Tetrahedron, 1964, Vol. 20, pp. 271 to 279. Pergamon Press Ltd. Printed in Northern Ireland

CONCERNING THE MECHANISM OF THE INDUCED DECOMPOSITIONS OF t-ALKYL AND ARALKYL HYDROPEROXIDES

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(*Received 5 August* 1963)

Abstract—The induced decompositions of t-alkyl and aralkyl hydroperoxides into the corresponding t-alcohol and oxygen have been studied. It has been found that the reaction is markedly influenced by structural variations in the hydroperoxides. The additives or promoters all appear to operate by generating peroxy and/or alkoxy radicals at temperatures lower than those under which the hydroperoxides give radicals. The means by which the promoters form radicals are discussed. It is believed that the oxygen forming reaction is the same for all of the decompositions and involves bimolecular combination of ROO·.

THE decomposition of t-butyl and cumyl hydroperoxides into the appropriate alcohol and oxygen can be effected by a number of additives and catalysts.[2]

$$2R_3COOH \rightarrow 2R_3COH + O_2$$

Although various mechanisms have been proposed for these decompositions, only one has received sound experimental verification. In general this involves initial production of the appropriate peroxy radical which undergoes bimolecular decomposition to oxygen and alkoxy radicals. The alkoxy radicals then abstract hydrogen atoms from the hydroperoxide and thus regenerate peroxyradicals. The major support for this mechanism

$$(1) \qquad R_3COOH \rightarrow R_3COO\cdot$$

$$(2) \qquad 2R_3COO\cdot \rightarrow 2R_3CO\cdot + O_2$$

$$(3) \qquad R_3CO\cdot + R_3COOH \rightarrow R_3COH + R_3COO\cdot$$

has been supplied by Traylor and Bartlett.[3] They have demonstrated that reaction (2) must occur during the autooxidation of cumene.

The additives and catalysts which have been used to promote these decompositions include combinations of nitriles and base,[4] metal ions which are capable of oxidation-reduction,[5] light[6] and at higher temperatures base alone.[4,7]

Although it has been suggested[5,6] that metal ions and light promote decomposition by the path outlined above, the nitrile-base[4] and base[2a] promoted decompositions

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[1] Rutgers Research Council Faculty Fellow, 1963–1964.

[2] Reviews on this subject can be found in (a) A. G. Davies, *Organic Peroxides*, Butterworths, London (1961); (b) E. G. E. Hawkins, *Organic Peroxides*. Van Nostrand, Princeton, N.J. (1961) and (c) A. V. Tobolsky and R. B. Mesrobian, *Organic Peroxides*. Interscience, New York, N.Y. (1954).

[3] T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters* No. 24, 30 (1960).

[4] M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.* 17, 207 (1952).

[5] M. H. Dean and G. Skirrow, *Trans. Faraday Soc.* 54, 849 (1958).

[6] J. T. Martin and R. G. W. Norrish, *Proc. Roy. Soc.* A220, 322 (1953).

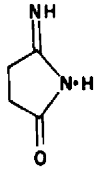
[7] V. A. Belyaev and M. S. Nemstov, *Zh. Obshch. Khim.* 31, 3855 (1961) and 32, 3113 (1962).

have been suggested to be non-radical reactions. Quite recently it has been proposed that oxygen can be formed and is formed by radical reactions other than (2).[8]

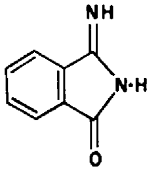
RESULTS

In general the results of Kharasch *et al.*[4] on the nitrile-base catalyzed decompositions of t-butyl hydroperoxide and cumyl hydroperoxide were confirmed. Attempts to decompose other t-alkyl hydroperoxides under conditions[9] which gave 74% and 99% yields of oxygen from cumyl and t-butyl hydroperoxide in ca. 30 minutes gave varying results. t-Amyl hydroperoxide gave a 51% yield of oxygen in two hours. *Trans*-9-decalyl hydroperoxide did not give oxygen under these conditions but ultimately gave a 54% yield of oxygen when more nitrile and base were added. No oxygen was formed from 1,1,3,3-tetramethylbutyl hydroperoxide even though most of the peroxide was decomposed when molar amounts of nitrile and base were used.

