[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL AND REFINING CO., BAYTOWN, TEX.]

The Decomposition of *p*-Methylbenzyl Hydroperoxide

BY WILLIAM J. FARRISSEY, JR.

RECEIVED SEPTEMBER 25, 1961

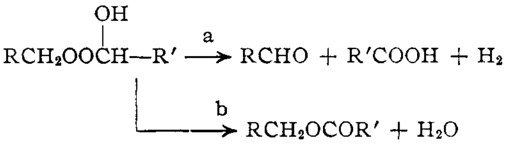
The thermal decomposition of *p*-methylbenzyl hydroperoxide (I) has been examined in several solvents. Decomposition *via* a hydroxyperoxide (III) is much less important than observed for primary aliphatic hydroperoxides. In the presence of *n*-heptaldehyde, the hydroxyperoxide IV becomes the major pathway for decomposition, particularly at lower temperatures. The degree of participation of III as a decomposition intermediate can be increased by acids, *p*-tolualdehyde and *p*-cresol. Decomposition in acetic acid results in formation of *p*-cresoxymethyl acetate (V).

Introduction

It is generally accepted that hydroperoxides play an important role in the autoxidation of hydrocarbons.[1,2] Their intermediacy has been demonstrated in a variety of autoxidation systems.[2] It is not surprising, then, that considerable work has been reported on the chemistry of hydroperoxides of various types. One important class of hydroperoxides, however, has received scant attention; namely, the primary benzyl hydroperoxides. Only two examples of this class are reported in the literature, benzyl[3] and *p*-methylbenzyl[3a,4] hydroperoxides, of which only the latter has been examined with regard to its decomposition behavior.

The synthesis of *p*-methylbenzyl hydroperoxide (I) was first reported by Hock and Lang,[4a] who determined that, in common with secondary hydroperoxides, it was unstable in the presence of strong base, decomposing to *p*-tolualdehyde. It was easily reduced with bisulfite to *p*-methylbenzyl alcohol. Kharasch examined the acid-catalyzed decomposition of I to *p*-cresol and *p*-tolualdehyde.[4b] Lorand and Edwards observed this same decomposition, although the amount of phenyl migration differed in the two cases.[4c] In addition, they observed an autocatalytic thermal decomposition of I, catalyzed by *p*-toluic acid. No mention was made of the product distribution from this reaction.

It was of interest to examine this thermal decomposition more closely, in view of the recent demonstration by Mosher[5] that primary aliphatic hydroperoxides decompose to a significant extent *via* a hydroxyperoxide (II) to hydrogen, acid and aldehyde. The extent to which hydroperoxide decomposes in this way depends upon the rate of formation of II and its equilibrium concentration. For aliphatic systems, this rate is very fast, and good yields of hydroxyperoxide can be obtained simply by mixing equivalent amounts of aldehyde and hydroperoxide. The lower susceptibility of aromatic aldehydes to nucleophilic attack,[6] however, may retard formation of II to an extent that it does not contribute greatly to the over-all decomposition reaction. This and other aspects of the thermal decomposition of I are the objects of this study.



$$RCH_2OO\overset{OH}{\overset{|}{C}}H\text{—}R' \xrightarrow{a} RCHO + R'COOH + H_2 \qquad (1)$$

$$\xrightarrow{b} RCH_2OCOR' + H_2O$$

II, $R = R' =$ alkyl
III, $R = R' = CH_3\text{-}p\text{-}C_6H_4\text{-}$
IV, $R = CH_3\text{-}p\text{-}C_6H_4\text{-}$
$R' = n\text{-}C_6H_{13}$

The synthesis of I was achieved essentially as described by Lorand and Edwards.[4c] After separation from the oxidation mixture by extraction with dilute sodium hydroxide solution, the hydroperoxide was purified by evaporative distillation and re-extraction, a procedure which afforded material containing greater than 90% of the theoretical active oxygen. Small amounts of unknown impurities were bothersome and gave erratic decomposition results. If the extractions and distillations were carried out with extreme care, however, material of usable purity was produced. The identity of all of the 5–7% of impurities present was not known, although 1.5–3% *p*-tolualdehyde was present. This did not seem to affect greatly the decomposition results.

Results and Discussion

The hydroperoxide was decomposed in a helium atmosphere at temperatures of 85–150°, as 0.3 *M* solute in appropriate solvents. Any evolved gas was collected and measured in a mercury buret. Prior to analysis, solvent was removed by aqueous extraction where possible or by distillation at reduced pressure. The resultant products were then analyzed by three different methods, no one of which was completely satisfactory for all constituents of the mixture. Mass spectral (M.S.) analysis was the quickest, but necessitated prior knowledge of and calibration for all products of the decomposition. This was not possible generally; first, because all of the minor products could not be identified and, second, because some of the known products exhibited no parent mass in the spectrum. Gas chromatography was suitable only for the more volatile components, alcohol, aldehyde and cresol. The accuracy of both methods could be checked by separation of the

---

(1) C. Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, N. Y., 1957, Chap. 9.

