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THE CHEMISTRY OF HYDROPEROXIDES. VI. THE THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE

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Many contradictions are to be found in the literature regarding the thermal stability of α-cumyl hydroperoxide. In this laboratory it has been found that *pure* α-cumyl hydroperoxide is stable, when dissolved in saturated hydrocarbon solvents, up to 130–140° (1). The apparent contradiction of results previously reported may be reconciled if it is borne in mind that decomposition of α-cumyl hydroperoxide may be induced (at lower temperatures) by compounds of various types, of which the following are representative.

A. Strong acids (in the Lewis sense). These initiate a chain reaction (through the formation of an intermediate cation $C_6H_5(CH_3)_2CO^+$) which results in the formation of phenol and acetone (2).

B. Tertiary alcohols. These, in the presence of traces of acids, react with hydroperoxides to form peroxides (symmetrical or unsymmetrical, depending upon the alcohol concerned) (3).

C. One-electron reducing agents. These initiate a chain reaction involving the intermediate formation of the free α-cumyloxy $[C_6H_5(CH_3)_2CO\cdot]$ radical (4). The ultimate products of the reaction depend in large part on the nature of the other substances present in the reaction system.

D. Two-electron reducing agents. In the presence of such reagents, of which sodium bisulfite is an example, α-cumyl alcohol is formed. The intermediate product is undoubtedly the same free radical postulated in the preceding example; further reduction leads to the carbinol.[1]

E. Free-radical sources. (See Discussion)

F. Reagents which induce oxygen evolution (intermolecular oxidation-reduction, yielding oxygen and carbinol).[2] Among these may be cited the following examples.

(a) Oxidizing agents, such as potassium permanganate, lead tetraacetate, chromic acid, and ceric sulfate. These under suitable conditions (*e.g.*, in high concentrations of hydroperoxide in acetic acid) induce decomposition of the hydroperoxide by a chain reaction. Some acetophenone is formed, perhaps by oxidation of α-cumyl alcohol.

(b) Traces of alkaline substances at 60° or above. These agents also give rise to the formation of some acetophenone, traces of benzoic acid, and some unidentified acids.

(c) Traces of alkali in the presence of traces of certain additives containing bifunctional groups (*e.g.*, succinonitrile, carbon disulfide, acrylonitrile, ethylene thiocyanate, etc.).

(d) Metallic complexes (*e.g.*, cobalt naphthenate, iron phthalocyanine, etc.).

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[1] See experimental part.

[2] Unpublished work.

PURITY OF REAGENTS

It is worthy of emphasis that grievous errors (both in fact and in interpretation) may arise in decomposition experiments if the hydroperoxides, solvents, and other reagents employed are not carefully purified. The unusual results cited by Fordham and Williams (5) may be explained on this basis. These investigators report that α-cumyl hydroperoxide dissolved in cumene decomposes completely in two hours at 100° to give phenol (10–11%), acetone (65%), and α-cumyl alcohol (17%). Actually, carefully purified α-cumyl hydroperoxide in purified cumene is relatively stable at 100°; little or no decomposition takes place in 48 hours.[3] At 128° more than 24 hours is required for complete decomposition.

DISCUSSION

Since free radicals are presumably formed in the thermal decomposition of α-cumyl hydroperoxide it is pertinent to review here the nature of the reactions taking place when free radicals (derived from the thermal decomposition of acetyl peroxide in the liquid phase) attack α-cumyl hydroperoxide at temperatures in the 70–100° range, in which α-cumyl hydroperoxide is thermally stable for relatively long periods (at least two days) (1). For the solvents cumene and ethylbenzene, a reaction scheme (I) consistent with the known properties of free radicals and their co-reactants, and with experimentally observed products is proposed in equations 1–7. (R is either $C_6H_5(CH_3)_2C\cdot$ or $CH_3(C_6H_5)CH\cdot$.)

REACTION SCHEME I

1. $[CH_3C(=O)O-]_2 \xrightarrow{\Delta} CH_3\cdot + CO_2 + CH_3C(=O)O\cdot$

2. $CH_3\cdot + RH \rightarrow CH_4 + R\cdot$

3. $C_6H_5(CH_3)_2C-OOH + R\cdot \rightarrow \{[C_6H_5(CH_3)_2C-OOH]\ [R\cdot]\}$ **A**[4]

4. $\mathbf{A} + [CH_3C(=O)O-]_2 \rightarrow C_6H_5(CH_3)_2C-OO-R + CH_4 + CH_3\cdot + 2\ CO_2$

5. $\mathbf{A} + RH \rightarrow C_6H_5(CH_3)_2COH + ROH + R\cdot$

6. $2\ \mathbf{A} \rightarrow C_6H_5(CH_3)_2C-OO-R + C_6H_5(CH_3)_2COH + ROH$

7a. $\mathbf{A} \rightarrow C_6H_5(CH_3)_2COH + RO\cdot$

7b. $\mathbf{A} \rightarrow C_6H_5(CH_3)_2CO\cdot + ROH$

α-Cumyl, α-phenylethyl (or, in general, R·) free radicals may add to the hydroperoxide to give a free radical complex **A**. At lower temperatures (70–80°), both this complex and acetyl peroxide are sufficiently stable to interact in the

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[3] No significance should be attached, therefore, to their calculated activation energy or to any deduction based on their data.

[4] The formation of the complex "**A**" is postulated because the following alternative explanations for the formation of the unsymmetrical peroxide do not appear attractive [*cf.*, Kharasch, Friedlander, and Urry, *J. Org. Chem.* **14**, 93 (1949)].

