The Effect of Structure on the Thermal Stability of Hydroperoxides

RICHARD R. HIATT AND WILLIAM M. J. STRACHAN

Chemistry Department of the University of Toronto, Toronto 5, Canada

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1-Phenyl-2-methylpropyl 2-hydroperoxide and 1-phenyl-2-methylpropyl 1-hydroperoxide have been prepared and subjected to thermal decomposition. From an examination of the rates and products it is concluded that they do not give concerted decomposition.

Investigations of peresters have shown that their thermal stability can be greatly modified by variations in the structure of the acyl radical.[1,2] This has been a strong argument for, in the degradation of some peresters, the simultaneous cleavage of both carbon–carbon and oxygen–oxygen bonds which has been called a concerted decomposition.

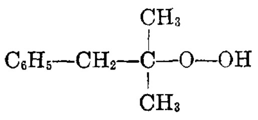
The thermal stability of hydroperoxides, on the other hand, seems to be unresponsive to structural changes.[3] This is not surprising if the primary rupture is confined to the oxygen–oxygen bond.

$$R_3C—O—O—H \longrightarrow R_3C—O\cdot + \cdot OH \qquad (1)$$

Conceivably the thermal decomposition could be analogous to those peresters which break in three, but for no hydroperoxides so far investigated has this been suggested. Product studies, where they have been done, have indicated the initial formation of an alkoxy radical[4,5] as in equation 1.

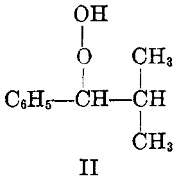
$$R_3C—O—O—H \longrightarrow R\cdot + R_2C{=}O + \cdot OH \qquad (2)$$

Nevertheless concerted decomposition remained an attractive possibility for a hydroperoxide suitably constructed; that is, where one of the R groups would make a particularly stable, free radical and where all of the groups were sufficiently bulky to cause some crowding. The following is an account of the preparation and thermal degradation of two closely related hydroperoxides, 1-phenyl-2-methylpropyl 2-hydroperoxide (I), where these conditions obtain, and 1-phenyl-2-methylpropyl 1-hydroperoxide (II), where they do not.



$$C_6H_5—CH_2—C(CH_3)_2—O—OH$$

I



$$C_6H_5—CH(O—OH)—CH(CH_3)_2$$

II

Experimental

1-Phenyl-2-methylpropyl 2-Hydroperoxide.—A 0.2-mole sample of 1-phenyl-2-methylpropanol-2 was mixed with 0.5 mole of 100% hydrogen peroxide and the temperature raised to 75°. A 0.07-ml. sample of 70% sulfuric acid was added with stirring over 10 to 15 min.[6] After 1 hr. the mixture was cooled and extracted with ether. Distillation gave an oil, b.p. 80–81° (0.01 mm.), which slowly crystallized. Recrystallization from pentane gave white needles, m.p. 44–44.6°, which on refluxing with acidified potassium iodide released 98% of the theoretical amount of iodine.

The infrared spectrum of the hydroperoxide differed from that of the alcohol only in the regions of 2.8–3 and 11–12 μ, indicating that no skeletonal rearrangement had occurred during the reaction. Reduction of the product with lithium aluminum hydride gave 1-phenyl-2-methylpropanol-2. The n.m.r. spectrum was consistent only with the expected structure on one other, 2-phenyl-2-methylpropyl 1-hydroperoxide, a possibility that was excluded by the foregoing observations and by the pattern of products from the thermal decomposition.

1-Phenyl-2-methylpropyl 1-hydroperoxide was prepared by a similar procedure from 1-phenyl-2-methylpropanol-1, except that the reaction was carried out at room temperature. The product was an oil, b.p. 50–51° (0.01 mm.), which liberated 99% of the theoretical amount of iodine. Its infrared spectrum was very similar to that of the starting alcohol.

***t*-Butyl hydroperoxide** was obtained from Lucidol Corp. It was separated from water and distilled, taking the fraction boiling at 33° (18 mm.).

Benzene used was Fisher reagent grade, dried over sodium, and distilled.

Kinetic Runs.—Dilute solutions of hydroperoxide in benzene were placed in sealed tubes and heated in a constant-temperature bath. The remaining amount of hyperoperoxide was determined iodometrically. The presence or absence of oxygen was found to have negligible effect on the rates of decomposition and no effort was subsequently made to remove it. Plots of the log of hydroperoxide concentration *vs.* time gave straight lines.

Product Studies.—Solutions of hydroperoxide, 0.9 *M* in benzene, were heated at 165° for at least ten half-lives. The resulting solution in benzene was analyzed with the Beckman GC-2 gas chromatograph.

Results and Discussion

In Table I are the first-order rate constants for the thermal decomposition in benzene of the two hydroperoxides as well as those of *t*-butyl hydroperoxide done under the same conditions for comparison. Table II

TABLE I

RATE CONSTANTS FOR THE THERMAL DECOMPOSITION IN BENZENE

Hydroperoxide I		Hydroperoxide II		*t*-Butyl hydroperoxide	
Temp., °C.	$k \times 10^6$ sec.$^{-1}$	Temp., °C.	$k \times 10^6$ sec.$^{-1}$	Temp., °C.	$k \times 10^6$ sec.$^{-1}$
144.2	5.04	133.8	3.18	154.5	4.29
154.5	12.1	143.9	8.95	161.7	9.27
165.5	29.2	153.9	20	169.3	20
176.0	69.7	163.7	40.3	174.6	40
		174	97.7		
ΔH^* 30 kcal.		29.2 kcal.		40.8 kcal.	
ΔS^* −11.5 e.u.		−12.5 e.u.		+12.2 e.u.	

