

ORGANIC  
PEROXIDES

*Their Formation and Reactions*

E. G. E. HAWKINS

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LONDON

E. and F. F. SPON LTD.

22 Henrietta Street, London, W.C.2

1961

## PREFACE

Although some of the reactions of organic peroxides have been described in a few recent books these have usually been limited to a particular aspect, e.g. the use of peroxides in polymerisation or the study of the radical processes involved in many of their decomposition reactions, and nothing has been devoted entirely to the organic chemistry of these compounds since Rieche's monograph *Alkylperoxyde und Ozonide* in 1931 and Criegee's short review in Houben-Weyl's *Methoden der Organischen Chemie* (Vol. 8; 1952). It was felt that the time was ripe to make available a summary of the major advances in a field which, like many others in organic chemistry, is broadening rapidly and in which a large number of new papers is constantly appearing in the journals. In addition to the formation and reactions of peroxides, their analysis and applications are also considered briefly in this book: further, a chapter on autoxidation is included to illustrate the close connection of this phenomenon with peroxide chemistry. References to the available literature up to the end of 1959 have been included, although these are not exhaustive. The kinetics of peroxide reactions and detailed discussion of the use of peroxides in polymerisation are outside the scope of this book, but are available elsewhere.

The method of classification used may not be ideal, but it is felt that the alternative methods which were considered suffered from a greater number of disadvantages. Some overlapping from chapter to chapter is bound to occur in this arrangement, but it is hoped that this has been kept to a minimum.

I should like to thank the Distillers Company Ltd. for the facilities which they have made available to me whilst writing this book, Dr. D. C. Quin for reading the manuscripts and offering valuable comments and a number of my colleagues for discussions and suggestions.

April, 1961.

E. G. E. HAWKINS

## INTRODUCTION

ALTHOUGH some peroxides, especially certain peracids and acyl peroxides, and the results of their formation during storage of materials—rancidity in edible vegetable and animal oils, bleaching of palm oils, loss of activity in vitamin A concentrates, gum formation in mineral oils, drying of paints and the formation of explosive substances in solvents—have been known for a considerable time, the systematic study of these compounds, particularly hydroperoxides and peroxides, has only made progress during the last thirty years or so. The rapid advance of knowledge of the chemistry of peroxides, both that concerned in their formation and that with their reactions, has been achieved by the studies of a large number of workers, but many of the major contributions to the understanding attained in this field are linked with the names of Rieche, Criegee, Hock, Schenck and Treibs in Germany, Kharasch and Milas in America, Dufraisse in France, and Farmer, Waters and A. G. Davies in Britain. These, and many others, have provided the evidence which has clarified the mechanisms involved in the preparation and decomposition of peroxides, and have shown that compounds of this nature may be produced from an ever-increasing number of chemical species. Other workers, particularly those in industrial research organisations, have found means of applying this fundamental knowledge to the development of commercially useful processes (e.g. phenol from cumyl hydroperoxide) and have had to face the initial problems of scaling-up the efficient production of compounds of doubtful stability and potential danger.

It is difficult to select the highlights in this field, but certain discoveries may, without doubt, rank as major advances and have provided the foundations for later studies.

Both Farmer and Criegee, by investigating the peroxides obtained from cyclic olefins, showed that these contained hydroperoxide ( $\text{-OOH}$ ) groups and were not the cyclic 1,2-peroxides earlier envisaged. At a later date peroxides derived from other classes of compounds (e.g. unsaturated ketones and phenylhydrazones) were similarly shown not to have the cyclic structure which had originally been attributed to them.

The early discovery by Staudinger that 1,1-diphenylethylene gave a polymeric peroxide on autoxidation has been followed over recent years by results which indicate that most vinyl monomers can also co-polymerise with oxygen

to yield polymeric peroxides—sometimes explosive in nature; this knowledge provided an explanation of the inhibiting effect of oxygen on many simple homopolymerisation reactions.

The studies of Rieche and his co-workers on the autoxidation of various ethers have led to an understanding of the nature of the explosive residues formed on storage of diethyl ether. The point of interest here is that the explosive compounds are not the initial hydroperoxides but other peroxides produced by their subsequent decomposition.

The theories proposed by Kharasch and Criegee to explain the mode of acid catalysed decomposition of hydroperoxides and their esters, and the mechanism of ozonolysis—also due to Criegee—were both of great importance. Of similar value were the results of work by Kornblum and de la Mare on the conversion of peroxides (particularly secondary-tertiary peroxides) to alcohols and ketones by bases.