1. $RO_2H + R_1\cdot \rightarrow RO_2\cdot + R_1H$
2. $RO_2\cdot + R_1\cdot \rightarrow RO_2R_1$

manner indicated in equation 4, leading to fairly good yields of either the symmetrical or an unsymmetrical peroxide. With cumene at 100° a lower yield of the symmetrical peroxide is obtained, while with ethylbenzene at 100° none of the unsymmetrical peroxide is formed.

A number of credible explanations, unfortunately none of them decisively indicated, might be suggested to account for the variation in products formed at different temperatures. These might include the instability at 100° of acetyl peroxide (resulting in suppression of reaction 4), or of the complex **A**, or of both, or to a predominance of reactions 5 and 6. Until more data are available it is profitless to speculate on these points.

TABLE I

EFFECTS OF TEMPERATURE AND SOLVENT ON RATE OF DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.5 G.) IN SEVERAL SOLVENTS (5 ML.) AS APPROXIMATED BY RATE OF EVOLUTION OF METHANE

SOLVENT	TEMPERATURE, (°C.)	CH_4 EVOLVED[b] (MOLE-%)	APPARENT HALF-LIFE (MIN.)[a]	
			Total Dec.	Initial Dec.
Dodecane	138.0	31	153	—
	147.5	33	120	150
	158.0	38	51	81
	168.0	40	23	66
Cumene	128.0	30	580	240
	158.0	46	43	62
Diisopropylcarbinol	137.0	68	54	54

[a] For reasons made clear in the preceding article (6) these values, arbitrarily calculated on the basis of first-order reactions, must be regarded merely as qualitatively indicative of relative reaction rates. [b] Methane was the only gaseous product formed in the reaction.

DECOMPOSITION OF α-CUMYL HYDROPEROXIDE IN SOLVENTS

The decomposition of α-cumyl hydroperoxide in (a) aliphatic hydrocarbons, (b) alkylated benzenes, (c) a secondary aralkyl alcohol, (d) a tertiary aliphatic alcohol, (e) a secondary aliphatic alcohol, (f) an olefin, and (g) organic acids was investigated (Tables I–VII).

These substances may be roughly divided into two classes. (*1*) Solvents in which no induced decomposition occurs (a, b). (*2*) Solvents in which an induced decomposition of α-cumyl hydroperoxide takes place (c, d, f, g). The evidence regarding the secondary aliphatic alcohol (e) is not clearcut.

The non-induced thermal decomposition of α-cumyl hydroperoxide. Any mechanism for the non-induced thermal decomposition of α-cumyl hydroperoxide in hydrocarbon solvents must take into account the following experimental facts: (a) the decomposition of α-cumyl hydroperoxide, although not first-order, is closer to first-order than to any other integral order (Table I); (b) the rate of decomposition varies considerably from solvent to solvent; (c) below 170° the rate of decomposition of α-cumyl hydroperoxide is appreciably slower than that of α-cumyl peroxide, or of *tert*-butyl α-cumyl peroxide, *tert*-butyl peroxide, or

TABLE II

PRODUCTS OF THE THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.1 MOLE) IN VARIOUS SOLVENTS (0.8 MOLE) (Except for high-boiling residues, yields are expressed in mole-%.)

SOLVENT (TEMP.)	CH_4	O_2	$CH_3COC_6H_5$	$C_6H_5(CH_3)_2COH$	C_6H_5OH	$(CH_3)_2CO$	H.-B. RES. (G.)
Decane (140°)	30.0	0.0[a]	20.0	54.0	0.7	0.7	6.2[b,c]
Cumene (128°)	32.0	.0	30.0	90.0	6.0	4.0[d]	4.5[c]
Cumene (158°)	46.0	.0	39.0	78.0	6.0	6.0	4.0[e]
Ethylbenzene (158°)	24.0	—	—	—	7.0	—	—
Diisopropylcarbinol (140°)	34.0[f]	—	34.0	59.0	—	—	1.0
α-Cumyl alcohol (170°)	63.0	7.0	—	—	—	—	—

[a] No oxygen was evolved in decane even at temperatures as high as 170°. [b] An acidic material (0.5 g.), probably aliphatic, was isolated from this residue. *Anal.* C, 65.2; H, 9.8. [c] All fractions boiling above 70°/16 mm. reduced lead tetraacetate in the cold. [d] Some of the acetone formed in this experiment may have been lost. [e] This residue was a mixture of bi-α-cumyl (1.2 g., 5%), resin (1.0 g.) and an oil distilling at 70–80°/0.01 mm. *Anal.* C, 82.1; H, 8.3; apparent mol. wt. (cryoscopic, benzene), 218. The oil undoubtedly contained some bi-α-cumyl. [f] The gas evolved in this experiment was not analyzed, but is reported as methane.

TABLE III

EFFECT OF ADDITIVES ON THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.1 MOLE) IN CUMENE (0.8 MOLE) AT 158°

ADDITIVE (MOLE-% ON BASIS OF HYDROPEROXIDE)	TIME OF 94% DECOMP'N (HRS.)	CH_4 EVOLVED (MOLE-%)	C_6H_5OH FORMED (MOLE-%)
None	3.0	46.0	6.0
α-Cumyl peroxide (2.0)	2.5	51.0	—
1,3,5-Trinitrobenzene (1.3)	3.5	5.5	—
Sodium salt of α-cumyl hydroperoxide (0.5)	—	47.0	0.3

TABLE IV

PRODUCTS OF THE THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.1 MOLE) IN SEVERAL ALCOHOLS AND IN 1-OCTENE AT 95–100° (Except for high-boiling residues, yields are expressed in moles × 10^{-1}.)