From decompositions of t-butyl, 1,1,3,3-tetramethylbutyl and cumyl hydroperoxide there was isolated 5-imino-2-pyrrolidone (I) when succinonitrile was used as an additive. Similarly phthalonitrile in the presence of t-butyl and cumyl hydroperoxides was converted to 3-iminophthalimide (II). When potassium hydroxide labeled with oxygen-18 was used in conjunction with phthalonitrile, the 3-iminophthalimide did not contain oxygen-18. The evolved oxygen did not contain excess oxygen-18.



I



II

The nitrile-base promoted decompositions were subject to inhibition. For example injection of styrene into an oxygen evolving reaction mixture resulted in the immediate cessation of oxygen evolution. The evolution of oxygen could not be realized when n-butyl ether and bis-β-ethoxyethyl ether were used in place of benzene as solvents.

In search for other initiators of this decomposition, 9 mole % of t-butyl hypochlorite was added to a benzene solution of t-butyl hydroperoxide. Irradiation of this mixture with an ordinary lamp led to a rapid evolution of oxygen. A 75% yield was obtained in ten minutes. Under the same conditions t-amyl hydroperoxide afforded a 22% yield of oxygen in twenty-five minutes. The evolution of oxygen ceased when styrene was injected into a decomposing mixture of t-butyl hypochlorite and t-butyl hydroperoxide.

The decomposition at 90° of cumyl or t-butyl hydroperoxide (0·025 mole) in the presence of 10% aqueous sodium hydroxide (0·005 mole) gave 61 and 68% yields of oxygen in ten minutes. 1,1,3,3-Tetramethylbutyl hydroperoxide failed to give oxygen under these conditions. The use of deionized water and reagent grade sodium hydroxide had little effect on the rate or yield of oxygen from cumyl hydroperoxide,

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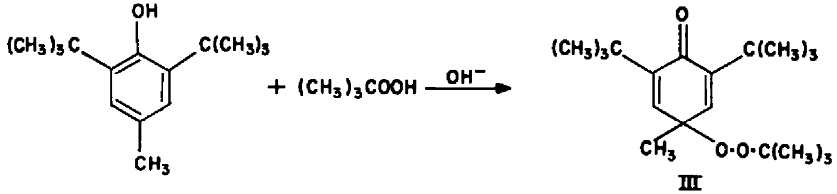
[8a] H. Berger and A. F. Bickel, *Trans. Faraday Soc.* 57, 1325 (1961); [b] H. Berger, *ibid.* 58, 1137 (1962).

[9] These conditions were 0·0283 mole of hydroperoxide, ca. 0·0025 mole of succinonitrile, ca. 0·0018 mole of potassium hydroxide and 20 ml benzene at room temperature.

nor was oxygen evolved when cumyl hydroperoxide was heated with tap water. Addition of 2 mole % (based on hydroperoxide) of the disodium salt of ethylenediaminetetraacetic acid to a standard reaction mixture of t-butyl hydroperoxide and base led to the virtually complete suppression of gas formation at 90°. Addition of 2 mole % and 10 mole % of the disodium salt of ethylenediaminetetraacetic acid to cumyl hydroperoxide reaction mixtures slowed the formation of oxygen by about a factor of three. The same amount of oxygen was ultimately formed.

The base promoted decompositions were subject to inhibition. For example no oxygen was evolved when cumyl hydroperoxide and aqueous base were heated in the presence of bis-β-ethoxyethyl ether. Injection of styrene into a decomposing reaction mixture of cumyl hydroperoxide and base caused cessation of oxygen evolution. An attempt to decompose t-butyl hydroperoxide with base in the presence of 2,6-di-t-butyl-4-methylphenol yielded no oxygen. The peroxide (III) was formed.



