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THE REACTION OF CHLORO-t-BUTYL HYDROPEROXIDE WITH BASE

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The alpha effect (1) suggests that neighboring peroxide group reactions should be facile compared to corresponding monoöxide analogs. Our interest in this field has lead us to investigate the reaction of chloro-t-butyl hydroperoxide with base.

Chloro-t-butyl hydroperoxide was prepared from isobutylene chlorohydrin (2) and hydrogen peroxide with sulfuric acid catalysis.[2] Purification was attempted by both simple and fractional distillation. Because of some decomposition to isobutylene chlorohydrin on prolonged distillation, simple distillation proved as satisfactory as fractionation.[3] Iodometric titration (4) indicates that the hydroperoxide can be obtained in 93-98% purity, where the contaminant is isobutylene chlorohydrin as determined by nmr.

Acetone and formaldehyde were formed from the reaction of chloro-t-butyl hydroperoxide with sodium hydroxide in 60% aqueous methanol containing 2 mole per cent (based on sodium hydroxide) of disodium ethylenediaminetetraacetic acid (5). Acetone was identified by comparison of the

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[1] National Science Foundation Undergraduate Research Participation.

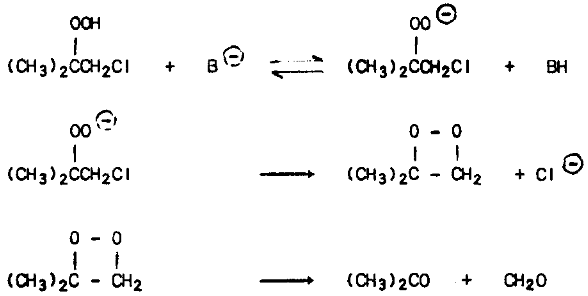
[2] Chloro-t-butyl hydroperoxide was previously prepared from the autoxidation of isobutyl chloride in 91% purity (3).

[3] On one occasion an explosion resulted after bleeding the system at the completion of the distillation.

gas-liquid chromatography (g.l.c.) retention time, infrared spectrum of the g.l.c. fraction and 2,4-dinitrophenylhydrazone (6) (m.p. 128-129°, lit. (7) m.p. 128°) with an authentic sample of acetone. Formaldehyde was isolated as the 5,5-dimethyl-1,3-cyclohexadione (dimedon) derivative (m.p. 191.5-192.5°, lit. (8) m.p. 191.4°). The best yield of acetone was 75%, based on reacted hydroperoxide. The yield decreased with increased base concentration relative to hydroperoxide concentration. In addition, yields decreased with increased reaction time with excess base. A control experiment with acetone (0.273 *M*), formaldehyde (0.258 *M*) and sodium hydroxide (0.250 *M*) in 60% aqueous methanol showed that 39% of the acetone underwent reaction after a normal reaction period of 3.5 hr. at 30°. The yields of acetone are understandably low due to base catalyzed condensation reactions with formaldehyde (9). The yield of formaldehyde reflects this condensation reaction also. Formaldehyde was obtained in 53% yield as the dimedon derivative. No gaseous products were observed, which excludes oxygen and isobutylene as possible products.

The reaction is first-order in chloro-*t*-butyl hydroperoxide. Zero-order dependence on base concentration results at high base strength ($\gtrsim$ 0.5 *M*) with 0.0100 *M* hydroperoxide concentration. Since the pKa's of hydroperoxides are less than 14 (10), the trend to zero-order dependence on base is expected. Thermal decomposition of the hydroperoxide did not interfere with the reaction in basic solution, since the half-life of chloro-*t*-butyl hydroperoxide in 60% aqueous methanol at 97.19° in the absence of base in 5.3 hr. In basic solution at 30°, the half-life is in the range of 7-18 min. The rate of chloro-*t*-butyl hydroperoxide reaction with base was unchanged in the presence of 2,6-di-*t*-butyl-*p*-cresol, which indicates that the reaction is not free radical. In addition, no decomposition of *t*-butyl hydroperoxide was observed at 30° under these basic conditions. Finally, the rate of the isobutylene chlorohydrin reaction with base is too fast to measure under our kinetic conditions. The kinetic data for chloro-*t*-butyl hydroperoxide is then valid, even though there is some contamination of the hydroperoxide by the chlorohydrin (11).

These data are consistent with the *non*-free radical mechanism below, where $B^{\ominus}$ is hydroxide or methoxide. The perepoxide[4] intermediate is of



$$(CH_3)_2\overset{\overset{OOH}{|}}{C}CH_2Cl \quad + \quad B^{\ominus} \quad \rightleftharpoons \quad (CH_3)_2\overset{\overset{OO^{\ominus}}{|}}{C}CH_2Cl \quad + \quad BH$$

$$(CH_3)_2\overset{\overset{OO^{\ominus}}{|}}{C}CH_2Cl \quad \longrightarrow \quad \begin{array}{l} \ \ \ \ \ \ \ \ \ \ \ O - O \\ \ \ \ \ \ \ \ \ \ \ \ \ | \quad\ \ | \\ (CH_3)_2C - CH_2 \end{array} \quad + \quad Cl^{\ominus}$$

$$\begin{array}{l} \ \ \ \ \ \ \ \ \ \ \ O - O \\ \ \ \ \ \ \ \ \ \ \ \ \ | \quad\ \ | \\ (CH_3)_2C - CH_2 \end{array} \quad \longrightarrow \quad (CH_3)_2CO \quad + \quad CH_2O$$

particular interest, since earlier workers suggested such intermediates in olefin autoxidation (12). Although most of the early work has been interpreted in terms of hydroperoxide rather than perepoxide intermediates (13), there are continuing reports of perepoxide intermediates (14). In addition, perepoxides are suggested as key intermediates in chemiluminescence reactions (15, 16). Our results suggest that the perepoxide of isobutylene is quite unstable, since little or no common ion rate depression was observed. Common ion rate depression has been used as a tool to detect

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[4] Alternate names are 3,3-dimethyl-1,2-dioxetane and isobutylene dioxide. See A. M. Patterson, L. T. Capell and D. F. Walker, "The Ring Index," Second Edition, Am. Chem. Soc. Publication, 1960, p. 6.

the lactone intermediate in the reaction of bromo-carboxylate compounds (17). Lastly, ring opening of isobutylene perepoxide yields predominantly carbonyl products, rather than oxygen and an olefin (15c), an α-glycol (14c) or an ester (14d).

Other peroxide anion and alkyl peroxide systems are under investigation where neighboring group reaction may intervene. Model compounds are also being studied to compare the magnitude of neighboring group participation.

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