[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE CHEMISTRY OF HYDROPEROXIDES. III. THE FREE-RADICAL DECOMPOSITION OF HYDROPEROXIDES

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Received December 7, 1949

In the first paper of this series (1), it was indicated that α-cumyl hydroperoxide, when decomposed under various conditions, gives many different reaction products. It was, however, established that this compound when dissolved in glacial acetic acid and treated with very small amounts of perchloric acid decomposes to give phenol and acetone exclusively.

$$C_6H_5(CH_3)_2C—OOH \xrightarrow[H^+]{HOAc} C_6H_5OH + CH_3COCH_3$$

However, when a water solution of ferrous ammonium sulfate is slowly added to a water suspension of α-cumyl hydroperoxide, and the reaction mixture is stirred, the products formed are indicated by the following equation.

$$1.\ C_6H_5(CH_3)_2C—OOH\ (1\ \text{mole}) \xrightarrow[(0.47\ \text{mole})]{Fe^{++}} CH_3COC_6H_5\ (71\%) + CH_3OH\ (44\%) + C_6H_5(CH_3)_2COH\ (12\%) + \text{gas}^1\ (15\%) + \text{high-boiling oil}\ (10\%)$$

The present paper deals with the latter type of decomposition.

DISCUSSION

The hydroperoxides decomposed by ferrous salts in the present study were of the following types: (a) α-cumyl, (b) *tertiary*-alkyl, and (c) triphenylmethyl.

(a) *Decomposition of α-cumyl hydroperoxide by ferrous salts.* The data recorded in Table I are best accounted for by assuming one or more of the reactions indicated in Chart I. It is assumed that the first step in the reaction is the one-electron reduction of the hydroperoxide[2]:

$$(A)\ C_6H_5(CH_3)_2C—OOH + Fe^{++} \rightarrow C_6H_5(CH_3)_2CO\cdot + FeOH^{++}$$

The formation of free RO· radicals in the decomposition of hydroperoxides by ferrous salts, or by heat, has been assumed without actual proof by many investigators (2). Excellent evidence of the initial formation (in the water phase) of such free radicals has been obtained by decomposing α-cumyl and other hydroperoxides with ferrous salts in the presence of olefins. Under the specified condi-

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[1] The 15% of gas obtained in the reaction accounts for 26% of the α-cumyl hydroperoxide; it consists of ethane (73%) and methane (27%). The amount of oxygen (if any) formed is small (maximum 0.2–0.4%).

[2] In the present discussion the exact mechanism of the oxidation of ferrous ion is irrelevant; however, the authors prefer the representation $FeOH^{++}$ to $Fe^{+++} + OH^-$. In this connection see: Rabinowitch, *Rev. Modern Physics*, **14,** 112 (1942); Farkas and Farkas, *Trans. Faraday Soc.*, **34,** 1113 (1938).

tions these radicals add to olefins to give identifiable adducts.[3] In the absence of reactive olefins, the free RO· radical may undergo a variety of reactions. Those possible for the RO· radical derived from α-cumyl hydroperoxide are indicated in the accompanying reaction scheme (Chart I).

Obviously, such a complication of potential reactions may be profoundly influenced not only by the materials added to the reaction mixture, but by the amount of α-cumyl hydroperoxide in the water phase. This latter factor is of course influenced by the amount of the inert hydrocarbon diluent added to the reaction mixture. The substances recorded in Table I were selected as additives in the hope that their properties (especially their respective solubilities in the water and oil phases) would throw some light on the behavior of the free $C_6H_5(CH_3)_2CO\cdot$ radical.

TABLE I

EFFECTS OF VARIOUS ADDITIVES ON THE REACTION OF α-CUMYL HYDROPEROXIDE[a] WITH FERROUS SALTS

ADDITIVE (equiv.)[b]	Fe^{++} CONSUMED (equiv.)[b]	PRODUCTS[c] (equiv.)[b]				
		GAS	$CH_3COC_6H_5$	$C_6H_5(CH_3)_2COH$	$(CH_3)_2CO$	OIL
None	0.47	0.15[d]	0.71	0.12	—	10% (wt.)
None[e]	?[e]	.12	.37	.63	—	—
Octane (5.0)	.58	.12	.65	.20	—	—
Octane (5.0) + Dextrose (0.27)	.08	.38[g]	.50	.30	—	14% (wt.)
$C_6H_5CHOHCH_3$ (2.0)	.43	.42[g]	1.20[h]	.61	—	—
2-Propanol (2.0)	.29	.38	0.42	+[f]	+	—
2-Propanol (6.0) + H_2SO_4 (0.22)	.29	.24	.21	.77	0.70	—
$C_6H_5(CH_3)_2COH$ (5.0)	.60	.20	.85	+	—	—
Cumene (5.0)	.62	.18[i]	.68	.30	—	—
HCO_2H (5.0)	.35	.60[j]	+	+	—	—