III

DISCUSSION

The widely varying means by which oxygen evolution has been promoted in these decompositions has led to almost as many different mechanistic proposals for its formation. The fact that the same products e.q. alcohol and oxygen are formed from these decompositions irrespective of the promoter or catalyst suggests that a common intermediate is involved in these reactions. The Traylor-Bartlett[8] experiment indicates radicals, ROO·, are the candidates for this role. With this in mind it seems imperative to scrutinize each promoter in terms of the basic mechanism, steps (1), (2) and (3).

The hypochlorite promoted decomposition can be very easily explained by the radical chain mechanism. Indeed its very simplicity adds fresh support to this mode of decomposition. It is well known that t-butyl hypochlorite decomposes on irradiation to give t-butoxy radicals and chlorine atoms.[10] In this way the radicals required to start the chain are formed.[11] It is interesting and important to note that t-butyl hypochlorite promoted decomposition of t-amyl hydroperoxide yielded only 22% oxygen versus 75% from t-butyl hydroperoxide. This is probably due in part to the fact that t-amyloxy radicals cleave to ethyl radicals and acetone faster than t-butoxy radicals cleave to methyl radicals and acetone.[12] Ethyl radicals are probably not as efficient chain carriers as alkoxy radicals.[13] The ethyl radicals probably react with

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[10] A. D. Yoffe, *Chem. & Ind.* 963 (1954).

[11] Abstraction of the peroxy hydrogen will be favored over methyl hydrogen, there being a difference of 5 kcal in bond dissociation energies. Both t-butoxy radicals and chlorine atoms should be able to abstract this hydrogen. The alcohol oxygen–hydrogen bond and the hydrogen–chlorine bond are at least 10 kcal stronger than the peroxy oxygen–hydrogen bond. The bond dissociation energies were taken from T. L. Cottrel, *The Strength of Chemical Bonds* (2nd Edition) pp. 270–271. Butterworths, London (1958).

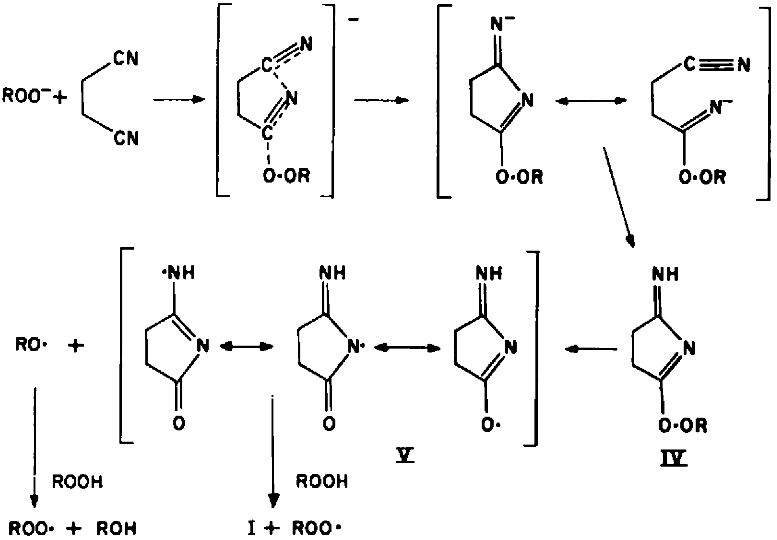
[12] P. Gray and A. Williams, *Chem. Revs.* **59**, 279 (1959).

[13] This reasoning is based on a simple bond dissociation energy argument and ignores polar factors etc. Nevertheless the carbon–hydrogen bond energy is ca. 5 kcal. less than the oxygen–hydrogen bond dissociation energy of an alcohol (ref. 11).

some of the oxygen which is formed thus further diminishing the amount of oxygen evolved.[14]

The inhibition of the hypochlorite promoted reactions by styrene is of course diagnostic of a free radical reaction.

