Tetrahedron Letters No.14, pp. 887-890, 1971. Pergamon Press. Printed in Great Britain.

THE ACID-CATALYZED DECOMPOSITION OF ALIPHATIC HYDROPEROXIDES: REACTIONS IN THE PRESENCE OF ALCOHOLS

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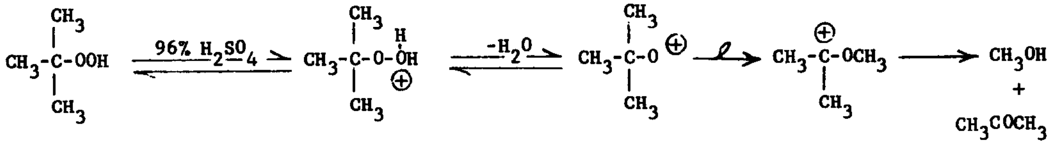
(Received in USA 25 January 1971; received in UK for publication 15 February 1971)

The recent publication by Deno[1] and co-workers on the reactions of aliphatic hydroperoxides in strong acid prompts us to report our results on the reactions of aliphatic hydroperoxides in strong acid, in dilute aqueous acid and in alcoholic sulfuric acid.

Clarification is needed for the earlier report by Leffler[2] which states that "isobutylene is the sole organic product from t-butyl hydroperoxide in the presence of acids", and has since been referred to in at least two books[3,4] on peroxide reactions. We have found that the products obtained from the acid-catalyzed decomposition of t-butyl hydroperoxide are dependent upon acid concentration. In 96% sulfuric acid t-butyl hydroperoxide rearranges to give a 95% yield of acetone and methanol[1,5] while in 50% sulfuric acid t-butyl hydroperoxide produces a 93% yield of di-t-butyl peroxide. Isobutylene was not detected in either reaction.

(1)


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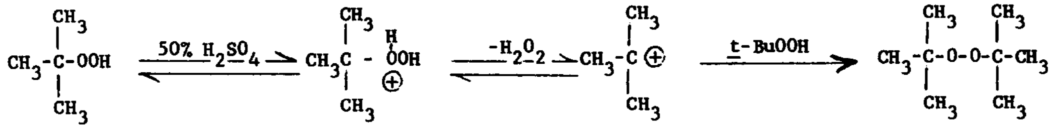
(2)


Reaction (1) proceeds via oxygen-oxygen bond heterolysis followed by methyl migration (probably a concerted reaction as described for cumene hydroperoxide)[6] to yield acetone and methanol. The nmr spectrum of the 96% sulfuric acid solution exhibits two sharp singlets at 2.92 p.p.m. and 4.08 p.p.m. assigned to protonated acetone and methyl hydrogen sulfate, respectively.

Reaction (2) proceeds via carbon-oxygen bond heterolysis to give di-t-butyl peroxide, which is stable and can be isolated by phase separation. This reaction requires the presence of unprotonated t-butyl hydroperoxide to attack the t-butyl cation, while in 96% sulfuric acid, less unprotonated hydroperoxide is present for nucleophilic attack and thus the pathway shown in (1) becomes more favorable.

The decomposition of t-pentyl hydroperoxide is also dependent upon acid concentration. In 96% sulfuric acid, 86% reacted via ethyl migration to give acetone and ethanol and 14% reacted via methyl migration to produce 2-butanone and methanol. In 50% aqueous sulfuric acid it produced di-t-pentyl peroxide.

The acid-catalyzed rearrangement of a series of secondary aliphatic hydroperoxides was reported by Pritzkow[7] to yield aliphatic ketones resulting from hydrogen migration. Deno[1] recently reported that sec-butyl hydroperoxide in strong acid reacted via both hydrogen and ethyl migrations to give 2-butanone and ethyl hydrogen sulfate in yields of 78 and 22%, respectively. We also studied the rearrangement of sec-butyl hydroperoxide in strong acid and noted that the product distribution was dependent upon the acid concentration. In 96% sulfuric acid sec-butyl hydroperoxide (97% pure by iodometric titration) reacted via hydrogen, ethyl and methyl migrations to produce 2-butanone, ethyl hydrogen sulfate and methyl hydrogen sulfate in yields of 48, 48 and 4%, respectively. In 70% sulfuric acid, only hydrogen and ethyl migrations occurred to produce 2-butanone and ethyl hydrogen sulfate in yields of 82 and 18%. The methylene groups of both ethyl hydrogen sulfate and 2-butanone appear in the nmr spectrum as clean quartets centered at 4.50 and 3.24 ppm, respectively and their band areas are used to calculate the relative amounts of ethyl and hydrogen migration.

t-Butyl hydroperoxide was then added to sulfuric acid in methanol (50 wt. % of 96% H_2SO_4 in methanol) and the major products were methyl t-butyl ether and methyl acetate. The reaction apparently proceeds via carbon-oxygen bond heterolysis to yield di-t-butyl peroxide (as in 50% aqueous sulfuric acid); however, in methanol the peroxide reacts slowly with methanol to yield methyl t-butyl ether. Hydrogen peroxide is decomposed to oxygen and water under these conditions.

