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THE CHEMISTRY OF HYDROPEROXIDES. XI. HYDROPEROXIDES AS OXIDIZING AND REDUCING AGENTS

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INTRODUCTION

The kinetics of the autoxidation of olefins and hydrocarbons (at temperatures above 60–70°) has been studied by many investigators. In most instances there is an induction period (which can be eliminated by adding reagents which under the experimental conditions generate free radicals), a period of fairly rapid oxygen absorption, and finally a period of slow oxygen absorption. In many instances only a small proportion of the reaction products have been characterized; hence it is difficult to construct a comprehensive picture to account for the many diverse observations.

It appeared reasonable, therefore, to approach the problem of such autoxidations by studying the chemistry of peroxides and hydroperoxides.[1] Previously it has been shown that the products formed in the decomposition of these compounds depend on whether the decomposition is caused by acids, by bases, or by a breakdown into free radicals (1). In all these reactions, a hydroperoxide may function as an oxidant, as a reductant, or both. There are, however, several different mechanisms for the action of a hydroperoxide as an oxidant, *i.e.*, it may act by abstraction of one electron, or two electrons, from an electron donor or by donation of an oxygen atom to an acceptor.

DISCUSSION

(*A*) *Acid-induced oxidations.* The product formed by reaction of a tertiary hydroperoxide and a tertiary alcohol (or an appropriate olefin) in the presence of a small amount of a strong (Lewis) acid is determined by the following factors: (a) the basicity of the alcohol as compared with that of the hydroperoxide; (b) the stability of the hydroperoxide toward acid. With hydroperoxides which are stable toward acids, addition of a tertiary alcohol yields a symmetrical or an unsymmetrical peroxide.[2] Thus, when α-phenyl-α-*p*-tolylethanol (dissolved

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[1] It is now well established that the oxidation of a simple olefin gives rise to a hydroperoxide and not to a moloxide [Criegee, Pilz, and Flygare, *Ber.*, **72**, 1799 (1939)]. Note that the compound postulated by Kohler [*Am. Chem. J.*, **36**, 177 (1906)] to have a moloxide structure, has been shown [Rigeaudy, *Compt. rend.*, **226**, 1933 (1948)] to be a hydroperoxide.

[2] The outcome of addition of an acid to a mixture of a tertiary alcohol and a hydroperoxide (which by itself is unstable to acid) will depend in part on the acidity of the carbonium ion formed from the alcohol, and in part on the stability of the hydroperoxide toward acids. Thus, α-tetralyl triphenylmethyl peroxide is formed upon addition of perchloric acid to a mixture of triphenylmethanol and α-tetralyl hydroperoxide. Decomposition of the unsymmetrical peroxide by perchloric acid gives the products observed in the decomposition of α-tetralyl hydroperoxide by perchloric acid (70%), and triphenylmethyl peroxide (30%). The latter product is probably formed by a displacement of an α-tetralyl

in acetic acid) is treated with *tert*-butyl hydroperoxide in the presence of a small amount of perchloric acid, the unsymmetrical peroxide is formed.[3] Addition of a somewhat larger amount of perchloric acid, however, results in the formation of *p*-cresol, acetophenone, and *tert*-butyl alcohol (2).

The rate of decomposition of a hydroperoxide by strong acids (in acetic acid) depends upon the particular hydroperoxide used and upon its concentration. In order to evaluate these two factors, the kinetics of the decompositions of α-cumyl and α-tetralyl hydroperoxides by perchloric acid (in acetic acid) were investigated. The rate of decomposition of α-cumyl hydroperoxide (0.05% in acetic acid) is zero order (with respect to the hydroperoxide) when perchloric acid (20 mole-per cent of the hydroperoxide) is used; it becomes first-order when a full equivalent of the acid is used. On the other hand, the rate of decomposition of α-tetralyl hydroperoxide in acetic acid is first order (with respect to the hydroperoxide) when small amounts of perchloric acid (5 mole-per cent) are used. Note that under the conditions cited above a dilute solution of α-tetralyl hydroperoxide is decomposed faster by small amounts of perchloric acid than is a dilute solution of α-cumyl hydroperoxide, but that the reaction velocities are reversed in more concentrated solutions (Table I). Furthermore, the reaction order for both hydroperoxides increases as more concentrated solutions of the hydroperoxides are used. The acid-induced decomposition of α-cumyl hydroperoxide in acetic acid has all the earmarks of a chain reaction when the concentration of the hydroperoxide is equal to or greater than 15 per cent.

TABLE I

ACID-CATALYZED DECOMPOSITION OF HYDROPEROXIDES AT *ca.* 25°

HYDROPEROXIDE	ROOH (g.)	HOAc (ml.)	$HClO_4$ (mole-%)[a]	REACTION ORDER[b]	RATE CHARACTERISTICS
α-Cumyl	0.5	1000	20.0	0	0.025 g./hr.
	.5	1000	100.0	1st	½-life, 195 min.
	1.0	50	0.2	0	0.015 g./min.
	4.0	30	.1	—	Complete dec., 20 min.
α-Tetralyl	.7	1000	5.0	1st	½-life, 420 min.
	5.0	30	.1	2nd	½ decomp'n, 1 hr.

[a] Based on the amount of hydroperoxide used. [b] Approximate apparent reaction order with respect to ROOH.