The nitrile-base promoted decompositions also fit into the general radical mechanism. Addition of the hydroperoxy anion to the nitrile group undoubtedly is the first step. When succinonitrile and phthalonitrile are used, this addition is favored by delocalization of the negative charge onto the adjacent cyano group. Formation of an intermediate (IV) is indicated. Indeed Berger[8b] has succeeded in trapping a similar intermediate when a mononitrile was used. Decomposition of IV yields an alkoxy radical and the resonance stabilized radical (V). It should be noted that decomposition of IV should be faster than that of similar adducts derived from mononitriles because there is greater resonance stabilization in V than in the comparable radical derived from mononitriles. Generation of ROO· occurs then by reaction of V with hydroperoxide and by reaction of RO· with hydroperoxide.[15] The inhibitory



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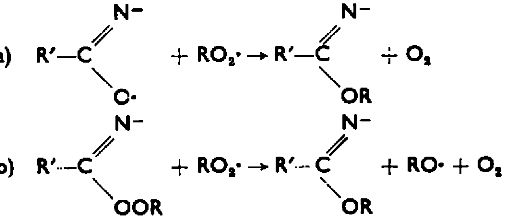
[14] E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, *Faraday Soc. Disc.* **10**, 246 (1951).

[15] Berger (ref. 8*b*) has also suggested that peroxy-anion adds to the nitrile to give an intermediate iminoperoxide. He prefers to envision the formation of oxygen as occurring not by dimerization of ROO· but rather by two paths. The major one being (*a*) and a minor one (b). Although the



$$\text{(a)}\quad R'-C\begin{matrix}\nearrow N^- \\ \searrow O\cdot\end{matrix} + RO_2\cdot \rightarrow R'-C\begin{matrix}\nearrow N^- \\ \searrow OR\end{matrix} + O_2$$

$$\text{(b)}\quad R'-C\begin{matrix}\nearrow N^- \\ \searrow OOR\end{matrix} + RO_2\cdot \rightarrow R'-C\begin{matrix}\nearrow N^- \\ \searrow OR\end{matrix} + RO\cdot + O_2$$

stoichiometry of these reactions is correct, it is difficult to understand just how these rather remarkable transformations are supposed to occur. In the absence of evidence which mitigates against the general mechanism there seems little reason to suggest new and recondite paths to give the products.

action of styrene, bis-β-ethoxyethyl ether and n-butyl ether support this mechanism. These materials act as chain transfer agents and destroy RO· and V with the production of radicals which do not abstract the peroxy hydrogen. The production of oxygen from t-amyl and *trans*-9-decalyl hydroperoxides was considerably less efficient than from t-butyl and cumyl hydroperoxides. This is to be expected because the alkoxy radicals derived from t-amyl and *trans*-9-decalyl hydroperoxides undergo β-fission more readily than t-butoxy and cumyloxy radicals. The alkyl radicals as mentioned before are not expected to be very reactive towards the peroxy hydrogen. In the case of 1,1,3,3-tetramethylbutyl hydroperoxide no oxygen was formed under the standard conditions. When molar amounts of succinonitrile and base were used I was formed but still no oxygen was evolved.[16] The 1,1,3,3-tetramethylbutyl alkoxy radical not only undergoes facile β-cleavage but also intramolecular hydrogen abstraction becomes an important decomposition path.[17] These reactions undoubtedly compete very effectively with the alkoxy-hydroperoxide reaction and also those ROO· radicals which are generated can combine with alkyl radicals to give unreactive peroxides.

The oxygen-18 experiments show that the imides are not artifacts derived by reaction of nitrile with base. The mechanism necessarily leads to oxygen gas which is free of excess oxygen-18 and this is in accord with experiment. It is satisfying to conclude that no new postulates are required to explain the effect of nitrile additives on these decompositions.[18]

The mechanism of the base catalyzed decomposition of cumyl hydroperoxide and t-butyl hydroperoxide at elevated temperatures has been the subject of considerable

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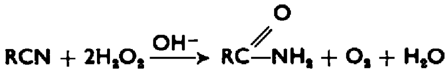
[16] It will be recalled that *trans*-9-decalyl hydroperoxide only gave oxygen when extra nitrile-base was added.