[a] One mole of α-cumyl hydroperoxide, suspended in 300 cc. of water, was gently agitated during gradual addition of the iron solution. [b] Moles per mole of hydroperoxide. [c] Methanol is always present among the reaction products, but its quantitative isolation from the reaction mixtures is troublesome. In no experiment here reported was α-cumyl peroxide detected. [d] The gas consists of approximately 73% ethane and 27% methane, with possibly 1% oxygen. [e] To 6 moles of a stirred 0.5-molar solution of ferrous ammonium sulfate was added dropwise one mole of α-cumyl hydroperoxide in water suspension. [f] The sign (+) indicates that the material was present in the reaction mixture, but that the amount was not determined. [g] The gas was chiefly methane (<7% ethane). [h] About 0.4 mole of acetophenone is formed from the hydroperoxide; the remainder is formed by oxidation of 1-phenylethanol. [i] The gas was nearly pure ethane (apparent mol. wt., 29.2). [j] The gas was a mixture of carbon dioxide (50%) and methane (50%).

[3] These results will be presented in another article of this series.

The extensive experience with free $RO\cdot$ radicals accumulated in this laboratory, (only part of which is reported here) can best be interpreted by assuming that, when α-cumyl hydroperoxide (suspended in water) reacts with a water solution of a ferrous salt, the free $RO\cdot$ radicals are formed in the water phase. The major reaction products are then readily accounted for by the reactions *a* and *b*, which are chain-terminating events, and *c*, f_1, and f_2, which are chain-sustaining steps leading to the formation of methanol and acetophenone (Chart I).

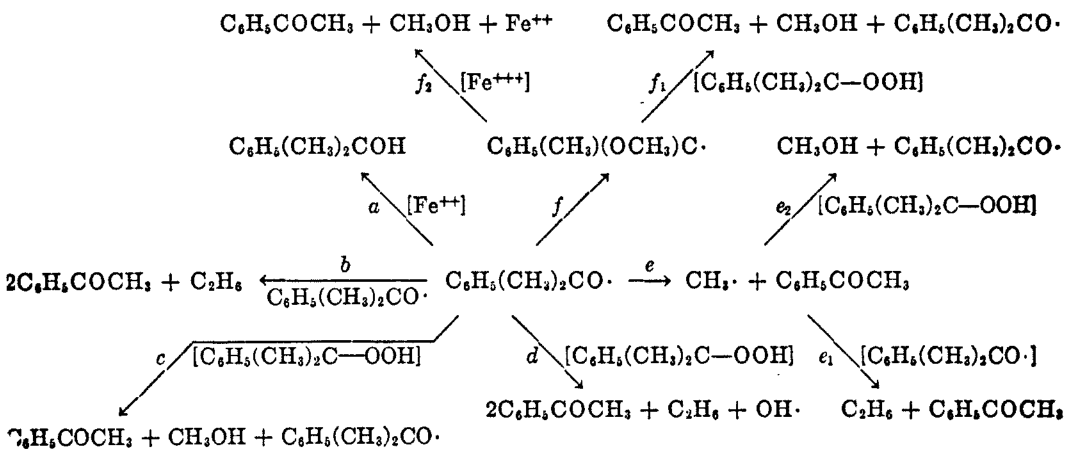
The total amount of gas formed when ferrous ammonium sulfate is slowly added to a slightly agitated water suspension of α-cumyl hydroperoxide is small (about 15 mole-per cent on the basis of the hydroperoxide used). The consumption of ferrous ion is high (indicating short chains). The gas is a mixture of ethane (73%) and methane (23%). Here the decomposition of the free-radical plays but

$$(e)\ C_6H_5C(CH_3)_2CO\cdot \rightarrow C_6H_5COCH_3 + CH_3\cdot$$

a minor part.[4] The methane formed in the reaction must arise from the interaction, in a manner indicated later, of the free $C_6H_5(CH_3)_2CO\cdot$ radical with some hydrogen "donor" which, in this instance, may be a reaction product. The carbinol is undoubtedly formed by the interaction of the free radical with a ferrous ion. This reaction leads to termination of the chain.

These views are substantiated by a study of the gaseous and other reaction products formed when α-cumyl hydroperoxide is decomposed in water solution

CHART I



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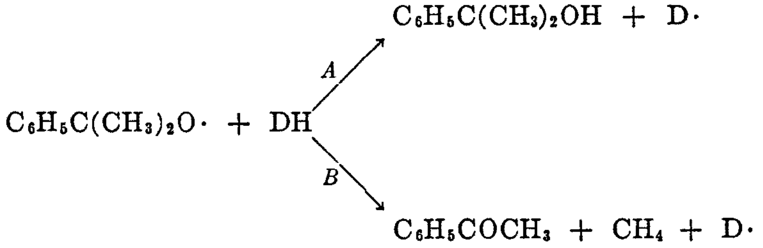
[4] The following are some of the reasons why the decomposition reaction is considered to be relatively unimportant. (a) The data in Table I indicate that the formation of ethane is a chain-terminating event. (b) It is known from previous experience that the formation of ethane by the dimerization of two methyl radicals in solution is highly improbable. (c) In the case of *tert*-amyl hydroperoxide decomposition analogous to (*e*) (Figure 1) should lead to both ethylene and butane; only butane was found.

