5]	$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{OC}_2\text{H}_5$	1.4065	
di- <i>n</i> -propyl peroxydi-carbonate	[16066-38-9]	$n\text{-C}_3\text{H}_7\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-n\text{-C}_3\text{H}_7$	1.4091	
diisopropyl peroxydicarbonate	[105-64-6]	$i\text{-C}_3\text{H}_7\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-i\text{-C}_3\text{H}_7$	1.4034	8–10
dibutyl peroxydicarbonate	[16215-49-9]	$n\text{-C}_4\text{H}_9\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-n\text{-C}_4\text{H}_9$	1.4129	
di- <i>sec</i> -butyl peroxydicarbonate	[19910-65-7]	$\text{C}_4\text{H}_9\text{-}sec\text{-O}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{O-}sec\text{-C}_4\text{H}_9$	1.4112	
dicyclohexyl peroxydicarbonate	[1561-49-5]			46
dibenzyl peroxydicarbonate	[2144-45-8]	$\text{H}_2\text{CC}_6\text{H}_5\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{OC}_6\text{H}_5\text{CH}_2$		101–102
di(2-ethylhexyl) peroxydicarbonate	[16111-62-9]	$\text{C}_2\text{H}_5\text{CH}(\text{H}_2\text{C})_3\text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3(\text{CH}_2)_3\text{CHCH}_2$ C_2H_5	1.4366	
di(2-phenoxyethyl) peroxydicarbonate	[41935-39-1]	$\text{H}_2\text{CH}_2\text{COC}_6\text{H}_5-\overset{\text{O}}{\parallel}\text{C}-\text{OO}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2$		97–100 ^c

di(<i>cis</i> -3,3,5-trimethylcyclohexyl) peroxydicarbonate	[31314-19-9]		78–79 ^d
di(4- <i>tert</i> -butylcyclohexyl) peroxydicarbonate	[15520-11-3]		91–92 ^{e,f}
di(isobornyl) peroxydicarbonate	[40716-59-4]		92–93 ^e
didodecyl peroxydicarbonate	[24356-04-5]		28–30
ditetradecyl peroxydicarbonate	[53220-22-7]		40–42
dihexadecyl peroxydicarbonate	[26322-14-5]		50–53 ^g

^a Refs. (18,44), and 187.

^b All of the listed peroxides are unstable in the liquid state above ca 20°C; some decompose violently.

^c Ref. 190.



^d Ref. 191.

^e Ref. 192.

^f Ref. 193.

^g Ref. 194.

Table 12. Melting Points of Some Organosulfonyl Peroxides^a

Organo-sulfonyl peroxide	CAS Registry number	Structure	Mp, °C ^b
di(methane-sulfonyl) peroxide	[1001-62-3]	$\text{CH}_3\text{--S(O)}_2\text{--O--}]_2\text{--}$	77
acetyl <i>tert</i> -butane-sulfonyl peroxide	[26305-18-0]	$t\text{-C}_4\text{H}_9\text{--S(O)}_2\text{--OO--}\overset{\text{O}}{\parallel}\text{CCH}_3$	35–37 ^{c,d}
acetyl cyclo-hexane-sulfonyl peroxide	[3179-56-4]		35–36 ^d
acetyl <i>sec</i> -heptane-sulfonyl peroxide	[33970-43-3]	$\text{sec-C}_7\text{H}_{15}\text{S(O)}_2\text{--OO--}\overset{\text{O}}{\parallel}\text{CCH}_3$	liquid ^e
acetyl (1-methy-cyclo-hexane)-sulfonyl peroxide	[32666-40-3]		liquid ^e
di(benzene-sulfonyl) peroxide	[29342-61-8]	$[\text{C}_6\text{H}_5\text{--S(O)}_2\text{--O--}]_2\text{--}$	53–54
di(<i>p</i> -toluene-sulfonyl) peroxide	[1886-68-6]	$[p\text{-CH}_3\text{--C}_6\text{H}_4\text{--S(O)}_2\text{--O--}]_2\text{--}$	50

^a Refs. 33 and 44.^b Most of the listed peroxides decompose at mp; some decompose violently.^c Ref. 195.^d Ref. 196.^e Ref. 197.