(2) H. S. Blanchard, *J. Am. Chem. Soc.*, **82**, 2014 (1960); C. E. H. Bawn, A. A. Pennington and C. F. H. Tipper, *Faraday Soc. Disc.*, **10**, 282 (1951); C. E. H. Bawn and D. P. Morgan, *J. Inst. Petroleum*, **44**, 290 (1958); H. Kropf, *Ann.*, **637**, 73, 93 (1960).

(3) (a) A. D. Boggs, Ph.D. Thesis, Ohio State University, 1954; (b) C. Walling and S. A. Buckler, *J. Am. Chem. Soc*, **77**, 6032 (1955).

(4) (a) H. Hock and S. Lang, *Ber.*, **76B**, 169 (1943); (b) M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 150 (1951); (c) E. J. Lorand and E. I. Edwards, *J. Am. Chem. Soc.*, **77**, 4035 (1955); W. Pritzkow and R. Hofmann, *J. prakt. Chem.*, [4] **12**, 11 (1960).

(5) H. S. Mosher and C. F. Wurster, *J. Am. Chem. Soc.*, **77**, 5451 (1955); C. F. Wurster, L. J. Durham and H. S. Mosher, *ibid.*, **80**, 327 (1958); L. J. Durham, C. F. Wurster and H. S. Mosher, *ibid.*, **80**, 332 (1958).

(6) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 245, 250.

mixture into its major constituents. Acid and cresol were obtained by successive extractions with sodium bicarbonate and sodium hydroxide solutions. Aldehyde was precipitated and determined as its semicarbazone. Chromatography of the residue on alumina was employed for separation and estimation of ester and alcohol. This tedious procedure was used only as a check of the other procedures or when serious discrepancies existed between the M.S. and G.L.P.C. analyses. In general, deviations from the average of product analyses for duplicate runs were less than 20%.

In Table I are shown the products obtained from the decomposition of I in several solvents. The amount of hydrogen produced was not large, amounting to 11 mole per cent. in chlorobenzene solution. Carbon monoxide, carbon dioxide, and, in some cases, oxygen were present in small amounts. In none of the solvents was the hydrogen yield as great as that obtained for the aliphatic hydroperoxides.[5]

TABLE I

SOLVENT EFFECTS ON THE DECOMPOSITION OF 0.3 *M* SOLUTIONS OF *p*-METHYLBENZYL HYDROPEROXIDE[a]

	Temp. and solvent				
Products	130° Chlorobenzene	130° *p*-Xylene	130° *n*-Octane	130° Ethylene glycol	100° Acetic acid
H_2	0.11	0.05	0.09	0.06	0.14
O_2	.01	..	.01	..	..
CO	.01	0.01	.003	..	0.002
CO_2	.02	.03	.003	..	0.009
Ester	.05	.01	.03		
Acid	.22	.08	.27	0.02	[b]
Alcohol	.25	.46	.32	.15	[b]
Aldehyde	.24	.48	.22	.39	0.3
p-Cresol	.01	..	.004		[b]
Others		0.08[c]		0.29[d]	≈0.25[e]

[a] Expressed in moles per mole of hydroperoxide. [b] Results not obtained; see text and Experimental. [c] 4,4′-Dimethylbibenzyl. [d] 2-(*p*-Methylphenyl)-dioxolane. [e] *p*-Methylphenoxymethyl acetate (V).

The major non-gaseous products of the decompositions were *p*-tolualdehyde, *p*-methylbenzyl alcohol, *p*-toluic acid and *p*-methylbenzyl *p*-toluate. Some *p*-cresol was formed also, though usually in small amounts. The most rapid decomposition occurred in ethylene glycol[7] solution with formation of *p*-tolualdehyde and its dioxolane. Little alcohol, acid and hydrogen were produced. Considerably more acid and alcohol were obtained from the decomposition in chlorobenzene solution, along with some ester and *p*-cresol. These products do not afford an adequate oxidation balance for the system; the reduction products (alcohol and hydrogen) outweigh the observed oxidation products (acid, carbon monoxide, carbon dioxide and oxygen) to an appreciable extent. Presumably, among the unidentified residues[8] comprising the balance of the reaction mixture may be found sufficient oxidized material to account for this discrepancy.

An increased alcohol yield resulted from the decomposition of I in hydrogen-rich solvents such as *p*-xylene. Abstraction of hydrogen by xylyloxy radicals becomes an important product-determining step in this solvent (3). Oxidation of the resulting alcohol by hydroperoxide[9] accounts for the increased aldehyde yields also (6). The greater importance of these reactions in *p*-xylene diminishes the extent of decomposition *via* the hydroxyperoxide III. Hence, lower yields of hydrogen (1a) and ester (1b) result.