fbyerrous salts in the presence of a hydrogen donor (DH). Under these conditions the reactions are *A* and *B* rather than *b*, *c*, *d*, *e*, and *f* (Chart I).



$$C_6H_5C(CH_3)_2O\cdot + DH \xrightarrow{A} C_6H_5C(CH_3)_2OH + D\cdot$$

$$C_6H_5C(CH_3)_2O\cdot + DH \xrightarrow{B} C_6H_5COCH_3 + CH_4 + D\cdot$$

When poor hydrogen donors (*e.g.*, dextrose) are used, the part played by reaction *B* becomes more prominent.

Moreover, as indicated in Table II, the ratio of methane to ethane may be widely varied (in the presence of dextrose) by changes in the concentration of α-cumyl hydroperoxide in the water phase.

TABLE II

Decomposition of α-Cumyl Hydroperoxide (1 mole) by Ferrous Salts (0.08 mole) in Water[a]

ADDITIVES	MOLE-% OF GAS[b]	COMPOSITION OF GAS, (%)	
		CH_4	C_2H_6
1. Dextrose[a] (0.3 mole)	35	55	38
2. Dextrose (0.3 mole) + heptane (18 moles)[b]	45	81	15
3. Dextrose (0.3 mole) + heptane (72 moles)[b]	50	95	5

[a] The mixture was gently agitated. Here, presumably, the rate of diffusion would be the rate-determining step. [b] Calculated on the basis of the amount of α-cumyl hydroperoxide used.

These results are readily explicable by consideration of the relative concentrations of the free RO· radical in the respective water phases. In the presence of a large excess of heptane, the concentration of the hydroperoxide in the water phase is very low and consequently the concentration of free radicals is also low; these radicals, therefore, react preferentially with the "donor" molecule (as in *B*); reactions *b*, *d*, *e*, and f_1 are excluded, and the gas is almost pure methane. With less solvent, the concentration of the hydroperoxide and thus concentration of the RO· radicals in the water is increased; the free RO· radical, therefore, reacts not only as in *B* but also with another RO· radical (*b*, Chart I) giving rise to ethane.

The extremely long chain noted for the decomposition of α-cumyl hydroperoxide by ferrous salt in the presence of dextrose (0.08 mole per mole of hydroperoxide), is probably not due to the regeneration of ferrous ions from ferric by the dextrose, but to the rapid interaction of the ferric ion with the free donor radical formed in *B*.[5,6]

$$D\cdot + Fe^{+++} \rightarrow D^+ + Fe^{++}$$

The strongly reducing sugars formed by the oxidation of the dextrose may also play an important role in sustaining the chain.

The views here developed suggest that, in the presence of excellent hydrogen donors, the free $C_6H_5(CH_3)_2CO\cdot$ radical may give α,α-dimethylbenzyl alcohol exclusively. This reaction does occur when an aqueous ethanolic solution of α-cumyl hydroperoxide and hydroquinone is treated with a trace of ferrous salt. In the absence of ferrous salts, the mixture is stable for many hours; but as little as 0.002 mole of ferrous ion causes an immediate exothermic reaction, and (when a large excess of hydroquinone is used) the separation of quinhydrone. Furthermore, no gas is formed under these conditions. Probably the reaction here proceeds according to the following scheme:

$$(C)\ C_6H_5(CH_3)_2C{-}OOH \xrightarrow{Fe^{++}} C_6H_5(CH_3)_2CO\cdot + FeOH^{++}$$

$$(D)\ C_6H_5(CH_3)_2CO\cdot + HOC_6H_4OH \rightarrow C_6H_5(CH_3)_2COH + \cdot OC_6H_4OH$$

$$(E)\ C_6H_5(CH_3)_2CO\cdot + Fe^{++} \xrightarrow{H_2O} C_6H_5(CH_3)_2COH + Fe^{+++}$$

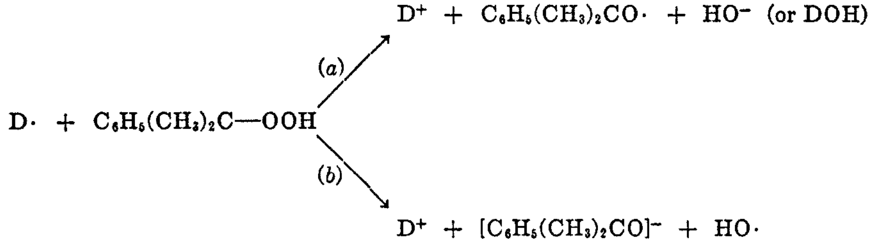
From this point on, the reaction may be represented schematically by a chain reaction involving either step *F* or *H*, or both.