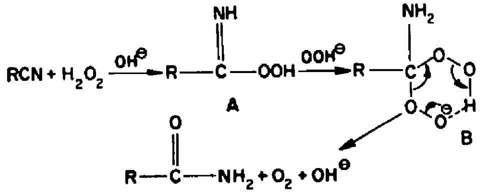
[17] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith and P. H. Zanet, *J. Org. Chem.* **28**, 55 (1963).

[18] It is interesting to consider the conversion of nitriles to amides by hydrogen peroxide and base. This reaction was discovered by B. Radziszewski, *Ber. Dtsch. Chem. Ges.* **17**, 1389 (1884) and later studied by K. B. Wiberg, *J. Amer. Chem. Soc.* **75**, 3961 (1953), who showed that the reaction is first order in nitrile, hydrogen peroxide and base. Recently G. B. Payne, P. H. Deming and P. H.



$$RCN + 2H_2O_2 \xrightarrow{OH^-} RC(=O){-}NH_2 + O_2 + H_2O$$

Williams, *J. Org. Chem.* **26**, 659 (1961) have shown that initial reaction leads to a peroxy carboximidic acid (A) which is relatively stable under neutral conditions. In the presence of base and hydrogen peroxide rapid decomposition with the formation of amide and oxygen occurs. This is not a chain reaction. We would like to suggest that this occurs by addition of another hydro-

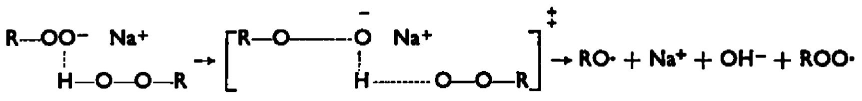


peroxy anion to give B which then undergoes intramolecular decomposition to form the observed products. This process is very similar to that proposed by J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.* **58**, 1846 (1962) for the decomposition of aromatic peracids in the presence of base.

speculation.[19] In general non-radical mechanisms have been proposed. The results of the work reported here do not support a non-radical mechanism but are in accord with a free and radical process.

In particular the formation of III indicates that t-butyl peroxy radicals were formed in the reaction mixture. Trapping of peroxy radicals by phenols is a very efficient process[20] and would be expected to inhibit oxygen formation if peroxy radicals are involved in generating oxygen. Similarly the effects of bis-β-ethoxyethyl ether and styrene are explainable if the formation of oxygen proceeds by a radical path. A radical mechanism also explains the lack of oxygen formation from 1,1,3,3-tetramethylbutyl hydroperoxide. The same reasoning applies as was used in the nitrile-base induced decomposition of this hydroperoxide.

Perhaps the major reason for suggesting a non-radical path for the formation of oxygen has been that no reasonable mode of radical initiation has been advanced. The experiments with the disodium salt of ethylenediaminetetraacetic acid, a well known heavy metal ion scavenger, clearly implies trace metal catalysis as the means of initiating the decomposition of t-butyl hydroperoxide. The base probably provided the trace metal ions. The situation is not so clear with the cumyl hydroperoxide decompositions. Trace metal catalysis is indicated since the reaction was slowed by the addition of the scavenger, however the reaction was not stopped. This may be due to low scavenger efficiency in this heterogeneous system, or there may be another mode of initiation not available to t-butyl hydroperoxide. It is well known that in the heterogeneous reaction mixture of decomposing cumyl hydroperoxide the hydroperoxide and its salt are highly associated.[4,7] Presumably this involves hydrogen bonding and ionic interaction. Complex formation of this type may provide the means by which the activation energy for homolysis is lowered sufficiently so that the reaction can occur at the moderate temperatures involved. A possible process is illustrated by the following equation.[21]



$$\begin{matrix} R{-}OO^- \; Na^+ \\ \vdots \\ H{-}O{-}O{-}R \end{matrix} \rightarrow \left[\begin{matrix} R{-}O\text{------}\overset{-}{O} \; Na^+ \\ \vdots \\ H\cdots\cdots O{-}O{-}R \end{matrix}\right]^{\ddagger} \rightarrow RO\cdot + Na^+ + OH^- + ROO\cdot$$

It is quite clear that the so-called "base catalyzed reaction" requires further investigation, however the data presently available indicate that the reaction which produces oxygen rapidly is a free radical chain reaction.

