

THE CHEMISTRY OF HYDROPEROXIDES. V. THE THERMAL DECOMPOSITION OF *tert*-ALKYL PEROXIDES

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Received July 31, 1950

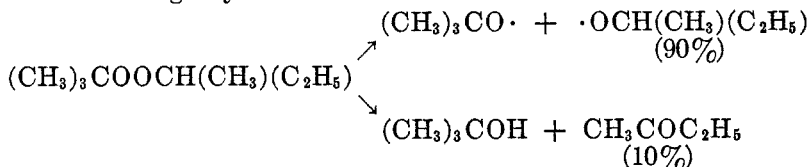
## INTRODUCTION

A great deal of work has been done in this laboratory on the chemistry of hydroperoxides, including the thermal decomposition of these substances in solvents. Because, in some instances, for an adequate explanation of the observed results it is necessary to assume the intermediate formation of peroxides, an examination of the thermal behavior of some peroxides became necessary. The peroxides investigated were  $\alpha$ -cumyl peroxide and *tert*-butyl  $\alpha$ -cumyl peroxide.<sup>1</sup>

## PREVIOUS WORK

Raley, Rust, and Vaughan (1) found that the decomposition of *tert*-butyl peroxide is a first-order reaction, and that its rate is nearly independent of concentration or of the solvent used. The products of decomposition of this peroxide were: *tert*-butyl alcohol, acetone, and methane, the relative amounts of which varied from solvent to solvent.

These authors concluded that the initial reaction (and rate-determining step) is a breakdown of the peroxide into two free *tert*-butoxy radicals. The activation energy determined for this reaction in different solvents was 37,500–39,100 cal. The ratio of acetone to *tert*-butyl alcohol, in a given solvent, increased with increasing temperature, indicating, according to these authors, that "with increasing temperature the *tert*-butoxyl radicals become more subject to loss of methyl rather than abstraction of hydrogen atoms from solvents". Rust, Seubold, and Vaughan (2) studied the decomposition of *tert*-butyl alkyl peroxides in cyclohexene (in the vapor phase) at 195°. They assume that the ratio of acetone to *tert*-butyl alcohol formed from free *tert*-butoxy radicals is independent of the origin of *tert*-butoxy radicals. To account for the ketone-alcohol ratio, they assume that *tert*-butyl *sec*-butyl peroxide (and *tert*-butyl *n*-butyl peroxide) decompose in the following way:



However, no rate studies were made to prove that the decomposition of these unsymmetrical peroxides in cyclohexene follows first-order kinetics.

<sup>1</sup>The thermal decompositions of *tert*-butyl triarylmethyl peroxides have also been studied in this laboratory and will be reported later.

## PRESENT WORK

The present authors decomposed *tert*-butyl  $\alpha$ -cumyl peroxide,  $\alpha$ -cumyl peroxide, and *tert*-butyl triphenylmethyl peroxide in a variety of solvents. The rates

TABLE I  
KETONE-ALCOHOL MOLE RATIOS IN PRODUCTS ARISING FROM THE ATTACK OF FREE ALKOXY RADICALS FROM DIFFERENT SOURCES ON CUMENE AT 138°

RADICAL AND SOURCE	KETONE/ALCOHOL RATIO
<i>tert</i> -C <sub>4</sub> H <sub>9</sub> O· from <i>tert</i> -C <sub>4</sub> H <sub>9</sub> OOC(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.15
<i>tert</i> -C <sub>4</sub> H <sub>9</sub> O· from ( <i>tert</i> -C <sub>4</sub> H <sub>9</sub> O—) <sub>2</sub>	.50
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CO· from [C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CO—] <sub>2</sub>	1.40
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CO· from <i>tert</i> -C <sub>4</sub> H <sub>9</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3.00