SOLVENT (MOLE)	CH_4	O_2	$CH_3COC_6H_5$	$C_6H_5(CH_3)_2COH$	PEROXIDES	H.-B. RES. (G.)
α-Cumyl alcohol (0.15)	—	0.07	0.25	—	0.50	1.2
tert-Amyl alcohol (0.24)	0.02	.15	.26	0.39	.05[a]	3.8[b]
α-Phenylethanol (0.17)	.02	.15	.70	.55	—	0.6
1-Octene (0.18)	—	.06	.25	.50	Trace	10.0[c]

[a] α-Cumyl peroxide (0.02 × 10^{-1} mole) and *tert*-amyl α-cumyl peroxide (0.03 × 10^{-1} mole) were detected. The former was isolated in crystalline form; the latter was estimated by iodometric titration (9) of the fraction distilling at 70–100°/12.0 mm. [b] This oil had an apparent molecular weight (cryoscopic, benzene) of 297. [c] This oil had an apparent molecular weight (cryoscopic, benzene) of 332; n_D^{21} 1.4732.

tert-butyl triphenylmethyl peroxide (6); (d) the thermal decomposition of α-cumyl hydroperoxide at 158° in dodecane, decane, cumene, or ethylbenzene is probably not a chain reaction, or any chains initiated are very short;[5] (e) thermal cleavage of the hydroperoxide into ions does not occur to any appreciable extent (note non-formation of phenol and acetone in decane and dodecane, and the

TABLE V

RATE OF THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.1 MOLE) IN SEVERAL ALCOHOLS AT 95–100° AND IN 1-OCTENE AT 103°

SOLVENT (MOLE)	DECOMP'N IN 48 HRS., %.
α-Phenylethanol (0.17)	70.0
tert-Amyl alcohol (0.24)	75.0
1-Octene (0.18)	86.0
α-Cumyl alcohol (0.14)	75.0
α-Cumyl alcohol (0.14) + 1% alkali	14.0
α-Cumyl alcohol (0.14) + 2% α-cumyl chloride	(80.0)[a]

[a] Reaction temperature, 90°; reaction time, 2.5 hrs.

TABLE VI

EFFECT OF ADDITIVES ON THE PRODUCTS OF THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.1 MOLE) IN CARBOXYLIC ACIDS AT 93–98° (Except for high-boiling residues, yields are expressed in moles × 10^{-1}.)

ACID (MOLE) + ADDITIVE (MOLE) × 10^{-3}	DE-COMP'N TIME (HRS.)	O_2	C_6H_5OH	$CH_3CO_2C_6H_5$	$CH_3COC_6H_5$	$CH_3(C_6H_5)C=CH_2$ + $C_6H_5(CH_3)_2COH$[a]	$[C_6H_5(CH_3)_2CO\text{-}]_2$[b]	H.-B. RES. (G.)
Niacet acetic (0.30)	2	0.00	0.27	0.00	—	—	0.180	0.2
Cryst'd acetic (0.30)	1	.00	.78	.00	0.03	0.007	.095	.1
Cryst'd acetic (0.37) + H_2O (70.0)	3	.015	.82	.00	—	.050	.010	1.0
Cryst'd acetic (0.50) + NaAc (3.0)	11	.08	.39	.07	.08	.200	—	2.0[c]
Cryst'd acetic (0.30) + $C_6H_5(CH_3)_2COH$ (5.0)	6	.03	.42	—	.02	.100	.060	2.0
Cryst'd acetic (0.30) + Aldol (0.6)	—	—	.59	—	.027	—	.185	—
Benzoic (1.23)[d]	20	—	.30	—	.060	.120	.200	0.3

[a] These products were determined jointly by conversion to the olefin-thioglycolic acid adduct (1). [b] Note that one mole of α-cumyl peroxide is equivalent to two moles of α-cumyl hydroperoxide. [c] *Anal.* C, 81.0; H, 7.7; apparent mol. wt. (cryoscopic, benzene), 325. [d] This decomposition was carried out at 105°.

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[5] This conclusion is based on the observation that the rate of decomposition of α-cumyl hydroperoxide is not altered by the addition of α-cumyl peroxide, a compound which breaks down into free α-cumyloxy radicals at 140° (Table III).

relatively small amount of phenol formation in cumene and ethylbenzene—Table II); (f) oxygen is not present among the reaction products (therefore intermolecular oxidation-reduction is not a contributary factor in the decomposition of the hydroperoxide); (g) methane, acetophenone, and "dimeric" products are formed (presumably, therefore, free radicals are formed during the decomposition of this hydroperoxide).

A reaction scheme (II) consistent with the observations cited, and with the relative amounts of the various reaction products isolated (Table II), for the decomposition of α-cumyl hydroperoxide in cumene is proposed in equations 8–14. Three simultaneous modes of decomposition [8, 9, and 10], varying in importance, are postulated.

TABLE VII

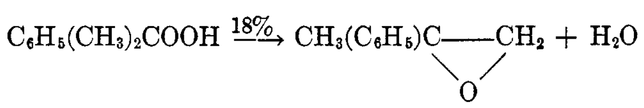
EFFECTS OF TEMPERATURE AND DILUTION ON PRODUCTS OF THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE (0.1 MOLE) IN ACETIC ACID (Except for high-boiling residues, yields are expressed in moles × 10^{-1}.)