Other landmarks in peroxide chemistry included the discovery of the formation of cyclic photoperoxides from substituted anthracenes by Dufraisse and his co-workers, and the syntheses of a number of hydroperoxides, previously unobtainable by other methods owing to their instability or for other reasons, by the new technique of low temperature photosensitised oxidation due to Schenck.

More recently, it has been found that peroxides can be produced from organic compounds containing tin, germanium, phosphorus, boron, silicon or cadmium (Rieche, Hock and Davies), and this list may well be extended in the near future. The syntheses of hydroperoxides from Grignard compounds and of alcohols from aluminium alkyls by oxidation processes both involve organometallic peroxides as intermediates.

Consideration of the reactions taking place during the formation and decomposition of peroxides, as described in the following chapters, shows that either homolytic (radical) or heterolytic (ionic, polar) mechanisms may be involved: which type operates in a particular instance may be dependent on the reaction conditions, e.g. temperature, solvent, catalyst and pH. The suggestion that many peroxide reactions could be satisfactorily explained on the basis of radical formation and interaction put forward by Waters and Hey<sup>1, cf. 2, 3</sup> allowed a much wider understanding of the mechanism of such reactions, and overcame the problems associated with fitting many of these into a pattern based on heterolysis.

Thus, the formation of hydroperoxides by autoxidation normally takes place by a radical process; the reaction is initiated thermally or by the addition of a compound known to provide radicals easily (e.g. a peroxide or azo-compound):

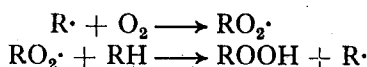


1. W. A. Waters and D. H. Hey, *Chem. Reviews*, 1937, **21**, 169.

2. W. A. Waters, *The Chemistry of Free Radicals*, Oxford University Press, Oxford, 1946 (2nd edition, 1948).

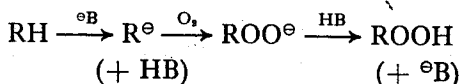
3. C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957.

This stage is followed by one of propagation by a chain mechanism:



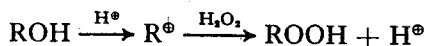
The chain usually ends by combination or disproportionation of such radicals, although in practice such a process is complicated by radical transfer to solvent or to reaction fragments, considered later. Further, such autoxidation processes may be prevented by the addition of a substance (antioxidant or inhibitor) which may act as an efficient radical trap: the practical applications of this are met in the addition of phenols or amines to monomers to prevent polymerisation, and in the presence of antioxidants (e.g. tocopherol) in a number of naturally-occurring, unsaturated, fatty materials. Such organic inhibitors do not act catalytically and when they reach the end of their useful life autoxidation proceeds normally. In this way the autoxidation of benzaldehyde to benzoic acid is inhibited by the presence of small quantities of olefins, but continues again when all the olefin has been converted to epoxide, glycol or carbonyl compounds.<sup>4</sup>

On the other hand, it has been suggested that substituted fluorenes, which autoxidise easily in pyridine solution, in the presence of a basic catalyst (Triton B), do so by an ionic route,<sup>5</sup>



and oxidation of carbonyl compounds in strongly basic solutions, to give acids and aldehydes by chain scission, may well proceed by a mechanism requiring the presence of carbanions.

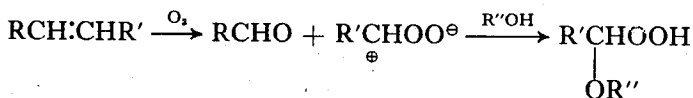
The method of synthesising hydroperoxides by the acid-catalysed reaction of alcohols (or esters) with hydrogen peroxide provides an illustration of a heterolytic process in which carbonium ions take part:



The formation of peroxides from hydroperoxides and alcohols proceeds similarly:



Criegee<sup>6</sup> has shown that the peroxides produced by ozonolysis of unsaturated compounds in a reactive solvent also arise by an ionic route:



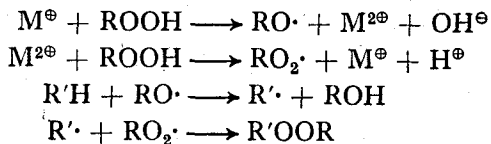
4. G. Wittig, *Annalen*, 1947, **558**, 201.

5. Y. Sprinzak, *J. Amer. Chem. Soc.*, 1958, **80**, 5449.

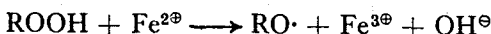
6. R. Criegee and G. Wenner, *Annalen*, 1949, **564**, 9; R. Criegee and G. Lohaus, *ibid.*, 1953, **583**, 6.