Table 13. Properties of Some *tert*-Alkyl Peroxyesters^a

Name	CAS Registry number	R	Mp, °C	Bp, °C (kPa) ^b
<i>tert</i> -butyl peroxy-formate	[819-50-1]	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$		28.3 (1.33)
<i>tert</i> -butyl peroxy-carbamate	[18389-96-3]	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{NC}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$	51	
<i>tert</i> -butyl peroxy-acetate	[107-71-1]	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$		22 (0.133)
<i>tert</i> -butyl <i>N,N</i> -di-methyl peroxy-carbamate	[42930-04-1]	$\begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3)_2\text{NC}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$		43–45 (0.013–0.027)
<i>tert</i> -butyl peroxyiso-butyl-rate	[109-13-7]	$\begin{array}{c} \text{O} \\ \parallel \\ i\text{-C}_3\text{H}_7\text{C}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$	45.7	
<i>OO</i> - <i>tert</i> -butyl <i>O</i> -isopropyl mono-peroxy-carbonate	[2372-21-6]	$\begin{array}{c} \text{O} \\ \parallel \\ i\text{-C}_4\text{H}_7\text{OC}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$		52–55 (0.133)
<i>OO</i> - <i>tert</i> -butyl <i>O</i> -hydrogen mono-peroxy-maleate	[1931-62-0]	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}_2\text{CCH}=\text{CHC}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$	114–116	
<i>tert</i> -butyl peroxy-pivalate	[927-07-1]	$\begin{array}{c} \text{O} \\ \parallel \\ t\text{-C}_4\text{H}_9\text{C}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$	oil	
di- <i>tert</i> -butyl diperoxy-carbonate	[3236-56-4]	$\begin{array}{c} \text{O} \\ \parallel \\ t\text{-C}_4\text{H}_9\text{OOC}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$		54–55 (0.067)
di- <i>tert</i> -butyl diperoxy-oxalate	[1876-22-8]	$\begin{array}{c} \text{O} \\ \parallel \\ t\text{-C}_4\text{H}_9\text{OO}-\text{C}(\text{O})\text{C}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$	50.5–51.5°	
<i>tert</i> -butyl cyclo-hexane peroxy-carboxylate	[20396-49-0]	$\begin{array}{c} \text{O} \\ \parallel \\ \text{cyclo-C}_6\text{H}_{11}\text{C}-\text{OO}-\text{C}(\text{CH}_3)_3 \end{array}$		83–89 (4.0–4.67)

Table 13. (Continued)


Name	CAS Registry number	R	Mp, °C	Bp, °C (kPa) ^b
<i>tert</i> -butyl peroxybenzoate	[614-45-9]	$\text{C}_6\text{H}_5\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	8	75–77 (0.267)
<i>tert</i> -butyl 2-ethyl- peroxy-hexanoate	[3006-82-4]	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	< –30	
<i>tert</i> -butyl 2-phenyl- peroxy-acetate	[3377-89-7]	$\text{C}_6\text{H}_5\text{CH}_2\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	oil	
<i>tert</i> -butyl 2-carboxy- peroxy-benzoate	[15042-77-0]	$2\text{-HO}_2\text{CC}_6\text{H}_4\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	104–104.5	
<i>tert</i> -butyl peroxy-nanoate	[22913-02-6]	$n\text{-C}_8\text{H}_{17}\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$		52–55 (0.0013)
<i>tert</i> -butyl peroxydecanoate	[16474-36-5]	$n\text{-C}_9\text{H}_{19}\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	–6.5	
di- <i>tert</i> -butyl diperoxy-adi- pate	[22158-52-7]	$t\text{-C}_4\text{H}_9\text{OO}-\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_2)_4\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	42–43	
<i>tert</i> -butyl 1-naph- thalene-peroxy-carboxy- late	[13061-74-0]		53–55	
di- <i>tert</i> -butyl diperoxy- phthalate	[2155-71-7]	$2\text{-(}t\text{-C}_4\text{H}_9\text{OO}-\text{C}(=\text{O})\text{OO}-\text{C}_6\text{H}_4\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	57.0–57.5	
<i>tert</i> -butyl 2,2-diphenyl- peroxy-acetate	[13144-32-6]	$(\text{C}_6\text{H}_5)_2\text{CHC}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	58.2–60	
<i>tert</i> -butyl peroxy-stearate	[2123-89-9]	$n\text{-C}_{17}\text{H}_{35}\text{C}(=\text{O})\text{OO}-\text{C}(\text{CH}_3)_3$	38.9–39.3	

