In the porous structure of fossil coals there appeared forces bonding the coal with the gas which made possible the creation and retention up to the present of the natural equilibrium of the "gas–coal" system. The valence bonds between the carbon atoms in the hexagonal-cyclic parts of the coal macromolecule are characterised by close action and large bonding forces ($\sim 10^2$ kcal mole^{-1}); the forces bonding the cyclic part of the molecules with the side chains have an energy an order of magnitude less (10^1 kcal mole^{-1}); the van der Waals forces which bond the coal substance with the gases have a bond energy again a whole order of magnitude less (10^0 kcal mole^{-1}), but are characterised by a comparatively large sphere of influence, non-specificivity, and additivity.

The van der Waals forces, which determine the sorption capacity of fossil coals with respect to gases, begin to appear noticeably when water is lost from the coals during metamorphism and side-groups are removed, which screened the sorption surface of the coal.

Hence, as a result of the physical and physicochemical processes taking place throughout the genesis, diagenesis, and metamorphism of coals, there was created in them the specific structure which conferred on the coals the properties of active natural sorbents and was the prerequisite for setting up the "gas–coal" natural system.

A thorough study of such a system has great significance for theoretical and practical problems in not only the mining, but also the utilisation of coals, since in many instances one should now speak not of coal, but of methane–coal deposits.

Study of the "gas–coal" system includes a series of problems, the most important of which are: study of the form of the bond of the coal with the absorbed gases, the sorption and collector properties of coal, the physical and physicochemical conditions of equilibrium of the system at various depths and in different geological circumstances, the conditions of the shift in the equilibrium in the system during changes in pressure, temperature, mechanical influences, etc.

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SYNTHESES INVOLVING REACTIONS OF PEROXIDE COMPOUNDS WITH SALTS OF TRANSITION METALS IN SOLUTION

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Oxidation–reduction systems comprising peroxides and salts of metals of variable valency are well known as vinylic polymerisation initiators and are widely used in the production of many interesting low-molecular compounds. The free radicals produced in such systems can react with the solvents, or can dimerise, disproportionate or be oxidised or reduced by the metal ions; and under the influence of the metal salts the peroxides themselves can undergo heterolytic rearrangements or catalysed heterolytic reaction with the solvents. These various processes produce various products.

The object of this paper is to provide, without any pretence at complete exhaustiveness, a review of these reactions, intensive study of which has, in recent years, opened new possibilities for organic synthesis and made a substantial contribution towards the chemistry of free radicals in solution.

1. THE H_2O_2–Fe^{2+} SYSTEM (FENTON'S REAGENT)

This system has been much investigated since its discovery in 1894. Its use as polymerisation initiator in the oxidation of aliphatic compounds and the hydroxylation of aromatic compounds has been reviewed by Semenov[1] and Walling[2].

The accepted mechanism is that proposed by Haber and Weiss, according to which the active particle produced in the system is a free hydroxyl radical:

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + HO^- + Fe^{3+}. \quad (1)$$

In the absence of an organic substrate, the latter can undergo the following series of reactions:

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^-, \quad (2)$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}, \quad (3)$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow HO^{\cdot} + H_2O + O_2, \quad (4)$$

$$HO_2^{\cdot} + H_2O \rightarrow H_3O^+ + O_2^-, \quad (5)$$

$$O_2^- + H_2O_2 \rightarrow {}^-OH + {}^{\cdot}OH + O_2. \quad (6)$$

In 1958 Coffman and coworkers[3] used Fenton's reagent for the production of bifunctional compounds from unifunctional, according to the reactions†

$$RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O, \quad (7)$$

$$2R^{\cdot} \rightarrow R{-}R. \quad (8)$$

The dilution and pH were selected so as to produce the dimeric compounds as the main reaction products in good yield, the reaction being conducted at room temperature by adding aqueous solutions of equimolar quantities of hydrogen peroxide and iron(II) sulphate to an excess of the aliphatic compound (as an aqueous solution or emulsion). The reaction is not a chain reaction — each mole of reacted aliphatic compound requires one mole of hydroxyl radical. This method was used for the dehydrodimerisation of lower aliphatic carboxylic acids, nitriles, amides, amines, alcohols, and ketones.

The attack of the hydroxyl radicals on the molecule of the aliphatic compound is not specific[3]: the hydroxyl abstracts hydrogen not only from the position α to the functional group, but from more distant positions also; as a result a series of bifunctional isomers is obtained, the yield sometimes reaching 60% (calculated on the hydrogen peroxide).

For example, the reaction of propionitrile with Fenton's reagent gives a mixture of approximately equal amounts of adipodinitrile, $\alpha\alpha'$-dimethylsuccinodinitriles, and α-methylglutarodinitrile (total yield 60%). Acetic acid gives a low yield (4%) of succinic acid. Individual dehydrodimers are only obtained when the C–H bonds in the starting material are all equivalent; thus trimethylacetic acid gives $\alpha\alpha\alpha'\alpha'$-tetramethylsuccinic acid (37% yield), and t-butyl alcohol gives $\alpha\alpha\alpha'\alpha'$-tetramethylbutane-1,4-diol (36% yield).

The applicability of the method is limited by the requirements that the starting material should have a suitable solubility in water and should not undergo oxidative decomposition. Best results are obtained at pH 2 and at a dilution of 1 g-mole H_2O_2 to 2 litres water.

Comparison of their experimental results with literature data on the activity of chlorine atoms in reaction with propionic and butyric acid[4,5] led Coffman and coworkers to infer that free hydroxyl radicals and atomic chlorine exhibit a similar strength of attack on C–H bonds.

The carbonyl group deactivates the α-position in carboxylic acids in respect of attack by the hydroxyl radical; according to their data the C–H bonds in pivalic acid $(CH_3)_3CCOOH$ are nine times as reactive as in acetic acid.

Razuvaev and Boguslavskaya investigated the reaction of methyl esters of aliphatic carboxylic acids and alkyl acetates with Fenton's reagent under the conditions of the Coffman synthesis[6–9], and obtained dimeric and oligomeric esters and oxidation products of the starting esters.

The dehydrodimers of the methyl esters are mixtures of the dimethyl esters of isomeric dicarboxylic acids; those of the alkyl acetates are glycol diacetates. The yields of dimers and oligomers sometimes reach 60% (based on H_2O_2) or 70% (based on starting ester). For example, the reaction of methyl isobutyrate with Fenton's reagent gave the following products, the percentage yields, based on H_2O_2 and reacted ester respectively, being given in parentheses: dimethyl $\alpha\alpha'$-dimethyladipate (12, 14), dimethyl $\alpha\alpha\alpha'$-trimethylglutarate (14, 17), dimethyl $\alpha\alpha\alpha'\alpha'$-tetramethylsuccinate (2, 2.5), oligomers (trimers and tetramers) of methyl isobutyrate (29, 35), monomethyl esters of C_8-dicarboxylic acids (2, 2.5), acetone (-, 2), and isobutyric acid (-, 24) [reactions (9)–(15)]. Similarly, isopropyl acetate gave 1,4-dimethylbutane-1,4-diol (11, 28), oligomers of isopropyl acetate (6, 14), acetone, and acetic acid (-, 58) [reactions (16)–(20)].

In the reaction of esters containing chains of several carbon atoms in the alcohol and acid parts of the molecule, mixed dehydrodimers are formed. These are obtained by dimerisation of radicals formed as a result of attack by hydroxyl on the alcohol and acid parts of the ester molecule. Thus ethyl propionate gives diethyl adipate, diethyl $\alpha\alpha'$-dimethylsuccinate, ethyl 5-propionylhydroxyvalerate and ethyl 2-methyl-4-propionylhydroxybutyrate, with

† Abstraction of hydrogen initially bonded to carbon.

traces of unidentified dimers (total yield 21% on the initial ester).