The above observations may be accounted for if it is assumed that α-cumyl hydroperoxide is a stronger base than α-tetralyl hydroperoxide and that the

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group, in the unsymmetrical peroxide, by a triphenylmethylcarbonium ion, $[(C_6H_5)_3C]^+$, [Kharasch and Burt, *J. Org. Chem.*, **16**, 131 (1950)]. However, the triphenylmethylcarbonium ion, $[(C_6H_5)_3C]^+$, is a strong enough acid to decompose α-cumyl hydroperoxide. This is indicated by the formation of phenol and acetone (90%) and triphenylmethyl peroxide (10%), when perchloric acid (0.2 g.) is added to a mixture of triphenylmethanol (5 g.) and α-cumyl hydroperoxide (2 g.) in glacial acetic acid (75 g.).

[3] Note that $CH_3(C_6H_5)(4\text{-}CH_3C_6H_4)COH$ is a stronger base than the hydroperoxide, and *tert*-butyl alcohol a weaker base.

cation formed from α-tetralyl hydroperoxide is less stable than the one formed from α-cumyl hydroperoxide. The stability of hydroperoxides toward acids depends, therefore, in part on their ability to add a proton (oxonium complex formation), and in part on the half-life of the cation $[RR_1R_2COOH_2]^+$. In the acid-induced chain decomposition of α-cumyl hydroperoxide (concentrations $\overset{=}{>} 15\%$), the cation $[C_6H_5(CH_3)_2COOH_2]^+$ breaks down as follows:

$$1.\quad [C_6H_5(CH_3)_2COOH_2]^+ \rightarrow \underset{\text{“A”}}{[C_6H_5OC(CH_3)_2]^+} + H_2O$$

and the cation "A" thus formed acts as the chain carrier:

$$2.\quad [C_6H_5OC(CH_3)_2]^+ + C_6H_5C(CH_3)_2OOH \\ \rightarrow C_6H_5OH + CH_3COCH_3 + [C_6H_5OC(CH_3)_2]^+.$$

In this instance the effect of the acetic acid as a proton acceptor is small. However, when the less basic α-tetralyl hydroperoxide is used, acetic acid successfully competes with the hydroperoxide (note equations 1 and 2) and the acid-induced chain decomposition no longer plays such an important role.

A hydroperoxide unstable to acid undergoes breakdown in preference to attacking another molecule which may act as a reductant. Thus, α-cumyl hydroperoxide (dissolved in acetic acid) breaks down into phenol and acetone when treated with a trace of perchloric acid even in the presence of a large amount of hydroquinone. On the other hand, the relatively stable *tert*-butyl hydroperoxide (dissolved in acetic acid) reacts rapidly with hydroquinone in the presence of a trace of perchloric acid. Here *tert*-butyl alcohol and quinhydrone are the reaction products. Obviously, under the conditions cited the ion $[ROOH_2]^+$ is the oxidant which accepts the electrons from the reductant. The ion $[ROOH_2]^+$ is, however, not a strong enough oxidant to attack another molecule of tertiary hydroperoxide. Note also that no oxygen has ever been observed as a reaction product when hydroperoxides are decomposed by acids.

(*B*) *Reduction and oxidation of hydroperoxides.* It is well known that hydrogen peroxide may act either as an oxidant or as a reductant depending upon the reagent with which it is used. In the presence of ferrous salts hydrogen peroxide decomposes by a chain reaction. The mechanism suggested by Haber and Weiss (3) is given below:

$$3.\quad Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + OH^- + HO\cdot$$

$$4.\quad HO\cdot + H_2O_2 \rightarrow HOH + HO_2\cdot$$

$$5.\quad HO_2\cdot + H_2O_2 \rightarrow O_2 + H_2O + HO\cdot$$

$$6.\quad HO\cdot + Fe^{++} \rightarrow Fe^{+++} + OH^-$$

However, it is very doubtful, that this mechanism (without considerable modification) will account for numerous additional facts uncovered in recent years. The question has even been raised whether the kinetic data justify the assumption that free hydroxyl radicals are the sole agents responsible for the chain propagation (4). The findings on the decomposition of hydroperoxides (ROOH) by ferrous salts indicate that the free (RO·) radicals here formed[4] do not participate in chain reactions with the hydroperoxide as suggested for hydrogen peroxide (equations 4 and 5).

TABLE II

CATALYZED DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (5.0 g.) IN ACETIC ACID (Temperature, *ca.* 25°; time, to cessation of O_2 evol'n)

EXPT. NO.	REACTION MEDIUM	DECOMP'N, %	PRODUCTS, %		
			O_2	C_6H_5-$(CH_3)_2COH$	CH_3-COC_6H_5
1	5.0 ml. HOAc + 0.15 g. $KMnO_4$	92	71	85	9
2	5.0 ml. exhausted mixture no. 1 + 0.04 g. MnO_2	—	67	—	10
3	15.0 ml. HOAc + 1.0 g. $KMnO_4$	90	26	62	28
4	15.0 ml. HOAc + 0.2 g. $KMnO_4$	51	36	—	9
5	5.0 ml. HOAc + 0.3 g. K_2CrO_4	—	70	—	+[a]
6	15.0 ml. HOAc + 5.0 g. $Ce(SO_4)_2$ + 2.0 g. NaOAc	—	20[b]	—	8[b]
7	20.0 ml. HOAc + 0.3 g. PbO_2	30	—	—	+[a]
8	5.0 ml. HOAc + 0.2 g. VCl_2	72	32	—	11
9	15.0 ml. HOAc + 0.3 g. $CoCl_2$ + 0.3 g. NaOAc	100	60	—	30

[a] In experiments 5 and 7 acetophenone was shown to be present, but was not determined quantitatively. [b] In experiment 6 the (extremely slow) oxygen evolution was no longer perceptible at the end of one day. In the same experiment oxygen evolution amounted to 15% at the end of three hours, but at that time no acetophenone could be detected.

