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HYDROPEROXIDES OF ALKYLARENES AND THEIR DERIVATIVES

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INTRODUCTION

The main course of petrochemical synthesis is the oxidation of hydrocarbons[1,2]. Most petrochemical products can be obtained by direct oxidation of petroleum hydrocarbons, of products of the petroleum-processing industry, or of by-product and natural gases. At the present time higher paraffin hydrocarbons are transformed industrially into aliphatic alcohols and acids by catalytic liquid-phase oxidation[3]. During recent years investigators have shown exceptional interest in the liquid-phase autoxidation of hydrocarbons to hydroperoxides by means of atmospheric oxygen. The interest in autoxidation is explained by the fact that similar processes occur widely in nature and are employed commercially for the synthesis of products of great economic importance.

Many hydroperoxides are quite stable compounds, and have been isolated in a pure form and characterised. In the USSR important investigations on the liquid-phase oxidation of hydrocarbons to hydroperoxides have been carried out by Ivanov[4-9], Sergeev[10-15], Yurzhenko[16-21], Erofeev *et al.*[22,23] and others[24-26]. These investigations have provided methods for preparing concentrated hydroperoxides, analysing them qualitatively and quantitatively in solution, isolating them in a pure form, and converting them into products of economic value.

Organic peroxides and hydroperoxides have formed the subject of several monographs[4,27,28] and reviews[29-31], and have been included in special sections of textbooks of organic chemistry[32]. In the periodical literature many original papers are published annually on the autoxidation of hydrocarbons. For 1958 alone the Chemistry Section of the *Referativnyi Zhurnal* contained more than 60 abstracts of papers and patents. All this indicates the immense importance which is now attached to the autoxidation of hydrocarbons.

The present review deals only with the liquid-phase oxidation of aromatic hydrocarbons and their derivatives by molecular oxygen, *i.e.* the so-called autoxidation process. Such oxidation results in the formation of hydroperoxides. Depending on the catalyst, temperature, time, and rate of introduction of oxygen or air, these may be either the final or the intermediate products of oxidation.

LIQUID-PHASE AUTOXIDATION OF ALKYLARENES

The autoxidation of alkylarenes to hydroperoxides or so-called "Dioxes" (organic peroxy-compounds)[33] is becoming more and more an independent field in a state of broad and intensive development. Hydroperoxides of alkylbenzenes have already acquired great industrial importance both in their own right and as intermediates, *e.g.*

in the synthesis of phenols, aliphatic, and aliphatic-aromatic ketones and alcohols. Hydroperoxides of mono- and di-isopropylbenzenes are used as weed-killers[34], as additives to solvents for the cleaning of apparatus from polymers in the production of "cold rubber"[35], as additives to improve the inflammability of motor fuels[36-39], as oxidants in the bleaching of textiles, and as efficient initiators in the low-temperature copolymerisation of butadiene with styrene and other unsaturated compounds[40-48]. Special interest as polymerisation initiators attaches to the hydroperoxides of cyclohexylbenzene, *p*-isopropylcyclohexylbenzene, 1,1-diphenylethane, *p*-isopropyl-t-butylbenzene, and 1,3,5-tri-isopropylbenzene. It appears that in the future the scale of production of hydroperoxides will be determined solely by the demand for those products which will be manufactured from them, since their technology is comparatively simple, and the raw-material basis unlimited. The synthesis of alkylbenzenes, which are necessary for the manufacture of hydroperoxides, was carried out on an industrial scale, even during the pre-war period, by the catalytic alkylation of benzene and its homologues with olefines.

A survey of the investigations shows that, in the liquid-phase autoxidation of alkylarenes, oxygen always attacks the alkyl carbon atoms directly attached to the aromatic nucleus, independently of the size and structure of the groups. Oxidation is carried out with oxygen or air in the presence and in the absence of catalysts, under the action of ultra-violet radiation, at atmospheric and at high pressures, in the presence and the absence of solvents. The course of the liquid-phase oxidation depends on the rates of formation and decomposition of the hydroperoxides, but the rate is determined by the structure and purity of the hydrocarbons, the nature of the catalyst, the temperature, the time, and the velocity at which the oxygen or air is passed through.

As a rule, oxygen enters more readily at a tertiary C–H bond. Primary carbon–hydrogen bonds are the most resistant to oxidation. But, as will be seen, in many cases this rule is not observed. It has not yet proved possible to oxidise an aromatic carbon–hydrogen link to a hydroperoxide, but, judging from data in patents, benzene has already been oxidised to phenol with oxygen or oxygen-containing gases under pressure[49-55]. Alkylarenes are not oxidised to hydroperoxides if quaternary carbon atoms are present in the α-position. Thus only those alkylarenes in which hydrogen atoms are attached to the α-carbon atoms undergo autoxidation. Toluene, the xylenes, and mesitylene, which contain only primary α-carbon atoms, are oxidised very slowly. Ethylbenzene is somewhat more readily oxidised, t-butylbenzene is not oxidised at all by atmospheric oxygen to a hydroperoxide, and isopropylbenzene, s-butylbenzene, *p*-cymene, *p*-di-isopropylbenzene, *p*-di-s-butylbenzene, and cyclohexylbenzene, which contain tertiary α-carbon atoms, are very readily oxidised.

The ease of oxidation of monoalkylbenzenes usually increases with increase in the degree of branching and in the length of the alkyl groups, but steric hindrance must be taken into account here, as a result of which the isopropyl group, for example, is usually more easily oxidised than the more ramified and longer s-butyl group.

Successive introduction of identical alkyl groups increases the oxidisability of hydrocarbons to a greater extent the more symmetrical the structure of the polyalkylbenzenes. If the alkyl groups differ in structure, those containing tertiary α-carbon atoms are oxidised first of all (in the case of dialkylbenzenes and symmetrical trialkylbenzenes). With unsymmetrical trialkylbenzenes the attack of oxygen is directed firstly at the α-carbon atom of the most remote radical, *e.g.* in 1,2,4-tri-isopropylbenzene at the group in position 4. If two or three groups having tertiary α-carbon atoms are attached to the benzene nucleus, the attack of oxygen is usually directed to the α-carbon atom of the larger alkyl group. The introduction of a methyl group *para* to an alkyl radical containing a tertiary α-carbon atom lowers the oxidisability, as can be seen on comparing the rates of oxidation of isopropylbenzene and *p*-cymene, s-butylbenzene, and *p*-s-butyltoluene. The last-named compound approaches the methylbenzenes in rate of oxidation. Autoxidation is facilitated by the presence of a double bond in the vicinity of an α-carbon atom. The attack of oxygen is then directed to the C–H bond of the carbon atom in the α-position with respect to the double bond.

Several investigators[56] link the different rates of oxidation of hydrocarbons with the values of the energy of rupture of the C–H bond, which is in general agreement with the experimental results, as can be seen from the Table.

Hydrocarbons	Bond	Bond energy kcal
Benzene	C_6H_5—H	102
Methane	CH_3—H	101
Propane	n-C_3H_7—H	100
Propane	i-C_3H_7—H	94
Butane	n-C_4H_9—H	102
Isobutane	t-C_4H_9—H	89
Propene	CH_2=CH—CH_2—H	77
Toluene	$C_6H_5CH_2$—H	77.5
Ethylbenzene	$C_6H_5CH(CH_3)$—H	75
Isopropylbenzene	$C_6H_5C(CH_3)_2$—H	74

The extent of autoxidation and the maximum concentration of hydroperoxides of alkylarenes depend on the stability of the hydroperoxides, the purity of the original hydrocarbon, temperature, time, type of catalyst, and other factors. The stability of the hydroperoxides rises with increasing number of alkyl groups attached to the α-carbon atoms, tertiary hydroperoxides of alkylbenzenes being the most stable, and the primary compounds the least stable[26]. In the absence of catalysts at room or not very high temperatures (up to 65°) autoxidation hardly occurs at all or only very slowly; the production of a considerable amount of oxidation products requires the prolonged action of oxygen or air on the hydrocarbon. As a result, the final products are usually aldehydes and acids in the case of the oxidation of hydrocarbons containing primary alkyl groups, and ketones in the case of compounds containing secondary alkyl radicals. Under conditions of liquid-phase oxidation with molecular oxygen, tertiary alkyl groups are not oxidised at all, as already mentioned.

Catalysts accelerate autoxidation and shorten the induction period, but many of them also bring about decomposition of the hydroperoxides which have been formed, and

promote further oxidation to ketones and tertiary alcohols [53]. Thus the stearates and acetates of cobalt possess the ability to initiate and terminate reaction chains, so that in the presence of a certain concentration of these salts the autoxidation process is initiated, but increasing the concentration reduces or slows down the oxidation [57]. The naphthenates of cobalt, chromium, manganese, nickel, and other metals also often cause the formation of non-radical oxidation products and contribute to a more far-reaching oxidation [58].

In the autoxidation of alkylarenes there is nearly always observed at first an induction period, the duration of which depends on the type of catalyst, the nature and purity of the hydrocarbon, and other factors. This is followed by a rapid accumulation of hydroperoxide, and after some slowing down in the rate of oxidation a maximum concentration of hydroperoxide is reached, which then begins to diminish owing to decomposition of the hydroperoxide into ketones and alcohols or acids (depending on the structure of the hydrocarbon). When oxidation is resumed after being interrupted for 10–12 h, an induction period is also observed at first, after which the rate gradually levels out, and the process proceeds normally [59].

The autoxidation of the following monoalkylbenzenes has been studied: toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, n-butylbenzene, s-butylbenzene, and isobutylbenzene [10,14,60-63]. All these hydrocarbons, on vapour-phase oxidation with air in the presence of V_2O_5 + + MnO_2 at 300°–500°, form benzoic acid and maleic anhydride [60]. Alkylaromatic hydrocarbons containing primary and secondary α-carbon atoms often form as the main final products alcohols or ketones on oxidation with oxygen in the liquid phase, owing to the readiness with which the hydroperoxides of such hydrocarbons are cleaved [64-66].

Methyl-substituted arenes are oxidised very slowly by molecular oxygen to hydroperoxides, and under severe conditions are usually converted into higher oxidation products. Toluene, for example, is oxidised to benzaldehyde and benzoic acid under the prolonged action of oxygen in the absence of a catalyst [67-69] or in the presence of anthraquinone [70] or a copper, bismuth, iron, vanadium, or silver salt [71].

The autoxidation of toluene to a hydroperoxide has been achieved by several investigators [14,72-75], and has been studied in special detail by Sergeev and Fedorova [10] in the presence of manganese resinate as catalyst and isopropylbenzene peroxide as initiator. These workers found that, after air had been passing through for 44 h, the content of hydroperoxide in the toluene solution had reached 0.6%, and then began to diminish. They were able to isolate *via* the sodium salt a preparation containing 68.8% of benzyl hydroperoxide.

When ethylbenzene is oxidised with atmospheric oxygen in the presence of an oxide of copper or iron, 75–80% of acetophenone and 20–25% of α-phenylethyl alcohol are formed [65,66,76]. Oxides and hydroxides of iron, manganese, and cobalt, iron benzoate [77], ferric chloride, copper nitrate [78,79], and other substances [80] can also be used as catalysts for this oxidation. In the absence of catalysts, the prolonged action of oxygen at room temperature [67,68] or at 110° [81] oxidises ethylbenzene to acetophenone. Under milder conditions Hock [72] was able to oxidise ethylbenzene to a hydroperoxide, which was isolated in the free state *via* the sodium salt. Ethylbenzene is oxidised by oxygen to a hydroperoxide in the presence of esters of β-keto acids or of the hydroperoxide of isopropylbenzene and NaOH [82]. In a similar way, the prolonged action of oxygen on n-propylbenzene converts the latter into propiophenone [81].

Alkylbenzenes containing tertiary α-carbon atoms are very readily oxidised to hydroperoxides in the presence of metal oxides, hydroxides, and salts of organic acids [53,83-85]. As an example of such hydrocarbons, the oxidation of isopropylbenzene has been especially well studied. Among the products of organic synthesis few compounds can be found which have attracted such attention from research workers. This is explained primarily by the availability of isopropylbenzene and the ease of conversion of its hydroperoxide into phenol and acetone, 2-phenylpropan-2-ol and α-methylstyrene or acetophenone. The importance of these products is well known [86-88].

In 1926, Stephens [81] first studied the oxidation of isopropylbenzene, and showed that the action of oxygen on it at 80°–104° for 3–5 weeks yielded acetophenone and formic acid. Later several patents were taken out for the oxidation of isopropylbenzene to acetophenone and 2-phenylpropan-2-ol [76,77,89,90]. The catalysts recommended were calcium hydroxide; chromic oxide and calcium carbonate; ferric, manganese, cobalt, copper, and silver oxides and hydroxides; and iron benzoate.

In 1944, Hock and Lang [91] first prepared isopropylbenzene hydroperoxide, in 7.5% yield, by the oxidation of isopropylbenzene with atmospheric oxygen under the influence of ultra-violet radiation. Udris, Sergeev, Nemtsov, and Kruzhalov [92,93] made a detailed study of the oxidation of isopropylbenzene to the hydroperoxide in the presence of manganese resinate. This hydroperoxide is now manufactured in many countries of the world for the production of phenol and acetone. In the USSR the first large-scale plant for the production of phenol and acetone *via* isopropylbenzene hydroperoxide was put into operation in 1946 [86]. In Canada the first plant with an annual production of 6000 tons of phenol, 3500–4000 tons of acetone, and 5000 tons of α-methylstyrene [94,95] started work in 1953. Several enterprises of this type are operating in the USA with a total output exceeding 40 000 tons of phenol and ~ 25 000 tons of acetone per year [96-99]. Similar works exist in England, Poland [100,101], France [102,103], Western Germany, Belgium, Japan, and other countries [104].

The process for obtaining phenol and acetone consists in alkylating benzene with propene, oxidising the isopropylbenzene to the hydroperoxide with atmospheric oxygen, and splitting the hydroperoxide into phenol and acetone [86,105,106]. Autoxidation is carried out in homogeneous liquid phase at 85°–130° in the presence of catalysts and various additives, or in alkaline emulsion. The recommended oxidation initiators are naphthenates, linoleates, and acetates of manganese, cobalt, and lead [84,107,108] and salts of alkali and alkaline-earth metals with strong acids [109]. In several patents the liquid-phase oxidation of isopropylbenzene in the presence of finely ground sodium carbonate or bicarbonate suspended in the reaction mixture is proposed [110,111]. Hydroperoxyisopropylbenzene is obtained by this procedure in 83% of the theoretical yield. Oxidation of isopropylbenzene with atmospheric oxygen in the presence of sodium bicarbonate at 75° yields up to 57.6% of hydroperoxide in the reaction mass [112], but in the presence of powdered calcium carbonate or barium carbonate the yield may reach 94% based on the isopropylbenzene. When the reaction is carried out in the presence of carbonates there is no induction period [113]. The gradual decrease in activity of the calcium carbonate may be overcome by periodic

addition of sodium carbonate. Calcium carbonate can be employed up to relatively high temperatures while maintaining a high rate of oxidation.