The decomposition reactions of peroxides may also involve homolysis, with the production of radicals ( $\text{RO}_2\cdot$ ,  $\text{RO}\cdot$  or  $\text{R}\cdot$ ), or heterolysis, with the formation of ions or ion pairs ( $\text{RO}_2^\ominus$ ,  $\text{RO}_2^\oplus$ ,  $\text{RO}^\ominus$ ,  $\text{RO}^\oplus$  or  $\text{R}^\oplus$ ): the conditions under which each is most likely to take place and consideration of the kinetic mechanisms involved are considered by Tobolsky and Mesrobian.<sup>7</sup>

Peroxy ( $\text{RO}_2\cdot$ ) radicals, formed, together with alkoxy ( $\text{RO}\cdot$ ) radicals, from hydroperoxides by a redox mechanism in the presence of catalytic quantities of the salts of certain multivalent metals (copper, cobalt and manganese), give substitution products with many reactive molecules (olefins, ketones, alkylbenzenes, ethers, etc.) when these are present in the reaction system, although addition may occur to molecules of polymerisable compounds or in the formation of epoxides during autoxidation of olefins. The following simplified scheme shows the net result of such reactions, although it seems possible in the light of recent work that radical-ion complexes may be involved:<sup>8</sup>



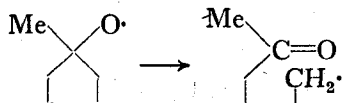
Ferrous compounds have been found to be convenient reagents for producing alkoxy radicals from hydroperoxides:



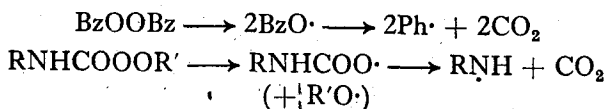
Radicals obtained by this method or by pyrolysis of hydroperoxides or peroxides may then add to vinyl compounds,



may rearrange,



abstract hydrogen,  $\text{RO}\cdot + \text{R}'\text{H} \longrightarrow \text{ROH} + \text{R}'\cdot$ , or decompose, e.g.  $\text{CMe}_3\text{O}\cdot \longrightarrow \text{OCMe}_2 + \text{Me}\cdot$ , and the new radicals formed enter into further reactions. Pyrolysis of dialkyl peroxides and peroxyesters has been utilised as a means of producing alkoxy (and hence alkyl) radicals for their further study, whilst acyloxy radicals derived from acyl peroxides or peroxy-carbamates may react as such or decarboxylate:

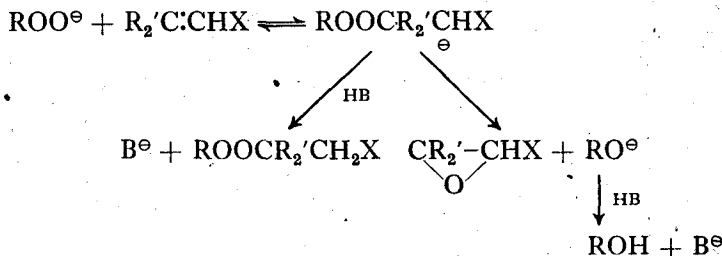


7. A. V. Tobolsky and R. B. Mesrobian, *Organic Peroxides; their Chemistry, Decomposition and Role in Polymerisation*, Interscience, New York, 1954; p. 57 et seq.

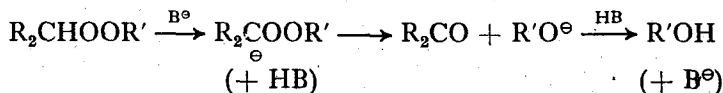
8. M. S. Kharasch and A. Fono, *J. Org. Chem.*, 1959, **24**, 606.

The subsequent reaction of radicals produced by these routes are considered in later chapters.

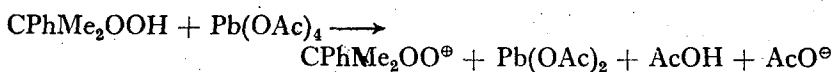
The interaction of hydroperoxides with reactive olefins under basic conditions takes place *via* a peroxy anion<sup>9</sup> and may lead to either an epoxide or peroxide, depending on the nature of the activating group X:



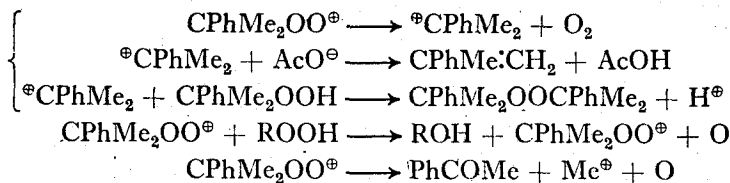
An alkoxy anion is also produced during the base-catalysed decomposition of many peroxides:<sup>10</sup>



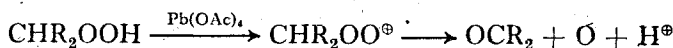
Although it was originally suggested that the decomposition of hydroperoxides by ceric salts and lead tetra-acetate proceeded with the formation of peroxy radicals,<sup>11</sup> a recent study of the reaction of tertiary hydroperoxides with lead tetra-acetate<sup>12</sup> has provided strong evidence that in this case at least peroxy cations are produced.