Furthermore, although free α-cumyloxy (or free *tert*-butoxy) radicals may act as oxidants toward secondary alcohols they act exclusively as reductants toward hydroperoxides (reaction 14).

$$7.\quad C_6H_5(CH_3)_2CO\cdot + (CH_3)_2CHOH \rightarrow C_6H_5(CH_3)_2COH + (CH_3)_2(OH)C\cdot$$

$$\searrow$$

$$CH_4 + C_6H_5COCH_3 + (CH_3)_2(OH)C\cdot$$

At no time has oxygen ever been noted as a product of the reaction between a hydroperoxide and a reductant (*i.e.*, ferrous salt).

The evolution of oxygen from hydroperoxides may, however, be brought about in three different ways: (a) by treating the hydroperoxide with a powerful oxidant, capable of abstracting one electron, (b) by heating tertiary hydroperoxides with alkali, or (c) by treating the hydroperoxide with an "additive" and alkali at room temperature. The highest yields (up to 95 per cent) of oxygen were obtained in the presence of "additives".

[4] The decomposition of hydroperoxide by ferrous salts, $ROOH + Fe^{++} \rightarrow ROFe^{++} + HO\cdot$, has never been noted by us or reported by other investigators. Note furthermore the high yield of RO· radicals in this reaction [Kharasch, Nudenberg, and Arimoto, *Science*, **113**, 392 (1951); *J. Org. Chem.*, **16**, 1556 (1951)].

Method (*a*). The oxidants which oxidize hydroperoxides to yield molecular oxygen fall into two classes: (I) oxidants which give about one equivalent of oxygen based on the amount of oxidizing agent used; (II) oxidants which decompose hydroperoxides into oxygen by a chain reaction and which, therefore, need be present only in small amounts. For example, ceric salts and lead tetraacetate belong to the first class, cobaltic acetate to the second. Members of both classes of oxidants probably act similarly on the hydroperoxide, according to the reaction

8. $ROOH + Oxid \rightarrow RO_2\cdot + H^+ + (Oxid + \epsilon).$

The lead and cerous salts thus formed are not reoxidized by the hydroperoxide; but cobaltous acetate is reoxidized to the cobaltic state and thus induces a chain reaction (Table II).

It follows from the observations just cited that the free $RO_2\cdot$ radical does not participate in a chain reaction with the hydroperoxide to yield gaseous oxygen. This product must therefore be formed in a different way. Of the two schemes indicated below, scheme 10 must play a dominant role, since, with ceric salts and lead tetraacetate, the yield of oxygen is almost one unit per unit of hydroperoxide (5) and because reaction products usually formed from free $RO\cdot$ radicals are not formed.[5]

9. $RO_2\cdot + ROOH \rightarrow RO\cdot + ROH + O_2$

10. $RO_2\cdot + Oxid \rightarrow R^+ + O_2 + (Oxid + \epsilon).$

There are additional complications when reagents which act both as oxidants and reductants (*e.g.* cobaltous acetate) are used, for the free alkoxy radicals formed by the interaction of the hydroperoxide with the cobaltous acetate may initiate a free-radical chain decomposition of the hydroperoxide, which may be represented schematically, as follows:

11. $C_6H_5(CH_3)_2COOH + Co^{++} \rightarrow C_6H_5(CH_3)_2CO\cdot + OH^- + Co^{+++}$

12. $C_6H_5(CH_3)_2COOH + Co^{+++} \rightarrow C_6H_5(CH_3)_2CO_2\cdot + H^+ + Co^{++}$

13. $C_6H_5(CH_3)_2CO\cdot + Co^{++} \rightarrow [C_6H_5(CH_3)_2CO]^- + Co^{+++}$

14. $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2COOH \rightarrow C_6H_5COCH_3 + CH_3OH + C_6H_5(CH_3)_2CO\cdot$

15. $C_6H_5(CH_3)_2CO_2\cdot + Co^{+++} \rightarrow [C_6H_5(CH_3)_2C]^+ + O_2 + Co^{++}$

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[5] The mechanism, $2\ RO_2\cdot \rightarrow 2\ RO\cdot + O_2$, is suggested by Seubold Jr., Rust, and Vaughan, *J. Am. Chem. Soc.*, **73**, 18 (1951), to account for the formation of acetone when *tert*-butyl hydroperoxide is decomposed at 195° in the presence of *tert*-butyl peroxide and oxygen. This interpretation is reasonable and attractive under the conditions imposed in their experiments. It does not follow, however, that at ordinary temperatures and in solution, free $RO_2\cdot$ radicals will disproportionate to yield oxygen. The evidence outlined appears to favor reaction scheme 10.

Reactions 13 and 14 are competitive reactions.[6] Hence, the evolution of oxygen from a hydroperoxide by a chain reaction is never quantitative, and the amount evolved varies considerably with the nature of the hydroperoxide and with the reaction conditions. The catalytic decomposition (with cobaltous acetate) of α-cumyl hydroperoxide gives 60 per cent of oxygen and 30 per cent of acetophenone, but only 24 per cent of oxygen is formed from α-tetralyl hydroperoxide.