AMOUNT ACID (MOLES)	DECOMP'N TEMP. (°C.)	TIME OF DECOMP'N (HRS.)	C_6H_5OH	$CH_3COC_6H_5$	$[C_6H_5(CH_3)_2CO-]_2$	H.-B. RES. (G.)
0.40	74–78	20.0	0.84	0.00	0.05	0.2
.30	93–98	1.0	.78	.03	.10	.1
.35	104–106	0.7	.69	.05	.10	.3
6–30[a]	117	48.0	.45	.40	—	1.7
0.12	93–98	5.0	.80	—	—	—
.065	93–98	7.0	—	—	—	—

[a] An acetic acid solution of the hydroperoxide was slowly dropped into boiling acetic acid. In a dilution of 1:300 the hydroperoxide appears to be thermally stable in the temperature range here investigated.

REACTION SCHEME II

8. $C_6H_5(CH_3)_2C{-}OOH \xrightarrow[{[+C_6H_5(CH_3)_2CH]}]{45\%} 2\ C_6H_5(CH_3)_2COH$

9. 

$$C_6H_5(CH_3)_2COOH \xrightarrow{18\%} CH_3(C_6H_5)\underset{\diagdown\ O\ \diagup}{C{-}{-}CH_2} + H_2O$$

10. $C_6H_5(CH_3)_2COOH \xrightarrow{30\%} C_6H_5(CH_3)_2CO\cdot + HO\cdot$

11a. $C_6H_5(CH_3)_2CO\cdot \rightarrow CH_3COC_6H_5 + CH_3\cdot$

11b. $CH_3\cdot + C_6H_5(CH_3)_2CH \rightarrow CH_4 + C_6H_5(CH_3)_2C\cdot$

12. $HO\cdot + C_6H_5(CH_3)_2CH \rightarrow H_2O + C_6H_5\ (CH_3)_2C\cdot$

13. $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2CH \rightarrow C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\cdot$

14. $2\ C_6H_5(CH_3)_2C\cdot \rightarrow [C_6H_5(CH_3)_2C{-}]_2$

The over-all process indicated for the sake of simplicity by equation 8 should not be interpreted as necessarily implying a bimolecular reaction of α-cumyl hydroperoxide with cumene. The authors are somewhat more inclined to the assumption that the process is initiated by α-cumyl radicals originating in such reactions as those indicated by equations 11b, 12, and 13.

8a. $C_6H_5(CH_3)_2COOH + C_6H_5(CH_3)_2C\cdot \rightleftharpoons$ Complex **A**

8b. Complex **A** $+ C_6H_5(CH_3)_2CH \rightarrow 2\ C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\cdot$

Reaction 8a is probably reversible. The higher the temperature the less the tendency toward complex formation, and the greater tendency toward the formation of bi-α-cumyl, which is formed in negligible amounts at lower temperatures (100°). Without the use of labelled molecules it is impossible to assess the relative importance of the various reactions in the over-all decomposition. The role played by complex **A** might be ascertained by determining whether or not the bi-α-cumyl (or its equivalent) formed contains a labelled group originally present in the α-cumyl hydroperoxide.

The heavy oils formed in these reactions probably arise from an attack on the readily available hydrogen atoms of the epoxide by free hydroxy, free α-cumyloxy, or free methyl radicals.[6]

An interpretation similar to the one outlined for the decomposition of α-cumyl hydroperoxide in cumene accounts satisfactorily for the decomposition of this hydroperoxide in decane and dodecane.

The formation of small, but equimolecular, amounts of phenol (6%) and acetone (6%), when α-cumyl hydroperoxide is decomposed in cumene at 128° and 158° (Table II), indicates a common origin for these products. [In this respect the results of the present study differ significantly from those reported by Fordham and Williams (5) (who isolated 10% phenol and 65% acetone)]. The tempting hypothesis that, despite the rigorous purification, the reagents contain traces of acidic impurities is rendered less plausible by the fact that in decane and dodecane only traces of phenol (0.7%) are formed. The α-cumyl hydroperoxide used was carefully purified to remove traces of acidic impurities, and the cumene was washed with a base, or refluxed for three hours over metallic sodium. If this treatment may be accepted as assurance of the absence of extraneous acid, it appears a necessary conclusion that in alkylated benzenes with labile hydrogen atoms reaction 15, followed by 16, takes place to a *minor extent.*

15. $C_6H_5(CH_3)_2C\text{—}OOH \rightarrow [C_6H_5(CH_3)_2CO]^+ + (OH)^-$

16. $\underset{\mathbf{B}}{[C_6H_5(CH_3)_2CO]^+} \xrightarrow{\text{rearrangement}} \underset{\mathbf{C}}{[C_6H_5O(CH_3)_2C]^+}$

The cation **C** is capable of participating in a chain reaction with α-cumyl hydroperoxide to give phenol and acetone. In support of this hypothesis it is found that if traces of alkali (such as the sodium salt of α-cumyl hydroperoxide) are added to cumene the decompositon of the α-cumyl hydroperoxide in that

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[6] The formation of an epoxide, according to reaction 10, is postulated because the reaction products react in the cold with lead tetraacetate.

mixture gives only traces of phenol and acetone (Table III). The base may be considered here as a powerful competitor for the carbonium ion **C**.

THE INDUCED THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE IN CARBINOLS AND OLEFINS

α-Cumyl hydroperoxide decomposes at a measurable rate at 90–100° in *tert*-amyl alcohol, α-cumyl alcohol, α-phenylethanol, and 1-octene (Table V). The products of decomposition in the above solvents are oxygen, acetophenone, α-cumyl alcohol, variable amounts of peroxides, traces of methane (much less than acetophenone), and high-boiling oils, the natures of which depend upon the solvents (Table IV).