TABLE II  
EFFECTS OF TEMPERATURE AND SOLVENT ON RATES OF DECOMPOSITION OF ALKYL PEROXIDES IN VARIOUS SOLVENTS

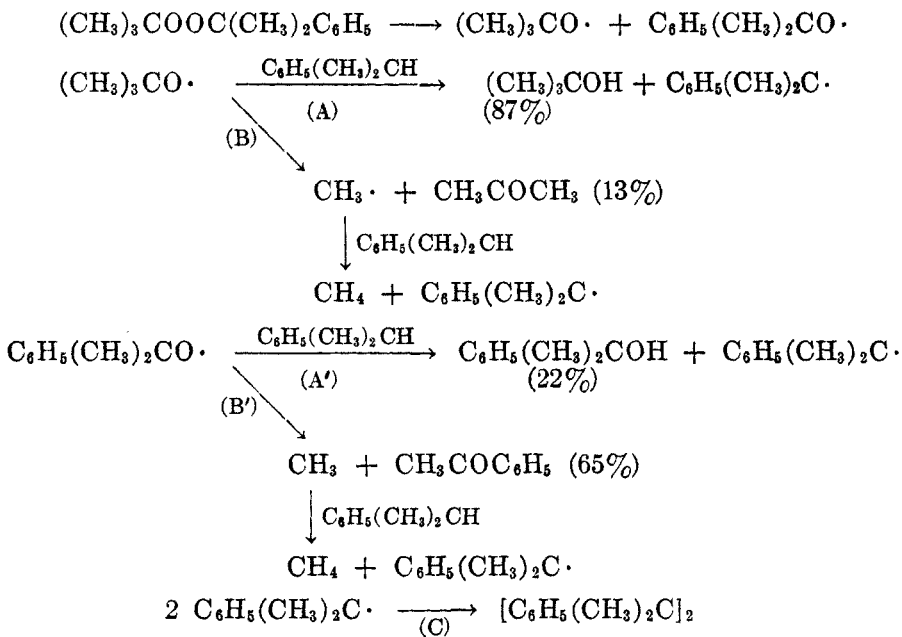
PEROXIDE (2.0 mmoles) SOLVENT (5.0 ml.)	TEMPERATURE (°C. $\pm$ 0.5°)	CH <sub>4</sub> EVOLVED (Mole-% $\pm$ 2%)	HALF-LIFE (Minutes $\pm$ 5%)
<u><i>tert</i>-C<sub>4</sub>H<sub>9</sub>OOC(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub></u>			
Dodecane	128.0	66	260.0
	138.0 <sup>a</sup>	71 <sup>a</sup>	83.0 <sup>a</sup>
	147.5	88	36.0
	158.0	95	13.0
Cumene	138.0	92	80.0
	158.0	108	13.0
<i>tert</i> -Butylbenzene	138.0	103	78.0
	158.0	110	12.0
<u>[C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>CO—]<sub>2</sub></u>			
Dodecane	128.0	70	132.0
	138.0	75	50.0
	147.5	88	21.5
	158.0	95	6.3
Cumene	138.0	108	45.0
	158.0	123	7.6
<i>tert</i> -Butylbenzene	158.0	—	6.7
Diisopropylcarbinol	138.0	148	36.6

<sup>a</sup> The same results were obtained when a large amount of glass wool was inserted into the reaction flask.

of decomposition of these peroxides (temperature dependence) and the reaction products were studied. In all cases, the rates of decomposition of *tert*-butyl  $\alpha$ -cumyl peroxide, and of  $\alpha$ -cumyl peroxide were first-order (decomposition carried

out to 97%) (Table II). The rates were nearly independent of the solvent used and there was no surface effect. Furthermore, when  $\log k$  was plotted against  $1/T$  (between 128–158°) a straight line was obtained. The gas evolved in all cases was pure methane. (No oxygen or ethane was formed, or at most only negligible quantities.) However, the ratio of ketone to alcohol varied from solvent to solvent (Table III), and increased with increase in temperature. The activation energy in dodecane as a solvent was 35 kcal. for *tert*-butyl  $\alpha$ -cumyl peroxide, and 33.5 kcal. for  $\alpha$ -cumyl peroxide (see Table II).

The products formed when *tert*-butyl  $\alpha$ -cumyl peroxide is decomposed in cumene at 140° (Table III) are best accounted for on the basis of the following reaction scheme.<sup>2</sup>



The following point should be noted. At any given temperature, the ratio of the reactions leading to ketones (B and B') and the ones leading to alcohols (A and A'), in different solvents, is (in our estimation) a measure of the availability of carbon-to-hydrogen bonds readily attackable by alkoxy radicals (Table IV). If the ketone-alcohol ratio is high, the hydrogen atoms are not readily removed by free alkoxy radicals.<sup>3</sup>

<sup>2</sup> For the sake of simplicity the breakdown of the free *tert*-butoxy or of the free  $\alpha$ -cumoxy radical is represented as a monomolecular decomposition into a free methyl radical and acetone or acetophenone, respectively. However, it is altogether possible that the decompositions are not spontaneous, but occur only when the free radicals collide with activated solvent molecules, *e.g.*:



<sup>3</sup> Due caution must, however, be exercised in the interpretation of these data. Thus, it would appear that *tert*-butoxy radicals (derived from *tert*-butyl peroxide or the unsym-

The ketone-alcohol ratio permits arrangement of the hydrocarbons in a linear order insofar as their reactivity towards free alkoxy radicals is concerned. Thus, it appears that *p*-methoxypropylbenzene is the most reactive of the hydrocarbons investigated, followed by dodecane, cumene, *tert*-butylbenzene, and diisopropylcarbinol in decreasing order of activity. The same linear order is maintained whether one considers the free *tert*-butoxy or the  $\alpha$ -cumyloxy radicals (Table IV).