TABLE III

Decomposition (70%) of α-Cumyl Hydroperoxide in (10%) Aqueous Sodium Hydroxide Solution at 90°

NaOH/ROOH (moles)	TIME (min.)	O_2 (mole-%)	$CH_3COC_6H_5$ (mole-%)	ACIDS (wt.-%)
0.18	48	58	4.5	2
1.80	240	50	10.0	11

TABLE IV

Freezing-point Depression of Benzene by ROOH, ROONa, and ROOH-ROONa Mixtures

R = α-cumyl = $C_6H_5(CH_3)_2C$

SAMPLE COMPONENTS, ML.			FREEZING-POINT DEPRESSION, °C.
Benzene	ROOH sol'n[a]	ROONa sol'n[b]	
9.0	0.0	0.0	0.000
6.0	3.0	.0	1.132
0.0	.0	9.0	1.252
6.0	.0	3.0	.458
6.5	1.5	1.0	.508
5.0	3.0	1.0	1.188
5.0	1.0	3.0	.676
4.0	2.0	3.0	.889
3.0	3.0	3.0	1.117

[a] This solution was compounded by adding 2.0 ml. of α-cumyl hydroperoxide to 20.0 ml. of benzene. [b] This solution was compounded by treating a mixture of 2.0 ml. of α-cumyl hydroperoxide and 20.0 ml. of benzene with sodium powder, and filtering the resultant suspension. It contains some free hydroperoxide and some α-cumyl alcohol (attributable to sodium reduction). With phenolphthalein as indicator, 3.00 ml. of solution is neutralized by 6.87 ml. of 0.1 *N* hydrochloric acid solution; 1.00 ml. of solution is equivalent to 9.60 ml. of 0.1 *N* sodium thiosulfate solution.

Method (*b*). Under similar conditions, hydroperoxides vary widely in their stability towards both dilute and concentrated alkali. Under the influence of alkali most secondary hydroperoxides decompose at or above room temperature to give alcohols, ketones and other oxidation products. No oxygen evolution

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[6] A chain-ending step of the type $RO\cdot + RO_2\cdot \rightarrow O_2 + RO^- + R^+$ is possible, but as yet there is no direct evidence in support of this formulation.

has been noted (or recorded) when primary or secondary hydroperoxides such as α-cyclohexenyl (6), α-tetralyl (7), isopropyl (8), *p*-menthenyl (9), *p*-xylyl (10), *p*-isopropylbenzyl (11), or α-indanyl (12) are treated with dilute alkali. On the other hand, tertiary hydroperoxides, such as α-cumyl, when treated with alkali, readily yield oxygen (Table III). The extent of this reaction is determined by the experimental conditions.[7]

An aqueous solution of α-cumyl hydroperoxide decomposes very slowly at 90° when a large excess of alkali is used. The decomposition (into oxygen, α-cumyl alcohol, acetophenone, benzoic acid and other acids as yet unidentified) is very much faster with 20 mole-per cent than with a full equivalent of alkali. These experiments suggest that, in water solution, the anion RO_2^- is the oxidant which attacks the undissociated molecule of the hydroperoxide (ROOH). Similarly, a solution of the sodium salt of α-cumyl hydroperoxide in hydrocarbon solvents (benzene, toluene, etc.) gives no oxygen when heated to 60–90°, but decomposes to α-cumyl alcohol, benzoic acid, etc. However, under these conditions, oxygen is formed when α-cumyl hydroperoxide is added to the solution. *A priori*, it might be expected that a small amount of the sodium salt of α-cumyl hydroperoxide should be sufficient to break down large amounts of α-cumyl hydroperoxide in organic solvents. This would probably be the case, were it

TABLE V

BASE (ROONa)-CATALYZED THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (ROOH) IN *tert*-BUTYLBENZENE[a]

REACTION-SYSTEM COMPONENTS, ML.			O_2 EVOL'N AT VARIOUS TEMPS., ML.[b]				
			78°		100°		107°
ROOH	*tert*-$C_4H_9C_6H_5$	ROONa[c]	1st Min.[d]	Total	1st Min.[d]	Total	1st Min.[d]
1.0	10.0	0.5	0.14	5.6	0.50	3.0	0.90
1.0	10.0	1.0	.37	20.0	1.50	13.0	4.00
1.0	10.0	2.0	1.40	46.0	8.00	34.0	15.00
1.0	10.0	4.0	2.90	63.0	—	—	—
1.0	20.0	2.0	—	—	4.40	25.0[e]	—
2.0	20.0	2.0	—	—	4.20	22.0	—

[a] When ln $(M - M_t)$, in which M is the total number of moles of oxygen evolved, and M_t is the number of moles of oxygen evolved in measured time, is plotted against time (t), a linear graph is obtained. [b] The amount of O_2 theoretically equivalent to 1.0 ml. of ROOH is 82.0 ml. [c] This component is a solution of ROONa in *tert*-$C_4H_9C_6H_5$; 1.0 ml. of solution contains ROONa equivalent to 0.031 ml. of ROOH. [d] The data here recorded were actually derived by averaging the amount of O_2 evolved during the first several (*ca.* 5) minutes of reaction. [e] O_2 evolution comes to a halt as acidic oxidation products react with ROONa, precipitating sodium salts. When, after cessation of O_2 evolution, an additional 1.0 ml. of ROONa solution was added to this reaction mixture, an additional 12.0 ml. of O_2 was evolved.