The processes occurring in the reaction of esters with Fenton's reagent are shown in the following series of reactions:

Methyl esters (example: methyl isobutyrate)

$$CH_3CH(CH_3)COOCH_3 + \cdot OH \rightarrow \begin{cases} CH_2\dot{C}(CH_3)COOCH_3 & (I) \\ CH_2CH(CH_3)\dot{C}OOCH_3 & (II) \\ CH_2CH(CH_3)COO\dot{C}H_2 & (III), \end{cases} \quad (9)$$

$$2\,(I) \rightarrow (CH_3)_2CCOOCH_3 \,|\, (CH_3)_2CCOOCH_3, \quad (10)$$

$$(I) + (II) \rightarrow C(CH_3)_2COOCH_3 \,|\, CH_2CH(CH_3)COOCH_3$$

$$2\,(II) \rightarrow CH_2CH(CH_3)COOCH_3 \,|\, CH_2CH(CH_3)COOCH_3,$$

$$(CH_3)_2\dot{C}COOCH_3 + \cdot OH \xrightarrow{[H_2O_2]} (CH_3)_2CCOOCH_3 \,|\, OH \rightarrow (CH_3)_2C{=}O, \quad (11)$$

$$CH_3CH(CH_3)COO\dot{C}H_2 + \cdot OH \xrightarrow{[H_2O_2]} CH_2CH(CH_3)COOCH_2OH \rightarrow CH_2CH(CH_3)COOH \quad (12),$$

$$CH_2CH(CH_3)COOCH_3 \,|\, CH_2CH(CH_3)COOCH_3 + \cdot OH \rightarrow \begin{cases} \dot{C}HCH(CH_3)COOCH_3 \,|\, CH_2CH(CH_3)COOCH_3 & (A) \\ CH_2\dot{C}(CH_3)COOCH_3 \,|\, CH_2CH(CH_3)COOCH_3 & (B) \\ CH_2CH(CH_3)COOCH_3 \,|\, CH_2{-}CHCOOCH_3 \,|\, \dot{C}H_2 & (C) \\ CH_2CH(CH_3)COOCH_3 \,|\, CH_2CH(CH_2)COO\dot{C}H_2 & (D), \end{cases} \quad (13)$$

$$(A), (B), (C), (D) + (I), (II), (III) \rightarrow \text{trimers, tetramers, and higher oligomers,} \quad (14)$$

$$(D) + \cdot OH \xrightarrow[[H_2O_2]]{} CH_2CH(CH_3)COOCH_3 \,|\, CH_2CH(CH_3)COOCH_2OH \rightarrow CH_2CH(CH_3)COOCH_3 \,|\, CH_2CH(CH_3)COOH, \quad (15)$$

Alkyl acetates (example: isopropyl acetate)

$$CH_3CH(CH_3)OCOCH_3 + \cdot OH \rightarrow \begin{cases} CH_3\dot{C}(CH_3)OCOCH_3 & (IV), \\ \cdot CH_2CH(CH_3)OCOCH_3 & (V), \end{cases} \quad (16)$$

$$2\,(V) \rightarrow CH_3CH(CH_3)OCOCH_3 \,|\, CH_3CH(CH_3)OCOCH_3, \quad (17)$$

$$(IV) + \cdot OH \xrightarrow{[H_2O_2]} CH_3C(CH_3)OCOCH_3 \,|\, OH \rightarrow (CH_3)_2C{=}O, \quad (18)$$

$$CH_3CH(CH_3)OCOCH_3 \,|\, CH_3CH(CH_3)OCOCH_3 + \cdot OH \rightarrow \begin{cases} \dot{C}HCH(CH_3)OCOCH_3 \,|\, CH_3CH(CH_3)OCOCH_3 & (E) \\ CH_2CH(CH_3)OCOCH_3 \,|\, CHCHOCOCH_3 \,|\, \cdot CH_3 & (F) \\ CH_2\dot{C}(CH_3)OCOCH_3 \,|\, CH_3CH(CH_3)OCOCH_3 & (G), \end{cases} \quad (19)$$

$$(E), (F), (G) + (V) \rightarrow \text{trimers, tetramers, and higher oligomers} \quad (20)$$

The oligomers are a complex mixture of structural isomers.

Under identical reaction conditions, the maximal yield of dimers and oligomers of methyl esters is obtained with methyl isobutyrate, and that of dimers and oligomers of alkyl acetates with n-propyl acetate (Figs. 1 and 2).

The presence of a large quantity of oligomers makes it difficult to calculate the positions of free-radical attack; however, with methyl isobutyrate an approximate calculation shows that the α-position is more reactive than the β-position.

Complex-forming metal ions (Fe^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}) form complexes with the free alkyl radicals, and so decrease their ability to react and hence favour dimerisation [10]. When Fe^{3+} is used as complex-forming ion, the addition of NaF, which binds Fe^{3+} into a stable complex, produces a considerable decrease in the quantity of dimer formed.

Razuvaev and Boguslavskaya investigated the influence of additions of equimolar amounts of various metal salts on the reaction of aliphatic esters with Fenton's reagent. Addition of Ni, Co, or Mn salts or NaF have no substantial effect on the yield or composition of the products. In the presence of an equimolar amount of NaCl there is practically no dehydrodimerisation of the esters; chlorinated derivatives of the initial esters are produced in small amounts. Chloride ions are known to reduce the rate of oxidation with Fenton's reagent [11,12]:

$$\cdot OH + Cl^- + H^+ \rightarrow Cl\cdot + H_2O. \quad (21)$$

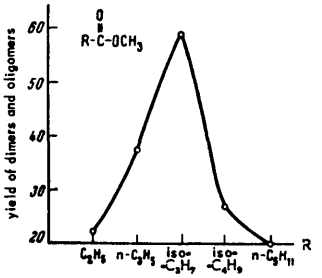


Fig. 1. Yield of dimers and oligomers of esters $RCOOCH_3$ as a function of the size and structure of the radical R.

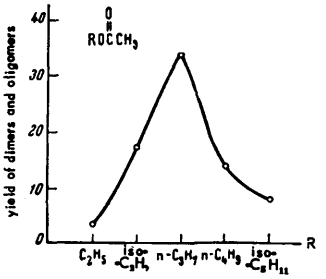


Fig. 2. Yield of dimers and oligomers of esters $ROCOCH_3$ as a function of the size and structure of the radical R.

An equimolar amount of $CuSO_4$ also suppresses the dehydrodimerisation of esters practically completely. It is known that Cu^{2+} can oxidise alkyl radicals [13,14]:

$$R^{\cdot}+M^{+n} \rightarrow \begin{cases} \text{alkene} + M^{+n-1} + H^+ \\ R^+ + M^{+n-1} \end{cases}, \quad (22)$$

$$R^+ + H_2O \rightarrow ROH + H^+, \quad (23)$$

The addition of $CuSO_4$, for example, to the system methyl butyrate–$FeSO_4$–H_2O_2 would therefore be expected to produce esters of unsaturated and hydroxy-acids (or their further oxidation products: aldehydo- and keto--acids), but these products have not been observed. Small amounts of unsaturated esters are formed in the absence of $CuSO_4$ as well as in its presence. The considerable decrease in the yield of dimers is probably due to the reduced equilibrium concentration of hydroxyl radicals in the presence of excess of Cu^{2+}:

$$Cu^{2+} + H_2O_2 \rightleftarrows Cu^+ + HO_2^{\cdot} + H^+ \text{ (see Semenov[1])}. \quad (24)$$

The reaction of various amines and ethers with Fenton's reagent has been investigated [15]; the corresponding dehydrodimers are produced in very low yields (0.5–10%), *NN'*-diethylbutenediamine is obtained from diethylamine (yield ~ 10%) and *NN'*-diethyl-*NN'*-diphenylbutenediamine from ethylaniline (yield < 10%).

Addition of 1,3-dienes to the Fe^{2+}–H_2O_2– substrate system produces addition dimers [16,17]:

$$RH + {\cdot}OH \rightarrow R^{\cdot} + H_2O,$$
$$R^{\cdot} + M \rightarrow RM^{\cdot}, \quad (25)$$
$$2RM^{\cdot} \rightarrow RMMR, \quad (26)$$

where M is a molecule of the 1,3-diene. These dimers are straight-chain (H) and branched-chain (J), (K) compounds produced by 1,4- and 1,2-addition to the diene:

$$R(CH_2{-}CH{=}CHCH_2)_2R; \quad RCH_2CH{=}CHCH_2\underset{\displaystyle CH{=}CH_2}{\underset{|}{C}}HCH_2R; \quad RCH_2\underset{\displaystyle CH{=}CH_2}{\underset{|}{C}}HCH_2R.$$
$$\text{(H)} \qquad \text{(J)} \qquad \text{(K)}$$

Addition dimerisation is favoured by adding equivalent amounts of the iron(II) salt, H_2O_2, and the diene simultaneously to a large excess of the substrate in water at -5° to 0° at a definite pH.

Substrates used have been carboxylic acids, alcohols, ketones, esters, acetaldehyde, propionitrile, and cyclohexylamine. Butadiene has been the main diene used, but chloroprene, isoprene, cyclopentadiene, acrylonitrile, and maleic acid have also been employed. The yield of addition dimers has reached 70–77% in some cases. The yield of products containing more than two butadiene units in the molecule is less than 10%.

The production of dichlorinated conjugated dienes by addition dimerisation has been patented [18]; thus butadiene reacts with the radicals produced in the H_2O_2–$FeCl_2$ system in solution in acetone to give $(ClC_4H_6)_2$. A new method for the addition of two azide groups to alkenes using Fenton's reagent has been developed [19]:

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + HO^- + Fe^{3+},$$
$$HO^{\cdot} + (FeN_3)^{2+} \rightarrow (FeOH)^{2+} + N_3^{\cdot}. \quad (27)$$

$$N_3^{\cdot} + \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \rightarrow N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{\cdot}, \quad (28)$$

$$N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{\cdot} + (FeN_3)^{2+} \rightarrow N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}N_3. \quad (29)$$

This reaction has been used with styrene, butadiene, hex-1-ene, cyclohexene, etc.