Kolmakov *et al.*[114] have shown that the autoxidation of isopropylbenzene in the presence of azobis(isobutyronitrile), NaOH or sodium carbonate, in contrast to the industrial process using manganese resinate, occurs at a higher velocity, gives a higher concentration of hydroperoxide, and is less sensitive to inhibition of the reaction by formic acid. For the initiation of oxidation the following are recommended as well as the catalysts mentioned: oxides, hydroxides, and salts of metals of variable valency (*e.g.* manganese or cobalt), hydroxides of the alkali and alkaline-earth metals and their salts with formic, stearic, oxalic, benzoic, and other organic acids, as well as gaseous ammonia[115-128]. Aliphatic alcohols accelerate the oxidation[129], and esters of β-keto acids (*e.g.* ethyl acetoacetate and benzoylacetate) proved to be suitable for this purpose[63,130].

The metals copper and silver are active catalysts for the autoxidation of isopropylbenzene[131], and are supposed to act as stabilisers for the hydroperoxide. It is therefore sometimes recommended that, to prevent decomposition of the hydroperoxide at temperatures above 50°, the internal surface of the reaction vessel should be covered with copper, silver, gold, or their alloys[132]. According to other patents, copper causes decomposition of the hydroperoxide, and the use of copper reaction vessels is not recommended[109]. Metallic catalysts were suggested for the oxidation of alkylbenzenes as early as 1931[78].

Several patents cover the oxidation of isopropylbenzene in aqueous alkaline emulsion[62,64,105,133-142,148]. The rate of oxidation is then 3–7% of hydroperoxide per hour. The reaction is affected by the pH of the medium, the temperature, the relative volumes of the phases, and the intensity of agitation. For optimum conditions the medium should have a pH of 7–11. When the autoxidation of isopropylbenzene is initiated with barium peroxide (1%), the peroxide, the hydroperoxide, or other products are formed depending on the conditions[143].

In many patents hydroperoxycumene, either by itself[144,145], with alkaline additions[82,146-150] or with copper and silver salts[128], is recommended as initiator for the oxidation of isopropylbenzene. The use of hydroperoxides as oxidation initiators shortens or eliminates the induction period: hence it accelerates autoxidation and diminishes the formation of by-products.

The induction period is shortened and the yield of by-products diminished when hydrocarbons of general formula $ArCHR_2$ are treated with ozonised oxygen or air containing ozone in the presence of substances which combine with acidic products[151-155].

Preliminary purification of isopropylbenzene and other similar hydrocarbons from impurities which inhibit oxidation is regarded as of very great importance for increasing the velocity and the extent of oxidation[72,141,156,157]. Before oxidation, commercial isopropylbenzene is usually treated with concentrated sulphuric acid (permanganate, hypochlorite), caustic soda, heated over metallic sodium, and distilled. Several patents[158] suggest treating the hydrocarbon with alkylation catalysts before oxidation. Particularly good results are achieved by treating isopropylbenzene with sulphuric acid and carrying out autoxidation in a Pyrex glass reaction vessel. For this purpose porous alumina[159,160] or an aqueous solution of mercuric acetate[161,162] can also be employed. Autoxidation of isopropylbenzene with oxygen or gases containing oxygen occurs also in the absence of catalysts[163]. Homologues of cumene are capable of undergoing liquid-phase oxidation under the influence of ultra-violet radiation or in the presence of alkali-metal peroxides; formates, oxalates, and benzoates of the alkali and alkaline-earth metals; formaldehyde; organic hydroperoxides; and compounds which can be used as alkylation catalysts (*e.g.* fluorosulphonic acid, aluminium chloride, and BF_3–HF)[74,164-169].

During recent years a great deal of attention has been paid in research and patent specifications to the liquid-phase oxidation of s-butylbenzene, which, like isopropylbenzene, can be obtained among the readily available hydrocarbons of the petroleum-processing industry, and is readily converted, *via* the hydroperoxide, into phenol and butan-2-one. The latter is of great practical interest as a selective solvent.

s-Butylbenzene, like cumene, is oxidised by oxygen comparatively rapidly after an induction period[170], the concentration of α-hydroperoxy-α-ethyl-α-methyltoluene reaches a maximum, and then begins to fall owing to its decomposition. The induction period is smaller in the presence of hydroperoxy-s-butylbenzene, and completely disappears with large quantities of the latter.

The liquid-phase oxidation of s-butylbenzene is carried out in the presence of manganese resinate[62], calcium hydroxide[125], hydroperoxides[144], and other initiators which can be used for the oxidation of cumene[171]. The addition of barium peroxide is recommended[172-174] as it increases the yield of s-butylbenzene hydroperoxide. In the opinion of the investigators, BaO_2 is not a catalyst, but takes part in suppressing side reactions, *e.g.* in the formation of acetophenone.

Oxidation of s-butylbenzene to the hydroperoxide under the influence of ultra-violet radiation was first accomplished by Ivanov *et al.*[175] In the absence of catalysts and initiators, s-butylbenzene is oxidised by air considerably more slowly than is isopropylbenzene (Fig. 1), in spite of their similarity in structure[176]. The reaction is less sensitive to various additives, and occurs very slowly at 100°–110°. The rate of oxidation increases with rise in temperature, and the length of the induction period decreases. Addition of manganese resinate (0.25 mg litre^{-1})

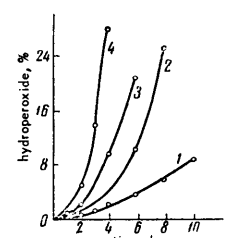


Fig. 1. Oxidation of s-butylbenzene (*1*, *3*) and cumene (*2*, *4*), at 120° (*1*, *2*) and 140° (*3*, *4*) in the absence of catalysts or initiators.

accelerates the oxidation of s-butylbenzene. As the amount of manganese resinate increases, the rate of oxidation increases, but the maximum achievable concentration of hydroperoxide in the reaction mass decreases (Fig. 2). Also with rise in temperature over the range 110°–150° the rate of oxidation increases, but the concentration of hydroperoxide in the reaction mixture decreases (Fig. 3).

This reaction has been studied in detail by Sergeev *et al.*[177] according to whom the optimum conditions for the oxidation of s-butylbenzene to a hydroperoxide content of 14–15% in the reaction mixture are a temperature of 110°–112° and a time of 8 h with 5 mg of manganese resinate per mole of the hydrocarbon. Addition of a minute amount of hydroperoxide considerably accelerates the autoxidation. The side-products of the oxidation are acetophenone, α-ethyl-α-methylbenzyl alcohol, and benzoic acid. Ethyl acetate and acetaldehyde have also been detected.

Investigation of the effects of various liquid, gaseous, and solid additions[176] on the rate of oxidation of s-butylbenzene has shown that cumene, barium carbonate, sodium sulphate, ammonia (0.1% added to the air), and barium sulphate (2%) have practically no effect on the rate of oxidation.

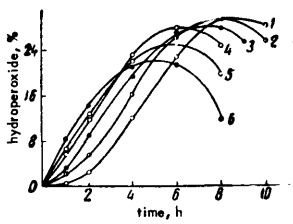


Fig. 2. Oxidation of s-butylbenzene at 140° in the presence of manganese resinate (mg litre^{-1}):
1) 0.0; 2) 0.25; 3) 9.0; 4) 18; 5) 36; 6) 62.

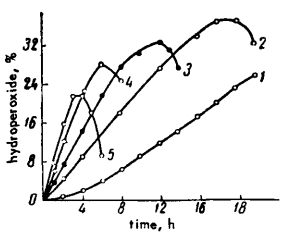


Fig. 3. Oxidation of s-butylbenzene in the presence of manganese resinate (18 mg litre^{-1}) at different temperatures:
1) 110°; 2) 120°; 3) 130°; 4) 140°; 5) 150°.

Phenol, the sulphates of nickel, manganese, and copper, hydrogen sulphide, and oxides of chromium, nickel, and copper retard the accumulation of the hydroperoxide. α-Ethyl-α-methylbenzyl alcohol, chlorine, and hydrogen chloride have an inhibiting effect. Sulphur dioxide has a particularly strong effect in diminishing the rate of oxidation, which practically ceases with a content of 0.001% of SO_2 in the air.

s-Butylbenzene is comparatively readily oxidised to the hydroperoxide in aqueous alkaline emulsion[178]. Oxidation of s-butylbenzene in the presence of sodium stearate, cobalt naphthenate, and sodium carbonate in aqueous solution yields α-ethyl-α-methylbenzyl alcohol and acetophenone[142].

The autoxidation of n-butylbenzene and isobutylbenzene with atmospheric oxygen to the corresponding hydroperoxides has been studied in the presence of ultra-violet radiation[64] and of various initiators[62,82,122].

Cyclohexylbenzene is comparatively slowly oxidised by molecular oxygen to hydroperoxide, but with appropriate choice of conditions a concentration of up to 23% of the latter in the reaction mass can be achieved. Suitable oxidation initiators are manganese resinate, formates, oxalates, and benzoates of the alkali and alkaline-earth metals, hydroperoxides, esters of β-keto acids, and formaldehyde[4,61,63,94,144,179–183].

LIQUID-PHASE OXIDATION OF DIALKYLBENZENES

Until very recently little information, and that mainly in the patent literature[85,115,169,183,184], was available on the liquid-phase oxidation of dialkylbenzenes to hydroperoxides. Dialkylbenzenes are oxidised by molecular oxygen in the presence of the same catalysts as with monoalkylbenzenes. Depending on the conditions, either monohydroperoxides or higher oxidation products are formed. Up to the present the dihydroperoxides of *p*-di-isopropylbenzene, *p*-isopropyl-s-butylbenzene, *p*-di-s-butylbenzene, and *p*-di-s-pentylbenzene have been isolated.

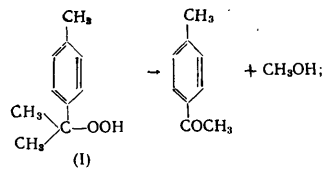
All the xylene isomers, on prolonged oxidation with oxygen either in the presence or in the absence of catalysts, are usually converted into the corresponding aldehydes or mono- and di-carboxylic acids[67–70,185–187]. A detailed review of the oxidation of xylenes has been given in a lecture by Toland and Nimer[188]. The monohydroperoxide of *p*-xylene was obtained by Hock and Lang[72] by shaking up *p*-xylene with oxygen and irradiating with light from a mercury source. This hydroperoxide can be prepared in 82% of theoretical yield by treating *p*-xylene with oxygen in the presence of di-t-butyl peroxide[74]. According to Lorand and Edwards' results[189] oxidation of *p*-xylene with molecular oxygen in the presence of di-t-butyl peroxide yields, in addition to *p*-methylbenzyl hydroperoxide, the following side-products: tolualdehyde, toluic acid, *p*-methylbenzyl alcohol, and 4,4′-dimethylbenzil and its polymeric homologues.

Sergeev and his coworkers[61] have studied the oxidation of *p*- and *m*-xylenes with air in the presence of manganese resinate and cumene hydroperoxide at 110°, and have shown that the monohydroperoxides which are then formed are very unstable and readily decompose during the oxidation. He was able to isolate preparations containing 67% of *p*-methylbenzyl hydroperoxide and 72% of the *meta*-isomer. Tolualdehydes and toluic acids were separated as by-products.

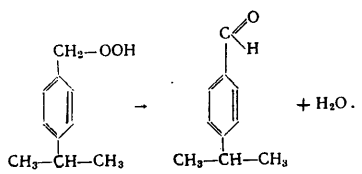
On oxidation in the presence of oxides of chromium and cobalt, *o*-, *m*-, and *p*-diethylbenzenes form the ethylacetophenones in yields of 14–19, 32–42, and 25–30% respectively[190,191]. The absence of the diacetylbenzenes among the oxidation products suggested that the acetyl group in the ethylacetophenones exerts an inhibiting action and prevents further oxidation. Sergeev and Sladkov[12] showed that, in the case of the oxidation of *p*-isopropylacetophenone, an acetyl group in the *para* position may even accelerate the oxidation of the isopropyl to a hydroperoxy group. Zavgorodnii[59] confirmed this view in the case of the oxidation of *p*-s-butylacetophenone. Later Sergeev and Sladkov[192] oxidised *p*-diethylbenzene with air in the presence of nickel benzoate and obtained *p*-ethyl-α-methyl-α-hydroperoxytoluene, separating it from the alkaline layer by treatment with CO_2. *p*-Ethylacetophenone was found among the by-products of the oxidation.

Research on the autoxidation of *p*-cymene is extensive. The liquid-phase oxidation of this hydrocarbon shows a failure of the rule that attack by molecular oxygen always occurs as a tertiary α-carbon atom.

The oxidation of *p*-cymene has been studied under various conditions, and some authors have assumed from the products isolated that oxidation occurs at the primary carbon atom of the methyl group[193,194] and others that the attack of oxygen is directed to the tertiary carbon atom of the isopropyl group[22,195]. In fact, the oxidation of *p*-cymene involves attack by oxygen on both the primary and the tertiary α-carbon atom with the formation of hydroperoxides of the two types (I) and (II)[61,67-69,81,196], which during the oxidation are partly decomposed into *p*-methylacetophenone and 4-aldocumene:



(I)



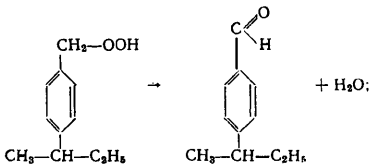
(II)

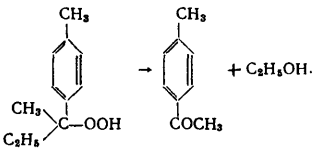
Serif *et al.*[197] studied the comparative ability of the methyl and isopropyl groups of *p*-cymene to undergo liquid-phase oxidation by Armstrong's emulsion method[133] and Helberger's photochemical method[194], and found that when *p*-cymene is oxidised in aqueous emulsion at 85° the isopropyl group is oxidised four times as readily as the methyl group. The same products are obtained at 60°, but under these conditions the hydroperoxides, formed initially, undergo less profound changes. Photochemical oxidation at 60° takes place at a lower rate than emulsion oxidation, and is not accompanied by cleavage of the primary oxidation products, so that the final products are only 4-methyl-α,α-dimethylhydroperoxytoluene and 4-(α-hydroperoxymethyl)cumene. The comparative capacity for oxidation of the tertiary α-carbon atom of the isopropyl group and of the primary methyl group in *p*-cymene is the same as with emulsion oxidation, *i.e.* 3.5 : 1. Thus the method affects the rate but not the direction of oxidation.