EXPERIMENTAL

Oxygen-32 : oxygen-34 ratios were determined on a Consolidated Isotope Ratio Mass Spectrometer. IR spectra were obtained with a Perkin-Elmer Infracord. Gas analyses were performed with an F and M Model 500 Gas Chromatograph. A 5 ft. Linde 5-A molecular sieve column was used at 60° and a flow of 60 ml of helium/min. Under these conditions oxygen had a retention time of 0·9 min; nitrogen 1·7 and methane 2·3.

Hydroperoxide analysis. The method of Silbert and Swern[22] was used with little modification.

[19] (*a*) Ref. 2^a pp. 186–187; *b* Ref. 4; *c* V. A. Belyaev and M. S. Nemstov, *Zh. Obshch. Khim.* **32,** 3483 (1962); *Chem. Abstr.* **58,** 12377 (1963).

[20] K. U. Ingold, *Chem. Revs.* **61,** 577 (1961).

[21] Further work on the decomposition in the presence of base was not undertaken when it was learned that Prof. J. O. Edwards, Brown University is carrying out a detailed investigation of these reactions.

[22] L. S. Silbert and D. Swern, *Analyt. Chem.* **30,** 385 (1958).

Materials. Cumyl hydroperoxide was purified by conversion to its sodium salt by the method of Kharasch *et al.*[23] Material thus purified assayed as being 96·7% hydroperoxide. t-Butyl hydroperoxide was distilled in vacuo b.p. 49–52° (40 mm); assayed for 92·5% peroxide. t-Amyl hydroperoxide was prepared according to Davies *et al.*[24] b.p. 44–45·5° (11 mm) (lit.[24] 50–51, 20 mm). Assay indicated 100% hydroperoxide. 1,1,3,3-Tetramethylbutyl hydroperoxide was prepared by Hoffmans method.[25] Titration indicated 74·4% purity. The IR spectrum had carbonyl absorption. This was probably due to acetone. *trans*-9-Decalyl hydroperoxide[26] had after crystallization from hexane, m.p. 92·5–93·5° (lit.[26] 95–96°). Succinonitrile was purified by distillation, b.p. 267° (lit.[27] 265–267°). Phthalonitrile had after recrystallization from water, m.p. 139° (lit.[28] 141°). Glutaronitrile, adiponitrile, pimelonitrile and benzonitrile were commercial materials and were used as such.

Nitrile-base induced decompositions. The standard apparatus consisted of a 50 ml flask with a nippled side-arm (through which gas samples could be removed with a syringe). The flask was connected to a reflux condenser, trap and gas-collecting bottle. The reaction mixtures were stirred magnetically. The reagents were always added in the indicated order: 0·0025 mole of dinitrile (0·005 mole of benzonitrile), 20 ml benzene, 0·0283 mole hydroperoxide[29] and ca. 0·002 mole alkali in pellet form. The results of these experiments are collected in Table 1.

TABLE 1. NITRILE-BASE INDUCED DECOMPOSITIONS OF VARIOUS HYDROPEROXIDES

Hydroperoxide	Nitrile	% Oxygen Yield	Time (min)
Cumyl	Succino	75	30
t-Butyl	Succino	99	30
t-Amyl	Succino	51	120
trans-9-Decalyl[a]	Succino	54	30
Cumyl	Phthalo	75	30
t-Butyl	Phthalo	99	30
Cumyl	Glutaro	7·4	30
Cumyl	Adipo	3·7	33
Cumyl	Pimelo	20	90
t-Butyl	Benzo	16	150
t-Butyl	Benzo	71	12 hr

[a] Extra nitrile and base were added to initiate the decomposition.