$$(F)\ [\cdot OC_6H_4OH] + C_6H_5(CH_3)_2C{-}OOH \rightarrow \text{Quinone} + C_6H_5(CH_3)_2CO\cdot + H_2O$$

$$(G)\ 2[\cdot OC_6H_4OH] \rightarrow \text{Quinhydrone}$$

$$(H)\ HOC_6H_4OH + Fe^{+++} \rightarrow Fe^{++} + \cdot OC_6H_4OH$$

[5] Another way of sustaining the chain reaction is:

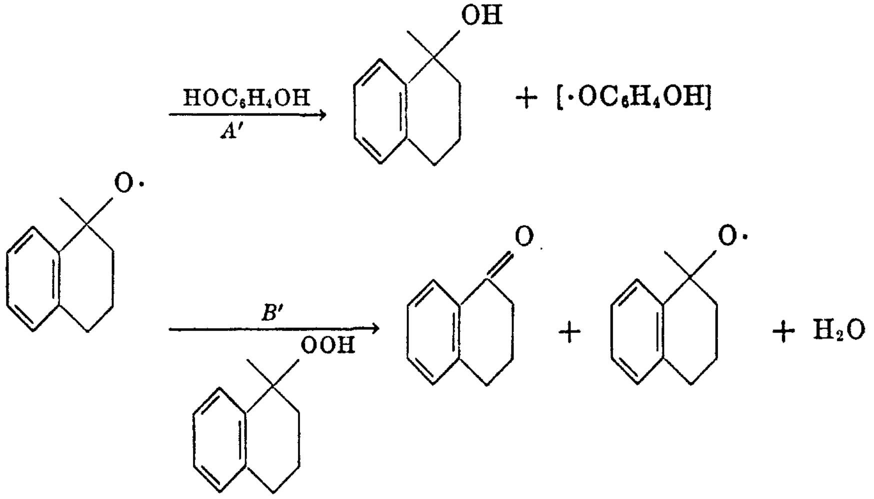


$$\begin{tikzcd}
 & D^+ + C_6H_5(CH_3)_2CO\cdot + HO^- \text{ (or DOH)} \\
D\cdot + C_6H_5(CH_3)_2C{-}OOH \arrow[ur, "(a)"] \arrow[dr, "(b)"'] & \\
 & D^+ + [C_6H_5(CH_3)_2CO]^- + HO\cdot
\end{tikzcd}$$

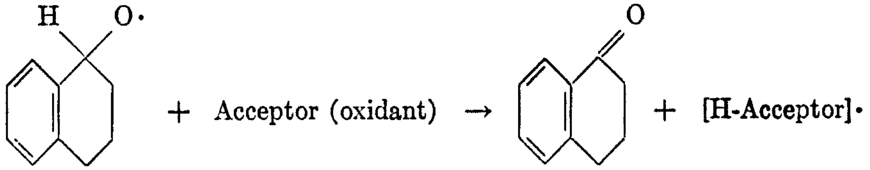
The above reaction plays an important part when α-cumyl hydroperoxide is decomposed by ferrous salts in the presence of 2-propanol. Here the chain length is about six, and the formation of methanol (c, e_2, f_1, f_2, Chart I) is suppressed even more than it is by dextrose, although this latter compound decreases methanol formation to the extent of 70% as compared with a reaction in which ferrous ion alone is the reductant.

[6] In these reactions, the presence of ferrous ion in the solution was demonstrated by the immediate production of a blue color when $K_3Fe(CN)_6$ was added to an acidified sample of the reaction mixture. On the other hand, no ferrous ion could be demonstrated, even after many hours, when a solution of a ferric salt was treated with dextrose. These facts are additional corroborative evidence that the regeneration of the ferrous ions proceeds by a mechanism different from the one usually postulated, *i.e.*, the reduction of the ferric ion by dextrose.

The above statements do not imply that all free RO· radicals react with hydroquinone or pyrogallol to give exclusively ROH compounds. Probably most of the free radicals derived from *tertiary*-alkyl hydroperoxides do react in this way; but some of those derived from secondary hydroperoxides behave differently. In fact, α-tetralyl hydroperoxide is decomposed by ferrous salts, even in the presence of a large excess of hydroquinone, to give appreciable amounts of α-tetralone. This fact may well mean that, of the two possible reactions *A′* and *B′*, *A′* is the slower.



Here the difference between the free secondary and free tertiary radicals may be due to a rapid decomposition of the secondary radical into tetralone and a hydrogen atom:



This reaction would endow the radical with reducing properties, and would therefore favor the reaction with the oxidant (α-tetralyl hydroperoxide).