$$\mathrm{RCH_2OOH \longrightarrow RCH_2O\cdot + HO\cdot} \qquad (2)$$

$$\mathrm{RCH_2O\cdot + R'CH_3 \longrightarrow RCH_2OH + R'CH_2\cdot} \qquad (3)$$

$$\mathrm{R'CH_2\cdot + R'CH_2\cdot \longrightarrow R'CH_2CH_2R'} \qquad (4)$$

$$\mathrm{R'CH_2\cdot + RCH_2OOH \longrightarrow R'CH_2OH + RCH_2O\cdot} \qquad (5)$$

$$\mathrm{R'CH_2OH + RCH_2OOH \longrightarrow R'CHO + RCH_2OH + H_2O} \qquad (6)$$

$$\mathrm{R = R' = CH_3\text{-}}p\mathrm{\text{-}C_6H_4\text{-}}$$

The *p*-xylyl radicals produced in eq. 3 may dimerize (4) or attack the hydroperoxide (5).[10] To determine that the latter reaction plays a significant role in this system, a similar decomposition in *p*-chlorotoluene solvent was examined. In addition to the usual products from I, several chlorine-containing compounds were observed in the mass spectrum of the product, corresponding to *p*-chlorobenzaldehyde, *p*-chlorobenzyl alcohol and 4,4′-dichlorobibenzyl. That these compounds contained chlorine was readily apparent from the ratio of the *M* and *M* + 2 peaks which agreed nicely with the natural abundance of the ^{35}Cl and ^{37}Cl isotopes. (For the bibenzyl compound, the *M*,*M* + 2 and *M* + 4 peaks were used.) Since very little oxygen could have been present in the system, the oxygenated products must have resulted from attack of solvent radicals on I (eq. 5 and 6, R′ = Cl-*p*-C_6H_4-).

n-Octane solvent was intermediate to chlorobenzene and *p*-xylene in its effect on the decomposition products. Some increase in alcohol yield was observed, suggesting some hydrogen abstraction from solvent. In this case, however, only very small amounts of solvent dimer were detected. Neither the presence of octenes, from disproportionation of octyl radicals, nor the formation of octanols or octanones could be established with certainty.

The effect of the various products on hydrogen formation for the decompositions in chlorobenzene solution was examined (Tables II and III). Whereas *p*-methylbenzyl alcohol caused a depression in hydrogen yield, the others (aldehyde, acid and cresol) caused an increase in hydrogen evolution to varying degrees. In contrast to the striking differences in decomposition behavior observed for aliphatic hydroperoxides in the presence of their corresponding aldehydes,[5] *p*-tolualdehyde exerted only moderate influence on the decomposition rate and product composition. Both hydrogen and ester yields were increased to some extent. These products become even more prominent at lower temperatures. Radical traps such

---

(7) C. F. H. Tipper, *J. Chem. Soc.*, 1675 (1953), observed a very rapid decomposition of decalin hydroperoxide in this solvent.

(8) A number of high mass peaks of low intensity were observed in the mass spectrum. Some appeared to contain chlorine and may have resulted from radical attack on solvent.

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

(10) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952); H. E. De La Mare, *J. Org. Chem.*, **25**, 2114 (1960).

as 2,6-di-*t*-butyl-*p*-cresol (DBPC) and styrene inhibited hydrogen formation, an effect observed also for I in the absence of added aldehyde.

Table II

Effect of Aldehydes on the Decomposition of I[a]

Products	Conditions					
	100° *p*-Tolualdehyde	130° *p*-Tolualdehyde	150° *p*-Tolualdehyde	85° *n*-Heptaldehyde	100° *n*-Heptaldehyde	130° *n*-Heptaldehyde
H_2	0.23	0.14	<0.05	0.6	0.53	0.38
O_2		.002				
CO	.003	.007		.08[b]	.15[b]	.36[b]
CO_2	.01	.01				.005
Ester	.2	.12		.02	.02	.03
Acid	.4	.38		.11	.05	.09
Alcohol	.2	.32		.21	.23	.27
Aldehyde	(− .2)[c]	(− .1)[c]		.61	.45	.42
Cresol	.01	.01		.01	.01	
Others				.62[d]	.54[d]	.46[d]

[a] Moles per mole of hydroperoxide. [b] Moles per mole of *n*-heptaldehyde. [c] Corrected for aldehyde initially added. [d] *n*-Heptanoic acid.

Table III

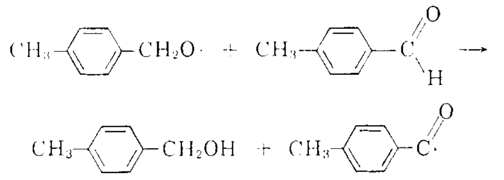
Effect of Reaction Products on Decomposition of I at 130°

Products	Conditions		
	p-Toluic acid 0.082 *M*/*M*[a]	*p*-Cresol 0.07 *M*/*M*	*p*-Methylbenzyl alcohol 0.95 *M*/*M*
H	0.17	0.23	0.04
O_2		.004	.007
CO	.006	.01	.004
CO_2	.02	.01	.005
Ester	.15	.10	.03
Acid	.26[b]	.17	.09
Alcohol	.27	.23	.16[b]
Aldehyde	.29	.32	.52
Cresol	.02	(−0.03)[b]	..
Other			.03[c]

[a] Expressed in moles per mole of hydroperoxide. [b] Corrected for added component. [c] Di-(*p*-methylbenzyl) ether.