The substances recommended as initiators for the liquid-phase oxidation of *p*-cymene are hydroperoxy-*p*-cymene[144,198,199], di-t-butyl peroxide[74], benzoyl peroxide[200,201], esters of β-keto acids[63], magnesium naphthenate[155], sodium stearate, manganese acetate and NaOH[198], sodium carbonate[202], and others[119]. In all cases oxidation products of both the isopropyl and the methyl group are formed.

Yamamoto and Hata[203] obtained a 63% yield of *p*-cymene hydroperoxides, representing a mixture of the 7-, 8-, and 9-hydroperoxides, by the autoxidation of an emulsion of the hydrocarbon in the presence of benzoyl peroxide. *o*-Cymene is oxidised to hydroperoxides by molecular oxygen in the presence of manganese resinate at only half the rate observed with *p*-cymene[22].

p-s-Butyltoluene, like *p*-cymene, is oxidised by molecular oxygen in the presence of manganese resinate to form 4-methyl-α-ethyl-α-methyl-α-hydroperoxytoluene and 4-(s-butyl)-α-hydroperoxytoluene[61,196]. *p*-s-Butylbenzaldehyde and *p*-methylacetophenone were also detected among the oxidation products. They are formed by decomposition of the primary and tertiary hydroperoxides:





During recent years many investigations and patent specifications have been published on the liquid-phase oxidation of di-isopropylbenzenes, especially the *para*-isomer, which is obtained in considerable quantities as a by-product in the manufacture of cumene, and can be used *via* the mono- and di-hydroperoxides for the synthesis of *p*-isopropylphenol and quinol.

A survey of the investigations shows that *p*-di-isopropylbenzene is very readily oxidised by molecular oxygen to the mono- and di-hydroperoxides, especially if it has first been treated with sulphuric acid or finely ground, porous alumina[161]. The oxidation of di-isopropylbenzenes is carried out in the presence of alkali and alkaline-earth metal salts of formic, acetic, oxalic, benzoic, and stearic acids[122,126,204], metal oxides and hydroxides[62,119], manganese resinate either alone or with alkaline additions[205-207], esters of β-keto acids[63,109], barium peroxide[155], gaseous ammonia[208], and organic peroxides and hydroperoxides[82,144,209-213]. High pressures or periodic ozonisation of the oxygen which is passed through has an extremely favourable effect on the reaction[78]. A mixture of mono- and di-hydroperoxides is usually formed.

Our investigations have shown[206,207] that, in the presence of manganese resinate without added alkali, the liquid-phase oxidation with air of *p*-di-isopropylbenzene yields a maximum concentration of 25% of hydroperoxide, even if the hydrocarbon has been carefully purified from

impurities by treatment with sulphuric acid. Alkalis, *e.g.* NaOH, KOH, $Ca(OH)_2$, and Na_2CO_3, are not very effective by themselves and have almost identical effects, but when added to manganese resinate in amounts of 0.5–1.0 g per mole of the hydrocarbon, they accelerate the oxidation process and enable a higher concentration of hydroperoxide to be obtained. Oxidation is particularly vigorous if *p*-di-isopropylbenzene is first oxidised in the presence of alkali to a hydroperoxide content of 2–3% in the reaction mixture, and then manganese resinate is added and the passage of air continued. The *p*-di-isopropylbenzene prepared in this way can be oxidised in the presence of manganese resinate to a content of 78% of hydroperoxide in the solution.

A mixture of manganese resinate and cobalt acetate containing added calcium hydroxide initiates the oxidation more vigorously than do manganese resinate and cobalt acetate taken separately with this same addition. Addition of sodium stearate to a mixture of manganese resinate, cobalt acetate, and calcium hydroxide accelerates the oxidation and enables a 71% yield of the hydroperoxide to be obtained in 17 h, whereas when these initiators are employed in the absence of sodium stearate, the amount of oxidation is 33% of hydroperoxide in 16 h. *p*-Di-isopropylbenzene is comparatively easily oxidised to mono- and di-hydroperoxides in the presence of NaOH and hydroperoxides in an inert solvent, *e.g.* t-butylbenzene or a halogenobenzene [214].

Dihydroxyperoxy-*p*-di-isopropylbenzene is precipitated after its concentration in the solution exceeds 40%. This suggests that autoxidation of *p*-di-isopropylbenzene first yields a monohydroperoxide, but when the latter has reached a considerable concentration the oxygen begins to attack the second isopropyl group, ending with the formation of the dihydroperoxide. The effect of temperature on the rate of oxidation of *p*-di-isopropylbenzene is illustrated in Fig. 4.

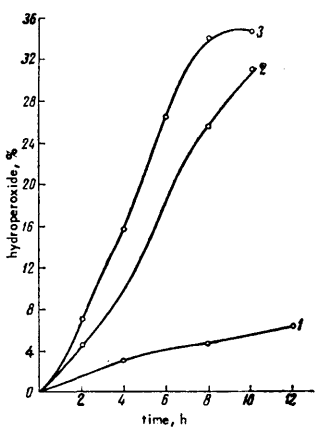


Fig. 4. Rate of oxidation of *p*-di-isopropylbenzene in the presence of manganese resinate and calcium hydroxide at temperatures of:
1) 85°; 2) 110°; 3) 130°.

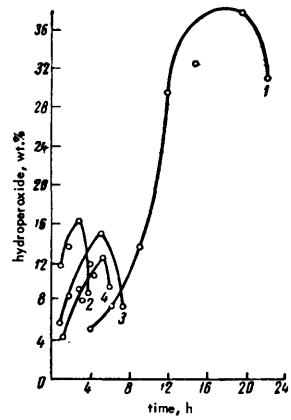


Fig. 5. Rate of oxidation of *p*-ethyl-isopropylbenzene at 85°:
1) manganese resinate, cobalt acetate, calcium hydroxide, and caustic soda;
2) manganese resinate, cobalt acetate, calcium hydroxide, and sodium stearate;
3) manganese resinate, cobalt acetate, and calcium hydroxide;
4) cobalt acetate and calcium hydroxide.

Oxidation of *p*-di-isopropylbenzene occurs readily in aqueous alkaline emulsion [183,215]. *m*-Di-isopropylbenzene is oxidised by atmospheric oxygen in the presence of alkali to a mixture of mono- and di-hydroperoxides [216,217], decomposition of which yields, in addition to resorcinol, *m*-isopropylphenol and *m*-isopropenylphenol.

Eventova *et al.* [218,219] found that the resistance to liquid-phase oxidation with oxygen at 175° falls in the series: *o*-, *m*-, and *p*-di-isopropylbenzenes, the *para*-isomer being oxidised three times as rapidly as the *ortho*-isomer. Among the oxidation products were found phthalic acids, phenol, acetophenone, formic acid, acetic acid, *m*-acetylbenzoic acid, resorcinol, and *m*-diacetylbenzene. It was confirmed that, in this case too, the action of the oxygen is directed at the tertiary α-carbon atom with the formation of hydroperoxides.

We have studied the liquid-phase oxidation of *p*-ethyl-isopropylbenzene. The initiator used was manganese resinate with addition of calcium hydroxide, caustic soda, sodium stearate, and cobalt acetate [207]. Under the conditions studied this hydrocarbon was found to oxidise very slowly (influence of the ethyl group in the *para*-position). The hydroperoxide formed is unstable and usually starts to decompose after 3–6 h. The main product of acid cleavage is *p*-isopropylphenol. Hence it follows that the attack of molecular oxygen is directed in the first place at the secondary α-carbon atom, in spite of the presence in the molecule of the tertiary α-carbon atom in the isopropyl group. The effect of manganese resinate on the rate of oxidation in the presence of various additives is shown in Fig. 5.

p-t-Butylcumene is oxidised by atmospheric oxygen to the corresponding monohydroperoxide. The liquid-phase oxidation of this hydrocarbon has been studied in detail by Sergeev and Kruzhalov[220]. It has been shown that one mole of the well-purified hydrocarbon requires 2.5 mg manganese resinate or 0.02–0.03 g caustic soda for the oxidation to occur at a rate of 5–7% hydroperoxide per hour. The extent of oxidation or the percentage conversion of the hydrocarbon into the hydroperoxide reaches 30 wt.% and more. In several experiments the concentration of hydroperoxide in the reaction mixture reached 42–45 wt.%. Hydroperoxy-*p*-t-butylcumene has limited solubility in the reaction mixture, so that, on standing, up to 50% of it separates as crystals. It can be isolated in this form by washing the oxidation products with n-pentane[221].

In the presence of peroxides and hydroperoxides *p*-s-butylcumene is oxidised in the liquid phase to its mono- and di-hydroperoxides. According to Tsutsumi and Odaira's results[222] the α-carbon atom of the isopropyl group is the one more readily attached by oxygen. According to our own results[223,224], *p*-s-butylcumene, in the presence of manganese resinate alone or with $Ca(OH)_2$, NaOH, Na_2CO_3, BaO_2, or sodium stearate, at 95°, 115°, or 120°, is very easily oxidised by air even without any special additional purification. Addition of calcium hydroxide to the manganese resinate allows the oxidation to be carried out during the first 5 h at a rate of 10% of hydroperoxide per hour, and to obtain after 10 h a maximum concentration of 71% of hydroperoxide. If sodium carbonate is added instead of calcium hydroxide to the manganese resinate, oxidation occurs still more rapidly. The maximum concentration of hydroperoxide is reached in 6 h and amounts to 71.1%. Thus additions of alkali not only accelerate the oxidation of *p*-s-butylcumene but also increase its extent.

Cleavage of hydroperoxy-*p*-s-butylcumene with sulphuric acid yields acetone, ethyl methyl ketone, quinol, and a mixture of *p*-isopropylphenol and *p*-s-butylphenol. The presence of these products shows that the oxidation of *p*-s-butylcumene involves the formation of 4-(s-butyl)-α,α-dimethyl-α-hydroperoxytoluene and 4-(α-methyl-α-ethyl-α-hydroperoxy)cumene and the dihydroperoxide.

p-Cyclohexylisopropylbenzene, previously purified by washing with sulphuric acid, is comparatively readily oxidised by air in the presence of manganese resinate alone or with added alkali at 95°–120°. The attack by oxygen is then directed mainly at the tertiary carbon atom of the isopropyl radical and results in the formation of hydroperoxy-*p*-cyclohexylisopropylbenzene. The tertiary carbon atom of the cyclohexyl radical is oxidised with greater difficulty under these conditions, and therefore 4-(hydroperoxycyclohexyl)cumene is formed in negligible yield[225]. In this case, too, autoxidation involves the formation of a maximum concentration of hydroperoxide, which on prolonged oxidation completely disappears from the reaction mixture. The effect of added alkali on the autoxidation is clear from Fig. 6.

In the presence of manganese resinate alone, *p*-cyclohexylisopropylbenzene is oxidised to a lesser extent than when alkali is also present. Sodium carbonate and calcium hydroxide have roughly the same effect.

The course of the oxidation of *p*-cyclohexylisopropylbenzene in the presence of manganese resinate, calcium hydroxide, cobalt acetate, and sodium stearate is unusual. The maximum content of hydroperoxide in the solution is 6% and is reached in 6 h; then it begins to diminish, and after

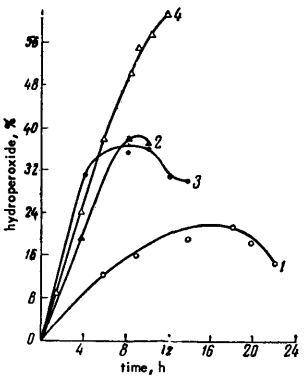
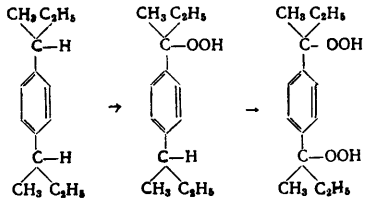


Fig. 6. Effect of added alkali on autoxidation of *p*-cyclohexylisopropylbenzene at 118°–120° with an air flow of 30 litres h^{-1}: 1) manganese resinate; 2) manganese resinate and sodium carbonate; 3) manganese resinate and calcium hydroxide; 4) manganese resinate, sodium carbonate, and barium peroxide.

10 h the hydroperoxide disappears from the reaction mass and cannot be detected after the lapse of tens of hours. The products of the reaction are *p*-cyclohexylacetophenone and *p*-cyclohexylphenol.

