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Organic Peroxides of Alkali Metals (Alkali Salts of Hydroperoxides)

N.A.Sokolov and Yu.A.Aleksandrov

Methods of making non-solvated lithium, sodium, and potassium salts of hydroperoxides in hydrocarbon media are considered. Results on the kinetics and mechanism of thermal decomposition of alkali organic peroxides and the reactions of these compounds with alcohols, aldehydes, ketones, esters, and nitriles are discussed. The role of complex formation by the alkali salts of hydroperoxides with donors of protons and Lewis bases is considered. Methods of making organic and organoelemental peroxides based on salts of the hydroperoxides are discussed. 167 references.

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I. INTRODUCTION

Organic peroxides of Group I metals (salts of organic hydroperoxides) are peroxide compounds of the general formula ROOM, where R is an alkyl, aryl, or acyl radical, and M is a metal of Periodic Group I.[1] Organic peroxides (OP) of lithium, sodium, and potassium are now known. Analogous compounds of rubidium and caesium or of the metals of the copper subgroup have not been described.

Alkali metal OP's are of interest to investigators as starting materials for making the OP of elements of other groups[1-5], as intermediates in the autoxidation of organic derivatives of alkali metals, for the oxidation of hydrocarbons in the presence of alkalis, etc.

Ten years has elapsed since progress in the field of the chemistry of organic peroxides of the alkali metals was discussed[1]. This period has been marked by considerable range of investigations of metal-containing OP. Some of the results obtained for the OP are important in principle. All this has stimulated the preparation of the present review. It discusses, as far as possible, all the works on methods of synthesis and the investigation of the properties of the anhydrous OP, and also the kinetics and mechanism of conversion of salts of the hydroperoxides in aqueous or non-aqueous solutions. Works on the kinetics and mechanism of deformation decomposition of alkali salts of peroxo-acids and H_2O_2 are not included since this could be the subject of a special review.

II. METHODS OF PREPARATION

The simplest and most widely used method of making the alkali metal OP is based on the reaction of hydroperoxides with the metal hydroxide or alkoxide in aqueous or alcoholic solution respectively. This method is used widely for the separation and purification of hydroperoxides and in the preparation of dialkyl peroxides and esters of peroxo-acids. However, when hydroperoxides react with a hydroxide or alkoxide, usually crystalline solvates of hydroperoxide salts with water[6-9] or alcohol[10-12] are obtained. The water or alcohol cannot be removed completely from such solvates without decomposition of the initial peroxide.

Kharasch and coworkers[13] were the first to obtain sodium cumyl peroxide in hydrocarbon solution by reaction of the hydroperoxide with sodium or its amalgam. However, during this process 20-45% of the hydroperoxide, depending upon the nature of the solvent, was reduced to the alcohol and the alcohol and alkoxide formed are very difficult to separate from the sodium salt of the hydroperoxide. It seemed impossible to obtain the pure salt by this method[13,14]. A product containing 70-75% sodium cumyl peroxide was obtained by the reaction of cumyl hydroperoxide with metallic sodium in ether. The impurities were 1-methyl-1-phenylethanol (15-20%) and its alkoxide (10%).[14]

The alkali OP are formed as intermediates in the autoxidation of the corresponding organometallic compounds (OMC). However, the pure salt of the hydroperoxide usually also cannot be obtained by this method owing to its rapid reaction with the OMC [1]:

$$RM + O_2 \rightarrow ROOM \ ,$$
$$RM + ROOM \rightarrow 2ROM \ .$$

Peroxides were obtained in significant yield only in the oxidation of alkyl-lithium[15,16]. Thus the hydroperoxide was obtained in 28-67% yield in the autoxidation of butyllithium in ether or hydrocarbon solution at −75°C after hydrolysis of the lithium butyl peroxide formed[15,16]. 75-85% of the active oxygen was obtained in the autoxidation of indenyl-3-lithium in ether at −75°C.[16]

Non-solvated alkali metal OP were obtained by reaction of hydroperoxides with alkali metal amide, hydride, or t-butoxide at 0-20°C in an aprotic solution. Only slight reduction of the hydroperoxide took place. The gaseous products formed (ammonia, hydrogen) are easily removed; the solvent and t-butyl alcohol in the reaction with lithium t-butoxide) are also distilled off at reduced pressure[17].

The non-solvated salts were obtained from hydroperoxides by the action of lithium or sodium hydride in tetrahydrofuran or ether[18]:

$$ROOH + MH \rightarrow ROOM + H_2 \ .$$

It was shown, by the examples of the reactions of tetralin hydroperoxide [1,2,3,4-tetrahydro-1-naphthyl hydroperoxide] with NaH in ether, and also of peracetic acid with LiH and NaH in tetrahydrofuran, that here (unlike the reaction

of a hydroperoxide with a metal) it is not reduced [18]. However, it was recently noted [19] that when triphenylmethyl hydroperoxide reacts with NaH in ether the yield and purity of the sodium salt of the hydroperoxide are not very satisfactory.

Unlike peroxo-acids, the alkyl and arylalkyl hydroperoxides react very slowly with LiH at 20°C. Thus lithium hydride reacts rapidly, with evolution of heat, with perdecanoic acid [17], but for cumyl hydroperoxide the conversion is negligible even after 48 h.

The method most widely used for obtaining sodium and potassium OP is based on the reaction of a hydroperoxide with sodium [20-23] or potassium [24,25] amides in a hydrocarbon:

$$ROOH + MNH_2 \rightarrow ROOM + NH_3 .$$

Pure sodium cumyl and triphenylmethyl peroxides were obtained for the first time by this reaction as were their solutions in a hydrocarbon free from significant amounts of impurities (alkoxide, alcohol, or hydroperoxide). [22,23] Hydroperoxides react rapidly with ground sodium or potassium amide at 0–20°C. Removal of ammonia from the reaction mixture by reducing the pressure facilitates an increase in the reaction rate [23-25]. It is noteworthy that an alkali metal amide should not contain as impurities ions of variable-valency metals, which decompose hydroperoxides readily. Therefore amides obtained by the reaction of a metal with liquid ammonia in the presence of an iron salt should not be used. Sufficiently pure sodium and potassium amides are easily obtained by passing ammonia through molten alkali metal at 350°C. [23,26]

When cumyl hydroperoxide reacts with sodium amide in toluene the sodium salt which is formed passes into the solution. After the almost complete removal of the toluene at reduced pressure and the addition of ether large crystals of sodium cumyl peroxide containing 99.5–99.8% of the main substance is obtained [22]. This compound readily absorbs moisture in the air but in a sealed vessel at 0°C remains without appreciable decomposition for several months [22].

Belyaev and Nemtsov [14] obtained a complex of sodium cumyl peroxide with cumyl hydroperoxide ROONa.ROOH. Cryoscopy showed that at a concentration of 0.08 M the complex is a dimer $[ROONa.ROOH]_2$ but dissociates to the monomer during dilution. In the infrared spectrum of the complex (in CCl_4), in addition to the narrow band of the vibrations of the OH group in the 3500 cm^{-1} range there is a broad band 350 cm^{-1} away in the lower frequency range. The displacement of the band of the OH vibrations is due to the formation of a hydrogen bond. The monomer of the complex is formed due to the hydrogen bond and the dimer is due to dipole–dipole interaction [14].

The thermodynamics of dissociation of the complex ROONa.ROOH (where R is cumyl) into the initial components was investigated by NMR. [27] The temperature dependence of the chemical shift of the proton of the OOH group was used to calculate the heat of dissociation of the complex, 12.7 ± 1.0 kcal $mole^{-1}$. The energy of the hydrogen bond in the complex is three times that in the hydroperoxide associate.

Potassium cumyl and t-butyl peroxides, sodium t-butyl peroxide, and also their complexes with hydroperoxide [24,25,28] have been obtained. Potassium t-butyl peroxide and its complex with the hydroperoxide were precipitated as they were formed in toluene or heptane. Under analogous conditions potassium cumyl peroxide appears in the solution. After removing the excess of potassium amide and distilling off the solvent at 20°C a viscous mass remains; when this is heated at 50°C and 0.1–0.5 mmHg a colourless solid containing 96–97% potassium cumyl peroxide is obtained. This compound deliquesces rapidly in air. In the absence of moisture at 0°C the active oxygen content had not decreased after 50 days. The salt thus obtained dissolved well in aromatic and aliphatic hydrocarbons and in ethers [25]. However crystalline potassium cumyl peroxide obtained by spontaneous crystallisation from toluene solution at 20°C does not dissolve in aprotic solvents [29].