These results are consistent with the mechanism proposed by Mosher involving prior formation of a hydroxyperoxide, at least for that portion of the reaction producing hydrogen (1a) and ester (1b). The small extent of these reactions with *p*-tolualdehyde is due to the lesser reactivity of the aromatic aldehyde toward nucleophilic attack.[6] The infrared spectrum of an equimolar mixture of I and *p*-tolualdehyde provided no evidence for formation of an appreciable concentration of III, even after the mixture was allowed to stand for long periods at room temperature. Thus, no enhancement in hydrogen yield was observed from decomposition of such a mixture. With decreasing temperature, however, decomposition by way of III, a reaction path of lower activation energy, becomes more important and more hydrogen and ester result.

Because only a limited amount of I is involved in formation of III, the general nature of the decomposition is characteristic of the free hydroperoxide. Thus, DBPC, which is known to accelerate the decomposition of *t*-butyl hydroperoxide,[11] catalyzes the decomposition of I and eliminates hydrogen formation, irrespective of the presence or absence of aldehyde. Also, the increase in alcohol yield probably indicates some attack of alkoxy radicals on the aldehyde (7). Subsequent oxidation of the *p*-toluyl radicals accounts for the corresponding increase in acid yield.



(7)

The most striking effect on hydrogen formation was produced by an aliphatic aldehyde, *n*-heptaldehyde.[12a] At 85° in chlorobenzene solution, 60% yields of hydrogen, *p*-tolualdehyde and *n*-heptanoic acid were obtained with this system. The greatly increased rate of decomposition was unaffected by α-methylstyrene, although the decarbonylation of *n*-heptaldehyde was completely inhibited. Furthermore, hydrogen evolution was diminished but slightly, compared to the effect of α-methylstyrene on I alone[13] or to the results previously mentioned with DBPC and *p*-tolualdehyde.

The infrared spectrum of a mixture of I and *n*-heptaldehyde is consistent with the moderately rapid formation of IV at room temperature. The decomposition data can be interpreted adequately on the basis that the major portion of the hydroperoxide decomposes *via* IV. Hence α-methylstyrene, which affects the free hydroperoxide only,[13] has little influence on the decomposition rate and product composition. Also, in agreement with the stoichiometry of eq. 1, a reasonable correspondence in the yields of hydrogen, *p*-tolualdehyde and *n*-heptanoic acid was observed. Preliminary enthalpy and entropy values obtained from the hydrogen evolution data indicate a highly ordered transition state of low energy.

Since it is probable that the hydroxyperoxide is the most important source of ester in the decompositions,[5] it is interesting that the system in which IV participates significantly produces little of the heptanoate ester. Presumably rearrangement of IV to ester is less favorable energetically than decomposition to hydrogen, aldehyde and acid. Support for the intermediacy of the hydroxyperoxide for ester formation was forthcoming from an examination of esterification rates. In the absence of mineral acid, heating a mixture of *p*-toluic acid and *p*-methylbenzyl alcohol at the decomposition temperature for prolonged periods produces very little ester. Furthermore, decomposition of I in the presence of benzoic acid yields the toluate ester predominantly. On the basis of the hydroxyperoxide mechanism, the toluate ester is the only one which could be produced, since *p*-tolualdehyde in this instance is the only aldehyde available for hydroxyperoxide formation. The small amount of benzoate ester that is produced probably results from transesterification. By catalyzing formation

---

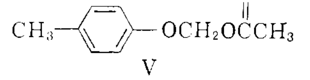
(11) T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 1469 (1952).

(12) (a) H. B. van Leeuwen, J. P. Wibaut, A. F. Bickel and E. C. Kooyman, *Rec. trav. chim.*, **78**, 667 (1959); (b) A. W. R. van Steveninck and E. C. Kooyman, *ibid.*, **79**, 413 (1960).

(13) C. Walling and Y. Chang, *J. Am. Chem. Soc.*, **76**, 4878 (1954).

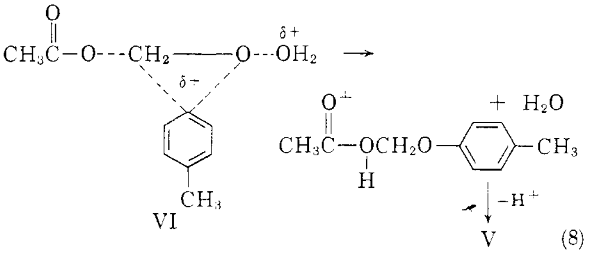
of III, both toluic and benzoic acids cause an increase in hydrogen and ester yields. In addition, increased *p*-cresol was found, in accord with its origin as an acid-catalyzed rearrangement product.