The following facts are pertinent to a logical interpretation of the data recorded in Table IV. (a) α-Cumyl hydroperoxide decomposes to the extent of 95% when heated in α-cumyl alcohol for 72 hours at 95°. (b) The addition of as little as one percent of the sodium salt of α-cumyl hydroperoxide decreases tremendously the rate of decomposition in α-cumyl alcohol. Thus, after 48 hours only about 14% decomposition had taken place (Table V). (c) The addition of α-cumyl chloride (2%), enhances the decomposition of α-cumyl hydroperoxide in α-cumyl alcohol (80% in 2.5 hours) with formation of the following products: α-cumyl peroxide (0.54 mole per mole of α-cumyl hydroperoxide); a high-boiling oil (probably the dimer of α-methylstyrene) (16%); oxygen (2%); and traces of phenol. No acetophenone is formed in this reaction.

These data (on the thermal decomposition of the α-cumyl hydroperoxide in carbinols and in 1-octene) may best be interpreted by assuming that the decomposition occurs in two mutually independent ways. The first [17–19] accounts for the formation of peroxides (diperoxides), acetophenone, some of the α-cumyl alcohol, and the products arising from attack on the solvent. The second [20] accounts for the formation of equivalent amounts of oxygen and α-cumyl alcohol.

In the first case the initial reaction is the formation of a peroxide by interaction of the hydroperoxide with the solvent.

17a. $C_6H_5(CH_3)_2C—OOH \xrightarrow{C_6H_5(CH_3)_2COH} [C_6H_5(CH_3)_2CO\cdot]_2$

The peroxide is less stable than α-cumyl hydroperoxide and at the prevailing temperatures breaks down slowly into alkoxy radicals.

17b. $[C_6H_5(CH_3)_2C—O\cdot]_2 \rightarrow 2\ C_6H_5(CH_3)_2CO\cdot$

The decomposition of the hydroperoxide is, therefore, induced by the decomposition of the peroxide, and is not a primary breakdown of the hydroperoxide into free radicals. The alkoxy radicals start a sequence of reactions the nature of which varies somewhat from solvent to solvent (depending upon whether the peroxide first formed is symmetrical or not). Specifically, the α-cumyloxy radicals, may initiate either of the following chain reactions (4):

18. $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2C—OOH$

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

19a. $C_6H_5(CH_3)_2CO\cdot + RH \rightarrow R\cdot + CH_4 + CH_3COC_6H_5$

19b. $C_6H_5(CH_3)_2CO\cdot + RH \rightarrow R\cdot + C_6H_5(CH_3)_2COH$

Reactions 19a, b would take place most readily in solvents such as α-phenylethanol, which have readily available hydrogen atoms, while reaction 18 would predominate in solvents similar to α-cumyl alcohol, in which the hydrogen atoms are not readily available.

The free radicals (R·) formed in 19 would attack the hydroperoxide further. Those formed by abstraction of a hydrogen atom from α-phenylethanol [$HO(CH_3)(C_6H_5)C\cdot$] react with α-cumyl hydroperoxide to give acetophenone and an α-cumyloxy radical (see Scheme I). Other radicals, *e.g.*, those derived by abstraction of a hydrogen atom from *tert*-amyl alcohol {$CH_3[HO(CH_3)_2C]CH\cdot$}, may interact with α-cumyl hydroperoxide to give an unsymmetrical peroxide (see Scheme I).

It is postulated that peroxides are initially formed from hydroperoxides (see equation 17) by an ionic, and not free-radical, mechanism. In support of this view it may be cited that the addition of a small amount of α-cumyl chloride to α-cumyl hydroperoxide in α-cumyl alcohol increases the rate of formation of peroxide[7], and that small amounts of alkali profoundly decrease the rate of thermal decomposition of the hydroperoxide in carbinols at 100° {note that α-cumyl chloride would tend to give rise to a large concentration of carbonium ions, $[C_6H_5(CH_3)_2C]^+$, while alkali would have the opposite effect}.

The decomposition of the α-cumyl hydroperoxide into oxygen and α-cumyl alcohol (second mechanism), in the absence of metal catalysts takes place, in the opinion of the present authors, only when basic materials are present. Carbinols may be regarded as the bases, for, under the experimental conditions imposed, they participate in the following equilibrium:

20. $C_6H_5(CH_3)_2C{-}OOH + C_6H_5(CH_3)_2COH$

$$\rightleftharpoons [C_6H_5(CH_3)_2C{-}OO]^- + [C_6H_5(CH_3)_2COH_2]^+\cdot$$

The presence of this anion in the reaction medium is an important contributor to the evolution of oxygen (perhaps by an intermolecular oxidation-reduction with the hydroperoxide).[2] Oxygen evolution in carbinols as solvents occurs to some extent even at 170°, where the major part of the hydroperoxide decomposes in a manner similar to that occurring in hydrocarbon solvents. Diisopropyl carbinol (when used as a solvent) is apparently not sufficiently basic to initiate formation of an unsymmetrical peroxide with α-cumyl hydroperoxide. Therefore, the decomposition in that solvent is not an induced decomposition, and follows first-order kinetics (Tables I and III). For this reason, the hydroperoxide is more stable in that solvent. No measurable decomposition sets in until 140°. In this respect diisopropyl carbinol resembles in its behavior the hydrocarbon class of solvents rather than the *tert*-alkyl alcohols.