These ions may then give rise to alcohols, ketones, olefins or peroxides:



Secondary hydroperoxides, under identical conditions, yield ketones:



The mechanism of many acid-catalysed reactions of hydroperoxides and peroxyesters can be understood on the basis of the formation of intermediate

9. N. C. Yang and R. A. Finnegan, *J. Amer. Chem. Soc.*, 1958, **80**, 5845.

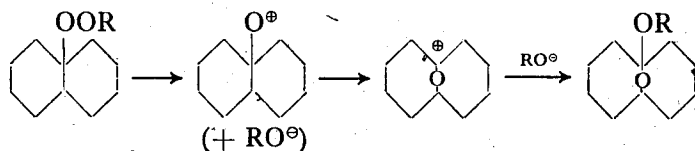
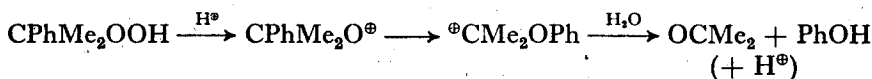
10. N. Kornblum and H. E. De La Mare, *ibid.*, 1951, **73**, 880.

11. M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.* 1952, **17**, 207.

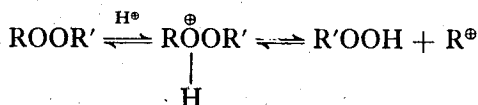
12. H. Hock and H. Kropf, *Chem. Ber.*, 1958, **91**, 1681.



alkoxy cations: examples of this include the well-known conversion of cumyl hydroperoxide to phenol and acetone<sup>13</sup> and the almost equally familiar rearrangement of decalyl peroxyesters:<sup>14</sup>



Finally, acid-catalysed alkyl-oxygen heterolysis of certain hydroperoxides and peroxides containing strongly electron-releasing groups, to give carbonium ions (R<sup>⊕</sup>), has been described.<sup>15</sup>



Such carbonium ions subsequently react with nucleophilic reagents present in the reaction mixture.

The further reactions of the radicals or ions produced in such methods of decomposition of peroxides as those exemplified above are multifarious, and some attempt has been made on the following pages to show how they behave in different environments. The mechanisms of reactions, where given, are generally those proposed by the workers concerned, but are often only tentative and may require modification in the light of later results. Some uncertainty generally arises through the transient nature of the fragments (radical or ionic) whose existence can often be deduced only from examination of the reaction products. Discussion on the mechanisms of the reactions of peroxides has been given in reviews<sup>16,17</sup> and occurs in detail in the books mentioned previously.<sup>2,3</sup>

Although, as will be evident, tremendous strides have been made in this field, and some order has been achieved in the chemistry of peroxides, there would appear to be potential scope for future work, both from the theoretical aspect and in applications directed towards their industrial utilisation.

13. M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, 1950, 15, 748.

14. R. Criegee, *Annalen*, 1948, 560, 127.

15. A. G. Davies, R. V. Foster and R. Nery, *J. Chem. Soc.*, 1954, 2204.

16. J. E. Leffler, *Chem. Reviews*, 1949, 45, 385.

17. C. E. Frank, *ibid.*, 1950, 48, 155.

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## CHAPTER 1

### HYDROPEROXIDES. ROOH: WHERE R IS (A) ALKYL, (B) ALKENYL AND (C) ALKYNYL

#### A. R: ALKYL

##### Formation

##### BY OXIDATION AND AUTOXIDATION

###### a. Hydrocarbons

Although the production of peroxides must have frequently occurred during storage of paraffinic (and other) hydrocarbons or as intermediates during their oxidation to ketones, alcohols and acids, concentration and isolation of such peroxidic compounds have not been attempted until recent years. There is little doubt that the main reason for this was the relative instability of such peroxides, particularly in the impure state or when formed during autoxidation in the presence of catalysts: the tendency, even under controlled conditions of temperature and degree of conversion, is for the peroxide concentration to rise to a maximum (often fairly small) and then for the rate of decomposition to overtake the rate of formation. The same is true of the autoxidation of many other types of compound, hydrocarbon and non-hydrocarbon, and the subsequent decompositions occurring during autoxidation are considered later (Chapter 12).