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[7] A notable exception is *trans*-decalyl hydroperoxide, which remains unaltered when heated with methanolic potassium hydroxide [Criegee, *Ber.*, **77**, 2219 (1944)].

not for the formation of benzoic acid (and other acidic materials) which neutralize the alkali and thereby stop any further decomposition of the hydroperoxide.

The solubility of the sodium salt of α-cumyl hydroperoxide in hydrocarbons is exceptional. Neither the corresponding lithium or potassium salts are soluble in such solvents, nor is the sodium salt of *tert*-butyl hydroperoxide. The sodium salt of α-cumyl hydroperoxide is highly associated in benzene (and presumably other organic solvents) with α-cumyl hydroperoxide, as well as with α-cumyl alcohol[8] (Table IV).

TABLE VI

BASE (ROONa)-CATALYZED DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (ROOH) IN BENZENE AT 78°[a]

REACTION-SYSTEM COMPONENTS, ML.			O_2 EVOLUTION[b]	
ROOH	C_6H_6[c]	ROONa[d]	1st Min.[e]	Total
1.0	10.0	1.0	1.1	23.0
1.0	10.0	2.0	3.1	46.0
1.0	10.0	4.0	5.8	59.0
5.0	10.0	2.0	2.6	26.0
2.0	10.0	2.0	1.2	34.0
1.0	40.0	2.0	1.4	16.0
2.0	10.0	1.0	—	12.0
1.0	10.0	0.5	—	3.2
—	—	20.0[f]	9.5	38.0

[a] When ln $(M - M_t)$, in which M is the total number of moles of oxygen evolved, and M_t is the number of moles of oxygen evolved in measured time, is plotted against time (t), a linear graph is obtained. [b] The amount of oxygen theoretically equivalent to 1.0 ml. of ROOH is 82.0 ml. [c] The C_6H_6 used was reagent grade (Merck). Technical C_6H_6 contains CS_2 which brings about ROOH decomposition even at room temperature. ROONa is less stable even in reagent-grade C_6H_6 than in $t\text{-}C_4H_9C_6H_5$. [d] This component is a solution of ROONa in C_6H_6; 1.0 ml. of solution contains ROONa equivalent to 0.31 ml. of ROOH. [e] The data here recorded were actually derived by averaging the amount of O_2 evolved during the first several (*ca.* 5) minutes of reaction. [f] ROOH equivalent to 16% of ROONa originally present was recovered. $C_6H_5CO_2H$ equivalent to 8.5% of the ROOH present was isolated, but only traces of $CH_3COC_6H_5$ were detected. Complete quantitative decomposition into O_2 and $C_6H_5(CH_3)_2COH$ would have yielded 118.0 ml. of O_2.

Rate studies of the base-catalyzed thermal (60–100°) decomposition of α-cumyl hydroperoxide in benzene and *tert*-butylbenzene have on the whole been unsuccessful. Qualitatively, it has been demonstrated that at a given temperature and with a given amount of alkali there is an optimum dilution at which the rate of decomposition attains a maximum (Tables V and VI).

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[8] The sodium salt of α-cumyl hydroperoxide (free of water) is difficult to prepare in the pure state. A solution of the salt in organic solvents is readily obtained by adding sodium (powder) or sodium amalgam to a solution of the hydroperoxide in the organic solvent. Unfortunately, some reduction of the hydroperoxide to the carbinol takes place (20% in cumene, ether, and ligroin; 45% in toluene). The solutions (presumably colloidal) of the sodium salt in organic solvents are rather unstable, and, depending upon the solvent, separation of the salt will occur in 2–48 hours.

Method (*c*). In the decomposition of α-cumyl hydroperoxide in the presence of a base at 60–100°, the $(RO_2)^-$ anions attack not only the α-cumyl hydroperoxide to give oxygen and the carbinol, but also attack this latter reaction product to give eventually acetophenone, benzoic acid, and other acidic oxidation products. It is, therefore, not surprising that, in none of these decompositions are carbinol and oxygen the sole reaction products. A quantitative decomposition of α-cumyl hydroperoxide into the carbinol and oxygen may, however, be accomplished at room temperature. If to a benzene solution containing α-cumyl hydroperoxide and 3 mole-per cent (on the basis of the hydroperoxide) of the sodium salt of α-cumyl hydroperoxide there is added about 3–4 mole-per cent of succinonitrile there is a rapid evolution of oxygen (95% of calculated amount).

TABLE VII

EFFECTS OF VARIOUS CATALYSTS[a] (0.00125 MOLE) ON THE DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (ROOH, 0.0133 MOLE) IN THE PRESENCE OF $ROONa \cdot 4H_2O$ (0.0009 MOLE) IN BENZENE (10 ML.) AT 25°

CATALYST	OXYGEN EVOLVED, (Mole-%)				
	2 Min.	3 Min.	5 Min.	10 Min.	Total
Succinonitrile	—	—	33	—	96
Phthalonitrile	—	—	31[b]	—	88[b]
Ethylene thiocyanate	54	—	—	—	54
Ninhydrin	—	—	15	—	33
Chloranil	—	—	54	—	54
Carbon disulfide	—	—	53	—	59
Fumaronitrile[c]	—	109	—	—	109
Diethyl acetylenedicarboxylate	—	43	—	—	43
Dimethyl malononitrile[c]	—	—	36	—	106
Dimethyl fumarate[c]	31	—	—	—	31
Adiponitrile[c]	—	—	21	—	70
Acrylonitrile[c]	—	—	—	32	84
Methyl acrylate[c]	—	—	—	23	32
Crotononitrile[c]	—	—	—	21	94