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[7] The formation of oxygen (2% in this instance) could arise from hydrolysis of the hydroperoxide and decomposition of the hydrogen peroxide thus formed.

The decomposition of α-cumyl hydroperoxide in 1-octene is described in Tables IV and V. This reaction takes place at 103°, a temperature at which the hydroperoxide is thermally stable in saturated hydrocarbons (decane, cumene, etc.). The authors are inclined to the view that this also is an induced decomposition, involving the intermediate formation of peroxide (in a manner analogous to that illustrated for the *tert*-alkyl alcohols, except that 1-octene here serves as the proton acceptor).

For the sake of simplicity the reaction scheme (III) postulated is illustrated specifically for the decomposition of α-cumyl hydroperoxide in α-phenylethanol (reactions 21–29). The choice of α-phenylethanol is dictated by the consideration that in this case all products have been isolated, identified, and quantitatively determined.

REACTION SCHEME III

The Decomposition of α-Cumyl Hydroperoxide in α-Phenylethanol at 100°

21. $C_6H_5(CH_3)_2C\text{—}OOH + CH_3(C_6H_5)CHOH$

(acid) (base)

$\rightleftharpoons [C_6H_5(CH_3)_2C\text{—}OO]^- + [CH_3C_6H_5CHOH_2]^+$

(conjugate base **D**) (Conjugate acid **E**)

22. $\mathbf{D} + C_6H_5(CH_3)_2C\text{—}OOH$

$\xrightarrow{30\%} C_6H_5(CH_3)_2COH + O_2 + [C_6H_5(CH_3)_2CO]^-$

23. $\mathbf{E} + C_6H_5(CH_3)_2C\text{—}OOH \rightarrow C_6H_5(CH_3)_2C\text{—}OO\text{—}CH(CH_3)C_6H_5 + H_3O^+$

24. $C_6H_5(CH_3)_2C\text{—}OO\text{—}CH(CH_3)C_6H_5 \rightarrow C_6H_5(CH_3)_2CO\cdot + CH_3(C_6H_5)CHO\cdot$

25. $CH_3(C_6H_5)CHO\cdot + C_6H_5(CH_3)_2C\text{—}OOH$

$\rightarrow CH_3COC_6H_5 + H_2O + C_6H_5(CH_3)_2CO\cdot$

26. $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2C\text{—}OOH$

$\xrightarrow{43\%} CH_3COC_6H_5 + CH_3OH + C_6H_5(CH_3)_2CO\cdot$

27a. $C_6H_5(CH_3)_2CO\cdot + CH_3(C_6H_5)CHOH$

$\xrightarrow{25\%} C_6H_5(CH_3)_2COH + HO(CH_3)(C_6H_5)C\cdot$

27b. $C_6H_5(CH_3)_2CO\cdot + CH_3(C_6H_5)CHOH$

$\xrightarrow{2\%} CH_3COC_6H_5 + CH_4 + HO(CH_3)(C_6H_5)C\cdot$

28. $HO(CH_3)(C_6H_5)C\cdot + C_6H_5(CH_3)_2C\text{—}OOH$

$\rightarrow CH_3COC_6H_5 + H_2O + C_6H_5(CH_3)_2CO\cdot$

29. $2\ HO(CH_3)(C_6H_5)C\cdot \rightarrow CH_3COC_6H_5 + CH_3(C_6H_5)CHOH$

It is important to point out here that the decomposition of α-cumyloxy radicals (derived from α-cumyl peroxide) in saturated hydrocarbons gives rise to equal quantities of acetophenone and methane. However, in the presence of added hydroperoxides (below 120°), this relationship does not hold, for under these conditions the α-cumyloxy radicals participate with the hydroperoxide in a chain reaction leading to acetophenone and methanol (equation 26). At higher temperatures (140° and above), the α-cumyloxy radicals are unstable; therefore, even in the presence of hydroperoxide equal quantities of methane and acetophenone are again produced.

THE INDUCED THERMAL DECOMPOSITION OF α-CUMYL HYDROPEROXIDE IN ACETIC AND BENZOIC ACIDS

Pure α-cumyl hydroperoxide, dissolved in glacial acetic acid (crystallized two or three times), is stable at room temperature. At higher temperatures (80–90°) decomposition occurs. A satisfactory elucidation of this decomposition must take into consideration not only the identities and relative yields of the reaction products [phenol, 78%; acetone, 78%; acetophenone, 3%; α-cumyl peroxide, 19.0%; and α-methylstyrene, 0.7% (Table VI)], but the following additional observations (Table VI). (a) Aldol (in small amounts) doubles the yield of the peroxide (from 19% to 32%). (b) Sodium acetate (3% on the basis of the α-cumyl hydroperoxide) lowers the rate of decomposition and decreases the yield of phenol (from 78% to 39%). In addition, small amounts (7%) of phenyl acetate, a new product for this reaction, and oxygen (8%) are formed, and the yield of α-methylstyrene is increased from 0.7% to 20%. (c) α-Cumyl alcohol (5% on the basis of α-cumyl hydroperoxide) decreases the phenol yield to half of its former value, and the yields of oxygen and α-methylstyrene are increased.[8] (d) The rate of decomposition of α-cumyl hydroperoxide in glacial acetic acid depends on the concentration (Table VII). In very dilute solution (1:300) the hydroperoxide appears to be stable even at the boiling point of acetic acid. (e) The decomposition of α-cumyl hydroperoxide in acetic at 70° gives an insignificant amount of acetophenone.