Table 14. *tert*-Butyl Areneperoxysulfonates^a

Benzeneperoxy sulfonate	CAS Registry number	Structure	Mp, °C
<i>tert</i> -butyl benzeneperoxy sulfonate	[18637-19-9]	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{S}-\text{OO}-t\text{-C}_4\text{H}_9 \\ \parallel \\ \text{O} \end{array}$	^b
<i>tert</i> -butyl <i>p</i> -chloro-benzeneperoxy sulfonate	[77482-48-5]	$\begin{array}{c} \text{O} \\ \parallel \\ p\text{-Cl-C}_6\text{H}_4\text{S}-\text{OO}-t\text{-C}_4\text{H}_9 \\ \parallel \\ \text{O} \end{array}$	30–35 ^c
<i>tert</i> -butyl <i>p</i> -methyl-benzeneperoxy sulfonate	[77482-49-6]	$\begin{array}{c} \text{O} \\ \parallel \\ p\text{-CH}_3\text{-C}_6\text{H}_4\text{S}-\text{OO}-t\text{-C}_4\text{H}_9 \\ \parallel \\ \text{O} \end{array}$	36.5–37
<i>tert</i> -butyl <i>p</i> -methoxy-benzeneperoxy sulfonate	[77482-50-9]	$\begin{array}{c} \text{O} \\ \parallel \\ p\text{-CH}_3\text{O-C}_6\text{H}_4\text{S}-\text{OO}-t\text{-C}_4\text{H}_9 \\ \parallel \\ \text{O} \end{array}$	47 ^c

^a Refs. 33 and 44.^b $n_D^{25} = 1.4629$.^c Explodes at mp.Table 15. Effect of *tert*-Alkyl Peroxyester Structure on 10-h HLT, R-C(O)-OO-R'^a

R	CAS Registry number	10-h HLT, °C (solvent)
C ₆ H ₅ -C(O)-OO- <i>t</i> -C ₄ H ₉	[614-45-9]	104 (dodecane)
CH ₃ -C(O)-OO- <i>t</i> -C ₄ H ₉	[107-71-1]	102 (decane)
(CH ₃) ₂ CHO-C(O)-OO- <i>t</i> -C ₄ H ₉	[2372-21-6]	99 (benzene)
(CH ₃) ₂ CH-C(O)-OO- <i>t</i> -C ₄ H ₉	[109-13-7]	82 (dodecane)
(CH ₃) ₃ C-C(O)-OO- <i>t</i> -C ₄ H ₉	[927-07-1]	58 (TCE) ^b
C ₆ H ₅ CH ₂ -C(O)-OO- <i>t</i> -C ₄ H ₉	[3377-89-7]	66 (chlorobenzene) ^c
(C ₆ H ₅) ₂ CH-C(O)-OO- <i>t</i> -C ₄ H ₉	[13144-32-6]	37 (cumene) ^d
(C ₆ H ₅) ₃ C-C(O)-OO- <i>t</i> -C ₄ H ₉	[10357-71-8]	11 (cumene) ^e
<i>t</i> -C ₉ H ₁₉ -C(O)-OO- <i>t</i> -C ₄ H ₉	[26748-41-4]	48 (TCE)
<i>t</i> -C ₉ H ₁₉ -C(O)-OO- <i>t</i> -C ₄ H ₉	[68299-16-1]	46 (TCE)
<i>t</i> -C ₉ H ₁₉ -C(O)-OO- <i>t</i> -C ₄ H ₉ ^f	[51240-95-0]	44 (TCE)
<i>t</i> -C ₉ H ₁₉ -C(O)-OO- <i>t</i> -C ₄ H ₉	[26748-47-0]	38 (TCE)
<i>t</i> -C ₉ H ₁₉ -C(O)-OO- <i>t</i> -C ₄ H ₉	[95718-78-8]	37 (TCE)
<i>t</i> -C ₄ H ₉ -OO-C(O)-C(O)-OO- <i>t</i> -C ₄ H ₉	[1876-22-8]	26 (benzene) ^g