Of interest is the novel synthesis of carboxylic acids by passing carbon monoxide into a Fe^{2+}–H_2O_2– substrate system [20]:

$$RH + CO + H_2O_2 \xrightarrow{Fe^{2+}} RCOOH + H_2O. \quad (30)$$

The formation of the acids is accompanied by dimerisation of the radicals R· into RR; thus t-butyl alcohol has given the carboxylation product (β-hydroxyisovaleric acid) and the dehydrodimerisation product (ααα'α'-tetramethylbutane-1,4-diol) in yields of 0.23 and 0.33 g-mole per mole H_2O_2 respectively.

The carboxylation proceeds at room temperature by introducing H_2O_2, $FeSO_4$, and CO simultaneously into a vigorously stirred mixture containing an excess of the organic reactant. The optimal H_2O_2 : $FeSO_4$ ratio and CO pressure is selected for each organic reactant. In some cases carboxylation takes place at atmospheric pressure. The following mechanism has been suggested:

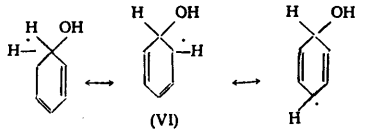
$$HO{\cdot} + RH \rightarrow R{\cdot} + H_2O,$$
$$R^{\cdot} + CO \rightarrow RC{=}O, \quad (31)$$
$$RC{=}O + Fe^{3+} \rightarrow \overset{+}{R}C{=}O + Fe^{2+}, \quad (32)$$
$$\overset{+}{R}C{=}O + \bar{O}H \rightarrow RCOOH. \quad (33)$$

If the reaction medium contains NaF, which binds Fe^{3+} into a stable complex, the yield of carboxylation products is markedly reduced.

Aromatic compounds are oxidised by Fenton's reagent by a non-chain mechanism [21–23]; hydroxylation occurs, and, with benzene and toluene, dehydrodimerisation also. The total yield of reaction products (based on H_2O_2) is always very low (< 5%). Merz and Waters have suggested the following mechanism [22]:

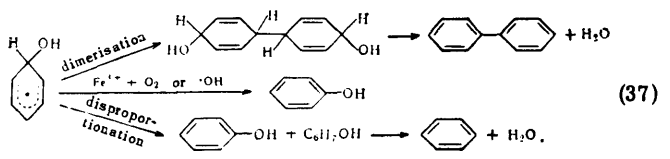
$$ArH + {\cdot}OH \rightarrow Ar^{\cdot} + H_2C, \quad (34)$$
$$2Ar^{\cdot} \rightarrow Ar{-}Ar, \quad (35)$$
$$Ar^{\cdot} + {\cdot}OH \rightarrow ArOH. \quad (36)$$

The oxidation of benzene and toluene by Fenton's reagent has recently been investigated in some detail [24]. The oxidation of benzene produces phenol and biphenyl. The formation of $C_6H_5^{\cdot}$ radicals is excluded, because of the absence of any isotope effect in the analogous oxidation of deuterobenzene. In the suggested mechanism, a hydroxyl radical first adds on to benzene to form the resonance--stabilised adduct (VI):



(VI)

which then dimerises, disproportionates, or is oxidised to produce the final products (phenol, biphenyl, and benzene):



(37)

It is difficult to evaluate the importance of each step in the overall process, but an important characteristic is that the relative amount of phenol produced is decreased by excluding Fe^{3+} (by adding fluoride) and oxygen.

In the oxidation of toluene, which apparently also proceeds by way of the analogous intermediate adduct (as well as by oxidation of the $-CH_3$ group), the following compounds have been obtained, in the indicated relative percentage contents: benzyl alcohol and benzaldehyde (38.3), benzoic acid (18), 1,2-diphenylethane (30.5), phenol (2.9), *o*-cresol (3), *m*-cresol (0.2), *p*-cresol (1), *o*-hydroxybenzaldehyde (3.2), diphenylmethane (1), and bi-*o*-tolyl (2.1).

Brodskii and Vysotskaya[25] used ^{18}O to investigate the mechanism of hydroxylation of phenol with Fenton's reagent, and showed that the oxygen in the resulting pyrocatechol comes from the hydrogen peroxide. They conclude that free hydroxyl radicals do not participate in the hydroxylation.

The same conclusion was reached by Hamilton and Friedman[26], who studied the hydroxylation of anisole with Fenton's reagent. They suppose the hydroxylation to proceed by a type of electrophilic substitution.

Cier and Nofre[27] investigated the mechanism of hydroxylation of benzoic acid and *N*-acylanilines in aqueous solution with hydrogen peroxide in the presence of transition metal ions in their lower valency state, and found the activity of the metals to fall in the series $Fe^{2+} > Co^{2+} > > Cu^{+} > Mn^{2+}$. Addition of ascorbic acid increases the activity of the systems and changes the order of reactivity: $Cu^{+} > Co^{2+} > Fe^{2+} > Mn^{2+}$. Complexing agents such as ethylenediaminetetraacetic acid activate or inhibit the reaction, depending on their nature and the metal ion. The hydroxylation of benzoic acid gives *o*-, *m*-, and *p*-hydroxybenzoic acids, and is accompanied by partial decarboxylation. The carboxy-group orientates the entering OH group in the ratio $o:m:p = 9:6:5$. For *N*-acylaniline this ratio is 11 : 5 : 4. A free-radical mechanism is accepted for the hydroxylation, and the analogy is pointed out between the reactions studied and biochemical hydroxylation in an organism. The action of a modified Fenton's reagent on purine[28] and pyrimidine bases[29] has been studied, to provide a model for the indirect action of ionising radiations on fundamental biochemical molecules in aqueous media. To increase the catalytic action of the Fe^{2+} ion, it was chelated with sodium pyrophosphate, which allowed the Fenton's reagent to be used at pH 7. The purine bases reacted to the extent of 0.5–1%, and hydroxylation of the pyrimidine bases took place with a yield of approximately 1–6.5%.

In the presence of iron(III) ethylenediaminetetraacetate and ascorbic acid (a model of a peroxidase system) salicylates are oxidised in aqueous solution by hydrogen peroxide (or oxygen) into 2,3- and 2,5-dihydroxybenzoic acids (yield 50–70% on salicylate)[30].

Phenoxyacetic acid and its halogen-substituted analogues are readily oxidised by Fenton's reagent to form CO_2, formaldehyde, phenol, and 1,2-diphenoxyethane[31]; the formation of the last compounds is unexpected, and is explained by the reactions:

$$ArOCH_2COOH + \cdot OH \rightarrow ArOCH_2COO^{\cdot} + H_2O \quad (38)$$

$$ArOCH_2COO^{\cdot} \rightarrow ArO\dot{C}H_2 + CO_2\,. \quad (39)$$

$$2ArO\dot{C}H_2 \rightarrow ArOCH_2CH_2OAr\,. \quad (40)$$

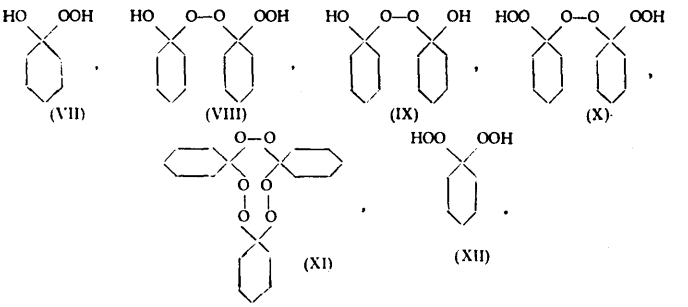
The following is also thought to be a probable mechanism:

$$ArOCH_2COOH + \cdot OH \rightarrow ArO\dot{C}HCOOH \xrightarrow{\text{migration of H}}$$

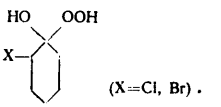
$$\xrightarrow{\text{migration of H}} ArOCH_2COO^{\cdot} \rightarrow ArO\dot{C}H_2 + CO_2\,. \quad (41)$$

2. SYSTEMS COMPRISING ALICYCLIC HYDROPEROXIDES AND METAL SALTS

Cyclohexanone reacts with hydrogen peroxide to give a mixture of the peroxides (VII)–(XII); the structure of these has been much studied[32-36]



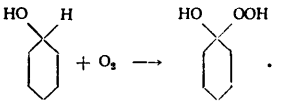
Depending on the method of preparation, one or other of these structures predominates. All the other conversions of the derivative of peroxide cyclohexanone can be considered as reactions of (VII) (1-hydroperoxycyclohexanol); this has not been isolated pure, but Kharasch[36] has prepared the α-halogeno-analogues from the α-halogenocyclohexanone and hydrogen peroxide:



(XIII)

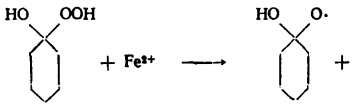
These peroxides (XIII) are individual solid substances and do not form dimeric peroxides of types (VIII)–(XII)[36].