[a] Among substances which proved ineffective as catalysts were: glutaronitrile, benzil, malononitrile, ethylmalononitrile, terephthalonitrile, dimethyl diethylmalonate, methyl methacrylate, succinic anhydride, maleic anhydride, dimethylmaleic anhydride, α,α′-dimethylsuccinic anhydride, methyl cinnamate, pimelonitrile, tetramethylsuccinonitrile, isophorone, sorbonitrile, and *tert*-butyl hydroperoxide-acrylonitrile addition product. [b] When one-half the specified amount of catalyst was used, oxygen evolution amounted to 20 mole-% in five minutes, and eventually totalled 65 mole %. [c] In these experiments 15.0 ml. of benzene was used.

$$16.\ 2\ C_6H_5(CH_3)_2COOH \xrightarrow[\text{“Additive”}]{NaOH} 2\ C_6H_5(CH_3)_2COH + O_2$$

Acetophenone is not formed during this decomposition.

A number of other substances catalyze the room-temperature decomposition of a solution of α-cumyl hydroperoxide and its sodium salt. To obtain compa-

TABLE VIII

CATALYZED HYDROPEROXIDE REDUCTIONS IN ALKALINE MEDIA[a]

HYDROPEROXIDE, (G.)	SOLVENT, (ML.)	CATALYST, (G.)	REDUCING AGENT, (ML.)	AQU. NaOH,[b] (ML.)	ROOH DEC., (%)	KETONE FORMED, (%)[c]
α-Cumyl (3.0)	None	Succinonitrile (0.30)	*i*-C_3H_7OH (30)	0.1	30	70
α-Cumyl (3.0)	*tert*-C_4H_9OH (25)	Succinonitrile (0.30)	$(C_6H_5)_2CHOH$ (6)	.1	75	95
α-Cumyl (2.0)	*tert*-C_4H_9OH (17)	Succinonitrile (0.04)	$(C_6H_5)_2CHOH$ (3)	.1	35	98
α-Cumyl (2.0)	*tert*-C_4H_9OH (15)	Acrylonitrile (0.10)	$(C_6H_5)_2CHOH$ (3)	.2	50	—
α-Cumyl (2.0)	*tert*-C_4H_9OH (15)	CS_2 (0.26)	$(C_6H_5)_2CHOH$ (3)	.2	33	—
α-Cumyl (2.0)	*tert*-C_4H_9OH (20)	None	$(C_6H_5)_2CHOH$ (3)	.4	29[d]	—
α-Cumyl (2.0)	$(C_2H_5)_2O$ (15)	Succinonitrile (0.10)	$(C_6H_5)_2CHOH$ (3)	.4	36	—
α-Cumyl (2.0)	*tert*-C_4H_9OH (20)	Succinonitrile (0.10)	Tetralyl hydroperoxide (2)	.4	80	—
tert-Butyl (1.5)	*tert*-C_4H_9OH (20)	Succinonitrile (0.10)	$(C_6H_5)_2CHOH$ (3)	.5	42	—
tert-Butyl (1.5)	*tert*-C_4H_9OH (20)	None	$(C_6H_5)_2CHOH$ (3)	.5	8[e]	—
tert-Butyl (2.0)	H_2O (15)	Succinonitrile (0.20)	*i*-C_3H_7OH (2)	1.0	62[i]	—
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.20)	*i*-C_3H_7OH (5)	1.0	76	—
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.05)	*i*-C_3H_7OH (5)	1.0	50	—
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.10)[f]	*i*-C_3H_7OH (5)	1.0	95	80
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.02)[g]	C_2H_5OH (5)	1.0	72	—
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.03)[g]	$[HO(CH_3)CH—]_2$ (5)	1.0	0	—
tert-Butyl (2.0)	H_2O (15)	CS_2 (0.16)[h]	$[HO(CH_3)CH—]_2$ (5)	1.0	70	—
tert-Butyl (2.0)	H_2O (10)	CS_2 (0.04)	*i*-C_3H_7OH (5)	1.0	25	—
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.03)[g]	$H_2C(CH_2OH)_2$ (5)	1.0	64	—
tert-Butyl (2.0)	H_2O (10)	Succinonitrile (0.02)	$[HOCH_2CH_2—]_2$ (5)	1.0	60	—

[a] No oxygen evolution was observed in any experiment, except as cited in *i*. [b] This solution was prepared by dissolving 6.0 g. of NaOH in 10.0 ml. of H_2O. [c] Based on the amount of hydroperoxide decomposed. [d] The reaction mixture was titrated for hydroperoxide after twenty-four hours; the corresponding catalyzed reactions were complete in less than two hours. [e] The reaction mixture was titrated for hydroperoxide after six hours; the corresponding catalyzed reactions were complete in less than two hours. [f] A 10% succinonitrile solution was added slowly to the reaction mixture. [g] A 10% succinonitrile solution was added to the reaction mixture in 0.1-ml. portions. [h] Carbon disulfide was added to the reaction mixture in four equal portions. [i] Before the catalyst was added the reaction mixture was allowed to stand for three hours, at the end of which time the hydroperoxide titer had decreased less than 1%. One-half hour after addition of the catalyst reaction was complete. Oxygen gas, 8% on the basis of the hydroperoxide consumed, was obtained.

rable data, these reactions were studied under a standard set of conditions and the results are summarized in Table VII.