A thorough study has been made of the liquid-phase oxidation of *p*-di-s-butylbenzene, which is obtained as a by-product of the manufacture of s-butylbenzene and has not yet found any industrial use. The oxidation of *p*-di-s-butylbenzene has been investigated mainly by the Japanese chemists Tsutsumi, Odaira, and Torii[142,215] and Yamada and Matsumoto[226,227]. They showed that this hydrocarbon is oxidised by oxygen, in either the presence or the absence of catalysts, to form mono- or di-hydroperoxides or higher oxidation products. One secondary butyl group is especially easily oxidised. In the presence of water, sodium carbonate, and sodium stearate at 80° and 30 atm, *p*-di-s-butylbenzene is oxidised with the formation of α,α′-dihydroxy-*p*-di-s-butylbenzene, *p*-diacetylbenzene, and *p*-s-butylacetophenone. In the presence of the same catalysts and benzoyl peroxide or the hydroperoxide of the original hydrocarbon at 95°, the mono- and di-hydroperoxides are formed with a maximum concentration of 39.5%. Fedorova and Sergeev made a detailed study of the liquid-phase oxidation of *p*-di-s-butylbenzene[61,228] and showed that, in the presence of manganese resinate, the hydrocarbon is oxidised at a mean rate of 3.0–3.5% hydroperoxide per hour, the maximum concentration of hydroperoxide reaching 48.5%. They estimated the rate of formation of mono- and di-hydroperoxides of *p*-di-s-butylbenzene by periodically determining the available oxygen in the reaction mass and analysing the products of sulphuric-acid cleavage. Zavgorodnii[59] studied the oxidation of *p*-di-s-butylbenzene, both the by-product of the experimental production of s-butylbenzene and the synthetic material, purified with sulphuric acid, and the unpurified material, containing 3–4% of the *ortho*-isomer. Oxidation was carried out in the presence of manganese resinate and

added alkali at 95°–120° and a rate of flow of air of 25–120 litres h^{-1} per mole of hydrocarbon. Conditions were found under which *p*-di-s-butylbenzene could be oxidised to a hydroperoxide concentration of 62.2% (arbitrarily based on the monohydroperoxide) or practically entirely converted into mono- and di-acetylbenzenes. *p*-Diacetylbenzene is formed in 57% yield of the theoretical in a single oxidation. On the basis of these results the author assumes that the oxidation of *p*-di-s-butylbenzene takes place in stages. The monohydroperoxide is formed initially, and no dihydroperoxide is present among the reaction products. When a definite concentration of the monohydroperoxide is reached, the oxygen attacks the α-carbon atom of the second s-butyl group, resulting in formation of the dihydroperoxide. On prolonged passage of air the hydroperoxides are split into ketones. The oxidation can be represented by the scheme:



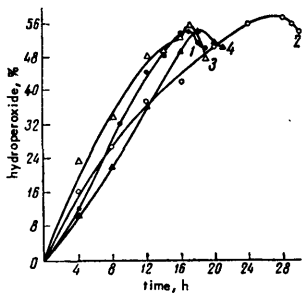


Fig. 7. Effect of added alkali on autoxidation of *p*-di-s-butylbenzene at 118°–120° with an air flow of 30 litres h^{-1}:
1) manganese resinate; 2) manganese resinate and calcium hydroxide; 3) manganese resinate and sodium carbonate; 4) manganese resinate and cobalt acetate.

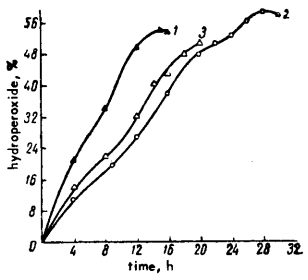


Fig. 8. Autoxidation of *p*-di-s-butylbenzene in the presence of manganese resinate and sodium carbonate at 110°–120° and air flows of litres h^{-1}:
1) 5; 2) 30; 3) 60.

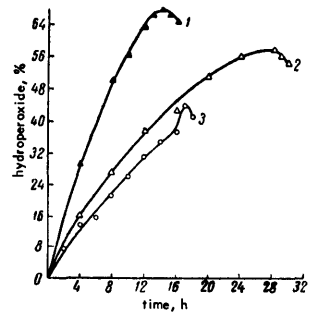


Fig. 9. Autoxidation of *p*-di-s-butylbenzene from different sources in the presence of manganese resinate and calcium hydroxide at 118°–120°:
1) pure synthetic; 2) containing 3–4% of the *ortho*-isomer; 3) isolated from the polybutylbenzene residues from experimental production.

The effects of added alkali, the rate of flow of air, and the purity of the hydrocarbon on the velocity and character of the oxidation of *p*-di-s-butylbenzene are shown in Figs. 7–9.

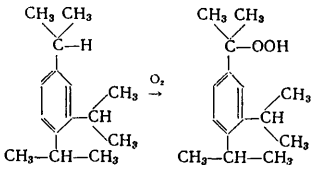
LIQUID-PHASE OXIDATION OF TRIALKYLBENZENES

The oxidation of trialkylbenzenes to hydroperoxides has hardly been studied at all. According to the literature, the prolonged action of oxygen on 1,2,4-trimethylbenzene and mesitylene yields the corresponding dimethylbenzoic acids[67,69]. Recently Sergeev and coworkers[61] have been able to oxidise mesitylene in the presence of manganese resinate to the monohydroperoxide, the maximum concentration of which after 40 h was 4.13%. This hydroperoxide is very unstable, and readily decomposes during oxidation, so that the oxidation products include also α-aldomesitylene and α-carboxymesitylene.

Among other trialkylbenzenes the oxidation has been studied of 1,3,5-tri-isopropylbenzene to the mono-, di-, and tri-hydroperoxides[229–232]. The main aim of the investigations, as was emphasised by Proft at the annual meeting of the Chemical Society of the GDR,[233] was to oxidise the hydrocarbon to the trihydroperoxide and cleave the latter to phloroglucinol, *i.e.* to accomplish the synthesis of this interesting but inaccessible trihydric phenol.

Oxidation of 1,3,5-tri-isopropylbenzene by a current of oxygen in ultra-violet radiation, or at 110° in the presence of a small amount of concentrated caustic soda solution, does not yield the desired results, owing to rapid decomposition of the reaction products (in the former case after absorption of 12% of the required amount of oxygen, and in the latter after absorption of 17%). The maximum yield (30%) of hydroperoxy-1,3,5-tri-isopropylbenzene was obtained by oxidising the hydrocarbon in a faintly alkaline emulsion at 85°. The use of NaOH, KOH, $Ca(OH)_2$, or hydroperoxides is recommended to eliminate the induction period. In order to obtain the monohydroperoxide, oxidation is continued to the extent of 30% conversion; for the di- and tri-hydroperoxides up to 80–90% conversion is required (calculated on the monohydroperoxide).

We have studied[231] the liquid-phase oxidation of 1,2,4- and 1,3,5-tri-isopropylbenzenes. The former is oxidised by atmospheric oxygen in the presence of manganese resinate and sodium carbonate to a maximum hydroperoxide concentration in the solution of 53%. Only the isopropyl group standing alone then undergoes autoxidation, the two groups mutually *ortho* blocking one another and remaining practically unoxidised. As a result, only the monohydroperoxide is formed:



1,3,5-Tri-isopropylbenzene in the presence of manganese resinate and sodium carbonate is oxidised extremely rapidly by atmospheric oxygen, the mean initial velocity being 20–30% of hydroperoxide per hour. Volkov[234] has shown that the oxidation takes place with the successive formation of a mixture of the mono-, di-, and tri-hydroperoxides of 1,3,5-tri-isopropylbenzene. Tri-isopropylbenzene peroxide is also obtained as a by-product.

There are indications, although only in the patent literature[232], that *meta*-substituted phenols can be obtained by oxidising 1,3,5-triethylbenzene, 1,2-di-isopropyltoluene, 1,3,5-tri-s-butylbenzene, 1,3,5-tri-n-pentylbenzene, 1,3,5-tricyclopentylbenzene, and 3,5-dichlorocumene, instead of 1,3,5-tri-isopropylbenzene. The resulting hydroperoxides are employed to obtain the corresponding alcohols and acetylphenols, and are also used as components of explosives and initiators for free-radical polymerisation.

LIQUID-PHASE OXIDATION OF POLYNUCLEAR ARENES

A. Oxidation of Hydrocarbons Containing Separated Benzene Nuclei

Descriptions have been published of the liquid-phase oxidation of diphenylmethane[91,142], di-*p*-tolylmethane[235], 1,1-diphenylethane[16,20,236-240], 1-phenyl-1-*p*-tolylethane, 1-*p*-ethylphenyl-1-phenylethane, 1-*p*-isopropylphenyl-1-phenylethane, 1-phenyl-1-*p*-t-butylphenylethane, 1,1-di-*p*-tolylethane, 1,1-diphenylpropane[21,241], 1,1-diphenylbutane, 1,1-diphenylpentane, 1,1-diphenylhexane, tribenzylmethane, tris(β-phenylethyl)methane, 1,2-diphenylethane, 1,3-diphenylpropane, 1,4-diphenylbutane, 1,5-diphenylpentane, and 1,6-diphenylhexane[240,242]. The same catalysts are recommended for these oxidations as for those of alkylbenzenes. The simplest of these hydrocarbons, diphenylmethane, is oxidised comparatively slowly, a yield of up to 12% of diphenylmethanol being obtained in the presence of water, sodium carbonate, and sodium stearate.

The oxidation of 1,1-diphenylethane has been most thoroughly studied, probably owing to the ease with which the hydroperoxide of this hydrocarbon can be isolated and its excellent initiating properties for the low-temperature copolymerisation of butadiene with styrene. When oxygen is passed at a rate of 6–8 ml min^{-1} through 1,1-diphenylethane at 65°–70°, the hydroperoxide concentration reaches 28.5%. The hydroperoxide can be isolated in the form of crystals or it can be decomposed, without being isolated, with sulphuric acid into phenol and acetophenone[237].

Eventova *et al.*[239] have found that the rate of oxidation of 1,1-diphenylethane at 175° is 28.9% after 3 h. Higher oxidation products were obtained (the hydroperoxide decomposes above 120°), but it was considered that under these conditions also the oxidation proceeds *via* formation of the hydroperoxide.

Yurzhenko and Puchin[236] worked out a technical method for oxidising 1,1-diphenylethane to the hydroperoxide in the presence of diphenylethane hydroperoxide and NaOH. After 25–30 h, the concentration of the hydroperoxide was 32–35%. When the reaction mixture was allowed to stand for 2–3 days, up to 64% of hydroperoxide came down in the precipitate, and could be readily separated. The oxidation of 1,1-diphenylpropane occurs similarly *via* the formation of a hydroperoxide having the structure $(C_6H_5)_2.C(OOH).C_2H_5$.[239]

The other 1-alkylphenyl-1-phenylethanes mentioned above are oxidised to the corresponding hydroperoxides in a similar way by oxygen in the presence of NaOH, although considerably more slowly than are t-alkylbenzenes (0.25–0.35% of hydroperoxide per hour). The hydroperoxides can readily be separated and purified by chromatography on Al_2O_3. In the case of the liquid-phase oxidation of 1,1-diphenylbutane, 1,1-diphenylpentane, and 1,1-diphenylhexane the tendency for hydrocarbons of this type to undergo oxidation increases with increase in the number of carbon atoms in the chain, independently of whether it is odd or even, but hydrocarbons of this series are less resistant to oxidation than are hydrocarbons of the 1,6-diphenylhexane series[240].

Triphenylmethane is oxidised by oxygen to the hydroperoxide, which can be obtained also from triphenylmethyl chloride and hydrogen peroxide[243-245].

Methylcyclohexylphenylmethane (I), dicyclohexylphenylmethane (II), cyclohexadienyldiphenylmethane (III), and cyclohexylcyclohexylidenephenylmethane (IV) are oxidised to hydroperoxides[246]. The rate of oxidation increases in the order II, I, IV, III. Examination of the reduction and acid cleavage products of the hydroperoxides showed that oxidation occurs not only at the central methane carbon linked to the cyclohexyl and phenyl radicals but also at the first and second carbon atoms of the cyclohexyl radical; as a result, a mixture of hydroperoxides having a concentration in the solution of ≥ 7% is formed.

In the liquid-phase oxidation of tribenzylmethane and tris(β-phenylethyl)methane at 175°, the oxygen attacks the α-carbon atoms directly linked to the benzene nucleus[247,248] in spite of the presence of a tertiary carbon atom in the aliphatic chain. This results in the formation of α,α′-dihydroperoxides, which split into benzoic, acetic, and formic acids. The same rule is observed in the liquid-phase oxidation of 1,2-diphenylethane, 1,3-diphenylpropane, 1,4-diphenylbutane, 1,5-diphenylpentane, and 1,6-diphenylhexane. In this series of diphenylalkanes the tendency to oxidation increases with molecular weight. Hydrocarbons containing an odd number of carbon atoms in the aliphatic chain are more resistant to oxidation than are those containing an even number.

Kuznetsov and Ivanov[242] constructed a circulatory-flow apparatus for investigating the kinetics of the oxidation of hydrocarbons by molecular oxygen, established optimum conditions for the oxidation of diphenyl- and dicyclohexyl-alkanes, and showed that the rate of oxidation decreases

with increase in the velocity of circulation of oxygen above 24–25 ml min^{-1} and in temperature above 140°–160°.

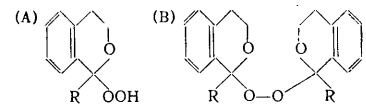
B. Oxidation of Hydrocarbons Containing Fused Benzene Nuclei

The oxidation to hydroperoxides of several alkylnaphthalenes, alkylhydronaphthalenes, alkylbiphenyls [*sic* (Ed. of Translation)], and other aromatic hydrocarbons containing fused benzene rings has now been studied. 2-Methylnaphthalene in the presence of organic peroxides — in particular of di-t-butyl peroxide — is oxidised to a hydroperoxide which on acid cleavage is converted into 2-naphthol and formaldehyde [74]. 2-Isopropylnaphthalene, on liquid-phase oxidation with oxygen or gases containing oxygen in the presence of hydroperoxides, alkali-metal carbonates or bicarbonates, cobalt linoleate, or peroxides, form a hydroperoxide with the peroxy-group attached to the α-carbon atom of the isopropyl group [84,249-251]. In a mixture of 1- and 2-isopropylnaphthalenes, the latter isomer is oxidised considerably more readily than the former [252]. 1,4-Dihydronaphthalene [37,253] and 1,2-dihydro-1-methylnaphthalene [254] are oxidised in the liquid phase to the corresponding hydroperoxides. Tetralin is readily oxidised to the hydroperoxide [4,255-257]. Chizhevskaya and Idel'chik [258] suggested a faster method for obtaining hydroperoxytetralin by oxidising the hydrocarbon in the presence of 0.01% of manganese stearate or cobalt stearate. Oxidation of tetralin proceeds well at 60°–80° under normal or high pressures with simultaneous illumination of the reaction mixture by red and yellow light in the presence of chlorophyll, which has a sensitising action [259]. In the oxidation by atmospheric oxygen of commercial tetralin, containing 0.1% of magnesium stearate, in tubes made of brass, copper, Monel, stainless steel, and iron at 70°–75° in a thermostat, the respective yields of 1-hydroperoxy--1,2,3,4-tetrahydronaphthalene obtained after 50 h were 37.5, 36.0, 35.2, 29.4, and 21.1%. In a silver-plated tube the yield of hydroperoxide amounts to 35.6% [260]. 1,2,3,4--Tetrahydro-1-methylnaphthalene [255,261,262], 1-ethyltetralin, 1,4-dimethyltetralin, and 1,4-diethyltetralin [263] are readily oxidised to the hydroperoxides in the presence of various catalysts, *e.g.* sodium carbonate. Decalin is oxidised in the liquid phase to the 9-hydroperoxide [264,265]. A mixture of *cis*- and *trans*-decahydronaphthalenes (90% of the *cis*--isomer), on oxidation with atmospheric oxygen in the presence of cobalt, manganese, and zinc oleates, gives products containing 80% of a solid hydroperoxide [266].