(b) *Decomposition of tertiary-alkyl hydroperoxides by ferrous salts.* It is of considerable interest that the ferrous ion-induced decompositions of the two *tertiary*-alkyl hydroperoxides (Table III) are not chain decompositions. The reactions of types *c*, e_2, and *f* (Chart I), where the O—O bond is broken by the RO· radical do not occur. Thus, when a dilute solution of ferrous salt is added to a water solution or suspension of either *tert*-butyl or *tert*-amyl hydroperoxide, at least one mole of ferrous ion is required for complete decomposition.

The course of the decomposition of *tert*-butyl hydroperoxide (Table IV) is influenced by additives in a fashion similar to that observed in the decomposition of α-cumyl hydroperoxide. But, in interpreting some of the results, the greater water-solubility (12%) of the *tert*-butyl hydroperoxide should be considered. Thus, when the decomposition was carried out in the presence of dextrose as the only additive, no chain decomposition was observed until the concentration of the *tert*-butyl hydroperoxide (and consequently of the RO· radicals) in the water phase had diminished appreciably. The presence of inert organic solvent diminishes the concentration of the RO· radicals in the water phase, and thus the probability of ending the chain by disproportionation (scheme *b*, Chart I) is decreased.

TABLE III

DECOMPOSITION OF *tertiary*-ALKYL HYDROPEROXIDES WITH FERROUS SALTS

HYDROPEROXIDE	Fe^{++} CONSUMED[a]	GAS[b]			ACETONE
		CH_4	C_2H_6	C_4H_{10}	
tert-Butyl[c]	1.25	0.16	0.16	None	0.5[d]
tert-Amyl[c]	1.00	None	.37	.16	.7[d]

[a] All products are calculated in moles per mole of the hydroperoxide. [b] The behavior of organic hydroperoxides toward ferrous salts and potassium iodide is in striking contrast to the behavior of hydrogen peroxide toward these reagents. The latter substance in the presence of traces of potassium iodide or somewhat larger amounts of ferrous salts is decomposed quantitatively into oxygen and water; whereas the *tertiary*-alkyl hydroperoxides under these conditions give practically no oxygen. [c] The amount (if any) of methyl ethyl ketone formed in this reaction is very small. [d] Besides the product here mentioned, the corresponding alcohols and small quantities of the corresponding peroxides are also formed. The quantitative isolation of these products was not attempted.

TABLE IV

EFFECT OF ADDITIVES ON THE REACTION OF *tert*-BUTYL HYDROPEROXIDE WITH FERROUS SALTS

ADDITIVE	MOLES Fe^{++}/MOLE HYDROPEROXIDE	MOLES OF GAS
None	1.25	0.32
Heptane (10 moles)	1.25	.12[a]
Dextrose (1 mole)	0.88[b]	.40
Dextrose (0.33 mole)	.88[b]	.40
Dextrose (0.33 mole) + Heptane (10 moles)	.10	.47
2-Propanol (3 moles) + Heptane (10 moles)	.20	.035[c]
2-Propanol (3 moles) + Dextrose (0.5 mole) + Heptane (10 moles)	.15	.12
Hydroquinone (3 moles)	.001	none

[a] The gas is pure methane. [b] When the ferrous salt solution was slowly added to the reaction mixture the amount of gas evolved was proportional to the amount of iron solution added until 0.84 mole of ferrous ion had been added and 0.28 mole of gas evolved. From this point on only 0.04 mole of iron salt was required to evolve the remaining 0.12 mole of gas. [c] The amount of gas evolved depends upon the rate of addition of the ferrous solution, *i.e.*, faster addition increases, slower addition decreases, the total amount of gas formed.

The results obtained in the decomposition of *tert*-butyl hydroperoxide differ from those with α-cumyl hydroperoxide in the following respects:

(a) In the absence of potential hydrogen donors, no chain decomposition can be observed [the $(CH_3)_3CO\cdot$ radical does not break the O—O bond].

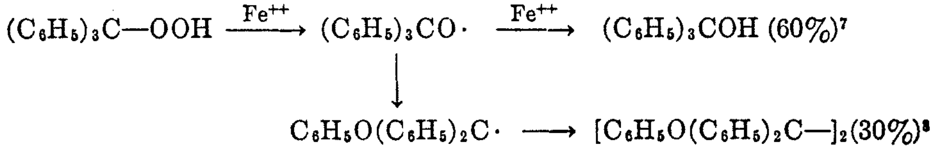
(b) In the reaction with 2-propanol, the amount of gas formed is negligible. This result indicates that in the presence of donor reagents reaction *A* rather than reaction *B* tends to occur.

(c) When heptane is the sole additive only small amounts of gas are formed (as in the similar decomposition of α-cumyl hydroperoxide with ferrous salts); here, however, the gas formed is pure methane. The absence of ethane indicates that with the $(CH_3)_3CO\cdot$ radical the reaction is *a* rather than *b* (Figure 1).