When solutions of cumyl hydroperoxide and its potassium salt in heptane are mixed the complex

$$C_6H_5C(CH_3)_2OOK \cdot HOOC(CH_3)_2 \cdot C_6H_5$$

is precipitated [25]. It seems that the hydrogen bond in the complex with the potassium salt should be stronger than those in the analogous sodium and lithium compounds, owing to the greater basicity of the K salt. The complexes of the hydroperoxide and its alkali salt are considerably less stable thermally than the non-solvated salts [14,22,25]. The decomposition temperature of potassium cumyl peroxide, determined thermographically, is 140–150°C, that is, 70–80 K higher than for its complex with cumyl hydroperoxide [25]. This is evidently due to weakening of the O–O bond in the complex under the influence of the hydrogen bond [30].

A method recently proposed for making salts of hydroperoxides was by the reaction of hydroperoxides with sodium bistrimethylsilylamide in ether [19]:

$$\underset{R = n\text{-}C_4H_9,\ t\text{-}C_4H_9,\ (C_6H_5)_3C}{ROOH + NaN[Si(CH_3)_3]_2} \rightarrow ROONa + HN[Si(CH_3)_3]_2 ,$$

This is a fast reaction. The sodium salt of the hydroperoxide was precipitated in high yield.

An attempt to obtain sodium triphenylsilyl peroxide $(C_6H_5)_3SiOONa$ by this method was unsuccessful. This compound decomposes in the presence of the strong base $NaN[Si(CH_3)_3]_2$, NaH, $NaNH_2$, or n-C_4H_9Li even between −80° and −20°C with the formation of phenoxide and $[(C_6H_5)_2SiO]_x$. [19]

Lithium alkyl peroxides are obtained by the reaction of hydroperoxides with lithium t-butoxide in an aprotic solvent [17]:

$$ROOH + (CH_3)_3COLi \rightarrow ROOLi + (CH_3)_3COH.$$

The reaction takes place readily at 0–20°C. Lithium t-butoxide has several advantages over alkoxides of primary and secondary alcohols and also over the analogous sodium and potassium compounds [17]. It is soluble in hydrocarbons therefore its solutions are readily obtained by heating the metal with a hydrocarbon solution of the alcohol [17,31,32]. t-Butyl alcohol and its alkoxides are stable in the presence of oxygen [32] or peroxides [33], whereas alcohols containing an α-hydrogen are oxidised readily by peroxides [33-36]. Alkoxides of primary and secondary alcohols are oxidised very readily by oxygen [32,37-39] and apparently by peroxides. Owing to steric hindrance and the acidic properties, t-butyl alcohol has less tendency to form complexes, especially with lithium salts, which have a lower basicity than the analogous sodium and potassium compounds. The lithium salts of the tertiary hydroperoxides are isolated after the solvent and t-butyl alcohol have been distilled off in a vacuum at 20°C. Thus lithium cumyl and lithium t-butyl hydroperoxides of 99.0–99.8% purity were first obtained in heptane [17]. Lithium cumyl peroxide is a white hygroscopic powder soluble in aromatic hydrocarbons. This peroxide ignites spontaneously when

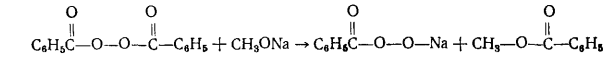
heated to 100–115°C. Lithium t-butyl peroxide is readily soluble in various organic solvents; when heated without a solvent it ignites spontaneously at 130–135°C.[17]

The lithium, sodium, and potassium salts of the primary hydroperoxides are insoluble in aprotic solvents and are immediately precipitated during the preparation[40,41]. The alkali salts of the secondary aliphatic hydroperoxides apparently also cannot be obtained in hydrocarbon or ethereal solution[41]. The poor solubility of the alkali salts of the primary and secondary hydroperoxides in aprotic solvents seems to be explained by the high degree of association of these salts. Even salts of tertiary hydroperoxides (namely, lithium and potassium cumyl peroxides) are associated into tetramers in benzene and cyclohexane[29].

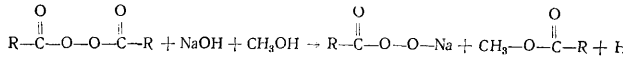
Lithium salts of secondary arylalkyl hydroperoxides can be obtained in solutions. For example, solutions of lithium 1-phenylethyl peroxide in ether, heptane, and ethylbenzene have been obtained. However, after the solid salt had been isolated it did not redissolve in aprotic solvents. When 1-phenylethyl hydroperoxide reacts with lithium t-butoxide in ether, which is then removed at 0–20°C, a salt of the hydroperoxide (97% pure) is obtained, it ignites spontaneously at 91–92°C.[41]

It is difficult to obtain the corresponding non-solvated salts by the reaction of hydroperoxides with potassium or sodium t-butoxide, since they rather firmly bond alcohol in a complex, unlike the analogous lithium compounds. The alcohol is difficult to remove from the complex ROOK.HOC$(CH_3)_3$ (where R is cumyl) even by heating in a vacuum[25]. True, potassium t-butyl hydroperoxide with a little t-butyl alcohol as impurity is obtained by heating the complex at 50°C in a high vacuum[42]. Apparently it is no less complicated to obtain a non-solvated salt by the reaction of a hydroperoxide with sodium methoxide[43]. Here in addition to the formation of a stable solvate with methanol, the alcohol and its alkoxide can be oxidised.

The sodium salts of acyl hydroperoxides (peroxo-acids) are made by reaction with sodium hydroxide. Anhydrous salts can be obtained with the aid of this reaction[44]. Sodium perbenzoate is usually made by the reaction of sodium methoxide with benzoyl peroxide in a mixture of alcohol and chloroform:



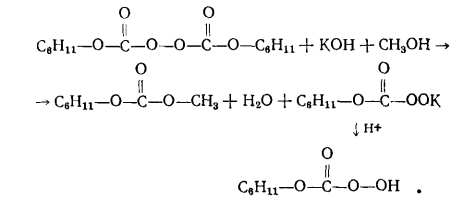
The same products are formed if instead of the alkoxide the alkali hydroxide in ethanol[45] or methanol[46] is taken:



The explanation[46] is that when the water concentration is low the equilibrium of the reaction

$$CH_3OH + {}^-OH \rightleftarrows CH_3O^- + H_2O$$

is shifted almost completely to the right[47]. The methoxide ion formed is more nucleophilic than the hydroxide ion[48]. *O*-cyclohexylmonoperoxocarbonic acid was obtained and isolated in the pure state by the reaction of dicyclohexylperoxodicarbonate with potassium hydroxide in methanol followed by the action of acid. It is evidently the first representative of an *O*-alkylmonopercarbonic acid[46].



Individual alkali metal OP and methods for making them are listed in Table 1.

Table 1. Methods of making organic peroxides of the alkali metals.

Peroxide	Method of preparation	Ref.
$(CH_3)_3COOLi$	ROOH + $(CH_3)_3COLi$ (heptane, 20°)	17
$C_6H_5C(CH_3)_2OOLi$	ROOH + $(CH_3)_3COLi$ (heptane, 20°)	17
$C_6H_5CH(CH_3)OOLi$	ROOH + $(CH_3)_3COLi$ (ethyl ether, 20°)	41
$CH_3C(O)OOLi$	ROOH + LiH (tetrahydrofuran)	18
$C_6H_5C(CH_3)_2OONa$	ROOH + $NaNH_2$ (toluene, 20°)	22
$(C_6H_5)_3COONa$	ROOH + $NaNH_2$ (toluene, 20°)	23
$(CH_3)_3COONa$	ROOH + $NaN[Si(CH_3)_3]_2$ (ether)	19
$CH_3CH_2CH_2CH_2OONa$	ROOH + $NaN[Si(CH_3)_3]_2$ (ether)	19
	ROOH + NaH (ether)	18
$CH_3C(O)OONa$	ROOH + NaH (ether)	18
$CH_3CH_2CH_2C(O)OONa$	ROOH + NaOH (water, alcohol, 0°)	44
$HC(O)OONa$	ROOH + NaOH (water, alcohol, 0°)	49
$C_6H_5C(CH_3)_2OONa.HOOC(CH_3)_2C_6H_5$	ROONa + ROOH (cumene, pentane)	14
$C_6H_5C(CH_3)_2OONa.HOOC(CH_3)_2C_6H_5$	ROONa + ROOH (toluene, heptane)	22
$(CH_3)_3COONa.HOOC(CH_3)_3$	2ROOH + C_2H_5ONa (toluene + ethanol, 20°)	28
$(CH_3)_3.COONa.(CH_3)_3COH$	ROOH + $(CH_3)_3CONa$ (t-butyl alcohol)	10
$C_6H_5(CH_3)_2COOK$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK$	heating $(CH_3)_3COOK.(CH_3)_3COH$ in a high vacuum, 50°	42
$(C_6H_5C(CH_3)_2OOK.HOOC(CH_3)_2C_6H_5$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK.HOOC(CH_3)_3$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK.2HOOC(CH_3)_3$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK.(CH_3)_3COH$	ROOH + $(CH_3)_3CONa$ (t-butyl alcohol)	10
$(CH_3)_3COOK.C_2H_5OH$	ROOH + KOH (ethanol, 0–2°)	12

III. THERMAL DECOMPOSITION

Studies of the decomposition of the alkali metal OP can be divided into three groups, depending upon the subject and conditions of the investigation. The first group comprises investigations [13,22,29] in which the thermal decomposition of the non-solvated compounds in hydrocarbons was studied. The second group covers the investigation of the thermal decomposition of complexes of the alkali OP with water and hydroperoxide in hydrocarbon solutions. Most of the papers relate to the third group; they describe an investigation of the decomposition of hydroperoxides in aqueous–alkaline solutions. An alkali salt of the hydroperoxide is an intermediate product of this reaction.