Thus, earlier work had shown that oxidation of pentane, hexane and octane<sup>1</sup> provided a crude product containing peroxides, whilst long-chain paraffins<sup>2</sup> oxidised at 100–200° yielded material with a peroxide content of only *ca.* 5% based on oxygen absorbed. Larger-scale oxidation of kerosene fractions in the presence of a weak base (magnesium oxide) provided sources of peroxide concentrates.<sup>3</sup>

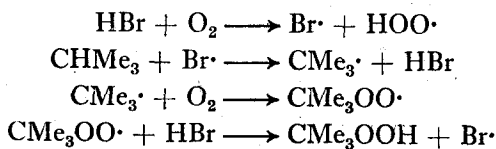
Workers of the Shell Development Co., in a study of the controlled vapour-phase oxidation of various hydrocarbons (paraffinic, olefinic and aralkyl) in the presence of a hydrogen bromide catalyst, were able to direct the reaction towards the production of either ketones and acids or hydroperoxides and

1. P. Mondain-Monval and B. Quanquin, *Compt. rend.*, 1930, **191**, 299.

2. P. George, E. K. Rideal and A. Robertson, *Nature*, 1942, **149**, 601.

3. Union Oil Co., U.S.P. 2,447,794.

peroxides by suitable variation of conditions.<sup>4,5</sup> Primary and secondary alkanes yielded mainly acids and ketones, but tertiary paraffins were the main source of peroxides. Thus isobutane, oxidised at 158° and with a contact time of three minutes, was found to give a 42% yield of di-t-butyl peroxide together with t-butanol and some butyraldehyde; variation of the reaction conditions led to the formation of 75% t-butyl hydroperoxide. The mechanism proposed involved the following steps:<sup>4</sup>



In a similar fashion isobutyl chloride was converted to chloro-t-butyl peroxide. Such a route to t-butyl hydroperoxide and di-t-butyl peroxide made these compounds readily available, and consequently their reactions have been studied to a greater extent than those of any other alkyl peroxide. A later report<sup>6</sup> also described the liquid phase oxidation of isobutane, at 100–150°, to t-butyl hydroperoxide.

In contrast to the production of such well-defined peroxides from isobutane oxidation, it was found that oxidation of propane and ethane, using a 9:1 ratio of hydrocarbon to oxygen at temperatures of *ca.* 450° and short contact times (4 sec.), gave a mixture of products, containing organic peroxides, hydrogen peroxide, aldehydes, alcohols, oxides of carbon, water, olefins and hydrogen.<sup>7</sup> The organic peroxides here probably consisted largely of hydroxyhydroperoxides and dihydroperoxides, derived from the interaction of the aldehydes (e.g. formaldehyde) and hydrogen peroxide known to be present. A more recent claim has been made<sup>8</sup> for the conversion of ethane into hydroperoxides by oxidation at 10–80° in the presence of U.V. light and a metal vapour sensitiser (mercury, zinc or cadmium); however, the conversion per pass in this process was very low (0.1%).

A discussion of the evidence of the presence of hydroperoxides as intermediates formed during the slow, vapour-phase combustion of hydrocarbons has been given by Tipper,<sup>9</sup> and it has recently been shown by careful examination of the products of oxidation of n-heptane at 250–275° that isomeric heptyl hydroperoxides were actually present, in addition to peroxide-aldehyde condensation compounds.<sup>10</sup>

4. F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, 1949, **41**, 2595; E. R. Bell, F. H. Dickey, J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, p. 2597; P. J. Nawrocki, J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, p. 2604; E. R. Bell, G. E. Irish, J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, p. 2609.
5. Shell Dev. Co., U.S.P. 2,395,523, 2,403,771–2, 2,434,888, 2,435,763, 2,446,797, 2,449,347, 2,570,487.
6. Shell Dev. Co., U.S.P. 2,845,461.
7. P. L. Kooijman, *Rec. Trav. chim.*, 1947, **66**, 5, 49; P. L. Kooijman and W. L. Ghijsen, *ibid.*, p. 205.
8. I.C.I., U.S.P. 2,730,495.
9. C. F. H. Tipper, *Quart. Reviews*, 1957, **11**, 313.
10. J. Cartlidge and C. F. H. Tipper, *Proc. Chem. Soc.*, 1959, 190.