When t-butyl hydroperoxide was added to 50% methanolic sulfuric acid and stirred for 2 hours at 50°C, the yields of di-t-butyl peroxide, methyl t-butyl ether and methyl acetate were 68, 9 and 17%, respectively. When the reaction time was increased to 60 hours, all the di-t-butyl peroxide reacted and the yields of methyl t-butyl ether and methyl acetate were 55 and 20%.

The methyl t-butyl ether forms at the expense of di-t-butyl peroxide; however, the reaction is complicated by the acid cleavage of methyl t-butyl ether as the reaction time is increased. This was demonstrated by examining the stability of methyl t-butyl ether with time. Methyl t-butyl ether was stirred for 18 hours in 50% methanolic sulfuric acid at 50° and 90% was recovered; after 60 hours only 69% was recovered. When di-t-butyl peroxide was employed as the starting reactant under the above conditions for 50 hours, the yields of methyl t-butyl ether and methyl acetate were 60 and 10%. The above results are explained by the following mechanism.

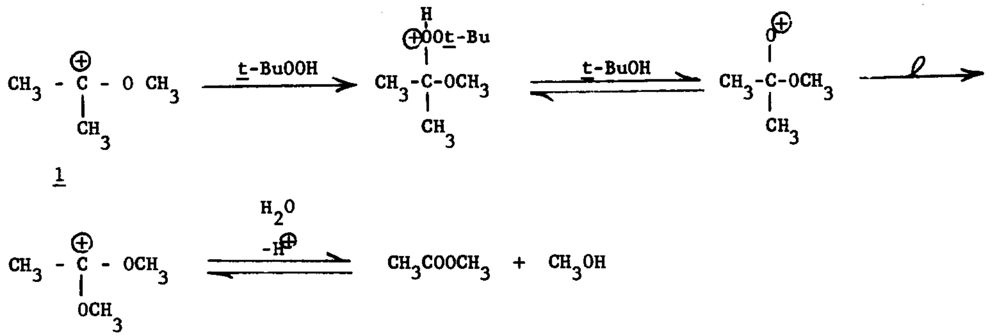
$$(3)\quad t\text{-BuOOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[t\text{-Bu}O\overset{H}{O}H\right]^{\oplus} \longrightarrow t\text{-Bu}^{\oplus} + H_2O + 1/2\ O_2$$

$$(4)\quad t\text{-Bu}^{\oplus} + t\text{-BuOOH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} t\text{-Bu}_2O_2 + H^{\oplus}$$

$$(5)\quad t\text{-Bu}^{\oplus} + CH_3OH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} t\text{-BuOCH}_3 + H^{\oplus}$$

$$k_2 >> k_3 > k_{-2}$$

An ionic mechanism is offered to explain the formation of methyl acetate. Some of the charged t-butyl hydroperoxide reacts via the t-butoxy cation, and after methyl migration, the carbonium ion 1 is attacked by the powerful nucleophile, t-butyl hydroperoxide. As discussed previously the heterolytic cleavage and methyl migration appear to proceed in a concerted reaction.[6]



$$CH_3-\overset{\oplus}{C}(CH_3)-O\,CH_3 \xrightarrow{t\text{-BuOOH}} CH_3-C(\overset{H}{\oplus O}Ot\text{-Bu})(CH_3)-OCH_3 \underset{}{\overset{t\text{-BuOH}}{\rightleftharpoons}} CH_3-C(O^{\oplus})(CH_3)-OCH_3 \xrightarrow{\ell}$$

$$CH_3-\overset{\oplus}{C}(OCH_3)-OCH_3 \underset{}{\overset{H_2O,\ -H^{\oplus}}{\rightleftharpoons}} CH_3COOCH_3 + CH_3OH$$

When the above reaction was carried out in ethyl alcohol and isopropyl alcohol, the yields of ethyl t-butyl ether and isopropyl t-butyl ether were less than 10%.

The addition of t-butyl hydroperoxide to 15-20% methanolic sulfuric acid with catalytic quantities of ferrous sulfate produced an 80% yield of methyl t-butyl ether and a 75% yield of methylal (based on charged t-butyl hydroperoxide) as a co-product. When t-butyl hydroperoxide was added to sulfuric acid in ethyl- or isopropyl alcohol (15-20 wt. %), the yields of ethyl t-butyl ether and isopropyl t-butyl ether were 50 and 15%, respectively.

Whereas the previous reaction without ferrous sulfate in 50% sulfuric acid proceeded via a heterolytic pathway as described above, the reaction with metal proceeds via a free radical pathway to give t-butyl alcohol and formaldehyde (Fenton reaction)[8] and these then reacted heterolytically with methanol to yield the methyl t-butyl ether and methylal.

ACKNOWLEDGEMENT: The author wishes to thank Mr. Arthur Brown for his laboratory assistance.

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