The thermal decomposition of the alkali OP in hydrocarbons at 80–130°C has been investigated [29]. The decomposition of potassium cumyl peroxide is described by a first-order kinetic equation. The hydrocarbon used as solvent has little effect on the rate of decomposition of the peroxide (Table 2). The decomposition products are given in Table 3.

Table 2. Kinetic parameters of the thermal decomposition of the alkali organic peroxides (c_0 = 0.1 M). [29]

Peroxide	Solvent	$10^5 k$, s^{-1} (at 110°C)	E, kcal mole^{-1}	lg A
$C_6H_5C(CH_3)_2OOK$	n-nonane	13.3	28.6	12.3
$C_6H_5C(CH_3)_2OOK$	cumene	7.0	29.0	12.4
$C_6H_5C(CH_3)_2OOK$	*m*-xylene	7.1	29.3	12.6
$C_6H_5C(CH_3)_2OOK$	t-butylbenzene	7.2	29.2	12.6
$(C_6H_5)_2CCH_3OOK$	t-butylbenzene	30.7	24.2	10.3
$(C_6H_5)_3COOK$	t-butylbenzene	18.4	21.4	8.5
$C_6H_5C(CH_3)_2OONa$	t-butylbenzene	19.7*	25.2	11.6

*$10^4 k$, litre mole^{-1} s^{-1}.

A decomposition mechanism has been proposed [29]:

$$ROO(L)_n \rightarrow RO^{\cdot} + {}^{\cdot}OK + nL \quad ,$$
$$^{\cdot}OK + SH \rightarrow KOH + S^{\cdot} \quad ,$$
$$RO^{\cdot} + SH \rightarrow ROH + S^{\cdot} \quad ,$$
$$RO^{\cdot} \rightarrow C_6H_5C(O)CH_3 + {}^{\cdot}CH_3 \quad ,$$
$$C_6H_5C(O)CH_3 + 3ROOK \rightarrow C_6H_5C(O)OK + HC(O)OK + 2ROH + ROK \quad ,$$
$$S^{\cdot} + S^{\cdot} \rightarrow S{-}S \quad .$$

During the decomposition of the associates there is a breaking of one peroxide bond after the act. The other peroxide molecules in the associate can be ligands (L) in relation to the decomposing molecule. A decrease in the strength of the peroxide bond being changed can be expected, as was noted for solvates with hydroperoxide and water [50]. The acetophenone formed in the partial decomposition of the cumyloxy-radicals readily undergoes a molecular reaction with potassium cumyl peroxide [51]. The yield of benzoic acid (a product of the oxidation of acetophenone) can be used to determine that the decomposition of the potassium salt of the hydroperoxide takes place by 60–80% by a free-radical reaction and 40–20% by a molecular reaction with the ketone. The ratio of the rates of these reactions depends on the nature of the solvent. The greater the rate of reaction of the free radical with the solvent, the less the part played by the molecular reaction.

Ethane is formed in the decomposition of potassium cumyl peroxide in n-nonane, but there are no gaseous products when the reaction is carried out in aromatic hydrocarbons. The explanation could be that the methyl radicals are added to the aromatic ring of the solvent [52] but are dimerised in nonane with formation of ethane [29]. The $^{\cdot}OK$ radical evidently removes hydrogen from the solvent [53] with the formation of an alkali hydroxide. The absence of gaseous oxygen and of oxidation products of the solvent is characteristic [29]. The absence of oxygen in the decomposition of sodium cumyl peroxide in a hydrocarbon was noted earlier [13].

Table 3. Decomposition products of alkali organic peroxides (c_0 = 0.2 M). [29]

Peroxide	Reaction temp., °C	Solvent	Reaction time, h	Yield, moles per mole peroxide decomposed				
				$C_6H_5C(CH_3)_2OH$	$C_6H_5C(CH_3)_2OM$	$C_6H_5C(O)OM$	HC(O)OM	MOH
$C_6H_5C(CH_3)_2OOK$	110	n-nonane*	6	0.90	0.05	0.05	0.05	0.74
$C_6H_5C(CH_3)_2OOK$	110	cumene**	6	0.89	0.07	0.08	0.08	0.65
$C_6H_5C(CH_3)_2OOK$	110	t-butylbenzene	6	0.82	0.08	0.09	0.10	0.78
$C_6H_5C(CH_3)_2OONa$	120	t-butylbenzene	6	0.80	0.09	0.10	0.08	0.75
$C_6H_5C(CH_3)_2OOLi$	80	benzene	12	0.60	0.20	0.22	0.21	0.30
$C_6H_5C(CH_3)_2OOLi$	90	t-butylbenzene	6	0.83	0.09	0.11	0.11	0.74

*The decomposition products contain 0.03 mole ethane per mole peroxide decomposed.
**The bicumyl in the products was determined qualitatively.

Sodium and lithium cumyl peroxides decompose analogously. However, the kinetics of the processes differ significantly: the decomposition of the sodium salt is described by a kinetic equation for a second-order reaction, but the lithium salt decomposes with a clear induction period. Table 2 gives the kinetic parameters for the decomposition of sodium cumyl peroxide. The activation energy for the decomposition of lithium cumyl peroxide, calculated from the temperature dependence of the induction period, is 23.0 kcal mole^{-1}. [29]

The difference in the formal kinetics of the decomposition of the peroxides is explained by the influence of the reaction products, above all the alkoxides. It seems that the formation of a complex of the peroxide with the alkoxide can change the strength of the O–O bond [29].

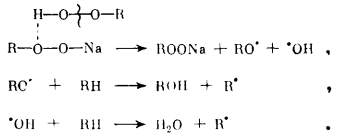
The decomposition of the salts in a hydrocarbon is greatly accelerated by additions of hydroperoxides, which is explained by the formation of the complexes ROOM.HOOR, which are less stable thermally [14,22,28,50]. The kinetics and mechanism of the decomposition of the complex

$$C_6H_5C(CH_3)_2OONa \cdot C_6H_5C(CH_3)_2OOH$$

in cumene have been studied [54,55]. The kinetic order with respect to the complex is 1.35, which the investigators explained by the occurrence of parallel reactions for the decomposition of the monomer and dimer of the complex (the latter is less stable thermally). The activation energy for the decomposition of the complex is 18.0 kcal mole^{-1}. [27,55] The decomposition of the complex initiates the polymerisation of styrene in bulk at 20–60°C more effectively than the

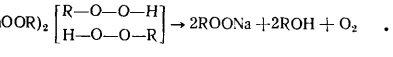
decomposition of cumyl hydroperoxide. Belyaev and Nemtsov[55] think that the O–O bond of the hydroperoxide in the complex is broken, being weakened by the hydrogen bond. In the molecule of the salt, which is an acceptor of a proton, they think that the O–C and O–O bonds become stronger. However, other results[50] which will be considered below do not support these conclusions.

A mechanism for the decomposition of the complex is proposed:



Acetophenone is formed as a result of the decompositon of the RO• radical. Belyaev and Nemtsov[55] explain the yield of acetophenone being lower than in the thermal decomposition of the hydroperoxide by the increased strength of the $C-CH_3$ bond in the complexes. We think the small yield of acetophenone in the decomposition of these complexes is explained by ketones containing α-hydrogen being readily oxidised by salts of hydroperoxides and their complexes[51].