Probably the hydroperoxide would decompose even if exceedingly small amounts of these "additives" were used, provided that the latter were not destroyed by the reagents employed. The chain character of their action is, however, unmistakable, even when the hydroperoxide decomposes without evolution of oxygen in the presence of alkali. Thus, when alkali is added to α-tetralyl hydroperoxide dissolved in *tert*-butyl alcohol, the hydroperoxide decomposes into water, tetralone, and higher oxidation products. The rate of this decomposition is doubled by addition of 4 mole-per cent of succinonitrile.

The high specificity of the "additives" which (in the presence of strong bases) bring about oxygen evolution from tertiary hydroperoxides (dissolved in a solvent not easily oxidized, *e.g.*, ether, ligroin, *tert*-butyl alcohol) is of considerable interest.[9] Furthermore, in solvents such as isopropyl alcohol or in the presence of easily oxidized compounds (*e.g.*, benzhydrol) these "additives" cause the tertiary hydroperoxide to react without evolution of oxygen gas. Instead, the alcohols are oxidized. A wide variety of "additives" (succinonitrile, acrylonitrile, carbon disulfide, etc.) accelerate the rate at which tertiary hydroperoxides (α-cumyl, *tert*-butyl) oxidize secondary alcohols to ketones in inert solvents (Table VIII).

The sodium salts of most tertiary hydroperoxides (excepting α-cumyl hydroperoxide) are insoluble in organic solvents (ether, ligroin, benzene, cumene, etc.). To obtain optimum results it is advantageous to work with homogeneous systems. This can be done by using water for water-soluble hydroperoxides (*tert*-butyl, etc.), or by using a mixture of water and *tert*-butyl alcohol for water-insoluble hydroperoxides. Thus, a water solution of *tert*-butyl hydroperoxide oxidizes propanol, ethanol, trimethylene glycol, and tetramethylene glycol, without oxygen evolution in the presence of alkali and succinonitrile. 2,3-Butanediol is not oxidized under these conditions but is easily oxidized (without oxygen evolution) if the catalyst ("additive") is carbon disulfide. Evidently, oxygen evolution and oxidation of the alcohol are potentially competitive reactions. Hence, to suppress oxygen evolution either in the presence or in the absence of "additives", it is necessary to use a very large excess of the alcohol (or diol).

In the alkaline oxidation of alcohols by hydroperoxides at room temperature the essential role of the "additive" is to accelerate a reaction which under these conditions is slow. Once, the temperature is raised (50–60°), a rapid decomposition occurs even in the absence of "additives".[10]

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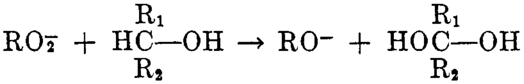
[9] The effective "additives" all contain two functional groups, and are capable of forming chelate complexes.

[10] Besides the organic additives already mentioned, there are quite a few metallic organic compounds (cobalt naphthenate, cobalt 2-ethylhexoate, iron phthalocyanin, and cuprous cyanide) which in benzene catalyze the decomposition of tertiary hydroperoxides into oxygen and carbinol. The rate of these reactions is increased several fold by traces of alkali. Furthermore, in acetic acid solution, α-cumyl hydroperoxide is decomposed (in part into oxygen and α-cumyl alcohol, in part into oxidation products of α-cumyl alcohol)

The question naturally arises whether or not the oxygen evolution from tertiary hydroperoxides in alkaline solution, and the oxidation of organic molecules (alcohols) are initiated by the same intermediates, the course of the reaction depending upon the concentration of the reactive components. Very probably this is the case. If so, the course of these reactions may be presented schematically as follows:

17. $ROOH + NaOH \rightleftharpoons RO_2^- + Na^+ + H_2O$

18.


$$RO_2^- + H\overset{R_1}{\underset{R_2}{C}}{-}OH \rightarrow RO^- + HO\overset{R_1}{\underset{R_2}{C}}{-}OH$$

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

Oxygen is directly transferred ("oxygenation") from the RO_2^- anion to the reducing component of the system, *i.e.*, alcohol or the undissociated peroxide (note that, in the presence of a large amount of alkali, tertiary hydroperoxides are stable at room temperature). With alcohols, therefore, the amount of oxygen evolution from hydroperoxides depends on the reducing power of the alcohol used as compared with that of the hydroperoxide, as well as on the relative concentrations of these two reactants.

The mechanism of oxygen evolution from tertiary hydroperoxides in the presence of a base and an "additive" thus differs from the mechanism of oxygen evolution where a powerful oxidant (ceric salts, lead tetraacetate, etc.) is employed. Under the latter conditions free $RO_2\cdot$ radicals are involved, whereas in the former instance no free radicals are involved; instead there is direct transfer of an oxygen atom.[11]

The precise function of the catalyst ("additive") in accelerating the rate of alkaline decomposition of hydroperoxides is still under investigation. Very probably complexes of the hydroperoxide and the "additives" are formed. Some support for this view has come from a study of the one-to-one complexes formed by hydroperoxides and 1,2-diamines. Thus, ethylenediamine, diethylenetriamine, and triethylenetetramine form one-to-one complexes with α-cumyl hydroperoxide; but this hydroperoxide forms no such complex with 2,3-dimethyl-2,3-diaminobutane.[12] Furthermore, in the presence of alkali, the "additive" succinonitrile rapidly decomposes α-cumyl hydroperoxide dissolved in benzene; the yield of oxygen under these conditions is almost quantitative, but, under similar conditions, tetramethylsuccinonitrile is without effect. Note also the effectiveness (Table VII) of phthalonitrile and ineffectiveness of terephthalonitrile.