With acetic acid as solvent, an interesting acetate ester was obtained. The mass spectrum of this material was indicative of two compounds of masses 150 and 180. Despite repeated distillation, these two masses were retained in the mass spectrum of all samples. The n.m.r. spectrum of this material was in agreement with a structure containing an acetate ester, a methyl attached to an aromatic nucleus and a methylene group to which were attached *two* electronegative substituents. From the basic hydrolysis of the ester were obtained *p*-cresol and the dinitrophenylhydrazone of formaldehyde. Saponification equivalent and elemental analyses were in accord with an ester of the formula $C_{10}H_{12}O_3$. These data can be accommodated by structure V. It has been assumed that the extra mass spectral peak is due to decomposition during the analysis. Because of the instability of II toward G.L.P.C. and M.S. analyses, it was not possible to determine precisely the product composition for the runs in acetic acid. However, in addition to V, aldehyde, alcohol, acid and cresol were produced (see Experimental).



V

In the rearrangement of peresters under ionizing conditions, the product ester contains the original acyl moiety[14]; that is, the rearrangement takes place completely intramolecularly.[15] It now appears, however, that in the acid-catalyzed rearrangement of hydroperoxides at least those of the primary benzyl type, solvent molecules may be incorporated in the product. This difference may be ascribed to the lesser degree of ionization of the peresters which facilitates internal return of the leaving group to the rearranged carbonium ion.[15] For the hydroperoxides, however, as the O–O bond breaks with an assist from the neighboring *p*-methylphenyl group,[12b,16] the developing positive charge on the methylene group is solvated extensively with acetic acid molecules. Loss of water, formation of the C–O bond to acetic acid and loss of H$^+$ gives V (8). If water molecules are the solvating agents, a hemiacetal is formed[12b] which rapidly breaks down to formaldehyde and *p*-cresol, the usual products of rearrangement of I.[4]



(8)

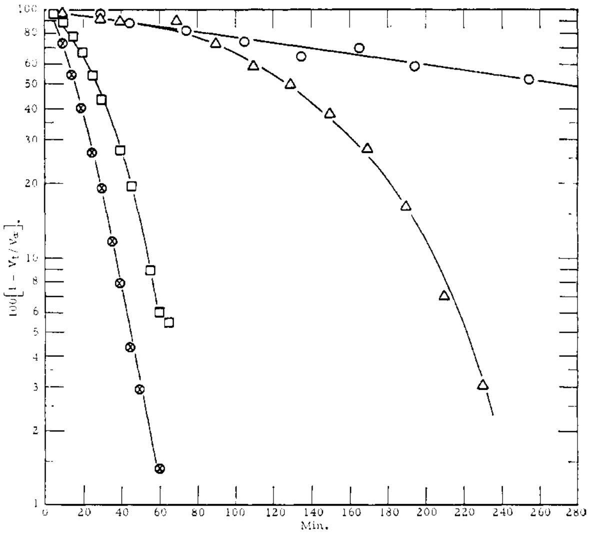


Fig. 1.—Effect of acid on the decomposition of I: O, no acid; Δ, unknown acid; □, *p*-toluenesulfonic acid; ⊗, *p*-toluenesulfonic acid + *p*-tolualdehyde.

In some early experiments in chlorobenzene solution, greatly increased yields of hydrogen and *p*-cresol were obtained.[17] A first-order plot of hydrogen evolution with time exhibited a marked curvature, characteristic of an auto-accelerated reaction, in contrast to the linear plots usually observed (Fig. 1). The cause of this erratic behavior seemed to be the presence of strong acids in the system; at least the same effect could be duplicated reasonably well with trace amounts of *p*-toluenesulfonic acid (Table IV). The increase in hydrogen production caused by acid stems from the formaldehyde produced along with *p*-cresol in the acid-catalyzed rearrangement of I. It is not unreasonable to suppose, from the results with heptaldehyde, that formaldehyde would react rapidly with I to form a hydroxyperoxide, decomposition of which would give hydrogen and formic acid along with *p*-tolualdehyde. Formic acid and *p*-methylbenzyl formate were detected among the products. It is interesting to note, in support of this mechanism, that the excess hydrogen formed corresponds nicely to the increase in *p*-cresol yield. Formaldehyde formation accounts for the auto-acceleration also. As more formaldehyde is produced, decomposition *via* the hydroxyperoxide is accelerated.

---

(14) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948); H. Hock and H. Kropf, *Ber.*, **88**, 1544 (1955); H. J. Shine and R. H. Snyder, *J. Am. Chem. Soc.*, **80**, 3064 (1958); R. H. Snyder, H. J. Shine, K. A. Leibbrand and P. O. Tawney, *ibid.*, **81**, 4299 (1959).

(15) P. D. Bartlett and J. L. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953); D. B. Denney, *ibid.*, **77**, 1706 (1955); D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).

(16) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952); S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); P. D. Bartlett and B. T. Storey, *ibid.*, **80**, 4953 (1958).

(17) The erratic nature of the decompositions in this solvent was not due to the hydroperoxide, since the same batch could be made to give the "high" and "low" hydrogen and *p*-cresol yields at will. Two sources of the difficulty were uncovered: the glass reactor itself, which required thorough soaking with dilute ammonia to neutralize acidic sites[12]; and a particular brand of rubber septum, employed in some of the early experiments, through which the hydroperoxide was injected into the hot solvent[18] (see Experimental).