This scheme does not explain the formation of oxygen and 1-methyl-1-phenylethanol (1.5 moles per mole hydroperoxide decomposed). It is suggested therefore[55] that molecular decomposition of the dimer of the complex is more probable:



The oxygen which has been formed by a chain free-radical mechanism oxidises cumene to its hydroperoxide, the decomposition of which also gives an additional amount of 1-methyl-1-phenylethanol.[55]

The decomposition of the complexes ROOK.ROOH and ROOK.$2H_2O$ (where R = cumyl) in benzene and toluene has been investigated[50]. The thermal decomposition of these complexes in solution is rather rapid even at 70–80°C. The main products of the reaction are 1-methyl-1-phenylethanol, potassium benzoate, and oxygen (Table 4). Potassium formate is also formed during decomposition in benzene[56].

Table 4. Decomposition products of the complexes with water and a hydroperoxide[50] (concentration 0.2 M).

Complex	Reaction temp., °C	Solvent	Yield, moles per mole complex decomposed		
			1-methyl-1-phenyl ethanol	potassium benzoate	oxygen
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	80	toluene	1.0	0.29	none
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	70	benzene	0.8	0.18	0.11
$C_6H_5C(CH_3)_2OOK \cdot C_6H_5C(CH_3)_2OOH$	70	toluene	2.0	0.38	0.24

The decomposition of the complex with water in benzene or toluene is described well by a first-order kinetic equation, as is the decomposition of the complex with the hydroperoxide in toluene. However the decomposition of this complex in benzene slows down sharply after the concentration of the peroxide compound has fallen to approximately half the initial value[50]. Table 5 gives the effective rate constants and activation energies for the decomposition of the complexes in benzene or toluene. The thermal decomposition of the complexes with loss of peroxide oxygen proceeds more readily than the decomposition of the potassium salt or the hydroperoxide separately.

Table 5. Rate constant and effective activation energies for the decomposition of the complexes of potassium cumyl peroxide with water and with a hydroperoxide (concentration 0.1 M).[50]

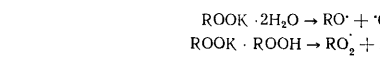
Complex	Solvent	10^5k, s^{-1} at 70°C	E, kcal $mole^{-1}$
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	benzene	19.4	25.3
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	toluene	11.9	22.6
$C_6H_5C(CH_3)_2OOK \cdot C_6H_5C(CH_3)_2OOH$	toluene	40.8	19.3
$C_6H_5C(CH_3)_2OOK \cdot C_6H_5C(CH_3)_2OOH$	benzene	3.67*	23.9*

*10^5w_0, mole $litre^{-1}$ s^{-1}.

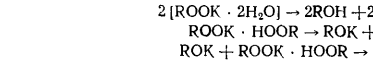
**Calculated from the temperature coefficient of the initial rate.

Additions of an inhibitor (1-naphthylamine) do not affect the decomposition of the complex of potassium cumyl peroxide with water in toluene. This shows that a molecular reaction of the inhibitor with the peroxide compound does not occur, just like the chain reaction for decomposition.

The rate of loss of peroxide oxygen in the decomposition of the complex in cumene increases with the concentration of 1-naphthylamine. The explanation is that 1-naphthylamine inhibits the radical-chain oxidation of cumene to its hydroperoxide by the oxidation formed in the decomposition of the complexes. The rate of decomposition of 1-naphthylamine in benzene showed that 10–20% of the complex decomposes with formation of free radicals:



The complexes decompose predominantly by molecular reactions:



The occurrence of the last exchange reaction is explained by the fact that decomposition of the complex of potassium cumyl peroxide with the hydroperoxide in benzene is greatly retarded after the concentration of peroxide oxygen has been reduced to approximately half.

The cumyloxy-radical detaches hydrogen from cumene and toluene to form 1-methyl-1-phenylethanol and a radical of the solvent, which is oxidised by the oxygen formed. In benzene, the cumyloxy-radical decomposes into the methyl radical and acetophenone, which is readily oxidised by potassium cumyl peroxide by a molecular mechanism[51]. In the decomposition of the complexes in toluene at 70° and 80°C, benzoic acid is formed due to oxidation of the solvent.

The lower thermal stability of the complex with water apparently shows the considerable drop in the dissociation energy of the O–O bond in the formation of a hydrogen bond. The influence of water cannot be explained by the formation of hydroperoxide due to the hydrolysis of its salt, since the degree of hydrolysis under the conditions of the reaction is low owing to the acidity of the hydroperoxide being much greater than that for water[50].

The decomposition of complexes of sodium t-butylperoxide with the hydroperoxide and water was investigated[28]. Sodium cumyl peroxide hexahydrate decomposes slowly at 60–70°C.[9] It loses active oxygen completely after 2 h at 115°C. Decomposition proceeds mainly according to the scheme:

$$C_6H_5C(CH_3)_2OONa \cdot 6H_2O \rightarrow C_6H_5C(CH_3)_2OH + \frac{1}{2}O_2 + NaOH + 5H_2O \ .$$

This main process is accompanied by the formation of acetophenone and methanol, which react with the initial compound:

$$C_6H_5COCH_3 + 4C_6H_5C(CH_3)_2OOH + 3NaOH \rightarrow$$
$$\rightarrow C_6H_5C(O)ONa + Na_2CO_3 + 3H_2O + 4C_6H_5C(CH_3)_2OH;$$
$$CH_3OH + 2C_6H_5C(CH_3)_2OOH + NaOH \rightarrow HCOONa + 2H_2O + 2C_6H_5C(CH_3)_2OH \ .$$

The formation of a little bicumyl shows that free-radical decomposition of the hexahydrate takes place[9]:

$$C_6H_5C(CH_3)_2OONa \cdot 6H_2O \rightarrow C_6H_5C(CH_3)_2O^{\cdot} + {}^{\cdot}ONa + 6H_2O \ .$$

The radical which is formed removes hydrogen from the solvent. The solvent radicals are oxidised by the oxygen released in the molecular decomposition of the peroxide or are dimerised. Additions of the hydroperoxide accelerate the decomposition of sodium cumyl peroxide hexahydrate in cumene at 80°C.[8] The highest reaction rate was observed at a molar ratio of 2 : 1 between the hydroperoxide and its salt. Decomposition of the salt without addition of hydroperoxide was slower by a factor of almost 2. Kharasch and coworkers[13] obtained analogous results.

When mixtures of sodium cumyl peroxide hexahydrate with the hydroperoxide or 1-methyl-1-phenylethanol in cumene was heated briefly to 80°C and then cooled rapidly a crystalline trihydrate was precipitated. The formation of this compound is explained by the existence of the equilibrium[8]:

$$ROONa \cdot 6H_2O + n\,A \rightleftharpoons ROONa \cdot 3H_2O + n\,A \cdot 3H_2O \ ,$$

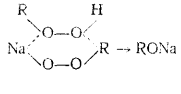
where A is an acceptor of water.

Kharasch and coworkers[13] proposed an ion-molecular mechanism for the decomposition of hydroperoxide:

$$RO_2^- + ROOH \rightarrow RO^- + ROH + O_2 \ .$$

They think[13] that free radicals are not formed and postulate the direct transfer of the oxygen atom from the peroxide anion to a reductant, which could be the non-dissociated hydroperoxide molecule or an alcohol with an α-hydrogen atom.

A mechanism of alkaline decomposition of hydroperoxide into a six-membered cyclic active complex was proposed[3,57]:



Apparently, molecular decomposition of the complexes of alkali OP with hydroperoxide and water takes place in the six-membered cyclic active complex. However, as an analysis of the products shows[29] that such a mechanism does not take place in the decomposition of the non-solvated alkali OP on hydrocarbons. It seems that an important part in the molecular decomposition of salts of hydroperoxides with release of oxygen is played by their solvation with the formation of a hydrogen bond.

The decomposition of a hydroperoxide and its salt in water by a free-radical mechanism could be due to traces of metals of variable valency. This is shown by the decrease in the rate of formation of oxygen by additions of small quantities of EDTA.[58]

The kinetics of decomposition of cumyl hydroperoxide in the presence of NaOH in various solvents was studied recently[59]. The alkaline decomposition of *m*- and *p*-di-isopropylbenzene dihydroperoxides in aqueous solution and also the decomposition of the crystalline hydrates of their disodium salts were investigated[60,61]. The primary product of the alkaline decomposition of the dihydroperoxides are hydroxyhydroperoxides, and the final products are carbinols, acetylbenzenes, carbonic acids. Belen'kii and coworkers[61] suggest the formation of atomic oxygen, which oxidises the primary decomposition products. We think the formation of the acids is explained by the reaction of the dihydroperoxide salt with the ketone formed as intermediate product.

A method of alkaline decomposition of hydroperoxides on an ion-exchange resin containing an active group of a quaternary ammonium base has been proposed[62].