Since pure α-cumyl hydroperoxide is stable in saturated hydrocarbons up to 130°, its decomposition in solvents at lower temperatures must be an induced reaction, and in view of the dilution effect (see 4 above), the induced decomposition must be a chain reaction. The observations cited in the foregoing summary (a–e) are readily accounted for on the basis of the assumption that the decomposition of α-cumyl hydroperoxide in acetic acid at elevated temperatures follows two distinct paths: (*a*) a decomposition induced by free radicals and (*b*) an acid-catalyzed decomposition. It is postulated that the initial reaction in process *a* is the formation of α-cumyl peroxide or α-cumyl peracetate by an ionic mechanism (equation 30.) These compounds may break down at 90° and above into α-cumyloxy and acetoxy free radicals. The α-cumyloxy radicals initiate a chain reaction as indicated in Scheme IV, reaction 37. In the acid-catalyzed decomposition (*b*) the cumyloxy cations, $[C_6H_5C(CH_3)_2O]^+$, are the chain carriers.

[8] With sodium acetate or α-cumyl alcohol as additives high-boiling oils are formed.

These cations may be formed from the peracetate as indicated in Scheme IV, reaction 31, or in some other manner.

REACTION SCHEME IV

Decomposition of α-Cumyl Hydroperoxide in Acetic Acid

30. $C_6H_5(CH_3)_2C{-}OOH + CH_3CO_2H \rightleftharpoons C_6H_5(CH_3)_2C{-}OO{-}C({=}O)CH_3 + H_2O$

31. $C_6H_5(CH_3)_2C{-}OO{-}C({=}O)CH_3 \xrightarrow{> 70^\circ} [C_6H_5(CH_3)_2CO]^+ + CH_3CO_2^-$

32. $[C_6H_5(CH_3)_2CO]^+ \rightarrow [C_6H_5O(CH_3)_2C]^+$

33. $[C_6H_5O(CH_3)_2C]^+ + C_6H_5(CH_3)_2C{-}OOH \rightarrow C_6H_5OH + CH_3COCH_3 + [C_6H_5(CH_3)_2CO]^+$

34. $[C_6H_5(CH_3)_2C]^+ + C_6H_5(CH_3)_2C{-}OOH \rightarrow [\text{Complex } \mathbf{F}]^+$

35. $[\text{Complex } \mathbf{F}]^+ + C_6H_5(CH_3)_2C{-}OOH \rightarrow [C_6H_5(CH_3)_2CO{-}]_2 + [C_6H_5(CH_3)_2C]^+ + H_2O_2$

36. $C_6H_5(CH_3)_2C{-}OO{-}C({=}O)CH_3 \xrightarrow{> 90^\circ} C_6H_5(CH_3)_2CO\cdot + CH_3CO_2\cdot$

37. $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2C{-}OOH \rightarrow CH_3COC_6H_5 + CH_3OH + C_6H_5(CH_3)_2CO\cdot$

Several equally plausible schemes may be written for the formation of carbonium ion, $[C_6H_5(CH_3)_2C]^+$, and no choice among them is here made on the basis of the inadequate data available. Equations 34 and 35 merely convey the essential fact that the peroxide is formed by the attack of a carbonium ion on the hydroperoxide.

Obviously, such a scheme, involving ionic species, would be most sensitive to acid-base catalysis.[9] The additives, therefore, influence the reaction insofar as they are potentially acids or bases in acetic acid. Thus, sodium acetate interferes with the chain-propagating step in equation 33 (decreasing the yield of phenol from 78 to 39%) because the acetate ion can react with rearranged carbonium ion, $[C_6H_5O(CH_3)_2C]^+$, to give phenyl acetate, a product actually isolated (7%), under these and no other conditions.

38. $[C_6H_5OC(CH_3)_2]^+ + CH_3COO^- \rightarrow C_6H_5OCOCH_3 + CH_3COCH_3$

An increase of oxygen evolution (8%) is also to be noted in this instance, because of the possibility of forming, under these conditions, the anion of α-cumyl hydroperoxide (see the preceding discussion of the decomposition of this anion).

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[9] The influence of strong acids on the decomposition of α-cumyl hydroperoxide has been discussed in a previous paper (1).

The increase in the yield of α-cumyl alcohol and α-methylstyrene (20%, instead of 0.7% without this additive) is attributable to the reaction that gives rise to the increased oxygen evolution and to no other cause.

Furthermore, bases (in acetic acid), such as α-cumyl alcohol and aldol decrease appreciably (by about one half) phenol formation when present in small quantities. Larger quantities of cumyl alcohol completely suppress the formation of phenol.

EXPERIMENTAL PART

Reagents. α-Cumyl hydroperoxide. To a cooled (0°) solution of 200 g. of commercial α-cumyl hypdroperoxide in 200 ml. of low-boiling ligroin, 160 ml. of a cooled 25% aqueous solution of sodium hydroxide was added. The sodium salt, which separated, was washed thoroughly with 100 ml. of 25% sodium hydroxide solution and then with a large amount of low-boiling ligroin (7). This salt was then suspended in ligroin, and the hydroperoxide was liberated by treatment either with carbon dioxide or with less than an equivalent amount of acetic acid. The ligroin layer was thoroughly washed with water and then distilled. α-Cumyl hydroperoxide distills at 60°/0.1 mm. It must be emphasized that mineral acids as well as sodium hydroxide are very soluble in α-cumyl hydroperoxide. In order to eliminate the last traces of acids a thorough washing of the ligroin extract with bicarbonate is usually necessary. In order to free it from alkaline impurities it must be distilled.