The decomposition of *tert*-butyl hydroperoxide in the presence of a mixture of dextrose and 2-propanol indicates that 2-propanol is a better hydrogen donor than dextrose. This observation substantiates the claim that reaction *A* is favored with good hydrogen donors.

One may also conclude that in *tert*-butyl hydroperoxide the O—O bond is stronger than the corresponding bond in α-cumyl hydroperoxide, and that the $(CH_3)_3CO\cdot$ radical is more reactive than the $C_6H_5(CH_3)_2CO\cdot$ radical.

(c) *Decomposition of triphenylmethyl hydroperoxide with ferrous salts.* In none of the examples cited is there any clue which justifies a single choice among the many elimination mechanisms indicated in Chart I. On the other hand, a careful study of the reaction of triphenylmethyl hydroperoxide with ferrous salts shows unequivocally that the compound reacts as follows:



$$\begin{tikzcd}
(C_6H_5)_3C\text{—}OOH \arrow[r, "Fe^{++}"] & (C_6H_5)_3CO\cdot \arrow[r, "Fe^{++}"] \arrow[d] & (C_6H_5)_3COH\ (60\%)^{7} \\
& C_6H_5O(C_6H_5)_2C\cdot \arrow[r] & [C_6H_5O(C_6H_5)_2C\text{—}]_2 (30\%)^{8}
\end{tikzcd}$$

The formation of benzopinacol diphenyl ether has previously been observed in the decomposition of triphenylmethyl peroxide (3) and of triphenylmethyl hyponitrite (4).

On the basis of the evidence now at hand, it appears unlikely that free radicals in which at least two of the groups are aliphatic and one is aromatic rearrange as follows:

$$Ar(Alk)_2CO\cdot \rightarrow ArO(Alk)_2C\cdot$$

Further study of this problem is under way. The relative tendencies of radicals R, R′, and R″ to migrate from carbon to oxygen in the free radical RR′R″CO· is also under investigation.

[7] Losses in recrystallization are probably responsible for the 10% deficit of organic matter.

[8] The experimental part of this paper should be consulted for details of the proof of structure for this compound. Note also that one of the compounds which Wieland obtained by treating this substance with zinc dust and glacial acetic acid, and which he claimed to be "a third isomer of triphenylmethyl peroxide" (m.p. 198°) should be stricken from the literature; the compound is actually benzopinacolone.

EXPERIMENTAL

Reagents. Commercial α-cumyl hydroperoxide (Hercules Powder Company[9]) was purified by the method of Hock and Lang (5). In most experiments the peroxide regenerated from the sodium salt was distilled at reduced pressure (0.1 mm.); in others, the peroxide, generated from the sodium salt, was used as such. The α-cumyl hydroperoxide used was 98–100% pure.

Ferrous ion was added in the form of a 0.5 N solution of ferrous ammonium sulfate, [$Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$, Mallinckrodt].

The carbinols (free of acetophenone) used as additives were prepared as described in the preceding paper of this series.

Gaseous reaction products were collected, fractionated from materials which remain condensed below 0°, and determined by the method described by Kharasch, Lewis, and Reynolds (6). The relative amounts of methane and ethane were estimated by molecular-weight determination of the hydrocarbon mixture, as well as by gas analysis with the Burrell modification of the Orsat apparatus.

Acetophenone was determined by the method described by Kharasch and Cooper (7).

α,α-Dimethylbenzyl alcohol was estimated by weighing its product with thioglycolic acid (8).

Decomposition of α-cumyl hydroperoxide by ferrous salts. The decomposition of α-cumyl hydroperoxide by ferrous salts was carried out as follows. Ferrous ammonium sulfate solution was introduced dropwise into a reaction vessel containing an aqueous suspension of α-cumyl hydroperoxide (0.1 mole of hydroperoxide and 30 cc. of distilled water) and, whenever so indicated, of the additive agent. The reaction mixture was stirred with the aid of a magnetic stirrer. The evolved gas was collected over water. The rate of addition of the iron salt was slow enough so that there was no appreciable temperature rise in the reaction vessel; when gas evolution had ceased the reaction was considered complete; a test for peroxides was negative. The results obtained in the presence of various agents are shown in Table I. The effect of an inert organic solvent on the decomposition of α-cumyl hydroperoxide in the presence of dextrose is shown in Table II. In these experiments, the total amounts of ferrous salt solution and dextrose indicated in the table were added at once to the hydroperoxide solution.