^a From or calculated from Ref. 22 unless otherwise noted.^b Trichloroethylene.^c Ref. 233.^d Ref. 234.^e Ref. 235.^f 1,1,3,3-Tetramethylbutyl.^g Ref. 222.

Table 16. Hazard Tests for Organic Peroxides^a

Hazard test	Test relevant to: ^b
impact sensitivity	H
burning test	H,S
SETA flash point ^c	H,S,L
pressure vessel test	H,S,T
rapid heat test	H
self-accelerating decomposition temperature (SADT) test	H,S,T,L
modified trauzl block test	H,S,T
thermal stability test	H,S,T
bulk vent tests ^d	H,S,T

^a Ref. 282, unless otherwise noted.^b H = handling, S = storage, T = transportation, and L = labeling.^c Ref. 283.^d Refs. 284 and 285.

Table 17. 10-h HLTs of Commercial Organic Peroxides^a

Organic peroxide	CAS Registry number	10-h HLT, ^b °C	Reference
diisobutyl peroxide	[3437-84-1]	21 (B); 25 (TCE)	72
3-hydroxy-1,1-dimethylbutyl peroxyneodecanoate	[95718-78-8]	37 (TCE)	22
<i>tert</i> -cumylperoxyneodecanoate	[26748-47-0]	38 (TCE)	22
<i>OO-tert</i> -butyl <i>O</i> -docosyl monoperoxyoxalate	[116753-76-5]	38	223
acetyl cyclohexanesulfonyl peroxide	[3179-56-4]	31 (B); 40 (TCE)	209
3-hydroxy-1,1-dimethylbutyl peroxyneohexanoate	[110972-57-1]	41 (AMS)	22
<i>tert</i> -cumyl peroxyneohexanoate	[104852-44-0]	43 (TCE)	22
<i>tert</i> -amyl peroxyneodecanoate	[68299-16-1]	46 (TCE)	22
<i>tert</i> -butyl peroxyneodecanoate	[26748-41-4]	48 (TCE)	22
di(2-ethylhexyl) peroxydicarbonate	[16111-62-9]	49 (TCE)	22
diisopropyl peroxydicarbonate	[105-64-6]	50 (TCE)	72
di(<i>sec</i> -butyl) peroxydicarbonate	[19910-65-7]	50 (TCE)	22
<i>tert</i> -amyl peroxyipivalate	[29240-17-3]	55 (TCE)	22
di(2,4-dichlorobenzoyl) peroxide	[133-14-2]	54 (B)	72
<i>tert</i> -butyl peroxyipivalate	[927-07-1]	58 (TCE)	22
di(3,5,5-trimethylhexanoyl) peroxide	[3851-87-4]	59 (B); 61 (TCE)	(72,22)
didecanoyl peroxide	[762-12-9]	61 (B); 65 (TCE)	(72,22)
didodecanoyl peroxide	[105-74-8]	62 (B); 64 (TCE)	(72,22)
2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy) hexane	[13052-09-0]	73 (DC)	22
diacetyl peroxide	[110-22-5]	69 (B)	72
<i>tert</i> -amyl 2-ethylperoxyhexanoate	[686-31-7]	75 (D)	22
<i>tert</i> -butyl 2-ethylperoxyhexanoate	[3006-82-4]	77 (D)	22
dibenzoyl peroxide (BPO)	[94-36-0]	73 (B)	22
<i>tert</i> -butyl peroxyisobutyrate	[109-13-7]	82 (D)	22
1,1-di(<i>tert</i> -amylperoxy)cyclohexane	[15667-10-4]	93 (D)	22
1,1-di(<i>tert</i> -butylperoxy)-3,3,5-trimethylcyclohexane	[6731-36-8]	96 (D)	22
1,1-di(<i>tert</i> -butylperoxy)cyclohexane	[3006-86-8]	97 (D)	22
<i>OO-tert</i> -butyl <i>O</i> -hydrogen monoperoxymaleate	[1931-62-0]	87 (AC)	22
<i>OO-tert</i> -butyl <i>O</i> -isopropyl monoperoxycarbonate	[2372-21-6]	99 (B)	22
<i>OO-tert</i> -butyl <i>O</i> -(2-ethylhexyl) monoperoxycarbonate	[34443-12-4]	100 (D)	22
2,5-di(benzoylperoxy)-2,5-dimethylhexane	[2618-77-1]	100 (B)	22
<i>tert</i> -butyl peroxy-3,5,5-trimethylhexanoate	[13122-18-4]	102 (B)	72
<i>tert</i> -amyl peroxyacetate	[690-83-5]	100 (D)	22