Reaction of 1,1,3,3-*tetramethylbutyl hydroperoxide with succinonitrile and base.* A mixture of 0·0117 mole 1,1,3,3-tetramethylbutyl hydroperoxide, 0·0117 mole succinonitrile and 0·0117 mole KOH pellets in 20 ml benzene was stirred at room temp. An exothermic reaction occurred with a slight evolution of gas. Gas analysis indicated oxygen was consumed. Titration of an aliquot of the reaction mixture indicated that at least 85% of the hydroperoxide had been destroyed. The reaction mixture on standing in a refrigerator deposited a solid whose IR spectrum was identical to that of 5-imino-2-pyrrolidone (I).

Isolation of 3-*iminophthalimide* (II). A mixture of 2·5 g II and its potassium salt precipitated from a reaction mixture of 28 g (0·27 mole) t-butyl hydroperoxide, 3·07 g (0·024 mole) phthalonitrile and 0·95 g (0·017 mole) KOH in 200 ml benzene. The 3-iminophthalimide (0·38 g) was separated from the potassium salt by extraction with water. The material thus obtained had m.p. 203° (lit.[28] 203°), no depression on admixture with an authentic sample prepared according to the procedure of Braun and Tcherniac.[28] The IR spectra of the two samples were identical.

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[23] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.* **16**, 113 (1951).

[24] A. G. Davies, R. V. Foster and A. M. White, *J. Chem. Soc.* 1541 (1953).

[25] J. Hoffman, *Organic Syntheses* Vol. 40; p. 76. John Wiley, New York, N.Y. (1960).

[26] A. C. Cope and G. Holtzman, *J. Amer. Chem. Soc.* **72**, 3062 (1960).

[27] I. Heilbron, *Dictionary of Organic Compounds*, Vol. IV, p. 385. Oxford University Press, New York, N.Y. (1953).

[28] A. Braun and J. Tcherniac, *Ber. Dtsch. Chem. Ges.* **40B**, 2709 (1907).

[29] Appropriate corrections were made on the basis of the analyses.

Isolation of 5-imino-2-pyrrolidone (I). This compound was isolated in 16% yield on the basis of succinonitrile from a reaction mixture identical to that described above except for the substitution of succinonitrile in place of phthalonitrile. Compound I had m.p. 238–240° d (lit.[20,21] 227–230° d, 250° d). It was converted to its anilino derivative, 5-phenylimino-2-pyrrolidone by the method of Elvidge and Linstead,[21] m.p. 216–217° (lit.[21] 219°).

Reaction of phthalonitrite and succinonitrile with t-butyl hydroperoxide in the presence of alkali enriched with oxygen-18. Potassium hydroxide, 2·8 g (0·05 mole) was dissolved in 20 g water containing 1·30 atom% oxygen-18. The solution was evaporated to dryness. The enriched alkali 0·95 g (0·017 mole) was added to 3·2 g (0·025 mole) phthalonitrile and 25·5 g (0·283 mole) t-butyl hydroperoxide dissolved in 200 ml benzene. The mixture of II and its potassium salt which precipitated was separated by extraction with ethyl acetate. Recrystallization from ethyl acetate gave material m.p. 203°. Oxygen-18 analysis[22] showed 0·00 atom % excess oxygen-18.

For the gas analyses, 1·0 g NaOH was dissolved in 3 ml water containing 1·75 atom % oxygen-18. The solution was evaporated to dryness and 0·0027 g of the alkali was allowed to react with 0·0283 mole of either t-butyl or cumyl hydroperoxide and 0·0025 mole of succinonitrile in 20 ml benzene. The evolved oxygen did not contain excess oxygen-18.

TABLE 2. DECOMPOSITION OF HYDROPEROXIDES IN THE PRESENCE OF ALKALI AT 90°

Hydroperoxide	Additives	Oxygen yield %	Time (min)
Cumyl	2 ml 10% NaOH	61	7
Cumyl	None	0	30
Cumyl	2 ml 10% NaOH	57	10
Cumyl	2 ml H_2O	0	30
Cumyl	10 ml 10% NaOH	11; 55	55; 120
t-Butyl	None	0	30
t-Butyl	2 ml 10% NaOH	68	10

Effect of inhibitors on the nitrile base induced decompositions. To 1·5 g (0·012 mole) phthalonitrile and 14·0 g (0·137 mole) t-butyl hydroperoxide in 100 ml benzene were added 15·5 g (0·15 mole) freshly distilled styrene and 0·48 g (0·0085 mole) KOH. No oxygen was evolved although titration showed that at least 0·025 mole hydroperoxide was decomposed. 3-Iminophthalimide (0·005 mole) was isolated as before from this reaction mixture.