The position of oxygen attack during oxidation of an *n*-alkane has been the subject of much discussion by a number of workers; this question will be considered more fully in Chapter 12. A careful study of the autoxidation of *n*-decane at 145° has shown that all the secondary decyl hydroperoxides are formed in equal amounts, whereas less oxidation occurs at the end (primary) carbon atoms.<sup>11</sup> The mixed hydroperoxides, isolated by counter-current extraction of the oxidate, had a purity of >97%, and their structures were demonstrated by conversion to the four corresponding secondary alcohols, in equimolar amounts, by catalytic reduction: only a trace of decan-1-ol was detected on chromatographic separation. In this work the carbon skeleton was largely retained, and 80% of the products were mono-functional: this was achieved by limiting the oxidation to a 2.5% peroxide concentration.

These results were confirmed by those obtained by Pritzkow and Müller,<sup>12</sup> who also found, by autoxidation of *n*-heptane, *n*-decane and *n*-dodecane, that mixtures of secondary hydroperoxides were produced: these were identified by conversion to the corresponding ketones and alcohols and the ketones further converted to oxamic esters for chromatographic separation. In this work the 1-, 2-, 3- and 4-heptyl hydroperoxides were also synthesised from the chlorides for comparison.

There seems little doubt from these results, and those on the autoxidation of *n*-octadecane by Geiseler, Asinger and Wien,<sup>13</sup> that during oxidation of a straight-chain paraffin random attack takes place as had previously been noted for chlorination, sulphochlorination, nitration and sulphoxidation reactions by Asinger and co-workers. It had been earlier suggested by Ivanov *et al.*<sup>14</sup> that *n*-heptane oxidation led mainly to the 2-hydroperoxide: these workers were led to this conclusion by the isolation of heptan-2-ol and preparation of the semicarbazone of heptan-2-one from the alkaline decomposition product of the crude hydroperoxide, obtained by concentration of their oxidate (0.5–0.6% peroxide). It has been pointed out by Asinger *et al.*<sup>15</sup> that this derivative may have been isolated owing to its lower solubility in the reaction solvent than that of the isomers, and possibly because of the greater reactivity of the heptan-2-one relative to the 3- and 4-ketones.

Introduction of branching into the paraffin chain in general leads to preferential oxidation at the tertiary carbon atom, and causes the formation of more stable hydroperoxides: the conversion of isobutane to *t*-butyl hydroperoxide, already mentioned, provides an example of this. When branching occurs at more than one position in the chain the final products of oxidation may contain more than one hydroperoxide group: thus exposure of 2,5-dimethylhexane to air for several years gave rise to a solid dihydroperoxide

11. J. L. Benton and M. M. Wirth, *Nature*, 1953, **171**, 269.

12. W. Pritzkow and K. A. Müller, *Annalen*, 1955, **597**, 167.

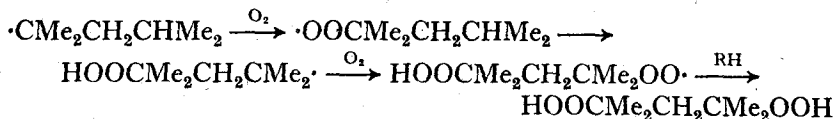
13. G. Geiseler, F. Asinger and H. Wien, *Chem. Ber.*, 1959, **92**, 958.

14. K. I. Ivanov, V. K. Savinova and V. P. Zhakhovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, 903.

15. F. Asinger, G. Geiseler and W.-D. Wirth, *Chem. Ber.*, 1957, **90**, 1987.

similar to that produced by treatment of 2,5-dimethylhexane-2,5-diol with hydrogen peroxide.<sup>16</sup>

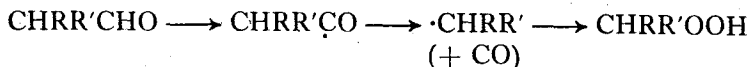
In a study of the autoxidation of a number of branched-chain alkanes (2,3- and 2,4-dimethylpentane, 2,5-dimethylhexane and 2,6-dimethylheptane) at 115–120° Rust<sup>17</sup> found that the products included both tertiary mono- and dihydroperoxides. The isolation of good yields of crystalline dihydroperoxides from 2,4-dimethylpentane and 2,5-dimethylhexane caused Rust to suggest that chain propagation might well be intramolecular in many cases, particularly where  $\beta$ - or  $\gamma$ -attack could occur:



The dihydroperoxide obtained from 2,5-dimethylhexane was identical with that isolated by Wibaut and Strang<sup>16</sup> and that prepared by Criegee and Paulig<sup>18</sup> from the corresponding glycol.