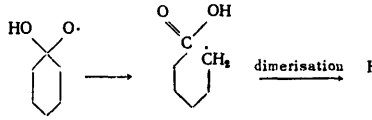
1-Hydroperoxycyclohexanol can be obtained by the autoxidation of cyclohexanol[37]:

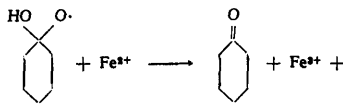


Treatment of the derivatives of peroxide cyclohexanone with an equimolar amount of iron(II) sulphate gives a good yield of decane-1,10-dicarboxylic acid, together with caproic acid, ω-hydroxycaproic acid, polymeric acids, and cyclohexanone[37-41]. Low temperature (-10° to 0°) favours formation of the decanedicarboxylic acid, and the

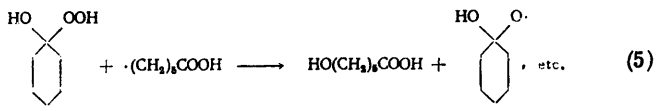
yields of this acid are considerably higher (up to 55%) from "liquid" peroxides of cyclohexanone[41]. These reactions proceed by a free-radical mechanism:


(1)


(2)


(3)

$$HOOC(CH_2)_5\,Fe^{3+} + H_2O \rightarrow HOOC(CH_2)_4CH_2 + Fe^{3+} + OH\,. \quad (4)$$


(5)

Treatment of 2-chloro-1-hydroperoxycyclohexanol with iron(II) sulphate produces a dichlorodecane-1,10-dicarboxylic acid in which the disposition of the halogens has not been established; from subsequent work[14] it may be assumed that this acid is a mixture of isomers with structure (XIV) predominating:

$$HOOC(CH_2)_4CHCl{-}CHCl(CH_2)_4COOH\,.$$
(XIV)

Introduction of butadiene into the peroxide derivative of cyclohexanone $-Fe^{2+}$ system has given[40] C_{20} unsaturated dicarboxylic acids in 65–75% yield:

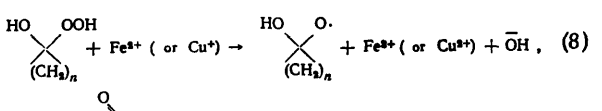
$$HOOC(CH_2)_5^{\cdot} + C_4H_6 \rightarrow \underset{(A)}{HOOC(CH_2)_5CH_2CH{=}CH{-}\dot{C}H_2} + \quad (6)$$

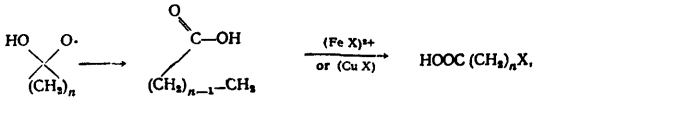
$$+ \underset{(A)}{HOOC(CH_2)_5CH_2\dot{C}HCH{=}CH_2}\,.$$

$$2A \xrightarrow{\text{dimerisation}} C_{20}\text{ unsaturated dicarboxylic acids.} \quad (7)$$

In the presence of an alcohol the corresponding esters are obtained. Similar products are obtained from cyclopentanone, but in lower yield.

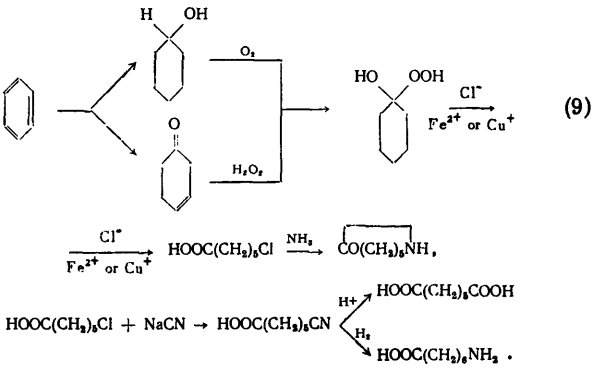
Several recent interesting processes are based on the redox reactions of peroxide derivatives of cyclohexanone and other alicyclic peroxides[14,42–49]. Treatment of 1-hydroperoxycycloalkanols with aqueous solutions of equimolar amounts of iron(II) or copper(I) salts in the presence of an excess of hydrogen halides (or their salts), or of alkali metal azides, cyanides, or other salts, at -30° to + 30° gives good yields of the corresponding ω-substituted alkanoic acids[43–48,50,51]:


(8)

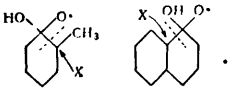


where X is Cl,[44] Br,[44] I,[44] N_3,[48] SCN,[50] CN,[48] S_2O_3Na,[50] or $ROCS_2$,[51] and n is 4 or 5. The ω-substituted acids are the only products of this reaction; the cycloalkanone which is also formed is the initial starting material and is recycled. Thus a peroxide derivative of cyclohexanone gives ε-chlorocaproic acid in a yield of more than 90% (based on ketone), and the product is readily isolated in satisfactorily pure form (> 99%).

This reaction is the basis of the proposed method for the production of the main starting materials for polyamide resins from benzene[42]:


(9)

Analogous reactions have also been carried out with alkyl-substituted cyclic ketones and perhydrohydroperoxynaphthol[47]. The main product in the decomposition of 1-hydroperoxy-2-methylcyclohexanol by copper(I) or iron(II) salts in the presence of halide anions is the ε-halogenoheptanoic acid, and perhydro-1-hydroperoxynaphth-1-ol gives mainly the γ-(2-halogenocyclohexyl)butyric acid; thus the rupture of the C–C bond when the oxygen radical isomerises occurs mainly on the side which the substituent occupies:



Treatment with alkali of ε-thiocyanocaproic acid produced by (8) gives εε′-dithiodicaproic acid in high yield[50]:

$$2\,HOOC(CH_2)_5SCN \xrightarrow{NaOH} HOOC(CH_2)_5SS(CH_2)_5COOH\,, \quad (10)$$

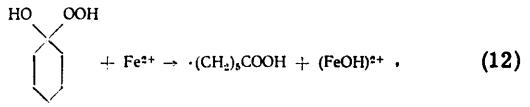
and the same product is obtained from the ε-substituted caproic acids $HOOC(CH_2)_5X$, where X is $-S-C\overset{S}{\underset{OC_2H_5}{<}}$ or S_2O_3Na.[50,51] Similarly δδ′-dithiodivaleric acid is obtained from a peroxide derivative of cyclopentanone[50,51].

The oxidation of the free radicals by metal salts — generally iron(III) or copper(II) halides, of type (8) — has been thought to proceed by ligand transfer[14,49], the reduction of the metal salt occurring with direct transfer of a halogeno-ligand to the free radical in the transition state (XV):

$$R^{\cdot} + M^{n+}X_n \longrightarrow \underset{(XV)}{[R{\cdot}X{-}MX_{n-1} \longleftrightarrow R{-}X\ MX_{n-1}]} \rightarrow RX + M^{+n-1}X_{n-1}\,. \quad (11)$$

In the absence of a suitable ligand the free radicals are oxidised, under analogous conditions, by a competing reaction involving electron transfer. For example, decanedicarboxylic acid is not produced when 1-hydroperoxycyclohexanol is reacted with a mixture of $FeSO_4$ and $CuSO_4$, the main reaction product being hex-5-enoic acid

(in 76% yield based on reacted ketone, or 61% based on H_2O_2)[14,49], which is formed by the mechanism:



(12)

$$\cdot(CH_2)_5COOH + Cu^{2+} \rightarrow CH_2{=}CH(CH_2)_3COOH + Cu^{+} + H^{+}, \quad (13)$$

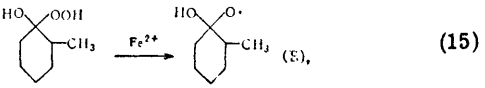
$$Cu^{+} + (FeOH)^{2+} \rightarrow Cu^{2+} + (FeOH)^{+}. \quad (14)$$

It is not thought that a classical carbonium ion is produced as an intermediate in this reaction, since when it is carried out in an aqueous or alcoholic medium only a very small quantity of substituted hexanoic acids is obtained. The optimal yield of hex-5-enoic acid cannot be obtained if catalytic quantities of the metal salts are used. In practice relatively large amounts of $FeSO_4$ (100–200% based on H_2O_2) and slightly smaller amounts of $CuSO_4$ (about 50 mole %) are required.

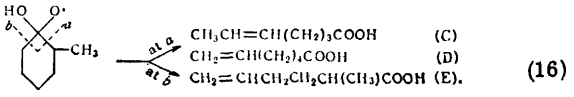
The used solution of $FeSO_4$ and $CuSO_4$ can be recycled, because of the low conversion of Fe^{2+} ions in the reaction.

In acidified aqueous methanol the reaction produces methyl hex-5-enoate, together with caproic acid formed as the result of abstraction of hydrogen from the solvent.