<i>tert</i> -amyl peroxybenzoate	[4511-39-1]	100 (D)	22
<i>tert</i> -butyl peroxyacetate	[107-71-1]	102 (DC)	22
<i>tert</i> -butyl peroxybenzoate	[614-45-9]	104 (D)	22
2,2-di(<i>tert</i> -butylperoxy)butane	[2167-23-9]	107 (D)	22
2,2-di(<i>tert</i> -amylperoxy)propane	[3052-70-8]	108 (D)	22
ethyl 3,3-di-(<i>tert</i> -amylperoxy)butyrate	[67567-23-1]	112 (D)	22
ethyl 3,3-di-(<i>tert</i> -butylperoxy)butyrate	[55794-20-2]	114 (D)	22
dicumyl peroxide	[80-43-3]	117 (DC)	22
1,3-di(α -(<i>tert</i> -butylperoxy)isopropyl)-benzene	[25155-25-3]	119 (D)	22
2,5-di(<i>tert</i> -butylperoxy)-2,5-dimethylhexane	[78-63-7]	120 (D)	22
di- <i>tert</i> -amyl peroxide	[10508-09-5]	123 (D)	22
di- <i>tert</i> -butylperoxide	[110-05-4]	129 (DC)	22
2,5-di(<i>tert</i> -butylperoxy)-2,5-dimethyl-3-hexyne	[1068-27-5]	131 (D)	22
<i>p</i> -menthane hydroperoxide	[26762-92-5]	133 (B) ^c	44
α -cumyl hydroperoxide	[80-15-9]	154 (B) ^c	296
<i>tert</i> -amyl hydroperoxide	[3425-61-4]	158 (B) ^c	296
<i>tert</i> -butyl hydroperoxide	[75-91-2]	165 (B) ^c	296
methyl ethyl ketone peroxide solutions	[1338-23-4]	172 (B) ^c	296
2,4-pentanedione peroxide solutions	[37187-22-7]	^d	292
peracetic acid	[79-21-0]	^e	292
3-chloroperoxybenzoic acid	[937-14-4]	^e	(34,165)
			18

^a General discussions of decomposition temperatures of organic peroxides are given in Refs. (14,21,22), and 44.

^b 0.2 M solution in the solvent indicated in parentheses: AC = acetone, AMS = α - methylstyrene, B = benzene, D = dodecane, DC = decane, EA = ethyl acetate, OMS = odorless mineral spirits, and TCE = trichloroethylene.

^c Hydroperoxides are generally used with reducing agents, eg, iron salts, in redox emulsion polymerization systems.

^d These peroxides are used with activators, eg, cobalt carboxylates, and half-life data are of little significance.

^e Used as an epoxidizing, oxidizing, or bleaching agent; half-life data are of little significance.