Injection of 4 ml (0·04 mole) styrene into a reaction mixture whose rate of evolution of oxygen was 25 ml/min caused the immediate cessation of the oxygen evolution.

A mixture of 2·95 g (87% by titration) t-butyl hydroperoxide, 0·2 g succinonitrile and 0·1 g KOH in 20 ml bis-β-ethoxyethyl ether failed to give any oxygen. Similarly 4·31 g cumyl hydroperoxide, 0·2 g succinonitrile and 0·1 g KOH in 20 ml bis-β-ethoxyethyl ether failed to give any oxygen in 24 hr.

t-Butyl hypochlorite initiated reactions. To 0·0283 mole hydroperoxide in 20 ml benzene was added 0·27 g (0·0025 mole) t-butyl hypochlorite. The system was flushed with nitrogen and a 100 watt desk lamp was directed at the reaction flask. A dry ice-acetone cooled trap was placed between the reaction flask and the gas collection cylinder. Removal of the light source did not stop the reaction once oxygen evolution had started. Under the above conditions t-butyl hydroperoxide yielded 75% of the theoretical amount of oxygen in 10 min. t-Amyl-hydroperoxide afforded 22% in 25 min. Injection of 2 ml styrene into a decomposing mixture of t-butyl hydroperoxide and t-butyl hypochlorite stopped the evolution of oxygen.

Decompositions in the presence of base. The standard reaction conditions consisted of heating 0·025 mole hydroperoxide and 2 ml 10% NaOH (0·005 mole) under a N_2 atmosphere at ca. 90°. The results of these experiments are collected in Table 2. Treatment of 1,1,3,3-tetramethylbutyl hydroperoxide, 0·022 mole with 2 ml 10% NaOH in an air atmosphere led to the consumption of the oxygen present in the reaction system rather than the evolution of oxygen.

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[20] M. Protiva, V. Rericha and J. O. Jilek, *Chem. Listy.* **44**, 231 (1950); *Chem. Abstr.* **45**, 7953 (1951).

[21] J. A. Elvidge and R. P. Linstead *J. Chem. Soc.* 442 (1954).

[22] W. E. Doering and E. Dorfman, *J. Amer. Chem. Soc.* **75**, 5595 (1953).

A standard decomposition mixture of cumyl hydroperoxide except for the addition of 2 ml bis-β-ethoxyethyl ether gave no oxygen in 21 min whereas in the absence of the ether a 61% yield was obtained in 7 min. Injection of 2 ml styrene into a standard mixture of decomposing cumyl hydroperoxide and base stopped the evolution of oxygen.

No oxygen was evolved when 2·25 g (0·025 mole) t-butyl hydroperoxide, 2 ml (0·005 mole 10% NaOH and 0·81 g (0·0037 mole) 2,6-di-t-butyl-4-methylphenol were heated for 1 hr at 90°. A precipitate formed when the reaction mixture was cooled. It was crystallized from methanol:water (1:1) to give material m.p. 88–89° (lit.[8b] 86°). NMR and IR spectra of this material were in complete accord with the assigned structure.

The decompositions in the presence of the disodium salt of ethylenediaminetetraacetic acid were conducted in essentially the same manner as those outlined above although different apparatus and reagents were used. In each case a control experiment was run where everything was identical except no scavenger was added. In two control experiments no more oxygen was evolved from a t-butyl hydroperoxide base reaction mixture after 20 min. When 2 mole % of the scavenger was added only a small amount 30 ml vs. 210 ml of gas was evolved after heating for 1·5 hr. In the case of cumyl hydroperoxide inclusion of 2 and 10 mole % of the scavenger increased the total time for oxygen evolution from 45 min to 2 hr. Analysis of the gas showed it was oxygen and no methane was formed.