Primary and secondary hydroperoxides decompose in an alkaline medium much more rapidly than the tertiary compounds. However, the sodium salts of hydroperoxides which contain α-hydrogen can also be obtained and in certain instances isolated[63]. The main products from the alkaline decomposition of primary and secondary hydroperoxides are the corresponding aldehydes or ketones; alcohols and acids can also be formed. Hydrogen is produced in the alkaline decomposition of the lower primary alkyl hydroperoxides. A brief review of the reactions in the alkaline decomposition of primary alkyl hydroperoxides has been published[64].

Methyl hydroperoxide decomposes in alkaline solution to form hydrogen, methanol, and formic acid[65]. Ethyl hydroperoxide decomposes with release of a very small amount of gas but when formaldehyde is added hydrogen is released. It is formed as a result of the alkaline decomposition of an alkyl hydroxymethyl peroxide, which is an intermediate product.

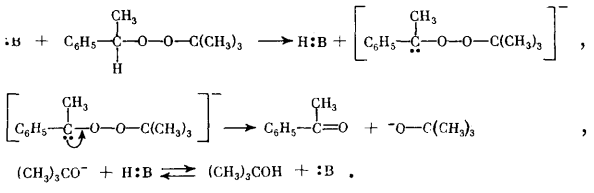
$$CH_3OOH \rightarrow CH_2O + H_2O$$
$$CH_3OOH + CH_2O \rightarrow CH_3-O-O-\underset{OH}{\underset{|}{CH_2}} \ .$$

Rieche[66] obtained hydroxymethyl methyl peroxide and ethyl hydroxymethyl peroxide. It was confirmed that these peroxides decompose in an alkaline medium with the formation of hydrogen, formic acid, and an alcohol, and in the second instance acetaldehyde also.

It was shown later[64] that n-butyl 1-hydroxyethyl and n-butyl 1-hydroxybutyl peroxides, unlike n-butyl hydroxymethyl peroxide, decompose in the presence of a base with the formation of a very small amount of gas. It was therefore concluded that hydrogen is formed from the hydroxymethylperoxo-group $O-O-CH_2OH$.

Not only hydroperoxides but also peroxides containing a hydrogen atom in the α-position decompose readily in an alkaline medium[67]. Peroxide compounds with either arylalkyl or alkyl radicals decompose readily. For example, 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide is converted

into α-tetralone [3,4-dihydro-1(2H)naphthalenone]. Isopropyl hydroperoxide rapidly forms acetone[68]. Kornblum and De La Mare[67] proposed a mechanism for the decomposition of peroxide compounds containing α-hydrogen, in the presence of a base (B):



This mechanism is widely encountered (for example, cf. Hawkins[69]), but the formation of a carbanion in the decomposition of peroxide compounds, especially alkyl ones, in water or low-polar solvents, seems improbable.

Acrylonitrile does not retard the alkaline decomposition of tetralin hydroperoxide [1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (Ed. of Translation)] in alcohol–water solution. The formation of a polymer during this reaction also is not observed, unlike the similar reaction in neutral solution. The explanation could be that free radicals are not formed in the alkaline decomposition of the hydroperoxide[70].

Syrkin and Moiseev[71] suggested that the alkaline decomposition of dialkyl peroxides containing an α-hydrogen proceeds in a cyclic transition state.

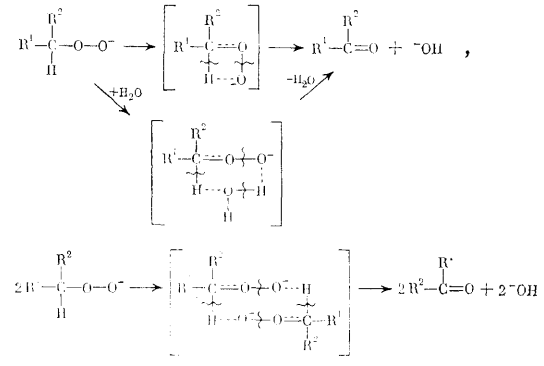
The kinetics of the alkaline decomposition of hydroperoxides with an α-hydrogen have been studied recently[40,41,72]. Hofmann and coworkers[72] investigated the kinetics of the decomposition of 4-n-heptyl, cyclohexyl, 1,2,3,4-tetrahydro-1-naphthyl, 1-phenylethyl, and cumyl hydroperoxides in methanol in the presence of sodium or potassium hydroxide. In addition to ketones, the decomposition products contained the corresponding alcohols. In investigating the kinetics of the process they obtained reproducible results only for 1,2,3,4-tetrahydro-1-naphthyl and 1-phenylethyl hydroperoxides. Additions of a little Complexone III did not alter the rate of decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide, but somewhat retarded the decomposition of 1-phenylethyl hydroperoxide and depressed the decomposition of the other hydroperoxides investigated (at 40°C). The inhibiting influence of the complexone is explained by these hydroperoxides decomposing according to a radical mechanism under the action of traces of heavy metal ions. The formation of alcohols is explained by the occurrence of free-radical reactions. The proportion of alcohols in the decomposition of the 1,2,3,4-tetrahydro-1-naphthyl and 1-phenylethyl hydroperoxides is insignificant. It is concluded that alkaline decomposition of these hydroperoxides proceeds according to the Kornblum–De La Mare mechanism.

The kinetics of decomposition of alkali salts of s-butyl and 1-phenylethyl hydroperoxides[41] and also of a substituted benzyl hydroperoxide[40] in aqueous solutions have been investigated. The rate constant of the first-order decomposition of a peroxide increases linearly with its initial concentration. The explanation could be that the decomposition proceeds by first- and second-order reactions in parallel:

$$w_{\text{eff}} = k_1 c + k_2 c^2;\ k_{\text{eff}} = k_1 + k_2 c\ .$$

The straight lines obtained in coordinates of k_{eff} against c_0 were used to calculate the rate constants of the first- and second-order reactions at various temperatures. The rate of decomposition of the hydroperoxide salt in water is independent of the nature of the alkali cation (lithium, sodium, potassium)[40,41]. For the decomposition of the salt of s-butyl hydroperoxide, $k_1 = 4.1 \times 10^8 \times \exp(-21\,000/RT)\ \text{s}^{-1}$, $k_2 = 3.2 \times 10^{11} \times \exp(-24\,700/RT)$ litre mole^{-1} s^{-1}; for the decomposition of the salts of 1-phenylethyl hydroperoxide $k_1 = 5.0 \times 10^6 \times \exp(-16\,500/RT)\ \text{s}^{-1}$, $k_2 = 6.7 \times 10^{11} \times \exp(-23\,000/RT)$ litre mole^{-1} s^{-1}.[41] The replacement of the ethyl group of the secondary hydroperoxide by a phenyl group considerably accelerates the decomposition of its alkali salt. The rate of decomposition of the sodium salts of the isomeric butyl hydroperoxides at 90°C fall in the order: primary > secondary > tertiary[41].

The simple composition of the products (during the decomposition of a salt of 1-phenylethyl hydroperoxide, acetophenone and the alkali hydroperoxide are formed quantitatively) and the low activation energy shows that decomposition of the peroxide anion with α-hydrogen takes place in a cyclic transition state. A six-membered transition state is the most favourable energetically, therefore the formation of such a state involving water is probable. Formation of an eight-membered cyclic transition state is suggested for a second-order reaction:



IV. REACTIONS WITH ORGANIC COMPOUNDS

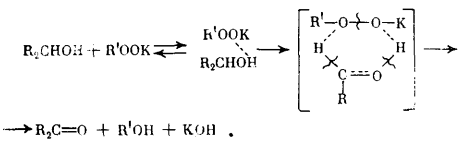
The alkali OP readily undergo nucleophilic substitution, addition, and elimination. The peroxide anion is a nucleophile with increased reactivity owing to the so-called α-effect.

The reactions of these peroxides with alkyl halides and acyl halides are nucleophilic substitutions and proceed with retention of the O–O bond and formation of dialkyl peroxides and peroxoacid esters respectively. Analogous reactions with organoelemental halogeno-derivatives are the main method for obtaining the OP of various elements. The primary stages of the reaction of hydroperoxide salts with carbonyl compounds and their heteroanalogues are nucleophilic additions. The decomposition of the salts of primary and secondary hydroperoxides with the formation of aldehydes and ketones are nucleophilic eliminations, as was discussed above[41,67,72].

The reactivity of the non-solvated alkali peroxides has been studied only recently[51,73–77]. Previously[78–86] the reaction of aqueous alkali salts of hydroperoxides with hydrocarbons[79,80], alcohols[13], aldehydes[81], ketones[81–84], and nitriles[13,58,78,86] were investigated. The reaction of the complex ROONa.ROOH with acetophenone and benzoquinone is also reported to take place comparatively readily[54,55]. It was found that even the addition of small quantities of water to a non-solvated peroxide greatly reduces its reaction rate with organic compounds[51] and can also change the composition of the products formed[75].