Commercial *cumene* was shaken with 5% aqueous sodium hydroxide solution and was then carefully distilled. An alkaline wash is absolutely necessary to free the cumene from acidic impurities.

Commercial *ethylbenzene* was carefully fractionated and was stored over anhydrous potassium carbonate. It was redistilled immediately prior to use.

Commercial *decane and dodecane* (The Connecticut Hard Rubber Company) were distilled prior to use.

A carefully distilled sample of *diisopropylcarbinol* was used.

The sample of *α-cumyl alcohol* used was crystallized several times from ligroin (m.p., 36°).

α-Phenylethanol was prepared as previously described (1).

tert-Amyl alcohol and 1-octene were carefully distilled prior to use.

The same results were observed with *glacial acetic acid* obtained from the General Chemical Company and with acetic acid that had been crystallized several times.

Kinetic studies. The temperature was kept constant within half a degree. Gas was collected over saturated aqueous sodium chloride solution. All rate studies are carried out in an atmosphere of nitrogen gas.

Analysis of reaction products. The gases formed in the reaction were analyzed as described previously (4). For oxygen absorption Fieser's solution was used.

Acetophenone was determined by the method of Kharasch and Cooper (8).

α-Cumyl alcohol and *α-methylstyrene* were determined after conversion to the olefin-thioglycolic acid adduct (1).

Peroxides were determined by dissolving a sample of the material in a mixture of glacial acetic acid (5 ml.) and hydriodic acid (5 ml.; sp. gr., 1.7). The reaction vessel was flushed with nitrogen gas and kept at 60–70° for 45 minutes. The sample mixture was then diluted with 50 ml. of isopropanol and was titrated with 0.1 N aqueous sodium thiosulfate solution (9).

Phenol was converted to tribromophenol.

Acetone was estimated on the basis of its iodoform equivalent.

Phenyl acetate was estimated on the basis of the phenol, liberated upon saponification of the neutral fraction of the reaction product.

The decomposition of α-cumyl hydroperoxide in carbinols was followed by iodometric titration (10).

The reduction of α-cumyl hydroperoxide with sodium bisulfite. One mole of α-cumyl hydroperoxide was added over a period of 12 hours to 1.2 moles of 20% aqueous sodium bisulfite solution. Petroleum ether was then added, the organic layer was thoroughly washed with water, and the solvent removed. The residue (130 g.) was α-cumyl alcohol, which contained 15.5% acetophenone. The α-cumyl alcohol was purified by crystallization from petroleum ether at −80°. The melting point of the α-cumyl alcohol thus obtained was 36°.

The reduction of α-cumyl hydroperoxide with sodium bisulfite in the presence of styrene. A solution of α-cumyl hydroperoxide (0.1 mole) in styrene (0.4 mole) was dropped, over a period of 16 hours, into a stirred mixture of styrene (0.4 mole) and sodium bisulfite (0.4 mole, 25% aqueous solution). The reaction was carried out in an atmosphere of nitrogen gas. At the completion of the reaction, ether was added, and the organic layer was isolated, dried, and distilled. α-Cumyl alcohol (0.05 mole), contaminated with a trace of acetophenone, was thus obtained.

The distillation residue (8 g.) is probably a polymer of styrene containing some α-cumyloxy radicals. It is insoluble in alcohol and petroleum ether, but soluble in benzene and ethyl acetate.

Anal. C, 83.9; H, 7.5; apparent mol. wt. (cryoscopic, benzene), 2600.

The aqueous layer was treated in the manner described by Kharasch, Schenck, and Mayo (11). The products isolated were: sodium α-phenylethanesulfonate (37%), and sodium α-hydroxy-α-phenylethanesulfonate (52%) (It was shown by permanganate titration that the latter product contained less than 5% of sodium α-phenylethylenesulfonate).

The formation of the styrene-bisulfite adducts suggests that the reduction of the hydroperoxide by the bisulfite anion takes place through a one-electron transfer (11).

SUMMARY

1. The thermal decomposition of α-cumyl hydroperoxide in saturated hydrocarbon solvents proceeds at a measurable rate only above 130°, and is not an induced decomposition. It is suggested that the thermal decomposition of α-cumyl hydroperoxide in these solvents takes place in a number of ways: (*a*) by breakdown into free α-cumyloxy and free hydroxyl radicals; (*b*) by two-electron oxidation of the solvent; (*c*) by intramolecular breakdown into α-methylstyrene oxide and water. Schemes *a*, *b*, and *c* are not of equal importance, and are not necessarily independent of one another.

2. In tertiary alcohols, olefins, and organic acids, induced thermal decomposition of α-cumyl hydroperoxide takes place at relatively low temperatures (70–90°). The processes responsible for the induced decomposition are as follows: (*a*) intermediate formation of peroxide, which is thermally less stable than the hydroperoxide and breaks down into free alkoxy radicals, which in turn initiate a chain reaction with α-cumyl hydroperoxide; (*b*) formation (under alkaline conditions) of the anion $[C_6H_5(CH_3)_2C{-}OO]^-$, which is an intermediate in the intermolecular oxidation-reduction of α-cumyl hydroperoxide, leading to the formation of oxygen and α-cumyl alcohol; (*c*) formation (under acidic conditions) of the cation $[C_6H_5(CH_3)_2CO]^+$, which initiates a chain reaction leading to the formation of phenol and acetone. Schemes *a*, *b*, and *c* may be made to proceed independently of one another.

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