TABLE III

PRODUCTS OF THE THERMAL DECOMPOSITIONS OF ALKYL PEROXIDES (0.1 MOLE) IN VARIOUS SOLVENTS

(Yields, except for high-boiling residues, are expressed in moles  $\times 10^{-1}$ . All yields, except those for *tert*-butyl alcohol, which are calculated on the basis of quantitative exploratory experiments, are determined directly.)

PEROXIDE SOLVENT (TEMP.)	CH <sub>4</sub>	CH <sub>3</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> COH	(CH <sub>3</sub> ) <sub>2</sub> CO	(CH <sub>3</sub> ) <sub>2</sub> COH	SOLVENT "DIMER"	HIGH- BOILING RESIDUE (g.)
<i>tert</i> -C <sub>4</sub> H <sub>9</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>							
Cumene (109-113°)	0.71	0.64	0.10	Trace	—	0.50	3.8
Cumene (139-141°)	.90	.65	.22	0.13	(0.87)	.62	—
<i>p</i> -Methoxypropylbenzene (135-138°)	.65	.45	.37	—	—	.24 <sup>a</sup>	22.0
Dodecane (138-142°)	.66	.36	.21	.04	(.96)	.27 <sup>b</sup>	5.5
<i>tert</i> -Butylbenzene (135-140°)	.10	.58	.06	.24	(.76)	—	8.9 <sup>c</sup>
Nitrobenzene (135-140°)	.30	.68	—	.11	—	—	—
[C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CO—] <sub>2</sub>							
Cumene (138°)	1.08	1.16	.82	—	—	—	—
Dodecane (138°)	0.75	0.61	.90	—	—	—	—
( <i>tert</i> -C <sub>4</sub> H <sub>9</sub> O—) <sub>2</sub>							
Dodecane (138°)	—	—	—	.22	(1.78)	—	—

<sup>a</sup> Hexestrol dimethyl ether. <sup>b</sup> *Anal.* Calc'd for C<sub>40</sub>H<sub>82</sub>: C, 85.2; H, 14.8. Found: C, 85.0; H, 14.9. <sup>c</sup> Saturated oil; apparent mol. wt. (cryoscopic, benzene), 535; *Anal.* C, 85.3; H, 9.2.

Most interesting and significant is the comparison of the ketone-alcohol ratios when *tert*-butyl peroxide, *tert*-butyl  $\alpha$ -cumyl peroxide, and  $\alpha$ -cumyl peroxide are decomposed (under the same conditions) in cumene at 138°. In these experiments (Table I) about 90% of the reactants are accounted for.

It has already been noted that for all these peroxides the thermal decompositions follow first-order kinetics, and that the rates of decomposition are independent of the solvents used. It is, therefore, a necessary conclusion that the rate-

metrical peroxide here cited) attack dodecane (as indicated by the ketone-alcohol ratio) more readily than cumene. However, it must be borne in mind that for each tertiary hydrogen atom per molecule of cumene there are twenty secondary hydrogen atoms per molecule of dodecane. With fairly active radicals this preponderance of secondary hydrogen atoms may outweigh the greater ease of removal of the tertiary hydrogen atom in cumene.

determining step is the breakdown of the peroxide into free alkoxy radicals. The question therefore arises why the ketone-alcohol ratio is dependent upon the origin of the free alkoxy radical. At this time, no explanation (which correlates all our data) suggests itself except that the behavior of the free alkoxy radicals in solution is not independent of the source from which they are derived.