As already stated, the thermal decomposition of the non-solvated alkali OP in hydrocarbon solutions takes place at a significant rate only at 80–130°C.[29] However, in hydrocarbons in the presence of aldehydes, ketones, alcohols (with α-hydrogen), and esters these peroxides decompose rapidly even at 10–50°C.[51,73,76,77]. The rate of decomposition of the peroxide in the presence of these compounds increases in the order ROOLi < ROONa < ROOK. These reactions take place through intermediate complexes (with an alcohol) or peroxide compounds. Therefore when there is an excess of an organic compound the decomposition of the peroxide is described by a first-order kinetic equation and has zero or even negative order with respect to the other component[51,73,76].

As the initial concentration of diphenylmethanol is increased there is first an increase in the rate constant of the decomposition of potassium cumyl peroxide, which passes through a maximum at the equimolar ratio of the reagents, then decreases. This type of relation shows the formation of a 1 : 1 complex of the peroxide with the alcohol, a complex which decomposes readily with loss of the peroxide oxygen. The complex can be formed because of a hydrogen bond. The decomposition mechanism proposed for such complexes is through a six-membered cyclic transition state[73]:



$\longrightarrow R_2C{=}O + R'OH + KOH$.

The calculated kinetic parameters for the decomposition of the complexes of potassium cumyl peroxide with diphenylmethanol and 1-phenylethanol in benzene. For the complex with diphenylmethanol $k = 2.0\times 10^9\times \exp(-18\,300/RT)\ s^{-1}$, and for the complex with 1-phenylethanol $k = 2.5\times 10^9\times \exp(-18\,500\ RT)\ s^{-1}$.

Table 6. Kinetic parameters for the decomposition of lithium cumyl peroxide (0.1 M) in the presence of XC_6H_4CHO (0.4 M) in benzene.[76]

Substituent X	10^5k, s^{-1} (at 30°C)	E, kcal mole^{-1}	lg A
H	17.0	22.8	12.7
p-Cl	13.8	22.0	12.0
p-Br	15.8	22.8	12.7
p-CH_3O	29.2	18.3	9.7

The kinetics and mechanism of the reaction of lithium cumyl peroxide with benzaldehyde and substituted benzaldehydes at 20–40°C have been investigated in detail[76]. As the initial concentration of aldehyde is raised the rate constant for the decomposition of the peroxide first increases linearly, and then the increase slackens and stops. The analogous relation was obtained for the reaction of potassium cumyl peroxide with acetophenone, acetone, and ethyl methyl ketone.[51] This type of dependence of the rate of decomposition of the peroxide upon the concentration of the carbonyl compound is explained by the formation of an intermediate peroxide owing to the reversible nucleophilic addition of the peroxo-group to the carbonyl carbon. The decomposition of the intermediate peroxides proceeds through a cyclic transition state[76]:

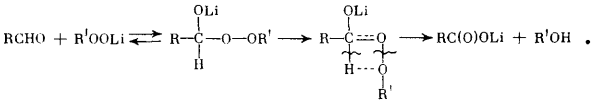
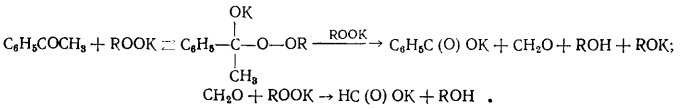


Table 6 gives the kinetic parameters of the decomposition of lithium cumyl peroxide in benzene in the presence of benzaldehyde or substituted benzaldehydes. The measurements were made in an excess of the aldehyde, when the equilibrium is shifted almost completely to the side of formation of an intermediate peroxide compound.

The reaction of potassium cumyl peroxide with acetophenone can be represented as[51]:



$CH_2O + ROOK \rightarrow HC(O)OK + ROH$.

Table 7. Kinetic parameters for the decomposition of potassium cumyl peroxide (0.1 M) in the presence of ketones (0.4 M) in benzene.

Ketone	10^4k, s^{-1} (at 20°C)	E, kcal mole^{-1}	lg A
Acetophenone	5.5	16.4	9.0
Ethyl methyl ketone	2.8	14.7	7.4
Acetone	4.7	15.5	8.2

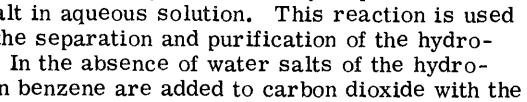
Table 7 gives the kinetic parameters for the decomposition of potassium cumyl peroxide in the presence of ketones. The results were obtained in an excess of the ketone, when a further increase in its concentration has little effect on the rate of decomposition of the peroxide. The kinetic parameters for Tables 6 and 7 relate to the slowest stage—the decomposition of the intermediate peroxide.

The alkali OP react with esters according to the scheme[77]

$$CH_3C(O)OC_2H_5 + 2ROOK \rightarrow 2CH_3C(O)OK + 2ROH \text{ (at 20°)},$$
$$C_6H_5C(O)OC_2H_5 + 2ROOK \rightarrow C_6H_5C(O)OK + CH_3C(O)OK + 2ROH \text{ (at 70°)}.$$

The first stage of the reaction is evidently also nucleophilic addition of a peroxo-group to the carbonyl carbon. In this instance this stage is the slowest. Therefore the reaction is first order with respect to each reagent and second order overall.

Carbon dioxide readily releases a hydroperoxide from its alkali salt in aqueous solution. This reaction is used widely for the separation and purification of the hydroperoxides. In the absence of water salts of the hydroperoxides in benzene are added to carbon dioxide with the formation of the alkali salts of arylalkyl monopercarbonic acids[74,75]:



$R = C_6H_5C(CH_3)_2$, M = Li, Na, K

These compounds are hydrolysed by water with the formation of a hydroperoxide and when acidified carbon dioxide is also released. It seems that initially an unstable arylalkylmonopercarbonic acid is formed, which is decomposed into a hydroperoxide and carbon dioxide [74,75]:

$$R-O-O-\overset{\overset{O}{\|}}{C}-O-M + H_2O \rightarrow \left[R-O-O-\overset{\overset{O}{\|}}{C}-O-H\right] + MOH \rightarrow ROOH + MHCO_3,$$
$$MHCO_3 + HCl \rightarrow MCl + H_2O + CO_2$$

The reactions of hydrocarbons, aldehydes, and ketones with t-butyl and cumyl hydroperoxides in the presence of potassium hydroxide have been investigated [79-84]. An intermediate product is undoubtedly a hydrated salt of the hydroperoxide which is formed rapidly. Hydrocarbons (benzene, cumene, *p*-xylene, ethylbenzene, t-butyltoluene, tetralin, and *p*-isopropyltoluene) reduce hydroperoxides to alcohols at 70–80°C; oxygen is released only on heating in benzene. The alkyl groups of aromatic hydrocarbons are oxidised to alcohols, aldehydes, ketones, or carboxyl groups [79,80]. Thus *p*-xylene is mainly converted into *p*-methylbenzaldehyde and the corresponding acid, *p*-t-*p*-t-butyltoluene is oxidised to *p*-t-butylbenzyl alcohol, *p*-t-butylbenzaldehyde, and *p*-t-butylbenzoic acid, and ethylbenzene to acetophenone and benzoic acid. Goto and coworkers [79] suggested that the potassium salt of the hydroperoxide gives a complex with the hydrocarbon which is rearranged with the formation of oxidation products. However, it was shown later [50] that the decomposition of potassium cumyl peroxide hydrate in a hydrocarbon partly takes place with the formation of free radicals, which initiate the radical-chain oxidation of the hydrocarbons by the oxygen released.

Formaldehyde, acetaldehyde, and propionaldehyde are oxidised by hydroperoxide in aqueous alkaline solution at 25–35°C to the corresponding acids [81]. The reaction takes place through an intermediate peroxide which is formed in the reversible addition of the peroxide anion to the carbonyl carbon and decomposes by an ionic mechanism [81].

The reaction of t-butyl hydroperoxide with ketones in the presence of potassium hydroxide in chlorobenzene at 80°C has been investigated [82-84]. Diaryl ketones (benzophenone, *p*-nitrobenzophenone, and fluorenone) [82] do not change under these conditions. The main oxidation products of the arylalkyl ketones are the corresponding benzoic acid and an alcohol, obtained from the alkyl group of the ketone [83]:

$$Ar-C(O)-R \xrightarrow[KOH]{(CH_3)_3COOH} ArC(O)OH + ROH \quad .$$

Thus in the oxidation of acetophenone and *p*-methylacetophenone the main products are methanol and the corresponding benzoic or *p*-toluic acid.