Table 18. **Estimated 1993 Consumption of Organic Peroxides by Principal Types,^a t**

Peroxide type	United States	Worldwide
diacyl peroxides	6,400	19,000
peroxydicarbonates	2,900	8,000
hydroperoxides ^b	1,700	5,500
dialkyl peroxides	4,100	13,000
methyl ethyl ketone peroxides	7,000	22,000
peroxyesters	9,300	29,000
peroxyketals and others	2,300	7,100
<i>Total</i>	<i>33,700</i>	<i>103,600</i>

^a Estimates from Elf Atochem North America, Inc.

^b Does not include hydroperoxides produced for captive use.

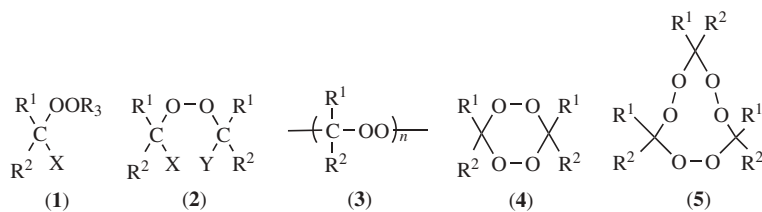


Fig. 1. Varieties of α -oxygen-substituted hydroperoxides and dialkyl peroxides. R^1 , R^2 , $R^3 = H$ or alkyl; X , $Y = OH$, OOH , OR^4 , $OSiR_3$, or OOR^5 ; R^4 , $R^5 = alkyl$; and R^3 and R^5 may also be acyl, $C(=O)R^6$.

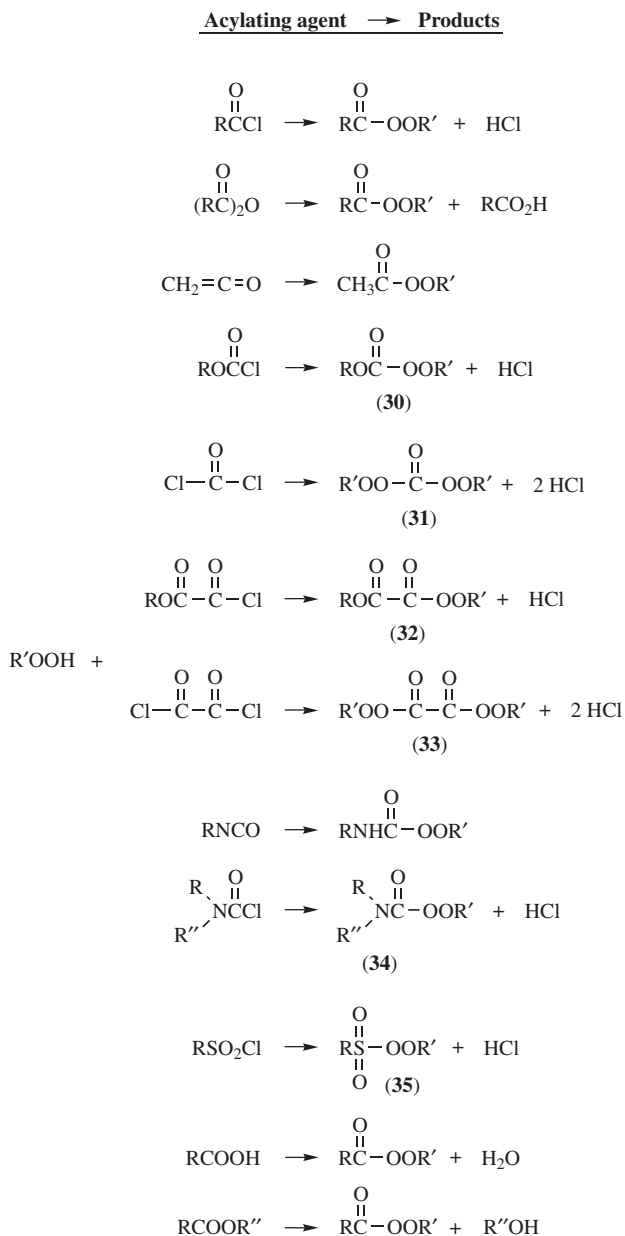


Fig. 2. Synthetic routes to alkyl peroxyesters. The acylating agent reacts with R'OOH in each case.