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(1) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(2) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

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

(4) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

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

(6) This preparation was attended by some hazard and was always carried out behind a safety screen. Occasionally a weird light was seen to flicker over the surface of the mixture during the addition and this was sometimes, but not always, followed by explosion. Subsequent findings indicate that the danger lies in addition of sulfuric acid to an alcohol–hydrogen peroxide mixture. Acidification of the concentrated hydroperoxide prior to its addition to the alcohol has eliminated the occurrence of explosions in preparation of other hydroperoxides. However, this does not obviate the need for all normal precautions in the use of concentrated hydrogen peroxide. We are grateful to a referee for indicating that this hydroperoxide may be prepared in 40–60% yields, using 30–50% hydroperoxide.

TABLE II

PRODUCTS OF THE THERMAL DECOMPOSITION IN BENZENE

Hydroperoxide I Product	Mol. %	Hydroperoxide II Product	Mol. %
Acetone	81	*i*-Butyraldehyde	2
Toluene	28	Acetone	65
Benzyl alcohol	6	*i*-Propyl alcohol	3
Benzaldehyde	9	Benzaldehyde	44
1-Phenyl-2-methyl-propanol-2	4	Benzoic acid	28
Benzoic acid	8	Methanol	Trace
Methanol	Trace		

shows the major products of these decompositions determined by gas chromatography.

Measurement of the rates of homolysis of hydroperoxides has always been complicated by their tendency to exhibit induced decomposition. The difficulty has been usually overcome by extrapolation to zero of rate measurements at several initial concentrations,[4] or by the inclusion of radical traps in the solution.[3] The rates reported here were done with initial concentrations of hydroperoxide of 0.05 and 0.033 M, considerably lower than those generally used. Initial concentrations lower than these did not affect the rate constants obtained appreciably and it was concluded that induced decomposition was negligible at these concentrations.

If, as expected, 1-phenyl-2-methylpropyl 2-hydroperoxide were to decompose in a concerted manner, it should show a marked decrease in thermal stability relative to other hydroperoxides. Instead, the rates of decomposition of the three hydroperoxides are remarkably similar. Both hydroperoxides I and II have activation enthalpies considerably lower than *t*-butyl hydroperoxide, but this is balanced almost completely by the large decrease in activation entropy. In fact a ΔH^* of about 30 kcal. is usual for the homolytic cleavage of hydroperoxides,[3] and it is *t*-butyl hydroperoxide that is the anomalous one.

The presence of 1-phenyl-2-methylpropanol-2 in the products from hydroperoxide I seems to prove that it cannot be undergoing a concerted decomposition. The benzyldimethylmethoxy radical survives long enough to abstract a hydrogen atom from the surrounding medium.[7] The other products are as expected and easily explicable in terms of hydrogen abstraction radical fragmentation and recombination, and induced decomposition which undoubtedly occurs in the concentrated solutions used for the product study. The large amount of acetone from hydroperoxide II is a bit surprising. Apparently cleavage of the initially formed radical to benzaldehyde and isopropyl radical is very facile. Decomposition of this radical to give isobutyraldehyde was also noted, but no isobutyrophenone could be found.

Do these hydroperoxides, then, give a concerted decomposition? Generally speaking, the arguments in support of this mechanism fall into three categories: the rate of decomposition relative to that for similar compounds, entropies and energies of activation relative to these same standards, and the products of reaction. Comparing only hydroperoxide I with *t*-butyl hydroperoxide, it would appear that concerted decomposition was quite possible. However, then one would have to admit hydroperoxide II to the ranks of concerted decomposers, as well as a number of other hydroperoxides which from structural considerations seem unlikely to homolyze in this manner.[3] Convincing evidence for a concerted mechanism is, therefore, lacking.

While 1-phenyl-2-methylpropyl 2-hydroperoxide may or may not undergo induced decomposition, the analogous perester, *t*-butyl phenylperacetate, does. The difference may be explained by referring to the gain in energy from producing carbon dioxide by the perester, relative to that from producing acetone by the hydroperoxide. In a simpler case where direct comparison is possible, this difference amounts to 20 kcal.

$$CH_3{-}CO_2\cdot \longrightarrow CH_3\cdot + CO_2 + 17 \text{ kcal.}^{8}$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + (CH_3)_2CO - 3 \text{ kcal.}^{9}$$

Probably the fragmentation of benzyldimethylmethoxy radical is exothermic, but not enough to provide the kick necessary for the concerted decomposition.

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[7] However, it is possible that the small amount of alcohol arises from some α,α-dimethylphenethyl radical produced not by homolytic cleavage of the hydroperoxide, but by induced decomposition. The results of Kochi [J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962)] on the metal ion-catalyzed decomposition of this hydroperoxide showed equivalent amounts of the parent alcohol in the products. This did not prevent speculation on a metal ion assisted, concerted mechanism for decomposition.

[8] I. Jaffe, E. J. Prosen, and M. Scwarc, *J. Chem. Phys.*, **27**, 416 (1957).

[9] P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).