(18) A preliminary report of this work was presented before the 137th Meeting of the American Chemical Society, April, 1960, Cleveland, Ohio, p. 16-Q, before this source of error was recognized. Some of the data reported as "thermal" decompositions undoubtedly represent acid-catalyzed reactions.

Table IV

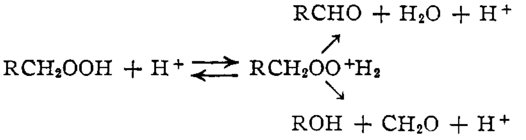
Effect of Acid on the Decomposition of I at 130°

	Acid and Solvent					
Products	None chloro-benzene	Un-known acid chloro-benzene	p-TSA[a] chloro-benzene	p-TSA[a] + p-toluald. chloro-benzene	p-TSA[a] + p-toluald. n-octane	Un-known acid n-octane
H_2	0.11	0.26	0.30	0.27	0.37	0.26
O_2	.01					
CO	.01			.003		
CO_2	.02			.002	.01	
Ester	.05	.07	.06	.08	.24	.18
Acid	.22	.11	.09	.18	.29	.13
Alcohol	.25	.11	.07	.14	.06	.03
Aldehyde	.24	.35	.27	.03[d]	(−.2)[d]	.25
Cresol	.01	.14	.14	.11	.04	.03
Others		+[b]	.04[b] .08[c]	.02[b]	.007[b]	

[a] *p*-Toluenesulfonic acid. [b] *p*-Methylbenzyl formate. [c] Di-(*p*-methylbenzyl) ether. [d] Corrected for added aldehyde; since these values were obtained from the difference of two large numbers, they may be considerably in error.

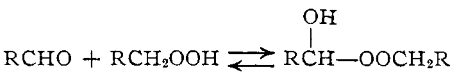
The octane solutions exhibited a different behavior with trace acid. Hydrogen production was greatly enhanced also, but without the attendant large increase in *p*-cresol formation. Instead, it is proposed that acid catalyzes formation of III[19] which results in high yields of ester and hydrogen. Some of the ester may be formed by direct esterification, also catalyzed by the acid present. Rearrangement of I to *p*-cresol does not occur to a great extent in this solvent (9b). Such decomposition of I by acid which does occur must be confined predominantly to production of *p*-tolualdehyde (eq. 9a).[4b,c]

A similar product distribution was obtained from the decomposition of equimolar mixtures of I and *p*-tolualdehyde with *p*-toluenesulfonic acid. Again less *p*-cresol was formed in *n*-octane than in chlorobenzene, although more hydrogen was produced in the former solvent. The differences in hydrogen yield for these two solvents reflects, presumably, their differing effect on the equilibria involved in protonation of I or *p*-tolualdehyde and formation of III (eq. 9–12). The extent to which I decomposes with acid, *via* 9a or 9b, or *via* the hydroxyperoxide (eq. 10–12), will depend on the rate at which these equilibria are established and the magnitude of the several equilibrium constants. It seems reasonable to suppose that solvent will affect these equilibria and the course of the decomposition.



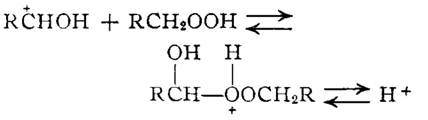
$$RCH_2OOH + H^+ \rightleftharpoons RCH_2OO^+H_2 \begin{cases} \nearrow RCHO + H_2O + H^+ & (9a) \\ \searrow ROH + CH_2O + H^+ & (9b) \end{cases}$$

$$RCHO + H^+ \rightleftharpoons RCH\overset{+}{O}H \longleftrightarrow R\overset{+}{C}HOH \qquad (10)$$



$$RCHO + RCH_2OOH \rightleftharpoons RCH(OH){-}OOCH_2R \qquad (11)$$

III



$$R\overset{+}{C}HOH + RCH_2OOH \rightleftharpoons RCH(OH){-}\underset{+}{O}(H)OCH_2R \rightleftharpoons H^+ \qquad (12)$$

III

Assurance that hydrogen was not a product of a radical reaction was sought by decomposing the hydroperoxide in the presence of radical traps such as styrene, α-methylstyrene,[20] 2,6-di-*t*-butyl-*p*-cresol,[11] iodine, N-phenyl-α-naphthylamine[21] and *p*-cresol. Of these, all but the last did decrease the yield of hydrogen, but also accelerated the decomposition (Table V). This accelerating effect of 2,6-disubstituted phenols and styrenes on peroxide decompositions has been observed previously.[11,13a,22] Iodine catalyzed another reaction which resulted in formation of a substantial amount of oxygen as product. The results with the amine were somewhat erratic and may not be reliable. It appears that in this instance also, a rapid direct reaction of the amine with the hydroperoxide takes place to a limited extent.[23] *p*-Cresol, however, did not suppress hydrogen production nor did it accelerate the decomposition. The yields of hydrogen and ester were increased, although the over-all decomposition rate was decreased.