The isomerisation of 2-substituted 1-hydroxycyclohexyloxy-radicals occurring in reactions involving electron or ligand transfer has been investigated; thus a mixture of heptenoic acids is obtained (in 43% yield based on the ketone) in the reaction of 1-hydroperoxy-2-methylcyclohexanol with $FeSO_4$ and $CuSO_4$:



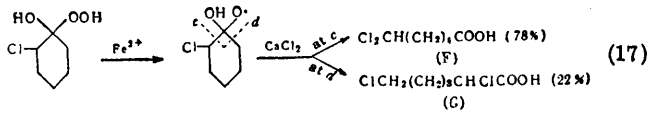
(15)



(16)

The acid (E) is present in a concentration of 5 mole %, and hence when the radical (B) isomerises the rupture of the C–C bond proceeds almost completely from the side of the methyl group. The acids (C) and (D) are present in the mixture in amounts of about 60% and 40%.

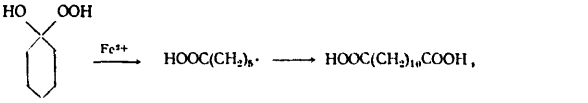
Treatment of 2-chloro-1-hydroperoxycyclohexanol with $FeSO_4$ and $CuSO_4$ gives a low yield of chlorohexenoic acids (~10%). With $FeSO_4$ and $CuCl_2$, dichlorocaproic acids are produced, in 37% yield based on the ketone:



(17)

The relative amounts of the isomers (F) and (G) show that rupture of the C–C bond occurs about four times as frequently on the side of the chloro-substituent as on the unsubstituted side.

Aliphatic acids and esters are obtained in the decomposition of 1-hydroperoxycyclohexanol with iron(II) salts in the presence of various halogen compounds and thiols[52], and are produced by recombination and transfer of the radicals formed in the system:



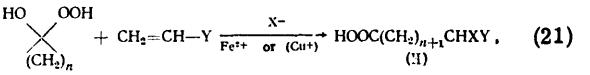
$$\cdot(CH_2)_5COOH + CCl_4 \rightarrow Cl(CH_2)_5COOH + \cdot CCl_3, \quad (18)$$

$$\cdot CCl_3 + \cdot(CH_2)_5COOH \rightarrow CCl_3(CH_2)_5COOH, \quad (19)$$

$$2\cdot CCl_3 \rightarrow C_2Cl_6. \quad (20)$$

In carbon tetrachloride, the reaction produces ϵ-chlorocaproic, decanedicarboxylic, and ω-trichloroheptanoic acids in yields of 17, 30, and 6% respectively; in methanethiol, the products are caproic acid, decanedicarboxylic acid, and 6-(methylthio)hexanoic acid $CH_3S(CH_2)_5COOH$ in yields of 26, 21, and 12%.

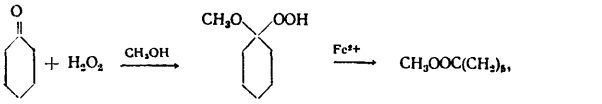
Acrylonitrile (or acrylates) and halogen have been added on to the carboxyalkyl radicals by the reaction[53,54]:



(21)

where n is 4 or 5, Y is CN or COOR, and X is Cl or Br. The ω-halogenoalkanoic acids are also formed. Saponification of hydration of the compounds (H) gives the corresponding dicarboxylic acids in yields of 20–30 mole % (based on the initial ketone).

Kochi and Rust[55] have studied the competing processes occurring in the reaction of 1-hydroperoxycyclohexanol in methanol with butadiene (or chloroprene, styrene, or acrylonitrile) in the presence of $FeSO_4$ and $CuSO_4$. Under these conditions the 5-(methoxycarbonyl)pentyl radical adds on butadiene, and the resulting radical is oxidised by the copper(II) salt to give a good yield of methyl methoxydecenoates. The competing reactions are the oxidation of 5-(methoxycarbonyl)pentyl radicals by the copper(II) salt to give methyl hex-5-enoate and 5-methoxyhexanoate, and dimerisation of the radicals:



$$CH_3OOC(CH_2)_5\cdot + C_4H_6 \rightarrow [CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH]\cdot, \quad (22)$$

$$2\,[CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]\cdot \rightarrow \text{three isomeric dimethyl eicosadienedioates}, \quad (23)$$

$$[CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]\cdot + Cu^{2+} \rightarrow [CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]^{+} + Cu^{+}, \quad (24)$$

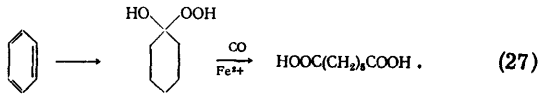
$$[CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]^{+} + CH_3OH \xrightarrow{-H^{+}} \begin{cases} \rightarrow CH_3OOC(CH_2)_6CH{=}CHCH_2OCH_3 \\ \rightarrow CH_3OOC(CH_2)_6CH(OCH_3)CH{=}CH_2, \end{cases} \quad (25)$$

$$CH_3OOC(CH_2)_5\cdot + Cu^{2+} \rightarrow \begin{cases} \rightarrow CH_3OOC(CH_2)_3CH{=}CH_2 \\ \rightarrow CH_3OOC(CH_2)_4CH_2^{+} \xrightarrow[-H^{+}]{CH_3OH} CH_3OOC(CH_2)_6OCH_3. \end{cases} \quad (26)$$

The ability of alkenes to add to the 5-(methoxycarbonyl)-pentyl radical decreases in the series‡: $CH_2{=}CHCH{=}CH_2$, $CH_2{=}C(CH_3)CH{=}CH_2 > CH_2{=}C(CH_3)CH{=}CH_2 > C_6H_5CH{=}CH_2 > > CH_2{=}CHCN > CH_2{=}C(CH_3)CH_2Cl > CH_2{=}CHBr > CH_2{=}CCl_2$.

‡ Presumably one of the isoprenes should be chloroprene (Ed. of Translation).

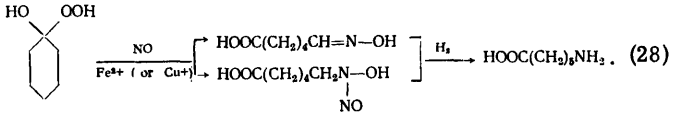
Carbon monoxide has also been added to the carboxyalkyl radicals obtained from 1-hydroperoxycyclohexanol[56,57]. Best results are obtained at pressures above 10 atm. The process may be utilised to prepare $\alpha\omega$-dicarboxylic acids, especially pimelic acid, from benzene:



(27)

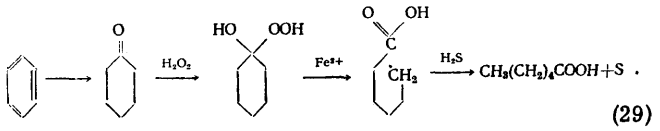
The decomposition of hydroperoxides in the presence of sulphur dioxide proceeds analogously, with the formation of sulphonic acids[57]; however, the greater activity of SO_2 as compared with CO enforces the use of dilute solutions, so as to avoid reduction of the peroxide to cyclohexanone.

Addition of nitrogen monoxide to the carboxyalkyl radicals followed by hydrogenation of the resulting nitrogen compounds produces amino-acids[58-60].



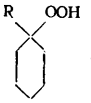
(28)

The decomposition of cyclic hydroperoxy alcohols in the presence of an iron(II) salt and hydrogen sulphide is the basis of a new method for the conversion of cyclic ketones into monocarboxylic acids having the same number of carbon atoms[61]. It may be utilised in the production of hexanoic acid from benzene[42]:



(29)

The autoxidation of alicyclic hydrocarbons or ethers[62,63] produces the hydroperoxides:

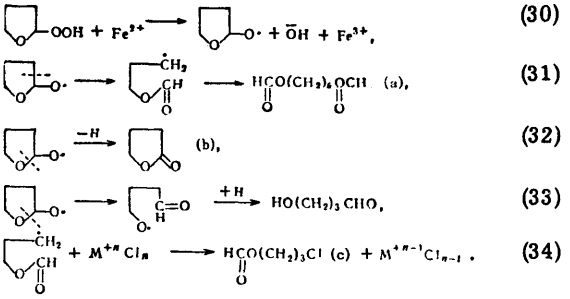


where R is alkyl or alkoxy.

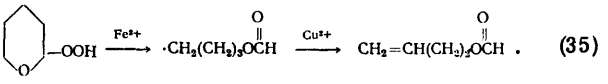
The reaction of methylcyclopentyl and methylcyclohexyl hydroperoxides with $FeSO_4$ has given[64] dodecan-2,11-dione and tetradecan-2,13-dione respectively, in yields of 40–55%. When 1,3-dienes are introduced into such systems, long-chain unsaturated diketones are obtained[65], of the general formula RMMR, where R is a ketoalkyl group and M is a butadiene or isoprene residue; the yield of such unsaturated ketones may reach 70%.