If it be assumed provisionally that the "hotter" or more energetic free radicals break down more readily into ketone and free methyl radicals [in accordance

TABLE IV

KETONE-ALCOHOL MOLE RATIOS IN PRODUCTS ARISING FROM THE ATTACK OF FREE ALKOXY RADICALS FROM DIFFERENT SOURCES ON VARIOUS SOLVENTS AT 138-140°

PEROXIDE SOLVENT	KETONE-ALCOHOL RATIOS	
	$\frac{(\text{CH}_3)_2\text{CO}^a}{(\text{CH}_3)_2\text{COH}}$	$\frac{\text{CH}_3\text{COC}_6\text{H}_5^b}{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{COH}}$
$[(\text{CH}_3)_3\text{CO—}]_2$		
<i>tert</i> -Butylbenzene	(2.90) <sup>c</sup>	—
Cumene	(0.50) <sup>c</sup>	—
Dodecane	.12	—
$(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_2\text{C}_6\text{H}_5$		
<i>tert</i> -Butylbenzene	.32	9.70
Cumene	.15	3.00
Dodecane	.04	1.70
<i>p</i> -Methoxyisopropylbenzene	—	1.20
$[\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CO—}]_2$		
Diisopropylcarbinol	—	2.80 <sup>d</sup>
Cumene	—	1.40
Dodecane	—	0.68

<sup>a</sup> Only acetone was determined directly; *tert*-butyl alcohol was calculated as indicated in Table III. <sup>b</sup> Values calculated from acetophenone and  $\alpha$ -cumyl alcohol isolated; substantially the same values were calculated on the basis of methane evolved. <sup>c</sup> These values are calculated from the data obtained at 135° and 145° by Raley, Rust, and Vaughan (1). The arithmetic mean of the two calculated values was used. <sup>d</sup> Calculated on the basis of methane evolved.

with the observation cited (1) that "with increasing temperature the *tert*-butoxy radicals become more subject to loss of methyl than abstraction of hydrogen atoms from solvents," (see also Table I)], then it follows that the free *tert*-butoxy radicals derived from *tert*-butyl peroxide contain more energy than the *tert*-butoxy radicals derived from *tert*-butyl  $\alpha$ -cumyl peroxide. A similar line of reasoning suggests that  $\alpha$ -cumyloxy radicals derived from  $\alpha$ -cumyl peroxide contain less energy than those derived from *tert*-butyl  $\alpha$ -cumyl peroxide. One must be careful not to associate high energy content of free radicals with what may be called reactivity, namely, the ability to abstract hydrogen atoms (as measured by the formation of carbinols) because of the possible difference in the half-life of the "hotter" free radicals.<sup>4</sup> In brief, it is perhaps profitless to discuss the behavior of a free

<sup>4</sup> It should be pointed out here that similar conclusions may be drawn from the ketone-alcohol ratios when the peroxides listed in Table IV are decomposed in dodecane and *tert*-

alkoxy radical unless the method of its generation is also stated. The same views may apply to free alkyl radicals generated by different methods.

The small amount of methane and the large amount of ketones formed when *tert*-butyl  $\alpha$ -cumyl peroxide is decomposed in nitrobenzene is of interest. It would appear that the free methyl radicals formed by the breakdown of the free alkoxy radicals are absorbed in appreciable amount (over 50%) by the nitrobenzene.

It is also of interest that the decomposition of the free alkoxy radicals in dodecane gives rise to a compound which is a saturated "dimer" of dodecane, and that no dodecene is formed in the reaction.

*Determination of order of decomposition of peroxides.*<sup>5</sup> It is submitted that pressure measurements, *without isolation of reaction products*, should not be accepted uncritically as a basis for evaluation of the kinetics of reactions of this type. For example, Raley, Rust, and Vaughan (3) followed the rate of vapor-phase decomposition of *tert*-amyl peroxide by pressure measurements, and observed a deviation from first-order kinetics. The reaction appeared to speed up toward the end. Such a method is in our estimation valueless since pressure measurements do not indicate the specific first step in the decomposition. Their results could be readily reconciled if we assume that the ethane-butane ratio increases as the reaction proceeds, because of the attack of the free ethyl radical [or the free radical  $C_2H_5(CH_3)_2CO\cdot$ ] on the methyl ethyl ketone. This assumption accounts for the high-boiling oils formed in the reaction, and for the preponderance of ethane (19.5%) over ethylene (5.2%) in the gaseous products (disproportion of the free ethyl radical should give equal quantities). A precise method (namely, the measure of the rate of disappearance of the peroxide) was used later by Raley, Rust, and Vaughan (1) in the study of the rate of decomposition of *tert*-butyl peroxide. This method gave excellent agreement with first-order kinetics.