Ferrous ion-induced decomposition of hydroperoxides in the presence of hydroquinone. Hydroquinone fails to react at an appreciable rate with hydroperoxides in the absence of catalysts. To a mixture of α-cumyl hydroperoxide (0.1 mole) and hydroquinone (0.18 mole) in aqueous methanol (100 cc. of water, sufficient methanol to produce a homogeneous solution) was added 0.5 cc. of 0.5 N ferrous ammonium sulfate solution (0.25 mole-%). A vigorous reaction ensued, with complete depletion of the peroxide within two minutes. The quinhydrone formed separated as crystals which were collected, washed carefully with aqueous methanol, and dried on a clay plate; m.p. 168°. The amount of quinhydrone thus isolated was 0.088 mole. The filtrate was shaken vigorously with sodium hydrosulfite solution, made alkaline, and then extracted with ether. The ether was removed, and the residue was distilled at 105°/25 mm. The distillate solidified (m.p. 36°), and when this was mixed with authentic α,α-dimethylbenzyl alcohol there was no melting-point depression. The alcohol thus obtained amounted to 98% of the calculated amount based on the hydroperoxide used. No acetophenone was found. When less than equivalent amounts of hydroquinone were used only quinone was formed.

Similar results were obtained with *tert*-butyl hydroperoxide and hydroquinone in the presence of ferrous salts.

The description of the decomposition of α-tetralyl hydroperoxide by ferrous salts under various conditions is summarized in Table V.

Decomposition of tert-butyl hydroperoxide by ferrous salts. To 0.083 mole of *tert*-butyl

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[9] We are grateful to the Hercules Powder Company for a generous supply of the hydroperoxide.

hydroperoxide (93% titre), suspended in 30 cc. of water, was added dropwise a solution of ferrous ammonium sulfate (0.5 *N*). Gas was evolved as soon as the first drop was added. After the addition of 0.1 mole of ferrous ammonium sulfate the evolution of gas ceased. At this point the peroxide was completely consumed. The volume of gas evolved was 590 cc. The results are recorded in Table III. The amount of gas produced (0.032 mole) accounted for 0.48 mole of the *tert*-butyl hydroperoxide consumed. The acetone formed (0.051 mole) was estimated by reaction of an aliquot portion of the solution with 2,4-dinitrophenylhydrazone, and determination of the weight of product formed. The large amount of iron required for complete utilization of the hydroperoxide indicates that 31% of the peroxide was converted by two-electron reduction to *tert*-butyl alcohol. No attempt was made to isolate the alcohol nor the small amounts of *tert*-butyl peroxide which may have been formed.

The results obtained with *tert*-butyl hydroperoxide in the presence of additives are shown in Table IV.

Decomposition of hydrogen peroxide with (a) ferrous salts and (b) potassium iodide. When 50 equivalent-percent of ferrous ammonium sulfate solution (18 cc., 0.5 *N*) was added dropwise to an ether solution of hydrogen peroxide (20 ml. of 3% H_2O_2 in ether) 180 cc. of oxygen was evolved. When neutral potassium iodide was used in place of the ferrous salt in a similar experiment with hydrogen peroxide only catalytic amounts of the iodide were required to decompose the peroxide quantitatively into oxygen and water. It is noteworthy that no oxygen evolution occurs with the organic hydroperoxides here studied.

TABLE V

EFFECT OF ADDITIVES ON THE DECOMPOSITION OF α-TETRALYL HYDROPEROXIDE BY FERROUS IONS

ADDITIVE	EQUIV. Fe^{++a}	GAS	PRODUCTS (MOLES)	
			α-Tetralone	Quinhydrone
None	0.2–0.4	None	0.88	—
None	5.0[b]	None	.79	—
Hydroquinone	0.002	None	.51[c]	0.22
Pyrogallol	.002	None	.54[c]	—

[a] To a stirred solution of crystalline tetralin hydroperoxide (0.05 mole) in 50 cc. of ethanol was added dropwise an aqueous solution (0.5 *N*) of ferrous ammonium sulfate. The tetralone formed was estimated as the 2,4-dinitrophenylhydrazone. [b] To 5 moles of a stirred solution of 0.5 *N* ferrous ammonium sulfate was added dropwise an alcoholic solution of 1 mole of α-tetralyl hydroperoxide. [c] The other reaction product is probably α-tetralol.

Decomposition of tert-amyl hydroperoxide by ferrous salts. To *tert*-amyl hydroperoxide 0.075 mole (98% titre), suspended in 50 cc. of water, sufficient aqueous 0.5 *N* ferrous ammonium sulfate (0.075 mole) was added dropwise to cause complete decomposition of the hydroperoxide. The gas evolved, (900 cc.), contained no oxygen. It was scrubbed with silver sulfate-nickel sulfate-sulfuric acid solution (9) for removal of olefins; however, none were detected. Vapor pressure measurements, after removal of the ethane, indicated butane to be the only other constituent. An aliquot portion of the reaction mixture was treated with 2,4-dinitrophenylhydrazine, and the resulting hydrazone was fractionally crystallized. All crude fractions melted above 120°; (ethyl methyl ketone dinitrophenylhydrazone melts at 115°). On recrystallization the melting points were raised to 128–130°, and the material proved to be identical with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone. The total amount of acetone formed in the reaction was 0.07 mole. The organic layer was washed well with water, and dried. It weighed 1 g., and boiled with decomposition at 150°; the material reduced permanganate; the molecular weight of this fraction in benzene (cryscopic) was 165. These properties correspond closely with those of *tert*-amyl peroxide (mol. wt., 174).