By introducing halide ligands into a system consisting of a cyclic hydroperoxide and Fe^{2+} (or Cu^{+}) ions, Minisci and Belvedere[66] have developed efficient methods for the production of ω-halogenated ketones and esters; thus methylcyclopentyl and methylcyclohexyl hydroperoxides give 6-chlorohexan-2-one and 7-chloroheptan-2-one respectively, in yields of ~ 50%. The reaction of methylcyclohexyl hydroperoxide with $FeSO_4$ and $CuSO_4$ produces hept-6-en-2-one in yields of up to 90%.[14] The mechanism of these reactions is identical with that already considered in respect of the hydroperoxyalcohols.

The above reactions have been extended to the hydroperoxides of cyclic ethers, which can be obtained by autoxidation of the ethers. The reaction of a tetrahydrofuryl hydroperoxide with $FeSO_4$ has given[67] hexamethylene diformate, see (a) below, 13.8% yield; γ-butyrolactone (b), 31.4% yield; and traces of 4-hydroxybutanol. In the presence of metal halides, no dimerisation of the radicals to produce (a) occurs, and 3-chloropropyl formate is obtained (c), 42% yield. The reactions involved are:



The reaction of tetrahydropyran-2-yl hydroperoxide with $FeSO_4$ gives octamethylene diformate in good yield[68]. In the presence of $FeSO_4$ and $CuSO_4$ but-3-enyl formate is obtained in 20% yield[14]:



(35)

If $CuCl_2$ is introduced into this system, 4-chlorobutyl formate is produced in 36% yield[69].

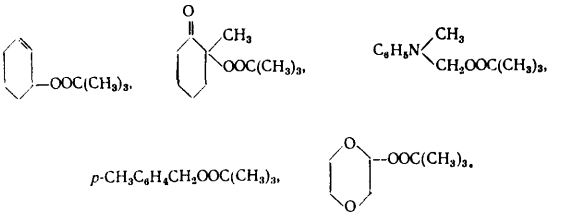
The reductive decomposition of tetrahydro-2,5-dimethylfuranyl hydroperoxide[70,71] gives 1-methylheptamethylene diacetate (46%) and s-butyl acetate (32%); in the presence of CCl_4, no s-butyl acetate is obtained, but 4-chlorobut-2-yl acetate (19%) is formed.

3. SYSTEMS COMPRISING ACYCLIC PEROXIDES AND METAL SALTS

The addition of catalytic quantities of copper(I) and certain other transition metal salts profoundly affects the course of the reaction between organic peroxides and certain organic compounds in solution[72,73]. In some cases such addition reduces the rate of or inhibits the reactions, and in others the reverse, causing rapid decomposition of the peroxides[75] and catalysing reaction of the peroxides with the solvents to give products which are unusual for normal free-radical reactions[73,74].

These investigations have led to some new and efficient synthetic methods. Thus a new method has been developed[74] for the introduction of peroxide groups into organic molecules by the reaction of t-butyl (or cumyl) hydroperoxide with many types of organic compound in the presence of catalytic amounts of copper, cobalt, or manganese salts at 70–100°. The peroxide group can be introduced in this way, with excellent yields, into compounds such as cyclohexene, 2-methylcyclohexanone,

cyclohexanone, dimethylaniline, xylene, and dioxan, to produce



The peroxide group replaces the most labile hydrogen atom.

A mechanism for the reaction has been proposed which involves the formation of intermediate complexes of the free radicals with molecules of the hydroperoxide:

$$ROOH + M^{+} \rightarrow RO\cdot + M^{2+} + \bar{O}H \quad (M=Cu,\ Mn,\ Co), \tag{1}$$

$$RO\cdot + R'H \rightarrow ROH + R', \tag{2}$$

$$R'\cdot + ROOH \rightarrow R'HOOR \ (complex), \tag{3}$$

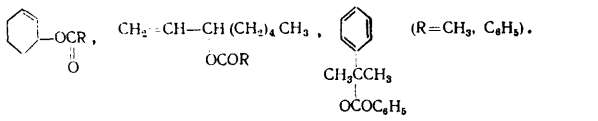
$$ROOH + M^{2+} \rightarrow ROO\cdot + M^{+} + H^{+}, \tag{4}$$

$$ROO\cdot + R'H \rightarrow R'HOOR \ (complex), \tag{5}$$

$$R'HOOR + oxidant \rightarrow R'OOR + (oxidant + e) + H^{+}. \tag{6}$$

The oxidant may be the M^{2+} ion or the hydroperoxide. The formation of free carbonium ions by the reaction R^{+} + oxidant $\rightarrow R'^{+}$ + (oxidant + e) is excluded, since practically no acetates are formed when acetic acid is used as reaction medium, but the yield of peroxide is not reduced.

t-Butyl peroxy-esters react smoothly with alkenes in the presence of catalytic amounts of copper or cobalt salts, producing allyl esters in good or moderate yields[73,76]; thus cyclohexene, oct-1-ene, and cumene have given 3-acyloxycyclohexenes, 3-acyloxyoct-1-enes, and $\alpha\alpha$-dimethylbenzyl benzoate respectively:



While in the absence of catalyst such reactions usually lead to a mixture of isomers, in the presence of copper or cobalt salts the reaction is specific: the acyloxy-group substitutes in the α-position to the double bond.

The use of gas–liquid chromatography for the separation and identification of the reaction products has shown[77-79] that the reaction between t-butyl peroxy-esters and alk-1-enes under the influence of catalytic amounts of copper salts produces not only the 3-acyloxyalk-1-enes, but also their isomers, the 1-acyloxyalk-2-enes. This gives grounds for assuming that the reaction involves the formation of relatively free carbonium ions which undergo rearrangement in the course of reaction. The reaction mechanism proposed by Kochi[77,78] and Walling[79] comes down to the multistage process represented by:

$$CH_3COOOC(CH_3)_3 + Cu^{+} \rightarrow CH_3COO^{-} + Cu^{2+} + (CH_3)_3CO\cdot, \tag{7}$$

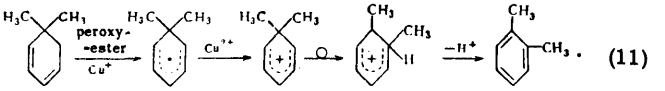
$$(CH_3)_3CO\cdot + RH \rightarrow (CH_3)_3COH + R\cdot, \tag{8}$$

$$R\cdot + Cu^{2+} \rightarrow R^{+} + Cu^{+}, \tag{9}$$

$$R^{+} + CH_3COO^{-} \rightarrow ROCOCH_3. \tag{10}$$

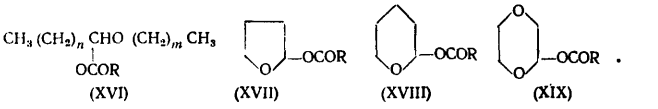
This is a chain reaction maintained by the Cu^{I} and Cu^{II} states of copper.

An interesting rearrangement with 1,2-transition of alkyl groups has been observed by Walling and Lawitsas[79] in the reaction between t-butyl peracetate and 6,6-dimethylcyclohexa-1,3-diene in the presence of copper salts; o-xylene was produced in 6% yield, but it is not formed in the absence of the copper or the peroxy-ester. The production of o-xylene clearly demonstrates the intermediate formation of a carbonium cation:



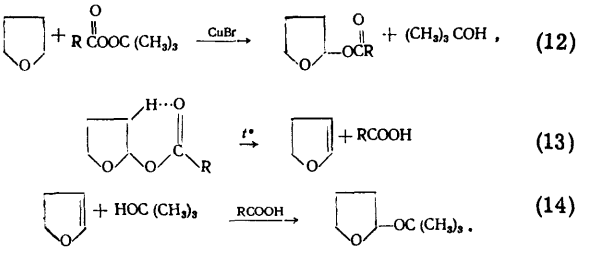
(11)

Aliphatic, aromatic, and cyclic ethers react smoothly with t-butyl peroxy-esters at 67–90° in the presence of CuCl or CuBr[76,80-88]. The primary reaction products are the acyloxy-substituted ethers — for example (XVI)–(XIX) — but these are unstable under the experimental conditions, and partially decompose into the corresponding carboxylic acids and unsaturated ethers[82]:



(XVI) (XVII) (XVIII) (XIX)

2,3-Dihydrofuran (13) is obtained in 66% yield from 2-benzoyloxytetrahydrofuran (XVII). The unsaturated ethers add on the t-butyl alcohol, giving the corresponding acetal (14); this stage is catalysed by the carboxylic acid:



(12)

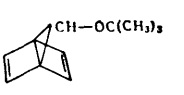
(13)

(14)

The reaction is general for ethers containing two methylene groups adjacent to the ether oxygen. Diethers such as dioxan give more stable acyloxy-derivatives, which on prolonged heating are slowly converted into the corresponding acetals (in low yield).

The analogous sulphur compounds are obtained in good yields by reaction of thioethers with t-butyl peroxy-esters[83,89,90].