In the presence of peroxides and hydroperoxides, alkylbiphenyls are comparatively readily oxidised to hydroperoxides by molecular oxygen. For example, 4-isopropylbiphenyl in the presence of di-t-butyl peroxide and $NaHCO_3$ at 148°–153° on oxidation had a hydroperoxide content of 32.8% after 1 h, and 34.6% after 2 h. The hydroperoxide of 3-isopropylbiphenyl was obtained in a similar manner. In the presence of sulphuric acid the former is split into 4-phenylphenol, and the latter into 3-phenylphenol [267]. A mixture of 3- and 4-isopropylbiphenyls, on oxidation with air in the presence of calcium hydroxide at 165°–170°, is converted after 24 h to the extent of 35.8% into "α-diphenylylacetophenone" and 11.9% into 4-biphenylyldimethylmethanol [268]. 4-s-Butylbiphenyl, in the presence of manganese resinate and hydroperoxycumene is oxidised by air to a hydroperoxide, whose concentration reaches 22% after 32 h. [269]

Aromatic hydrocarbons and several of their derivatives having more highly fused ring systems are capable of autoxidation to form the corresponding hydroperoxides. The oxidation to hydroperoxides has been described of indane [27,270], 1,3,3-trimethylindane [271,272], perhydroindane [27,262], fluorene [261], 1,2,3,4,10,11-hexahydrofluorene [273], octahydroanthracene [274], tetrahydroacenaphthylene or tetraphene [275], isochroman and di-isochroman [276,277], alkylisochromans [278], and symmetrical and unsymmetrical hexahydropyrenes [279]. 1,2,3,4,10,11-Hexahydrofluorene on liquid-phase oxidation gives a 76% yield of the 11-hydroperoxide. Autoxidation of tetraphene at 60°–80° in a glass flask yields di-11-tetraphenyl† peroxide and small quantities of 5-tetraphenone, which is probably a product of the spontaneous dehydration of the intermediate 5-hydroperoxytetraphene. When oxygen is blown through tetraphene in a quartz vessel at 40°, 11-hydroperoxytetrahydroacenaphthylene is obtained.

Isochroman, 1-methylisochroman, 1-isopropylisochroman, and 1-benzylisochroman are readily oxidised in the light to the corresponding hydroperoxides [276]. The hydroperoxides of isochroman and 1-methylisochroman are converted under the action of H_2SO_4 into dimeric peroxides (B):



The analogous peroxides of 1-ethylisochroman and 1-cyclohexylisochroman, as well as the peroxide of bis--5,6-benzoisochroman-1-yl, are obtained by direct autoxidation of the corresponding isochromans without separation of the intermediate products.

Symmetrical and unsymmetrical hexahydropyrenes, 1,2,3,4,5,8,9,10,11,16-decahydropyrene, and hexadecahydropyrene undergo autoxidation [279].

Steroid compounds containing isolated double bonds are readily converted into hydroperoxides in the presence of photosensitisers [280,281]. Thus irradiation of cholesterol and haematoporphyrin with a mercury lamp in a current of oxygen gives a 49.2% yield of 5α-hydroperoxycholesterol [281]. Photo-oxidation of Δ^5-cholesten-3-one in the presence of dichlorotetraiodofluorescein in $C_6H_6-CH_3OH$ mixture by irradiation with a sodium lamp results in the formation of the carcinogenic 6β-hydroperoxy-Δ^5-cholesten-3-one in 9.3% yield. This suggests a link between carcinogenic hydroperoxysteroids and cancerous diseases caused by ultra-violet radiation. Ergosterol on ultra-violet irradiation in the presence of 1,8-dihydroxyanthraquinone gives a 33% yield of hydroperoxide [281]. Hydroperoxides of pregnenolone have been obtained.

LIQUID-PHASE OXIDATION OF SUBSTITUTED ALKYLBENZENES

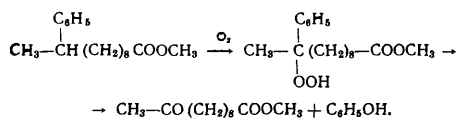
(*a*) Oxidation of alkylhalogenobenzenes. We have studied the liquid-phase oxidation of *p*-fluoroisopropylbenzene and *p*-cyclohexylfluorobenzene to the corresponding hydroperoxides by atmospheric oxygen in the presence of manganese resinate, cobalt acetate, and

† For numbering of rings see Treibs and Thörmer, ref. 275, p. 95 (Ed. of Translation).

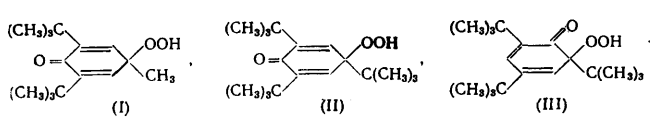
NaOH.[282] The halogenated alkylbenzenes are oxidised more slowly and form lower maximum concentrations of hydroperoxides than the alkylbenzenes themselves. Thus oxidation of *p*-fluoroisopropylbenzene in the presence of caustic soda yielded a maximum concentration of 23.2% of the hydroperoxide. Oxidation of *p*-cyclohexylfluorobenzene in the presence of NaOH, cobalt acetate, and manganese resinate gave a maximum hydroperoxide concentration of 12%. *p*-Chloroisopropylbenzene in the presence of hydroperoxycumene and NaOH is oxidised to the hydroperoxide[283]. In a similar manner 4-chloro-, 2-chloro-, 4-methyl-, 3-chloro-4-isopropyl-, and 2,4-dichloro-isopropylbenzene are oxidised to the corresponding hydroperoxides.

(*b*) Oxidation of oxygen-containing aromatic compounds. Among oxygen-containing compounds the oxidation to hydroperoxides has been studied of *p*-methylacetophenone[13], *p*-isopropylacetophenone[12,15], *m*-isopropylacetophenone[284], *p*-s-butylacetophenone[59], the methyl and ethyl esters of phenylacetic[14], toluic[285], isopropylbenzoic, and 10-phenylundecanoic acids[286,287], several alcohols[288,289], and alkylphenols[290,291].

p-Methylacetophenone in the presence of nickel benzoate is oxidised by atmospheric oxygen to give 2% of the hydroperoxide after 20 h, but this is very unstable, so that the end-product is *p*-acetylbenzoic acid in 70% yield after 56 h. Methyl and ethyl phenylacetates on similar oxidation are converted into the esters of phenylglyoxylic acid[14]. The dimethyl and diethyl esters of *cis*-3,6-diphenyl-Δ^4-cyclohexene-1,2-dicarboxylic acid are oxidised to the respective 5-hydroperoxides[292]. *p*-Isopropylacetophenone in the presence of nickel benzoate is oxidised to the corresponding hydroperoxide, which also, like the hydroperoxide of *m*-isopropylacetophenone, is cleaved by sulphuric acid into ketophenols employed in the synthesis of drugs. Methyl 10-phenylundecanoate in the presence of the sodium salt of cumene hydroperoxide is oxidised according to the scheme:



Phenols are known to inhibit autoxidation. Trialkylphenols, added in the autoxidation of isopropylbenzene, are themselves partly oxidised to derivatives of alkyl 4-hydroxyaryl ketones and 1,2-di-*p*-hydroxyphenylethane[293]. Bicke and Gersmann[290] showed that 4-methyl-2,6-di-t-butylphenol and 2,4,6-tri-t-butylphenol in alkaline medium in an atmosphere of oxygen form hydroperoxides in 75% yield, the first compound forming a single hydroperoxide (I), and the second yielding two hydroperoxides (II and III):



(*c*) Oxidation of alkylnitrobenzenes. *o*-Ethylnitrobenzene[294] in the presence of $K_2Cr_2O_7$, $KMnO_4$, and HNO_3 is usually oxidised to *o*-nitrobenzoic acid. *p*-Isopropylnitrobenzene in the presence of nickel benzoate at 100° is oxidised by air to the hydroperoxide, the concentration of which reaches 38.5% after 55 h. The pure hydroperoxide on standing for a long time in the light gradually darkens, and on heating to 150°–160° it decomposes with a flash and the separation of soot[11,295]; when oxygen is blown through *p*-isopropylnitrobenzene in the presence of caustic soda at 130°, the yield of hydroperoxide reaches 89.6% after 15 h. Oxidation can be carried out in the presence of hydroperoxycumene[296].

The following hydroperoxides were obtained in an analogous manner: 4,3-$CH_3(NO_2)C_6H_3.C(CH_3)_2.OOH$, *p*-$NO_2.C_6H_4.C(CH_3)_2.OOH$, etc.[297]

p-Nitrotoluene on oxidation with air under pressure in the presence of manganese and cobalt naphthenates forms *p*-nitrobenzoic acid in 55–75% yield[298].

Arylmagnesium halides, *e.g.* *p*-bromophenylmagnesium bromide, phenylmagnesium bromide, and mesitylmagnesium bromide, are oxidised by oxygen at low temperatures forming the hydroperoxides in yields of 9.3, 5.2, and 3% respectively[299].

ISOLATION AND SEPARATION OF HYDROPEROXIDES

The most varied methods are used for isolating hydroperoxides from the reaction mixture in a pure or highly concentrated form. However, the most widely employed method is to convert them into the sodium salts. It is possible in this way to isolate even the relatively unstable hydroperoxides of toluene, the xylenes, and mesitylene in a quite concentrated form.

Steam distillation is often employed to concentrate the hydroperoxides. A considerable proportion of the unoxidised original hydrocarbon usually distils over with the steam, and a more concentrated hydroperoxide remains in the flask[142,300].

Stable hydroperoxides are isolated by distillation under reduced pressure. Thus distillation of cyclohexylbenzene hydroperoxide at 0.1 mm yielded a preparation containing 90.53% of the hydroperoxide[48]. Extractive distillation of mixtures[301,302] and treatment with hydrogen peroxide in the presence of mineral acids are employed[303].

Mixtures of hydroperoxides are usually separated by first treating the oxidation products with alkaline solutions of various concentrations, then selectively extracting the hydroperoxides from the latter with volatile, water-immiscible solvents such as CH_2Cl_2, $CHCl_3$, $C_2H_4Cl_2$, $(C_2H_5)_2O$, etc. In this way it was possible to separate the primary and tertiary hydroperoxides of the cymenes[304] and of *p*- and *m*-di-isopropylbenzenes[305].

Hydroperoxides are often isolated and purified by chromatography, which is specially suitable for the isolation of crystalline hydroperoxides, *e.g.* hydroperoxy-1,1-diphenylethane[241].

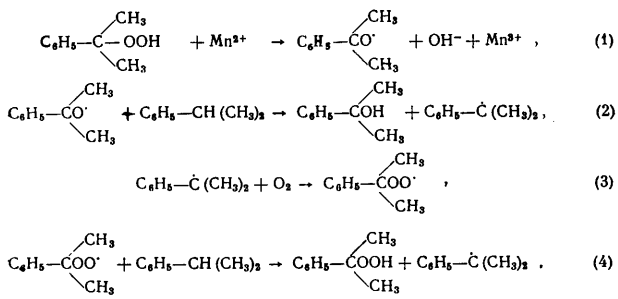
When a hydroperoxide is crystalline and may be precipitated (*e.g.* the dihydroperoxides of *p*- and *m*-di-isopropylbenzenes and of *p*-di-s-butylbenzene), it is filtered off from the cooled reaction mixture and well washed with petroleum ether[220,306]. If it is desired to extract the dihydroperoxide completely the filtrate is treated at a low temperature with benzene or petroleum ether, after which the precipitated dihydroperoxide is again separated, the residue treated with caustic alkali and the hydroperoxide isolated *via* the sodium salt[213].

MECHANISM OF LIQUID-PHASE OXIDATION OF ALKYLARENES

The question of the mechanism and the velocity of the liquid-phase oxidation of hydrocarbons in general, and in particular of alkylarenes with molecular oxygen, has been extensively studied and the results described in review papers [56,86,307]. However, we still do not have a definite solution for all stages of the mechanism, possibly owing to the extraordinary complexity of this reaction [308].

Attempts have been made to find a relationship between the structure of alkylarenes and their reactivity towards oxygen, and to establish the laws governing the oxidative reactivity of hydrocarbons [67,68,73,309-312]. Since individual investigators have used hydrocarbons of varying purity in their work, and have judged the reactivity from data on the oxidation products or from the oxygen absorbed, the conclusions have often been inconsistent. This is indeed understandable, since the rate of oxidation is greatly affected by the purity of the oxidisable species, and the oxygen is not only used up in forming the primary oxidation products, the hydroperoxides, but must also take part in many secondary reactions.

Underlying the mechanism of the liquid-phase oxidation of alkylarenes is Bakh's peroxide theory [313], later developed by Semenov [314] as a free-radical chain mechanism. A characteristic feature of the autoxidation reaction is its great sensitivity to various impurities capable of reacting with active free radicals and thus terminating the reaction chains. The mechanism of the oxidation of one of the most thoroughly studied hydrocarbons, isopropylbenzene, in the presence of manganese salts [88,114,315,316] can be represented by the equations:



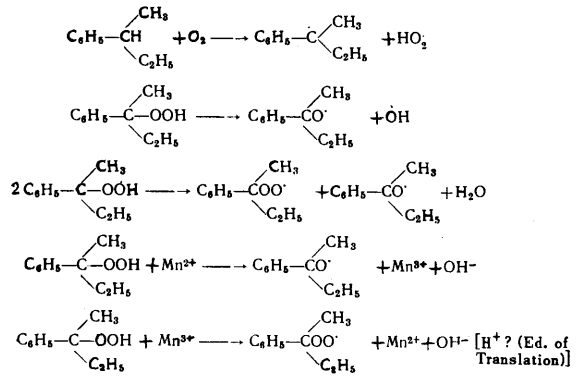
It is evident from these schemes that the principal stable product of the initial oxidation is hydroperoxyisopropylbenzene [317]. A by-product is α,α-dimethylbenzyl alcohol, which lowers the rate of oxidation. The chain reaction is maintained by the phenylisopropyl radical, formed according to Eqn. (2). The role of the catalysts, the manganese salts, consists in splitting up the hydroperoxide which is formed.

Hock and Kropf [149] have shown that the oxidation of isopropylbenzene in the presence of PbO_2 and hydroperoxycumene can occur simultaneously by different mechanisms.