In contrast to the above results it was earlier reported by Ivanov, Savinova and Zhakhovskaya<sup>19</sup> that oxidation of 2,7-dimethyloctane gave a 2-mono-hydroperoxide and a 2,3-dihydroperoxide. The formation of such an  $\alpha\beta$ -dihydroperoxide is not in agreement with Rust's  $\beta$ -attack, and even if intermolecular propagation took place it might have been anticipated that the remaining tertiary position ( $C_7$ ) rather than the secondary one ( $C_3$ ) would have been involved. Further discussion of paraffin oxidation is provided in Chapter 12.

As will be seen later, co-oxidation of olefins and aldehydes usually leads to the formation of esters of  $\alpha\beta$ -glycols or peroxyacids, depending on the proportions of the reactants, but it has been recently claimed<sup>20</sup> that alkyl hydroperoxides may be produced by a similar route. Although normal aldehydes ( $\text{CHRR}'\text{CHO}$ ;  $\text{R}' = \text{H}$ ) can be used in this process, branched-chain compounds ( $\text{R}' = \text{alkyl}$ ) are preferred, and the olefins should have a tertiary carbon atom  $\alpha$ - or  $\beta$ - to the double bond; for optimum yields of hydroperoxides ( $\text{CHRR}'\text{OOH}$ ) the ratio of olefin to aldehyde is controlled at *ca.* 3 : 1 and the oxidation carried out at 60–90°. Yields of up to 64% hydroperoxide (based on aldehyde) have been claimed, with carboxylic acid as a by-product. The mechanism of this reaction is in doubt, but bears a close resemblance to that in which ketones are formed by oxidation of  $\alpha$ -alkylalkanols (e.g. 2-ethylhexanol),<sup>21</sup> presumably *via* hydroperoxides:



16. J. P. Wibaut and A. Strang, *Proc. K. Ned. Akad. Wet.*, 1951, **54B**, 102.

17. F. F. Rust, *J. Amer. Chem. Soc.*, 1957, **79**, 4000.

18. R. Criegee and G. Paulig, *Chem. Ber.*, 1955, **88**, 712.

19. K. I. Ivanov, V. K. Savinova and V. P. Zhakhovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1948, **59**, 703.

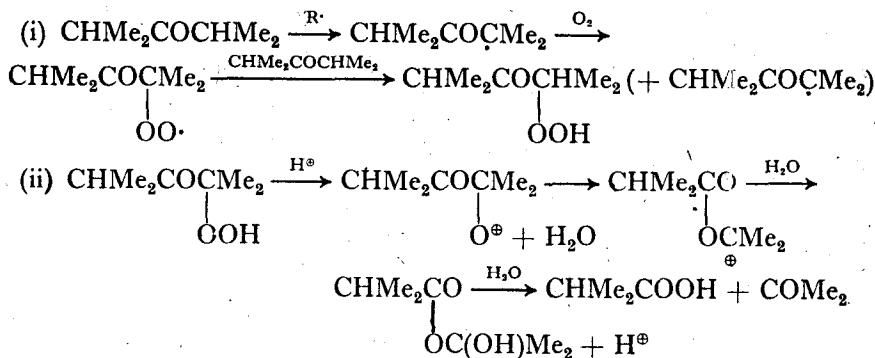
20. Standard Oil Co., U.S.P. 2,831,023.

21. P. Thüring and A. Perret, *Helv. Chim. Acta*, 1953, **36**, 13.

## b. Non-hydrocarbon

The autoxidation of certain acyclic compounds (e.g. propan-2-ol, diethylene glycol, di-isopropyl ether) yields peroxides of such structures that they fall into groups considered in later sections.

It was found by Paquot<sup>22</sup> that oxidation of di-n-propyl ketone, in the presence of a nickel phthalocyanine catalyst, yielded as main products n-butyric and propionic acids, and this was confirmed by others workers<sup>23</sup> on non-catalytic oxidation of the same ketone at 110° when low concentrations of peroxide were also detected. Concentrates of the hydroperoxides from this ketone and from butan-2-one and 2,4-dimethylpentan-3-one (di-isopropyl ketone) were later isolated from the products of autoxidation of these ketones;<sup>24</sup> that they were hydroperoxides was demonstrated by oxygen liberation on treatment with lead tetra-acetate,<sup>25</sup> and the structure of the hydroperoxide from butan-2-one was proved by catalytic reduction to acetoin. The hydroperoxides of the straight-chain ketones were generally unstable, particularly to acid, but that derived from di-isopropyl ketone withstood purification by distillation;<sup>26</sup> even here the use of too high a bath temperature during distillation led to complete decomposition to acetone and isobutyric acid. It has been suggested by Pritzkow that the formation (i) of such hydroperoxides proceeds by the normal radical process, but the decomposition (ii) by an ionic mechanism:



The similar formation and decomposition of a well-known group of ketone peroxides, known as Kohler's peroxides, will be described later (Chapter 3).