A particular type of substitution occurs[91,92] in the reaction of t-butyl peroxy-esters with norbornadiene under the influence of catalytic amounts of CuBr; this produces 7-t-butoxynorbornadiene in 26% yield:



The mechanism of the catalytic action of copper salts on the reactions of organic peroxides has been considered by Kochi[14,77,78,93-95] and by Walling[79].

In the presence of large quantities of copper salts, the products obtained depend to a considerable extent on the nature of the anion; for instance, $CuCl_2$ and $CuBr_2$ oxidise the alkyl radicals to the corresponding alkyl halides, while under analogous conditions $CuSO_4$ gives unsaturated compounds and solvolysis products. Primary alkyl radicals in the presence of $CuSO_4$ give mainly unsaturated compounds, and tertiary alkyl, benzyl, and allyl radicals give solvolysis products. A desired product can therefore be obtained by suitable choice of reaction conditions. The examples given below illustrate these general statements (see also Section 2).

The reaction between t-butyl hydroperoxide and butadiene in the presence of $FeSO_4$ produces t-butoxy radicals, which readily add on to butadiene, and the resulting t-butoxybutenyl radicals dimerise [96]. When carried out in aqueous methanol in the presence of $FeSO_4$ and $CuSO_4$, [14,94] this reaction gives a good yield (55–60%) of the isomeric methyl ethers of t-butoxybutenols of the composition

$$(CH_3)_3COCH_2CH(OCH_3)CH=CH_2 \quad (\sim 66\%),$$
$$trans\text{-}(CH_3)_3COCH_2CH=CHCH_2OCH_3 \quad (\sim 32\%),$$
$$(CH_3)_3COCH_2CHOH.CH=CH_2 \quad (\sim 2\%).$$

The mechanism of such reactions has already been discussed in Section 2.

The reaction of t-butyl hydroperoxide with butadiene in the presence of the Fe^{3+}/Fe^{2+} or Cu^{2+}/Cu^{+} system and Cl^-, Br^-, SCN^-, or N_3^- ions gives good yields of compounds $(CH_3)_3CO(C_4H_6)X$, where X is Cl, Br, SCN, or N_3. [19,97] For example, the reaction between t-butyl hydroperoxide (0.63 g-mole), butadiene (0.30 g-mole), $FeCl_3.6H_2O$ (0.55 g-mole), $FeSO_4.7H_2O$ (0.32 g-mole), and LiCl (0.56 × × g-mole) at -10° to -15° produces a mixture of 1-chloro--4-t-butoxybut-2-ene and 3-chloro-4-t-butoxybut-1-ene in a yield of 98% on the diene or 47% on the peroxide [97].

Investigation of the reactions of the t-butoxy-radical, which is fairly strongly electrophilic in the presence of chloride, azide, and thiocyanate anions and alkenes, has shown the direction of reaction to depend on the donor–acceptor properties of the substituents in the alkene molecule [19]. With butadiene the reaction is:

$$(CH_3)_3COOH + Fe^{2+} \rightarrow (CH_3)_3CO\cdot + Fe^{3+} + \bar{O}H, \quad (15)$$
$$(CH_3)_3CO\cdot + C_4H_6 \rightarrow (CH_3)_3COC_4H_6^{\cdot}, \quad (16)$$
$$(CH_3)_3COC_4H_6\cdot + (FeX)^{2+} \rightarrow (CH_3)_3COC_4H_6X + Fe^{2+}. \quad (17)$$

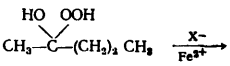
Cyclopentadiene behaves analogously to butadiene. Under the same conditions, styrene forms 1-chloro-1-phenylethyl t-butyl ether in the presence of chloride ions, and a mixture of $C_6H_5CHN_3CH_2OC(CH_3)_3$ and $C_6H_5CHN_3CH_2N_3$ in the presence of sodium azide. Clearly, in the latter case two parallel processes take place:

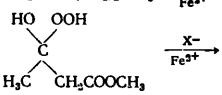
$$(CH_3)_3CO\cdot + C_6H_5CH=CH_2 \rightarrow C_6H_5\dot{C}HCH_2OC(CH_3)_3 \xrightarrow{(FeN_3)^{2+}} \xrightarrow{(FeN_3)^{2+}} C_6H_5CHN_3CH_2OC(CH_3)_3, \quad (18)$$
$$(CH_3)_3CO\cdot + (FeN_3)^{2+} \rightarrow N_3\cdot + Fe^{3+} + (CH_3)_3CO^-, \quad (19)$$
$$N_3\cdot + C_6H_5CH=CH_2 \rightarrow C_6H_5\dot{C}HCH_2N_3 \xrightarrow{(FeN_3)^{2+}} C_6H_5CHN_3CH_2N_3. \quad (20)$$

A t-butoxy-radical of reduced reactivity is observed in the decomposition of t-butyl hydroperoxide in the presence of the Fe^{3+}/Fe^{2+} system, chloride ions, and acrylonitrile, when α-chlorobutyronitrile is obtained as main reaction product. This is because the strongly electrophilic t-butoxy-radical cannot react with the ethylenic bond of the acrylonitrile, which is electron-deficient in nature, and it therefore decomposes to give a methyl radical, which has nucleophilic properties:

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3^{\cdot}, \quad (21)$$
$$CH_3\cdot + CH_2=CH-CN \rightarrow CH_3CH_2\dot{C}HCN \xrightarrow{(FeCl)^{2+}} CH_3CH_2CHClCN + Fe^{3+}. \quad (22)$$

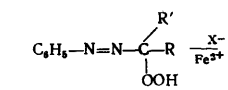
The decomposition of peroxides of acyclic ketones with iron(II) or copper(I) salts in the presence of Cl^-, SCN^-, or N_3^- ions gives the corresponding substituted alkanes [56]:


$$\xrightarrow[Fe^{2+}]{X^-} CH_3CH_2CH_2X + CH_3COOH, \quad (23)$$

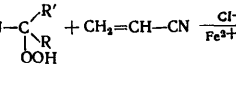

$$\xrightarrow[Fe^{2+}]{X^-} CH_3OCOCH_2X + CH_3COOH. \quad (24)$$

The reaction of peroxides of acyclic diketones or keto--esters with iron(II) sulphate in the presence of butadiene produces diketones and esters of long-chain dicarboxylic acids [98,99].

The reaction of hydroperoxides of ketone phenylhydrazones with iron(II) or copper(I) salts in the presence of Cl^-, Br^-, SCN^-, or N_3^- follows the course of the Sandmeyer reaction, with the formation of the correspondingly substituted aryl compounds [100]:


$$\xrightarrow[Fe^{2+}]{X^-} C_6H_5X + R'COR + N_2. \quad (25)$$

The reaction of these hydroperoxides with acrylonitrile or acrylates under analogous conditions (the Meerwein reaction) [101] gives good yields of the α-substituted β-phenylpropionitriles or β-phenylpropionate esters respectively:

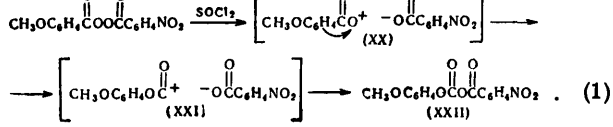

$$+ CH_2=CH-CN \xrightarrow[Fe^{2+}]{Cl^-} C_6H_5CH_2CHClCN + R'COR + N_2. \quad (26)$$

4. IONIC REACTIONS OF PEROXIDES UNDER THE INFLUENCE OF LEWIS ACIDS

Recent years have seen the accumulation of much experimental material which shows that certain peroxides can decompose in solution by an ionic, as well as a radical, mechanism [102–107].

The ionic reactions of peroxides are catalysed by polar solvents [102,103], strong acids [102–107] and Lewis acids ($AlCl_3$, $SbCl_5$, $FeCl_3$, BF_3, etc.) [104,106,108–114].

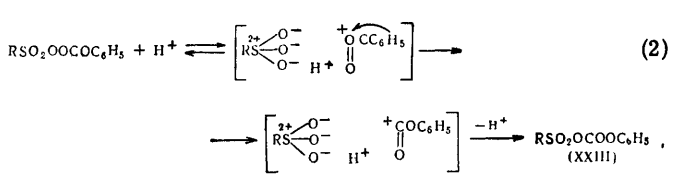
Heterolytic decomposition of peroxides leads most frequently to intramolecular rearrangement [102–105,110,113], and hence to loss of the ability to initiate radical polymerisation [102,103]. For example, *p*-methoxybenzoyl--*p*-nitrobenzoyl peroxide decomposes by a radical mechanism in benzene, but by an ionic mechanism in the strongly polar thionyl chloride, producing a mixed anhydride of *p*-nitrobenzoic acid and mono-(methoxyphenyl) carbonate (XXII) [102]:



(1)

The *p*-methoxyphenyl radical in the cation (XX) migrates to the peroxidic oxygen to form the carbonium cation (XXI); recombination of the ions then gives the mixed anhydride (XXII).