The subject of direct oxygen transfer ("oxygenation") is projected as the subject of a future publication.[13]

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by catalytic amounts of inorganic additives such as manganese dioxide, chromic oxide, and vanadous chloride.

[11] This hypothesis could readily be tested by tracer technique using a tertiary hydroperoxide containing isotopic oxygen and an alcohol (benzhydrol).

[12] Note that in the presence of polyamines (unpublished work, Kharasch, Nudenberg, and White) tertiary hydroperoxide reacts with butadiene and ferrous salts to give not the "dimers" $(ROC_4H_6)_2$, but compounds of the type $RO(C_4H_6)OH$.

[13] Direct "oxygenation" may occur in the formation of epoxides from olefins and organic peracids.

EXPERIMENTAL

The hydroperoxides used in this study were purified by procedures described in previous publications.

Summaries of the results of most of the experiments of this study are assembled in Tables I to VIII. Some pertinent experiments, not recorded in the tables, are described below.

Oxidation of hydroquinone by tert-butyl hydroperoxide. A solution of *tert*-butyl hydroperoxide (5 g.) and hydroquinone (12 g.) in acetic acid (100 ml.) is stable at room temperature for several hours. However, the addition of perchloric acid (0.5 g.) causes a rapid drop in the peroxide titre. The reaction is complete within half an hour. The quinhydrone which separates accounts for 85% of the hydroperoxide used.

Decomposition of α-tetralyl hydroperoxide with potassium permanganate. Potassium permanganate (0.44 g., 0.0028 mole) was added to a solution of α-tetralyl hydroperoxide (11.5 g., 0.07 mole) in acetic acid (0.2 mole). Oxygen evolution (0.0028 mole) ceased at the end of 30 minutes. A titration indicated that 28% (0.0196 mole) of the hydroperoxide had decomposed. The oxides of manganese formed in the reaction caused a slow decomposition of the hydroperoxide—but no additional oxygen was evolved. At the end of 24 hours about 88% of the hydroperoxide had decomposed. α-Tetralone (60% of calculated amount) was recovered from the reaction mixture.

Decomposition of α-tetralyl hydroperoxide by cobaltous salts. A solution of α-tetralyl hydroperoxide (5 g.) and cobaltous chloride (0.3 g.) in acetic acid (15 ml.) is stable at room temperature. However, the addition of sodium acetate (0.3 g.) causes a violent exothermic reaction, and after 15 minutes no residual hydroperoxide can be demonstrated. On the basis of the hydroperoxide used, about 24% of gaseous oxygen is evolved.

Thermal decomposition of sodium salt of α-cumyl hydroperoxide in organic solvents. (*a*) *Toluene.* The sodium salt of α-cumyl hydroperoxide (16×10^{-3} mole) dissolved in toluene (15 ml.) was heated for 6 hours at 81°. At the end of that time, iodometric titration indicated the presence of 5.6×10^{-3} mole of the hydroperoxide. No oxygen gas was evolved during the reaction. From the reaction mixture benzoic acid (1.5×10^{-3} mole) and a trace of acetophenone were obtained.

(*b*) *Cyclohexene.* When the experiment described above was repeated except that cyclohexene (5 ml.) was added, the decomposition took place at a lower temperature. Thus, 14×10^{-3} mole of the hydroperoxide was decomposed in 1.5 hours at 58°. No evolution of oxygen was noted, and about 0.2×10^{-3} mole of benzoic acid was isolated. The residue was a high-boiling liquid which reacted readily with lead tetraacetate.

Effect of succinonitrile on the alkali-catalyzed decomposition of α-tetralyl hydroperoxide. To a solution of α-tetralyl hydroperoxide (2.5 g.) in *tert*-butyl alcohol (20 ml.), sodium hydroxide (0.4 ml.) (6 g. NaOH in 10 ml. of water) was added. About 30% of the hydroperoxide was decomposed in 55 minutes. A faster decomposition (30% in 35 minutes) took place in the presence of succinonitrile (0.1 g.).

Effect of succinonitrile on the alkali-catalyzed decomposition of hydrogen peroxide. To a mixture of hydrogen peroxide (2 ml. of 30% H_2O_2 in 10 ml. of H_2O) and isopropyl alcohol (15 ml.), sodium hydroxide (1 ml.; 6 g. NaOH in 10 ml. of H_2O) was added. The oxygen liberated was collected (40 ml. in 4 hours). The rate of oxygen evolution was greatly increased (43 ml. in 10 minutes) by the addition of succinonitrile (0.1 g.).

Tests for acetone showed that none was formed in the two preceding reactions.

SUMMARY

1. Hydroperoxides may act as oxidants or reductants or both, and certain aspects of acid-induced oxidations are discussed.

2. There are three different ways to evoke oxygen evolution from tertiary hydroperoxides: (a) by the aid of a powerful oxidant, (b) by the aid of heat and alkali, (c) by the aid of "additives" and alkali at room temperature.

3. "Oxygenation" of alcohols at room temperature may be brought about by the aid of a tertiary hydroperoxide, an "additive", and a base.

4. The mechanisms of the reactions outlined in 2 and 3 are discussed.

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