Aliphatic ketones react in two ways:

$$RC(O)R' \xrightarrow[KOH]{(CH_3)_3COOH} \begin{cases} \rightarrow RC(O)OH + R'OH \\ \rightarrow R'C(O)OH + ROH \end{cases} \quad .$$

Maruyama [83,84] proposed the reaction mechanism:

$$ROOH + KOH \rightarrow ROOK + H_2O$$
$$ROOK + X-C_6H_4-\overset{\overset{O}{\|}}{C}-R' \rightleftarrows \left[X-C_6H_4-\overset{\overset{O^-}{|}}{\underset{\underset{O-O-R}{|}}{C}}-R'\right] K^+ \xrightarrow{-OH} \rightarrow X-C_6H_4-C(O)OK + R'OH + RO^-;$$
$$RO^- + H_2O \rightarrow ROH + {}^-OH \quad .$$

The results of these investigations differ considerably from those obtained earlier [51]. In the oxidation of acetophenone by the aqueous potassium salt of a hydroperoxide in benzene at 70°C, benzoic and formic acids were observed [51]. Not one mole, but about three moles of the peroxide are decomposed per mole ketone oxidised.

Karasch and coworkers [13] found that the decomposition of cumyl hydroperoxide in the presence of 3 mole % of its sodium salt is strongly accelerated by an addition of 3–4% dinitriles, for example, succinonitrile. During this the hydroperoxide decomposes rapidly even at room temperature with the formation of 1-methyl-1-phenylethanol and oxygen. In this system secondary alcohols are oxidised rapidly to ketones. These investigators [13] suggested that nitriles form complexes with the hydroperoxide, which are readily decomposed without the formation of free radicals. A radical-chain mechanism was found later for the reaction [58,85,86]. Berger [86] proposed a scheme for the decomposition of t-alkyl hydroperoxides in the presence of a substituted benzonitrile and a base:

$$R'-CN + ROO^- \rightarrow R'-C(N^-)(OOR) \quad ,$$
$$R'-C(N^-)(OOR) + ROOH \rightleftarrows R'-C(NH)(OOR) + ROO^- \quad ,$$
$$R'-C(N^-)(OOR) + ROOH \rightleftarrows R'-C(N^-)(O\cdot) + RO\cdot \ldots HOOR \quad ,$$
$$RO\cdot \ldots HOOR \rightarrow RO_2^{\cdot} + ROH \quad ,$$
$$R'-C(N^-)(O\cdot) + RO_2^{\cdot} \rightarrow R'-C(N^-)(OR) + O_2 \quad ,$$
$$R'-C(N^-)(OR) + ROO^- \rightarrow R'-C(N^-)(OOR) + RO^- \quad ,$$
$$R'-C(N^-)(OR) + ROOH \rightleftarrows R'-C(NH)(OR) + ROO^- \quad ,$$
$$2\,RO_2^{\cdot} \rightarrow ROOR + O_2 \quad ,$$
$$R'-C(N^-)(O\cdot) + ROOH \rightarrow R'-C(N^-)(H^+\!\uparrow\downarrow OH) + RO_2^{\cdot} \quad .$$
$$R-C(NH_2)(O)$$

The first stage of the reaction is the addition of a peroxide anion to the nitrile group with the formation of an intermediate peroxide. This peroxide decomposes at the O–O bond with formation of an alkoxy-radical and a stable anion-radical

$$R'-C(N^-)(O\cdot) \quad .$$

The radicals react with the hydroperoxide to give a peroxy-radical. The reactions of the latter lead to the formation of oxygen. According to the scheme one molecule of the nitrile decomposes several molecules of the hydroperoxide; the nitrile is gradually converted into an amide.

The peroxide anion, which contains in its composition a nitrile group, is unstable. Thus the hydroperoxide

$$(CH_3)_2C(CN)OOH,$$

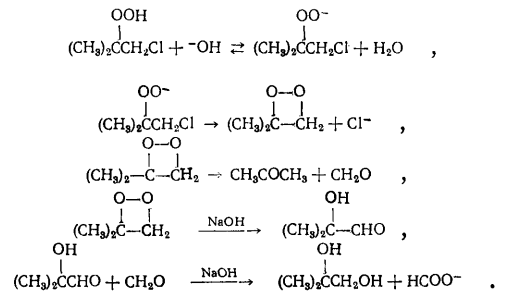
unlike other tertiary hydroperoxides, decomposes readily in the presence of alkali. The decomposition products are acetone and cyanate ion [87].

To investigate the factors which determine the size of the α-effect in nucleophiles, the reactivity of the peroxide anions in substitutions at the saturated and aromatic

carbon atom and also in reactions with carbonyl and nitrile carbon atoms in aqueous solution was studied [78].

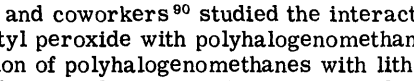
The kinetics of the reactions between organic halogen derivatives (*o*-chlorobenzyl chloride, allyl bromide, propyl bromide) and potassium t-butyl peroxide at 30° and 50°C in methanol have been investigated [88]. The activation energy is 21–23 kcal mole^{-1}. The activation energies for the reactions of organic halogeno-derivatives with alkoxides are similar.

The intramolecular reaction of the peroxide anion with the halogen derivatives takes place during decomposition of chloro-t-butyl hydroperoxide with an aqueous methanol solution of NaOH at 16–40°C. [89]



The decomposition of the intermediate 1,2-epidioxyethane is the limiting stage. At initially equimolar concentrations of hydroperoxide and alkali, 1,2-epidioxyethane decomposes with the formation of acetone and formaldehyde. When there is an excess of NaOH the rate of conversion of 1,2-epidioxyethane into the hydroxyaldehyde becomes considerable.

Petukhov and coworkers [90] studied the interaction of lithium t-butyl peroxide with polyhalogenomethanes. As in the reaction of polyhalogenomethanes with lithium alkyls the intermediate product is a halogenomethyl derivative of lithium, which decomposes with the formation of a halogenocarbene:



The formation of halogenocarbenes is proved by the production of a halogenonorcarane in the presence of cyclohexene.

V. USE

Preparation of Organic and Organometallic Peroxides

The method used most frequently is based on the reaction of nucleophilic replacement of a halogen atom in the corresponding organic or organometallic compound (cf. reviews on peroxides [1-5,91-97]):

R and R′ are organic or organoelemental radicals, X = Cl or Br, and M = Li, Na, or K.

In the preparation of peroxides stable against hydrolysis a hydrated salt obtained in the reaction of a hydroperoxide with a hydrated alkali hydroperoxide can be used [7,11,98]. The reaction takes place at 20°C or under gentle heating in an organic solvent in which the alkali halide is insoluble (hydrocarbon, alcohol, mixture of alcohol and ketone). [99]

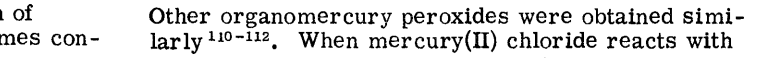
However, it must be taken into account that primary and secondary alcohols, and also ketones, are oxidised comparatively readily by salts of hydroperoxides [51,73].

Esters of peroxo-acids are obtained by the reaction of salts of hydroperoxides with acid chlorides [100-102].

The purest organometallic peroxides are obtained in the best yield from anhydrous salts formed in reaction between hydroperoxides and sodium [20-23] or potassium [25] amide, sodium hydride [18], and lithium t-butoxide [17]. The best solvents for making organometallic peroxides are hydrocarbons, which are the most inert to the initial compounds and to the peroxides obtained. Alcohol [103-105] can be used as the solvent when the initial organometallic compound and the peroxide product do not undergo alcoholysis. However, the salt obtained by the reaction of a hydroperoxide with sodium or potassium methoxide can contain a certain amount of alkoxide owing to the equilibrium [21].

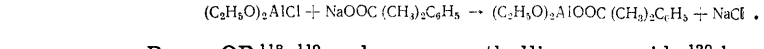
When the organometallic compound is hydrolysed slightly the hydrated salt obtained by the reaction between a hydroperoxide and KOH in hydrocarbon medium is used. However, it was noted recently that the method based on the reaction of a hydroperoxide with a base (KOH, pyridine) [106,107] cannot be employed for obtaining large quantities of dialkyl t-butyl peroxophosphates owing to side-reactions [108]. The method using an anhydrous hydroperoxide salt is better.