Table V

Effect of Radical Traps on the Decomposition of I[a]

	Conditions			
Products	I + DBPC (0.05)[a]	I + *p*-Toluald. + DBPC (2.0)[a]	I + α-Me-styrene (2.8)[a]	I + n-$C_6H_{13}CHO$ + α-Me styrene (2.0)[a]
H_2	0.06	0.009	..	0.31
O_2	.003			
CO	.02			.01
CO_2	.03	.001		
C_4H_8		.04[b]		
Ester	.03			
Acid	.2			
Alcohol	.4	.6[c]	0.5[c]	
Aldehyde	.4	.4[c]	.2[c]	
Cresol	.02			

[a] Chlorobenzene solution at 130°; reported in moles per mole of hydroperoxide. [b] Isobutylene; see J. J. Conradi and G. A. McLaren, *J. Am. Chem. Soc.*, 82, 4745 (1960). [c] Yields based on isolation.

The results with *p*-cresol illustrate the close competition between the radical decomposition of I and the non-radical decomposition *via* III. Slowing down the former by inhibiting the induced decomposition with *p*-cresol increases the relative importance of III as a decomposition intermediate. Hence, products derived from III (hydrogen and ester) are more prominent in the inhibited decomposition.

Experimental

Materials.—Eastman Kodak Co. chlorobenzene and ethylene glycol, and Phillips research grade *n*-octane and 99.3% *p*-xylene were distilled and stored in a nitrogen atmosphere. All were inert to potassium iodide in acetic acid. Acetic acid was J. T. Baker analyzed reagent. *n*-Heptaldehyde was Eastman Kodak Co. white label material. *p*-Tolu-

---

(19) C. N. Satterfield and L. C. Case, *Ind. Eng. Chem.*, **46**, 998 (1954).

(20) L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 4537 (1960).

(21) J. R. Thomas, *ibid.*, **77**, 246 (1955).

(22) A. Farkas and E. Passaglia, *ibid.*, **72**, 3333 (1950).

(23) J. R. Thomas, *ibid.*, **82**, 5955 (1960).

aldehyde was obtained from Bios Laboratories,[24] distilled and stored under nitrogen. Other reagents were commercial materials and were used without further purification.

***p*-Methylbenzyl Hydroperoxide (I).**—The procedure of Lorand and Edwards[4c] was used without major modification. *p*-Xylene, 300 g., and di-*t*-butyl peroxide, 30 g., were heated to 125° with vigorous stirring under a steady stream of oxygen from a fritted glass inlet tube. At the end of an hour, a further 15 g. of peroxide was added followed by 15 g. more 45 minutes later. After oxidation of the xylene, the oxidate was cooled to 0° and extracted with 5% sodium carbonate and then with ice-cold 2% sodium hydroxide solution. The caustic solution was then acidified with carbon dioxide gas to a *p*H of 8.5–9.0 and extracted with three 100-ml. portions of ether. After drying, the ether was evaporated to give a highly peroxidic yellow oil. Evaporative distillation at 50° and 0.07 mm. gave a nearly colorless oil with 10.8% active oxygen, 93% of theoretical. This material had $n^{27}\text{D}$ 1.5302, compared to $n^{20}\text{D}$ 1.5317 reported by Kharasch.[4b] From the ultraviolet spectrum, an estimated 1.9% *p*-tolualdehyde was present in the sample. A nuclear magnetic resonance spectrum was in agreement with this amount of aldehyde. No other contaminants could be detected.

Decompositions.—The reactor consisted of a small, round-bottomed, Pyrex flask equipped with a thermowell and side-arm closed with a rubber septum. When it was established that a particular kind of septum was a source of difficulty,[17] experiments were conducted in a flask without side-arm or with the side-arm closed with a silicone rubber puncture seal.[25] The reactor was cleaned in dichromate cleaning solution, soaked in dilute ammonia, rinsed thoroughly with distilled water and oven-dried. This procedure gave reproducible results if followed meticulously; it was particularly important to soak completely the reactor in a basic solution.

The decompositions were effected by two procedures, depending on whether or not the flask was equipped with a side-arm. If not, the flask with its hydroperoxide solution was attached to a condenser and mercury-filled buret and cooled in a Dry Ice-bath. The frozen mixture was pumped, flushed with helium, melted, refrozen and the flushing repeated. After the solution was warmed to room temperature and the volume on the buret noted, the solution was heated in an oil-bath maintained at ±1°. Volume changes were recorded at suitable times by means of the buret. When gas evolution had ceased, the flask was cooled to room temperature and the volume again noted. Since very little gas was evolved during the warm-up period, it was possible to determine the thermal expansion of the gas volume in the reactor and correct for it. The volume of gas evolved as determined in this way was in fair agreement with that obtained from the difference in the volume readings at room temperature before and after decomposition.