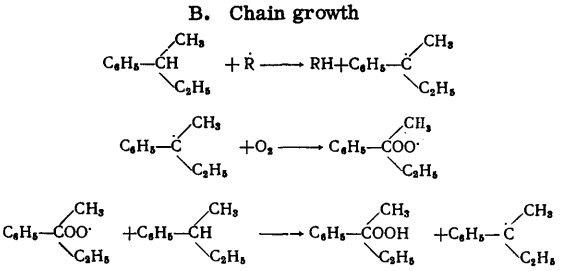
When NaOH is added to the reaction mixture, ions as well as radicals are formed, leading to an increase in the yield of α,α-dimethylbenzyl alcohol to 40%. On addition of Na_2O_2 the conversion of isopropylbenzene into acetophenone increases to 33%. The yield of the latter increases also on addition of ZnO, Al_2O_3, and MnO_2 (to 34–42%). The acidic oxides V_2O_5 and MoO_3 sharply diminish the percentage conversion of the isopropylbenzene.

A radical chain mechanism for the oxidation of s-butylbenzene, including chain initiation, growth, and termination, can be represented by reactions [176] such as:

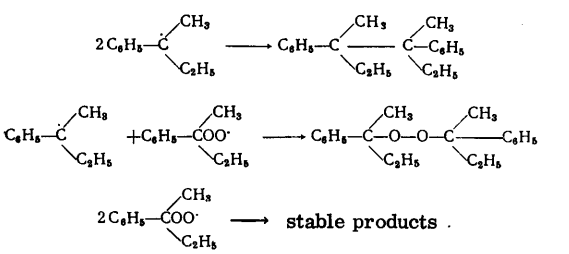
A. Initiation of reaction chains



B. Chain growth

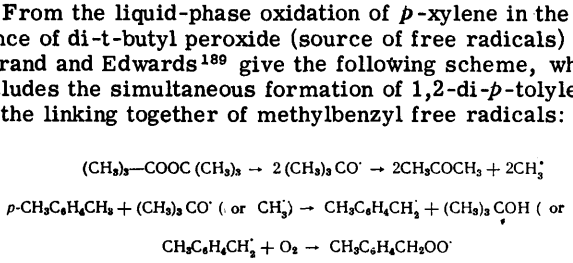


C. Chain termination



Apart from recombination of free radicals, chain termination can occur by the combination of radicals with by-products of the conversion of the alkylbenzene itself as well as of impurities.

From the liquid-phase oxidation of *p*-xylene in the presence of di-t-butyl peroxide (source of free radicals) Lorand and Edwards [189] give the following scheme, which includes the simultaneous formation of 1,2-di-*p*-tolylethane by the linking together of methylbenzyl free radicals:



Other by-products in this reaction are *p*-tolualdehyde, *p*-toluic acid, *p*-methylbenzyl alcohol, etc.

Erofeev and his coworkers [318] studied the kinetics of the oxidation of cumene mixed with $CH_3.COOH$, $(CH_3)_2CH.COOH$,

and $n\text{-}C_{17}H_{35}.COOH$ in the presence of cobalt acetate, and showed that additions of up to 1% of these acids increased the velocity of oxidation. As the concentration of the acids increased, the quantity of CO_2 increased at the same time, at least part of it being formed by decarboxylation of these acids; this is explained[318] by the occurrence of an associated decarboxylation with simultaneous autoxidation of the hydrocarbons according to the scheme:

$$C_6H_5C^{\cdot}(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OO^{\cdot},$$
$$C_6H_5C(CH_3)_2OO^{\cdot} + RCOOH \rightarrow C_6H_5C(CH_3)_2OOH + RCOO^{\cdot},$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2, \quad R^{\cdot} + C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C^{\cdot}(CH_3)_2 + RH,$$
$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}, \quad ROO^{\cdot} + C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C^{\cdot}(CH_3)_2 + RCOOH.$$

Razuvaev and his coworkers[319] studied the kinetics of the oxidation of cumene by atmospheric oxygen in the presence of manganese resinate and several other substances, and established that the reaction is autocatalytic. This is confirmed by the shortening of the induction period produced by previous addition of hydroperoxycumene (up to 0.2%) to the initial cumene. The induction period is still further shortened by adding the sodium salt of hydroperoxycumene, in conformity with numerous observations of the accelerating action of hydroxides and carbonates of the alkali and alkaline-earth metals. Introduction of small quantities of manganese resinate (up to 36 mg litre^{-1}) also shortens the induction period and increases the rate of formation of the hydroperoxide. Further increase in the concentration of manganese resinate produces a gradual fall in the rate of accumulation of hydroperoxide, owing to the ability of manganese resinate to accelerate not only the formation but also the decomposition of cumene hydroperoxide.

Many substances retard or inhibit the process of autoxidation. Among those which strongly inhibit the oxidation of isopropylbenzene are above all phenols, acids, alcohols, amines, and aromatic thiols. Their action is quite complicated, and probably consists in chain termination. In the opinion of many investigators, the first stage of inhibition is the removal of active hydrogen from the oxygen or the nitrogen of the inhibitor by means of a peroxy radical:

$$ArOH + RO_2^{\cdot} \rightarrow ArO^{\cdot} + ROOH,$$
$$ArNHR + RO_2^{\cdot} \rightarrow ArN^{\cdot}R + ROOH.$$

Boozer *et al.*[320,321] consider the first stage of inhibition to be complex formation between the inhibitor and a peroxy radical $RO_2^{\cdot}$ with subsequent cleavage of the complex. Phenol and formic acid exert an especially strong retarding effect on the oxidation; even at a concentration of 0.002 mole % they halve the reaction velocity[319]. Hey and Waters[293] investigated the autoxidation of isopropylbenzene in the presence of trialkylphenols, and established that about 2% of the latter is oxidised to derivatives of alkyl 4-hydroxyaryl ketones and 1,2-di-*p*-hydroxyphenylethane.

In the opinion of Barnard *et al.*[322] the inhibiting effect of mono- and di-sulphides on the autoxidation of squalene at 75° is due to the formation, in the course of the oxidation, of sulphoxides and thiosulphinates, the inhibiting action of which is considerably stronger than that of the original sulphides. The activity of sulphoxides of the type R.SO.R′ as antioxidants depends on the nature of the radicals R and R′, long alkyl substituents exhibiting the greater activity. The activity of thiosulphinates RSOSR′ is less dependent on the nature of R and R′, but dialkyl derivatives are more active than diaryl derivatives.

Ivanov and Vilyanskaya[323] have shown that the liquid-phase oxidation of petroleum hydrocarbons by molecular oxygen is completely inhibited, even in the presence of a source of free radicals, by retarding agents of the type of *p*-hydroxydiphenylamine and 4-methyl-2,6-di-t-butylphenol, for these substances react with R· to give inactive products. When oxidation is initiated by the radical $RO_2^{\cdot}$ of hydroperoxycumene + Co^{3+}, substances of the type of 4,4′-diaminodiphenyl sulphide are effective inhibitors, since they react both with $RO_2^{\cdot}$ and with hydroperoxides ROOH, whereas 4-methyl-2,6-di-t-butylphenol reacts with $RO_2^{\cdot}$, but not with the hydroperoxide, so that it merely retards the reaction without completely inhibiting it.

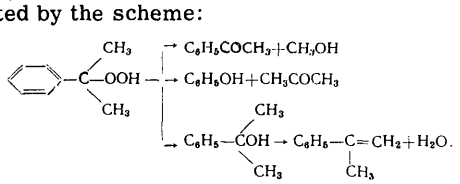
α,α-Dimethylbenzyl alcohol has a weaker effect than phenol or acids in inhibiting the oxidation of isopropylbenzene[319]. Di-isopropylbenzene, acetophenone, and cyclohexene have still feebler effects. Benzene, toluene, ethylbenzene, *p*-cymene, acetone, and chlorobenzene have hardly any effect on the reaction velocity even at a concentration of 4 mole %. Sulphur dioxide has the strongest retarding effect on the oxidation. A concentration of 0.001 vol.% completely stops the reaction. A smaller influence is exerted by Cl_2, HCl, and H_2S. The reaction is strongly poisoned by solid Fe_2O_3 and $FeCl_3$, and also $NiSO_4$ and $CuSO_4$. CuO and Cr_2O_3 accelerate the reaction in the initial stages, but then the content of hydroperoxycumene hardly rises at all.

In the initial stages of the oxidation of 1,2-diphenylethane[324] at 110°, 130°, 140°, and 150°, only peroxides are detected among the reaction products. The curves for their formation are practically identical with those for the absorption of oxygen, which is a direct proof of the formation of the monohydroperoxide. Other compounds are formed by decomposition of this hydroperoxide and subsequent oxidation of the products formed. The following radical-chain mechanism is suggested for the oxidation of 1,2-diphenylethane:

$$C_6H_5CH_2CH_2C_6H_5 + O_2 \longrightarrow C_6H_5C^{\cdot}HCH_2C_6H_5 + HO_2^{\cdot}$$
$$C_6H_5C^{\cdot}HCH_2C_6H_5 + O_2 \longrightarrow C_6H_5CH(OO^{\cdot})CH_2C_6H_5$$
$$C_6H_5CH(OO^{\cdot})CH_2C_6H_5 + RH \longrightarrow C_6H_5CH(OOH)CH_2C_6H_5 + R^{\cdot}$$
$$C_6H_5CH(OOH)CH_2C_6H_5 \longrightarrow C_6H_5CH{=}O + HO^{\cdot} + C_6H_5CH_2$$
$$C_6H_5CH(OOH)CH_2C_6H_5 \longrightarrow C_6H_5CH{=}O + C_6H_5CH_2OH$$
$$C_6H_5CH(OO^{\cdot})CH_2C_6H_5 + \text{inhibitor} \longrightarrow \text{products} + RO^{\cdot}$$
$$RO^{\cdot} + C_6H_5CH_2CH_2C_6H_5 \longrightarrow ROH + C_6H_5C^{\cdot}HCH_2C_6H_5$$
$$2RO_2^{\cdot} \longrightarrow \text{chain termination}$$

MECHANISM AND KINETICS OF THE CLEAVAGE OF HYDROPEROXIDES

Depending on the catalyst and other conditions, hydroperoxides of alkylarenes can be cleaved to form phenols and aliphatic ketones, aliphatic aromatic ketones, alcohols, and their dehydration products, arylolefines. In the case of isopropylbenzene hydroperoxide such cleavage can be represented by the scheme:

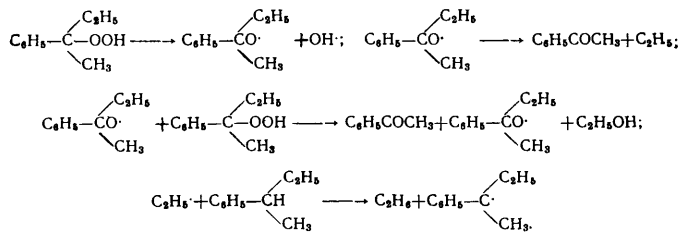


Acetophenone and methanol are formed by the thermal decomposition of hydroperoxycumene. Hydroperoxy-s--butylbenzene, on being heated in sealed tubes, begins to decompose at an appreciable rate at 132°–138°; vigorous decomposition occurs on heating to 145° and above. In this case, too, the principal decomposition product is acetophenone[177]. The decomposition of hydroperoxycumene in acid media, which was first observed by Udris *et al.*[98] in 1943, leads to the formation of phenol and acetone, but in alkaline media α,α-dimethylbenzyl alcohol is obtained.

Various opinions exist as to the mechanism of the decomposition of hydroperoxides. According to some investigators[325-329] it occurs by a unimolecular mechanism with rupture of an O–O bond. Other workers[170,307,330,331] cite data supporting a bimolecular decomposition of hydroperoxides with formation of water and of hydroxy- and peroxy-radicals, and several consider that decomposition occurs simultaneously by unimolecular and bimolecular reactions.

According to results obtained by Kharasch *et al.*[332] hydroperoxyisopropylbenzene reacts with strong acids by an ionic mechanism. With other reagents the hydroperoxide decomposes by a radical mechanism with formation of the $C_6H_5.C(CH_3)_2.O\cdot$ radical in the initial stages of the reaction.

Yamada[333] assumed the following mechanism for the decomposition of hydroperoxy-s-butylbenzene:



Kucher and Yurzhenko[334] studied the rate of decomposition of hydroperoxyisopropylbenzene in aqueous solutions of Nekal [generic name for a group of wetting and emulsifying agents (Ed. of Translation)] and potassium laurate and stearate, and established that in acid medium the primary thermal decomposition of the hydroperoxide occurs at the peroxy bond O–O resulting in the formation of two radicals:

$$C_6H_5.C(CH_3)_2.O-OH \rightarrow C_6H_5.C(CH_3)_2.O\cdot + \cdot OH.$$

The first radical then reacts with a molecule of the hydroperoxide:

$$C_6H_5.C(CH_3)_2.O\cdot + C_6H_5.C(CH_3)_2.O-OH \rightarrow \rightarrow C_6H_5.C(CH_3)_2.O\cdot + C_6H_5OH + CH_3.CO.CH_3.$$

This type of decomposition leads to recombination of free radicals, and is therefore inactive with respect to the initiation of emulsion polymerisation. The action of the emulsifiers on the decomposition of the hydroperoxide is, in the opinion of these workers, associated with their hydrophilic character, the surface activity of the soap being taken as a measure of this property. The more hydrophilic the soap, the more it protects the hydroperoxide molecule from decomposition, *i.e.* the more the latter is stabilised. Consequently, the more hydrophobic the emulsifier, the better it catalyses the decomposition of the hydroperoxide.

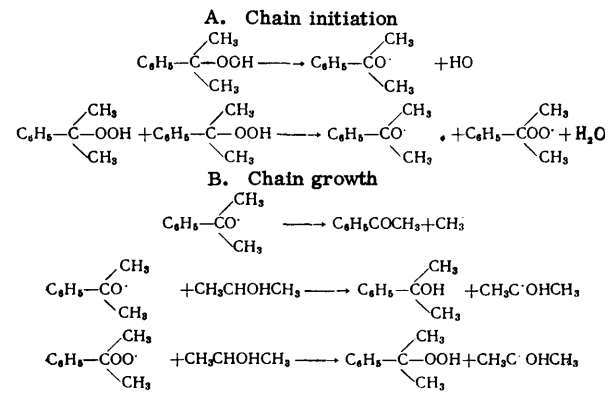
Shushunov *et al.* made a detailed study of the kinetics of the decomposition of hydroperoxy-isopropylbenzene and -s-butylbenzene and established that the rate of cleavage of the former into phenol and acetone is proportional to the concentration of the sulphuric acid, and obeys a first-order equation with respect to hydroperoxide concentrations below 0.02 M.[335] An autocatalytic effect is observed which is greater the higher the concentration of hydroperoxyisopropylbenzene: this is explained by the effect of the acetone formed, additions of which accelerate the reaction. Benzophenone and phenol do not affect the reaction velocity.