The reasons for the objection raised to following rates of decomposition of peroxides by pressure measurements are illustrated by the work of Szwarc and Roberts (4). These investigators measured the gas evolved when *tert*-butyl peroxide was decomposed in the presence of toluene vapor at 120–160°. It is gratuitously assumed that all free *tert*-butoxy radicals break down to free methyl radicals and acetone; the possible formation of *tert*-butyl alcohol is completely ignored. Since the free *tert*-butoxy radical is less stable as the temperature is increased, a larger amount of gas (per unit of peroxide decomposed) would result

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butylbenzene, although the results are not so clearcut. Higher yields of methane than of ketones are found, and the acetophenone and  $\alpha$ -cumyl alcohol are converted in part to products which appear as oxygen-containing oils of high molecular weight. [Cf., Kharasch, McBay, and Urry, *J. Am. Chem. Soc.*, **70**, 1273 (1948); and Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, **15**, 753 (1950), papers which describe the formation of high-boiling oils, when acetyl peroxide is decomposed in acetophenone and  $\alpha$ -cumyl alcohol.] These complications, however, do not invalidate the conclusions here drawn.

<sup>5</sup> The rate of thermal decomposition of *tert*-butyl triphenylmethyl peroxide in *p*-methoxypropylbenzene indicates a first-order reaction. In cumene and diisopropylcarbinol there are apparent deviations from first-order kinetics. The product isolated from the decomposition in cumene— $C_6H_5O(C_6H_5)_2CC(CH_3)_2C_6H_5$ —suggests a complex mechanism for the peroxide decomposition. The results of these experiments will be published shortly.

as the temperature is increased. Furthermore, the possibility of the loss of free methyl radicals by absorption in aromatic nuclei should not be overlooked. Experiments in this laboratory have demonstrated the formation of both toluene and xylenes when acetyl peroxide is decomposed in the presence of benzene.

## EXPERIMENTAL

*Reagents.* *tert-Butyl  $\alpha$ -cumyl peroxide* was prepared as previously described (6);  $n_D^{20}$  1.4792;  $d$  0.94. The peroxide was shown to be at least 96% pure by iodometric titration (5). Isopropanol, instead of water, was used as the diluent.  *$\alpha$ -Cumyl peroxide* was prepared as previously described (6). *Commercial tert-butyl peroxide* was redistilled. *Solvents* were all carefully fractionated before use.

*Rate studies.* Temperatures were controlled within one-half degree. Decomposition rates were followed by measuring the volume of methane evolved. The gas was collected over saturated salt solution, and estimated as previously described (7). In all cases the gas isolated was shown by analysis to be pure methane. About 25 readings were made in each experiment. In all decompositions studied (up to 97%) the rate-determining step was found to be first-order.

The calculated activation energy for the thermal decomposition of *tert-butyl  $\alpha$ -cumyl peroxide* in dodecane solution over the temperature range 128–158° (see Table II) was 35.0 kcal., with a frequency factor of  $10^{13.8}$ .

The calculated activation energy for the thermal decomposition of  *$\alpha$ -cumyl peroxide* in dodecane solution over the temperature range 128–158° (see Table II) was 33.5 kcal., with a frequency factor of  $10^{13.3}$ .

*Analytical methods.* Acetophenone was determined as its dinitrophenylhydrazone (8).  *$\alpha$ -Cumyl alcohol* was determined in the form of its reaction product with thioglycolic acid (6). Acetone was determined as iodoform. Bi- *$\alpha$ -cumyl* (9) was isolated by crystallizing from methanol the crude mixture of the high-boiling cumene reaction products. The same procedure was used to isolate hexestrol dimethyl ether (9) when *p*-methoxypropylbenzene was the solvent.

## SUMMARY

1. It has been shown that the rate of thermal decomposition of  *$\alpha$ -cumyl tert-butyl peroxide* and  *$\alpha$ -cumyl peroxide* is nearly solvent-independent and follows first-order kinetics.

2. The decomposition activation energy in the temperature range 130–170° (in dodecane as a solvent) was 35 kcal. for *tert-butyl  $\alpha$ -cumyl peroxide* and 33.5 kcal. for  *$\alpha$ -cumyl peroxide*.

3. The ketone-alcohol ratio in the thermal breakdown of the peroxides depends upon: (a) the temperature of decomposition; the ratio increases with temperature; and (b) the solvent present; the ratio decreases with the increase of readily available hydrogen atoms in the solvent.

4. It is suggested that the free *tert*-alkoxy radicals formed by the decomposition of a symmetrical peroxide may differ in energy content from the *tert*-alkoxy radicals formed by the decomposition of an unsymmetrical peroxide. High energy content of a free *tert*-alkoxy radical (which presumably favors breakdown into ketone and a free alkyl radical) should not be confused with high reactivity as evidenced by the ability to abstract a labile hydrogen atom from a solvent and form tertiary alcohol.

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