For the flask with side-arm, the procedure was the same except that the hydroperoxide was injected after the system had attained thermal equilibrium and a constant volume was noted on the buret. Although somewhat more accurate gas evolution data could be obtained with this procedure, no difference in the over-all decomposition products was noted. Samples of the gas were removed and analyzed by gas chromatography.[26]

The reaction mixture was extracted with sodium bicarbonate solution to remove *p*-toluic acid and the solvent removed by vacuum distillation. The residue was analyzed by gas chromatography and mass spectrometry.[26] In some instances the isolation procedure outlined below was employed.

Identification of Products.—From the decomposition of 2.76 g. (20.0 mmoles) of *p*-xylyl hydroperoxide in 75.0 ml. of chlorobenzene, 131.3 ml. of gas was evolved. After distillation of solvent, extraction of the residue with 5% sodium carbonate gave 135 mg. (1 mmole) of *p*-toluic acid. Extraction with 1 *N* sodium hydroxide solution provided 290 mg. (2.7 mmoles) of a brown oil, which smelled phenolic. This oil gave a benzoate which had, after sublimation, m.p. 70.5–71.5° undepressed on admixture with authentic *p*-cresyl benzoate. Treatment of the remainder with semicarbazide hydrochloride gave 860 mg. (4.8 mmoles) of a tan solid, m.p. 208–216°, reported[27] m.p. for *p*-tolualdehyde semicarbazone, 215°. The residue from semicarbazide treatment was water washed, the solvent distilled off, and the residue chromatographed on alumina. Several distinct fractions were obtained, one of which, 110 mg. of colorless oil, had an infrared spectrum identical to that of authentic *p*-xylyl *p*-toluate. The main fraction, 260 mg. of a yellow oil, gave on sublimation a white solid, m.p. 58.0° alone and mixed with a known sample of *p*-methylbenzyl alcohol.

***p*-Cresoxymethyl Acetate (V).**—A solution of 13.25 g. (0.096 mole) of I in 75 ml. of acetic acid was heated to 78–80° for several days, during which *ca.* 200 ml. of gas, mostly hydrogen, was evolved. After cooling and dissolving in 300 ml. of methylene chloride, the reaction mixture was washed free of acetic acid and the solvent removed. The residue, 13.03 g., was vacuum distilled. In addition to *p*-tolualdehyde (4.0 g., 0.03 mole), *p*-cresol (0.21 g., 0.002 mole) and *ca.* 2 g. of a mixture of *p*-methylbenzyl alcohol, *p*-methylbenzyl acetate and V, there were obtained 2.8 g. (0.016 mole) of nearly pure V. The pot residue, which solidified on cooling, was mostly *p*-toluic acid (*ca.* 4 g., 0.03 mole). Redistillation of the concentrate of V gave material boiling at 78–79° (0.6 mm.).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; sapon. equiv., 180. Found: C, 67.2; H, 6.85; sapon. equiv., 173.

Some of the error in these analytical figures is due to the small amount of *p*-toluic acid known to be present in the sample. The solution from the saponification equivalent (0.1626 g. of V, 0.90 mmole) was made strongly acid with 6 *N* hydrochloric acid and ether extracted. Evaporation of the ether gave 0.0935 g. (0.88 mmole) of *p*-cresol, identified by M.S. and G.L.P.C. From one-half of the aqueous solution, on treatment with 2,4-dinitrophenylhydrazine in diglyme solution, there was obtained 0.1072 g. (0.51 mmoles) of crude formaldehyde 2,4-dinitrophenylhydrazone, m.p. 161.0–165.5°. Recrystallization from ethanol gave m.p. 165.5–167.5°, undepressed on mixing with authentic formaldehyde 2,4-dinitrophenylhydrazone. The other half of the aqueous solution gave a positive formaldehyde test with chromotropic acid.[28]

The nuclear magnetic resonance spectrum of V is in accord with the structure suggested.[29] The resonance of the methylene hydrogens is shifted down field by the electron-withdrawing influence of the two substituents. Its position (1.6 p.p.m. from benzene) is considerably lower than that for *p*-methylbenzyl acetate (2.1 p.p.m.) and other benzyl esters.[30] For comparison, the resonance of the methylene group in chloromethyl benzoate is also low, at 0.95 p.p.m.

Acknowledgment.—The author is grateful to Dr. J. T. Horeczy for his continued support of this project and to Mr. Leroy C. Jennings for excellent technical assistance.

---

[24] This material was uncontaminated with the *ortho* isomer; see J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3443 (1953).

[25] Silicone seals, puncture type, Catalog No. 261-9-01, Burrell Corp., Pittsburgh, Pa.

[26] The author is indebted to V. H. Rushing and J. Dzilsky for the gas sample analyses and to G. R. Taylor and J. L. Taylor for the mass spectral analyses.

[27] "Table for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, O., 1960.

[28] F. Feigl, "Spot Tests in Organic Analysis," Elsevier Press, New York, N. Y., 1956, p. 331.

[29] The author is grateful to Mr. N. F. Chamberlain for the interpretation of the n.m.r. spectra.

[30] N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).