Razuvaev and Fedotova [109] were the first to obtain an organomercury peroxide by the reaction:



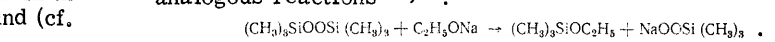
Other organomercury peroxides were obtained similarly [110-112]. When mercury(II) chloride reacts with ROONa in a mixture of benzene and ether, mercury bis(cumyl peroxide) is obtained [113], but with a peroxo-acid and NaOH in water the mercury salt of the peroxo-acid is obtained [114].

Razuvaev, Graevskii, and their coworkers [115-117] were also the first to obtain aluminium OP by the reaction:

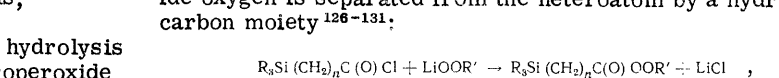


Boron OP [118,119] and an organothallium peroxide [120] have also been obtained similarly.

The preparation of the organometallic peroxides of Periodic Group IV elements was also described in detail in a review [121]. Salts of hydroperoxides have been used to obtain organometallic peroxides of silicon [19], germanium [21,122], tin [20,21,103-105,123], and lead [20,21] of the general formula R_3MOOR'. Thus the organosilicon peroxides R_3SiOOR' are obtained in especially good yield in the reaction of trialkyl- and triphenyl-chlorosilanes with an anhydrous salt R′OONa in an aprotic solvent [19]. The sodium salt of trimethylsilicon hydroperoxide, which can be obtained from a symmetrical peroxide undergoes analogous reactions [124,125]:



When silicon-containing acyl chlorides react with an anhydrous salt ROOLi in ether, esters of organosilicon peroxocarboxylic acids are obtained, in which the peroxide oxygen is separated from the heteroatom by a hydrocarbon moiety [126-131]:



A large number of phosphorus [108,132-140], arsenic [141-143], and antimony [141-144] OP have been made by using alkali salts of hydroperoxides.

The interaction of ROOK with tetra-alkylammonium[145] and quanidinium[146,147] halides in methanol has been used to obtain salts of hydroperoxides and corresponding nitrogenous bases:

$$R_4NCl + KOOR' \rightarrow R_4NOOR' + KCl \quad ,$$
$$R = CH_3,\ C_2H_5,\ \kappa\text{-}C_4H_9,\ R' = (CH_3)_3C,\ C_6H_5C(CH_3)_2 \quad ,$$
$$(RNH)_2C{=}NR \cdot HCl + KOOR' \rightarrow (RNH)_2C{=}NR \cdot HOOR' + KCl \quad .$$

Sym-triazine peroxides have been obtained by the reaction of salts of hydroperoxides with 2,4,6-trichloro-1,3,5-triazine.[148,149] The lithium salt of t-butyl hydroperoxide replaces only two chlorine atoms in the 2,4,6-trichloro-1,3,5-triazine molecule but under the action of the more reactive potassium salt of the hydroperoxide all three chlorine atoms are replaced by peroxide groups[149].

Organic peroxides can also be obtained by the addition of a peroxide anion to alkenes containing an electron-withdrawing substituent X.[150-152] A certain amount of epoxide is also formed:

$$ROO^- + CH_2{=}CHX \rightleftarrows ROO{-}CH_2{-}\bar{C}H{-}X \quad ,$$
$$ROO{-}CH_2{-}\bar{C}H{-}X + H_2O \rightleftarrows ROO{-}CH_2{-}CH_2{-}X{-}{}^-OH \quad .$$
$$\downarrow$$
$$CH_2{-}CH{-}X + RO^-$$
$$\diagdown O \diagup$$

Peroxoalkyl phosphonates are obtained by the reaction of salts of hydroperoxides with alkenyl phosphonates[153].

The reaction of salts of hydroperoxides with carbonyl compounds leads to α-hydroxyperoxides[51,76,154]:

$$R{-}\overset{\overset{O}{\|}}{\underset{\underset{R^1}{|}}{C}} + MOOR^2 \rightleftarrows R{-}\overset{\overset{OM}{|}}{\underset{\underset{R^1}{|}}{C}}{-}OOR^2 \xrightarrow{H_2O} R{-}\overset{\overset{OH}{|}}{\underset{\underset{R^1}{|}}{C}}{-}OOR^2 \quad .$$

R = H, alkyl; M = Li, Na, K

Fluorinated peroxides containing an alkali metal, which serve as initiators of the polymerisation of alkenes (especially fluoroalkenes), have been obtained in this way[155]:

$$F_3C{-}\overset{\overset{O}{\|}}{\underset{\underset{CF_3}{|}}{C}}{-}CF_3 + MOOC(CH_3)_3 \rightarrow F_3C{-}\overset{\overset{OM}{|}}{\underset{\underset{CF_3}{|}}{C}}{-}O{-}O{-}C(CH_3)_3 \quad .$$

M = Li, Na, K

As already stated, when anhydrous alkali salts of hydroperoxides react with carbon dioxide percarbonates are obtained

$$\bar{R}{-}O{-}O{-}C(O){-}OM$$

where M = Li, Na, or K and R = cumyl[74,75].

Preparation of Hydroperoxides, Alcohols, and Other Oxygen-Containing Compounds

Salts of hydroperoxides are obtained when organolithium and organomagnesium compounds are oxidised by oxygen at −75°C,[15,16] when the salts are acidified the hydroperoxide is released. The yield can reach 75 to 85%.[16]

Decomposition of salts of hydroperoxides with the formation of free radicals is used for initiating the oxidation of hydrocarbons, for example, cumene to a hydroperoxide[156-159]. Phenol and acetone are obtained in the acid decomposition of cumyl hydroperoxide but the product from alkali splitting is 1-methyl-1-phenylethanol, which is dehydrated to α-methylstyrene[160].

The preparation of hydroperoxide salts is widely used in the separation of hydroperoxides from the reaction mixtures obtained by the oxidation of hydrocarbons and also for purifying hydroperoxides[160,161].

Alkali Organic Peroxides—Intermediate Products in the Production of Inorganic Peroxide Compounds of Alkali Metals

Alkali alkoxides of secondary alcohols are oxidised readily at 0–20°C with the formation of alkali metal inorganic peroxide compounds[37-39,162]. Depending upon the conditions (nature of the alkali metal, solvent, additive) an alkali metal hydroperoxide, peroxide, or superoxide is formed. The intermediate oxidation products are the unstable alkali salts of hydroperoxides of secondary alcohols $R_2C(OH)OONa$ and $R_2C(ONa)OONa$, which decompose into the ketone and inorganic peroxide compound. The greatest interest is in the production of sodium superoxide NaO_2 in the catalytic oxidation of sodium under mild condition in aprotic polar organic solvents[163,164]. The catalysts are aromatic ketones, hydrocarbons, or nitrogen-containing compounds, which easily form organic (ketyl or complex) compounds with an alkali metal. During its oxidation the superoxide is formed and the catalyst is regenerated. This preparation of NaO_2 can be carried out at 0–20°C and atmospheric pressure. In industry NaO_2 is obtained by the oxidation of Na_2O_2 at high pressures and temperature[162].

Other Regions of Use

Salts of hydroperoxides are used as initiators of the polymerisation of alkenes[165]. The polymerisation of ethylene is carried out at 145–175°C and a pressure of 200–1000 at. in a medium of alcohol, hydrocarbon, or water. Copolymers of ethylene with styrene, α-methylstyrene, methyl vinyl ketone, vinylpyridine, acrylic and methacrylic acids, methyl and ethyl acrylate, or methacrylate can be obtained and also these individual vinyl compounds can be polymerised[165]. Salts of hydroperoxides were recently proposed for use as components of detergents[166].

Unlike the lithium, sodium, and potassium OP, there have been very few studies of the corresponding magnesium and alkaline earth compounds. This seems to be due to their insolubility in organic solvents. We know of only a few papers which describe the preparation of the OP of these metals by the reaction of hydroperoxides (or peroxo-acids) with the corresponding bases (oxide[10], hydride[18], organomagnesium compound[167]). Thus when hydroperoxides react with strontium or barium oxides the salts $M[OOC(CH_3)_3]_2$ are obtained[10], where M = Sr or Ba. Peracetates have been obtained in the reaction between calcium and barium hydrides with the peroxoacid in tetrahydrofuran[18].

The reaction of the organomagnesium compounds $ROMgC_5H_{11}$, $ROMgR^1$ and R^1_2Mg with cumyl hydroperoxide or with hydrogen peroxide in ether at 0°C the magnesium OP $ROMgOOR^2$, $ROMgOOMgOR$, and $R^1MgOOMgR^1$, where $R = (CH_3)_3C$, $R^1 = C_6H_5$, and $R^2 = C_6H_5C(CH_3)_2$, are obtained[167].

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Scientific Research Institute for Chemistry, Lobachevskii State University, Gor'kii