Alkanesulphonyl peroxides decompose in organic solvents (irrespective of their polarity) by an ionic mechanism[111], with the formation of the mixed anhydrides (XXIII); this reaction is catalysed by the alkanesulphonic acid which is produced by the initial homolytic decomposition of the peroxide[104,105]:

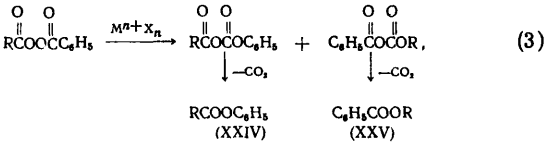


(2)

(XXIII)

where R is CH_3, C_2H_5, n-C_3H_7, or iso-C_3H_7. If the sulphonic acid is bound (for example, by means of dry powdered potassium carbonate[104,105]), the peroxides decompose predominantly by a radical mechanism; on the other hand, addition of a sulphonic acid or of aprotonic acids ($AlCl_3$, $SnCl_4$, or $SbCl_5$) directs the reaction towards the heterolytic isomerisation (2), the mixed anhydrides of alkanesulphonic acid and monophenyl carbonate (XXIII) being obtained in more than 85% yield.

Analogous rearrangements are undergone by benzoyl peroxide[102,108,109,115,116] under the influence of $AlCl_3$ or $SbCl_5$, and by unsymmetrically substituted analogues of benzoyl peroxide and other non-symmetric acyl peroxides under the influence of BF_3.[113] The acyl phenyl carbonates produced by the heterolytic rearrangement are unstable, and decompose in the presence of aprotonic acids to form the corresponding esters (in 70–95%) and CO_2:

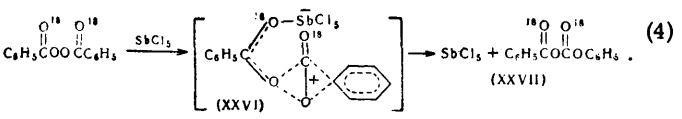


(3)

(XXIV) (XXV)

where $M^{n+}X_n$ is $AlCl_3$, $SbCl_5$, or BF_3, and R is C_6H_5, *p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$NO_2C_6H_4$, *o*-$CH_3C_6H_4$, *o*-ClC_6H_4, CH_3, $ClCH_2$, C_2H_5, etc. Depending on R, either (XXIV) or (XXV) may predominate; thus the reaction produces 100% (XXIV) when R is *p*-$NO_2C_6H_4$, and 100% (XXV) when R is *p*-$CH_3OC_6H_4$.

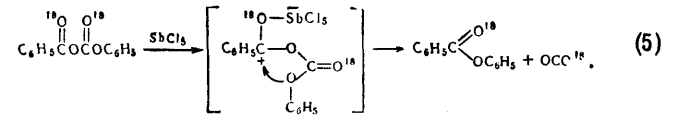
Denney and coworkers have investigated the heterolytic rearrangement, under the influence of $SbCl_5$, of benzoyl peroxide[115,116] and of some other peroxides[117-118], labelled with ^{18}O in the carbonyl group; the resulting ester — (XXIV) or (XXV), R = C_6H_5 — still contains ^{18}O in the carbonyl group, but the phenolic oxygen does not contain the remaining ^{18}O. It is therefore concluded that the heterolysis of the peroxide does not produce free carbonium cations, but that the rearrangement proceeds in the transitional complex (XXVI):



(4)

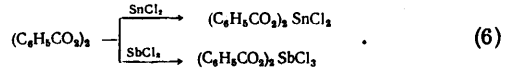
(XXVI) (XXVII)

Under the influence of the $SbCl_5$ the mixed carbonate (XXVII) rapidly decomposes as follows:



(5)

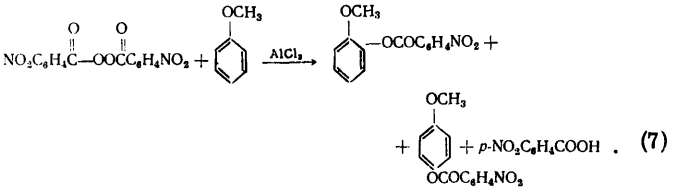
Benzoyl peroxide reacts quantitatively with $SnCl_2$ and $SbCl_3$ at room temperature as follows[119]:



(6)

Apparently, in these reactions the benzoyl peroxide splits homolytically at the O–O bond, and the resulting benzoyloxy-radicals react with the salt present, the Sn^{2+} and Sb^{3+} being converted into Sn^{4+} and Sb^{5+} respectively.

Edward and coworkers have recently shown[114] that under the influence of an equimolar amount of $AlCl_3$ *pp'*-dinitrobenzoyl peroxide can react with strongly nucleophilic solvents (anisole, mesitylene, 1,3-dimethoxybenzene) at 0–25° by a Friedel–Crafts type reaction, giving moderate yields of the corresponding *p*-nitrobenzoates:

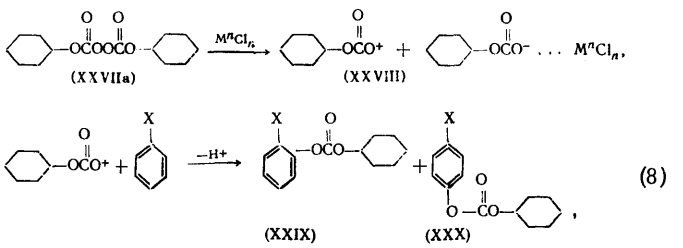


(7)

The peroxide apparently splits heterolytically at the O–O bond, and the resulting *p*-nitrobenzoyloxy-cation attacks the aromatic ring. This electrophilic attack is facilitated by electron-donating substituents, and does not occur with benzene or toluene.

The reaction between dicyclohexyl peroxodicarbonate (XXVIIa) and aromatic compounds under the influence of $FeCl_3$,[112] $SbCl_5$, $SbCl_3$, and $AlCl_3$ has been investigated. In the absence of the aprotonic acids, the peroxodicarbonate decomposes homolytically in toluene at 50–65° to form CO_2 and cyclohexyloxy-radicals, which partially disproportionate in a "cage" of solvent, and partially react with the toluene, the resulting benzyl radicals dimerising to produce 1,2-diphenylethane[120].

Catalytic amounts of aprotonic acids ($SbCl_5$, $FeCl_3$) do not affect the decomposition of the peroxodicarbonate, since they are removed from the sphere of reaction as solid complexes[120]. If the aprotonic acids are added in amounts of 10–50 mole %, the homolytic reaction with the solvents is suppressed, and the peroxodicarbonate enters into a Friedel–Crafts reaction with aromatic compounds, forming the corresponding mixed carbonates (XXIX, XXX):



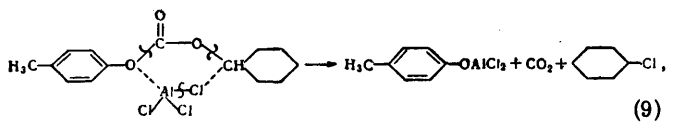
(8)

(XXVIIa) (XXVIII) (XXIX) (XXX)

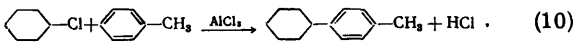
where X is H, CH_3, OCH_3, or Cl.

The cyclohexyloxycarboxy-cation (XXVIII) is fairly reactive and does not require activation of the aromatic ring by electron-donating substituents; under the influence of $FeCl_3$ it reacts with benzene to give a 17% yield of cyclohexyl phenyl carbonate, and with toluene to give cyclohexyl *o*-tolyl and cyclohexyl *p*-tolyl carbonates in yields of 34% and 7% respectively. Electron-donating substituents favour the electrophilic attack; thus even in the absence of Lewis acids anisole reacts to give cyclohexyl *o*-methoxyphenyl and cyclohexyl *p*-methoxyphenyl carbonates in good yield.

Strong Lewis acids, such as $AlCl_3$, can decompose the mixed carbonates. The main product of the decomposition of the peroxodicarbonate in toluene at 40–60° in the presence of 50 mole % $AlCl_3$ is *p*-tolylcyclohexane (40% yield), which is obtained as the result of decomposition of the initial cyclohexyl tolyl carbonates (XXIX) and (XXX):



(9)



(10)

When carried out in chlorobenzene the reaction produces *p*-chlorophenylcyclohexane. The reaction mechanism is confirmed by the quantitative liberation of hydrogen chloride.

The ionic reactions of peroxides with solvents are almost restricted to the examples given[112,114]. However, the growing interest in such processes suggest that in the near future the ionic reactions of peroxides will form the basis of new methods of synthesis.

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ADVANCES IN THE CHEMISTRY OF POLYETHYLENEIMINE (POLYAZIRIDINE)†

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† Since polyethyleneimine is an industrial product, and really a straight-chain compound, it has seemed advisable to retain this name in the translation, while the more systematic *aziridine* is used for the monomer (Ed. of Translation).