The study of the autoxidation of a variety of sulphides (saturated and unsaturated) by Bateman and co-workers<sup>27</sup> has shown that there are produced mainly sulfoxides and fission products, but it has been suggested that

22. C. Paquot, *Bull. Soc. chim.*, 1945, **12**, 450.

23. D. B. Sharp, S. E. Whitcomb, L. W. Patton and A. D. Moorhead, *J. Amer. Chem. Soc.*, 1952, **74**, 1802.

24. W. Pritzkow, *Chem. Ber.*, 1955, **88**, 572.

25. R. Criegee, H. Pilz and H. Flygare, *Ber.*, 1939, **72**, 1799.

26. D. B. Sharp, L. W. Patton and S. E. Whitcomb, *J. Amer. Chem. Soc.*, 1951, **73**, 5600.

27. L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1955, 1596; L. Bateman and F. W. Shipley, *ibid.*, p. 1996; L. Bateman, J. I. Cunneen and J. Ford, *ibid.*, 1957, 1539.



peroxides (or peroxy radicals) are formed as intermediates: presumably the sulphide group activates the neighbouring methylene system in a similar way as does an ether group.

Photosensitised oxidation of some amines at room temperature yielded hydroperoxides (e.g.  $\text{CHMe}_2\text{CH}(\text{OOH})\text{NH}_2$ ); that from isobutylamine provided oxygen on treatment with lead tetra-acetate, lost water to give isobutyramide ( $\text{CHMe}_2\text{CONH}_2$ ), and on reduction yielded isobutyraldehyde and ammonia *via*  $\text{CHMe}_2\text{CH}(\text{OH})\text{NH}_2$ .<sup>28</sup>

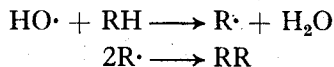
Although peroxides were not isolated from the products of autoxidation of acyclic disubstituted hydroxylamines, they were shown to be present;<sup>29</sup> moreover, the final products (aldehydes and monohydroxylamines) of oxidation indicated that hydroperoxides of the type  $\text{RCH}_2\text{N}(\text{OH})\text{CHR}(\text{OOH})$  were probable intermediates.

Semicarbazones also probably formed intermediate hydroperoxides on oxidation, but these proved too unstable to isolate.<sup>28</sup>

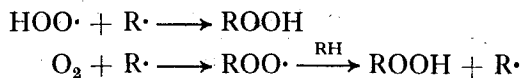
The hydroperoxides derived from phenylhydrazones are described later (Chapter 3).

Autoxidation of trialkylborons gives rise to peroxides, by rearrangement of the first formed peroxy radical, and not hydroperoxides:<sup>30</sup> alkylcadmium compounds behave rather similarly.<sup>31</sup>

A recent paper<sup>32</sup> has described the formation of hydroperoxides (and the corresponding alcohols) from a variety of compounds by use of the hydroxyl radicals present in flame propagation. An aqueous stream, containing the organic compound (alcohols, acids, amines and salts), was passed through a flame ( $>800^\circ$ )—near its inner cone—and the products trapped and separated; many of these products were of the RR type (e.g. t-butanol gave 1,1,4,4-tetramethylbutane-1,4-diol; acetic acid, succinic acid):



but the formation of hydroperoxides (from acetic, propionic and pivalic acids) was thought to involve  $\text{HOO}\cdot$  radicals or oxygen:



#### FROM HYDROGEN PEROXIDE

The reaction of hydrogen peroxide with olefins, alcohols and esters (e.g. sulphates, methanesulphonates, halides, hydrogen phthalates), in the presence of acid or alkali, has been the method of choice for the preparation of a large number of alkyl hydroperoxides and dihydroperoxides.

28. G. O. Schenck, *Angew. Chem.*, 1957, **69**, 579.

29. D. H. Johnson, M. A. T. Rogers and G. Trappe, *J. Chem. Soc.*, 1956, 1093.

30. M. H. Abraham and A. G. Davies, *J. Chem. Soc.*, 1959, 429; A. G. Davies and D. G. Hare, *ibid.*, p. 438.

31. A. G. Davies and J. E. Packer, *Chem. and Ind.*, 1958, 1177; *J. Chem. Soc.*, 1959, 3164.

32. C. S. Cleaver, L. G. Blosser and D. D. Coffman, *J. Amer. Chem. Soc.*, 1959, **81**, 1120.