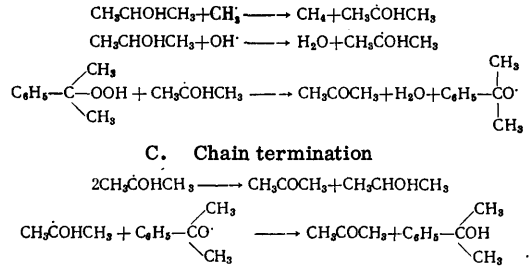
The sulphuric-acid catalysed decomposition of hydroperoxy-isopropylbenzene and -s-butylbenzene in dioxan is of the first order with respect to both the hydroperoxides and the catalyst[336]. Addition of glacial acetic acid has no effect, but addition of water strongly retards the acid-catalysed decomposition of these hydroperoxides. Acetic anhydride strongly accelerates the reaction. Additions of ethyl methyl ketone and phenol up to concentrations of 0.1–0.5 M have little effect on the rate of decomposition.

The rate of cleavage of hydroperoxyisopropylbenzene into acetophenone and α,α-dimethylbenzyl alcohol in the presence of Co^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, and Na^+ stearates in chlorobenzene is also proportional to the hydroperoxide and stearate concentrations[337]. The initial concentration of hydroperoxide does not affect the catalytic rate constant, which indicates the absence of any induced decomposition of the hydroperoxide. The catalytic activity falls in the sequence $Co^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Na^+$. Zinc stearate possesses no catalytic activity. It is assumed that the catalyst facilitates the first stage of the reaction — decomposition of the hydroperoxide molecule with rupture of the O–O bond to form the radicals $C_6H_5.C(CH_3)_2.O\cdot$ and $\cdot OH$.

The rate of reaction of hydroperoxyisopropylbenzene with triethylenetetramine in the presence of ferric sulphate in aqueous solution at 20°–25° depends on the time for which the Fe^{3+} solutions have been kept, and is identical for Fe^{3+} and Fe^{2+} at equal concentrations[338]. The decomposition products include acetophenone and α,α-dimethylbenzyl alcohol.

Decomposition of hydroperoxyisopropylbenzene in a mixture of isopropyl alcohol and benzene leads to the formation of acetone, α,α-dimethylbenzyl alcohol, acetophenone, and α-methylstyrene. The velocity of this reaction depends on the composition of the solvent, the concentration of hydroperoxide, and the temperature. Sokolov and Shushunov[339] propose the following chain mechanism for the decomposition of hydroperoxycumene in the presence of isopropyl alcohol:





C. Chain termination

Since these workers employed dilute solutions, they assume that chain initiation occurred according to the first reaction, and that bimolecular decomposition, as in the second reaction, did not occur.

Studies have been made of the kinetics of the heterogeneous decomposition of hydroperoxycumene on nickel sulphate[340] and on the ion-exchange resin KU-2.[341] Previously dehydrated nickel sulphate has been shown to accelerate the decomposition of hydroperoxycumene into acetone and phenol. In separate experiments the yield of phenol reached 94–97% of theoretical. Small amounts of α,α-dimethylbenzyl alcohol and acetophenone (traces) are formed in the reaction. Heterogeneous decomposition of the hydroperoxide into heptane on nickel sulphate occurs at an appreciable rate at 50°. The reaction velocity increases with rise in temperature. The initial rate of such decomposition of hydroperoxyisopropylbenzene is directly proportional to the catalyst concentration. In contrast to the acid-catalysed decomposition[335] the process occurs without self-acceleration. Additions of phenol and acetone have no effect, but addition of α,α-dimethylbenzyl alcohol strongly retards the reaction.

The heterogeneous decomposition of hydroperoxyisopropylbenzene on the ion-exchange resin KU-2 in the solvents n-octane, chlorobenzene, and acetone is accompanied by the formation of acetone and phenol in almost quantitative yield. The reaction is of the first order with respect to hydroperoxyisopropylbenzene.

CLEAVAGE OF HYDROPEROXIDES INTO PHENOLS AND ALIPHATIC KETONES

Metal sulphates and chlorides as well as acid catalysts (as just noted) usually cleave hydroperoxides into phenols and aliphatic ketones. Substances which are very frequently employed are dilute sulphuric acid[183,342-350], a mixture of concentrated or dilute sulphuric acid with acetone[351-357] or other inert solvents[358], porous material (pumice, kieselguhr) moistened with 85% sulphuric acid[359], orthophosphoric and acetic acids[332,360], hydrochloric acid[361], perchloric acid[362], arylsulphonic acids and their acid chlorides[363-365], sulphates of metals of Groups I and II, in particular copper and calcium sulphates[366,367], ferric chloride[368], boron trifluoride[369], sulphur dioxide and trioxide[156,357,370], and other catalysts[371-373].

The sulphuric-acid cleavage of α-hydroperoxytoluene yields phenol and formaldehyde[181,374,375]. Treatment of hydroperoxy-*p*-xylene with concentrated sulphuric acid in methyl alcohol yields *p*-cresol in 55% yield[375]. Hydroperoxy-*p*-di-isopropylbenzene in acetone at 56°–75° is cleaved by sulphuric acid into *p*-isopropylphenol in 83% yield[74].

Hydroperoxides containing the peroxy-group at a secondary or tertiary α-carbon atom are split by acids into phenols and aldehydes or ketones. Thus hydroperoxyethylbenzene in the presence of electrophilic catalysts (H_2SO_4, BF_3 in the form of its compounds with ethers and with orthophosphoric acid) is cleaved to phenol and acetaldehyde[376-378].

Many methods have been published for cleaving hydroperoxyisopropylbenzene of various concentrations and for isolating the resulting products. In industry cleavage is usually effected with concentrated sulphuric acid. When the hydroperoxide is cleaved with sulphuric acid diluted with water or acetone, phenol can be obtained in yields up to 98% and acetone in about 75% yield[91,105,348,356,379-381].

In order to obtain phenol in good yield, Bewley[382] recommends decomposing the residue in the vat in the presence of an acid catalyst at a high temperature, with subsequent treatment with water at 50°–100°. Several patents[383-385] propose cleaving hydroperoxyisopropylbenzene into phenol and acetone with sulphuric or perchloric acid in the presence of phenol. Perchloric acid in acetic acid cleaves this hydroperoxide almost quantitatively[332]. As an improved method for obtaining phenol and acetone, another patent[355] recommends completely freezing the reaction mixture from HCl (after separating the hydrocarbon from the cleavage products) by washing with a small quantity of a 1–2% solution of citric, tartaric, salicylic, or phthalic acid.

Cleavage of hydroperoxyisopropylbenzene occurs quite smoothly if hydrogen peroxide or substances which produce it are first added to the crude hydroperoxide[346,386]. For the cleavage of hydroperoxycumene suitable catalysts are, as indicated above, sulphates of metals of Groups I and II[366,387], elements of Groups V and VI of the Periodic System[388], activated clays[148,389], and ion-exchange resins, *e.g.* the sulphonated resins KU-1‡ and KU-2‡[390].

A recommended method for isolating phenol from mixtures formed by the cleavage of hydroperoxycumene, which always contain acetophenone, α,α-dimethylbenzyl alcohol, and α-methylstyrene, though in small amounts, is to treat the products with alkaline aqueous solutions with subsequent fractional distillation[391,392] or simply to fractionate the cleaved mixture on efficient plate columns[393-395] and several other methods[396-404]. Thus one patent[371] recommends neutralising the cleavage products of hydroperoxyisopropylbenzene with an equimolecular amount of a 10–60% aqueous solution of sodium phenoxide, and in this way avoiding the possible formation of a gelatinous deposit, as occurs on neutralising with solid or aqueous solutions of caustic alkalis. Phenol can be isolated and purified by treating the mixture of cleavage products from hydroperoxycumene with hexane after addition of water[405]. Bowen[406] recommends, after removing acetone, α-methylstyrene, and acetophenone from the mixture, subjecting the remaining *p*-cumenylphenol to pyrolysis at 200°–400°, and

‡ KU-1 is a strongly acidic bifunctional cation exchange resin with SO_3H and OH as the active groups. It is obtained by polycondensation of *p*-phenolsulphonic acids with formaldehyde in acidic media. KU-2 is a monofunctional, strongly acidic, cation exchange resin with SO_3H as the only active group. It is obtained by treating swollen copolymer of styrene and divinylbenzene with chlorosulphonic acid, with subsequent saponification of the sulphochloride derivative (Ed. of Translation).

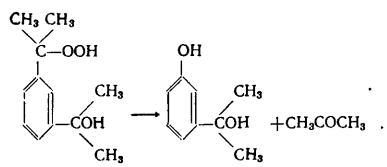
thereby increasing the yield of phenol and α-methylstyrene by means of the reaction

$$p\text{-}HOC_6H_4.C(CH_3)_2C_6H_5 \rightarrow C_6H_5OH + C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2.$$

The cleavage of hydroxyperoxy-s-butylbenzene takes place quietly and in good yield in the presence of arylsulphonyl chlorides[365], *e.g.* benzenesulphonyl chloride.

Mono- and di-hydroperoxides of dialkylbenzenes are cleaved in the presence of acid reagents into alkylphenols or dihydric phenols and aliphatic ketones. Thus acid cleavage of hydroperoxides of the cymenes (mainly 8-hydroperoxy-*p*-cymene) gives a good yield of cresols[228,369,407-409]. Monohydroperoxy-*p*-ethylisopropylbenzene on cleavage with sulphuric acid forms mainly *p*-isopropylphenol[207]. The monohydroperoxides of *p*- and *m*-di-isopropylbenzenes are converted by dilute sulphuric acid into *p*- and *m*-isopropylphenols respectively[183, 206, 343, 381, 410]. The dihydroperoxides of *p*-xylene and of *p*- and *m*-di-isopropylbenzenes are cleaved by sulphuric acid to quinol or resorcinol with yields of 90% and above[96,183,343,353,354,381,396,406,411-413]. The yield of monohydric and dihydric phenols can be increased by subjecting the residues in the vat, after removal of the main amounts of phenols, to thermal cleavage in the presence of inert organic solvents, *e.g.* tri-isopropylbenzene, alkylnaphthalenes[191,410].

m-α-Hydroxyisopropyl-α',α'-dimethyl-α'-hydroperoxytoluene in dry benzene is cleaved in the presence of H_2SO_4 into *m*-α-hydroxyisopropylphenol[364,414]:



The mono- and di-hydroperoxides of *p*-isopropyl-s-butylbenzene are split by sulphuric acid into *p*-isopropyl-(mainly and *p*-s-butyl-phenol and quinol[233]; those of *p*-di-s-butylbenzene into *p*-s-butylphenol, quinol, and ethyl methyl ketone[59,222,224]; hydroperoxy-*p*-isopropyl- and -*p*-cyclohexyl-fluorobenzene are converted by sulphuric acid into *p*-fluorophenol[282]. A mixture of the mono-, di-, and tri-hydroperoxides of 1,3,5-tri-isopropylbenzene is split in the presence of sulphuric acid into monoisopropylresorcinol, di-isopropylresorcinol, and phloroglucinol[231]. Hydroperoxy-1,2,4-tri-isopropylbenzene is cleaved to 3,4-di-isopropylphenol[231]. Similarly, hydroperoxycyclohexylbenzene hydroperoxide is split by dilute sulphuric acid into phenol and cyclohexanol[350], and hydroperoxy-*p*-cyclohexylisopropylbenzene into *p*-cyclohexylphenol[225]. Hydroperoxy-*p*-s-butylbiphenyl is converted by acidic reagents into *p*-hydroxybiphenyl[269].

Hydroperoxides containing aliphatic carbon atoms linked to two or three aryl radicals are readily cleaved in acid medium by means of steam[415]. The process is carried out by continuously feeding in the hydroperoxide and the steam, and distilling off the resulting phenol with the steam. Acid cleavage of hydroperoxy-1,1-diphenylethane yields phenol and acetophenone[416]. 1,1-Di-*p*-tolylethane gives *p*-cresol and *p*-methylacetophenone; hydroperoxytriphenylmethane in acid medium is also decomposed into phenol and benzophenone[257].

Under mild conditions hydroperoxides in contact with strong acids may condense to form diperoxides[417].

A 28% yield of 2-naphthol is obtained by cleaving hydroperoxy-2-isopropylnaphthalene with sulphuric acid[349,375]. 1,4-Dihydroperoxy-1,4-diethyltetralin on cleavage in this way gives catechol, *o*-4-oxohexanoylphenol, and octane-3,6-dione[263]. Hydroperoxy-1,3,3-trimethylindan-1-yl is cleaved by sulphuric acid with the formation of 2,4,4,-trimethylchrom-2-en and 2,4,4-trimethylchroman-2-ol. When the hydroperoxide is heated with alkanesulphonic acids, *e.g.* $C_4H_9SO_3H$ in acetone, 2,4,4-trimethylchroman-2-yl peroxide is formed together with other products[271].

CLEAVAGE OF HYDROPEROXIDES INTO ALCOHOLS, ALDEHYDES, OR KETONES

Mono- and di-hydroperoxides of alkylbenzenes having the peroxy-group attached to a tertiary α-carbon atom are readily reduced by sulphides of the alkali and alkaline-earth metals, caustic soda or potash, or sodium bisulphite or thiosulphate to the corresponding mono- and di-carbinols. Thus, for example, hydroperoxyisopropylbenzene in an aqueous solution of sodium sulphide is converted into α,α-dimethylbenzyl alcohol[418] and mono- and di-hydroperoxy-*p*-di-isopropylbenzenes are reduced by sodium thiosulphate, caustic soda, or caustic potash into *p*-isopropylphenyldimethylmethanol and *p*-(α,α'-dihydroxydi-isopropyl)benzene respectively[183,206]. Hydroperoxyisopropylbenzene and other hydroperoxides are reduced in the presence of Raney nickel, platinum, or cobalt to dimethylphenylmethanol[419]. Monohydroperoxy-*p*-s-butylisopropylbenzene on reduction with $Na_2S_2O_3$ is converted into *p*-s-butylphenyldimethylmethanol, while the dihydroperoxide forms $p\text{-}(CH_3)_2C(OH).C_6H_4.C(CH_3)(C_2H_5).OH$. Hydroperoxy-*p*-t-butylisopropylbenzene in an alkaline solution of sodium sulphate is readily converted into *p*-t-butylphenyldimethylmethanol[220]. Monohydroperoxy-*p*-di-s-butylbenzene is reduced by zinc dust and 30% caustic soda solution to *p*-s-butylphenylethylmethylmethanol, the yield being 96% of theoretical, and the dihydroperoxide under similar conditions is converted into *p*-(α,α'-dihydroxy-s-butyl)benzene with a yield of 92% of theoretical[59]. Similarly, the mono-, di-, and tri-hydroperoxides of 1,3,5-tri-isopropylbenzene are quantitatively reduced by excess of sodium to the corresponding tertiary alcohols[231]. Monohydroperoxy-1,2,4-tri-isopropylbenzene is reduced by zinc dust and caustic soda to 1-α-hydroxyisopropyl-3,4-di-isopropylbenzene[231], and the hydroperoxides of tetralin and 1,3,3-trimethylindan-1-yl into the corresponding alcohols[271].