Decomposition of triphenylmethyl hydroperoxide in the presence of ferrous salts. Triphenylmethyl hydroperoxide was prepared according to method of Wieland and Maier (10), with the slight modification that the calculated amount of 50% potassium hydroxide was added to the acetone solution of hydrogen peroxide and trityl chloride. The hydroperoxide used for this experiment melted at 78–80°. Triphenylmethyl hydroperoxide (1 g.) was dissolved in ethanol (10 cc.). To the well-stirred solution a solution of ferrous ammonium sulfate (3 g. in 10 cc. of water) was added. The reaction mixture was stirred for one hour after addition of the iron salt, and was then acidified to Congo Red with 2 *N* hydrochloric acid. The insoluble organic material was collected and washed with absolute ethanol. In this fashion the triphenylcarbinol was separated from the insoluble benzopinacol diphenyl ether. The triphenylcarbinol was crystallized from aqueous ethanol to give 0.6 g. of material which melted at 160° and did not depress the melting point of an authentic sample of triphenylcarbinol. The insoluble diphenyl ether of benzopinacol, after washing with hot ethanol and small amounts of ether, weighed 0.3 g. The crude product was crystallized from a chloroform-ethanol mixture. In an evacuated tube the crystals turned yellow at 180° and melted at 218°, to give a melt of deep red color. The product gave no melting-point depression with an authentic sample of the material prepared according to Wieland.

Anal. Calc'd for $C_{38}H_{30}O_2$: C, 88.03; H, 5.77; Mol. wt., 518.
Found: C, 87.91; H, 5.99; Mol. wt., 498.

Hydrolysis of benzopinacol diphenyl ether. To benzopinacol diphenyl ether (0.15 g.), suspended in glacial acetic acid, powdered zinc (0.15 g.) was added, and the mixture was refluxed (see Wieland, *loc. cit.*) until solution took place. Upon addition of water, benzopinacolone (0.1 g., 99% yield) separated. When crystallized from ethanol, the substance melted at 195–200° in an evacuated tube, and at 175–178° in an open tube. The melting point of this substance was not depressed upon mixture with an authentic sample of benzopinacolone.

Anal. Calc'd for $C_{26}H_{20}O$: C, 89.9; H, 5.79; Mol. wt., 348.
Found: C, 89.8; H, 6.0; Mol. wt., 343.

In the reaction with zinc and acetic acid the yields of benzopinacolone varied between 60 and 99%. The cause of these variations was not investigated. Where the yield was lower, the other product was benzohydrol, as reported by Wieland.

SUMMARY

1. In the presence of aqueous ferrous salt solutions α-cumyl hydroperoxide decomposes into acetophenone, methanol, ethane, and α,α-dimethylbenzyl alcohol. Methane can also be formed.

2. The results obtained suggest the following scheme.
   - (*a*) The first step is a one-electron reduction resulting in the formation of the $C_6H_5(CH_3)_2CO\cdot$ radical.
   - (*b*) The radical thus formed may be reduced by another ferrous ion; it may disproportionate into acetophenone and ethane; or, by attack on an α-cumyl hydroperoxide molecule, may form methanol, acetophenone, and a new $C_6H_5(CH_3)_2CO\cdot$ radical, thus sustaining a chain reaction.
   - (*c*) In the presence of a potential hydrogen donor (dextrose, 2-propanol, 1-phenylethanol, formic acid, hydroquinone) the $C_6H_5(CH_3)_2CO\cdot$ radical may abstract a hydrogen atom, thereby forming (a) α,α-dimethylbenzyl alcohol, or (b) methane and acetophenone. With loosely held hydrogen atoms (hydroquinone) reaction (a) is favored. The donor radical formed may contribute to sustaining a chain reaction.

3. The RO· radical formed from α-tetralyl hydroperoxide is less reactive towards hydrogen donors than that from α-cumyl hydroperoxide.

4. The reaction of *tert*-butyl, and *tert*-amyl hydroperoxides with ferrous salts follows a course similar to that of α-cumyl hydroperoxide. These hydroperoxides, however, differ in having a stronger O—O bond; thus the chain reaction to yield methanol and acetone, or ethanol and acetone is suppressed. Furthermore, the $(CH_3)_3CO\cdot$ radical is more reactive toward hydrogen donors than the $C_6H_5(CH_3)_2CO\cdot$ radical.

5. The relative tendency of groups R, R′, or R″ in the radical RR′R″CO· to participate in cleavage of the R—C bond increases in the order: phenyl, methyl, ethyl, hydrogen.

6. The $(C_6H_5)_3CO\cdot$ radical formed from triphenylmethyl hydroperoxide rearranges without elimination, and dimerizes to benzopincol diphenyl ether.

CHICAGO 37, ILLINOIS

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