Primary hydroperoxides of alkylbenzenes in the presence of metal salts are usually cleaved to the corresponding aldehydes, but the secondary and tertiary hydroperoxides are converted into acetyl derivatives. This also occurs as a side-reaction during the autoxidation of alkylarenes to hydroperoxides, and therefore aldehydes or ketones are always present among the products of the sulphuric-acid cleavage of hydroperoxides. Their amount depends on the initiators employed for the autoxidation and on the extent of oxidation. As has been shown above, in individual cases the acetyl derivatives may be the principal or even

the only products of the liquid-phase oxidation of alkylarenes. Ferrous sulphate solution is most often employed for the ketonic cleavage. For example, hydroperoxy-n-butylbenzene is split by ferrous sulphate at elevated temperatures into benzaldehyde[64], but hydroperoxy-s-butylbenzene gives acetophenone[175]. Hydroperoxyisopropylbenzene with ferric chloride is cleaved to acetophenone[4], but monohydroperoxy-*p*-di-s-butylbenzene is reduced to *p*-s-butylacetophenone. The dihydroperoxides of *p*-di-isopropylbenzene and *p*-di-s-butylbenzene are converted by ferrous sulphate solution into *p*-diacetylbenzene[183,222]. A mixture containing 53.7% of total mono- and di-hydroperoxides of *p*-di-s-butylbenzene on heating with aqueous 1 *N* $FeSO_4$ forms *p*-s-butylacetophenone and *p*-diacetylbenzene in yields of 58% and 60% respectively based on the hydroperoxide content[59].

1,4-Dihydroperoxy-1,4-diethyltetralin with $FeSO_4$ is converted into 1,4-naphthaquinone[263], but hydroperoxydecalin gives an 80% yield of 2-n-butylcyclohexanone.

Hydroperoxyisochroman on boiling with 2 *N* KOH is converted into isochroman-1-one in 66% yield, but with NaOH, Na_2SO_4, and H_2O it gives a 62% yield of *o*-2-hydroxyethylbenzaldehyde[276]. Hydroperoxy-*p*-isopropylnitrobenzene in the presence of $Cu(NO_3)_2.3H_2O$ decomposes into *p*-nitroacetophenone and dimethyl-*p*-nitrophenylmethanol[296].

FORMATION OF PEROXIDES

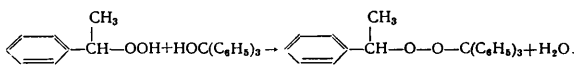
Alkyl and aryl hydroperoxides, in the presence of a small quantity (0.2%) of copper, cobalt, and manganese salts of glycollic and other acids, react with organic compounds containing reactive hydrogen atoms to form peroxides by replacement of the hydrogen by the peroxy-group[420]. In this way α-cumenyl-t-butyl peroxide and α-cumenylperoxycyclohexene have been obtained in 90% yield.

Alkyl and aryl hydroperoxides can be alkylated by ethers[421]. In the presence of a small amount of H_2SO_4 at 20° t-butyl hydroperoxide reacts with ethyl triphenylmethyl ether in $CH_3.COOH$ to form t-butyl triphenylmethyl peroxide:

$$(C_6H_5)_3C-O-C_2H_5 + C_4H_9OOH \rightarrow (C_6H_5)_3C-O-O-C_4H_9 + C_2H_5OH.$$

Similarly, hydroperoxycumene is alkylated by isopropyl triphenylmethyl ether to form the peroxide $C_6H_5.C(CH_3)_2.O.O.C(C_6H_5)_3$. t-Butyl hydroperoxide with bis(diphenylmethyl) ether gives the peroxide $C_4H_9.O.O.CH(C_6H_5)_2$.

Hydroperoxy-1-phenylethane is alkylated by triphenylmethanol to form 1-phenylethyl triphenylmethyl peroxide[422]:



Tertiary hydroperoxides of alkylarenes can react with alcohols with the formation of peroxides. Hydroperoxycumene with dimethylphenylmethanol in glacial acetic acid in the presence of a catalyst (H_2SO_4 or $HClO_4$) forms dicumenyl peroxide in 95% yield based on the hydroperoxycumene and 80% yield based on the dimethylphenylmethanol[423]. *p*-Isopropyl-s-butylbenzene hydroperoxide with dimethyl-*p*-s-butylphenylmethanol forms the peroxide $\{p\text{-s-}C_4H_9.C_6H_4.C(CH_3)_2.O\}_2$. Hydroperoxydiphenylmethane when heated with diphenylmethanol in the presence of $p\text{-}CH_3.C_6H_4.SO_3H$ and $CH_3.COOH$ to 80° for 1 h forms bis(diphenylmethyl) peroxide[424].

Alkyl and aryl hydroperoxides of general formula $R.C(CH_3)_2.OOH$ (R = CH_3 or C_6H_5) condense with orthoesters $RO.CR'(OC_2H_5)_2$ (R = C_2H_5, R'= CH_3 or H) to form per-orthoesters[425]:

$$R-C(OC_2H_5)_3 + R'C(CH_3)_2-OOH \rightarrow R'C(CH_3)_2-O-O-C(R)(OC_2H_5)_2 + C_2H_5OH,$$

where R = CH_3 or H; R' = CH_3 or C_6H_5.

Oxidation of cumene with air in the presence of PbO_2 at 50° forms 27% of hydroperoxycumene, 21% of dimethylphenylmethanol, 7% of cumene peroxide, 2% of acetophenone, and 42% of isopropylbenzene. With phenol in the presence of 96% H_2SO_4 this mixture forms *p*-α-cumenylphenol in 87–99% yield based on the carbinol[426]. Hydroperoxyisopropylbenzene with tetraethyl-lead in glacial acetic acid at 30° gives acetophenone, dimethylphenylmethanol, and dicumenyl peroxide in amounts of 0.32, 0.54, and 0.03 mole respectively per mole of hydroperoxycumene[427]. In the presence of this hydroperoxide in benzene solution, diphenyl sulphides are oxidised to symmetrical diphenyl sulphoxides[428].

Hydroperoxides of ethylbenzene, isopropylbenzene, tetralin, and decalin tend to increase the yield of benzene hexachloride and its γ-isomer content in the chlorination of benzene in the liquid phase[429].

INITIATION OF POLYMERISATION BY HYDROPEROXIDES

Several hydroperoxides are now employed in industry as initiators, *e.g.* for the emulsion copolymerisation of butadiene with styrene, which occurs by a free-radical mechanism, and, like other similar reactions, requires the presence of an activating agent to start the chain.

The initiation of the polymerisation of unsaturated compounds by hydroperoxides of aliphatic and alkylarenes is based on their ability, under certain conditions, to decompose into free radicals, which initiate the chain as follows:

$$ROOH \rightarrow RO\cdot + HO\cdot$$
$$RO\cdot + RH \rightarrow R\cdot + ROH$$
$$RH + HO\cdot \rightarrow R\cdot + H_2O$$
$$R\cdot + O_2 \rightarrow ROO\cdot$$
$$RH + ROO\cdot \rightarrow ROOH + R \quad \text{etc.}$$

Among the large group of hydroperoxides, tertiary hydroperoxides of alkylarenes are especially active initiators of polymerisation[4,29,430]. In the USSR hydroperoxyisopropylbenzene is employed for the copolymerisation of 1,3-butadiene with styrene to form rubbers. Americans use, in addition to this hydroperoxide and that of di-isopropylbenzene, hydroperoxy-*p*-menthane, etc. However, the problem of finding new, more active polymerisation initiators remains extremely urgent today.

Fedorova and Sergeev[48] tested as initiators for the low-temperature emulsion copolymerisation of butadiene with styrene, the tertiary hydroperoxides of *p*-cymene, *p*-s-butyltoluene, and cyclohexylbenzene, the monohydroperoxide and a mixture of the mono- and di-hydroperoxides of *p*-di-s-butylbenzene having a content of active oxygen of 9.54%. Hydroperoxy-*p*-isopropyl-t-butylbenzene was taken for comparison. In the presence of hydroperoxy-*p*-s-butyltoluene no polymerisation was observed during 4 h. Hydroperoxycyclohexylbenzene possesses the same activity as that of *p*-isopropyl-t-butylbenzene, but hydroperoxy-*p*-cymene exhibits rather less initiating activity.

As initiators for the low-temperature copolymerisation of butadiene with styrene we have tested, according to recipe SKS-30A §, the hydroperoxides of cyclohexylbenzene, *p*-cyclohexylisopropylbenzene, *o*-chloro-*p*-di-isopropylbenzene, *p*-di-isopropylbenzene, and *p*-di-s-butylbenzene[431]. The initiating properties of these hydroperoxides were studied at the same time and under similar conditions as those of the peroxides of isopropylbenzene, di-isopropylbenzene, and unsymmetrical diphenylethane. The most active initiator among the hydroperoxides studied was that of *p*-cyclohexylisopropylbenzene in bottle copolymerisation at 10° for 3 h. With this catalyst the rubber content of the latex is 25 g, and the conversion of the hydrocarbons 100%, whereas in the presence of the hydroperoxide of unsymmetrical diphenylethane, which is regarded as the most active initiator, the rubber content of the latex is 24.2 g and the conversion of hydrocarbons 94.4%. It may be mentioned for comparison that, in the presence of hydroperoxyisopropylbenzene, which is used at the present time in industry, the rubber content of the latex under these conditions is 19 g, and the conversion 65.8%. Somewhat better results are obtained in the presence of the hydroperoxides of di-isopropylbenzene, cyclohexylbenzene, and *o*-chloro-*p*-di-isopropylbenzene. In the presence of these hydroperoxides the quantity of rubber in the latex is 22–23 g.

Results of the same order were obtained also in experiments on the autoclave copolymerisation according to recipe SKS-30A at a temperature of +5°.

The hydroperoxides of *p*-cyclohexylisopropylbenzene and of unsymmetrical diphenylethane are more active than that of isopropylbenzene by factors of 2 and 3 respectively. With these hydroperoxides the conversion of hydrocarbons after 4 h is 59%. The physical and mechanical properties of rubbers obtained according to recipe SKS-30A in the presence of the various hydroperoxides do not differ appreciably.

Cumenyl peroxide has been tested[432] as initiator for the copolymerisation of styrene with divinylbenzene and 2,4-dimethylstyrene. Perfluoropenta-1,4-diene, 1,1,3,3,5,5-hexafluoropenta-1,4-diene, 4,5-dichloro--1,1,2,3,3,4,5,5-octafluoropentene, and 1-ethoxyperfluorocyclobutene are polymerised neither by a radical mechanism in bulk or as an emulsion, nor by an ionic mechanism in solution. However, they all copolymerise with butadiene, styrene, and vinyl acetate in the presence of hydroperoxides. With butadiene in the presence of hydroperoxy-*p*-menthane at 5° rubberlike copolymers are formed[433]. Hydroperoxides of tri-isopropylbenzenes are active initiators for emulsion polymerisation[434]. They give the same conversion as hydroperoxy-*p*-isopropyl-t-butylbenzene, but lower than that of hydroperoxycyclohexylbenzene.

Hydroperoxyisopropylbenzene and dihydroperoxy-*p*-di--isopropylbenzene in the form of their sodium and potassium salts are good initiators for the polymerisation of ethylene and the copolymerisation of ethylene with styrene, α-methylstyrene, methyl vinyl ketone, vinylpyridine, and other unsaturated compounds[435]. The polymerisation of styrene in the presence of various hydroperoxides in benzene solution is unimolecular with respect to the initiator¶, and is explained by reaction between the hydroperoxide and the styrene, leading to the formation of a free radical[436]. There are some indications that hydroperoxy-5-*p*-isopropylphenylpent-2-ene is an active initiator for the polymerisation of diene hydrocarbons to solid polymers[437]. A study has been made of the copolymerisation of methyl acrylate with di-t-butyl peroxide as initiator at a temperature of 60°–68°,[438] and of the polymerisation of vinyl, vinylidene, and diene compounds in the presence of hydroperoxyisopropylnaphthalene. This last hydroperoxide is recommended for the reclaiming of rubber, the process of flotation, and in kier-boiling, finishing, and other textile operations[252].

§ Designation for synthetic rubber made from butadiene with 30% styrene by low-temperature (5°) polymerisation (Ed. of Translation).

¶ The reader is advised to consult Schröder's[436] paper here (Ed. of Translation).

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IRREVERSIBLE POLAROGRAPHIC WAVES

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I. INTRODUCTION

The fundamental basis of classical polarographic theory[1-4], which has contributed to the wide and varied use of the polarographic method, is the hypothesis that the magnitude of the current is determined only by the rate of diffusion of the reacting substances, and the electrochemical reaction proceeds sufficiently quickly for electrochemical equilibrium to be attained at the electrodes. For many so-called "reversible" polarographic waves, these assumptions are quite justified. In the interpretation of such waves by means of the Nernst equation[5], the standard electrode potential φ^0, and hence also the half-wave potential $\varphi_{\frac{1}{2}}$, depend simply on the standard free energy $\Delta G^0 (-\Delta G^0 = nF\varphi^0)$[6,7].

For a series of inorganic, and the majority of organic, compounds the rate of electrode reaction is less than, or about the same as, the rate of supply of the depolariser to the electrode surface. During the passage of current the electrochemical equilibrium is disturbed. Polarographic waves obtained under these conditions are termed irreversible. Until recently, irreversible polarographic waves could be handled only by means of empirical expressions,